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SUBMICRON FILM DROP PRODUCTION BY BUBBLES IN SEAWATER

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Abstract. The marine droplet aerosol, composed of the film and jet drops produced by breaking bubbles, is at the origin of most of the sea salt particles found in the atmosphere. For a long time, it was believed that the number of film drops produced per bubble burst increased continuously with increasing bubble diameter. Recently, however, Blanchard and Syzdek (1988) reported a peak in film drop production in the bubble size range of 2- to 2.5-mm diameter, with much lower drop counts for larger bubbles. Experiments designed to investigate this peak over the bubble diameter range of 1.06-5.7 mm are reported. The results confirm the existence of a peak in the film drop count data at a bubble diameter of about 2.14 mm. The size distribution of the film drops accounting for the peak was estimated using a screen diffusion battery. Most of the drops were found to be of submicron dimensions and concentrated in the 0.05- to 0.3-μm-diameter size range.

Introduction

The recent discovery by *Blanchard and Syzdek* [1988] of a surprising and unexplained peak in film drop production from bursting bubbles in the 2- to 2.5-mm-diameter range has raised questions about the hitherto accepted rule of thumb that the number of film drops per bubble burst continuously increases with bubble size. It has also generated some controversy [*Wu,* 1990]. And rightly so. For if indeed 2-mm bubbles in seawater produce the greatest number of film drops per bubble burst, then they must play a significant role in the formation of the marine aerosol. We therefore need to know more about the number and size distributions of the film drops produced by these bubbles. The information obtained, in conjunction with available bubble spectra at sea, will help determine the importance that may be attached to the role of 2-mm-diameter bubbles in the sea-to-air transfer of particles. In their 1988 paper as well as in their reply *Blanchard and Syzdek* [1990] to *Wu*'s [1990] suggestion that the peak in drop production they observed might just have been an experimental artifact, Blanchard and Syzdek strongly dismissed this hypothesis, though they admitted that the cause of the peak was yet to be explained. This is an additional justification for an independent experimental attempt, not only to verify or test the existence of this peak, but also to obtain new information likely to explain its presence. The present paper is the result of that investigation.

Film drops produced by bursting air bubbles in seawater cover a wide size spectrum, ranging from submicron dimensions to well over 200 μm in diameter at the large end [e.g., *Cipriano and Blanchard,* 1981; *Resch et al.,* 1986; *Woolf et al.,* 1987; *Blanchard and Syzdek,* 1988; *Afeti and Resch,* 1990]. The drop count data obtained by *Resch et al.* [1986] and *Afeti and Resch* [1990], using a holographic imaging technique, covered drops larger than 8 μm in diameter. This lower limit was due to constraints associated with their experimental technique. Recently, using a Royco aerosol counter and a Kratel particle counting device, *Resch and Afeti* [1991] were able to obtain a better size resolution, detecting and counting drops as small as 0.8 μm. In all these investigations, the number of film drops produced per bubble appeared to increase continuously with increasing bubble diameter. No peak in drop production was detected. It is interesting to note, however, that in announcing the presence of the peak, Blanchard and Syzdek reported counting all the film drops produced down to about 0.03 μm in diameter (for a 100 % counting efficiency). The counting instrument they used was a TSI model 3020 condensation nucleus counter (CNC). It would seem therefore that if this peak really exists, then the drops accounting for it must be much smaller than 0.8 μm, probably ranging between 0.03 and 0.8 μm.

Experimental Methods

The experimental installation we used consisted of a bubble production and film drop aerosol generation unit, a TSI model 3760 condensation nucleus counter, a Royco model 5120 aerosol counter and a screen diffusion battery or particle size selector (PSS), model TSI 376060, arranged as shown schematically in Figure 1.

Single air bubbles having various diameters (1.60, 1.89, 2.04, 2.14, 2.20, 2.46, 2.51, 2.66, 4.60, and 5.70 mm)

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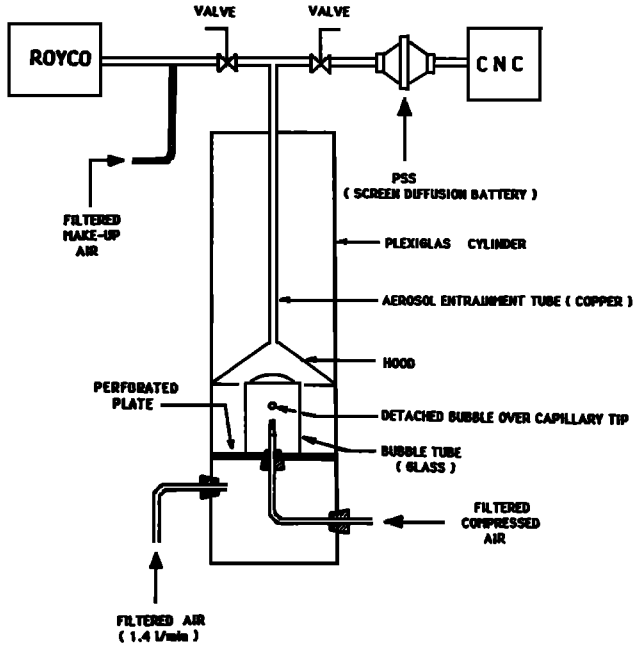

Fig. 1. Film drop aerosol generation and sampling system.

were produced by forcing filtered nucleus-free air through capillary tips of different sizes held at the bottom of a 3-cm-diameter and 15-cm-long glass tube filled with seawater. The diameter of the bubble produced depends on the internal diameter of the capillary tip used [*Blanchard and Syzdek,* 1977]. Bubble production as well as film drop generation was carefully monitored and accompanied by measures of cleanliness and bubble size verifications. In particular, at the start of each experiment, the glassware was thoroughly cleaned to remove any previous deposit of salt residue. The surface quality of the seawater sample was also constantly monitored and the sample replaced whenever appreciable bubble coalescence at the surface (due to increased accumulation of surface impurities) took place. Bubble sizes were verified by measuring the volume of water displaced in an inverted burette into which a known number of bubbles produced by a given capillary tip were injected. From a knowledge of the volume associated with a single spherical bubble, the corresponding bubble diameter is easily calculated. The salinity of the seawater samples, taken from the French Mediterranean coast, was 37 ‰. The bubble rise distance to the free water surface was about 3 cm on the average.

The droplets generated by the bursting bubbles were ejected into the dry and filtered entrainment air flowing at the rate of 1.4 L/min (see Figure 1). A collecting hood then directs the droplet aerosol into the 10-mm-diameter copper tube that leads into either the CNC or the Royco counter. During their journey through the 70-cm-long entrainment tube, the liquid droplets in the sampled air are transformed into smaller salt particles which are the residues of the parent seawater drops. Using the law of conservation of mass and considering that the concentration of salt in seawater is about 37g/L, it can be shown that the diameter of the salt residue is approximately one-quarter that of the parent drop [*Blanchard,* 1983].

Specific details of the Royco counter we used are given by *Resch and Afeti* [1991]. Briefly, light scattered by individual film drop particles as they traverse a viewing volume are picked up as pulses by a sensor and electrically amplified to provide a series of sizing information. The effective solid particle size detection range of the Royco was 0.2-5 μm. Because the counter internal pump is rated at an optimum design air flowrate of 28.3 L/min, it was necessary to dilute the sampled aerosol stream of 1.4 L/min with a filtered nucleus-free make-up air flowing at 26.9 L/min whenever readings were taken with the Royco instrument.

The principle of operation of the CNC is well known [*Agarwal and Sem,* 1980]. Schematically, as the aerosol sample enters the counter, it is saturated with alcohol (butanol) vapor from a large pool in the CNC. From there, the air sample passes into a condensing unit where the alcohol vapor condenses onto the airborne film drop particles. As a result, most of the ultrafine particles are able to grow into droplets that are large enough to be detected when they scatter light as they pass one at a time through a single-particle-counting sensor. The optical pulse produced by a particle traversing the light beam is collected, focused onto a photodetector, and transformed into an electrical signal. These electrical pulses are then counted and recorded for each series of bubble bursts.

For the CNC as well as the Royco, the average number of film drops produced per bubble burst is obtained by dividing the particle count over a specified time interval by the number of bubbles that burst over the same period of time under steady state conditions. In our experiments, the particle count readings were taken over 3- and 5-min intervals, while the bubbles were generated at the rate of 30-150 per minute (depending on bubble diameter). Before any condensation nucleus or particle readings were taken, clean filtered air was passed through the sampling system for about 20 min until no single nucleus could be detected. Afterward, another 10 min or so were allowed for steady state conditions to be established. The entire film drop aerosol generation and sampling unit was effectively protected against infiltration from the external ambient air.

Unlike the Royco counter, which furnishes both the number of film drop particles produced as well as their size

distribution, the CNC by itself gives only the drop count. Consequently, in order to estimate the size distribution of the ultrafine droplets passing through the CNC, we arranged in series with it a screen diffusion battery or particle size selector (see Figure 1). The underlying theory of the PSS is based on the fact that the motion of very fine particles is not linear but random, due to collisions with individual air molecules. The larger the particle size, the smaller its random motion and the greater the probability that it will pass through a given narrow passage without colliding with the passage walls. The PSS is composed of a series of narrow passages created by sandwiching together a number of fine-mesh stainless-steel screens. Depending on the number of screens, it is possible to prevent the passage of particles of a specified size. The number of screens used in the PSS therefore effectively determines the size of the smallest particles that eventually get through to the CNC, so that only particles bigger than the specified or cut off size are counted.

Results and Discussion

The film drop particle count data obtained by both the Royco and CN counters are given in Figure 2. The CNC results show a peak drop production of about 80-100 per bubble at a bubble diameter of 2.14 mm. On the left of this peak, drop production was less than 2, while to the right, the number of particles detected increased gradually from 8 per bubble (for a bubble of 2.66 mm in diameter) to about 15 for a 5.7-mm-diameter bubble. It is interesting to recall that *Blanchard and Syzdek* [1988] obtained a maximum drop count of 75 for a 2.1-mm-diameter bubble in seawater.

The data obtained using the Royco revealed no peak in drop production; the number of drop particles per bubble increased continuously with bubble diameter.

If the peak is real (and not an experimental artifact), why did the Royco counter fail to find it ? The most plausible answer is that the particles responsible for the peak were too small to be detected by the Royco. The Royco we used had an effective solid particle detection range of 0.2-5 μm compared with 0.014-2 μm for the CNC (Figure 2*b*). The film drop particles produced by the 2.14-mm bubbles must therefore have been smaller than 0.2 μm (or 0.8 μm as seawater drops). The size distribution data obtained using the PSS confirm this assertion (see Table 1). The results show that the majority of the film drops produced by the 2.14-mm bubbles had diameters between 0.05 and 0.3 μm. The number of screens used in the PSS, the 50 % cutoff values and the percentage of the film drops bigger than this 50 %

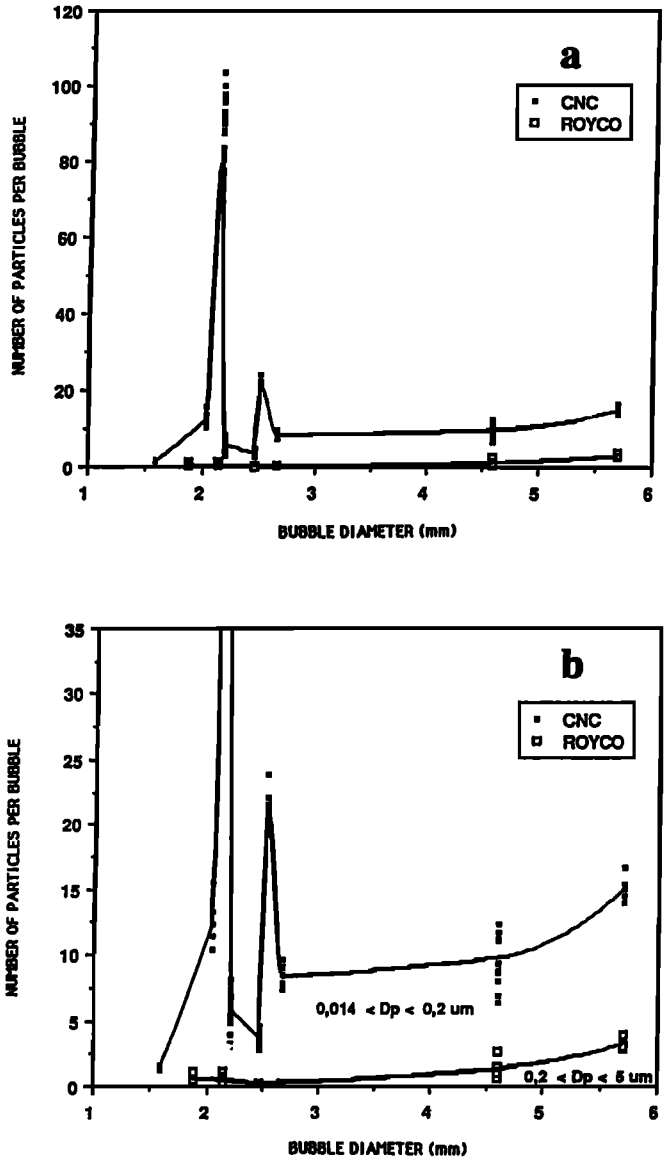

Fig. 2.(*a*) Number of film drop particles counted per bubble as a function of bubble diameter. (*b*) Enlarged view of the bottom half of Figure 2*a*.

cutoff are also given in Table 1. The 50 % cutoff value is the drop diameter corresponding to a collection/sizing efficiency of 50 % for a given number of screens. It is therefore evident from Table 1 that using eight screens in the PSS and assuming that only half of the total number of droplets produced are effectively sized, all but about 25 % of them have diameters below 0.3 μm. A summary of the drop diameters that could be measured by the present Royco and CNC devices and by the CNC *Blanchard and Syzdek* [1988] utilized is given in Table 2.

Though the mechanism responsible for the fertile production of film drops by bubbles of about 2-mm diameter is yet to be understood, it is interesting to note that the

TABLE 1. Size Distribution of the Drops for the 2.14 mm Bubbles

Number of Screens	50 % Cutoff, * μm	Percentage Greater Than 50 % Cutoff +
0	0.056	100
1	0.060	80±6.4
2	0.100	56±4.7
3	0.136	45.2±3.8
4	0.172	38.4±2.6
5	0.200	38.5±0.7
6	0.240	29.5±0.7
8	0.300	25.5±0.7

* Drop diameter.

+ Average over 4 measurements.

TABLE 2. Comparative Drop Sizes That Can be Measured by the CNC and Royco Instruments in the Present Work and the CNC of *Blanchard and Syzdek* [1988]

Instrument	Drop Size, μm	Reference
CNC TSI model 3760	0.056-0.8	Present work
Royco model 5120	0.8-20.0	Present work
CNC TSI model 3020	0.03-10.0	*Blanchard and Syzdek* [1988]

highest jet drop ejection heights have been associated with 2-mm bubbles [*Blanchard*, 1983]. Also, *Resch and Afeti* [1990, 1991] have determined a threshold bubble diameter of about 1.8 mm above which film drop production outweighs jet drop production. It seems likely therefore that a subtle drop production mechanism is at work when bubbles of about 2-mm-diameter break.

A final word about the fate of the jet drops produced in these experiments : The diameter of the smallest jet drops produced was about 160 μm (corresponding to one-tenth the diameter of the smallest bubble we generated). These large drops, because of gravitational fallout, cannot be entrained in the aerosol airstream up into the CNC or Royco counter. In effect, by considering the aerodynamic and buoyancy forces acting on a typical drop in the entrainment air circuit, it can be shown that all drops ≥ 100 μm will not be entrained. All the particles that reached the counting devices must therefore have been of film drop origin.

Concluding Remarks

It is important to emphasize that the results reported in this paper were obtained from a series of experiments carried out over several weeks involving both the CNC and the Royco aerosol counter. Also, on every occasion, though the film drop count varied, the drop production peaked at a bubble diameter of 2.14 mm for the CNC but not for the Royco. There is therefore no doubt that when measurement techniques capable of detecting submicronic particles are utilized, bubbles of about 2 mm produce by far the largest number of film drops. The majority of these drops have diameters between 0.05 and 0.3 μm. These ultrafine drops, because of their strong resistance to gravitational fallout and their ability to remain airborne over a considerable length of time, must play a significant role in the transport dynamics of particles in the marine atmosphere. Also of interest is the fact that jet drops produced by 2-mm-diameter bubbles attain the highest ejection heights and that bubbles smaller than about 2 mm produce more jet drops than film drops when they break. It follows that 2-mm-diameter bubbles are probably key actors in the bursting-bubble-induced sea-to-air transfer of particulate matter.

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