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Marine aerosol production: a review of the current knowledge

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The current knowledge in primary and secondary marine aerosol formation is reviewed. For primary marine aerosol source functions, recent source functions have demonstrated a significant flux of submicrometre particles down to radii of 20 nm. Moreover, the source functions derived from different techniques up to 10 μm have come within a factor of two of each other. For secondary marine aerosol formation, recent advances have identified iodine oxides and isoprene oxidation products, in addition to sulphuric acid, as contributing to formation and growth, although the exact roles remains to be determined. While a multistep process seems to be required, isoprene oxidation products are more likely to participate in growth and sulphuric acid is more likely to participate in nucleation. Iodine oxides are likely to participate in both nucleation and growth.

Keywords: marine aerosol; particle formation; nucleation; sea spray; sea salt

1. Introduction

The marine aerosol constitutes one of the most important natural aerosol systems globally. It contributes significantly to the Earth's radiative budget, biogeochemical cycling, impacts on ecosystems and even to regional air quality. The marine aerosol comprises primary and secondary aerosol components. The primary aerosol production results from the interaction of wind stress at the ocean surface and results in the mechanical production of sea-spray aerosol (sea spray being the combination of inorganic sea salt and organic matter). Sea spray is produced via the bubble-bursting process typically resulting from whitecap generation, producing film and jet drops, resulting in sea-spray particles in the range of the submicrometre size and up to a few micrometres. It is estimated that whitecap formation onset occurs at wind speeds of 4 m s^{-1} . At higher wind speeds, the direct tearing of wave crests can result if spume droplet formation occurs at sizes from tens to hundreds of micrometres. Globally, in terms of sea-salt production, the mass flux is estimated to be $1\text{--}3 \times 10^{16} \text{ g yr}^{-1}$ (Erickson & Duce 1988;

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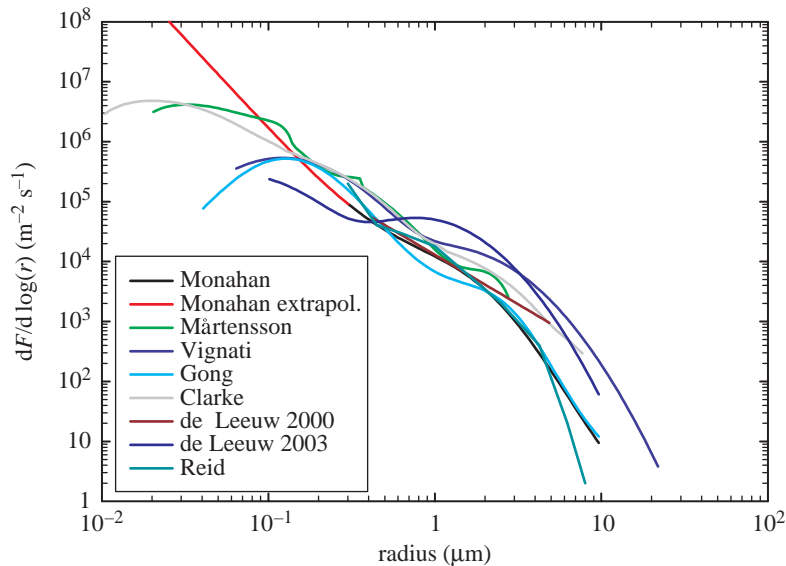


Figure 1. Compilation of sea-spray source functions published since 1998. Flux values are for a wind speed of 8 m s^{-1} .

Gong *et al.* 2002). Thirty-two per cent of the global flux comes from the Northern Hemisphere and 92% of the mass flux is attributed to the supermicrometre size range (i.e. $r > 0.5 \mu\text{m}$). Increase in sea-salt mass is primarily associated with increasing wind speeds with mass concentrations being measured up to $1000 \mu\text{g m}^{-3}$ at wind speeds of $15\text{--}20 \text{ m s}^{-1}$ (Lewis & Schwartz 2004). Although mass loadings can be high, marine aerosol number concentrations are typically low, of the order of $300\text{--}600 \text{ cm}^{-3}$ (O'Dowd *et al.* 1997; Yoon *et al.* 2007), of which up to $50\text{--}150 \text{ cm}^{-3}$ can be sea-salt particles under high wind conditions (O'Dowd & Smith 1993; Kreidenweis *et al.* 1998).

The interest in sea-spray aerosol has traditionally been focused on large particles ($> 1 \mu\text{m}$) owing to their influence, at high wind speeds, on sea–air transfer of water vapour and latent heat (e.g. Andreas 1998). The overview of sea-spray source fluxes presented by Andreas (2002), which includes most of the common source functions presented until 1998, shows a variation of approximately six orders of magnitude. A critical analysis of the source functions presented in Andreas (2002) is discussed in Schulz *et al.* (2004).

More recently, the interest in sea spray has been shifted to other applications such as its role in chemical reactions (for coupled nitric acid–sea salt see Sorensen *et al.* (2005); for coupled sulphate–sea salt cycles see O'Dowd *et al.* (1999a, 2000)) and, in particular, its role in climate change (IPCC 2001). Sea salt is the dominant submicrometre scatterer in most ocean regions (e.g. Kleefeld *et al.* 2002; Bates *et al.* 2006) and dominates the marine boundary layer (MBL) particulate mass concentration in remote oceanic regions, with a significant fraction occurring in the submicrometre size range (IPCC 2001). Sea salt contributes 44% to the global aerosol optical depth. Estimates for top-of-atmosphere, global-annual radiative forcing due to sea salt are -1.51 and -5.03 W m^{-2} for low and high emission values, respectively (IPCC 2001). Sea

spray not only affects climate by scattering of solar radiation, but also the spray particles act as cloud condensation nuclei and thus contribute to the indirect aerosol effect (O'Dowd *et al.* 1999b). Sea salt has also been linked to the MBL cycle through the activation of halogens, leading to ozone depletion (Vogt *et al.* 1996; McFiggens *et al.* 2000). For primary marine aerosol (PMA), a historical and detailed review of sea-salt production and resulting concentrations is discussed in Lewis & Schwartz (2005).

In terms of secondary marine aerosol production (i.e. particle production resulting from gas-to-particle conversion processes), historically, it has been thought that sulphur species have been the primary chemical component involved (Shaw 1983; Charlson *et al.* 1987). Secondary aerosol production occurs in the following two ways: (i) new particle formation occurs via the nucleation of stable clusters of the order of 0.5–1 nm in sizes (these clusters, once formed, can grow to larger sizes via condensation processes) and (ii) they also can grow via heterogeneous reactions and aqueous phase oxidation of dissolved gases in existing aerosol particles. In terms of the sulphur cycle, dimethylsulphide (DMS), a waste produced by phytoplankton, is released from the ocean into the atmosphere where it undergoes oxidation by the OH radical to form SO₂, which is further oxidized to form H₂SO₄ (see Charlson *et al.* (1987) for full discussion). H₂SO₄ is thought to participate in binary homogeneous nucleation with H₂O, and more recently, in ternary nucleation with H₂O and NH₃. While Clarke *et al.* (1998) found evidence for particle production linked to high DMS emissions in the Pacific, a more robust analysis of particle production from H₂SO₄ by Pirjola *et al.* (2000) pointed out that while binary nucleation was likely to occur in the polar regions, and ternary nucleation likely to occur in many other marine environments, there is typically insufficient H₂SO₄ vapour to contribute to growth of stable clusters into aerosol particles (operationally defined as particles with $D > 3$ nm). O'Dowd *et al.* (2002a) demonstrated that unless newly formed stable clusters can grow sufficiently fast, the clusters are scavenged by the pre-existing aerosol coagulation sink. For example, a 1 nm particle, under typical H₂SO₄ concentrations, will grow by condensation of H₂SO₄ vapour at a rate of 0.5×10^{-4} nm s⁻¹. This is compared with a coagulation loss rate of 2×10^{-3} s⁻¹, that is, there is a very low probability of survival for 1 nm particles. If, however, the source rate of condensable vapours is increased significantly above that for H₂SO₄, and the particle can grow rapidly to 3 nm, the coagulation loss rate reduces by an order of magnitude, and at 6 nm, the lost rate is reduced further by another order of magnitude. Thus, it is essential for new clusters to undergo rapid condensation growth immediately after formation if they are to have a reasonable probability for survival. The difficulty is that H₂SO₄ concentrations are insufficient to lead to the required growth rate for a significant number of nucleated embryos to survive into aerosol particles.

Recent studies in the coastal zone, where regular and significant particle nucleation events have been observed (O'Dowd *et al.* 1998, 1999c, 2002b), show that iodine oxides have been found to drive the nucleation and growth (O'Dowd *et al.* 2002b). This has raised the question whether or not iodine oxides can explain the production of new aerosol particles over the open ocean. Other issues to consider are that nucleation events over the ocean appear to be relatively infrequent and associated with significant washout after heavy precipitation events. Two questions yet to be answered are (i) is secondary particle production dominated by

Table 1. Sea-spray source functions and range of applicability. For Geever 100 nm <math>D < 1000\text{ nm}</math> $f(x) = ax^b$, $f(x)$ = Number flux, $a = 1.854 \times 10^{-3}$, x = wind speed 1–20 m s⁻¹, $r^2 = 0.8$, $b = 2.706$. For Geever 10 nm <math>D < 10\ 000\text{ nm}</math> $f(x) = ax^b$, $a = 9.204 \times 10^{-5}$, $b = 4.1$. SST, sea-spray temperature; WS, wind speed.

reference	method	formulation (m ⁻² μm ⁻¹ s ⁻¹)	validity		
			size (μm)	WS (m s ⁻¹)	SST (°C)
Monahan <i>et al.</i> (1986)	whitecap ^a /lab	$dF_{M86}/dr = 1.373 U_{10}^{3.41} r^{-3} (1 + 0.057 r^{1.05})$ $\times 10^{1.19} e^{-B^2}$ $B = (0.380 - \log r)/0.650$	$0.3 < r_{80} < 20$	n.a.	lab temp (approximately 20)
de Leeuw <i>et al.</i> (2000)	whitecap ^a /surf	$dF_N/dD = W \times 1.1 \times e^{0.23 \times U} \times D^{-1.65}$	$1.6 < D_0 < 20$	0–9	approximately 16
de Leeuw <i>et al.</i> (2003)	model/field	$dF_N/dr = c \left(\sum_{i=1}^2 A_i e^{-c_i * \ln(r/r_i)^2} \right)$ units: μm ⁻¹ m ⁻² s ⁻¹ $A_1 = 1.41u + 0.98$ $A_2 = 0.51u - 1.82$ $C_1 = -0.1u + 1.69$ $C_2 = 1.09$ $c = (0.24u + 0.4) \times 10^4$	$0.063 < R < 7.996$	0–9	approximately 16
Vignati <i>et al.</i> (2001)	model/field	$dF_{v00}(\log r_{80})/d \log r = \sum_{i=1}^3 N_i / (\sqrt{2\pi} \log \sigma_i)$ $\exp(-(\log r_{80} - \log R_i)/2 \log^2 \sigma_i)$ $d \log r = 0.1$ $i = 1; N_i = 10^{(0.095U + 0.283)}; R_i = 0.2; \sigma_i = 1.9$ $i = 1; N_i = 10^{(0.0422U - 0.288)}; R_i = 2; \sigma_i = 2$ $i = 1; N_i = 10^{(0.069U - 3.5)}; R_i = 12; \sigma_i = 3$	$0.04 < r_{80} < 13$	6–17	approximately 13
Mårtensson <i>et al.</i> (2003) ^b	whitecap ^a /lab	$dF_0/d \log D_p = W(A_k T_w + B_k)$, T_w is water temperature in K $A_k = c_1 D_p^4 + c_2 D_p^3 + c_3 D_p^2 + c_4 D_p + c_5$ $B_k = d_1 D_p^4 + d_2 D_p^3 + d_3 D_p^2 + d_4 D_p + d_5$ $k = 1$, size ranges $j = 1-13$, 0.018–0.168 μm $k = 2$, size ranges $j = 13-26$, 0.168–0.949 μm $k = 3$, size ranges $j = 26-38$, 0.949–5.700 μm ^b	$0.018 < D_d < 20$	n.a.	–2–25

(Continued.)

Table 1 (Continued.)

reference	method	formulation ($\text{m}^{-2} \mu\text{m}^{-1} \text{s}^{-1}$)	validity		
			size (μm)	WS (m s^{-1})	SST ($^{\circ}\text{C}$)
Gong (2003)	modified Monahan/lab	$\text{d}F_{M86}/\text{d}r = 1.373 U_{10}^{3.41} r^{-A} (1 + 0.057 r^{3.45}) \times 10^{1.19e^{-B^2}}$ $A = 4.7(1 + \theta r)^{-0.017r^{-1.41}}$ $B = (0.433 - \log r)/0.433$	$0.07 < r_{80} < 200.04 < r_d$	n.a.	see Monahan <i>et al.</i> (1986)
Clarke <i>et al.</i> (2006) ^c	whitecap ^a /surf	$(\text{d}F_N/\text{d} \log D_p) = w \sum_{i=1}^3 A_i$ $A_i = \beta_0 + \beta_1 D_p + \beta_2 D_p + \beta_3 D_p + \beta_4 D_p + \beta_5 D_p^c$	$0.01 < D_p < 8$	n.a.	approximately 25

^aWhitecap cover is most commonly formulated as (Monahan & O’Muircheartaigh 1980): $W(U_{10}) = 3.84 \times 10^{-6} U_{10}^{3.41}$, where U_{10} (m s^{-1}) is the wind speed at 10 m. ^bSee table 2 for values of the constants. ^cSee table 3 for values of the constants.

entrainment of sulphate clusters/particles from the free troposphere? And (ii) is the background particle concentration maintained by a slow source rate of secondary particles which are below the detection limit of current-day aerosol instrumentation? While we do not aim to answer these questions in this review, we provide the most current summary of recent advances in elucidating the marine secondary aerosol formation process based on current knowledge.

2. Primary marine aerosol source functions

The PMA source function describes the surface flux (typically at 10 m above the ocean) of sea-spray aerosol, i.e. the number of droplets produced per unit surface area and per unit of time. Measurements may provide total fluxes, i.e. the total number of particles in a given size interval or spectral fluxes. The latter are expressed in number of droplets for a range of size intervals, i.e. $\mu\text{m}^{-1} \text{m}^{-2} \text{s}^{-1}$. It is noted that the particle radius may be given as dry radius (r_{dry}), i.e. the radius the sea-salt particle would have at relative humidity $\text{RH}=0\%$, as the radius the particle would have when normalized to $\text{RH}=80\%$ (r_{80}) or as the radius at formation (r_0). The latter would be understood as a particle with the composition of seawater in an environment with the equilibrium RH over seawater ($\text{RH}=97\%$). The formulation depends on the way the source function has been derived. As a rule of thumb, $r_0 \approx 2r_{80} \approx 4r_{\text{dry}}$. Often the particle diameter is used instead of radius. In this review, we focus on a selection of source functions which span both submicrometre and supermicrometre sizes, with particular emphasis on the submicrometre flux.

The selected source functions are shown in [figure 1](#) for a wind speed of 8 m s^{-1} . The associated parametrizations are listed in [table 1](#) along with their range of applicability. Mostly, the source functions are presented as power-law functions and hence, at higher wind speeds, the source of sea spray increases in greater proportions than the wind speed increase. These include [Monahan *et al.* \(1986\)](#) who used the whitecap method that is based on combining the parametrization of the whitecap cover using field experimental data and the production of sea-spray aerosol per unit whitecap area determined from laboratory experiments. This parametrization applies to particle diameters in the range $0.3\text{--}10 \mu\text{m}$, which is the range of the particle counter used in their laboratory experiments. Monahan's parametrization has also been extrapolated down to 20 nm sizes, as shown in the figure; however, there is no scientific rationale associated with this extrapolation. It should be noted that although not included here, [Hoppel *et al.* \(2002\)](#) recommend a combined source function using [Monahan *et al.* \(1986\)](#) and a modified version of [Smith *et al.* \(1993\)](#). [Gong \(2003\)](#) modified Monahan's source function to account for the observed decrease in the particle concentrations for particles smaller than $0.1 \mu\text{m}$ radius ([O'Dowd *et al.* 1997](#)) although the results at the smallest sizes are likely to be questionable. [Vignati *et al.* \(2001\)](#) used an approach based on inverse modelling and also used the observations of [O'Dowd *et al.* \(1997\)](#).

[de Leeuw *et al.* \(2000\)](#) based their parametrization on surf zone experiments while [Reid *et al.* \(2001\)](#) used a concentration build-up method using aircraft measurements in an evolving internal boundary layer. A more recent scheme developed by [de Leeuw *et al.* \(2003\)](#) used the Vignati method for data collected in

Table 2. Values of constants used in [Mårtensson *et al.* \(2003\)](#).

size interval (μm)	c_1	c_2	c_3	c_4	c_5
0.018–0.168	-2.87×10^{28}	-1.30×10^{22}	1.94×10^{15}	-1.00×10^8	7.46×10^{-1}
0.168–0.949	-4.57×10^{24}	1.30×10^{19}	-1.34×10^{13}	5.76×10^6	-7.15×10^{-1}
0.949–5.700	-1.09×10^{21}	1.64×10^{16}	-8.43×10^{10}	1.59×10^5	-5.53×10^{-2}
	d_1	d_2	d_3	d_4	d_5
0.018–0.168	-8.37×10^{30}	3.81×10^{24}	-5.74×10^{17}	3.01×10^{10}	-2.21×10^2
0.168–0.949	1.25×10^{27}	-3.62×10^{21}	3.81×10^{15}	-1.67×10^9	2.17×10^2
0.949–5.700	2.93×10^{23}	-4.44×10^{18}	2.29×10^{13}	-4.32×10^7	1.52×10^1

Table 3. Values of constants used in [Clarke *et al.* \(2006\)](#). (Percentage values of constants in [Clarke *et al.* \(2006\)](#).)

coefficient	D_p range (μm)		
	0.01–0.132	0.132–1.2	1.2–8.0
β_0	-5.001×10^3	3.854×10^3	4.498×10^2
β_1	0.808×10^6	1.168×10^4	0.839×10^3
β_2	-1.980×10^7	-6.572×10^4	-5.394×10^2
β_3	2.188×10^8	1.003×10^5	1.218×10^2
β_4	-1.144×10^9	-6.407×10^4	-1.213×10^1
β_5	2.290×10^9	1.493×10^4	4.514×10^{-1}

the Pacific near Hawaii. [Mårtensson *et al.* \(2003\)](#) determined their source function from bubble-mediated laboratory studies to determine the flux as a function of whitecap coverage and then incorporated Monahan's wind speed and whitecap relationship to produce flux estimates. Their parametrization also includes temperature effects, finding that at lower temperatures, the dry size of the spray droplet reduced in size with reducing sea surface temperature. [Clarke *et al.* \(2006\)](#) determined the production over the surf zone and related that to open ocean production using whitecap cover, similar to de Leeuw, but extending the valid interval to the range 0.01–8 μm dry radius ([table 3](#)).

The data in [figure 1](#) show that the discrepancy between different formulations is much reduced with respect to the situation when Andreas did his review. The source functions shown in [figure 1](#) were obtained using different methods and physical principles but leading to consistent results. Comparison of the formulations by [Clarke *et al.* \(2006\)](#), a representative expression for the 'whitecap method', de Leeuw, Monahan and Reid and colleagues show that they lie within approximately a factor of 2 ([Clarke *et al.* 2006](#)). In addition, [Clarke *et al.*](#) compares very well with the [Mårtensson *et al.*'s \(2003\)](#) laboratory-based parametrization. This provides the level of confidence in PMA source functions over sizes from 0.01 to approximately 10 μm ([Clarke *et al.* 2006](#); [table 3](#)).

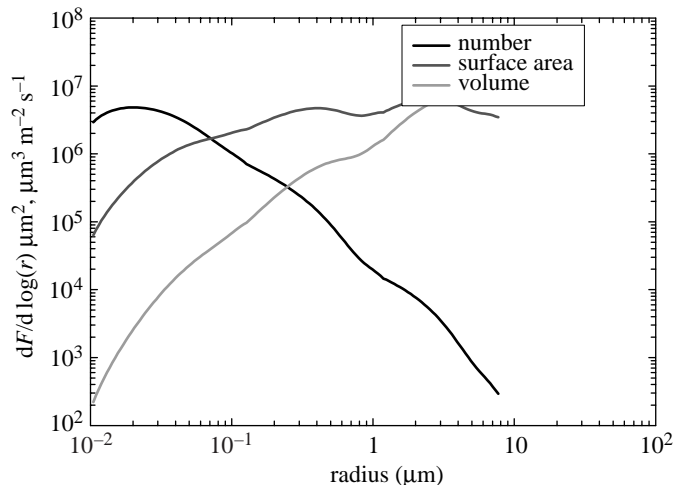


Figure 2. Number, surface area and volume source functions at 18 m s^{-1} using the source function from Clarke *et al.* (2006).

It is useful to also look at the higher order moments of the sea-spray source function distribution to estimate the sea-spray surface area and volume flux since these fluxes are important for chemical reactions and scattering processes. Figure 2 illustrates the number, surface area and volume flux at 18 m s^{-1} for the Clarke *et al.* (2006) parametrization (corresponding to a water temperature of 28°C). It can be clearly seen that while the number is dominated by submicrometre sizes, and in particular, sizes as small as 20 nm , the surface area flux is dominated by modes at 300 nm and $2\text{--}3 \mu\text{m}$. Volume is dominated by the $3 \mu\text{m}$ mode also; however, the trend indicates that the actual volume mode is at sizes greater than $10 \mu\text{m}$. This is consistent with the volume mode reported by O'Dowd *et al.* (1997).

The PMA source functions discussed above are based on indirect methods relying on measurements of particle concentrations, which in most cases can reliably be assumed to be sea spray (refractory measurements and profiles over the surf zone). Direct measurements of sea-spray fluxes are provided by the eddy covariance (EC) method that was first attempted by Nilsson *et al.* (2001) in the Arctic Ocean using an ultrasonic anemometer (Sonic) and a condensation particle counter (CPC) to measure the total number flux of particles larger than 10 nm . The advantage of this method, as opposed to the whitecap method, is that all particles within the detectable size range may be measured, and hence there is no restriction for bubble-mediated production. The technique was also used at a coastal station over the North East Atlantic by Geever *et al.* (2005). In the latter study, fluxes were quantified for total number concentration larger than 10 nm using a CPC, and larger than 100 nm using a particle measuring system active scattering aerosol spectrometer probe (ASASP-X). The data were carefully filtered to remove any potential surf zone effect and they demonstrated that the peak in the flux footprint for the filtered data was clearly $1\text{--}2 \text{ km}$ offshore. Geever *et al.* (2005) found that approximately 50% of the number flux occurred into the Aitken mode ($10\text{--}100 \text{ nm}$) and 50% into the accumulation mode ($100\text{--}1000 \text{ nm}$).

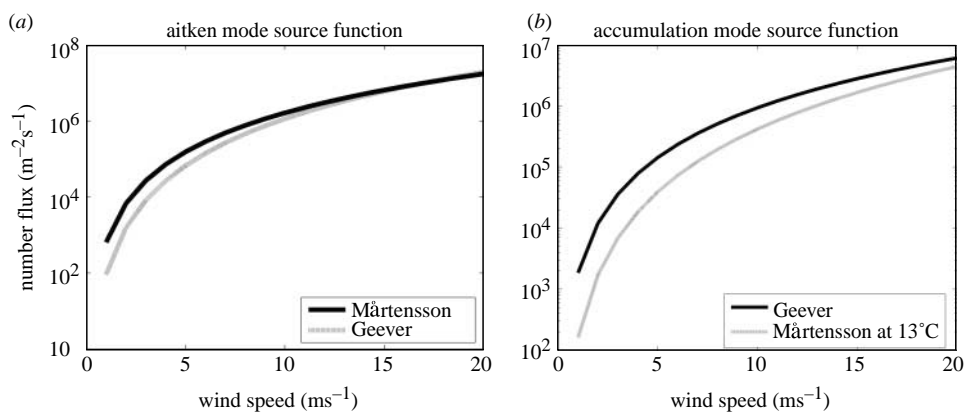


Figure 3. (a) Parametrized source function of total number concentration from Mårtensson and Geever for sizes larger than 10 nm. (b) Parametrized source function of total number concentration from Mårtensson and Geever for sizes larger than 100 nm. Mårtensson parametrization is derived for a sea surface temperature of 13°C.

They reported measurements up to 18 m s^{-1} . Figure 3 compares the Geever integrated number with that derived from Mårtensson at sizes $D > 10$ and 100 nm. For sizes $D > 10$ nm, the two parametrizations exhibit close agreement, while the agreement is not as close, but still reasonable for sizes larger than 100 nm.

3. Submicrometre size distribution structure

Over the last few years, three detailed studies on laboratory-generated sea-spray production were conducted. Mårtensson *et al.* (2003) conducted experiments using artificial seawater (using aquarium-grade sea salt) for four different water temperatures and three different salinities. At 25°C, there was a distinct mode at approximately 100 nm and a secondary mode at approximately 40 nm (diameter). Both modes appeared to shift to smaller sizes as the temperature was reduced to 5°C with an increasing amplitude for the smaller mode and a decreasing amplitude for the larger mode.

Sellegri *et al.* (2006) conducted experiments on artificial seawater alone and artificial seawater with added synthetic surfactant (SDS). At 23°C, the aerosol distribution resulting from the use of surfactant-free seawater comprised three modes (figure 4): (i) a dominant accumulation mode at 110 nm, (ii) an Aitken mode at 45 nm, and (iii) a third mode at 300 nm, resulting from forced bursting of bubbles. The forced bursting occurs when bubbles fail to burst upon reaching the surface and are later shattered by splashing associated with breaking waves and/or wind pressure at the surface. At 4°C, the accumulation mode diameter was reduced to 85 nm, the Aitken mode diameter was reduced to less than 30 nm and the 300 nm mode diameter was reduced to 200 nm. With the addition of SDS, the relative importance of the mode resulting from forced bursting increased dramatically.

Tyree *et al.* (in press) also conducted submicrometre aerosol measurements from controlled bubble-mediated production in the laboratory. They also found, for inorganic seawater, a dominant mode at 100 nm. They found that a reduction in salinity reduced the net flux of particles and also reduced the dominant mode

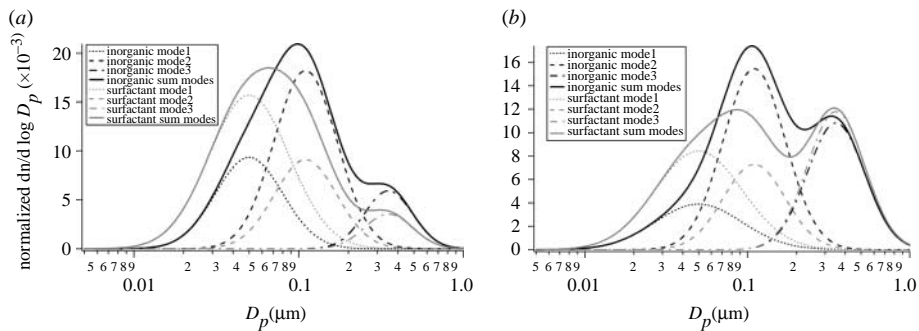


Figure 4. (a) Resulting size distribution for small sintered gas bubble system (mean bubble size $160\ \mu\text{m}$) for inorganic seawater and with added surfactant. (b) Same as (a) except for weir-generated bubbles with a mean size of $70\ \mu\text{m}$. Reproduced with permission from American Geophysical Union (Sellegri *et al.* 2007; doi:10.1029/2005JD006658). Copyright © American Geophysical Union.

size from $100\ \text{nm}$ at a salinity of 70% to $90\ \text{nm}$ at a salinity of 10% . This change in salinity reduced the number concentration by a factor of 2. In addition, they found that the addition of natural organic matter increased the droplet flux by a factor of 1.5.

These preliminary studies indicate a more complex submicrometre spectral structure that is significantly affected by salinity, temperature and surfactant concentration and suggest that more detailed studies are required for laboratory-generated sea-spray aerosol.

4. Chemical composition

Although the dominant mass fraction of sea-spray aerosol is inorganic sea salt, organic matter can also contribute to the overall mass and it has long been known that marine aerosols contain organic material (i.e. Blanchard 1964; Hoffman & Duce 1976). Recent field measurements clearly document the presence of organic matter in individual particles (Middlebrook *et al.* 1998) and a relevant contribution of organic species to fine aerosol mass in the unperturbed MBL (Putaud *et al.* 2000). However, the role of organic compounds in the remote marine aerosol, although recognized as potentially important (Matsumoto *et al.* 1997; Novakov *et al.* 1997), remains largely uncertain, mainly due to the lack of quantitative measurements of their size-dependent composition. Further, despite a large number of studies on the occurrence of individual compounds or classes of compounds, e.g. carboxylic acids (Kawamura & Sakaguchi 1999; Mochida *et al.* 2003), a comprehensive characterization of the chemical nature of organic matter in marine aerosols is currently not available.

The most comprehensive study to date on the organic fraction of sea-spray aerosol has been conducted by Cavalli *et al.* (2004) and O'Dowd *et al.* (2004). They found a significant and dominating fraction of organic matter in submicrometre sizes, while the supermicrometre size range was predominately inorganic sea salt. However, it should be noted that the absolute magnitudes of organic mass in the sub- and supermicrometre size ranges were equivalent and it was their relative

concentrations that differed significantly. Figure 5 illustrates the chemical composition of clean marine aerosol over the northeast Atlantic during winter and summer periods, corresponding to low and high biological activity periods (O'Dowd *et al.* 2004). Also shown is the distribution of chlorophyll *a* derived from the SeaWiFS satellite. O'Dowd *et al.* (2004) found that the majority of the organic matter was water insoluble and argued that this organic fraction and a large component of the water-soluble organic fraction were likely to be derived from bubble-mediated production. This thesis was based on the detailed characterization of the organic fraction by Cavalli *et al.* (2004) who found that the water-soluble organic carbon chemical composition comprises mainly aliphatic and only partially oxidized species and humic-like substances and results in appreciable surface-active properties. Further, the observed organic matter chemical features (size-dependent concentration, hydrophobic nature of a substantial fraction of the organic matter, low oxidized and surface-active WSOC species) were consistent with the hypothesis of a primary marine source; bubble-bursting processes, occurring at the surface of the North Atlantic ocean during phytoplankton blooms, effectively transfer organic matter into marine aerosol particles, particularly enriching the fine aerosol fraction. In summary, during periods of high biological activity, the organic fraction ranged from 40 to 60% of the submicrometre mass, while during low biological activity periods, the fraction reduced to approximately 10–15%. The measurements by Cavalli *et al.* (2004) and O'Dowd *et al.* (2004) were taken at a coastal station (Mace Head); however, a recent evaluation of offshore and coastal measurements around Mace Head confirmed the lack of any coastal effect influencing the results (Rinaldi *et al.* in preparation).

5. Secondary aerosol formation from iodine vapours

As outlined in §1, sulphuric acid may form stable clusters leading to particle formation, but there seems typically to be insufficient sulphuric acid which can lead to growth of sizes larger than 3 nm. In an effort to elucidate an alternative source of condensable vapour leading to particle production, a large body of work has emerged in the last few years on iodine-related particle production in the coastal zone and the main results are summarized here. During low tide and clean air conditions in the coastal zone, massive bursts of new particles can regularly be observed with concentrations rapidly rising up to 10^6 cm^{-3} (O'Dowd *et al.* 2002*b*). Figure 6 illustrates a typical event observed at Mace Head where the concentration increase occurs at low tide when inter-tidal algae are exposed to the atmosphere. It can be noted that the peak in sulphuric acid concentration occurs significantly later than the particle burst. In fact, during the burst, the nucleation mode acts as a sink for sulphuric acid as the condensation sink rises significantly. Following detailed field studies during the research programme New Particle Formation and Fate in the Coastal Environment (PARFORCE; <http://macehead.nuigalway.ie/parforce>), laboratory studies into the formation of aerosols from CH_2I_2 , conducted by Hoffmann *et al.* (2001) and Jimenez *et al.* (2003), confirmed significant particle production in the presence of UV-radiation and O_3 and a formation mechanism resulting in the polymerization of OIO into I_2O_4 was proposed (figure 7). Jimenez and colleagues suggested that while it was clear that significant particle production occurred from CH_2I_2 , an additional source of condensable material might be required to

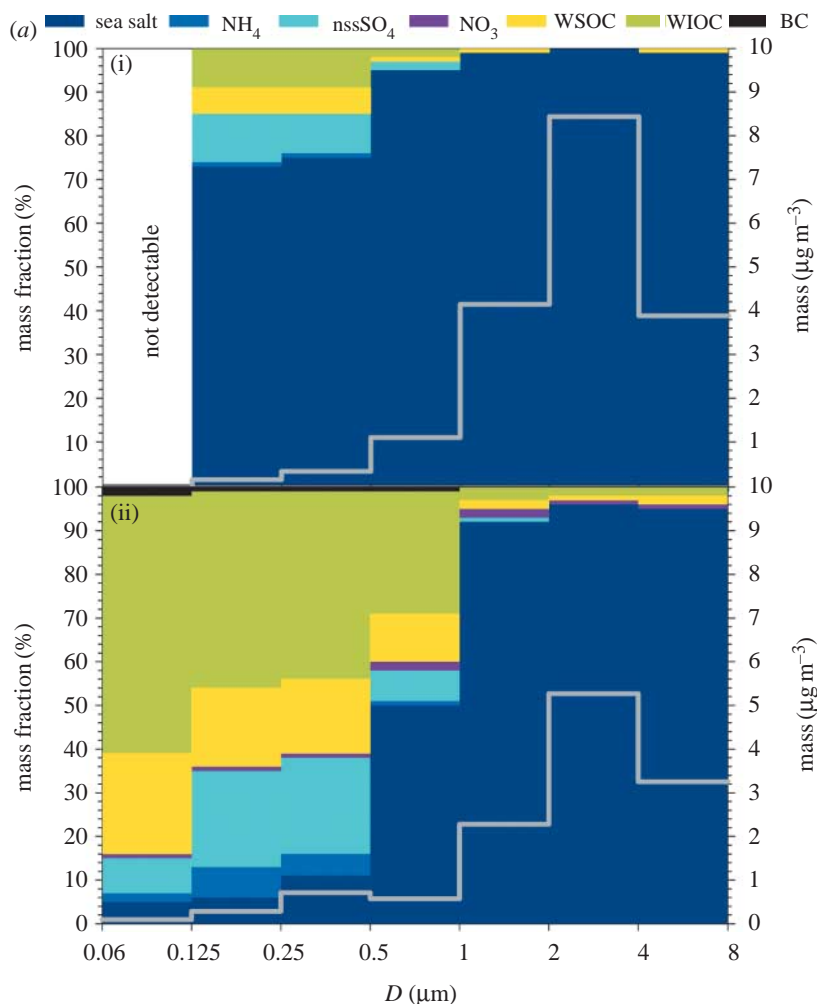
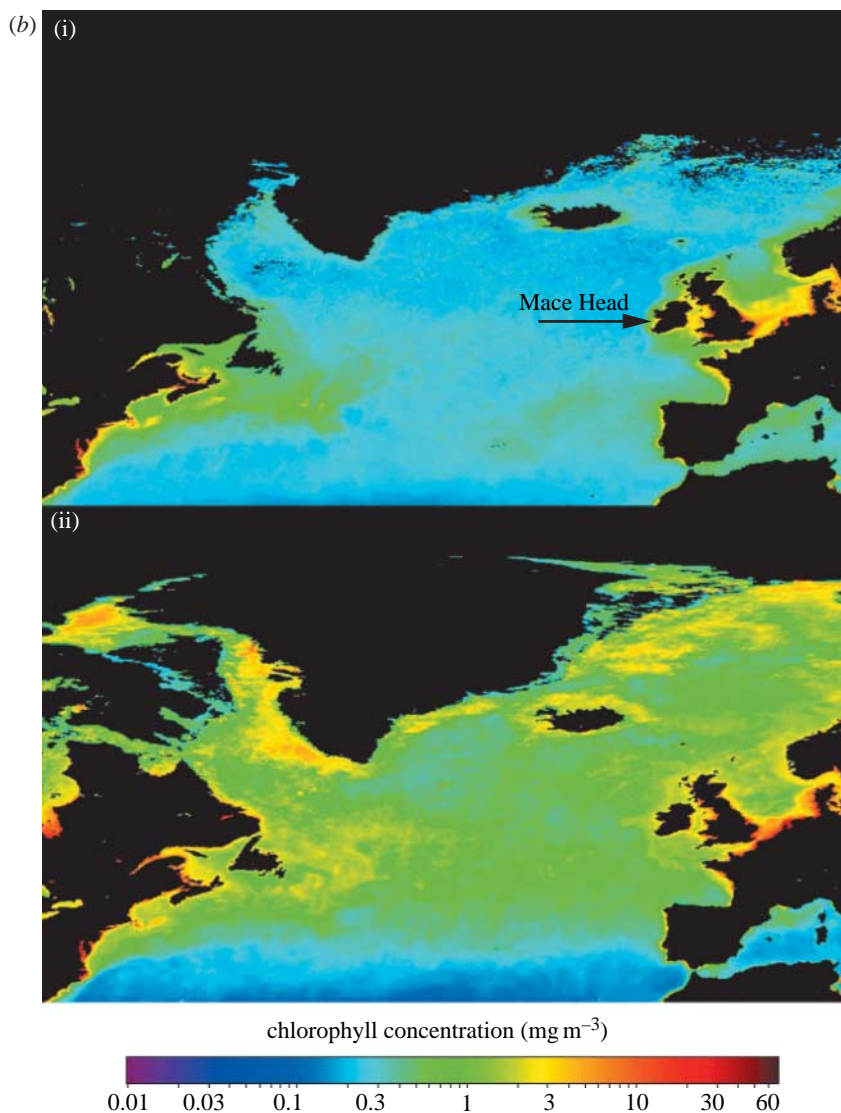


Figure 5. (*Continued.*) (a) Chemical and mass size distributions for North Atlantic marine aerosol during periods of (i) low biological activity and (ii) high biological activity. (b) Oceanic chlorophyll a concentrations over the North Atlantic for low and high biological activity periods (i) winter and (ii) spring.

explain the observations in the atmosphere. Preliminary modelling of the coastal nucleation system by Pirjola *et al.* (2002) revealed that a nucleation rate of the order of 3×10^5 – 3×10^6 $\text{cm}^{-3} \text{s}^{-1}$ was required and that the condensable vapour source rate needed to be of the order of 5×10^7 $\text{cm}^{-3} \text{s}^{-1}$, leading to a condensable vapour concentration of the order of 6×10^9 cm^{-3} . The conclusions from these modelling studies were that sulphuric acid concentrations could perhaps explain the nucleation of clusters in most events; however, there were typically three orders of magnitude too low sulphuric acid availability to explain growth into detectable sizes and for the concentrations encountered during these events.

Burkholder *et al.* (2004) were the first to attempt to completely model the iodine system from photolysis, to iodine oxide nucleation and on to aerosol growth. In their studies, they used a kinetic nucleation approach coupled to an aerosol dynamics

Figure 5. (*Continued.*)

model. Using their aerosol formation model, Burkholder and colleagues evaluated the possibility of OIO particle formation in the coastal zone and the open ocean through comparisons of measurements of both IO and OIO concentrations in oceanic regions. The IO measurements come from Mace Head and Tenerife and peak values range from 2 to 5 ppt (Alicke *et al.* 1999), while the OIO measurements were sources from Allan *et al.* (2001) and of the order of 0.5 ppt. The simulations concluded that steady-state concentrations of 10 ppt OIO would lead to a particle concentration of 10^6 cm^{-3} after 10–20 min, while concentrations of the order of 50–100 ppt IO would be required to produce significant particles. These concentrations are significantly higher than the reported observations of both IO

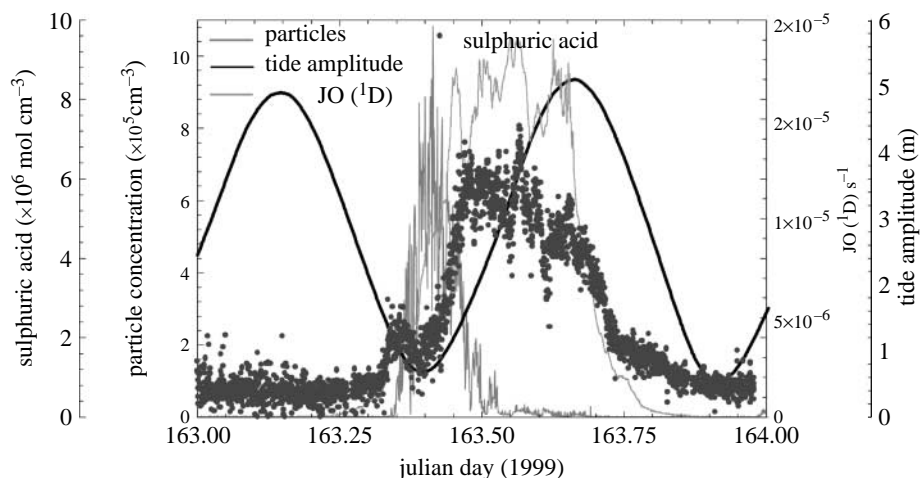


Figure 6. An example of a coastal nucleation event at Mace Head. Also shown are the tidal cycle, photolysis range $JO (^1D)$ and sulphuric acid concentrations. Reproduced with permission from American Geophysical Union (O'Dowd *et al.* 2002b; doi:10.1029/2001JD000555). Copyright © American Geophysical Union.

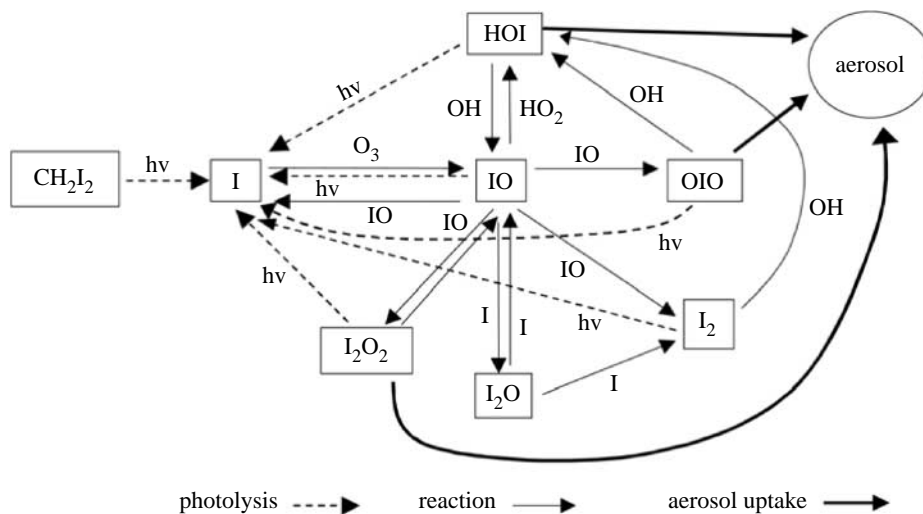


Figure 7. Formation mechanism of iodine oxide aerosol from biogenic organoiodine. Taken from O'Dowd *et al.* (2002b) and Jimenez *et al.* (2003). Reproduced with permission from American Geophysical Union (Jimenez *et al.* 2003; doi:10.1029/2002JD002452). Copyright © American Geophysical Union.

and OIO. It should, however, be noted that IO and OIO measurements at Mace Head were conducted using long-path DOAS measurements and thus, spanned a horizontal distance of 15 km. Given that the tidal regions are only a fraction of a kilometre, both IO and OIO concentrations could easily reach an order of magnitude higher than that reported by the DOAS measurements, and they concluded that iodine oxide particle production could be feasible in local 'hot-spots' where elevated concentrations of CH_2I_2 could drive the system.

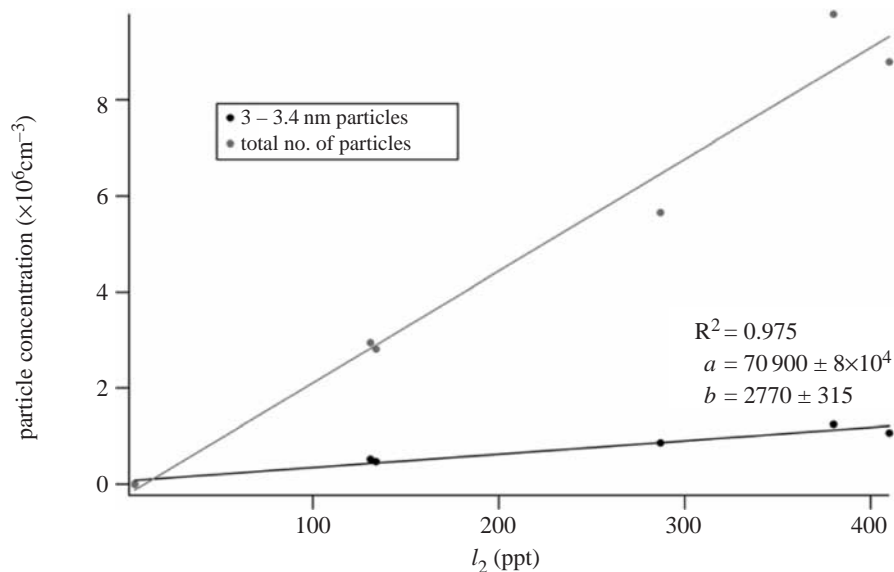


Figure 8. Relationship between particle concentrations as a function of molecular iodine (Sellegri *et al.* 2005).

While initially, CH_2I_2 appeared promising as the main source of coastal nucleation events, it became clear that its source rate was still insufficient to explain the observations. Subsequently, McFiggans *et al.* (2004) found that the iodine flux from molecular iodine was three orders of magnitude greater than that from CH_2I_2 . This high source of molecular iodine was able to explain the observed levels of OIO (3 ppt) and was supported by observations of I_2 ranging from 20 ppt in the daytime to more than 80 ppt at night (Saiz-Lopez *et al.* 2004, 2005). As a consequence, molecular iodine seemed the most probable precursor of the observed nucleation events. Around the same time, Sellegri *et al.* (2005) conducted chamber experiments on inter-tidal algae (*Fucus* and *Laminaria*). The experiments were designed to be as close to atmospheric conditions as possible and were conducted in a 2 m^{-3} perspex flow-through chamber with 50% UV transmission efficiency. Natural sunlight was used to drive the photochemistry and clean ambient air, filtered of background aerosol but not scrubbed of ozone, was used as the flow carrier. The main results revealed a strong correlation between I_2 concentrations and seaweed biomass. Further, the concentration of particles produced, both the total particle concentration and the concentration of particles between 3 and 3.4 nm, were linearly correlated with I_2 concentrations (figure 8). Peak I_2 concentrations of 400 ppt produced approximately 2×10^6 particles cm^{-3} in the 3–3.4 nm size range and approximately 10^7 particles cm^{-3} as a total particle concentration. For a seaweed mass of 2.5 kg m^{-3} , the flux of 3–3.4 nm particles was of the order of $1.5 \times 10^{10} \text{ m}^{-2} \text{ s}^{-1}$, which compared well with direct eddy-covariance flux measurements (Flanagan *et al.* 2005). Model simulations of the chamber experiments (Pirjola *et al.* 2005) derived a range of I_2 fluxes from 5×10^8 to $1.5 \times 10^9 \text{ cm}^{-3} \text{ s}^{-1}$. The calculations showed that for the lower I_2 flux, I_2 reached a steady-state concentration of $3.2 \times 10^9 \text{ cm}^{-3}$ and for the higher flux, a concentration of $1 \times 10^{10} \text{ cm}^{-3}$, which were in very close agreement with the observations.

Although it was clear that iodine oxides, most probably predominant from I_2 emissions were producing the observed nucleation events, there was some debate on the actual form of the iodine oxide. In particular, Saunders & Plane (2005) argued on the basis of *ab initio* modelling studies and elemental analysis of iodine oxide particles produced in laboratory chamber experiments that the form was more like I_2O_5 rather than I_2O_4 , requiring I_2O_4 to undergo a further reaction with O_3 to produce I_2O_5 . While the results clearly suggest the formation of I_2O_5 under laboratory conditions, this is not necessarily the case in the atmosphere. Väkevä *et al.* (2002) conducted measurements into nucleation mode aerosol uptake of water (i.e. hygroscopic growth) and found that under typical coastal particle production conditions, the new particles possessed very low hygroscopicity—an observation inconsistent with the proposed dominance of I_2O_5 , which is very water soluble in comparison to the non-water-soluble characteristics of I_2O_4 .

In terms of open ocean particle production, the situation is less clear, mainly due to the significantly lower biogenic emissions when compared with the coastal zone and also the less frequent observations of nucleation events to study. Studies have clearly linked iodocarbon production to phytoplanktonic processes (Yamamoto *et al.* 2001) suggesting that over the open ocean, there is likely to be an unaccounted and significant source of biogenic iodine which could perhaps contribute to particle production. In addition, there are also inorganic sources of iodine. For example, the direct photochemical oxidation of iodide at the sea–air interface (Miyake & Tsunogai 1963) is likely to be an important source as is the oxidation by ozone of seawater iodide, followed by the release of I_2 into the gas phase (Vrbka *et al.* 2004). The latter mechanism depends on ozone deposition at the ocean surface and the production of I_2 must take place at the air–sea interface for volatilization to occur.

Since the aforementioned processes have only been recently hypothesized as participating in open ocean particle production, there is little evidence gathered to date to evaluate the role of either organic or inorganic iodine in process. Future experiments should be designed to evaluate the sources and the role of iodine in open ocean particle production. As mentioned in the §1, the source strengths of precursors over the open ocean are quite low and often difficult to detect, particularly for iodine species which are very short lived, thus presenting significant challenges associated with addressing these hypotheses.

6. Secondary organic aerosol formation

The work by O'Dowd *et al.* (2004), and references therein, point to a significant source of both water-soluble and water-insoluble organic carbon in marine aerosol. They concluded that both classifications, and in particular, the water-insoluble organic carbon was most likely resulting from bubble-mediated primary production. However, it is possible that a notable fraction of the oxidized and water-soluble organic carbon could be produced via Secondary organic aerosol (SOA) formation processes. If this was indeed the case, some evidence of SOA composition should be visible in at least coastal nucleation mode particles. Such evidence was provided by Vaattovaara *et al.* (2006) for coastal nucleation events at Mace Head. They used a novel experimental system to examine organic

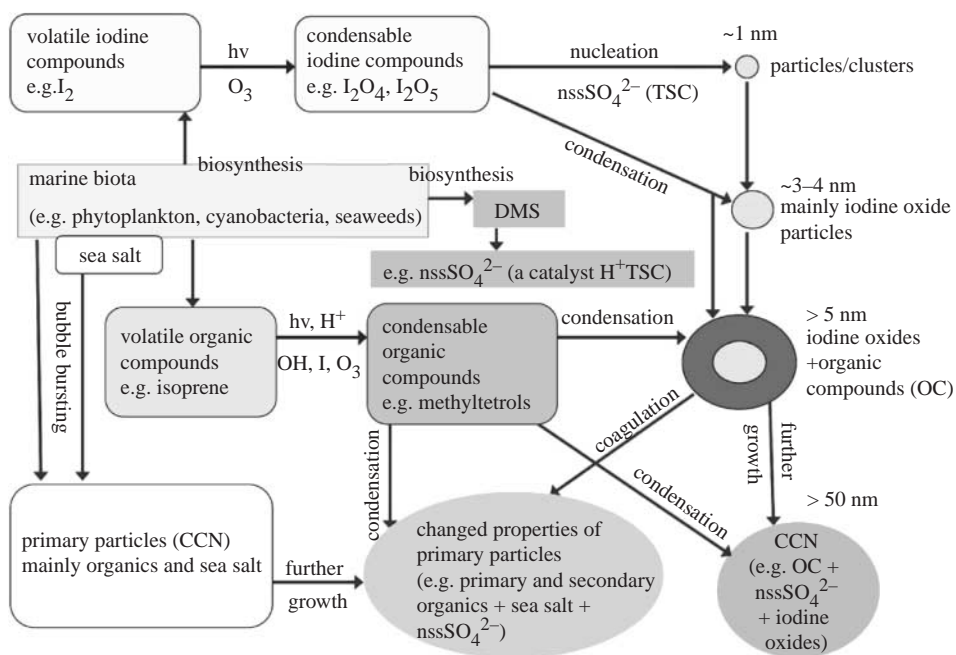


Figure 9. Schematic of both primary and secondary aerosol production and growth of marine aerosol (taken from Vaattovaara *et al.* 2006, Copyright EGU).

vapour uptake on recently formed 10 nm particles, the principle being that organic aerosols are significantly more soluble in organic vapours than inorganic aerosols (similar principle to water-based hygroscopic growth). They found that under certain event types, 11–47% of the mass fraction could be attributed to an organic fraction produced by SOA formation processes. They suggested that isoprene was a probable precursor to SOA. *In situ* (Greenberg *et al.* 2005) and remote-sensing studies (Palmer & Shaw 2005) estimated isoprene fluxes ranging from 10^7 to 10^9 molecules $\text{cm}^{-2} \text{s}^{-1}$ from marine biota which could account for a significant source of SOA. Chamber estimates of the aerosol yield of isoprene are of the order of 1–3% depending on the oxidation conditions (Kroll *et al.* 2005, 2006). Most recently, Meskhidez & Nenes (2006) suggested a dominant role for isoprene in the formation of SOA resulting from plankton emissions over the southern ocean. They suggested that the contribution to marine aerosol was so significant that it contributed to a notable indirect effect in terms of cloud reflection. Vaattovaara *et al.* (2006) concluded that SOA formation contributed to the growth of recently formed particles rather than being involved in driving the formation.

The current conceptual picture on marine aerosol formation and growth is summarized in figure 9 (taken from Vaattovaara *et al.* 2006). Clearly, there are many different processes and chemical species contributing to secondary marine aerosol formation and growth. Rather than looking for a single species to be responsible for aerosol production, there are clearly multiple steps involved. Both sulphuric acid and iodine oxides are likely to nucleate stable embryos; however, sulphuric acid cannot contribute to growth into aerosol sizes. This growth may

be supported by iodine oxide and isoprene oxidation products. An alternative is that iodine oxides nucleate and growth is accelerated by sulphuric acid and isoprene products. Both the above options are equally probable at different times due to sulphur and iodine species being emitted by different plankton species and/or different parts of the plankton life cycle.

In any event, it is unlikely that isoprene products are responsible for nucleation, but clearly can contribute to growth.

7. Conclusions

Considerable advances have been made in the last 5 years in terms of better understanding of both primary and marine aerosol formation. In terms of PMA, a number of studies have confirmed a significant flux of submicrometre sea-spray particles, even down to 10 nm sizes. Furthermore, the estimates of the sea-spray flux in submicrometre and micrometre size ranges exhibit close agreement despite the variety of methods used to derive the fluxes. While it is unclear if one flux scheme should be recommended over another, it is clear that like wind speed, sea surface temperature also affects the physical sea-spray source function, so future improvements on the source function should also account for sea surface temperature. In addition to the physical source function, the chemical source function also needs to be developed as there is a growing body of evidence that primary organic matter contributes significantly to the sea-spray source flux, and at times, can dominate in submicrometre sizes. As a strong recommendation, the chemical component must also be incorporated into the source function also, although this presents a challenge as it involved incorporating a biogenic factor into what has traditionally been a dynamic or physical source function.

In terms of secondary marine aerosol formation, significant advances have been made in identifying particle production, at least in coastal zones where iodine oxides are considered the dominant species leading to particle production (O'Dowd & Hoffmann 2005). Contributing to growth can also be SOA species (i.e. isoprene oxidation products) and sulphuric acids. Further, sulphuric acid and iodine oxides are perhaps equally likely to form stable clusters from the gas phase (i.e. nucleation); however, sulphuric acid on its own does not appear capable of growing the stable clusters to detectable sizes of 3 nm and larger. At that stage, iodine oxides and organic vapours are more likely to drive aerosol growth. The difficulty in truly elucidating this process relates to the very low levels of short-lived precursor gases over the ocean, combined with the difficulty associated with detection of low production rates of new particles, given current day aerosol instrumentation, and these difficulties present us with a considerable challenge in terms of really identifying the dominant processes and species and the source rate of new particles, formed *in situ*, in the MBL. On a more positive front, if the rate of instrumentation and analytical methods continue to develop as they have recently, along with the increased scientific focus on gas and aerosol emissions from the marine environment, the outlook for considerable advances is actually quite positive.

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