Uncertainties in the determination of global sub-micron marine organic matter emissions

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\begin{abstract}
Organic matter (OM) constitutes an important contribution to the composition of sub-micron sea-spray aerosol produced from biologically active waters. However, OM emission estimates vary by more than an order of magnitude. To estimate the uncertainties in the OM production estimates a sensitivity analysis has been performed in which various parameters have been varied. These include different sea-spray source functions, satellite-retrieved chlorophyll distributions, and a relationship correlating in situ organic mass measurements with satellite-retrieved chlorophyll data. The starting point was a baseline model from which the annual global emission of the water insoluble organic matter (WIOC) fraction in sea spray has been estimated to be 20.4 Tg. In this baseline the global WIOM emission is dominated by the contribution (80%) of the chlorophyll-poor regions (\textless 0.3 mg m\textsuperscript{-3}). Significant deviations from this estimate are introduced by the choice of the sea-spray source function and the assumed background organic mass fraction, each of which leads to an uncertainty of at least a factor of 2. In particular the chlorophyll-poor regions which dominate the WIOM contribution are strongly affected by the choice of the organic mass fraction parameterisation. The way the chlorophyll data are handled, such as different gap filling approaches, causes deviations in the OM emission that are in the order of 10% and is therefore of less importance. The present research indicates that special attention should be given to the low chlorophyll areas in e.g. the tropics, since there the parameterisations are most uncertain and at the same time these regions dominate total WIOM emissions.
\end{abstract}

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1. Introduction

Sea-spray aerosol constitutes one of the most important global aerosol systems (de Leeuw et al., 2011). OM substantially contributes to the composition of sea-spray aerosol, especially in biologically active regions (O’Dowd et al., 2004; Cavalli et al., 2004; Facchini et al., 2008). The organic fraction significantly affects the hygroscopicity of sea-spray aerosol particles (Fuentes et al., 2011) and therefore their size as a function of relative humidity (RH), as well as their refractive index (Ming and Russell, 2001). Consequently, the amount and type of organics in sea-spray aerosol have an impact on their scattering potential (Randles et al., 2004) and their ability to act as cloud condensation nuclei (CCN) (O’Dowd et al., 2004; Moore et al., 2008; Roelofs, 2008). Additionally, Zhou et al. (2008) showed that the OM in sea spray is both an important precursor/source as well as a dominant sink for the OH radical illustrating its role in marine atmospheric chemistry.

Small sea-spray particles may be mainly composed of OM with a decreasing contribution as particle size increases (Facchini et al., 2008). Facchini et al. (2008) observed that the size-dependent transfer of OM to sea-spray aerosol is mainly controlled by solubility and surface tension properties of marine OM. Sub-micron water insoluble organic carbon (WIOC) is primarily produced at the ocean surface while water soluble organic carbon (WSOC) is formed by a secondary process (Ceburnis et al., 2008; Facchini et al., 2008).

To quantify the role of the organic fraction of sea-spray aerosol its source strength needs to be known. A first attempt to include the organic fraction in a sea-spray source function was presented by O’Dowd et al. (2008). These authors proposed to use satellite-derived chlorophyll concentration data as a proxy for oceanic biological activity, and derived an OM-chlorophyll relationship by correlating chlorophyll satellite data and in situ measurements of OM. This relationship, and updates thereof, was used together with
microphysical sea-spray source functions to determine the surface flux of combined inorganic/organic sub-micron sea-spray particles as discussed below. The way this is done differs due to different choices made in the implementation. In this paper we investigate the effects of the different choices made, starting from a baseline estimate of the annual global emission of the sub-micron OM fraction of sea spray.

2. Methodology

Existing sea-spray source functions, satellite-retrieved chlorophyll distributions, and a relationship correlating in situ OM measurements with satellite-retrieved chlorophyll data have been combined to determine the emission strengths of OM in sub-micron sea-spray aerosol. Sub-micron sea-spray droplets in this study are droplets with radii at a RH of 80%, \( R_{80} \), smaller than 1 \( \mu m \). To a good approximation \( R_{80} \) equals the particle dry diameter, \( D_p \) (de Leeuw et al., 2011).

A baseline estimate was chosen as described in Section 2.1 to derive a first estimate of the total annual global emission of sub-micron OM which was used for comparison with estimates derived using other parameterisations and input data. An analysis of the inter-annual and regional variability of the global OM emission in sub-micron particles was performed for this base case.

2.1. Base case simulation

2.1.1. Model

The studies presented here were conducted using the off-line global chemistry transport model TM5 (Krol et al., 2005). TM5 was chosen because it uses pre-processed meteorological fields from the European Centre for Medium-Range Weather Forecasts (ECMWF) on a global grid (Segers et al., 2002) which includes meteorological input for both SST and \( U_{10} \) needed for the calculation of global emission estimates. Since this study deals only with emissions, operations for advection, convection, sources, and chemistry were omitted. All calculations were performed on a global 1 \( \times \) 1 grid.

2.1.2. Sea-spray source function

The Mårtensson et al. (2003) sea-spray source function was used in this study as a baseline since it provides production fluxes similar to those provided from other recent parameterisations (Clarke et al., 2006; de Leeuw et al., 2011). It has a large advantage in that it includes sea surface temperature (SST) in addition to wind speed. SST has a significant effect on the spatial distribution of sea-spray emission fluxes across the Earth (Jaeglé et al., 2011; Mårtensson et al., 2003; Sellegri et al., 2006).

2.1.3. OM-chlorophyll relationship

In the baseline study the Mårtensson et al. (2003) sea-spray source function is combined with a relationship originally derived by O’Dowd et al. (2008), and slightly revised by Vignati et al. (2010), correlating local in situ measurements of the OM fraction in sea-spray aerosol with regionally derived satellite-retrieved chlorophyll data:

\[
\% \text{OM} = 43.5 \times \text{Chl} \left[ \text{mg m}^{-3} \right] + 13.805, \quad \text{Chl} < 1.43 \text{ mg m}^{-3} \quad (1)
\]

with a coefficient of determination \( R^2 = 0.30 \). We acknowledge that this relationship is rather poor, which may be explained by a lack of weighting of the back trajectories (Vignati et al., 2010). Nonetheless, it is currently the best available and frequently used in global modelling exercises. Below we also investigate alternatives to the above mentioned fit.

Comparison of different papers in which relationship (1) has been used, shows different interpretations of organic carbon (OC) and OM. Facchini et al. (2008) mention that the conversion factor from OC to OM is 1.8 for water soluble organic matter (WSOM) and 1.4 for WIOC. These values are based on \(^1\)H NMR spectroscopy experiments by DeCesari et al. (2007). O’Dowd et al. (2008) used WIOC whereas WIOM was intended. As a consequence several authors have used this relationship and presented their results as OC, where it should have been OM. We recommend to use the OM-chlorophyll relationship to calculate emissions of the WIOM fraction of sea spray.

2.1.4. Chlorophyll data

In the OM-chlorophyll relationship we have chosen to use level 3 MODerate resolution Imaging Spectroradiometer (MODIS) chlorophyll data, daily mapped with a resolution of 4.6 km (res 4) (http://oceancolor.gsfc.nasa.gov/) based on arguments regarding performance, and the availability of co-located data (Albert et al., 2010). Ocean colour distributions obtained from satellite retrievals contain gaps due to clouds (and associated scattered light), optically thick aerosol layers, inter orbital gaps, sun glint, high solar zenith angles, and sensor tilts causing either obscuration or lack of sampling (Gregg and Casey, 2007). In the calculation of our base case estimate we have filled the gaps in the chlorophyll data by assuming that the last available non-zero value for a certain pixel remains the same until the next observation becomes available (Fig. 1). In our base case estimate we have used input data for only one year and thus the grid in the first days of the year is not completely filled until about the tenth day (Fig. 1b). At the end of the year, in regions without daylight, values were kept fixed during the dark period, as no new data was available (Fig. 1c).

2.2. Base case data analysis

For the base case estimate of the global annual sub-micron organic mass emission the year 2006 was chosen. However, we have run the model for 5 years, 2004—2008, to check whether 2006 is representative for the annual emission of sub-micron OM. Additionally, these runs serve to determine whether differences in estimates of the annual emission due to the use of different parameterisations, input data, and assumptions as described in Section 2.3, are significant compared to the inter-annual variability.

We have selected six regions (Fig. 2) with different chlorophyll concentration and wind speed conditions. R1 (region 1) was chosen to represent the tropics. R2 is located in the Southern Hemispheric storm track region which is characteristic for high emission of sea spray and has high chlorophyll concentrations throughout the year (Fig. 3). R3, in the Indian Ocean, was chosen to represent the lower-latitude region on the southern hemisphere which is characterized by moderate emission of sea spray. R4 and R5 were selected as being characteristic for the North Atlantic with relatively high sea-spray emissions and high chlorophyll concentrations. R6 was selected to cover more of the Southern Hemispheric storm track region but with lower annual mean chlorophyll concentrations as compared to R2. It is noted that region R5 was used in several previous investigations (e.g. Spracklen et al., 2008; Vignati et al., 2010) because of the proximity of the measurement station Mace Head, Ireland. In the current study R5 is also used because it covers the region for which the OM-chlorophyll relationship was derived. When interpreting global total emissions it should be taken into account that the tropics (i.e. region 1) have the largest surface area, and therefore have a relatively large contribution to the total global flux. To calculate the regions mean emission we did not include grid cells containing more than 90% land and/or ice.

2.3. Sensitivity simulations

The sensitivity of the emission estimate to different parameterisations and input parameters was investigated utilizing a series of simulations in which the most decisive parameters were
changed alternately while keeping the other parameters constant. The simulations were aimed at determining the impact of using:

- an alternative sea-spray source function,
- alternative OM relationships,
- alternative handling of chlorophyll data,
- an alternative chlorophyll product.

All sensitivity simulations were made for the year 2006.

2.3.1. Source function

Sea-spray source function formulations provide significantly different results (de Leeuw et al., 2011). To illustrate the effect of the sea-spray source function we have replaced the Mårtensson et al. (2003) source function used in the base case estimation with that derived by Gong (2003). Gong (2003) is based on the commonly-used Monahan et al. (1986) scheme, is often used in global models (Textor et al., 2006) and provides a lower estimate for the sub-micron sea-spray aerosol flux than Mårtensson et al. (2003).
Where Mårtensson et al. (2003) is at the high end of the existing formulations, Gong (2003) provides a relatively low estimate (de Leeuw et al., 2011).

2.3.2. OM relationship

A seasonal pattern linking WIOM and oceanic chlorophyll-a concentrations for an area of 1000 km × 1000 km over the North East Atlantic to the west of Mace Head, derived from Sea-viewing Wide Field-of-view Sensor (SeaWiFS) observations, has been observed (Yoon et al., 2007; O’Dowd et al., 2008). Fig. 4 shows reanalyses of the samples obtained by Yoon et al. (2007). The OM-chlorophyll relationship shown in Eq. (1) was obtained from these data as the linear trend line (O’Dowd et al., 2008; Vignati et al., 2010).

In view of the large uncertainty in these data, two alternative relationships were defined to investigate the impact of the slope and the background concentration, the y-intercept, of the fit: we have run both a sensitivity simulation with a constant background, $y = 13.805$ (Fig. 4, dashed line), and a simulation where the fit to the data was forced through the origin, $y = 60x$ (Fig. 4, dotted line). This alternative better covers the presence of the cluster of data points below the background value of 13.805% of the original fit.

Gantt et al. (2011) suggest that the OM enrichment decreases with wind speed and included that effect in their parameterisation which further includes the size dependence of the organic mass fraction based on the work of Facchini et al. (2008). We evaluated this new relationship by using it instead of the O’Dowd et al. (2008) parameterisation, while keeping all other settings as in the base case run.

2.3.3. Handling chlorophyll data

In the base case model we have used daily mapped chlorophyll data at a resolution of 4.6 km (res 4), and have assumed that we could fill data gaps by maintaining the last observation in a grid cell over time until it is replaced by a new valid observation. We have chosen this filling method based on the assumption that changes in chlorophyll concentration don’t appear on a daily basis due to the lifetime of the algae that produce the chlorophyll (typically 23 days (Marbà et al., 2007)). This assumption was evaluated through three tests:

1. A model run with daily mapped data and assuming a zero chlorophyll concentration in areas where no data were available.
2. A similar run but using a chlorophyll product at a coarser resolution of 9.2 km (res 9), effectively lowering the number of data gaps.
3. Using monthly chlorophyll data (http://oceancolor.gsfc.nasa.gov/) instead of daily data, both with and without gap filling with the last valid monthly observation.

2.3.4. Different chlorophyll product

To quantify the effect of using chlorophyll data that are obtained from retrievals from a different satellite sensor we have also performed a model run where MODIS data were replaced with SeaWiFS data. SeaWiFS mapped daily data is only available on a 9.2 km resolution (res9) which was compared with MODIS res 9.

3. Results

3.1. Global emission estimate (base case)

The annual average 10 m wind speed ($U_{10}$), chlorophyll concentration, and the calculated annual average WIOM emission rate for 2006 are shown in Fig. 5. The spatial distributions of the emission rate and $U_{10}$ show a clear similarity, as expected from the way organic emissions are calculated: first the total sea-spray emission, mainly driven by wind speed, is determined, and subsequently the organic mass fraction of the total emission is estimated based on chlorophyll concentrations. Thus, the chlorophyll signal (Fig. 5b) is visible on top of the wind-induced sea-spray emission pattern. In some areas, the chlorophyll concentration is high enough to show a maximum in organic mass emission distribution despite a lower wind speed. Examples are the area to the east of Argentina and nutrient-rich upwelling areas such as off the west coast of Africa. By integrating the emission rate we have arrived at an estimate for the total emitted global sub-micron organic mass fraction of sea spray of 20.4 Tg WIOM, or 14.6 Tg WIOC.

Table 1 displays the global annual sub-micron WIOM emission estimates from the base case simulation for the years 2004–2008. These results show that the inter-annual variability is relatively small, less than ±3% of the 5-year average. Therefore, 2006 can be considered representative for the estimation of the global annual emission of sub-micron OM.

There is large spatial variation in emission strengths. Fig. 6 shows the 5-year average WIOM emission rate for the six
selected regions (Fig. 2) with the corresponding wind speed, chlorophyll concentration and SST. There is a similar trend in the variation of wind speed and WIOM emission for the regions examined here. This applies to chlorophyll concentration and WIOM emission as well, except for R6: R6 is a region with a low chlorophyll concentration but a relatively high WIOM emission rate. This is due to the way organic emissions are calculated: R6 has the highest annual average wind speed and thus large emission of sea spray and organic material. The low chlorophyll concentration in region 6 (and region 1) is due to the absence of coastal regions which are generally richer in phytoplankton populations than open ocean regions, see Fig. 5b. The geographic distribution of the WIOM emission was found not to be correlated with SST.

The error bars (i.e. 1σ) in Fig. 6, show that the variation in wind speed from year to year is small. The inter-annual fluctuations in chlorophyll concentration are strongest in the regions with the highest concentrations. This is probably due to the fact that the conditions for algae blooming depend on strongly varying factors such as nutrient availability and light. R2 shows both higher average chlorophyll concentration and higher average wind speed as compared to R5, but R2 does not have the highest average emission rate of the two because here we considered annual average values, whereas the fluxes are calculated on an hourly basis. As a consequence, areas with the same annual mean wind speed conditions and chlorophyll concentrations may have different annual organic mass emissions depending on the extent that algae blooms and high wind speed conditions occur simultaneously. When comparing the WIOM emission rates for the different regions based on location it is noticed that the highest emission rates occur at higher latitudes close to the continents, whereas the emission rates in the tropics, which cover the largest ocean area, are relatively low.
3.2. Sensitivity analysis

The results from the various experiments on the sensitivity of the emission estimates to choices in parameterisations and input parameters are presented in Table 2. These results are discussed below.

3.2.1. Source function

The effect of the choice of a significantly different sea-spray source function is illustrated by replacing Mårtensson et al. (2003) with Gong (2003). This results in a decrease of the total global emission for 2006 by more than one third of the base case estimate to 12.5 Tg.

3.2.2. OM relationship

The first simulation on the effect of the formulation of the OM-chlorophyll relationship aimed at quantifying the impact of the background value. Replacing Eq. (1) with $y = 13.805$ (Fig. 4, dashed line) resulted in a global WIOM emission of 14.6 Tg yr$^{-1}$, i.e. more than 2/3 of the calculated global emission total of 20.4 Tg yr$^{-1}$ is determined by the choice of the background while the presence of chlorophyll is responsible for only a small part (5.8 Tg yr$^{-1}$) of the total OM emission in 2006.

Using the third alternative ($y = 60x$), without any assumed background and with a different slope, led to a reduction of the OM emission by a factor of two to 9.9 Tg WIOM yr$^{-1}$. The global annual average WIOM emission rate calculated using this fit is everywhere lower than the base case. The spatial distribution (Fig. 7) shows that in this simulation the variations in OM emission are governed by the variations in chlorophyll concentration rather than wind speed. Thus, in this case the wind speed signal is visible on top of the chlorophyll distribution pattern. The contrast in OM emissions between the tropics and mid-latitudes is stronger here than in the base case.

Using the OM relationship as defined by Gantt et al. (2011) resulted in a decrease in annual global WIOM emission to 2.2 Tg for 2006. The difference in OM emission strengths for high- and low-wind regions is less pronounced than in the base case (Fig. 8). The large difference with the base case annual global WIOM emission estimate is mainly due to the size-dependence in the parameterisation which leads to a much smaller organic mass fraction of the larger sea-spray particles which in turn dominate the sea-spray aerosol mass. Neglecting the size-dependency in the Gantt et al. (2011) formulation would lead to an annual global WIOM emission estimate of 18.2 Tg yr$^{-1}$. The wind-dependent part of the OM relationship as defined by Gantt et al. (2011) results in the lowest contrast between the tropics and mid-latitudes of all simulations.

3.2.3. Handling of chlorophyll product

Replacing missing chlorophyll data in the MODIS daily product by a zero concentration, an unrealistic value, leads to a decrease in the sub-micron organic mass emission estimate by approximately 20% to 16.3 Tg. When in addition the resolution is changed from res 4 to res 9, the annual emission estimate is 16.1 Tg. As we have used zero chlorophyll concentrations where no observations are available, these fluxes represent the lower limit.

Alternatively, we have used monthly instead of daily chlorophyll data. This results in a higher emission estimate compared to the base case value: 20.7 Tg. Monthly averaged distributions contain only few gaps due to e.g. persistent clouds. There are no data at high latitudes in local winter because the solar zenith angle limit is too low (Wang, 2002). By additionally filling the gaps in these monthly data we found an emission estimate of 21.4 Tg yr$^{-1}$.

3.2.4. Comparison of different chlorophyll products

Using chlorophyll data from SeaWiFS instead of MODIS hardly changes the estimated sub-micron organic mass emission. Where res 9 MODIS data resulted in an estimate of the total emission for 2006 of 20.2 Tg yr$^{-1}$, SeaWiFS data resulted in an estimate of 20.8 Tg for the same year.
Fig. 5. Input data and result of base case simulation for 2006: (a) Annual average of the input wind speed at 10 m above the ocean surface in m s\(^{-1}\), (b) Annual average of the input chlorophyll concentration in mg m\(^{-3}\), (c) annual average organic matter emission rate in ng m\(^{-2}\) s\(^{-1}\).
4. Discussion

The uncertainties in estimates of the global emission of OM associated with direct production of sea-spray aerosol have been studied. The base case simulation for 2006 provided a total annual estimate of 20.4 Tg WIOM, or 14.6 Tg WIOC. Uncertainties due to changes in parameterisations and input parameters are significant compared to inter-annual variability. The most important deviations are introduced by the choice of the sea-spray source function and the parameterisation of the OM fraction of the total emitted sea-spray mass. Handling of the chlorophyll data causes uncertainties of the order of 10%. Below we discuss these issues in more detail.

4.1. Discussion on uncertainties

A large uncertainty in organic emission estimates can be traced back to the large variations between different source functions (de Leeuw et al., 2011). Since in the base case the organic fraction is derived from the total emission this uncertainty is linearly carried over into the organics emission estimate. Sea-spray source functions might be improved by including factors, complementary to wind speed, which better account for the effects of a suite of meteorological and oceanographic factors but such efforts have thus far not been proven successful (de Leeuw et al., 2011). Formulations of the sea-spray source functions published in the last decade seem to converge to within a factor of 2–3 (Clarke et al., 2006). However, de Leeuw et al. (2011) concluded that the uncertainties are still very large. Another promising way forward may be the use of satellite-retrieved whitecap fraction data (Anguelova et al., 2006) which would provide a direct measurement of the ocean surface area producing sea-spray aerosol rather than parameterisations based on observations which show very large differences between different data sets (de Leeuw et al., 2011; Anguelova et al., 2006; Lewis and Schwartz, 2004).

Satellite observations of chlorophyll do not go without complications. These observations are only possible during daylight, in cloud-free conditions with solar zenith angles smaller than 75° (Wang, 2002), and are hampered by other disturbing factors such as sun glint and whitecaps (Gregg and Casey, 2007). Kwiatkowska et al. (2007) have shown that the approximate daily percentage of global ocean coverage is about 16% for SeaWiFS and about 13% for MODIS-Aqua at 9 km resolution. Most observations are available for regions with large amounts of sunlight and low cloud cover, which do not coincide with the regions with high sea-spray aerosol emissions. Especially in the storm track region on the southern hemisphere there are only about 30–100 new observations per year (Fig. 3, lower panel). However, we found maximum impact of about 20% for different ways of handling the data gaps, which is in line with the uncertainty estimate by Vignati et al. (2010).

The applied OM-chlorophyll relationship has been derived from measurement data that were obtained at the Mace Head research station, Ireland (O’Dowd et al., 2008). The derived relationship has a relatively large background and a dependence on chlorophyll concentration, which might be applicable to other regions with relatively high chlorophyll concentrations, such as the coastal region upwind of Mace Head. However, on a global scale these intensive blooms hardly occur, see Fig. 5b. Fig. 9 shows that the global WIOM emission is dominated by the contribution (80%) of low chlorophyll conditions (<0.3 mg m⁻³) in which the contribution of the background to the WIOM emission is high and the sensitivity to chlorophyll concentration is rather low (Fig. 4) as discussed in Section 3.2.2. Hence, an accurate OM-chlorophyll relationship is needed especially for low chlorophyll conditions since these dominate the global emission.

The effect of alternative fits to the data presented in Fig. 4 was illustrated in Section 3.2.2. The sea-spray emission rate is not very high in the tropics due to relatively low winds. The vast surface area in the tropics explains why a change in the background concentration has such a large impact on the global emission estimate. Fuentes et al. (2011) show that the organic enrichment is a function of the seawater organic concentration and type of organic exudate. Therefore they propose that differences in the composition and surface-active properties of the OM in the source seawater, which often originates from different oceanic regions, might explain discrepancies in the organic enrichment of primary particles generated in different studies. Based on analysis of ambient marine aerosol chemical composition Ganitt et al. (2011) also mention that the maximum organic enrichment of sea-spray aerosols can differ enormously between different measurement locations. Long et al.

Table 1
Total sub-micron WIOM emission estimates for different years. All simulations were performed using the base case settings (Section 2.1) and era interim meteorology.

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<tr>
<td>Sub-micron organic mass emission [Tg]</td>
<td>19.7</td>
<td>19.9</td>
<td>20.4</td>
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Fig. 6. 5 year average (2004–2008) WIOM emission rate estimates for the six regions indicated in Fig. 2 (olive green bars), with corresponding 1σ (a), chlorophyll concentration (b), and SST (c). The error bars indicate the standard deviation of the average values.
show that linearly extrapolated functions based on measurements, relating the OM mass fraction and the chlorophyll-a concentration in seawater, are highly sensitive to the chlorophyll-a concentrations in seawater from which the particulate OM mass originates: compared to the Langmuir functional relationship as defined by these authors measurements in productive marine regions give a relatively low OM to chlorophyll-a slope whereas measurements in oligotrophic waters result in a high slope, resulting in a net underestimate- and overestimate respectively, of the globally integrated OM flux.

In short, it can be questioned whether the applied OM-chlorophyll relationship is representative at the global scale. To improve the global applicability of a single OM relationship, sea-spray aerosol composition measurements are needed in both the high and low chlorophyll regions and the discussion above especially calls for additional measurements in tropical regions. It should be noted that the large change in the contrast between OM emission density in tropics and mid-latitudes as a result of neglecting the background in the OM-chlorophyll relationship may have a large impact on the associated indirect aerosol forcing since the amount of organics in sea-spray aerosol particles affects their ability to act as cloud condensation nuclei (CCN) (O’Dowd et al., 2004; Moore et al., 2008; Roelofs, 2008; Fuentes et al., 2011).

More fundamental, there may be some concern about (satellite-retrieved) chlorophyll concentration as a proxy for OM. Organic carbon originating from phytoplankton is extracellularly produced by photosynthesis and released into the seawater as a result of cell lysis (Myklestad, 2000). Therefore, Fuentes et al. (2010) have derived a first-order estimation of the total OM production as a mass balance of extracellular release, cell lysis, and biodegradation during the algae lifetime and used the uncertainty limits of the parameters as defined in this balance to derive a relationship between chlorophyll-a and OM which was found to be highly dependent on the specific conditions of the algal bloom.

Fuentes et al. (2010) mention that it should be considered that phytoplankton does not only die due to cell lysis but also by grazing and sinking below the photic layer, which affects the total amount of OM that is released: if phytoplankton dies untimely, excretion of organics will be lower. Additionally, the balance between phytoplankton death through lysis, grazing and sinking varies per oceanic region. Also the carbon to chlorophyll-a mass ratio in algal cells, one of the parameters used to define the production balance,
varies strongly, up to a factor of 40, due to effects of light, nutrients and temperature. According to Fuentes et al. (2010) it is therefore likely that a regional relationship between chlorophyll-a concentration and organic particle fraction cannot be extrapolated to a global scale. Another issue concerning chlorophyll as a proxy for OM is that many algae blooms occur not only directly on the ocean surface, making it hard to assess the total chlorophyll mass below the surface by satellite. Also, in the derivation of the OM-chlorophyll relationship is assumed that there is only a single algae species, whereas in reality there is a large variety (e.g. Sathyendranath et al., 2004). Moreover, chlorophyll concentrations provide information on living algae blooms whereas, as mentioned above, algae release OM into the seawater as a result of cell lysis (Myklestad, 2000). This may cause a delay between satellite- and field measurements.

Russell et al. (2010) found only weak to mild correlations in the North Atlantic and even negative correlations in the Arctic; Lapina et al. (2011) report the absence of a strong correlation between organic aerosol concentrations and chlorophyll-a measurements. In these studies, however, a correlation between simultaneous in situ chlorophyll concentrations from local water samples and OM measured in air samples may not have been found since the concentration footprint is expected to extend to the order of 100 km and thus cannot be directly compared to local water samples corresponding to spatial scales of less than a km. Fuentes et al. (2010) stress that ocean colour data only provides estimates on the phytoplankton distributions in the oceans and can therefore only be used as a first-order approximation. However, Gantt et al. (2011) report a higher correlation between OM mass fraction and chlorophyll than between OM mass fraction and particulate organic carbon (POC) or dissolved organic carbon (DOC). Also Long et al. (2011) choose chlorophyll-a as a proxy for surface-active OM in surface seawater. They considered the use of dissolved organic carbon (DOC) but no correlation was found between DOC and either chlorophyll-a or particulate OM mass. Long et al. (2011) stress that their chlorophyll approach is based on the results of only two studies resulting in limited observational constraints, preventing explicit evaluation of the reliability of chlorophyll-a as a proxy for OM. Next to additional field measurements as discussed above, applying algorithms for discriminating distinct groups (Sathyendranath et al., 2004) and classes (Uitz et al., 2010) of phytoplankton from ocean colour remote sensing may improve the regional representation of the emission estimates in the future.

4.2. Comparison to other emission estimates

To put our study into perspective, Table 3 shows a compilation of the annual sub-micron OM emission estimates presented in literature. Reported emission estimates were based on both bottom-up and top-down approaches. Our global emission estimate for WIOC emission, 14.6 Tg yr⁻¹, is in the higher range of earlier estimates, although three studies provide considerably higher values (Long et al., 2011; Roelofs, 2008; Westervelt et al., 2012). Long et al. (2011) have developed an alternative measurement-based sub-micron size-resolved production flux parameterisation of
(particulate OM as function of wind-driven air detrainment through the surface seawater column in which a Langmuir driven shape parameter was implemented to account for OM production. In their parameterisation they additionally introduce size-dependent variability based on measurements performed by Keene et al. (2007) and Facchini et al. (2008), showing increasing mass and volume ratios of OM to sea salt with decreasing particle size. For global simulations chlorophyll-α was used as a proxy for the presence of surface-active OM in surface seawater. Long et al. (2011) show that using a Langmuir functional relationship leads to a systematically higher globally integrated flux of particulate OM than the linear OM-chlorophyll extrapolation as defined by O’Dowd et al. (2008).

In contrast, the spatial distribution of particulate OM mass production shows the same pattern as in our studies: fluxes coincide with the wind-distribution with local minima and maxima associated with chlorophyll-α concentration. Bottom-up studies using the OM-chlorophyll relationship from O’Dowd et al. (2008) yield lower estimates than presented here. This is largely explained by the use of different sea-spray source functions as discussed above. Note that the lowest estimate by Langmann et al. (2008) was obtained using monthly mean meteorological data which can cause a dramatic underestimation, as compared to hourly data, due to the cubic dependence of whitecap fraction on wind speed. The uncertainty in top-down estimates is determined by the quality of the model that is used, and the quantity and quality of the measurements. Spracklen et al. (2008) used a global top-down analysis to produce a global estimate of the total oceanic OC source using a combination of observations of OC from 3 oceanic surface sites (Amsterdam Island, Azores and Mace Head), back trajectories, and remotely sensed chlorophyll-α concentrations, which were interpreted using a global chemistry transport model. Based on their analysis they found a global estimate of the total (primary and secondary) oceanic OC source of about 8 Tg OC yr⁻¹, of which about 5.5 Tg yr⁻¹ was suggested to reside in the sub-micron mode as WIOC. Assuming the observations to be reliable the uncertainty in top-down emission estimates is determined by the model uncertainty. In particular the removal parameterisations are quite uncertain and their efficiency can easily differ by a factor 2 to 3 (Textor et al., 2006; Manders et al., 2010). In the case of indirect observations such as cloud droplet number and effective radii used by Roelofs (2008), additional parameterisations are introduced, with their own uncertainty and thus increasing the overall model uncertainty.

### 4.3. Conclusion

At present, there is a large uncertainty as regards the importance, both in quantity and (climate) impact, of the organic content of sea-spray aerosols (O’Dowd et al., 2008; Bigg and Leck, 2008; Modini et al., 2010; Ovadnevaite et al., 2011). Our base case simulation for 2006 resulted in a total annual estimate of 20.4 Tg WIOM, or 14.6 Tg WIOC. However, large uncertainties are associated with the choice of the sea-spray source function and the definition of the OM relationship causing a large range in reported emission estimates as well as emission patterns over the Earth. To improve current understanding of the importance of the organic fraction of sea spray as well as its source strength, a stronger observational basis is highly necessary. The present research indicates that special attention should be given to the low chlorophyll areas, since there the parameterisations are most uncertain and at the same time these regions dominate total WIOM emissions.

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### References


