A combined organic-inorganic sea-spray source function

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[1] This study presents a novel approach to develop a combined organic-inorganic sub-micron sea-spray source function for inclusion in large-scale models. It requires wind speed and surface ocean chlorophyll-a concentration as input parameters. The combined organic-inorganic source function is implemented in the REMOTE regional climate model and sea-spray fields are predicted with particular focus on the North East Atlantic. The model predictions using the new source functions compare well with observations of total sea-spray mass and organic carbon fraction in sea-spray aerosol. During winter (periods of low oceanic biological activity), sea-salt dominates the sea-spray mass while in summer (when biological activity is high), water soluble organic carbon contributes between 60–90% of the submicron sea-spray mass. **Citation:** O'Dowd, C. D., B. Langmann, S. Varghese, C. Scannell, D. Ceburnis, and M. C. Facchini (2008), A combined organic-inorganic sea-spray source function, *Geophys. Res. Lett.*, *35*, L01801, doi:10.1029/2007GL030331.

1. Introduction

[2] Primary marine aerosol, or sea-spray, represents one of the most important aerosol species on the global scale as the oceans cover more than 70% of the Earth surface. Sea-spray aerosols contribute significantly to the Earth's radiative budget in terms of scattering of incoming solar radiation (the direct aerosol effect) [*Mulcahy et al.*, 2007], and the modification of cloud micro-physics and radiative properties (the indirect aerosol effect) [*O'Dowd et al.*, 1999]. Estimates for top-of-atmosphere, global-annual radiative forcing due to sea salt are -1.51 and -5.03 Wm^{-2} for low and high emission values, respectively [*Intergovernmental Panel on Climate Change*, 2001] while it is estimated that sea-salt increases cloud condensation nuclei concentrations by even 50% [*Pierce and Adams*, 2006].

[3] Although sub-micron sea-salt occurs in significant number concentrations [*O'Dowd and Smith*, 1993], most attempts to include a submicron component rely on arbitrary extensions of the *Monahan et al.* [1986] source function (see *O'Dowd and de Leeuw* [2007] for a review) although recent improved parameterisations for sub-micron sea-salt are now available from both field [*Clarke et al.*, 2006] and laboratory studies [*Mårtensson et al.*, 2003]. Moreover, there has been a serious omission of the organic aerosol component of sea-spray. It has been recognised for many decades [e.g., *Blanchard*, 1964] that organic matter concentrated at the ocean surface can be entrained into sea-spray through the bubble bursting process, however, this component of sea-spray has been particularly difficult to incorporate into a source function since there is a scarcity of understanding on the factors influencing this process. At this point we should define sea-spray as the hydrated droplets encapsulating dissolved sea-salt and entrained organic matter. In the context of this study, the following references to sea-spray refer to the dry aerosol mass associated with the spray droplets.

[4] Recent studies into marine aerosol physico-chemical properties have, however, resulted in new insights into marine aerosol production mechanisms. For example, *O'Dowd et al.* [2004], *Cavalli et al.* [2004], and *Yoon et al.* [2007] conducted extensive studies on North East Atlantic marine aerosol over a three year period and found that the submicron mode contained a dominant sea-salt contribution to the accumulation mode in winter and a dominant organic contribution to that mode in summer. This contrast was linked to periods of low and high biological activity as shown from comparison with chlorophyll-a concentrations derived from satellite. The predominant organic fraction was water-insoluble organic carbon (WIOC) with properties similar to that expected for organic matter derived from a primary source [*Cavalli et al.*, 2004]. The detailed study by *Yoon et al.* [2007] revealed the seasonal behaviour of the contribution of organic matter to the accumulation mode. In addition to the seasonal pattern observed in the aerosol chemistry, there also was a clear seasonal pattern observed in the aerosol micro-physical properties. In particular, the accumulation mode modal (dry-size) diameter was observed to increase from a winter minimum of 100 nm to a summer maximum of 180 nm. This increase in mean particle size was attributed to a combination of an increase in the mean size of primary-produced sea-spray as organic matter is concentrated in the bubble film and sea-surface temperature changes [*Sellegri et al.*, 2006]. Some of the aerosol mass, comprising of water soluble organic carbon (WSOC) is likely to be produced *via* secondary aerosol formation mechanisms for the water soluble organic carbon (WSOC) component due to photo-chemical oxidation processes associated with VOCs. Given that the water soluble component makes up typically 20–25% of the submicron mass [*Yoon et al.*, 2007], it hence contributes only about 7% to the change in modal diameter size.

[5] The source of WSOC and WIOC was further elucidated by gradient chemical flux measurements conducted at Mace Head during periods of high biological activity (D. Ceburnis et al., unpublished manuscript, 2007) - a clear upward flux was observed for sea-salt aerosol and WIOC and a clear downward flux was observed for non-sea-salt

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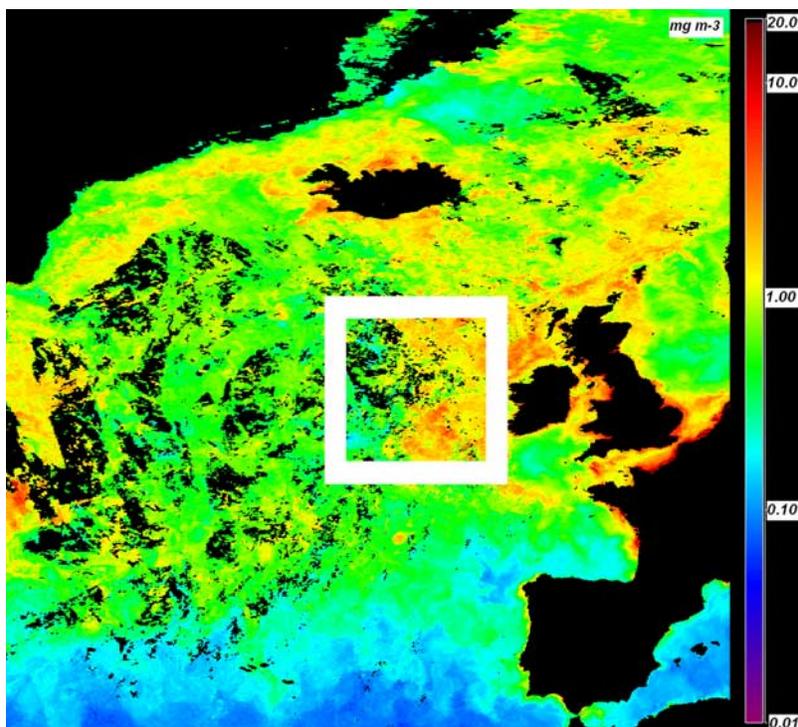
Figure 1. Chlorophyll-a concentrations in the North East Atlantic to the west of Mace Head. Black areas are land masks and cloud-contaminated pixels. The white box marks the grid area 1000 km × 1000 km through which clean air back trajectories pass during transit to Mace Head.

sulphate and WSOC. These results provide strong evidence that the majority of the WSOC is produced *via* secondary aerosol formation while the WIOC is predominantly produced *via* primary, or bubble-mediated production at the open surface.

[6] In terms of sub-micron sea-spray number flux, *Geever et al.* [2005] conducted the first direct flux measurements of sub-micron sea-spray over the Atlantic Ocean and found a strong dependency of flux on wind speed, as expected. Moreover, they found that approximately 50% of the number flux lay in the Aitken mode (10–100 nm) and 50% in the accumulation mode (100 nm–500 nm). The above results are brought together in this study to provide a combined organic-inorganic accumulation mode sea-spray source function for use in large scale models.

2. Methodology

[7] The most detailed aerosol chemical record over the N.E. Atlantic exists for Mace Head where a seasonal pattern linking both chlorophyll-a, used as a surrogate for oceanic biological activity, and WIOC [*Yoon et al.*, 2007] has been observed. Therefore, the correlation between chlorophyll-a and WIOC was explored as a method of estimating the impact of biological activity on the fractional contribution of WIOC to the sea-spray aerosol. For each clean air sample, over a 3 year period, where high resolution chemical aerosol data are available, the average monthly chlorophyll-a concentration (taken from MODIS) in oceanic waters upwind of Mace Head was compared to the observed WIOC fraction. This was achieved by selecting a grid area 1000 km × 1000 km to the west of Mace Head overwhich air parcels

would have advected for a period of approximately 48 hours prior to arrival at Mace Head (Figure 1). The average chlorophyll-a concentration in this grid was then calculated and correlated with the fractional concentration of WIOC to sub-micron sea-spray mass measured over the same period, assuming that sea-spray comprised predominantly of sea-salt and WIOC although with a minor WSOC component (arbitrarily set to 5% of the WIOC fractional contribution). The relationship between percentage mass contribution of WIOC in sea-spray and chlorophyll concentration is shown in Figure 2. The parameterization of WIOC fraction as a function of chlorophyll-a leads to a value of 10% at very low chlorophyll-a concentrations and is forced to saturate at 90% for concentrations above $1.27 \, \mathrm{mg \, m^{-3}}$ in accordance with the maximum observed in the chemical data.

[8] The derived fractional composition of sea-spray particles produced as a function of chlorophyll-a fields is then integrated into the physical sea-spray source function of *Geever et al.* [2005]. To do this, we utilize the accumulation mode number flux as a function of wind speed. *Geever et al.* [2005] presented the flux parameterization as a log-linear function of wind speed; however, at lowest wind speeds, this can introduce an artificial bias in sea-spray production. Consequently, the data were re-fitted as a power-law in the form of $N_{Flux}(10^6 \, \mathrm{m^{-2} \, s^{-1}}) = 1.854 \times 10^{-3} \, U_{22}^{2.706}$ ($r^2 = 0.8$) where U_{22} is the 22-meter wind speed in m s^{-1}. The supermicron flux function is taken from *Stier et al.* [2006], which in turn is taken from *Schulz et al.* [2004]. The seasonal variation in the sea-spray diameter has been prescribed based on that of *Yoon et al.* [2007]. The presumed secondary aerosol fraction, ranging from 5–50% by mass, was removed and the remaining monthly mean
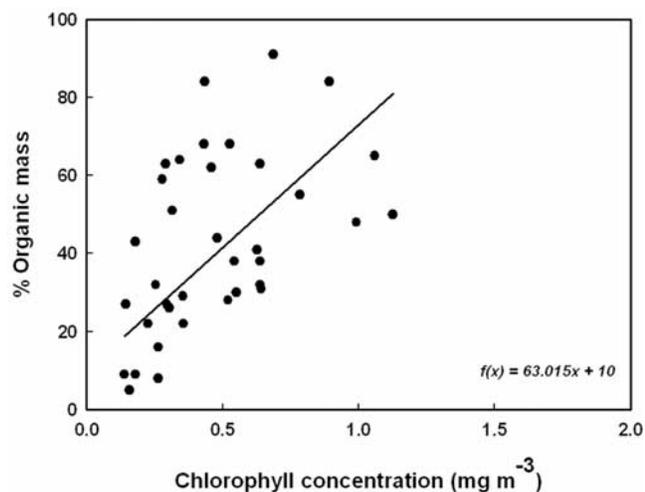
Figure 2. Correlation between fractional WIOC component of sea-spray as a function of grid-average chlorophyll-a concentration.

diameters were represented by the following equation: $D = 0.158 + 0.0148/(1 + (("month" - 6.65)/3.6)^2)$. With the combination of the modal diameter and number flux, we effectively get a volume flux, which is transformed into a sea-spray mass flux based on density estimates of the WIOC/sea-salt ratio: density of WIOC = 1 g cm^{-3} [*Cavalli et al.*, 2004] and density of sea-salt = 2.165 g cm^{-3}. Assuming that the sea-spray is internally mixed, we can constrain the sea-spray flux to a log-normal flux mode with known diameter, mass, number and chemical composition and this log-normal source function is directly interfaced with the M7 modal aerosol module [*Vignati et al.*, 2004] in the REMOTE (REgional MOdel with Tracer Extension) regional climate model [*Langmann*, 2000]. In the interfacing of the source function with a variable standard deviation, a conversion to equivalent mass has to be made since the modal standard deviation of the M7 accumulation mode is fixed is 1.59.

## 3. Regional Scale Simulations of Sea-Spray

[9] Simulations were conducted over an area covering the Northeast Atlantic and Europe for three 1-month periods, one in late spring (May 2002), the second in winter (January 2003) and the third early summer (June 2003) using a horizontal resolution of 0.5° and boundary conditions provided by ECMWF analysis data. The model was found to predict wind fields very well, although for a small fraction of the time, wind speed differences of up to 10–25% were encountered for the evaluation period of June 2003. Figure 3 illustrates the predicted total sea-salt (sampled as Total Suspended Particulate or TSP) mass at Mace Head for the same period.

[10] The simulated sea salt TSP (the sum of accumulation and coarse mode sea salt) concentration, for clean air samples only, agrees quite well with the measured concentration for most of the sample periods, although some periods exhibit an underestimation of the mass, partly due to the underestimation of the wind speed but also due to

model-measurement sampling time mis-matches. For the evaluated periods, we can conclude that the model predicts sea-salt mass reasonably well.

[11] The monthly average sub-micron mass distribution, and the WIOC fractional contribution, resulting from the combined inorganic and organic sea-spray is displayed in Figure 4 for the three selected months. In winter (January 2003), maximum accumulation mode sea-spray mass concentrations of ~ 3 μg m^{-3} are seen over the NE Atlantic and to the west of Ireland (and Mace Head). For this period, biological activity is at its lowest level and the WIOC fraction is more or less zero. By contrast, for the May and June periods of high biological activity (e.g. late spring and early summer), total sea-spray mass is lower, due to generally lower wind speeds, and lies in the range of $1-2$ μg m^{-3}. For these periods, the WIOC fraction has increased to $80-90\%$ in some regions. It should be noted that the lower sea-spray mass in May 2002 compared to June 2003 is due to 30% higher precipitation during the former period rather than to differences in wind speed (wind speeds were comparable during both periods). Similar seasonal contrasts are seen over the North Sea and the Baltic Sea.

[12] In Table 1, the model results are compared with three available observation datasets with size resolved chemical data from *Yoon et al.* [2007]. These data are different from the TSP data presented in Figure 3, the size resolved being over timescales of about 7 days and the TSP over $1-2$ days. It should be noted that it is not possible to do an exact comparison since the model time-step is 6 hours while the aerosol-chemistry sample periods are variable, depending on whether or not the air is within the clean sector or not. For example, a typical chemical sample period of 7 days actually comprises about $70-100$ hours of sampling time which will overlap, to varying degrees, with the model time resolution. In a given month, there are between 1 and 2 samples to compare to the model. Nevertheless, the modeled predictions compare quite favorably for some of the sea-salt and WIOC mass concentration comparisons and
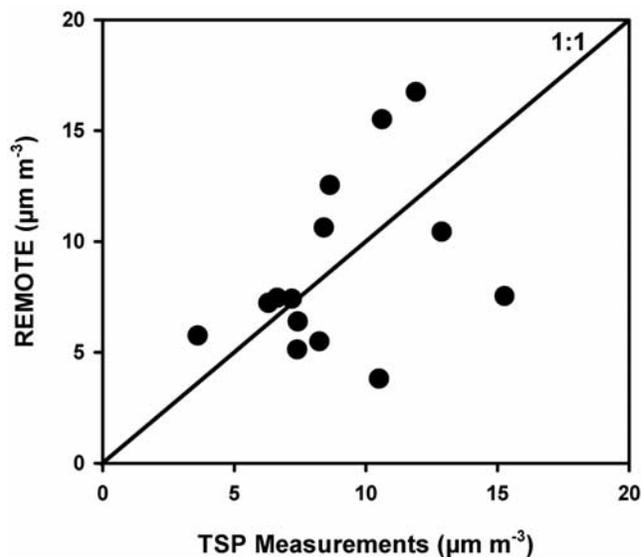
Figure 3. Comparison of measured and modeled sea-salt mass at Mace Head for June 2003.
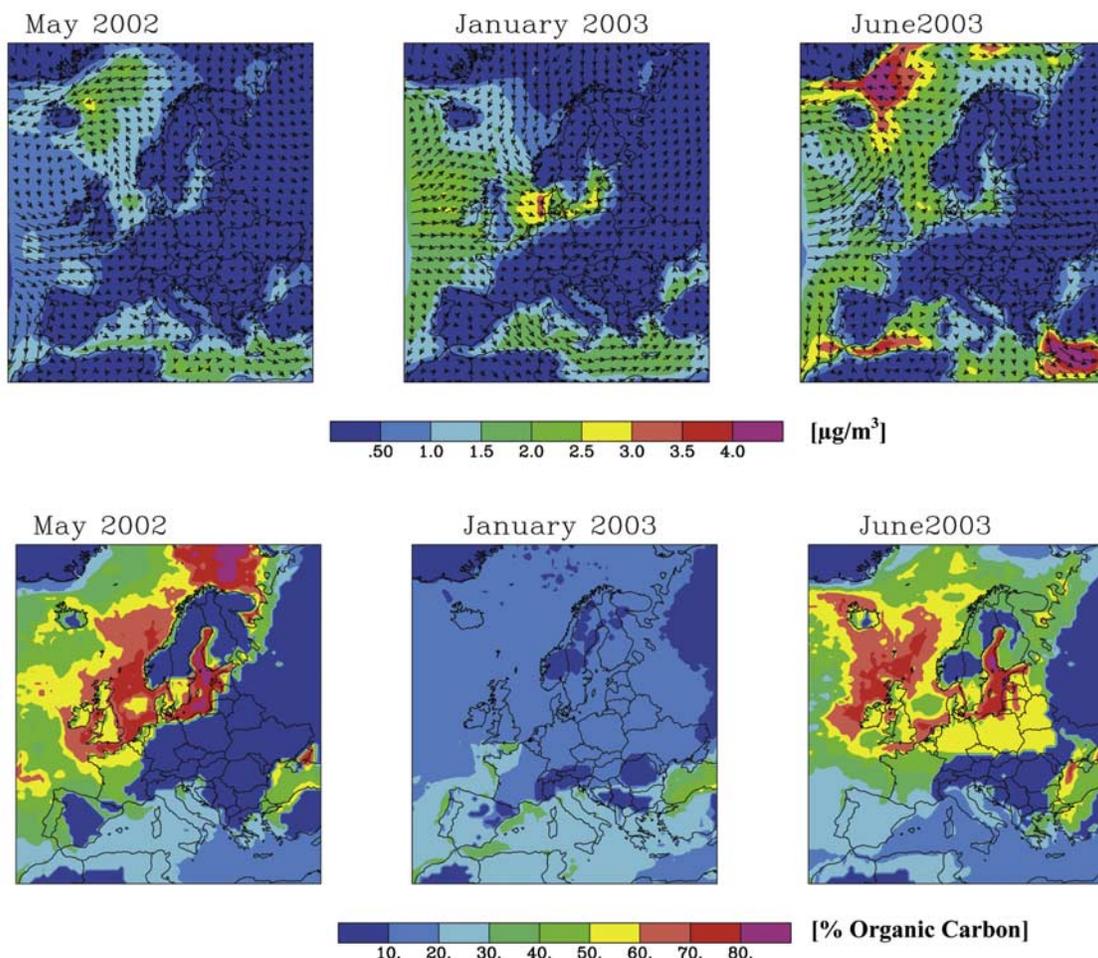
Figure 4. (top) Near surface sea-spray mass concentrations around the European regions and average wind vectors. (bottom) Percentage primary organic contribution to sea-spray mass.

less favorably for others. For the accumulation mode sea-salt mass in winter, the measured and modeled values agree within 25–30%; however, the agreement is poorer for the summer cases. For WIOC, agreement is similar in summer and in winter. Overall, there is no trend of over or under-estimation of sea-salt and WIOC mass. Given the different timescales of the two data sets, there is not necessarily expected to be perfect agreement, however, both the magnitudes of the inorganic and organic mass concentrations and their variation with season exhibit encouraging agreement.

4. Conclusions

[13] An approach to include a combined organic-inorganic sea-spray source function in large scale models is presented. The approach combines satellite measurements of chlorophyll-a data with a sea-spray number flux function and available information on marine aerosol chemical composition. The organic-inorganic source function is implemented in the REMOTE regional climate model and is interfaced to the M7 aerosol dynamics module. Evaluation of the new source function for periods of low (winter) and high (summer) biological activity compares well with observations of aerosol chemical composition. In winter, the observed dominant inorganic sea-salt component (90–100%) is reproduced very well while in summer, the increased WIOC fraction (60–90%) in sea-spray is equally well reproduced. Further improvements could be achieved through more detailed laboratory experiments relating the WIOC fraction to high-resolution chlorophyll-a measurements.

Table 1. Comparison of Measured and Modeled Sea-Salt and Organic Sea-Spray at Mace Head

Chemical Mass, $\mu g/m^3$	7–15 May 2002	24–30 May 2002	6–22 January 2002	Source
Sea salt	0.21	0.12	2.13	REMOTE
Sea salt	0.52	0.55	1.51	Measurements
Primary WIOC	0.30	0.22	0.25	REMOTE
WIOC	0.44	0.34	0.10	Measurements

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