

Uncertainties and importance of sea spray composition on aerosol direct and indirect effects

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[1] Although ocean-derived aerosols play a critical role in modifying the radiative balance over much of the Earth, their sources are still subject to large uncertainties, concerning not only their total mass flux but also their size distribution and chemical composition. These uncertainties are linked primarily to their source drivers, which is mainly wind speed, but are also linked to other factors, such as the presence of organic compounds in sea spray in addition to sea salt. In order to quantify these uncertainties and identify the larger knowledge gaps, we performed several model runs with online calculation of aerosol sources, removal, and underlying climate. In these simulations, both the direct and indirect aerosol effects on climate are included. The oceanic source of organic aerosols was found to be heavily dependent on the sea-salt parameterization selected. For only a factor of 2 change in assumed fine-mode sea-salt size, a factor of 10 difference in mass emissions was calculated for both sea salt and primary oceanic organics. The annual emissions of oceanic organics were calculated to range from 7.5 to 76 Tg yr⁻¹. The model's performance against remote oceanic measurements was greatly improved when including the high estimates of organics. However, the uncertainty could not be further reduced by bulk sea-salt measurements alone since most parameterizations tested agree reasonably well with measurements of both the (coarse-mode-dominated) sea salt and aerosol optical depth due to large changes in lifetime and optical properties of aerosols when different aerosol sizes are used.

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1. Introduction

[2] The ocean, which covers two thirds of the Earth's surface, is a major source of atmospheric aerosols. These particles affect Earth's radiative balance, both by scattering of the incoming solar radiation (aerosol direct effect), and by modifying cloud properties which in turn affect solar radiation (aerosol indirect effect). The latter is of particular importance in the remote atmosphere since the aerosol indirect effect is very sensitive to background atmosphere aerosol-cloud interactions [Pierce and Adams, 2009]. Despite the global oceans' large surface area and importance, there are still very large uncertainties associated with its source contribution to the global aerosol budget. It is generally acknowledged though that the ocean produces sea spray as a result of bubble

bursting, a mechanism which is closely linked with surface wind speed [Monahan *et al.*, 1986]. Other mechanisms that form aerosols, like direct tearing of spray from the wave tops [Monahan *et al.*, 1983], are not included in this parameterization. The total annual fluxes of sea salt, the major component of sea spray, has been estimated to be around 5000 Tg yr⁻¹ [Lewis and Schwartz, 2004] with a factor of 4 uncertainty based on both model results and a compilation of measurements, while the *Intergovernmental Panel for Climate Change (IPCC)* [2001] suggested 3340 Tg yr⁻¹ with an uncertainty of 80%. Sea-salt fluxes in models also vary by a large degree, from 1800 to 22,000 Tg yr⁻¹ [Textor *et al.*, 2006], while Dentener *et al.* [2006] suggested 7925 Tg yr⁻¹ for model calculations. A recent overview of uncertainties in sea spray aerosol mass production fluxes, including the effect of different sea spray aerosol source functions, was given in de Leeuw *et al.* [2011]. A reason for this large uncertainty can be attributed to several factors, including the uncertainty due to the source mechanisms, uncertainties due to the heterogeneity of different source regions which cannot easily be addressed by the current coarse-grid global models, as well as uncertainties in model calculations and parameterizations. Indeed, de Leeuw *et al.* [2011] reviewed that sea spray source functions provide significantly different sea spray fluxes, which can be as high as a factor of 2, affecting both sea salt and marine organics [Albert *et al.*, 2012].

[3] Among the different model parameterizations published in the literature, the method of Monahan *et al.* [1986],

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refined by *Gong* [2003] and further modified by *Jaeglé et al.* [2011], is one of the most popular ones in the modeling community. Still, due to the very strong dependence of the sea-salt source on wind speed, small wind speed changes result in very large uncertainties in the total sea salt fluxes, even within models that use identical parameterizations. Additionally, different model assumptions regarding the sea-salt size distribution affect both the total flux and lifetime of sea-salt aerosol. Even worse, measurement techniques make the validation with measurements very challenging, due to different cutoff sizes among sampling techniques and complications that arise from the very high hygroscopicity of sea salt.

[4] Until recently, sea spray aerosol was considered to consist of solely sea salt, especially in model studies. Although a few decades ago it was suggested that the ocean does not only emit sea salt but also organic compounds [*Hoffman and Duce*, 1976, 1977; *Duce et al.*, 1983], it was less than a decade ago when it was widely accepted that the ocean not only emits potentially important amounts of insoluble organic material in the atmosphere, but these organic compounds are being coemitted with sea salt [*O'Dowd et al.*, 2004]. Since then, a number of studies confirmed that sea salt and organic compounds are being coemitted from the ocean [e.g., *Facchini et al.*, 2008a, 2008b; *Russell et al.*, 2011], suggesting that the term sea spray should really be used for the oceanic primary aerosol fluxes instead of sea salt, as also proposed by *de Leeuw et al.* [2011]. *O'Dowd et al.* [2004] reported that 71% of the total submicrometer organic matter measured under clean conditions at Mace Head, Ireland during phytoplankton bloom periods was water insoluble, while *Facchini et al.* [2008b] measured that 94% of submicrometer particles are water insoluble. *O'Dowd et al.* [2008] parameterized the enrichment of sea spray with organic insoluble material, and later *Vignati et al.* [2010] improved that parameterization. *Meskhidze et al.* [2011] developed a parameterization that also takes into account the organic enrichment as a function of particle size. Qualitatively, the more chlorophyll *a* (a proxy of biological activity) is present in the surface of the ocean, the more the organic enrichment of sea spray, and this effect decreases with increasing emitted aerosol size.

[5] Very few model studies exist to date that include this organic enrichment [*Spracklen et al.*, 2008; *Roelofs*, 2009; *Gantt et al.*, 2009, 2011; *Vignati et al.*, 2010; *Myriokefalitakis et al.*, 2010; *Long et al.*, 2011; *Meskhidze et al.*, 2011]. These present a very wide range of global annual organic fluxes from the ocean, and it is very hard to validate which one of them is the most accurate. The large uncertainties of both the empirical sea spray fluxes and the organic enrichment propagate to the even larger uncertainties in the oceanic organic fluxes, while measurements that can be used to validate and constrain the models are extremely scarce. *Myriokefalitakis et al.* [2010] included a secondary source of organic aerosols from marine precursors (other than methanesulfonic acid (MSA)), and found that their contribution to the global marine organic source is negligible. This source will not be studied here. The present study quantifies where the most significant uncertainties lie, and demonstrates the importance of the presence of organic aerosols in sea spray for both the sea-salt lifetime and climate implications.

2. Model Description

[6] The climate model used, driven by fixed climatological sea surface temperatures, is an updated version of the GISS modelE GCM [*Schmidt et al.*, 2006] that will be used for the Fifth Assessment Report of the IPCC, with $2^\circ \times 2.5^\circ$ resolution and 40 hybrid sigma levels to 0.02 hPa. It includes gas phase chemistry [*Shindell et al.*, 2003], aerosols [*Koch et al.*, 2006, 2007; *Miller et al.*, 2006], gas-aerosol phase interactions [*Bell et al.*, 2005] and heterogeneous chemistry [*Bauer and Koch*, 2005; *Bauer et al.*, 2007], coupled with the model's climate (see *Schmidt et al.* [2006] and subsequent updates) and CMIP5 emissions [*Lamarque et al.*, 2010]. The model also includes secondary organic aerosol production (K. Tsigaridis *et al.*, manuscript in preparation, 2012), as described by *Tsigaridis and Kanakidou* [2007] and references therein. Aerosols affect climate via the direct [*Koch et al.*, 2006] and indirect effects [*Menon et al.*, 2008, 2010], and gas phase chemistry by affecting photolysis rates [*Bian et al.*, 2003]. Sea surface temperature (SST) and sea ice extent is the climatological monthly varying mean compiled by *Rayner et al.* [2003], averaged over the years 1996–2004. These fields are interpolated daily using a quadratic scheme that preserves the monthly mean value.

[7] There are currently two aerosol modules in GISS modelE. One is the mass-based scheme, where aerosols are treated as externally mixed and have prescribed size and properties [e.g., *Koch et al.*, 2006, 2007], with the exception of sea salt that has two distinct size classes, and dust that has four size classes and can be coated by sulfate and nitrate aerosols [*Bauer and Koch*, 2005]. The other is the aerosol microphysics module MATRIX [*Bauer et al.*, 2008] where explicit treatment of the evolution of aerosol size, number and mixing state with time is included. For the present study the mass-based scheme was used. The oceanic organic source described here will be included in the aerosol microphysics scheme in the future. All results presented here are 10 year means with year 2000 emissions, after 1 year of spin-up.

[8] The version of the model used only includes the first indirect effect, which is the effect of aerosols on cloud droplet number concentration (CDNC) and thereby on cloud albedo, cloud effective radii and radiation. Our treatment of the aerosol indirect effect is similar to the one used in *Menon et al.* [2008], but with some changes as described in *Menon et al.* [2010]. CDNC is obtained using a prognostic equation [*Morrison and Gettelman*, 2008] that includes source terms: newly nucleated CDNC depend on aerosol number concentration and cloud-scale turbulence [*Lohmann et al.*, 2007]. The aerosol number concentration is obtained from the aerosol mass for a lognormal distribution as described in *Menon and Rotstayn* [2006]. Sink terms include droplet loss through autoconversion, contact and immersion freezing [*Morrison and Gettelman*, 2008].

2.1. Sea Spray Production

[9] Several sea spray source parameterizations were tested. The original one was described by *Koch et al.* [2006] and is based on *Monahan et al.*'s [1986] empirical formulation, which allows the calculation of the number of sea spray particles emitted as a function of wind speed at 10 m height and aerosol size at 80% relative humidity. We initially tested

this formulation against three others: the statistically based source by *Lewis and Schwartz* [2004], an updated version of *Monahan et al.* [1986] by *Gong* [2003], and a very recent one by *Jaeglé et al.* [2011] that uses the *Gong* [2003] formulation but also includes a dependence on sea surface temperature (Figure 1). All approaches except *Lewis and Schwartz* [2004] agree reasonably well with each other in the size range where relevant measurements were available at the time these formulations were being developed, but *Monahan et al.* [1986] calculates very high sea spray aerosol number production at sizes below $0.1\ \mu\text{m}$ in radius. It should be noted though that the *Monahan et al.* [1986] parameterization was developed for particles in the $0.2\text{--}10\ \mu\text{m}$ size and should only be used within this range. On the other hand, the *Lewis and Schwartz* [2004] approach gives smaller sea spray number fluxes compared to the other three for submicrometer particles and larger for particles greater than $3\ \mu\text{m}$ in radius. An important consequence is that the total mass of the submicrometer particles calculated by the *Lewis and Schwartz* [2004] formulation will be significantly smaller than the other three, and the resulting total sea-salt mass will be greatly enhanced since coarse particles dominate the total aerosol mass. Recently, *Clarke et al.* [2006] and *Keene et al.* [2007] made measurements that span to smaller sizes, but these do not necessarily apply to remote oceanic regions since the former was performed at coastal breaking waves and assumed that their findings scale with open ocean conditions, and the latter was conducted in the laboratory. Extrapolating from such studies to global oceanic conditions, although it might prove in the future to be valid, at present has to be treated with extreme caution.

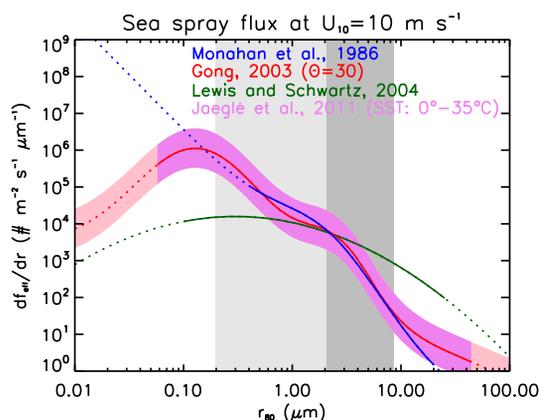


Figure 1. Aerosol number flux of sea spray as a function of size at 80% relative humidity and wind speed at 10 m height $U_{10} = 10\ \text{m s}^{-1}$. The lines represent three of the parameterizations studied here: blue, *Monahan et al.* [1986]; green, *Lewis and Schwartz* [2004]; red, *Gong* [2003] using the parameter $\Theta = 30$ as in *Vignati et al.* [2010]. Pink shading represents the *Jaeglé et al.* [2011] parameterization range for sea surface temperatures from 0°C to 35°C . Solid lines show the range where the corresponding formulations were meant to be used. Light gray shading presents the fine-particle range used by the model for the SS1 simulations (see text), and dark gray shading represents the coarse-particle range for the same simulations.

[10] In the model, we assume that sea spray consists of two modes: a submicrometer one (dry radii from 0.1 to $1\ \mu\text{m}$; light gray shading in Figure 1) with dry effective radius of $0.44\ \mu\text{m}$, and a supermicrometer one (dry radii from 1 to $4\ \mu\text{m}$; dark gray shading in Figure 1) with dry effective radius of $1.7\ \mu\text{m}$. For the hygroscopic growth of particles, we used the *Gerber* [1988] formulation for sea salt particles, in the absence of other methods that take into account the occurrence of primary marine organic compounds in sea spray. The resulting present-day annual mass fluxes per sea spray mode are presented in Table 1 and are compared with previous studies. The comparison between the different model estimates from the literature cannot be direct since different models have different assumptions for the sea-salt size representation, as noted in Table 1. This is evident from our study as well since changing the dry effective radius of fine sea salt by a factor of 2 (see sections 2.2 and 3.1) leads to a factor of 10 change in their mass flux, with only small changes to their lifetime. The effect these changes have on AOD and CDNC, which are calculated to be small, will be discussed later. The coarse-mode flux calculated presents less variability with assumed size, but the size representation in models is not identical, again making a direct comparison difficult.

[11] An additional simulation was performed and is also listed in Table 1, using the offline AEROCOM emissions of sea salt [*Dentener et al.*, 2006], derived from *Gong* [2003]. Note, however, that the AEROCOM coarse-mode emissions are for the range from 1 to $10\ \mu\text{m}$ dry radius (dry effective radius of $5\ \mu\text{m}$).

2.2. Alternative Sea Spray Size Parameterization

[12] In order to study the effect of the sea-salt size parameterization in the model's results, three different sea spray size assumptions have been used along with the *Gong* [2003] source function. The first is the default of the GISS modelE, which has fine sea spray with dry radii ranging from 0.1 to $1\ \mu\text{m}$ (dry effective radius of $0.44\ \mu\text{m}$) and coarse sea spray with dry radii ranging from 1 to $4\ \mu\text{m}$ (dry effective radius of $1.7\ \mu\text{m}$). This assumption was used for all sea spray formulations appearing in Figure 1 and is named SS1 throughout the text. In order to calculate the total mass flux from the number fluxes presented in Figure 1, we integrated over the prescribed sea-salt size range of the model. The second assumption, SS2, has the same fine sea spray representation as in SS1, but its coarse-mode dry radius extends to $10\ \mu\text{m}$ (dry effective radius of $5\ \mu\text{m}$), for consistency with the *Dentener et al.* [2006] data set. The third assumption, SS3, has almost the same aerosol size representation as in *Jaeglé et al.* [2011] and a very similar to the *Meskhidze et al.* [2011]: fine sea spray with dry radii ranging from 0.1 to $0.5\ \mu\text{m}$ (dry effective radius of $0.2\ \mu\text{m}$) and coarse sea spray with dry radii ranging from 0.5 to $4\ \mu\text{m}$ (dry effective radius of $1.7\ \mu\text{m}$). We do not use the very small size sea spray (dry radius of $0.01\text{--}0.1\ \mu\text{m}$) used by *Jaeglé et al.* [2011], an assumption that will not affect the total mass of sea spray, since its contribution is negligible. In addition, measurements over the remote marine ocean have shown that the larger particles within the fine sea-salt mode as well as the coarse mode dominate light scattering [*Quinn et al.*, 1998]. Still, since number production fluxes are more important globally in terms of the aerosol indirect

Table 1. Sea Spray Sources and Sinks as Calculated by the Different Approaches Used^a

Source (Tg yr ⁻¹)		Lifetime (days)		Reference
Fine	Coarse	Fine	Coarse	
<i>Sea Salt</i>				
24 ^b	6273 ^c			<i>Vignati et al.</i> [2010]
31 ^b	6259 ^c			<i>Myriokefalitakis et al.</i> [2010]
	1500 ^d			<i>Long et al.</i> [2011]
116 ^c	3427 ^f			<i>Meskhidze et al.</i> [2011]
59 ^g	2229 ^h	1.03 ^g	0.5 ^h	<i>Jaeglé et al.</i> [2011] (SST simulation)
471	1916	1.36	1.11	This work, using <i>Monahan et al.</i> [1986]
252	12210	1.32	1.10	This work, using <i>Lewis and Schwartz</i> [2004]
346	7044 ⁱ	1.43	0.42 ⁱ	This work, using <i>Dentener et al.</i> [2006]
357	2327	1.36	1.12	This work, using <i>Gong</i> [2003], SS1
284	2335	1.48	1.12	This work, using <i>Gong</i> [2003], SS1, plus organics replacing part of sea spray
360	2341	1.44	1.11	This work, using <i>Gong</i> [2003], SS1, but organics are added to sea spray
358	5100 ^j	1.37	0.41 ⁱ	This work, using <i>Gong</i> [2003], SS2
288	5179 ⁱ	1.49	0.41 ⁱ	This work, using <i>Gong</i> [2003], SS2, plus organics replacing part of sea spray
359	5117 ⁱ	1.47	0.41 ⁱ	This work, using <i>Gong</i> [2003], SS2, but organics are added to sea spray
36 ^j	2659 ^h	1.38 ^j	1.12 ^h	This work, using <i>Gong</i> [2003], SS3
28 ^j	2658 ^h	1.49 ^j	1.11 ^h	This work, using <i>Gong</i> [2003], SS3, plus organics replacing part of sea spray
36 ^j	2673 ^h	1.47 ^j	1.12 ^h	This work, using <i>Gong</i> [2003], SS3, but organics are added to sea spray
310	2019	1.33	1.11	This work, using <i>Jaeglé et al.</i> [2011], SS1
246	2026	1.42	1.12	This work, using <i>Jaeglé et al.</i> [2011], SS1, plus organics replacing part of sea spray
315	2047	1.40	1.11	This work, using <i>Jaeglé et al.</i> [2011], SS1, but organics are added to sea spray
<i>Oceanic Organic Aerosols</i>				
1.4	12.6			<i>Duce et al.</i> [1983]
5.5 ^j	2.5 ^k			<i>Spracklen et al.</i> [2008]
	75 ^k			<i>Roelofs</i> [2008]
4.1 ^l	27.2 ^l			<i>Gantt et al.</i> [2009]
8.2	9	2.2		<i>Vignati et al.</i> [2010]
7-8		4.5		<i>Myriokefalitakis et al.</i> [2010]
	29 ^k			<i>Long et al.</i> [2011]
7.9-9.4 ^c	18.6-23 ^f			<i>Meskhidze et al.</i> [2011]
2.8-5.6 ^k				<i>Gantt et al.</i> [2011]
20.4				<i>Albert et al.</i> [2012]
75		1.53		This work, using <i>Gong</i> [2003] plus organics replacing part of sea spray
76		1.48		This work, using <i>Gong</i> [2003], but organics are added to sea spray
76	i	1.54	i	This work, using <i>Gong</i> [2003] plus organics replacing part of sea spray
75	i	1.50	i	This work, using <i>Gong</i> [2003], but organics are added to sea spray
7.5 ^h	h	1.52 ^h	h	This work, using <i>Gong</i> [2003] plus organics replacing part of sea spray
7.5 ^h	h	1.48 ^h	h	This work, using <i>Gong</i> [2003], but organics are added to sea spray
65		1.48		This work, using <i>Jaeglé et al.</i> [2011] plus organics replacing part of sea spray
66		1.44		This work, using <i>Jaeglé et al.</i> [2011], but organics are added to sea spray

^aThe dry radius size range of fine sea salt is 0.1–1 μm, and it is 1–4 μm for the coarse sea salt, unless otherwise noted.

^bSea-salt dry radius size range is 0.05–0.5 μm.

^cSea-salt dry radius size range is larger than 0.5 μm.

^dSum of eight size bins.

^eSea-salt dry radius size range is 0.15–0.5 μm.

^fSea-salt dry radius size range is 0.5–5 μm.

^gSea-salt dry radius size range is 0.01–0.5 μm.

^hSea-salt dry radius size range is 0.5–4 μm.

ⁱSea-salt dry radius size range is 1–10 μm.

^jSea-salt dry radius size range is 0.1–0.5 μm.

^kUnits are Tg C yr⁻¹.

^lValues are 2.9 and 19.4 Tg C yr⁻¹ for fine and coarse sea salt, respectively, converted from organic carbon (OC) to organic matter (OM) by using OM/OC = 1.4 (N. Meskhidze, personal communication, 2011).

effect, our study has to be viewed as a lower limit with regard to the impact of submicrometer aerosol on climate.

2.3. Sea Spray Composition

[13] With the exception of the modeling studies listed in Table 1, all other studies to our knowledge that include oceanic aerosols assume that sea spray consists solely of sea salt. As suggested almost 30 years ago [*Hoffman and Duce*, 1976, 1977; *Duce et al.*, 1983] and is well established by now, this is not the case; sea spray is a complex mixture of sea salt, water and organic compounds originating from the ocean [e.g., *O'Dowd et al.*, 2004; *Facchini et al.*,

2008a, 2008b; *Russell et al.*, 2011]. A weak correlation between chlorophyll *a* levels and an organic enrichment factor of sea spray has been proposed by *O'Dowd et al.* [2008] and was revised (correlation coefficient 0.3) by *Vignati et al.* [2010]. Although probably not the optimal one, chlorophyll *a* is widely used as a proxy for calculating the oceanic fluxes by various groups, due to its availability of data on the global scale. *Vignati et al.* [2010] used chlorophyll *a* to constrain the fluxes directly, while *Long et al.* [2011] used it to constrain the organic material in the ocean. This parameterization is suitable for a global model because it provides the composite organic enrichment at various aging times

since during sampling it is not possible to separate the fresh from the aged marine organics. In the future this parameterization will be improved, as more detailed parameterizations will become available.

[14] In order to include this approach in the GISS modelE, the chlorophyll *a* measured by SeaWiFS was used to calculate the organic enrichment of sea spray as described by Vignati *et al.* [2010] by applying it to both the Gong [2003] and the Jaeglé *et al.* [2011] approaches mentioned in section 2.1. The organics committed with sea salt in the sea spray were assumed to be internally mixed with sea salt, in contrast to all other aerosol modes in GISS ModelE, in order to capture more accurately the impact of the mixed sea salt/organics modes on aerosol removal, lifetime and impact on clouds. This results in having lower solubility when compared to pure sea salt, which depends on the mass fraction of sea spray aerosol that consists of insoluble organic material. The solubility decrease increases sea salt's lifetime and reduces CDNC. This reduction is not very strong since sea salt has extremely high hygroscopicity. Indeed, Ovadnevaite *et al.* [2011] measured at Mace Head sea spray aerosol enriched in organic matter that had high CCN activation efficiency. The mean annual sea salt and organic aerosol fluxes calculated are listed in Table 1 and are compared with other studies from the literature, while the changes in CDNC will be discussed in section 4.2. The enhancement of the organic enrichment with decreasing submicrometer particle size [Facchini *et al.*, 2008b; Meskhidze *et al.*, 2011] was not taken into account. Two sets of simulations were performed: in the first, organics replace sea salt on sea spray (denoted MPOA), while in the second they are being added on top of the calculated sea-salt flux (denoted MPOA+). In all cases, the number fluxes of sea spray did not change.

3. Comparison With Measurements

3.1. Sea Salt

[15] The parameterizations tested in the present work were compared against the University of Miami data set

(J. Prospero and D. Savoie, personal communication, 2010). The measurements present the climatology of sea salt over several years of measurements at various oceanic locations around the world (Figure 2). The results of the comparisons of this data set with the model's calculated climatology at the surface (monthly mean data averaged over 10 years, after a year of spin-up) for each of the several parameterizations tested here are shown in Figure 3, the seasonality of the individual stations is presented in Figure 4, and the seasonality of wind speed against the National Centers for Environmental Prediction (NCEP) reanalysis data [Kalnay *et al.*, 1996] is shown in Figure 5.

[16] When comparing the station data (both wind speed and sea-salt concentrations) at the individual stations shown in Figure 3 and Figure 4, it is evident that the seasonalities of sea-salt concentrations are strongly linked with the seasonality of wind speed calculated by the model. This is expected since the sea spray fluxes are a strong function of wind speed. The larger variability on sea-salt concentrations are due to the different removal mechanisms which are related to differences in precipitation and the size assumptions in the different model simulations. The correlation in general is poor, which is something that appears also in previous modeling studies [e.g., Stier *et al.*, 2005; Jaeglé *et al.*, 2011], supporting the fact that global models are still underperforming with regard to sea-salt aerosol concentrations.

[17] In general, the model overpredicts sea salt, while it underpredicts wind speed, which can be due to either excessive sources or insufficient removal, or both. Since we use prescribed size distributions, we cannot accurately validate the removal via sedimentation, which should be explored with the use of a model that includes detailed aerosol microphysics, like the MATRIX that we plan to use in the future. As expected, the SS2 simulations are having an order of magnitude higher sedimentation fluxes when compared with all other ones (3500–5000 versus 300–400 Tg yr⁻¹), with the Lewis and Schwartz [2004] parameterization having 1800 Tg yr⁻¹. In addition, this latter parameterization is having the highest emissions (Table 1) and the highest wet removal

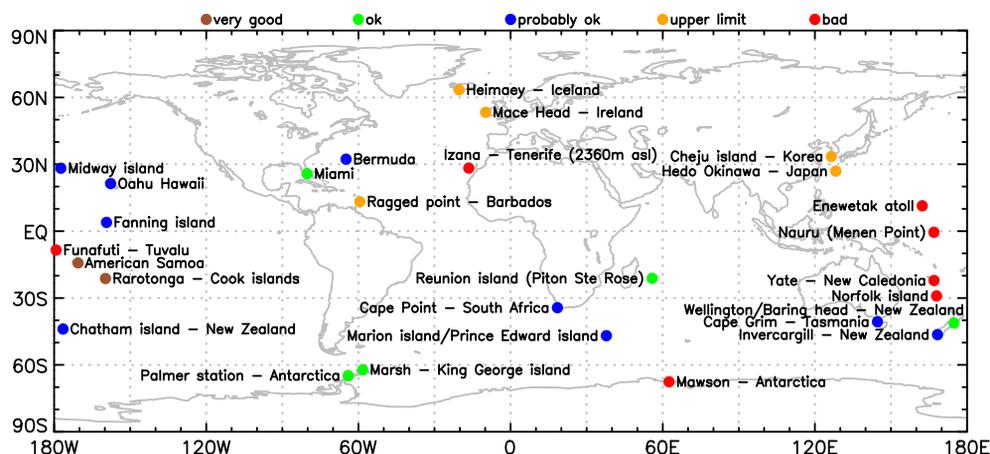


Figure 2. Sampling sites of the University of Miami data set. Different colors represent different quality data (J. Prospero and D. Savoie, personal communication, 2010) as follows: very good, brown; good, green; most probably good, blue; affected by local sources, orange; bad, red. Unless explicitly mentioned, bad measurements were not used in the analysis. Mawson, Antarctica, has been excluded due to persistent very strong katabatic winds, which affect the representativeness of the station when compared to the model's grid. In general, measurements were taken for over a decade per station.

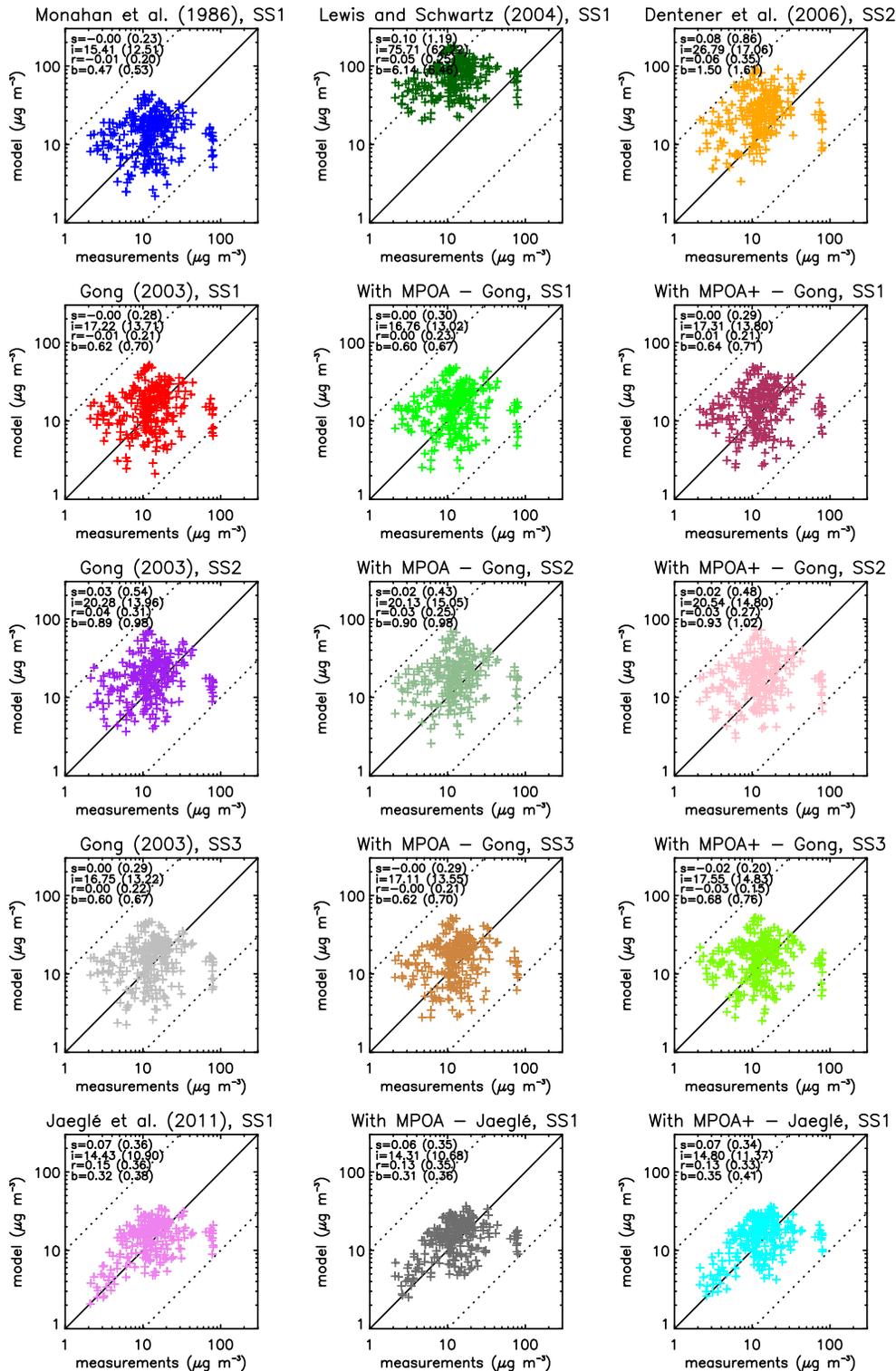


Figure 3. Comparison of the different sea spray source parameterizations with the University of Miami data set. Statistics are the slope of the linear correlation (s), the intercept (i), correlation (r), and mean normalized bias (b). Numbers outside parentheses are for all data, while numbers in parentheses exclude Rarotonga, the group of points that the model strongly underestimates, which are to the far right in each plot. See also Figure 4.

(9000 versus $<2000 \text{ Tg yr}^{-1}$ for all other simulations), which was not strong enough for keeping the total sea-salt burden low, resulting in 27 Tg sea-salt load, compared with the $7\text{--}9 \text{ Tg}$ for all other simulations. This clearly shows the

importance of the size distribution of sea spray calculations, a limitation that all modes without aerosol microphysics have. [18] As expected, the *Lewis and Schwartz* [2004] parameterization produces much higher sea-salt concentrations

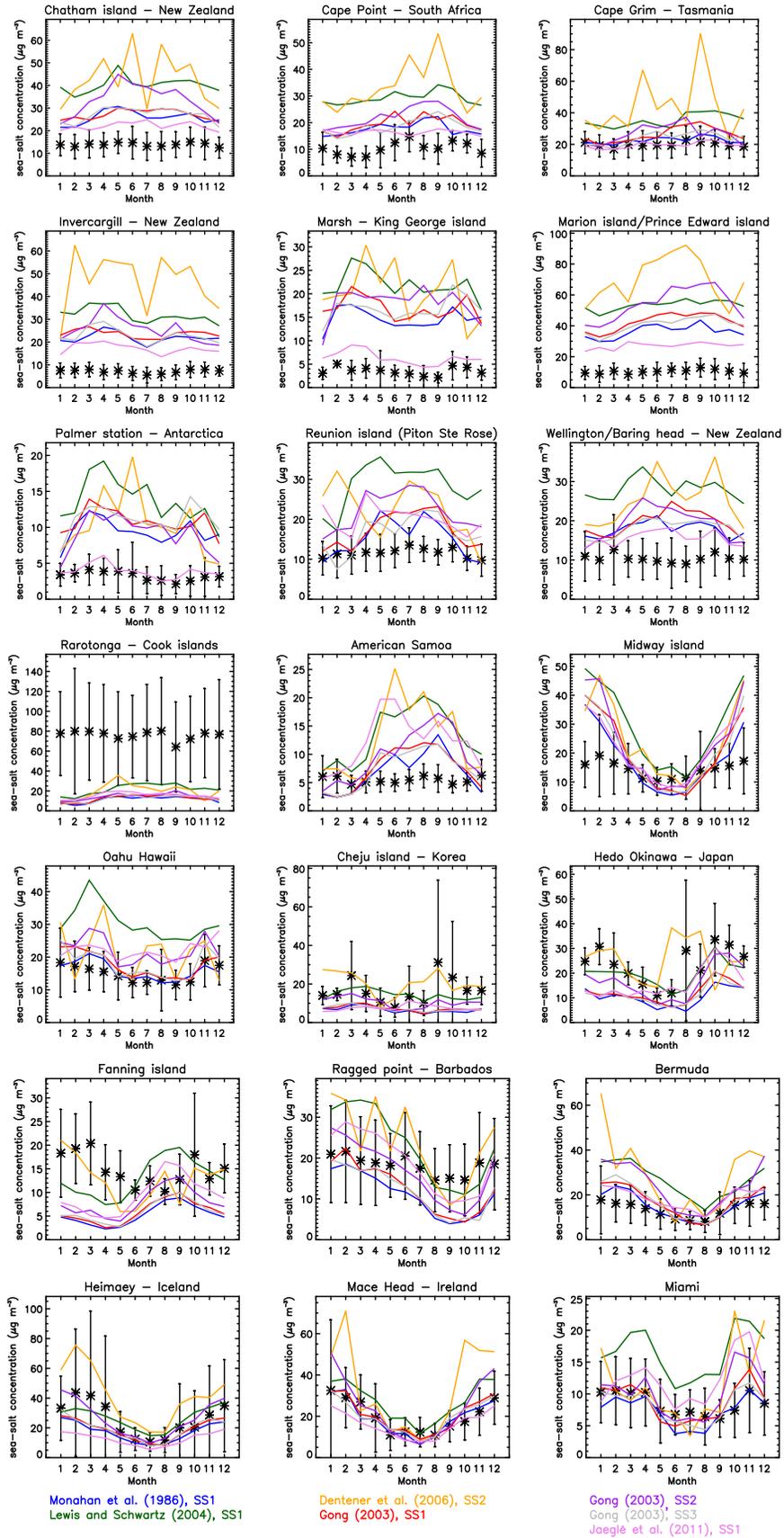


Figure 4. Comparison of the data seasonality (stars) with the models' results. The colors correspond to the ones in Figure 3. For clarity, only the simulations that do not include marine organics are presented. The results of the *Lewis and Schwartz* [2004] parameterization are divided by a factor of 3 (green line).

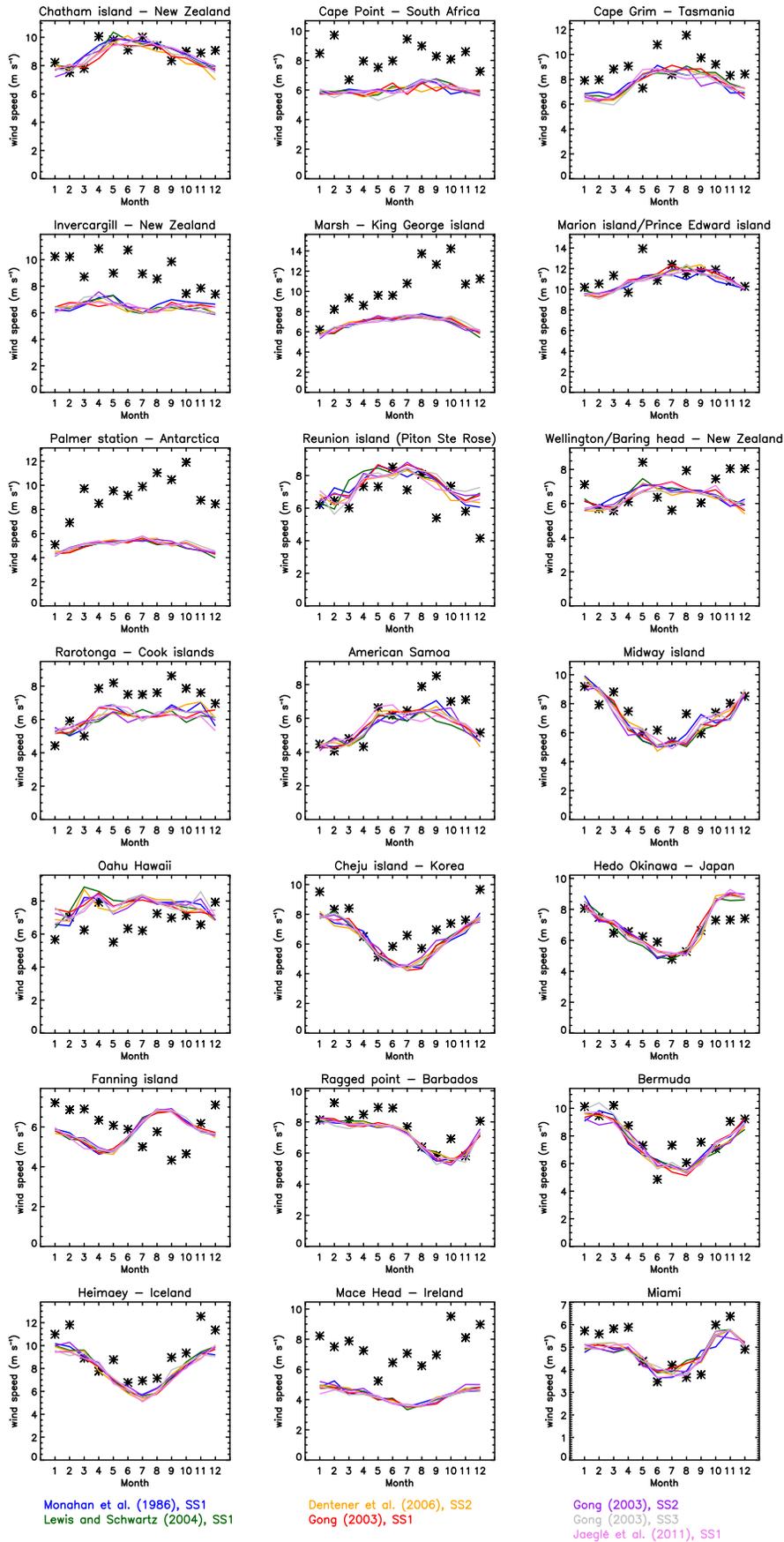


Figure 5. Same as Figure 4, but for wind speed. The stars represent wind speed data as provided by NCEP [Kalnay et al., 1996]. The factor of 3 mentioned in Figure 4 does not apply here.

due to the much larger coarse sea spray flux (results divided by 3 in Figure 4). Excluding the *Lewis and Schwartz* [2004] parameterization, sea-salt concentrations from the SS2 simulation with the *Dentener et al.* [2006] data are the highest at most Southern Hemisphere stations. Interestingly, the *Dentener et al.* [2006] parameterization captures well the seasonality of certain stations, such as Cheju (Korea), Hedo Okinawa (Japan), and Fanning Island, probably due to the better representation of meteorology, since it was constructed with a chemistry transport model which used reanalysis data and not model-calculated winds. On the other hand, the underestimation of wind speed by the model does neither systematically nor exclusively occur in the Southern Hemisphere (Figure 5), where *Dentener et al.* [2006] parameterization appears to be very high. From all other parameterizations and without taking into account the seasonality (see below), *Jaeglé et al.* [2011] is the one that appears to perform best since it is tuned (at least in part) against the same data set we are comparing with. All other parameterizations present similar correlation coefficients against measurements. The *Lewis and Schwartz* [2004] parameterization captures well the exceptionally high concentrations at Rarotonga (a factor of 4 or more higher compared to most other stations), where all other parameterizations are too low. However, given the very large error bars (which represent extremely high interannual variability), it is hard to say whether the *Lewis and Schwartz* [2004] parameterization is really better there, or some other meteorological parameter is responsible for such a variability. The seasonality of wind speed is captured well by the model at that station (correlation of about 0.8 for all simulations) and the general underestimation of about 1 m s^{-1} of its magnitude lies at the lower end of the modeled wind speed underestimation that occurs in several other stations (Figure 5). It appears probable that a year or more from the measurements had exceptionally high winds (and thus sea-salt fluxes) was the cause of the very wide error bars at this station.

[19] One feature that persistently appears in the comparison with measurements is that all simulations tend to overestimate measurements in the Southern Ocean (30°S – 60°S), with the exception of Cape Grim (Tasmania). This is due to the very strong winds calculated by the model, as opposed to reanalysis data, e.g., NCEP [*Kalnay et al.*, 1996]. This overestimation is also reflected in the organic aerosol concentrations at Amsterdam Island, as shown later. Unfortunately, the University of Miami data set only provides monthly means of sea-salt climatologies, which hinders any fine temporal resolution comparison with the model. Although this would have been possible for a comparison of the modeled wind speed against the NCEP reanalysis, it would have little value in lack of fine temporal sea-salt mass concentration comparison. In addition, we should note that reanalysis data is not real measurements; it is model results, heavily based on measurements. In remote marine locations, where meteorological measurements are very scarce, an agreement or disagreement of the model against reanalysis data should be treated with caution.

[20] The overall performance of the different parameterizations based on the mean monthly data is summarized in Figure 6, where every color bar represents the comparison of a single model simulation against all stations and

error bars represent the standard deviation of the statistical measure (mean, root-mean-square error (RMSE), standard deviation, and correlation) of that run among stations. Figure 6 also presents results from the simulations with marine organics (“with MPOA” and “with MPOA+”) which are described later. Most simulations calculate comparable mean sea-salt concentrations at the station locations (mean of station annual mean, Figure 6a), but their seasonal variability is higher than measured (mean of station annual standard deviation, Figure 6b). The correlation with measurements is neither bad nor great, with the seasonal variability of *Jaeglé et al.* [2011], as shown with the standard deviation of the monthly mean values in Figure 6b, being lower when compared with that of *Gong* [2003] and closer to measurements.

3.2. Organic Aerosols

[21] In order to study the marine organic aerosol source, we decided to use either the *Gong* [2003] approach, which is the most widely used by global models, or the newly developed one by *Jaeglé et al.* [2011] in order to study the sea surface temperature dependency. Only the sea spray formulation was modified; the organic enrichment remained the same in all simulations. The calculated differences on organic aerosol concentrations are due to the differences in sea spray fluxes and climate feedbacks, rather than the organic enrichment itself. These simulations were compared against sea-salt measurements (included in the figures already discussed in section 3.1) and show a similar pattern with the case of organics. Only the evaluation against organic aerosol concentrations will be presented here. For that comparison, we used the *Bahadur et al.* [2009] data set, which is a large collection of $\text{PM}_{2.5}$ organic carbon aerosol measurements that took place over the last 30 years. Several of these measurements are urban; many more are remote continental, while marine measurements, mostly from ship campaigns, are also included. The individual marine data were compared with the *Gong* [2003] SS1 model run (Figure 7), assuming an OM/OC ratio of 1.4. It is clear that the inclusion of primary oceanic organics drastically improved the comparison with organic aerosol measurements since the systematic underestimation (but not the considerable scatter) of marine measurements by the model ceased to exist.

[22] Looking at individual marine measurement locations, oceanic organics contribute to an enhancement, sometimes large, of the model’s calculated total OC concentration (Figure 8). In the model, organic aerosol sources other than the primary oceanic ones are terrestrial burning and oxidation products of terrestrial volatile organic compounds (SOC in Figure 8) and oceanic dimethyl sulfide (MSA in Figure 8). Interestingly, Amsterdam island measurements are much lower compared to the calculated ones. This might be due to the strong winds calculated by the model, resulting in high sea spray fluxes (see section 3.1), leading to very high primary oceanic organic fluxes. This does not appear to be the case in other places where measurements exist in the Southern Ocean though, where sea salt was overestimated. Clearly, not only the sea spray fluxes are highly uncertain, but the organic enrichment of sea spray as well. It also has to be noted that only the Amsterdam island measurements are long term [*Sciare et al.*, 2009] and are being strongly

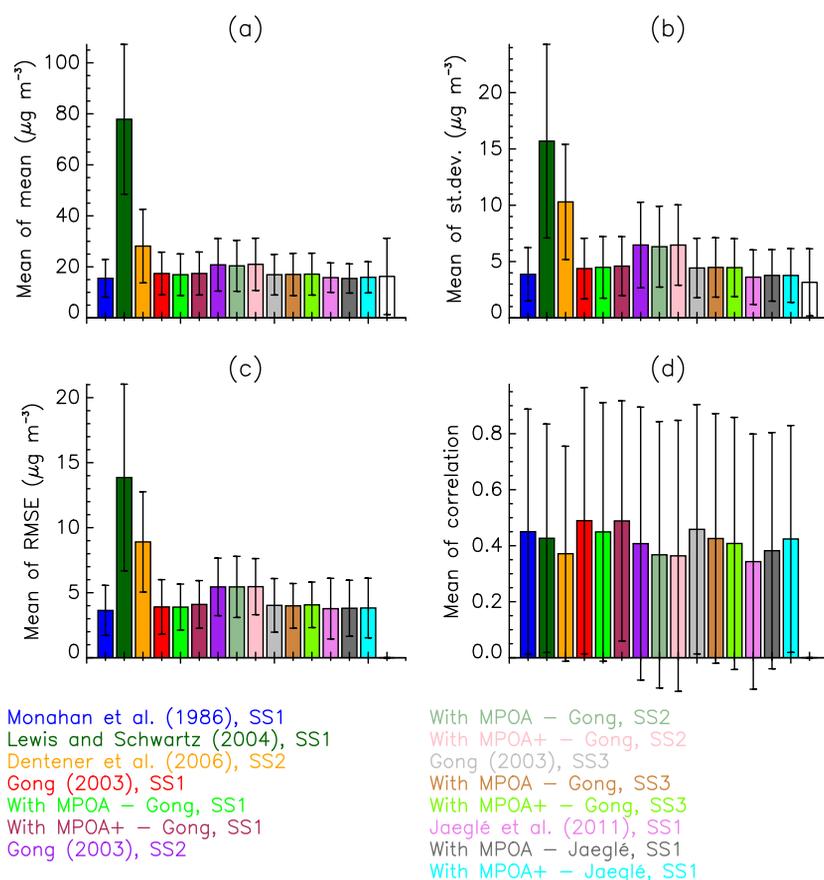


Figure 6. Comparison of the parameterizations' performance (colored bars) with measurements (white bars). Statistics were calculated per station and represent the model's ability to capture the measured seasonality. The mean statistics for all stations per model simulation are presented by the color bars, while the error bars represent the standard deviation among stations per simulation. (a) Mean, (b) standard deviation, (c) root-mean-square error, and (d) correlation.

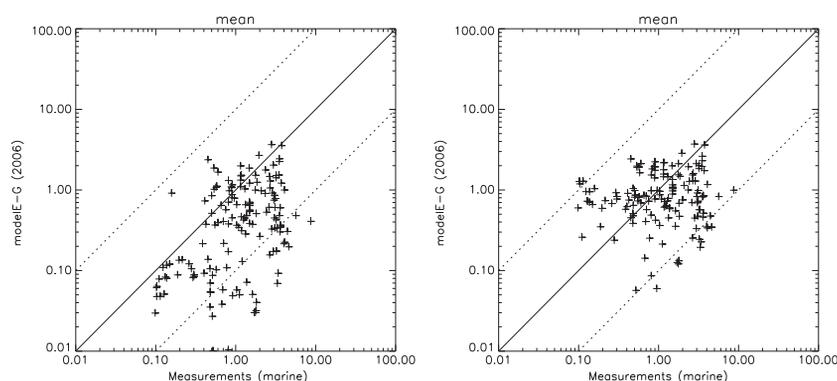


Figure 7. Comparison of marine OC measurements ($\mu\text{g m}^{-3}$) with the model (left) without and (right) with the oceanic organic source, using Gong [2003], SS1.

affected by the seasonality of the marine phytoplankton bloom, which has a strong north–south gradient that falls right on Amsterdam Island and heavily affects chlorophyll levels. The rest of the remote ocean measurements come from individual ship campaigns [Bahadur *et al.*, 2009, and references therein]. Nevertheless, using such a simple parameterization greatly improves the organic aerosols simulated by the model.

[23] In all simulations, the inclusion of organic aerosols does not significantly affect the comparison with sea-salt measurements (Figure 6). This is because the organic enrichment was only applied to fine sea spray, while the total sea-salt mass is dominated by the coarse sea spray fraction.

[24] The published values of the primary oceanic organic aerosol fluxes range by about an order of magnitude (Table 1). Although one might expect that the reason is the

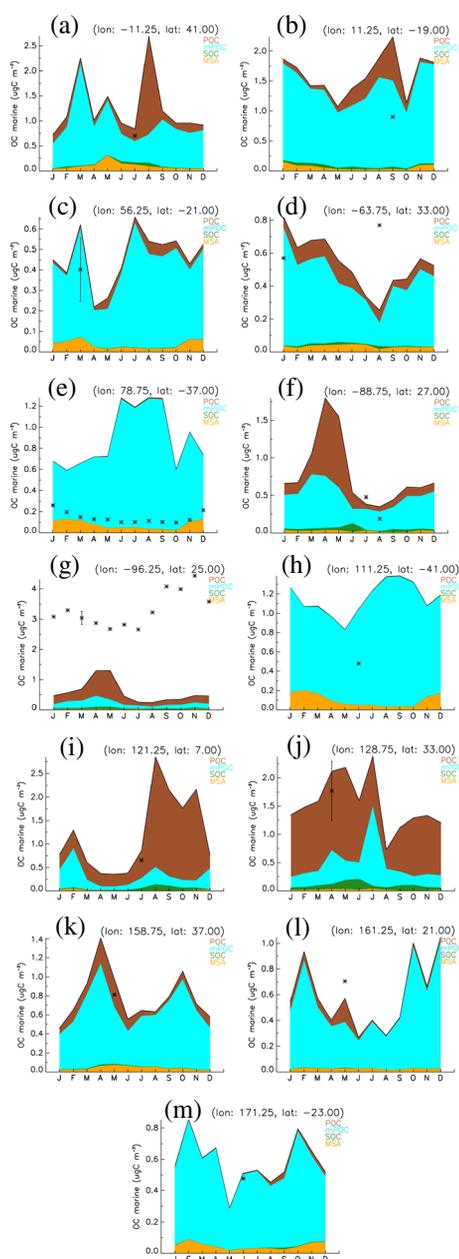


Figure 8. Contribution of the marine primary organic carbon (mPOC, cyan) to total OC at selected locations: (a) west of Portugal, (b) west of Namibia, (c) La Reunion island, (d) Bermuda, (e) Amsterdam Island, (f) Gulf of Mexico (north), (g) Gulf of Mexico (west), (h) southwest of Australia, (i) Philippines, (j) south of South Korea, (k) North Pacific Ocean, (l) North Pacific Ocean, and (m) New Caledonia. The coordinates show the center of the model's box where the measurements were made. The total organic carbon measurements are presented with a star, and the error bar (if any) presents the standard deviation of all measurements in the model's grid when more than one measurement was performed in the same month. Brown is the contribution of primary terrestrial OC (POC), orange is that of methanesulfonic acid (MSA), and green is that of secondary organic carbon (SOC).

weak correlation of chlorophyll *a* with the organic enrichment of sea spray, instead the discrepancy is mostly attributed to the sea spray treatment: when we changed the dry effective radius of fine sea spray by about a factor of 2 (from $0.44 \mu\text{m}$, the SS1 case, to $0.2 \mu\text{m}$, the SS3 case), the primary oceanic organic aerosol source was decreased by a factor of 10 (from 76 to 7.5 Tg yr^{-1} ; Table 1) since it is linked with the fine sea salt, which was also decreased by a factor of 10 (from 284 to 28 Tg yr^{-1} ; Table 1). The comparisons with sea-salt measurements of both SS1 and SS3 are marginal (correlation coefficient 0.23 and 0.21 with MPOA, respectively) and dominated by the coarse fraction, while the comparison of SS2 (larger coarse sea spray) is again about of equal quality (correlation coefficient 0.25 with MPOA), due to the reduced lifetime of coarse sea salt. This comparison does not appear to be conclusive on which sea spray size assumption is the best to follow. Using the organic aerosol measurements to draw conclusions is not safe since the only long-term measurements are present at one single location and suggest that SS1 is too high, but other measurements at many more locations show a much better agreement, but lack temporal information. More simultaneous size-resolved measurements of both sea salt and organic aerosols are clearly needed in remote oceanic regions in order to better understand the sea spray composition and to constrain the models. In addition, the comparison of the oceanic organic aerosols with models has to be treated with caution since different treatments of the sea spray size distribution leads to very different results.

[25] Our model lies at the upper range of oceanic organic fluxes from the literature (Table 1), and this is clearly due to the treatment of the sea spray size distribution. Modifying it to smaller sizes improves the agreement with other modeling studies, but not the comparison with measurements. Although this does not mean that the GISS modelE has a better size assumption for sea spray, it clearly points out that improving the parameterizations can only happen through targeted experiments and measurement campaigns where simultaneous measurements of sea salt and organics will take place. Due to the large area the oceans cover and their distance from inhabited regions, this is a very challenging task that requires considerably more coordinated experiments and field campaigns.

4. Effect on Climate

[26] In the atmosphere, changing the aerosol distribution, which is strongly affected by their sources, affects the radiation distribution via light scattering changes (aerosol direct effect) and cloud changes (aerosol indirect effect). This, in turn, results in changes in meteorology (e.g., wind speed, highly important in the present study) and aerosol wet removal, affecting aerosol distributions in a nonlinear and, frequently, nonintuitive way. These effects are all included in our model.

4.1. Aerosol Optical Depth

[27] Sea salt and oceanic organic aerosols contribute to clear-sky light extinction virtually exclusively via light scattering. Fine particles scatter light more efficiently at visible wavelengths, but coarse particles also play a significant role, due to their much larger aerosol mass. The

clear-sky 10 year mean aerosol optical depth over the Southern Ocean, calculated as described by *Koch* [2001], where marine aerosol is expected to dominate the total AOD, is presented in Figure 9 for all simulations and is compared with satellite retrievals [*Yu et al.*, 2006]. Note that we do use the appropriate sea-salt sizes in the Mie calculations, while the sizes for other aerosol types are typical from the literature [*Koch*, 2001]. We focus on the Southern Ocean because it is probably the only region in the globe that is not affected by intercontinental transport of pollutants, and also is a significant source of marine aerosols, both sea salt and primary organics, due to its vicinity to high marine biological activity areas. Accurate calculation of AOD is necessary in order to assess the direct effect of marine aerosols on climate.

[28] Starting from the coarse-mode sea spray AOD, which in our model is considered to be pure sea salt, using the *Lewis and Schwartz* [2004] formulation a strong overestimation of clear-sky AOD is evident, in line with the mass concentration comparison presented in section 3.1. This confirms that this source function strongly overestimates coarse sea spray production relative to the model removal rates. The different sets of sea spray parameterizations (section 2.2) appear to be insensitive to the coarse-mode AOD to the inclusion or not of the organic enrichment to the fine fraction of sea spray. The coarse-mode AOD is heavily influenced by the selection of the coarse-mode size range. When using much larger sizes (SS2, compared to SS1) the coarse-aerosol lifetime decreases due to increased effective size, and the mode as a whole scatters less efficiently at visible wavelengths due to reduced burden, resulting in lower AOD by more than a factor of 3. When using the same effective size but assuming a different cutoff of the tail of the distributions (SS3, compared to SS1), the coarse mode starts from smaller particle sizes and AOD increases by 13% are being calculated, mostly due to the lifetime and burden increase of coarse sea salt by 14%. *Monahan et al.* [1986] parameterization gives lower AOD compared to the *Gong* [2003] one due to about 18% lower coarse-mode fluxes over the Southern Ocean, while *Jaeglé et al.* [2011] appears lower due to the sea surface temperature effect which results in 13% lower fluxes over the same region.

[29] For the fine mode, the picture is more complicated. The effect of the size assumptions is again evident: for SS1 and SS2 with the *Gong* [2003] parameterization and when the oceanic enrichment does not affect the sea-salt fluxes (cases without MPOA and cases with MPOA+), AOD is fairly constant but lower than the coarse-mode sea-salt AOD. This also applies to the *Dentener et al.* [2006] simulation. *Monahan et al.* [1986] results in calculated AOD over the Southern Ocean are 30% higher due to 32% higher fluxes of the large fine-mode particles (Figure 1) over the same region, while *Jaeglé et al.* [2011] is 32% lower due to the sea surface temperature effect which results in 11% lower fine-mode fluxes. All simulations that include MPOA by replacing sea salt from the sea spray flux calculations have 20% lower fine-mode sea-salt AOD, but the same organic aerosol AOD. Overall, depending on the sea spray parameterization used, the oceanic enrichment enhances the organic aerosol contribution to the total Southern Ocean optical depth by 115% (SS1 with *Gong* [2003] parameterization), 126% (SS2), 11% (SS3), and 83% [*Jaeglé et al.*, 2011].

[30] The AOD of both SS2 and SS3 simulations (0.18 and 0.11, respectively) with the *Gong* [2003] parameterization appear to be closer to satellite retrievals (0.11 and 0.14 [*Yu et al.*, 2006]) over the Southern Ocean. The *Jaeglé et al.* [2011] simulation (with SS1 sizes) produces AOD of 0.13, which lies between both the simulations and the satellite retrievals. Still, it is hard to infer which parameterization is the most appropriate one for use in global models since, as mentioned earlier, the aerosol mass (which is being compared with measurements) is dominated by the coarse mode, while for the AOD both fine and coarse aerosols play a significant role. The parameterization with the effect of sea surface temperature is also not clearly better compared to the other ones that only take into account wind speed due to poorer representation of the seasonality of sea-salt measurements (Figure 6).

4.2. CDNC Changes and Climate Feedbacks

[31] The inclusion of an insoluble component homogeneously mixed with the very soluble sea salt does not affect the overall solubility of the mixed aerosol much, both due to the very high hygroscopicity of sea salt and the (on average) domination of sea salt on sea spray. The lifetime of fine sea

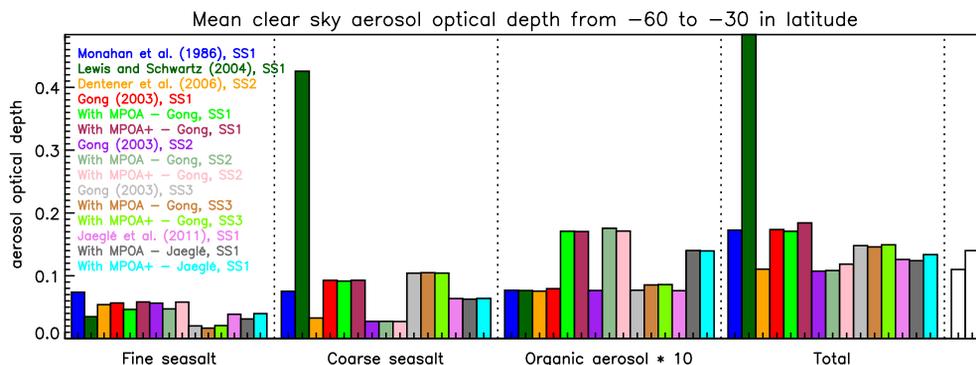


Figure 9. Mean clear-sky aerosol optical depth from 60°S to 30°S in latitude for fine and coarse sea salt, total organic aerosol, and all aerosols. Note that organic aerosol optical depth is multiplied by 10. The last two white columns are Moderate Resolution Imaging Spectroradiometer (MODIS) and Clouds and the Earth’s Radiant Energy System (CERES) A, respectively [*Yu et al.*, 2006].

salt is never changing by more than 10% due to the organic aerosol inclusion on sea spray (Table 1). However, small but significant changes to CDNC are calculated when organic aerosols are emitted with sea spray (Figure 10, top, for “Gong [2003] plus organics” simulation, as compared to “Gong [2003]” in Table 1). These changes, which are mainly present in the Southern Ocean where wind speed and phytoplankton are more prominent, are not attributed to organic aerosols or sea salt alone. There is no surprise in the fact that sea salt is reduced (Figure 10, middle) since part of the sea spray is now also assigned to organic aerosols instead of sea salt alone. It is still an open question whether organics replace sea salt or they are adding mass to sea spray.

[32] On an annual mean basis, wind speed is calculated to decrease almost everywhere due to reduced sea salt concentration (Figure 10, bottom). This is a positive feedback and can also be one of the reasons why sea-salt burden has gone down, other than the presence of organics on sea spray. It is not clear what the mechanism that drives the decrease in wind speed is, but it has to be linked to the energy balance of the atmosphere which is being disturbed when AOD is changing. Interestingly though, looking at the seasonality of these changes instead of the annual means (Figure 11), certain features are observed. The most striking one is that sea salt, on a monthly mean basis, and not only for January and July presented in Figure 11, has both positive

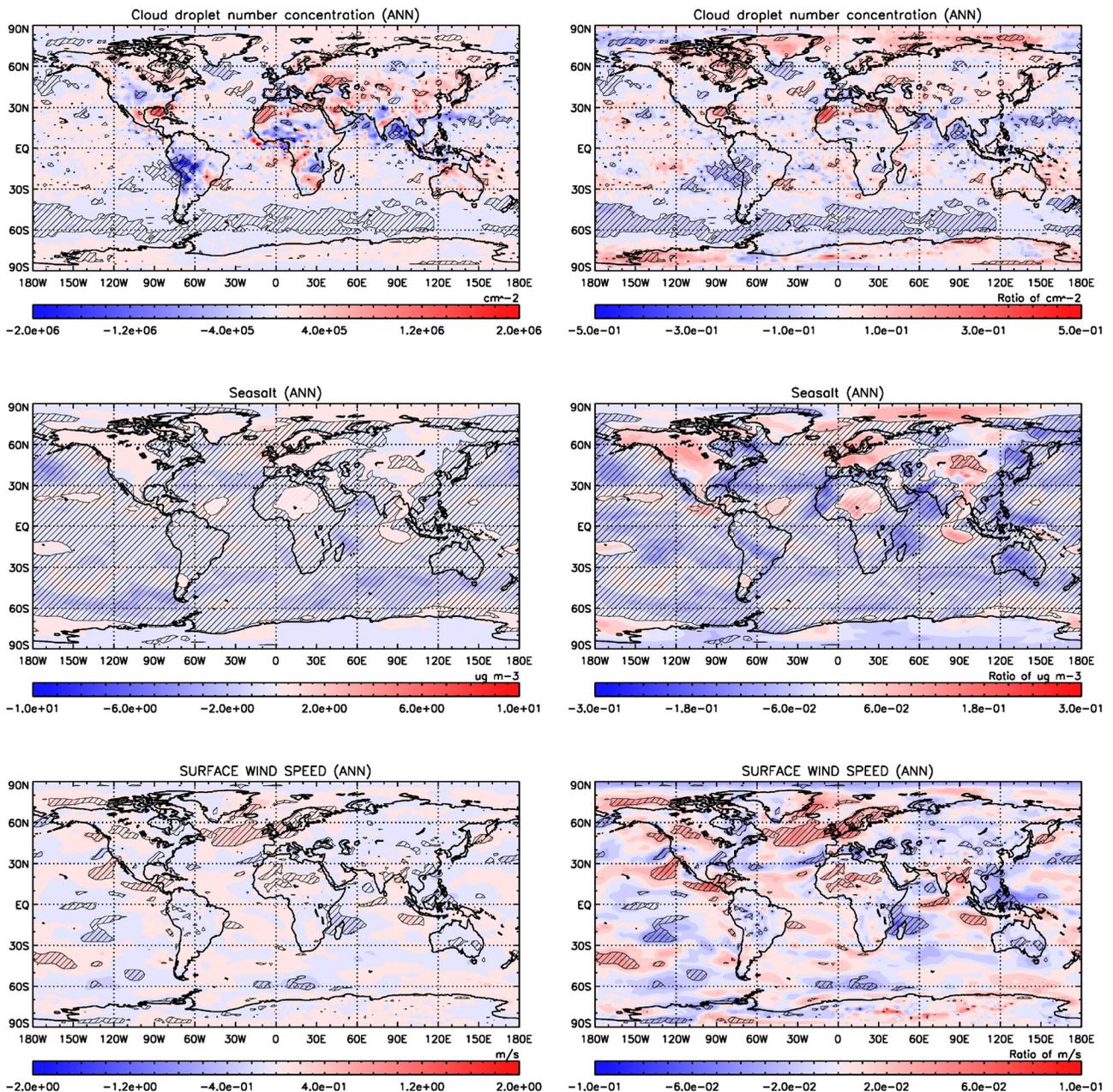


Figure 10. Annual mean change of (top) cloud droplet number concentration (CDNC), (middle) sea salt, and (bottom) surface wind speed changes when sea spray also includes organic compounds: (left) absolute and (right) relative. Hatch areas present 90% or higher confidence level.

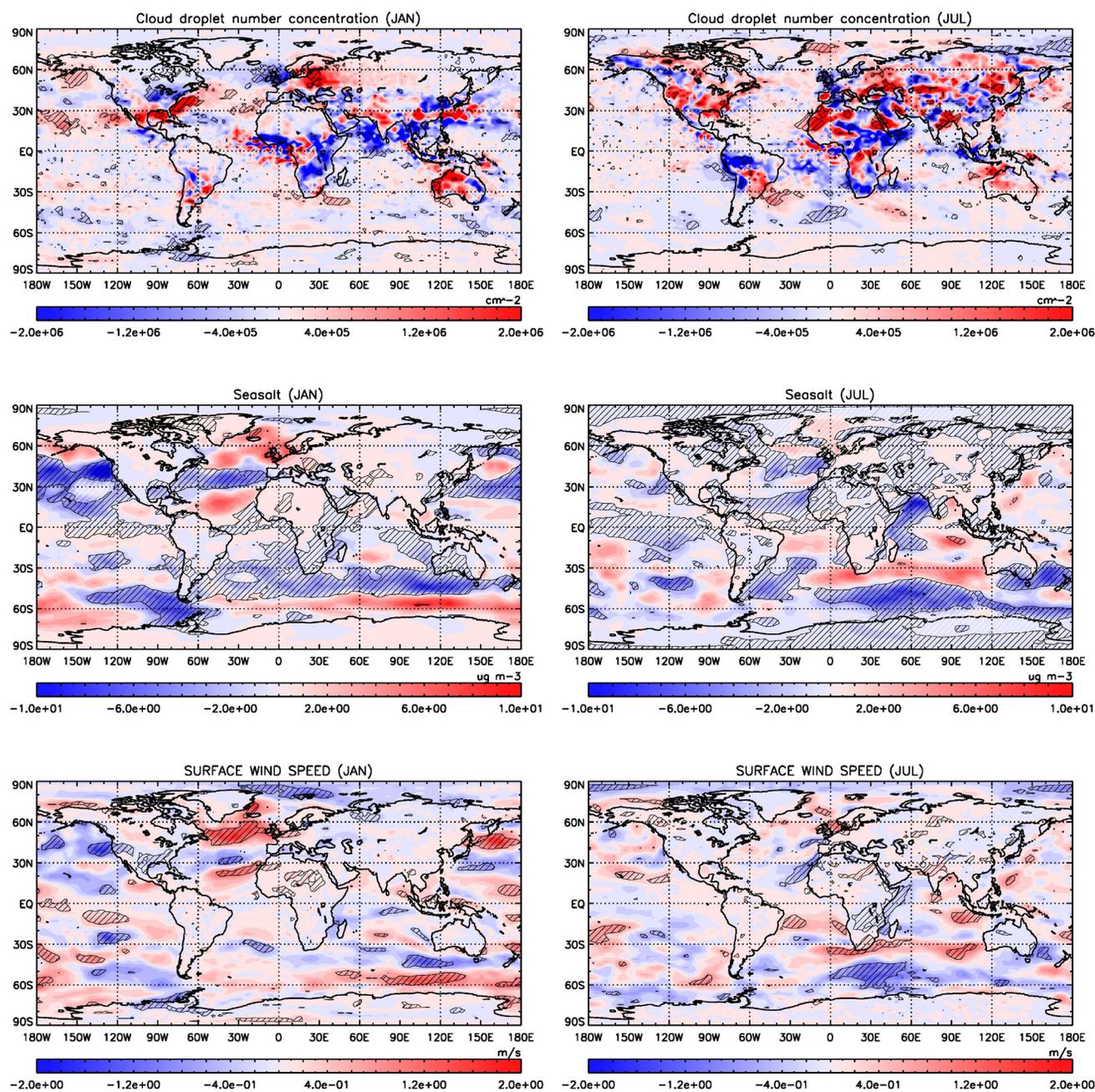


Figure 11. Absolute changes as in Figure 10, but for (left) January and (right) July.

and negative changes to its concentrations. The strong negative ones are always statistically significant (90% confidence level), while the positive ones never are. This applies to all 12 months of the year. Even more interesting is the wind speed: although most of the globe is dominated by negative wind speed changes, only the stronger ones are statistically significant. On the other hand, almost all positive changes appear to be significant for all 12 months (and the annual mean), but not as much as the sea salt changes. The positive surface wind speed changes always coincide with the positive (but not statistically significant) changes of sea-salt concentrations, which appear to be the driver for their increase. The significant CDNC changes appear not to be correlated with any of the two; these changes are driven primarily by the organic aerosol abundance on sea salt and not the sea salt

and/or wind speed changes, at least not as a first-order effect. AOD and CDNC changes are likely the primary driver for the calculated wind speed changes via cloud and radiation changes, but this is outside the scope of the present study.

5. Conclusions and Future Work

[33] The uncertainties related to the primary oceanic aerosol sources, abundance and effect on AOD, CDNC and climate have been discussed. The source function selection was found to strongly affect the total mass of aerosols present in the fine and coarse fractions; the model assumptions regarding the size range of aerosols affect mass fluxes and lifetime; the organic enrichment of sea spray affects aerosol composition, hygroscopicity and lifetime. The selection of

the best parameterization is not easy. More detailed analysis is required with focus on the effect of oceanic aerosols on aerosol optical depth and cloud formation in order to select the proper parameterization. Interestingly, the discrepancy between model studies concerning the marine primary organic aerosol source appears to be attributed mainly due to the sea spray parameterization and not to the (also very uncertain) sea spray organic enrichment. Coordinated studies of both sea salt and organic aerosols are required in order to reduce the uncertainty of the source, composition and effect on climate of oceanic aerosols.

[34] It has to be noted that an interactive climate model should not be seen as the best tool to constrain the efficacy of sea spray production functions since small errors in wind speed strongly affect the sea spray fluxes. This sensitivity may tend to overwhelm temperature or other effects that impact marine aerosol production. Dedicated field studies at a variety of oceanic conditions are needed in order to understand this mechanism and create parameterizations that are applicable for a global model simulation.

[35] The importance of the presence of organic aerosols on sea spray, as well as their size distribution which is extremely important for the coarse particles, appears to affect the model's climate in a nonnegligible way, which also feeds back to the oceanic aerosol source itself. Changing the energy distribution due to changes in optical depth and cloud properties affects the model's meteorology by changing winds, which directly affects oceanic aerosol fluxes themselves, among others. Dedicated studies to these feedbacks are clearly needed to understand and evaluate the importance of these feedback mechanisms.

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