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**Marine organic
aerosol and cloud
drop activation**

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A GCM study of organic matter in marine aerosol and its potential contribution to cloud drop activation

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Abstract

With the global aerosol-climate model ECHAM5-HAM we investigate the potential influence of organic aerosol originating from the ocean on aerosol mass and chemical composition and the droplet concentration and size of marine clouds. We present sensitivity simulations in which the uptake of organic matter in the marine aerosol is prescribed for each aerosol mode with varying organic mass and mixing state, and with a geographical distribution and seasonality similar to the oceanic emission of dimethyl sulfide. Measurements of aerosol mass and chemical composition serve to evaluate the representativity of the model initializations. Good agreement with the measurements is obtained when organic matter is added to the Aitken, accumulation and coarse modes simultaneously. Representing marine organics in the model leads to higher cloud drop number concentrations, smaller cloud drop effective radii, and a better agreement with remote sensing measurements. The mixing state of the organics and the other aerosol matter, i.e., internal or external depending on the formation process of aerosol organics, is an important factor for this. We estimate that globally about $75\,\mathrm{Tg\,C\,yr^{-1}}$ of organic matter from marine origin enters the aerosol phase. An approximate 35% of this occurs through formation of secondary organic aerosol and 65% through emission of primary particles.

1 Introduction

Aerosol particles influence optical characteristics and the lifetime of clouds through the so-called first and second aerosol indirect effects (e.g., Lohmann and Feichter, 2005). Anthropogenic activities have caused an increase of the atmospheric burden of aerosol and aerosol precursors compared to the pre-industrial atmosphere, and this may have altered regional and global radiative cloud forcings (e.g., Penner et al., 2001). The large spatial and temporal variability in size, chemical composition, and hygroscopicity of particles impede accurate estimation of the aerosol direct and indirect forcing (Textor

et al., 2006). Poor understanding of aerosol effects leads to large uncertainties in assessing the sensitivity of climate to human perturbations and in projections of climate change (Andreae et al., 2005).

An accurate quantification of the climate forcing from anthropogenic aerosol requires detailed knowledge of natural aerosol as well. Estimation of the amount of organic aerosol matter produced from vegetation emissions is characterized with many uncertainties associated with the chemical properties and emission strength of precursor gases, gas- and aqueous phase oxidation pathways and yield of reaction products, formation of secondary organic aerosol (SOA) through condensation of semi-volatile gases and the size distribution of the organic matter (e.g., Jacobson et al., 2000; Kanakidou et al., 2005). Other aerosol components are involved as well. Kulmala et al. (2000) mention that thermodynamically stable clusters formed in the atmosphere, for example of H_2SO_4-NH_3-H_2O, can undergo rapid growth to nucleation mode sizes and larger when mixed with air containing condensable organic gases. Current estimates of SOA production from continental vegetation display a large range, between 12–70 Tg SOA/yr from bottom-up approaches (Kanakidou et al., 2005) and 200–800 Tg C/yr from top-down approaches (Goldstein and Galbally, 2007).

Several decades ago, before a significant anthropogenic influence on marine aerosol was acknowledged, in an extensive review on marine aerosol Berg and Winchester (1978) reported studies that found that a strong chemical similarity exists between sea surface organic material and airborne organics, and that indicated that aerosol with relatively high organic aerosol content are associated with air masses that passed over ocean regions rich in organic material. It was concluded that the ocean must be an important source of the organic constituents in marine air, with the quantity of organic carbon in sea water, the amount of surfactants in sea water and the chemical and physical nature of oceanic organic compounds as important governing factors (Hoffman and Duce, 1976). Later, scientific attention switched to the anthropogenic contribution to remote aerosol, and studies on marine aerosol organics were mostly limited to DMS and the uptake of MSA in aerosol (Fitzgerald, 1991; O'Dowd et al., 1997; Heintzenberg

et al., 2000).

The study of natural organic aerosol in marine environments is receiving increasing attention in recent years. Measurements in Mace Head (Ireland) showed the presence of relatively large quantities of aerosol organics, $\sim$620 ng/m^3 in summer, in air masses advected from remote marine regions that were probably influenced by plankton bloom (O'Dowd et al., 2004). Isoprene emissions from the ocean surface were reported by Yokouchi et al. (1999). Claeys et al. (2004) showed that the oxidation of isoprene produces water-soluble methyl tetrols, implying potential influence of isoprene on cloud drop activation. Meshkidze and Nenes (2006) found a correlation between the seasonal variation of cloud drop effective radius in the southern Atlantic Ocean region and of isoprene emission by plankton.

Aerosol organics that originate from the ocean contribute to the natural atmospheric aerosol burden. The radiative properties of the natural atmosphere form the background against which the impact of anthropogenic activities on the Earth's energy budget is compared. Current estimates indicate on average that the anthropogenic aerosol indirect forcing over the ocean is 75% of that over land, with several studies estimating a larger forcing over the ocean than over land (see Lohmann and Feichter, 2005, their Fig. 3; Lohmann and Lesins, 2002). However, these studies did not take the marine organic emissions and their effect on aerosol and cloud properties into account, and therefore the actual anthropogenic aerosol indirect forcing over the ocean may be considerably smaller.

In this study we apply the aerosol-climate model ECHAM5-HAM, extended with a parameterization for cloud drop activation and size-dependent aqueous phase sulfur chemistry, to investigate the potential influence of aerosol organics originating from the ocean surface on aerosol and cloud characteristics in a marine environment. In a previous model study that considered only ocean emissions of sea salt and DMS the simulated effective radii (R_{eff}) of marine clouds exceeded observations from ISCCP (International Satellite Cloud Climatology Project) by about 5 μm in the Northern Hemisphere (NH) and 6 μm in the Southern Hemisphere (SH) (Roelofs et al., 2006). This

is equivalent with an underestimation of the cloud drop number concentration (CDNC) by a factor of 3 or 4. The present study investigates the potential effect of aerosol organics of marine origin on aerosol activation and cloud formation. Three research questions motivate this study: through which mechanisms does the organic matter enter the aerosol phase, in which aerosol mode or modes is the organic matter deposited, and does the study allow for an estimate of the annual and global amount of the aerosol organics originating from the ocean surface? Because the model does not calculate SOA formation explicitly a top-down approach is applied where specific amounts of organic matter are directly added to different aerosol modes. The observations of O'Dowd et al. (2004) and other observations of aerosol composition and cloud drop radius are used as a constraint to assess the representativity of the boundary conditions. Section 2 describes the aerosol-climate model ECHAM5-HAM and the cloud processing parameterization. Section 3 introduces the measurements of the aerosol chemical composition that will be used to assess the model representativity, and the boundary conditions of the sensitivity simulations. Section 4 presents the results of the sensitivity simulations, and Sect. 5 summarizes and discusses the results.

2   Model description

The study is performed with a version of the coupled aerosol-climate model ECHAM5-HAM similar to the one applied by Stier et al. (2005). ECHAM5-HAM consists of the general circulation model ECHAM version 5 and an aerosol module (HAM) that accounts for emissions of aerosol and aerosol precursors, chemical transformations, nucleation of new particles and condensation of semi-volatile H_2SO_4 on existing particles, coalescence between particles and dry and wet deposition. The core of HAM is the aerosol dynamical module M7 (Vignati et al., 2004; Wilson et al., 2001). M7 describes the aerosol population with four soluble and three insoluble aerosol modes composed of (mixtures of) sulfate, organic carbon, black carbon, sea salt and dust. The modes are lognormal and each mode is characterized by the particle number concentration and

mass of associated aerosol components, from which an average dry particle radius is derived. The size ranges considered are below 0.005 μm particle radius for the nucleation mode, between 0.005 and 0.05 μm particle radius for the Aitken mode, between 0.05 and 0.5 μm particle radius for the accumulation mode, and above 0.5 μm particle radius for the coarse mode. All emissions are treated as primary emissions except for the sulfur compounds. Hence, secondary organic aerosol (SOA) formation associated with organic emissions from vegetation and – in this study – from the ocean surface is not calculated explicitly. Instead, organics are emitted as primary particles. For further information on emissions considered in the model we refer to Stier et al. (2005) and Roelofs et al. (2006).

The bulk cloud chemistry scheme in ECHAM5-HAM has been replaced with a cloud processing parameterization. The parameterization consists of two steps, for cloud drop activation and for aqueous phase chemistry. First, the maximum supersaturation at the cloud base is estimated through an empirical approach derived from cloud parcel model simulations (Hänel, 1987) as described in more detail in Roelofs et al. (2006). The activation parameterization performs relatively accurately, i.e., the predicted supersaturation and CDNC are generally within 30% of cloud parcel model results. The second step in the parameterization calculates aqueous phase formation of sulfate and its distribution over the different activated modes, i.e., the modes that contribute to CDNC. The parameterization is linked to the climate model's large-scale cloud scheme, which has prognostic equations for cloud liquid water and ice (Lohmann and Roeckner, 1996).

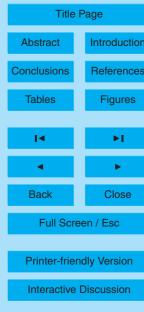## 3 Description of the sensitivity studies

The measurements of O'Dowd et al. (2004) of the organic fraction in marine aerosol sampled in Mace Head can be summarized as follows. The organic mass in the accumulation mode displays a significant seasonality with ~620 ng/m^3 in summer and 70 ng/m^3 in winter. Measured organic mass fractions in summer were 83% for parti-

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cles smaller than $0.125\,\mu$m diameter (comparable with the Aitken mode in ECHAM5-HAM), 65% for particles with a diameter between 0.125 and $1\,\mu$m (the accumulation mode in ECHAM5-HAM), and ~3% in particles with diameters exceeding 1 μm (the coarse mode in ECHAM5-HAM). The approximate mass fractions of nss-sulfate in the Aitken and accumulation modes are 12% and 25%, respectively. Since the measurements were performed on air samples advected from remote marine regions it can be assumed that the aerosol sulfate mainly originates from oxidation of DMS. In view of the observed ratio between organic and sulfate masses and the model global DMS source of ~23 Tg S/yr (Stier et al., 2005) we assume a global production of marine organic aerosol varying between 25 Tg C/yr and 75 T C/yr in the sensitivity simulations. The seasonality of the marine organic emissions is assumed to follow the emission of DMS. As in Roelofs et al. (2006) the organics are assumed to have a soluble fraction of 50%. The measurements indicate a smaller soluble fraction, ~25%, but Roelofs et al. (2006) showed that for relatively soluble organics a 25% change in solubility has an effect of only a few percent on the average CDNC.
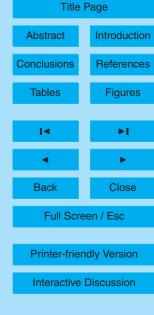
Data presented in this study are compiled from four years of simulation in the T21 resolution (approximately $5.6°\times5.6°$ with a 2400 s time step). The model uses 19 vertical layers in a hybrid σ-p-coordinate system, from the surface to 10 hPa. The simulated meteorology is generated by the climate model and does not reflect actual meteorological events. The computed cloud drop concentration does not feed back on large-scale cloud evolution and precipitation formation in order to eliminate meteorological effects in comparing the sensitivity simulations.

Table 1 presents the boundary conditions used in the sensitivity simulations. Organic aerosol matter originating from the ocean is deposited in the Aitken (labeled K), accumulation (labeled A) or coarse mode (labeled C), or a combination of these. O'Dowd et al. (2004) demonstrated that in theory the mixing state of the marine organics in the aerosol phase can have a large effect on the cloud forming properties of the aerosol. Therefore we apply different mixing states: external (labeled e or x, in x the organic mass is distributed over four times as many particles as represented in e) or internal

(labeled i), which reflect different aerosol formation mechanisms. Important processes for SOA formation are condensation of semi-volatile organics leading to new particle formation (external mixture) or growth of existing particles (internal mixture) (Kanakidou et al., 2005). Organics may also enter the atmosphere through mechanical forces, i.e., wind-driven generation of particles out of the organic mono-layer (external mixture) or of sea-salt mixed with organics (internal mixture) (Berg and Winchester, 1978, and references therein). Other processes that affect the aerosol mixing state, such as condensation of sulfuric acid, coagulation between particles and cloud processing, are explicitly represented in ECHAM5-HAM.

4 Results
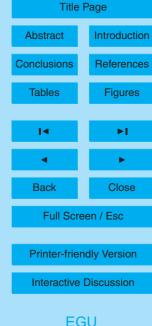
4.1 Aerosol mass and composition

In this section we compare the simulated aerosol mass and composition in the surface layer in the region 16° W–11° W, 50° N–55° N, i.e., over the ocean west of Ireland, with the measurements of O'Dowd et al. (2004). We focus on the summer months June, July and August (JJA) when simulated organic emissions from the ocean maximize, allowing for a more straightforward comparison with the measurements. The total observed particulate organic mass is about ten times larger in summer than in winter, and differences between the sensitivity simulations are more pronounced. Further, the organic mass associated with the Aitken mode was below the detection limit in the winter.

Simulated particle number concentrations for the Aitken and accumulation modes and averaged over JJA are shown in Fig. 1. Figure 2 shows the simulated modal aerosol mass and chemical composition averaged over JJA, and the observed values (labeled *OBS*) derived from O'Dowd et al. (2004). The observations, together with observed R_{eff} presented later, serve as benchmark to assess the representativity of the boundary conditions in the sensitivity simulations. We note that ammonia is not

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considered explicitly in the model, so we assumed that the simulated and observed sulfate is present as ammonium bisulfate. The mass fractions of the individual aerosol components in *OBS* may therefore differ slightly from O'Dowd et al. (2004). Figure 2 shows that the organic mass in the Aitken and accumulation modes in the base case simulation *CTRL* is underestimated compared to the observations, and the sulfate mass in the Aitken mode is also smaller than observed.
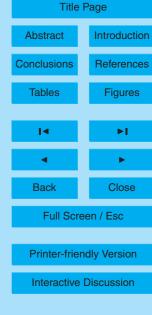
Ai, *Ae*, *Ax*. In these simulations a global amount of ~25 Tg C/yr of organics is added to the accumulation mode. The accumulation mode particle concentration in the simulation with internally mixed organics, *Ai*, is about the same as in *CTRL* (Fig. 1b). Number concentrations are larger when the organics are mixed externally (*Ae*, *Ax*), and in all three simulations the organic mass in the accumulation mode is larger than in *CTRL*. The total accumulation mode mass is largest in *Ax* and smallest in *Ai*, which probably reflects the size dependence of removal processes. The Aitken mode is not affected much by the additional organic matter in the accumulation mode, although removal of Aitken particles due to impaction by accumulation mode particles appears to be somewhat more efficient when accumulation mode particle concentrations are larger.

Ke, KeAi, KeAe, KeAx. In *Ke* a global amount of ~25 Tg C/yr of organics is added to the Aitken mode. Emission of marine organic aerosol as external mixture into the Aitken mode increases number concentration (Fig. 1a) and mass (Fig. 2a) of this mode. The Aitken mode mass in *Ke* is close to observed. Note that also the sulfate mass associated with the Aitken mode is larger than in *CTRL*. Due to the additional aerosol matter the total surface of the Aitken particles is larger enabling more efficient condensation of sulfuric acid. Further, the organics are partly soluble and thus facilitate cloud drop activation and enable cloud processing of the aerosol (see also Roelofs et al., 2006; Kerminen, 2001). The organics are partly transferred from the Aitken to the accumulation mode through impaction or cloud processing, and mass and number concentration of the accumulation mode are larger than in *CTRL* (Figs. 1b, 2b) but smaller than observed. *Ke2* is similar to *Ke* but twice the organic mass is added to the Aitken

mode. *Ke2* overestimates the Aitken organic mass compared to the observations but now the accumulation mode organic mass agrees better.

In *KeAi, KeAe* and *KeAx* organic matter is added to the Aitken mode as in *Ke*, and the same amount is added to the accumulation mode as external or internal mixture.
5 Comparison of the results for these simulations with *Ke* yields a qualitatively similar picture as the comparison of *Ai, Ae* and *Ax* with *CTRL* presented above. Now, however, the simulated accumulation mode mass is of the same order as observed (with *KeAi* somewhat smaller and *KeAx* somewhat larger; Fig. 2b), while also the simulated relative mass fractions (organics: ∼50%, ammonium bisulfate: ∼20%, sea salt: ∼30%)
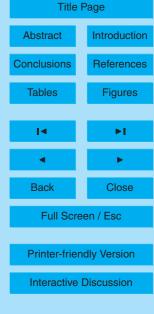10 agree better with the measurements.

Kx, KxAi, KxAe, KxAx. In *Kx* a global amount of ∼25 Tg C/yr of organics is added to the Aitken mode but it is distributed over four times the amount of particles, but these are smaller than in *Ke*. The computed Aitken particle number concentration is therefore larger while also the organic and sulfate masses are larger. The relative
15 differences in accumulation mode mass and concentration between these simulations are comparable to the differences between *Ke, KeAi, KeAe* and *KeAx*, or *CTRL, Ai, Ae* and *Ax* discussed previously.

Based on the results presented thus far it can be concluded that the best agreement between the modelled and observed Aitken and accumulation mode mass and chem-
20 ical composition is obtained when organics emitted from the ocean surface enter the aerosol phase through both modes. For the Aitken mode this involves new particle formation due to condensation of semi-volatile gases while for the accumulation mode both internal and external mixtures yield results that are in relatively good agreement with the observations. Relevant processes for this are condensation of semi-volatile
25 gases on existing particles and mechanical aerosol formation. Agreement within 20% between simulated and observed mass and chemical composition for both the Aitken and accumulation mode is obtained in *KeAi, KeAe* and *KeAx.* The Aitken mode mass is overestimated in *KxAi, KxAe* and *KxAx* but the agreement for the accumulation mode, that contains more than 90% of the fine mode aerosol mass, is also good. Since the

main difference between these six simulations apparently concerns particle number concentrations, the cloud drop effective radius must be considered for a better assessment of the representativity of the boundary conditions.

The measurements of O'Dowd et al. (2004) show that a small but significant organic fraction of ~3% is present in the coarse mode. The simulated transfer of mass from the Aitken and accumulation modes to the coarse mode, however, is insignificant. The production of atmospheric coarse mode organic matter thus appears to be directly coupled to the formation of sea salt aerosol, i.e., mechanical production of sea water droplets and subsequent evaporation of the water resulting in an internally mixed particle with inorganic and organic matter. This is in accordance with the observed similarities between marine aerosol organics and the organic composition of the sea water (Berg and Winchester, 1978). *KeAiCi* considers identical emissions as *KeAi* but an additional 25 Tg C/yr of organics is mixed internally into the coarse mode. The coarse mode organic mass fraction then increases from 0% in *CTRL* to 1.5% in *KeAiCi*, in better agreement but still smaller than the observations.

4.2   CDNC and R_{eff}

Figures 3 and 4 illustrate the effect of marine aerosol organics on simulated cloud parameters. They show the summer distribution of CDNC and R_{eff} over the North Atlantic Ocean simulated in *CTRL, KeAe* and *KxAx*. The model data are obtained by sampling the model domain as from a satellite, i.e., using the highest cloudy grid box from each model column, but at altitudes below 500 hPa and with a cloud cover larger than 10%. CDNC increases between *CTRL, KeAe* and *KxAx* due to the effect of aerosol organics, especially between 30° N–50° N and over the eastern North Atlantic. CDNC increases from 10–50 drops cm^{-3} in *CTRL* to values up to 140 cm^{-3} in *KeAe* and 200 cm^{-3} in *KxAx*. Over the remote North Atlantic, *KeAe* and *KxAx* simulate an average CDNC of 90–110 cm^{-3} and 100–150 cm^{-3}, respectively. The model results are in good agreement with values of CDNC retrieved from MODIS. These are 90±27 cm^{-3} for the remote North Atlantic and up to 180 cm^{-3} for the eastern North Atlantic (Ben-

nartz, 2007).

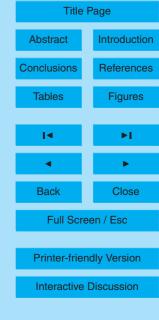R_{eff} decreases from 15–20 μm in *CTRL* to 11–15 μm in *KeAe* and 10–14 μm in *KxAx* (Fig. 4). The results from *KeAe* and *KxAx* agree with remotely sensed cloud drop radii over the NH Atlantic Ocean reported by Han et al. (1994) of 10–16 μm. In *CTRL* R_{eff} maximizes between 20° N and 40° N. The maximum shifts to sub-tropical latitudes in *KeAe* and *KxAx* because the effects of marine aerosol organics on CDNC and R_{eff} are most pronounced north of 30° N.

Figure 5 shows simulated CDNC in the remote marine boundary layer and averaged over JJA, and the contribution to CDNC from each mode. The data are from the region between 40° N–48° N and 40° W–20° W, but results are qualitatively similar for other regions over the North Atlantic Ocean. For *Ai, Ae* and *Ax* a good correlation exists between the accumulation mode number concentration shown in Fig. 1b and the contribution from this mode to CDNC. In *Ai* the organic matter is mixed internally and CDNC is the same as in *CTRL* . In the external mixture simulations *Ae* and *Ax* more particles are present and become activated. When the concentration of accumulation mode particles is relatively small substantial activation of Aitken mode particles may take place, as seen in *Ke* and *Kx*. Differences between *Ae* and *Ax*, however, are more pronounced than between *Ke* and *Kx*, illustrating that accumulation mode particles activate already at smaller supersaturations than Aitken mode particles. Finally, the organics added to the coarse mode in *KeAiCi* do not influence CDNC significantly.

4.3   Comparison with ISCCP

Figure 6 shows observed and simulated R_{eff} for the northern (40° N–48° N, 40° W–20° W) and the sub-tropical (15° N–25° N, 40° W–25° W) NH Atlantic Ocean. Observed radii are from ISCCP (http://isccp.giss.nasa.gov/). The data display a seasonal variation of R_{eff} with a summer maximum in the northern North Atlantic and a summer minimum in the equatorial North Atlantic.
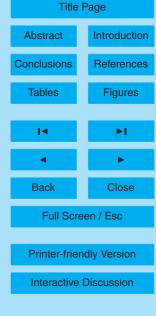
In *CTRL,* R_{eff} is larger than observed by 4 to 8 μm. Roelofs et al. (2006) argued that the overestimation of R_{eff} (or underestimation of CDNC) in marine regions is probably

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associated with too low concentrations of cloud condensation nuclei. When organics are added as an external mixture to the Aitken mode (*Ke*) R_{eff} decreases significantly (Figs. 6a, b). *Kx* and *Ke2* simulate higher concentrations of Aitken particles than *Ke* (Fig. 1) but perform only slightly better in terms of R_{eff}, which reflects that relatively high

5 supersaturation values are required for activation of smaller Aitken particles. When the organic mass is added to the accumulation mode instead (*Ai, Ae, Ax*) the simulated R_{eff} displays a larger range (Figs. 6c, d). In *Ai* R_{eff} is the same as in *CTRL* , whereas *Ae* and *Ax* are closer to the observations.

In *KeAe* and *KeAx,* R_{eff} decreases further but not in *KeAi* (Figs. 6e, f). Due to the

10 relatively high supersaturation required to activate Aitken mode particles the R_{eff} in *KeAe* does not differ significantly from *KxAe* in the summer (Figs. 6g, h) even though Aitken particle concentrations are much larger. However, in the winter in the northern North Atlantic, R_{eff} in *KxAe* is significantly smaller than in *KeAe*. The influence of the organic matter on the accumulation mode mass and number concentration is smaller

15 than in summer and the Aitken mode contribution to CDNC becomes more prominent.

In the northern part of the North Atlantic the observations are characterized by a summer maximum while the model simulates a summer minimum and overestimates R_{eff} in winter. We note that R_{eff} is also overestimated over the European continent in winter (Roelofs et al., 2006), and this may be partly caused by too small aerosol sulfate

20 concentrations (Stier et al., 2005). Underestimation of sulfate concentrations in winter over Europe is a common feature of global sulfur models, as discussed in Roelofs et al. (1998). However, over the remote ocean sulfate concentrations are relatively small and probably not the main reason that R_{eff} is overestimated. A plausible explanation may be that the typical size of new particles formed by condensation of non-volatile

25 gases depends on temperature or supersaturation. We assume in our simulations the same critical nucleus size for new particle formation throughout the year, as is also assumed for sulfuric acid (Wilson et al., 2001). However, the saturation mixing ratio of semi-volatile gases decreases with decreasing temperature. The ambient supersaturation for semi-volatile organic gases may be higher in winter than in summer, and

this results in a smaller critical size for nucleation (e.g., Girshick and Chiu, 1990). The number concentration of freshly formed particles per unit condensed mass may therefore be larger in winter. As a result the size distribution of aerosol organic matter may resemble *KeAe* or *KeAx* in the summer and to *KxAe* or *KxAx* in winter.

5   For the sub-tropical North Atlantic region the average simulated R_{eff} is also significantly improved when marine aerosol organics are considered, and the simulated seasonality is also in much better agreement with observations.

4.4   Southern Hemisphere

Although our study focuses on the NH Atlantic Ocean region, we will briefly discuss
10 the model representativity over the SH. Based on remotely sensed R_{eff} near the island of South Georgia east of south America, a location with a strong plankton bloom seasonality, Meskhidze and Nenes (2006) argue that aerosol organic matter originating from isoprene emissions from plankton significantly affects marine cloud characteristics. They inferred a possible concentration range for SOA from isoprene from $5\,ng\,m^{-3}$
15 in air relatively unaffected by the plankton bloom to $230\,ng\,m^{-3}$ when the isoprene flux into the atmosphere is relatively large. As a result, R_{eff} in clouds varies from 11–$13\,\mu m$ during high bloom activity in summer to 14–$16\,\mu m$ during low bloom activity in winter. Simulations *KeAi* and *KeAe* calculate monthly averaged R_{eff} of 12–$13\,\mu m$ in November and 14–$15\,\mu m$ in June, months with high and low bloom activity, respectively. In *KxAi*
20 and *KxAe* somewhat smaller radii are calculated for November, 11–$12\,\mu m$. Without marine organics in the aerosol (*CTRL*) the simulated R_{eff} during high bloom activity is significantly larger, 14–$17\,\mu m$. The simulated monthly averaged organic aerosol mass in summer near South Georgia, of the order of $200\,ng\,m^{-3}$ in *KeAiCi*, is close to the estimate by Meskhidze and Nenes (2006) for the period with high bloom activity. For
25 the region west of Tasmania, Boers et al. (2006) used MODIS data to derive a seasonal cycle of R_{eff} from 14–$16\,\mu m$ in summer to 21–$24\mu m$ in winter. The simulated R_{eff} west of Tasmania in winter ranges around $20\,\mu m$ in summer and $23\,\mu m$ in *CTRL*, but is significantly decreased due to the influence of organics in the sensitivity simulations.

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For example, in *KeAiCi* R_{eff} near Tasmania is 14 μm in summer and 19 μm in winter, respectively, in better agreement with the observations.

5 Conclusions

We used the global aerosol-climate model ECHAM5-HAM to investigate the potential influence of marine aerosol organics on simulated aerosol and cloud characteristics. Without these organics the model underestimates the aerosol organic mass and cloud condensation nuclei concentrations in the marine atmosphere, and overestimates cloud drop effective radii in marine clouds. By introducing organic matter in the Aitken and accumulation modes, separately or combined, the simulated and observed aerosol mass, aerosol chemical composition and cloud drop size can be brought in relatively good agreement with observations.

A bottom-up estimate of the amount of primary and secondary formation of aerosol organics and an evaluation of the influence of marine organics on cloud optical properties requires a qualitative and quantitative knowledge of ocean emissions and chemical reaction pathways that exceeds our current level of understanding. We used a relatively simple top-down approach where different organic yields and mixing states are prescribed for the relevant aerosol modes. Measurements of O'Dowd et al. (2004) for the aerosol mass and composition, and of ISCCP for cloud drop size were used to evaluate these boundary conditions.

The results indicate that organic matter from marine origin may contribute to a large extent to the mass and particle concentrations associated with fine mode aerosol of the natural atmosphere. Good agreement between simulated and observed chemical composition of the aerosol was obtained when globally about 75 Tg C/yr of organic matter is added to the marine aerosol phase, more or less equally divided between the Aitken, accumulation and coarse modes.
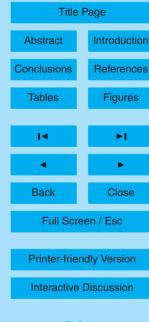
Different pathways of adding organics to the aerosol phase occur simultaneously, and it depends on the process if the particle number concentration also changes. In

the first place, new particle formation due to condensation of semi-volatile gases takes place, thereby increasing the number concentration of Aitken particles. Results indicate that the critical size of newly formed particles varies with season, with more and smaller particles in winter than in summer. Part of the organics in the Aitken mode
5 is transferred to the accumulation mode by particle coagulation. In the second place, organic matter emitted from the ocean is added to the accumulation mode, through condensation (internal mixture) or through mechanical generation of particles (external mixture). The latter process results in an increase of the accumulation mode particle concentration and this improves the agreement between simulated and observed
10 R_{eff}. In the third place, the observed presence of organic matter in the coarse mode suggests direct emission of marine organics into that mode, probably associated with wind-driven generation of sea-salt particles.

We estimate that about 30%–50%, or 25–40 Tg C/yr, can be associated with SOA formation in the Aitken and accumulation modes through new particle formation or
15 condensation on existing particles. Isoprene produced by plankton is a potentially important precursor of marine SOA (Meshkidze and Nenes, 2006). Since the yield of SOA from isoprene is limited to a few percent the actual organic mass emitted from the ocean surface may be at least an order of magnitude larger than 40 Tg C/y but other SOA precursors with higher yields than isoprene may play an additional role (e.g.,
20 Jacobson et al., 2000). The remaining 35–50 Tg C/yr is probably emitted as primary particles, originating from the organic microfilm at the ocean surface or from dissolved or undissolved organic matter in the ocean water. Given the discrepancy between the simulated and observed coarse mode organic mass this estimate may be a lower limit.

Considering the effect of marine aerosol organics on cloud formation may enhance
25 CDNC up to several times compared to the simulation without this, and R_{eff} is considerably reduced and in better agreement with observations. Our simulations indicate that organics emitted from the ocean surface may significantly contribute also to the seasonality of marine cloud optical properties. This makes the organic fraction of the marine aerosol an important contributor to the optical properties of the natural back-

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ground atmosphere. Representing this aspect in aerosol-climate studies may result in a considerable decrease of the estimated indirect forcing due to anthropogenic aerosol in marine regions compared to current estimates.
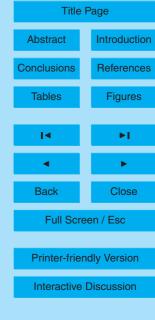
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Table 1. Simulations performed in this study.

simulation [*)]	description
CTRL	The control simulation without ocean organic emissions
Ai	Emission of 25 Tg C/yr globally, internally mixed in the accumulation mode
Ae	Emission of 25 Tg C/yr globally, externally mixed in the accumulation mode with a particle mass of 6×10^{-18} kg.
Ax	As Ae but with a particle mass of 1.5×10^{-18} kg.
Ke	Emission of 25 Tg C/yr globally, externally mixed in the Aitken mode with a particle mass of 6×10^{-19} kg.
KeAi	Emission of 50 Tg C/yr globally, Ke and Ai combined
KeAe	Emission of 50 Tg C/yr globally, Ke and Ae combined
KeAx	Emission of 50 Tg C/yr globally, Ke and Ax combined
Kx	As Ke but with a particle mass of 1.5×10^{-19} kg.
KxAi	Emission of 50 Tg C/yr globally, Kx and Ae combined
KxAe	Emission of 50 Tg C/yr globally, Kx and Ae combined
KxAx	Emission of 50 Tg C/yr globally, Kx and Ax combined
Ke2	Emission of 50 Tg C/yr globally, externally mixed in the Aitken mode with a particle mass of 6×10^{-19} kg.
KeAiCi	As KeAi with additional emission of 25 Tg C/yr globally, internally mixed in the coarse mode

[*)]K, A and C refer to the Aitken accumulation and coarse mode, respectively. Character i refers to aerosol with internally mixed organics, and e and x refer to aerosol with externally mixed organics. New particles formed in x contain 25% of the particulate mass considered in e while four times as many particles are formed.
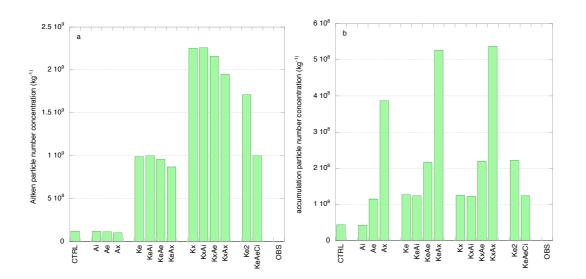
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Fig. 1. Simulated particle concentrations (kg^{-1}) averaged over June, July, August for **(a)** the Aitken mode and **(b)** the accumulation mode.
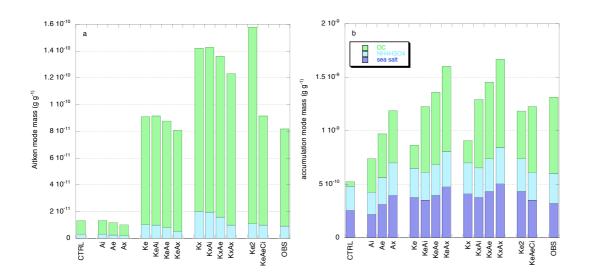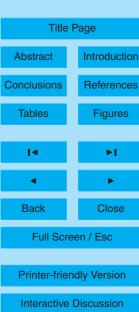
Fig. 2. Simulated aerosol mass and chemical composition (g g^{-1}) averaged over June, July, August for **(a)** the Aitken mode and **(b)** the accumulation mode.

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Fig. 3. Simulated cloud drop number concentration (cm^{-3}) averaged over June, July, August for **(a)** *CTRL*, **(b)** *KeAe*, and **(c)** *KxAx*. The model predicts no or little cloud occurrence over northern Africa.

Fig. 4. Simulated cloud drop effective radius (μm) averaged over June, July, August for **(a)** *CTRL*, **(b)** *KeAe*, and **(c)** *KxAx*.
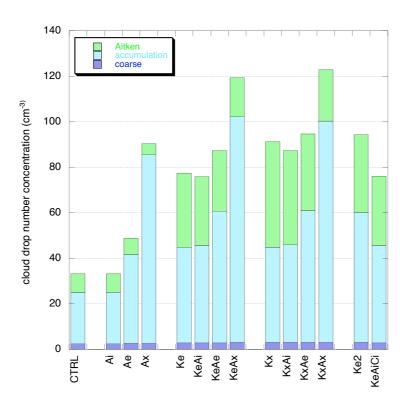
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Fig. 5. Simulated cloud drop number concentration and contribution by the individual aerosol modes (cm^{-3}), averaged over June, July, August for the region 40° N–48° N, 40° W–20° W.
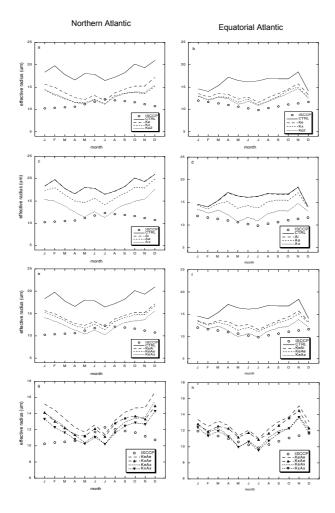
Fig. 6. Simulated monthly averaged cloud drop effective radius and ISCCP data for the regions 40° N–48° N, 40° W–20° W (**a**, **c**, **e**, **g**) and 15° N–25° N, 40° W–25° W (**b**, **d**, g, **h**).

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