Surfactants and submicron sea spray generation

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[1]   Laboratory experiments have been carried out to elucidate the role of surfactants on the primary marine aerosol production of submicron marine aerosols. A synthetic surfactant SDS was used in conjunction with artificially generated seawater, and the resultant bubble-mediated aerosol produced was observed. At 23°C, the aerosol distribution resulting from the use of surfactant-free seawater comprised three modes: (1) a dominant accumulation mode at 110 nm; (2) an Aitken mode at 45 nm; and (3) 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 <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. The laboratory results were compared to the observed seasonality of North Atlantic marine aerosol where a progression from mode radii minima in winter to maxima in summer is seen. The bimodality and the seasonality in modal diameter can be mostly explained by a combination of the three modes observed in the laboratory and their variation as a function of sea-surface temperature and seawater surfactant concentration. These results indicate that submicron primary aerosol modes would on a first approximation result from bubble bursting processes, although evidences of additional secondary processes leading, during summer, to a higher amplitude of the Aitken mode and mode 2 smoothed into mode 3 still need to be investigated.

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1. Introduction

[2]   Aerosol particles influence the Earth's radiative budget by directly intercepting the solar radiation, and indirectly by being activated into cloud droplets that will in turn intercept the solar radiative fluxes. Tropospheric aerosols are highly variable in space and time, and hence it is important to know how they are produced and transformed during transport. Marine aerosols in particular are of high interest because they are produced over large areas and hence are representative of a significant fraction of aerosols found in the atmosphere. Their production rate, according to wind speed or whitecap coverage has been extensively studied [*Monahan et al.*, 1986; *Smith et al.*, 1993; *Nilsson et al.*, 2001], first for the supermicron range, and, with the development of measurement and analysis techniques relative to smaller sizes, also for the submicron range. Recent pseudo-size-segregated flux measurements performed at Mace Head, Western Ireland, showed that, for conditions representatives of the open ocean, the Aitken mode contribution to total submicron particle flux was significant (50%) [*Geever et al.*, 2005]. A temperature dependence of the marine aerosol flux has also been observed in laboratory experiments [*Monahan and O'Muircheartaigh*, 1986; *Mårtensson et al.*, 2003].

[3]   Continuous measurements of the submicron aerosol size distribution at the Mace Head atmospheric research station have recently revealed that clean North East Atlantic aerosols show a seasonality in both size and concentration [*O'Dowd et al.*, 2004]. During the summer, the Aitken and accumulation mode diameters are 1.4 times as large as during the winter (going respectively from 28 to 40 nm and from 100 to 135 nm, up to a maximum of 197 nm). Seasonal changes in the size distribution of marine aerosols could be attributed to seasonal variability of seawater temperature quantified by *Mårtensson et al.* [2003]. However, the influence of surfactants and organic matter concentrated at the ocean surface has also been invoked to explain the trends [*O'Dowd et al.*, 2004; *Cavalli et al.*, 2004]. *Woodcock* [1948] already showed that drops produced by bubbles bursting in areas with high concentrations of plankton (dinoflagellates) in red tide could carry an organic irritant and it was further confirmed by *Blanchard and Syzdeck* [1970] that bacteria are concentrated at the sea surface, leading to enrichment of sea spray aerosol.

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[4] Foam is often produced in waters where surfactant concentrations are more concentrated. Foam is defined as a mass of bubbles of air or gas formed on or in a liquid because of agitation. In the case of the marine environment, foam is produced when bubbles (manifested by whitecaps) are formed close to or at the sea surface because of breaking waves. The seawater foam ability has been shown to be gradually higher when the salinity was increased, reaching a finite maximum at 35 ppt [*Peltzer and Criffin*, 1988]. Foam formation in slicks has been related to sea state [*Abe*, 1962] with a higher foam ability of the seawater presumably associated with higher wave amplitude. The presence of organic matter in seawater can modify the seawater foam ability in different ways depending on the nature of the organics and time. The bubble life time at the seawater surface was shown to be increased or decreased depending on the solubility of the surface active substances and the mechanical properties they provide to the surface, which is time dependant [*Garrett*, 1967]. The same contradictory effects have been observed in the relationship between seawater foam characteristics and aerosol production. In some cases a slick apparently enhances the production of film drops and CN [*Garrett*, 1968; *Woolf and Monahan*, 1988], and in other cases the organic film or slick inhibits film-drop and aerosol production [*Blanchard*, 1963; *Woolf and Monahan*, 1988]. It is clear that organic substances present in seawater cover a large range of species, and the effect that they can have on foam formation is a complex function of the nature of the surfactants and bubbling time. Up to present, no clear consensus on the relationship between foam formation and surfactants has been achieved. While surfactants increase the bubble stability, they also tend to decrease the friction velocity at the ocean surface, which in turn is likely to decrease the bubble formation rate due to reduction of entrainment of air. Thus these two competing effects make the relationship between aerosol production, foam formation and surfactant concentration quite complex.

[5] In regard to the seasonal variations in the natural atmospheric aerosol size and concentration observed at Mace Head, we aimed in this work to quantify the change of aerosol size in the submicron range, implied by the presence of a given surfactant in seawater. Results are presented from preliminary laboratory experiments of the effect of SDS (sodium dodecyl sulphate) on the primary production of aerosol particles by bubble bursting in seawater. The effect of SDS on aerosol production by bubble bursting and the seasonal change of particle size in the North Atlantic air masses are then compared, as a first attempt to understand these seasonal changes.

2. Experimental Section

[6] A 30 L Perspex tank was 1/3 filled with artificial seawater, sealed and continuously flushed with 6 L min^{-1} of filtered air. Bubbles were generated using two different methods: (1) a weir created by pumping water from the tank and streaming out at 10 cm above the water surface as a jet of circular cross section and (2) sintered glass filters of small, medium and large pore sizes, immersed at 2 cm below the water surface were used to create bubbles by forcing 50−100 ml min^{-1} of filtered air through them.

[7] The size distributions of the bubbles created with the four bubbling devices were measured directly in the water of the tank using an optical bubble measuring system (miniBMS) where the well-defined sample volume was illuminated by a light beam which was monitored with a video camera [*Leifer et al.*, 2003]. Bubbles between about 30 and 500 μm in diameter can be measured with the miniBMS.

[8] Droplets produced by bubble bursting were sampled through a nafion tube flushed with dry air. Dry aerosol size distributions were then measured using a Scanning Mobility Particle Sizer (SMPS), consisting of an electrostatic classifier (DMA, TSI model 3071) and a particle counter (TSI model 3010). A scan of particles in the diameter size range from 10 nm to 450 nm, at 35−40% RH (measured in the sheath and excess flows) took 120 s. In this study we focus only on the dry or residual aerosol size since the measurement of the spray droplet size is a strong function of RH and is also a rapidly varying parameter.

[9] In order to test the effect of surfactants on the aerosol production, various amounts of surfactant were added to synthetic seawater free of organic matter. The latter was made from Milli-Q water and synthetic sea salt mixture of the main sea-salt components, i.e., Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, Ca^{2+} and K^+, in the proportions mentioned by *Seinfeld and Pandis* [1998]. The surfactant used in this study was sodium dodecyl sulphate (SDS) with a solubility of 100 g L^{-1}. Prior to each experiment, the background aerosol concentration in the tank, while flushing with filtered air, was measured after stopping the bubbling devices. The background concentrations were lower than 20 particles cm^{-3}. After the bubbling started, steady aerosol concentrations were achieved within 5 to 10 min, after which five to ten size distribution spectra were averaged for each experimental condition. Experiments were made both at ambient water temperature (23°C) and in colder water of 4°C.

3. Results

[10] The three bubbling devices produced three different quasi monodisperse bubble size distributions (Figure 1) at 60−70 μm, 150 μm and 450 μm from the weir, small and medium sintered glass filters respectively. Bubbles produced by the sintered glass filter with large pores were 1 to 2 mm diameter and could not be detected with the BMS camera and thus their distribution is not shown on Figure 1. *Blanchard and Woodcock* [1957] published measurements of bubble distributions in the sea a few seconds after small waves had broken. Their distribution, with bubbles from 100 μm to about 500 μm, was heavily weighted toward the small end: most of the bubbles were smaller than 200 μm. An overview of oceanic bubble spectra [*de Leeuw and Leifer*, 2002] shows that they peak at 60−80 μm, with concentrations decreasing with size as $D^{-\nu}$, where ν varies between 1.8 and 5. This would correspond best to the spectra created by our weir. The mean number concentration of bubbles with a diameter of 150 μm in our experiment is 5 10^{-3} bubbles cm^{-3}, similar to oceanic measurements in a wind speed of 14 m s^{-1} [*de Leeuw and Cohen*, 2002].

[11] It is noted that oceanic bubble measurements are time averages that are representative of the average background concentrations; that is, the largest contributions are from
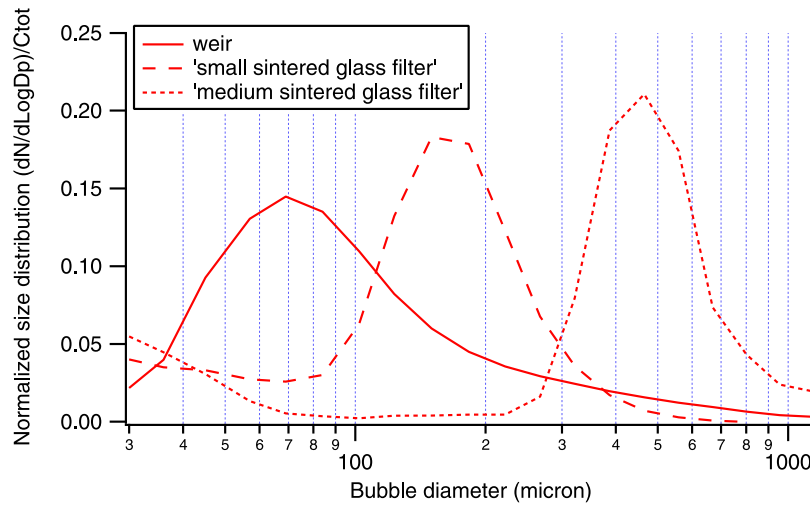
Figure 1. Normalized (to the total number concentration) bubble size distributions generated by various bubbling devices (water pump and sintered glass filters) and measured with the miniBMS camera type measuring system. The three bubbling devices produced three different quasi monodispersed bubble size distributions.

bubble plumes in the senescence phase. Right after breaking, the bubble size distribution is dominated by large bubbles which, because of their buoyancy, rise very fast to the surface and thus disappear within a fraction of a second [*Leifer and de Leeuw*, 2002]. The lifetime of the smaller bubbles is a few seconds and they may be observed tens of seconds after wave breaking and bubble plume formation. Therefore various sizes of bubbles are studied in this work.

[12] The dry size distributions of the aerosol particles produced as residues of droplets bursting from bubbles deriving from the use of these four different bubbling devices in synthetic seawater are shown in Figure 2. The weir produces significantly less aerosols than the sintered glass filters, and hence, in order to compare aerosol size distributions produced by the various bubble size spectra (due to the various bubble devices), the number concentrations (dN/dLogDp) (cm^{-3}) shown in Figure 2 are normalized to the
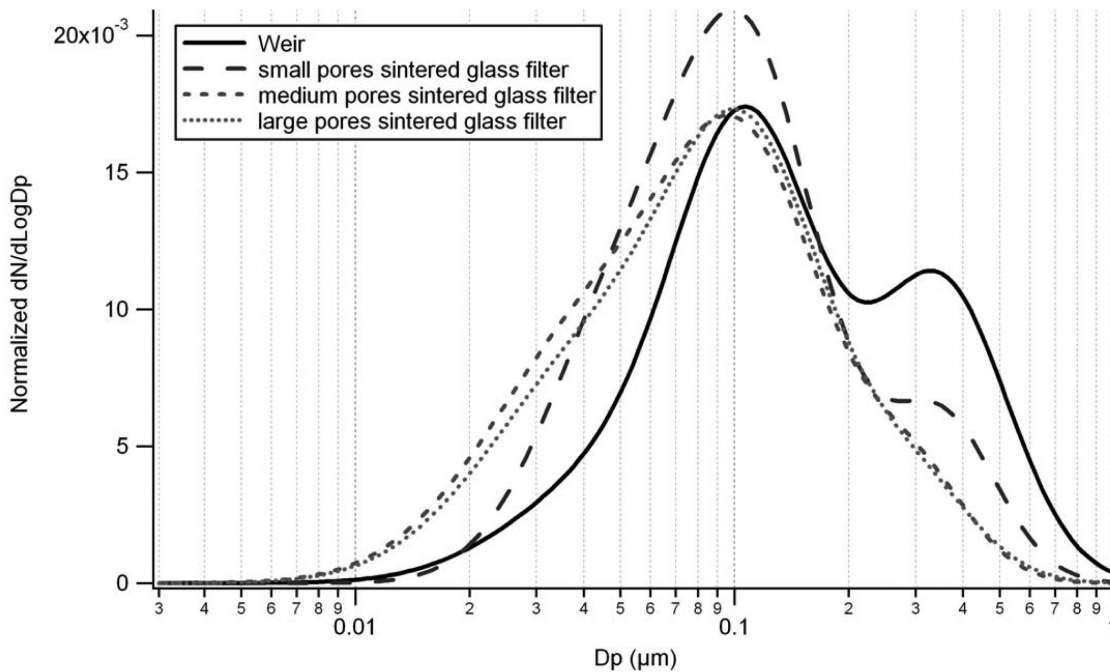

Figure 2. Normalized (to the total number concentration) aerosol size distributions deriving from the use of the four different bubbling devices in synthetic seawater, measured with a SMPS with a 2 min time resolution. The spectra are the results of averages over 5 to 10 size distributions for each device. The resulting size distributions have been fitted with lognormal distributions as described in Figure 3.
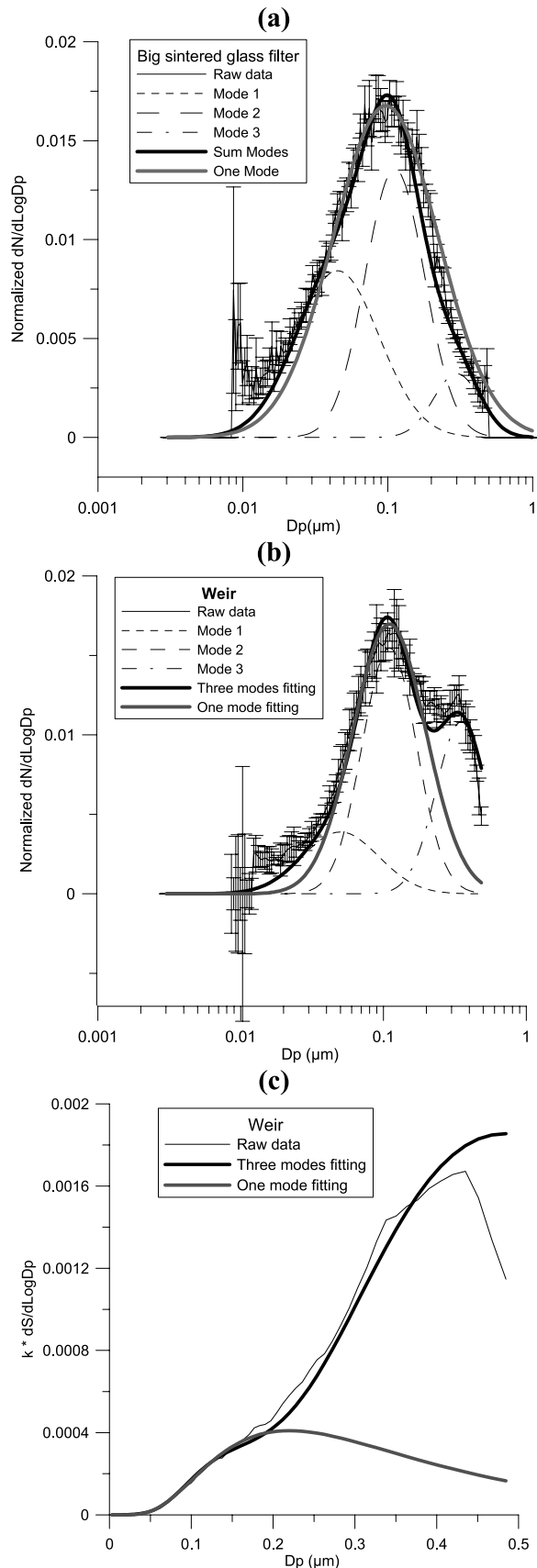
total number concentration (cm^{-3}) of particles (Ctot). Prior to normalization, typical aerosol concentrations for bubble-mediated production from sintered glass filters were from 2500 to 3000 cm^{-3} and between 150 and 850 cm^{-3} for aerosols produced by the weir.

[13] It is very clear from Figure 2 that irrespective of the bubbling device used, the size distributions measured with the SMPS peak at about 100 nm. This indicates that these are film droplets since jet droplet diameters are about 0.1 times the parent bubble diameter [*Blanchard*, 1963]. In addition to a primary mode at 100 nm, a notable mode or a clear "shoulder" in the size distribution is also observed in the size distribution at lower particle sizes. On Figure 3a, the standard deviation on raw data are calculated on the basis of size distributions obtained during four different experiments (performed on different days) under the same conditions (big pore sintered glass filter in synthetic seawater). It can be seen that the aerosol size distribution obtained with a given setup are very reproducible, and they can not be described by one single lognormal size distribution. In fact, each size distribution can be described effectively as the sum of three single lognormal modes (modes 1, 2 and 3), as shown on Figures 3a–3c. The necessity of using mode 3 (300 nm) is made clearer on the aerosol size distribution obtained with the weir by number (Figure 3b), but especially by surface (Figure 3c). It seems that the two smaller diameter modes are produced when rising bubbles burst on reaching the surface. Although many submicrometer colloids have been detected in seawaters [*Wells and Goldberg*, 1991], they do not seem to be captured by rising bubbles and be the cause of the modes observed in the resulting residual particles size distribution. Indeed, size distributions measured when air is bubbled through natural seawater, collected in the Mace Head area (not shown) are similar to the size distributions of particles produced with the same bubbling device in synthetic seawater. Whether modes 1 and 2 are actually two modes resulting from two different processes or it is one skewed distribution resulting from one production process is not clear. However, as will be seen later, dependant on the conditions, these apparent modes are certainly significant. The largest diameter mode at 300 nm, on the other hand, clearly seems to result from a different process, i.e., forced shattering or bursting of pseudostable bubbles that have not yet burst after reaching the air-water interface. This forced breaking is most evident in the weir system and occurs through splashing and bursting by the waterfall and by the pressure of air currents being blown into the pseudostable bubbles. This will be further discussed in section 3.3.

3.1. Effect of Low Temperatures (Winter Conditions)

[14] When the water temperature is decreased from 23°C to 4°C, all three modes are shifted toward smaller sizes, as shown in Figure 4 for the large pore sintered glass filter. A

Figure 3. Example of fitting, with the superposition of three single lognormal distributions of aerosol size distributions generated (a) with the big pore sintered glass filter in synthetic seawater by number, (b) by the weir in synthetic seawater by number and (c) by the weir in synthetic seawater by surface.
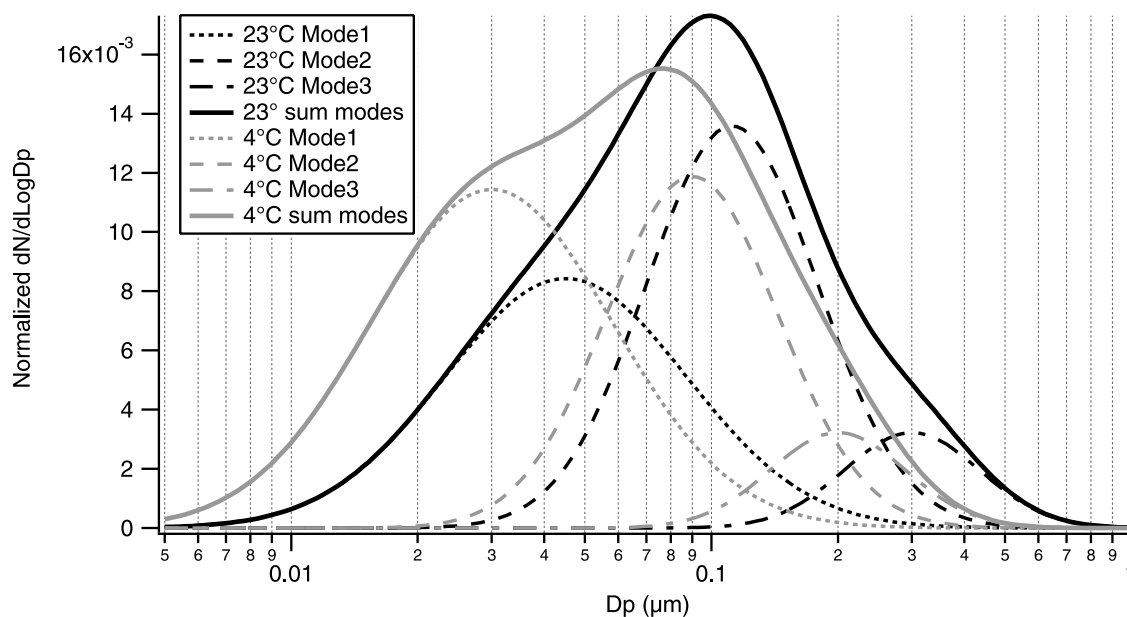
Figure 4. Example of the effect of temperature on the normalized aerosol size distribution, here generated by the large pore sintered glass filter in synthetic seawater. At low temperatures, all three modes are shifted toward smaller sizes.

similar effect has recently been observed by *Mårtensson et al.* [2003] in a study on the effect of seawater temperature on the production of primary submicron and supermicron marine aerosol using sintered glass filters. *Mårtensson et al.* [2003] show that below 70 nm, the number concentration decreases with increasing temperature. *Bowyer et al.* [1990] and *Woolf et al.* [1987] also showed that, while particles larger than 1.5 μm have an increasing number concentration with temperature, particles between 500 and 750 nm have a drastic increase in concentration for temperatures below 13°C. *Blanchard* [1963] also already showed that the ejection height of jet droplets increased with temperature, and that 200 μm diameter bubbles in seawater at 4°C were ejecting a drop whose diameter was 62 percent of that ejected by the same bubble in water at 24−26°C. However, the work of *Blanchard* [1963] was dealing with jet drops while we are, in this work, predominantly looking at film droplets. The change in viscosity of the seawater between 20°C and 0°C (about double) has been mentioned by *Bowyer et al.* [1990] to explain the change in number of small bubbles reaching the surface at different temperatures. *Pounder* [1986] shows that the number of bubbles increases, while their mean size decreases, with an increasing temperature, owing to a reduction of bubble coalescence. Because more film drops are produced by larger bubbles, this would explain an increase in film drop production in cold waters where bubbles rise to the surface slower than in warm waters, and hence have more time to coalesce.

3.2. Effect of Surfactant (High-Biological-Activity Conditions)

[15] The effect of the addition of 5 mg liter^{-1} of surfactant (SDS) is a relative increase of the contribution of mode 1 and a relative decrease of the contribution of mode 2 for all bubbling devices (Figure 5). The amplitude of mode 3 also decreases by 30−50% for all bubbling devices, except

for the weir. This exception will be explained later. The result appears like a size distribution shift toward smaller sizes. The apparent mode shift is very clear for concentrations of SDS starting from 3 mg liter^{-1}, but the relative importance of mode 1 to mode 2 does not increase with the amount of SDS. In fact, when the amount of surfactant dissolved in the seawater is increased to more than 6 mg liter^{-1}, the effect is difficult to evaluate, as a dense foam forms and bubble bursting is delayed while other effects are taking place (see next section). Hence we have only qualified the change of aerosol size distribution induced by the presence of surfactants, and we did not quantify the number of aerosol particle produced and so Figure 5 is shown with normalized concentrations, in order to compare the relative changes of modal amplitudes for all bubbling devices. However, *Blanchard* [1963] showed that the production of film drops are highly reduced by the presence of surfactants, because of the longer life time of the bubbles at the surface, while we did not detect a significant decrease in aerosol particle production. We suggest that Blanchard's results may be due to the smaller film drops produced in the presence of surfactant not having been detectable by the optical method he used.

[16] When synthetic seawater and surfactant are left to bubble over night, the mode shift is not observed anymore the next morning, while a whitish color of the seawater indicates that the compound has dissolved in the bulk of the water instead of staying at the surface.

[17] The effect of surfactants could not be studied at low temperatures because the SDS in seawater was observed to crystallize below $\approx$ 10°C: the foam previously formed by bubbling in synthetic seawater and the surfactant was suppressed when the temperature was decreased and white crystals were appearing in the bulk of the water. Natural seawater produces particle size distributions which are closer to the ones produced in synthetic seawater than
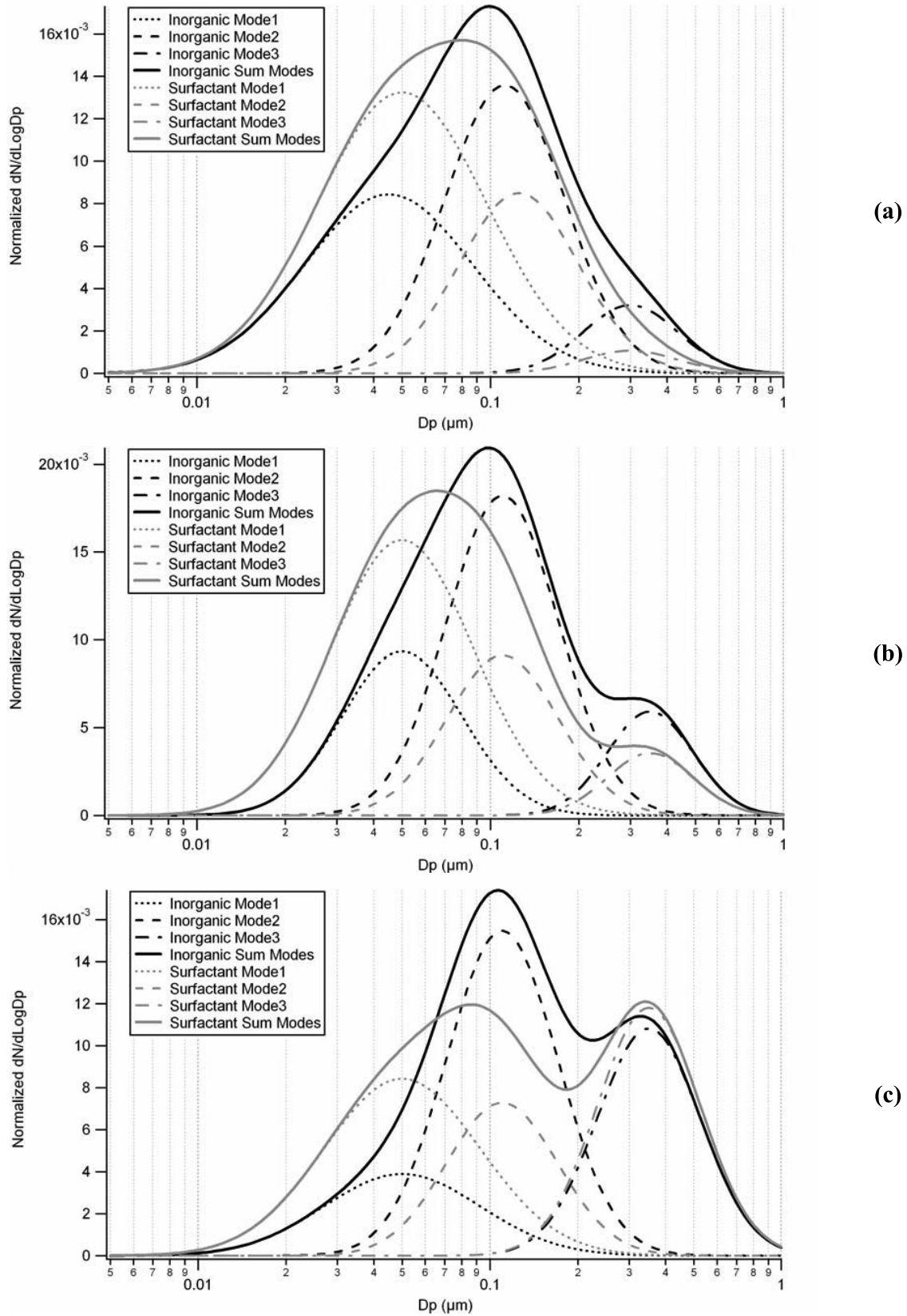
Figure 5. Effect of 5 mg liter^{-1} of SDS is an increase of mode 1 and decrease of mode 2 for three kinds of bubbling devices: (a) large pore sintered glass filter, (b) small pores sintered glass filter and (c) weir.
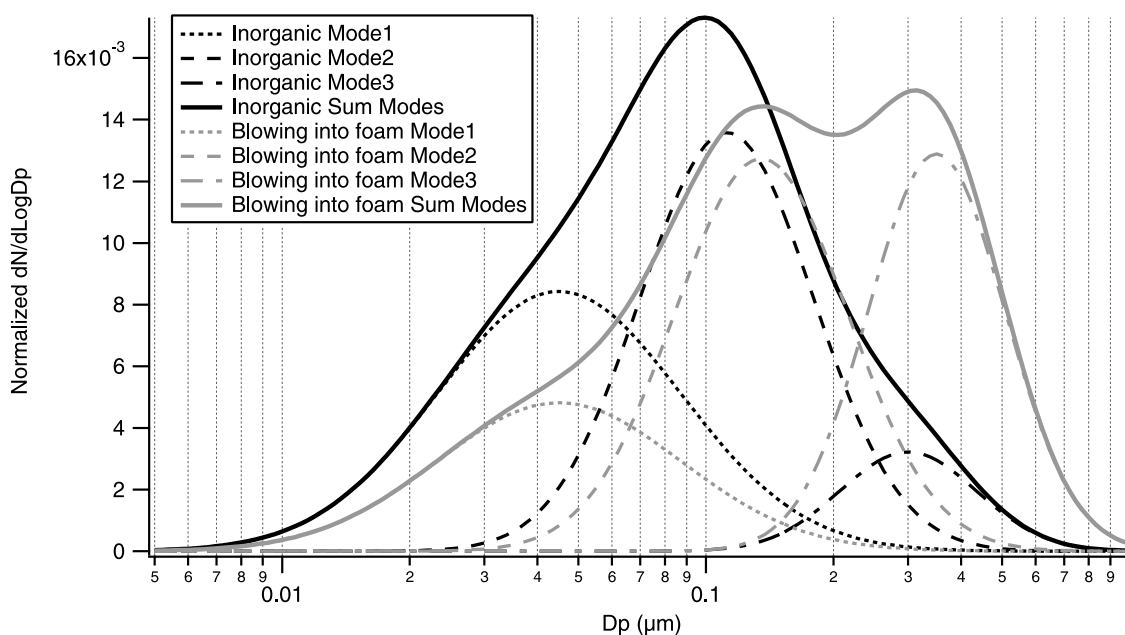
Figure 6. Example of the effect of blowing air into the foam generated by the presence of surfactant on the normalized aerosol size distribution, here generated by the large pore sintered glass filter in synthetic seawater. A 300 nm mode is clearly appearing, while mode 2 is decreased in favor of mode 1.

the ones produced in synthetic seawater with the addition of SDS.

3.3. Effect of Wind on Foam (Wind and High-Biological-Activity Conditions)

[18] Air currents with velocity of around 1 m s^{-1} were directed through a 0.635 cm diameter tubing into stabilized foam to "artificially" burst the stabilized bubbles. Compared to a "still" foam created in seawater enriched with surfactant, the effect of blowing air through the foam was to significantly increase the production of aerosols in the 300–350 nm size range (Figure 6). It can be seen in Figure 6 that mode 3 is clearly enhanced, relative to mode 2. This leads to an apparent shift of the distribution toward larger sizes of particles. The bimodal characteristic of the "accumulation mode" (mode 2 + mode3) observed during this experiment will be commented upon in section 4, in comparison with in situ atmospheric aerosol size distributions.

[19] When the bubbles are artificially broken by the wind (produced here by blowing air onto a very stable foam), the magnitude of mode 3 is increased relative to the mode at 100 nm, compared to a naturally reached breaking point. One explanation for this could be that for forced breaking the film is ruptured before it had time to drain, thin out, and naturally burst. Indeed, with increasing time, the drainage of seawater from the film can reduce its thickness [*Blanchard*, 1963]. When artificially broken, bubbles thus produce larger droplets, which, when dried out, leave larger particulate residues. With the addition of surfactants, a new effect is introduced. The surfactant stabilizes the bubble, which leads to an increasing time to drain, but at the same time an increasing time to be artificially broken. The results that we obtained in this work show that the presence of the 300 nm mode is increased when surfactants are present while air is blown through the foam. This would suggest that surfactants influence the way water drains out from bubbles upon

reaching the surface, by increasing the time for the bubble film to thin out.

[20] In fact, we also observed that aerosol size distributions produced by the weir, which splashes droplets partly in the direction of bubbles, always produces a distinct 300 nm mode (also in synthetic seawater, Figures 3 and 5). Hence, because surfactants are not necessary but more a catalyst, we believe that any mechanical artificial breaking of bubbles before they reach their natural bursting point leads to the production of larger particles than when they are in equilibrium.

[21] This could also be the reason why a smaller 300 nm mode was also generated by the small pores sintered glass filter, mainly in synthetic seawater. When using this filter, the number and volume density of the small bubbles generated are very high, and a significant number of them could be artificially broken by horizontally directed film drops of the nearby bubbles. Following *Spiel* [1997, 1998], bubbles with diameters smaller than 3 mm generate film drops that have nearly horizontal and downward trajectories. When these droplets collide with the surface, they are believed to generate spray by splashing or creating secondary bubbles and subsequent jet drops, as also reported by *Nystuen and Medwin* [1995]. With a dense population of bubbles (smallest sintered glass filter), or when the weir is used, the downward ejected film droplets each have a significant probability of hitting another bubble and thus leading to its likely rupture.

4. Link to in Situ Measurements of North East Atlantic Marine Aerosol

[22] We have observed three distinct and significant effects of the physical and chemical condition of the seawater on the size of submicron aerosol particles produced by bubble bursting:
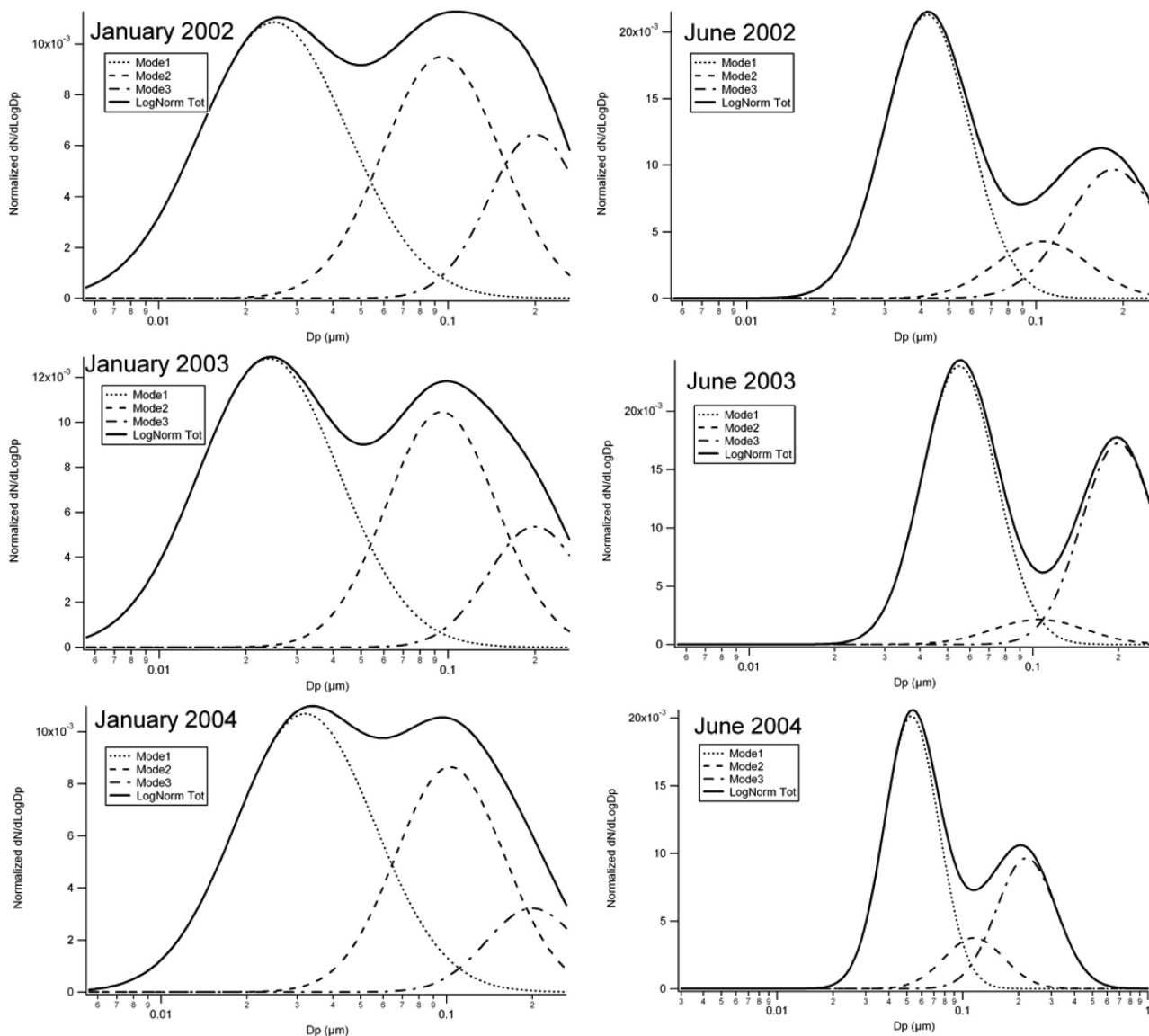
Figure 7. Fitting of normalized aerosol size distributions averaged over clean marine sector conditions during January and June 2002, 2003 and 2004 at Mace Head (for averaging periods from 9 hours to 6 days). Nonnormalized concentrations can be obtained by considering total concentrations of 200, 220 and 230 # cm^{-3}, respectively, for January 2002, 2003 and 2004 and 442, 493 and 483 # cm^{-3} for June 2002, 2003 and 2004.

[23] 1. Particles generated by bubbles in seawater of 4°C are significantly smaller than those produced in seawater of 23°C. In particular, the Aitken mode mean diameter is lowered from 46 nm to 28 nm and the Aitken mode concentrations are significantly enhanced relative to the accumulation mode concentrations.

[24] 2. The presence of a surfactant induces an apparent mode amplitude shift toward smaller sizes (mode 1 is enhanced relatively to mode 2) when the foam is undisturbed (no wind). However, it was observed that the surfactants we studied crystallize at low temperature and become inactive.

[25] 3. In the presence of a low wind or a splashing source (a subsequent wave for example), a clear 300 nm mode is generated. This 300 nm mode appears like a shift of

particles from the main 100 nm mode toward larger particles. This effect is enhanced when the bubble life time is increased by the presence of a surfactant, but not observed when the surfactant stabilized foam is undisturbed.

[26] In order to evaluate the consistency of these effects, we selected typical winter and summer aerosol size distributions observed in clean Atlantic air arriving at the Mace Head atmospheric research station (Figure 7). These bimodal particle size distributions can be decomposed into three individual lognormal modes as observed in the laboratory measurements reported above. As already mentioned in the work of *O'Dowd et al.* [2004], we observe that during the summer, the Aitken mode of clean marine North Eastern Atlantic aerosols is 1.4 times larger than during the winter (increasing from 28 to 40 nm). The accumulation mode is

Table 1. Aerosol Size Distribution Characteristics[a] Obtained Under Different Experimental Conditions of Bubbling, Described as Three Lognormal Modes (Calculated as Concentration = $((A/(\ln(\sigma) * 2.506628)) * \exp(-(\ln(Dp) - \ln(Dp_m))^2 / (2 * \ln(\sigma)^2))))$

	Mode 1	Mode 2	Mode 3
Mean Diameter, nm			
Inorganic sea salt	45	112	300
5 mg liter^{-1} surfactant	50	125	300
Low temperature (4°C)	30	90	200
Blowing into dense foam	45	135	350
Standard Deviation (σ)			
Inorganic sea salt	1.94	1.60	1.45
5 mg liter^{-1} surfactant	1.94	1.60	1.45
Low temperature (4°C)	1.94	1.60	1.45
Blowing into dense foam	1.94	1.60	1.45
Relative Amplitude (A)			
Inorganic sea salt	0.014	0.016	0.003
5 mg liter^{-1} surfactant	0.022	0.010	0.001
Low temperature (4°C)	0.019	0.014	0.003
Blowing into dense foam	0.008	0.015	0.012

[a]Mean diameter Dp_m (nm), standard deviation σ and amplitude A (cm^{-3}).

separated here into mode 2 and mode 3, with a clear decrease of mode 2 and a clear increase of mode 3 during summer compared to winter.

[27] During the winter, less surfactant is likely to be present in the seawater, and hence the aerosol size distributions observed during winter in the North Atlantic clean marine air masses would be closest to our laboratory observations in synthetic seawater at temperatures approaching 4°C. This is confirmed by the good agreement between Table 1 "Low temperature" and Table 2 "Jan 2002 to 2004." Figure 8 illustrates the difference in sea surface temperature between January and June in the Northern part of the Atlantic Ocean, from where most of the air mass back trajectories arriving at Mace Head originate. During winter, not only are colder temperatures found at the coasts around Mace Head, but more importantly, 72 hours clean marine air mass back trajectories seem to come from farther away from the North where the ocean temperature is cooler. Consequently, the average "path" or winter air masses are representative of cooler waters. Even though, in the laboratory, we used 4 and 23°C whereas Figure 8 shows that the water temperatures were higher than 4°C in winter and lower than 23°C in summer, *Mårtensson et al.* [2003] indicate that there is a gradual transition of the size distributions with temperature and *Bowyer et al.* [1990] showed that the effect of increasing number small particles (500– 750 nm) concentrations with decreasing temperature was effective below 13°C. The major difference between cold synthetic water laboratory measurements and winter North Atlantic measurements is in the amplitude of mode 3, more pronounced in the North Atlantic aerosol size distributions compared to the ones created in the laboratory for bubbling devices other than the weir. This is either indicative of the fact that real sea bubble size distributions are closer to the one achieved with the weir, or indicative of an "artificial breaking wind effect" on bubble bursting at Mace Head.

[28] During the summer, surfactant levels are expected to be higher, and the seawater warmer. Figure 9 illustrates the

change of chlorophyll concentrations in the seawater from January to June. Superimposed on the chlorophyll data are typical 72 hours air mass back trajectories, showing that air masses are transported over richer planktonic areas in June compared to January. Surfactants in seawater are expected to increase bubble life time, hence the June field measurements can be expected to be more closely duplicated in the laboratory "blowing into foam" results shown in Figure 6 and Table 1. Compared to winter, the Aitken mode diameter shift to larger sizes in summer is found in the laboratory, and can be due to the combined effects of (1) mode 1 diameter increasing to 50 nm because of the temperature rise and (2) mode 1 amplitude increasing because of the presence of surfactants. Another similarity is found between the summer size distribution and the "blowing into foam" laboratory conditions, in that the mode 3 contribution is enhanced in both cases, compared to winter, and to "low temperature" conditions. This shows that the effect of wind blowing into bubbles stabilized by surfactants might be a determining parameter in the size of the aerosols produced during summer. However, the relative contribution of the Aitken mode is much higher in the North Atlantic size distributions compared to the laboratory experiments. Indeed, in the laboratory experiments, the Aitken mode amplitude is 40– 50% smaller than that of mode 2 whereas marine aerosols at Mace Head (during summer) generally show an Aitken mode 50% higher than the accumulation mode. The laboratory measurements can hence explain only part of the Aitken mode observed during clean marine sector conditions at Mace Head. A significant fraction of this mode could be accounted for by secondary aerosol formation processes, which are also expected to be higher in summer because of increases of biogenic gas emissions and photochemical activity [*O'Dowd et al.*, 2002].

[29] In parallel, the contribution of mode 2 to the observed North Atlantic size distribution data is less than that

Table 2. Mode Characteristics (Same as in Table 1) During Winter and Summer Conditions at Mace Head for 2002, 2003 and 2004

|	Mode 1	Mode 2	Mode 3
Mean Diameter, nm			
Jun 2002	42	105	185
Jun 2003	55	105	200
Jun 2004	53	115	220
Jan 2002	24	95	200
Jan 2003	25	95	200
Jan 2004	32	103	200
Sigma			
Jun 2002	1.40	1.45	1.45
Jun 2003	1.35	1.45	1.35
Jun 2004	1.40	1.45	1.45
Jan 2002	1.75	1.55	1.45
Jan 2003	1.80	1.55	1.45
Jan 2004	1.75	1.55	1.45
Amplitude			
Jun 2002	0.018	0.004	0.009
Jun 2003	0.018	0.002	0.013
Jun 2004	0.017	0.0035	0.009
Jan 2002	0.018	0.0115	0.005
Jan 2003	0.017	0.012	0.006
Jan 2004	0.015	0.0095	0.003
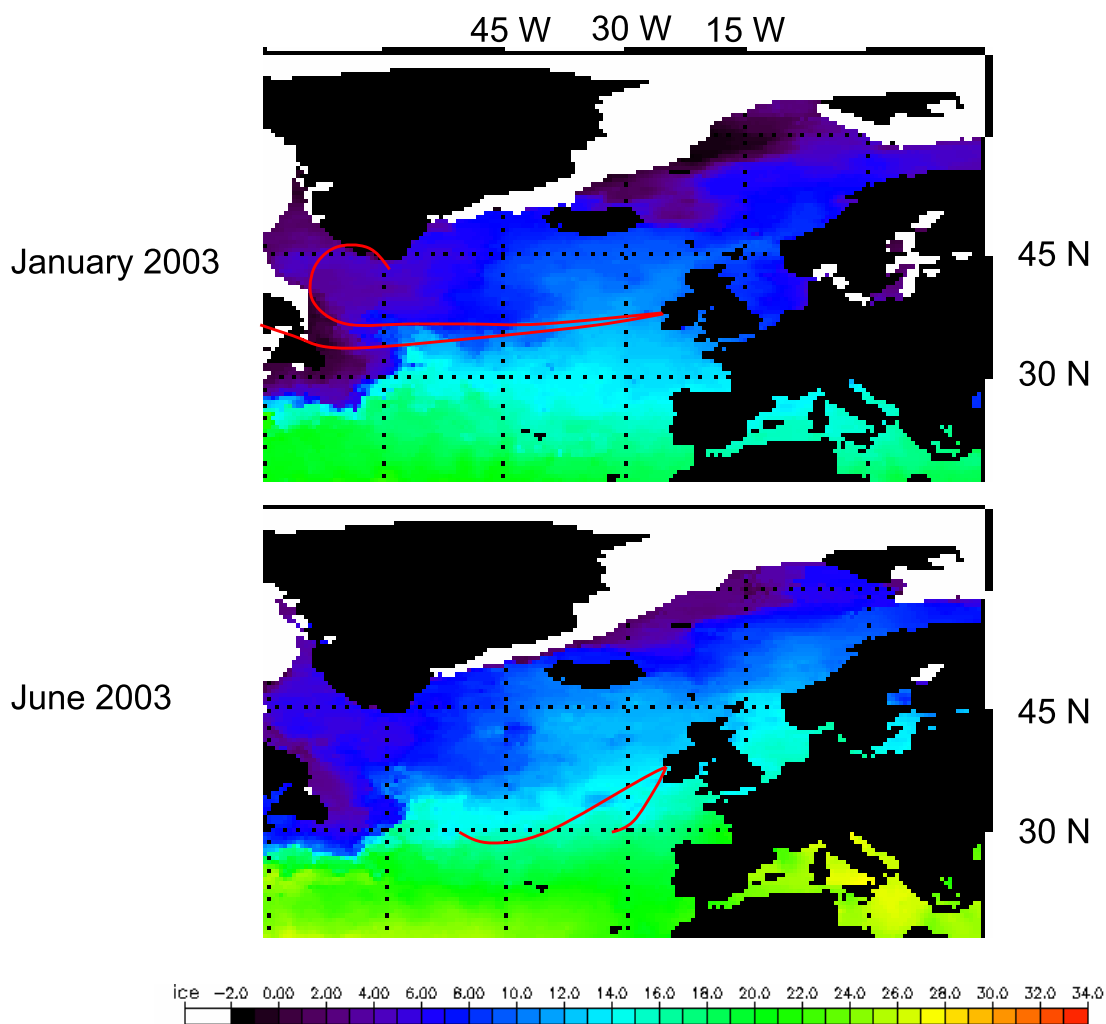
Figure 8. Maps of the sea surface temperatures in the Atlantic Ocean during winter and summer 2003. Two typical 72 hours air mass back trajectories calculated for clean marine wind sectors in January 2003 and during June 2003 (the dates chosen are representative of the data set used for Figure 7) are also superimposed in red. Trajectories have been calculated by the HYSPLIT NOAA model and then reproduced on the temperature map. During January 2003, winds were usually stronger and originate from higher latitudes than during June 2003. This effect enhances the source zone seawater temperature difference between the two seasons.

observed for the laboratory measurements, resulting in a lack of bimodality of the accumulation mode observed in the North Atlantic aerosol size distributions compared to the ones produced in the laboratory. Several explanations can be proposed for this discrepancy:

[30] 1. The nature of the surfactants and the wind speed are different in our laboratory experiments, compared to the natural environment. If the natural surfactants are more effective in stabilizing bubbles, and wind speed higher, we expect artificial breaking to be favored over natural breaking and hence mode 3 to be favored over mode 2.

[31] 2. In the North Atlantic samples, mode 2 and mode 3, which are quite close to each other, can possibly be smoothed into a single mode by chemical and physical transformations during transport to the measurement site (either condensation processes or cloud processing, even though studies showed that in-cloud sulphate formation occurring in marine aerosol does not lead to a significant growth of the accumulation mode [*O'Dowd et al.*, 2000]). It is not possible to further assess the influence of these secondary processes in the laboratory.

5. Conclusions

[32] Laboratory experiments on bubble-mediated aerosol production illustrate that the submicron aerosol produced can be fitted best with three modes. At 23C, there are typically modes at 45 nm, 110 nm and 300 nm. At 4C, the droplet diameter associated with these modes reduce in size to 30 nm, 85 nm and 200 nm. Out of these three modes, two clearly appear to result from different physical processes. The main 110 nm mode is predominantly produced by all bubbling devices, as well as by the weir. The largest 300 nm mode appears to result from forced bursting of bubbles by increasing pressure associated with air currents or breaking waves. When a surfactant is added to the seawater, the
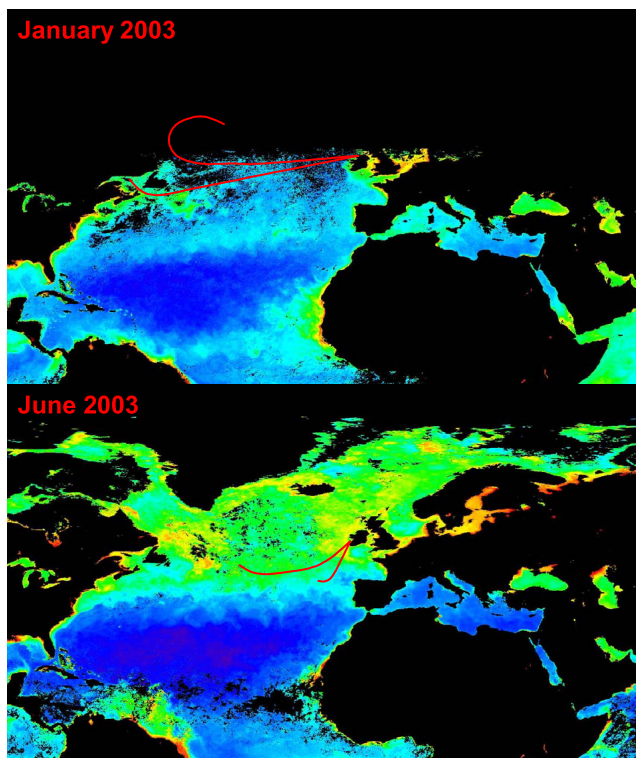
Figure 9. Maps of the sea chlorophyll in the Atlantic Ocean during January and June 2003 (from http://oceancolor. gsfc.nasa.gov/), with, as in Figure 8, the corresponding 72 hours air mass back trajectories.

bubbles are further stabilized and forced bursting of these bubbles significantly increases the contribution of the 300 nm mode to the size distribution. The laboratory experiments performed in this work are by no mean exhaustively representative of the real marine aerosol production, and SDS is only an example of the effect of surfactant that could be observed in the seawater for a similar compound. However, the regularly observed bimodal size distribution in marine air can mostly be explained by a combination of the three modes observed in these laboratory experiments. The laboratory measurements also show that the seasonal changes in the aerosol size distribution measurements in clean marine air could be partly explained by both the change in temperatures and air mass back trajectories between summer and winter, and the increase in the surfactant content in the seawater. As they extend the bubble surface life time, surfactants increase the chance that these bubbles are artificially broken by the wind or a following wave, leading to the generation of a significant 300 nm mode in the aerosol size distribution. However, winter clean marine aerosol size distributions are better reproduced in the laboratory than summer marine aerosol size distributions. During summer, additional secondary processes are likely to be involved. *McKay et al.* [1996] showed that gaseous hydrocarbons can be produced biotically either directly by plankton or indirectly from organics exuded during growth and degradation of plankton cells. Hence organic gases are released in greater quantities during plankton blooming. Most probably, some of these hydro-

carbon gases are oxidized into partly condensable species and can, on the one hand contribute to a significant fraction of the Aitken mode observed in situ, and on the another hand contribute to smooth the bimodal characteristic of the accumulation mode observed in the laboratory. The degree in which these secondary processes contribute to the mass of marine aerosols still needs to be quantified.

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