

Control of Jet Drop Dynamics by Organic Material in Seawater

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The ejection height of jet drops from bubbles bursting in seawater has been found to be a function of the time spent by the bubble rising to the surface. During this time, adsorption to the bubble of the surface active species of organic material in the water lowers the bubble surface free energy, the source of the kinetic energy of the jet drops. Experiments with a bubble aging tube have shown that the time rate of change of drop ejection height is a function of not only the amount of organic carbon in seawater but the species as well. Since changes in drop ejection height are paralleled by changes in drop size, the possibility exists that organics in the sea can play a role in modifying the drop size spectrum produced by the sea. On the other hand, the modification may be minimal, since the organic effect is most pronounced on the larger bubbles (about 1-mm diameter) and less so on the smaller and more numerous bubbles produced by natural processes in the sea.

It is generally accepted that the major source of sea-salt aerosol in marine atmospheres is jet and film drops produced by air bubbles bursting at the surface of the sea. The origin of the drops is a thin microlayer that forms the surface of the bubble [MacIntyre, 1972]. Thus it follows that any organic material adsorbed to the bubble surface will be found in the jet and film drops in a concentration far higher than that in bulk seawater. Hoffman and Duce [1976] have found that such a mechanism can account for at least part of the high enrichment factors (from several hundred to several thousand) for organic carbon on the marine aerosol [Blanchard, 1968; Barger and Garrett, 1970; Hoffman and Duce, 1974]. Detailed reviews of the relationship between bubbles and enrichments of organics and other materials on the marine aerosol have been prepared by Blanchard [1975] and Duce and Hoffman [1976].

The energy for jet drop ejection is derived from the surface free energy of the bubble [Blanchard, 1963]. Since the adsorption of organic material to a bubble rising through water will lower the bubble surface free energy, one would expect to find a lowering of the height to which the jet drops are ejected, and perhaps a decrease in their size, as a function of time spent by the bubble rising through the water before bursting. This has been found in experiments with a few samples of coastal seawater [Lee, 1972; Blanchard and Syzdek, 1974] and in work aboard ship with nearly 100 samples of open ocean seawater obtained near the Galapagos Islands and at various places in the North Atlantic [Blanchard, 1977]. However, no measurements of organic carbon were available for any of these seawater samples. It is the purpose of this paper to present data that relate the organic carbon content of seawater to the rate of change of jet drop ejection height with bubble age.

PROCEDURE

The ejection height versus bubble age data were obtained with a bubble aging tube (Figure 1). Details on the construction and use of the aging tube can be found elsewhere [Blanchard, 1963]. Only a brief description will be given here of the use of the tube in the present work. A stirring rod causes the water to move slowly in a counterclockwise direction. As it moves down through the constriction its speed increases to

about 30 cm s^{-1} , establishing a velocity gradient beneath the constriction. Accordingly, a bubble released from the capillary tip rises to the point where its rise speed is equal to the downwelling speed of the water, and there it remains. At the end of any desired time the stirring rod is turned off, the downwelling ceases, and the bubble rises to the surface to burst and eject jet drops into the air. The preparation of bubble-producing capillary tips has been described by Blanchard and Syzdek [1977].

Each day, and sometimes twice a day, the entire apparatus was taken apart and cleaned. The capillary tip was bubbled for 20 or 30 min in acetone and then rinsed in distilled water. The rest of the apparatus was scrubbed in a hot detergent solution, rinsed with hot tap water, and then rinsed with distilled water.

The air for the bubbles came from a small air pump. It was filtered through a column of cotton wool to remove particles and then through activated charcoal to remove any organic vapors that might be present.

The water supply was fed into the right-hand branch of the aging tube. The surface where the bubbles burst was overflowed from time to time to keep it free of organic monolayers. It was not necessary to maintain a continuous overflow, for it was found that the drop ejection heights depended primarily on the age of the bubble, provided the water surface was clean initially. Thus the experiments were done by using an overflow supplied by hand periodically from a beaker of the sample of seawater.

The bubbles did not burst immediately upon arrival at the surface. This surface residence time is not a part of the bubble age, which in this paper is the time spent by the bubble in rising from the capillary tip to the surface. For bubble ages $< 10 \text{ s}$ the residence time was generally high, sometimes several tens of seconds, but for ages $> 10 \text{ s}$ the residence time changed little, being in the range of 1–5 s. Residence times for bubbles at a saltwater surface have been found by Garrett [1967] to be an inverse function of the pressure exerted by a surface film, while Bikerman [1968] has shown that even in the absence of surface films, bubbles can have a residence time of the order of 1 s. However, whether the residence time was 1 or 50 s, the ejection height of the jet drops in this work was the same. It was a function only of the bubble age.

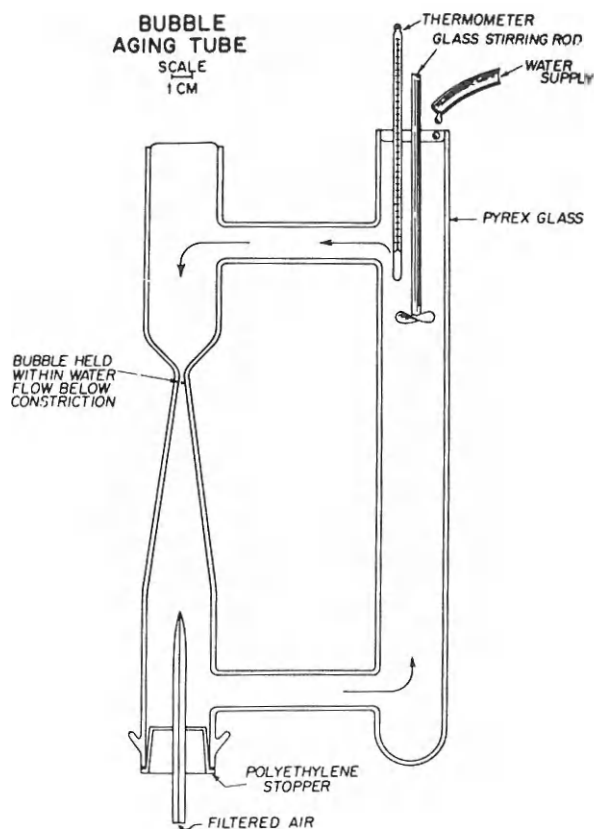


Fig. 1. The bubble aging tube, a device used to suspend air bubbles in a downward moving stream of water for any desired time.

The ejection height of the jet drops was estimated with the naked eye. A transparent plastic millimeter scale was mounted vertically over the water only 2–3 mm away from the vertical path followed by the jet drops. With the use of proper illumination it was a simple matter to determine within about 1 mm the drop ejection heights. Although several jet drops are ejected per bubble, observations were made on only the top drop.

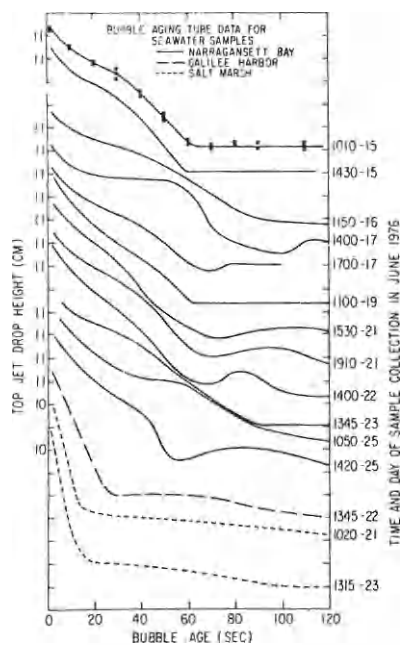


Fig. 2. Data obtained with the bubble aging tube. See text for details.

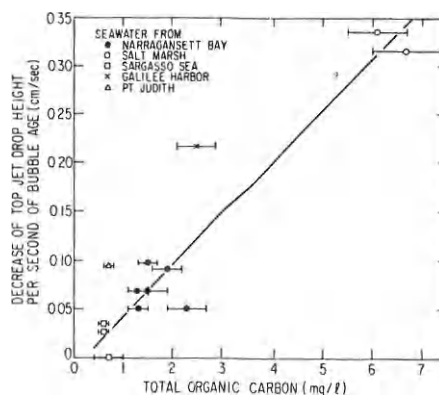


Fig. 3. Change in jet drop ejection height per second of bubble age as a function of the total organic carbon content of the water sample. See text for details.

Nearly 20 samples of seawater were studied in the aging tube. More than half were obtained in Narragansett Bay from the pier at the Graduate School of Oceanography of the University of Rhode Island. Others came from a nearby harbor (Galilee), Point Judith (near the entrance to Narragansett Bay), a salt marsh, and from a teflon-lined 55-gal drum of Sargasso seawater. All of the local samples of seawater were obtained in June 1976, about 10–20 cm beneath the surface in a 4-l polyethylene container. Although the temperature of the samples at the time of collection varied from about 16°C (Narragansett Bay) to 32°C (salt marsh), they were all run at about room temperature (20–22°C) several hours after collection.

Analyses were done on 13 of the samples. Unfiltered, they were analyzed for total organic carbon (TOC) by the *Menzel and Vaccaro* [1964] wet oxidation procedure, using an Oceanography International model 0524 total carbon analyzer. The values reported for TOC are based on four or five replicate analyses. The standard deviations of these analyses are indicated for each sample by the width of the bars in Figure 3. The blank was 0.2 mg OC/l. The samples were oxidized with persulfate within 2 hours after collection.

RESULTS

With the exception of the three Sargasso sea samples, one of which is shown in Figure 4, the aging tube runs for the samples are shown in Figure 2. Since only one capillary tip was used, the bubble size remained constant at about 0.9-mm diameter. Data points are shown for only one sample, that obtained at 1010, June 15, in Narragansett Bay. It was not felt necessary to give data points for all the samples, since the accuracy was similar to that shown for the first sample, and it is easier to see the gradual changes in the nature of the curves from one sample to the next. To compare the different curves more easily, they have been placed as close together as possible without overlapping. The drop height scale is the same for all samples. Adjacent to the ordinate is a number which identifies the top jet drop ejection height for the curve to the right. For example, the seawater sample for the top curve showed a drop height of about 11.3 cm at a bubble age of 1 s. The height decreased steadily with bubble age, reaching 6.2 cm at an age of 62 s. It remained at that height out to an age of 110 s, where the experiment ended.

Nearly all the curves show a rate of decrease of drop height with time, dH/dT , which at first is relatively great but at a particular time changes abruptly to either zero or a very low

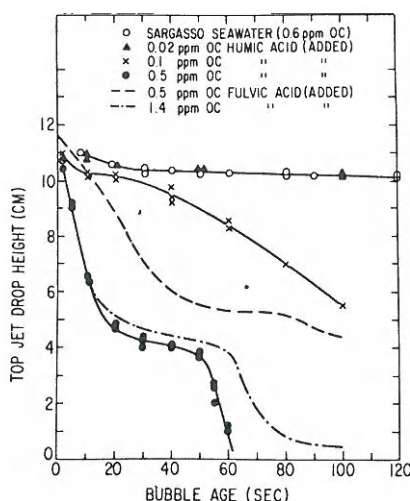


Fig. 4. Jet drop ejection height as a function of bubble age for various concentrations of humic and fulvic acid in Sargasso seawater.

value. A semiobjective determination can be made of the average dH/dT over the initial part of the curve (hereafter called slope) by noting the decrease in drop height up to the time where the abrupt change occurs. For the top curve of Figure 2 a decrease of 5.1 cm occurred in 62 s to give a slope of 0.082 cm s^{-1} . A similar procedure was used for all the seawater samples where a determination of total organic carbon was made. The relation between the slope and the organic carbon (OC) concentration is shown in Figure 3.

There are other ways to present these data. For example, one could have determined H for a constant T for each of the curves in Figure 2 and plotted it against OC. This, however, does not appear to be as meaningful as determining dH/dT . First, T would have to be $< 10 \text{ s}$, for the salt marsh samples show nearly a steady state H for $T > 10 \text{ s}$. Obtaining H for such small times can introduce error, since only about two determinations were made of H for $T < 10 \text{ s}$. Second, and perhaps more important, dH/dT is a direct measure of the rate at which the drop dynamics are changing, which probably is proportional to the rate at which surfactant molecules are being adsorbed at the surface of the rising bubble, which in turn should be proportional to the OC content of the water.

Since the slope was lowest with water from the Sargasso Sea, one of these samples was used as a control (Figure 4), while aging tube runs were made as successively larger amounts of organic carbon in the form of humic acid were added. This was done in an attempt to determine the concentrations of humic acid necessary to modify the slope significantly. For comparison, runs with fulvic acid are also shown in Figure 4.

The nature of the curves shown in Figure 2 is not only a function of organic carbon but also of the size of the bubble. This is shown in Figure 5, where bubbles of different sizes were used in the same sample of seawater. The two curves were obtained with an aging tube run made aboard ship within an hour or two after the sample was collected [Blanchard, 1977].

DISCUSSION

The aging tube runs with samples of seawater obtained in and near Narragansett Bay produced curves (Figure 2) with a variety of shapes. However, nearly all of these have their counterparts in the curves that were found for samples of seawater from the North Atlantic [Blanchard, 1977]. For example, the nearly identical curves found for the two samples of

June 15, and one for June 19, were commonly found in the North Atlantic, although the bubble age at which a steady state in jet drop height began was not necessarily about 60 s, as is the case in the present work. It is remarkable how abrupt the change is to the steady state. Whether this signifies the time beyond which no more surface-active material is adsorbed by the bubble [Detwiler and Blanchard, 1978] or whether the amount of material adsorbed at this time produces a steady state in some parameter controlling drop dynamics cannot be decided.

Another common curve, also found in the North Atlantic work, is represented by the samples of June 21, 22, and 25. This form of curve is similar to that above in that inflection points are found in the initial slope, but it differs in that after the minimum drop height is reached a steady state does not occur. Instead, the curve rises slightly before returning to a steady state at an increased bubble age. This increase of ejection height with bubble age no doubt parallels an increase in the kinetic energy of the drop as it leaves the jet, but this does not mean that the surface free energy of the bubble must also have a concomitant increase. There are other drops produced by the jet, and when the ejection height of the top drop increases with time, the height of the second drop generally decreases [Blanchard and Syzdek, 1972]. Thus there can be time changes in the partitioning of kinetic energy among the various drops in the jet set but in such a way that the total kinetic energy most likely either decreases with time or remains at a steady state. Why the partitioning of energy occurs in the way it does is not known. The consequence for this work is that a unique correlation between the slope and the time-rate-of-change of bubble surface free energy probably does not exist. However, since the top jet drop has more kinetic energy than any of the lower drops [Blanchard, 1963], it is probable that the energy partitioning plays a secondary role.

It is clear from Figure 3 that there is a correlation between the slope and the OC of the sample. The samples from the three main sources, the Sargasso Sea, Narragansett Bay, and the salt marsh, have a correlation coefficient of 0.97. The slope increases by about 0.05 for each milligram per liter of OC. The single sample from Galilee Harbor gave a slope nearly twice that given by the above relation, but perhaps this is not surprising. It is possible that an abnormally high proportion of the OC was composed of highly surface active material from the fishing and pleasure boats in the harbor. The slope of the Point Judith sample, also high for its low OC, was the only sample collected right at the shore among rocks where waves were breaking. Although one can speculate on the cause of the high slope, it would seem better to suggest further samples from these anomalous locations for testing. In passing, it should be noted that the TOC of seawater from the upper few meters of the open ocean is between 0.3 and 3 mg l^{-1} , usually between 1 and 1.5 mg l^{-1} [Riley and Chester, 1971; Sharp, 1973].

Although Figure 3 shows a correlation between the sample slope and OC, it is apparent from Figure 4 and from the above-mentioned comments on energy partitioning that this correlation can never be exact. It depends on the nature of the species of organic material that constitutes the OC as much as it does on the absolute amount of OC. In Figure 4 we see that the slope for a sample of seawater from the Sargasso Sea, with its low concentration of only $0.6 \text{ ppm (mg l}^{-1})$ OC, is quite small. No change was observed when 0.02 ppm OC was added in the form of humic acid. However, the addition of only 0.1 ppm of humic acid OC was enough to increase the slope

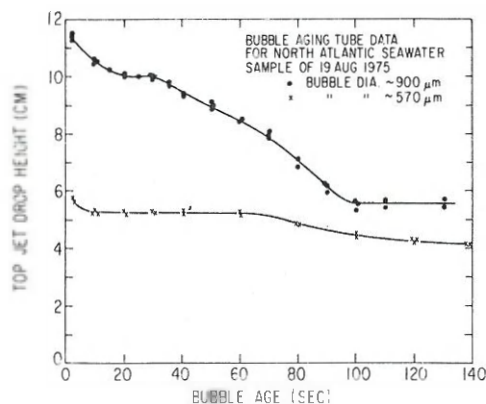


Fig. 5. Jet drop ejection height as a function of bubble age for two different bubble sizes.

markedly to about 0.05, a value approaching that found in the Narragansett Bay samples. When a total of 0.5 ppm of humic acid OC was added, the slope increased to about 0.37, a value in excess of that produced by the salt marsh samples with their OC of 6–7 ppm. It should be noted that the tendency of this curve to approach zero rapidly for a bubble age of about 60 s was never found in the other seawater samples of this work (Figure 2) nor in prior work [Blanchard, 1977]. In that respect the effect of humic acid OC is different from the normal OC found in seawater.

The curves shown in Figure 4 for fulvic acid OC resemble those for humic acid, though for similar concentrations the slope is less for fulvic acid. A fulvic acid concentration nearly 3 times that of humic acid (1.4 and 0.5 ppm, respectively) is barely adequate to produce equivalent slopes. This suggests that humic acid is more surface active than fulvic acid. Since humic acid has the higher molecular weight, it is less soluble in water and thus more likely to be adsorbed at interfaces. This species effect could be clarified with experiments using Sargasso seawater, to which were added known amounts of other classes of organic compounds found in seawater.

The results of Figure 4 are in qualitative agreement with the laboratory experiments of Hoffman and Duce [1976]. They produced numerous bubbles in Narragansett Bay seawater and analyzed the aerosol for the OC/Na ratio. They found that when they added only 0.45 ppm OC in the form of humic acid to seawater which contained about 1 ppm OC, the OC/Na ratio in the aerosol increased by about 7 times. The ratio also increased with the addition of a similar concentration of fulvic acid OC, but it was about 5 times less than that for humic acid. They concluded from this and other results that the nature of the chemical species of the OC in seawater might even be more critical than the amount in determining the OC/Na ratio on the aerosol.

The results with both humic and fulvic acids are interesting, since it appears that this largely uncharacterized class of compounds constitutes 5–20% of the total OC in seawater [Stuermer and Harvey, 1977], with fulvic acid present in higher concentrations than humic acid. While these acids can be used to simulate some of the effects of the OC in seawater experiments, it is clear from Figure 4 that they do not duplicate the OC in seawater. Similarities and differences have been discussed by Kerr and Quinn [1975] and Stuermer and Harvey [1974, 1977].

From a comparison of the present work with that of Hoffman and Duce [1976], one can conclude that the adsorption of surfactant to bubbles rising through the water not only results

in an increased OC/Na ratio in the aerosol but also produces complex changes in jet drop dynamics. This is a direct result of the role played by the surfactants in lowering the surface free energy, the energy source of jet drop formation.

An understanding of the mechanism of control of jet drop dynamics by organic carbon is further complicated by the finding that bubble size is an important parameter [Lee, 1972; Blanchard, 1977]. This is quite evident in Figure 5. The curve for the larger bubble (900 μm) shows a steady decrease in drop height during the first 100 s of bubble age, at which time a steady state is reached. None of this is found for the smaller bubbles (570 μm). After a small height decrease during the first 10 s the height remains nearly constant out to 60s, after which a slow but continual decrease occurs out to 140 s, where the experiment ended. On the basis of these and prior data, it appears that the control of jet drop dynamics by OC is a direct function of bubble size. However, it is not known why this should be so. Clearly, further work is needed including an investigation of the OC/Na ratio on the top jet drops from bubbles of different sizes as a function of bubble age and different amounts and types of organic carbon.

Hoffman and Duce [1976] compared laboratory data to field data and concluded that the enrichment of OC on the marine aerosol, commonly 1000 or more with respect to the OC in seawater, cannot be entirely explained by bubble-scavenging mechanisms in the sea. It appears that gas-to-particle conversion mechanisms may account for the major fraction of OC in the marine aerosol [Ketseridis et al., 1976; Hoffman and Duce, 1977]. Though this may prove to be the case, OC in seawater can play a role in jet drop dynamics and thus the drop size distribution produced by bubbles at the surface of the sea. Whether this will prove to be significant remains to be seen. Some evidence suggests it may be minimal. Most of the bubbles produced in the sea are less than 500 μm in diameter [Blanchard and Woodcock, 1957], and their jet drop ejection heights appear to be relatively unaffected by OC (Figure 5). Indeed, it may be found that the most useful application of the curves shown in Figures 2–5 is in understanding the adsorption of surfactants at the surfaces of air bubbles rising in water [Detwiler and Blanchard, 1978].

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