

Bubble Formation and Modification in the Sea and its Meteorological Significance

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Abstract

It is believed that the vast majority of the airborne salt nuclei arise from bursting bubbles at the air—sea water interface. Four natural mechanisms for the production of these bubbles have been studied. These are whitecaps, rain, snow and supersaturation of the surface waters of the sea due to spring warming. The bubble spectra from whitecaps and snowflakes have been measured and semi-quantitative and qualitative observations have been made on the bubble spectrum produced by raindrops. No evidence of bubble production by spring warming has been obtained.

All of the measurements show that a majority of the bubbles are < 200 microns diameter and, in the case of bubbles from snowflakes, < 50 microns. In the vicinity of a breaking wave the bubble production rate is about $30 \text{ cm}^{-2} \text{ sec}^{-1}$.

Due to the effects of surface tension in increasing the bubble internal pressure all bubbles < 300 microns will go into solution even at sea water air saturations of 102 percent. Bubbles < 20 microns will go into solution at saturations up to 115 percent! The solution time for small bubbles of about 10 microns is about 10 sec and is not markedly affected by the water saturation percentage.

It is concluded that the effects of the rate of solution of bubbles in sea water can, under some conditions, play a significant role in modifying the initial bubble spectrum. This, in turn, should influence the spectrum of airborne nuclei.

I. Introduction

It seemed evident from the work of WRIGHT (1940) and KÖHLER (1941) that large salt particles were playing an active role in visibility changes in the lower atmosphere and perhaps in cloud formation as well. It was not until the work of WOODCOCK (1949 and 1952) however that the existence of these particles throughout the entire subcloud and cloud layers in marine air was shown. CROZIER and SEELY (1950), TWOMEY (1955), and BYERS (1955)

have demonstrated that significant concentrations of these aerosols exist in air masses that had traveled many hundreds of miles over land. A consideration of the potential importance of these particles in the mechanism of rainfall production is, therefore, not limited to clouds over oceanic areas. LUDLAM (1951) and BOWEN (1950) have both shown, on a theoretical basis, that hygroscopic particles of the size of the salt nuclei found in the atmosphere are sufficiently large to grow rapidly into raindrops, by the process of coalescence with smaller cloud droplets. Recently WOODCOCK (1952) and WOODCOCK and BLANCHARD (1955) have compared the raindrop spectrum and the rainwater chlorinity with the salt nuclei spectrum in the sub-cloud layer. These results have suggested that each salt nucleus becomes a rain-

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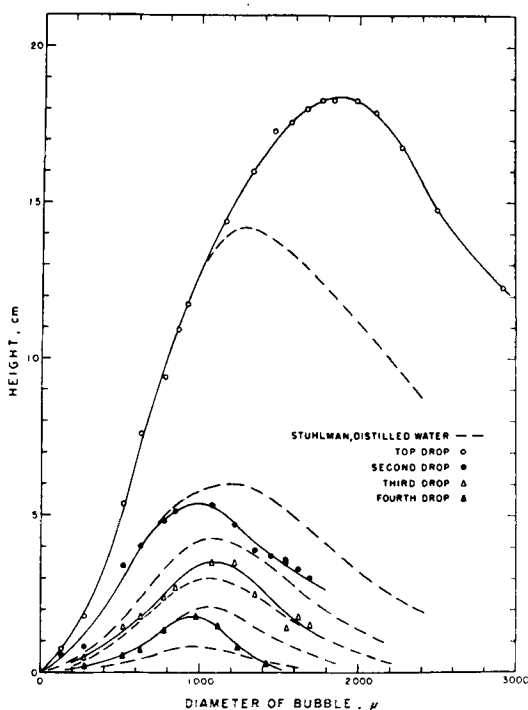


Fig. 1. This illustrates the heights of ejection of the several drops from the jet of a bubble bursting in sea water. STUHLMAN's (1932) findings are shown for the top drop from bubbles bursting in distilled water.

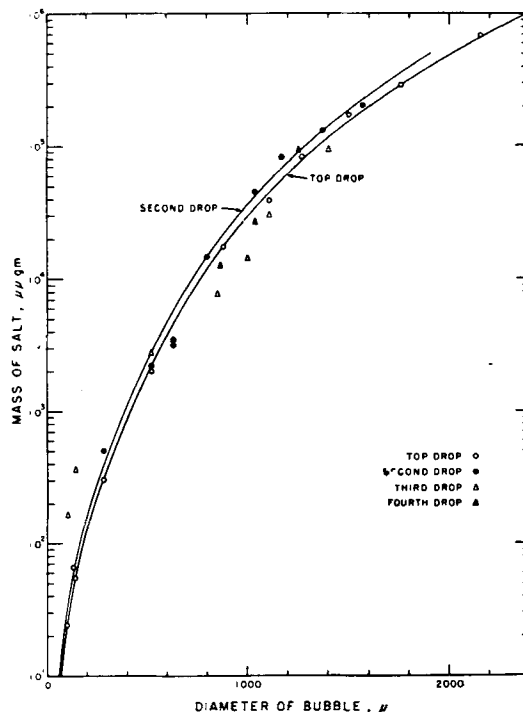


Fig. 2. This indicates the mass of salt contained in the drops that are ejected from bubbles bursting in sea water. This figure combined with Fig. 1 will give the ejection heights and drop size as a function of bubble diameter for the top four of the drops that evolve from the jet of a bursting bubble.

drop and that any modification of the sea salt spectrum will change the raindrop spectrum and possibly the manner of rainfall production. In the present paper we shall discuss the natural methods of production of salt particles at the sea surface and show that these methods should, in fact, be capable of modifying the existing salt nuclei spectrum.

The source of the airborne salt particles is, of course, the sea. Some of the first attempts at measurement of the salt spectrum were made near the sea surface by OWENS (1926). COSTE and WRIGHT (1935) showed that salt nuclei could be produced by spraying sea water and ALIVERTI and LOVERA (1939) produced small particles by bubbling air through sea water. KÖHLER (1941) forced air through sea water and found salt nuclei produced down to a radius of about 0.5 micron. None of these investigators, however, was greatly concerned with the exact mechanism of nuclei production; whether it was by mechanical disruption

of the water by breaking bubbles or some other process. In 1948 Woodcock suggested that salt particles were ejected into the air from breaking bubbles by a mechanism first suggested by STUHLMAN (1932). BOYCE (1951) carried out an experiment that suggested that relatively few salt particles were produced by the mere mechanical "tearing" of the water in a breaking wave but that a significantly greater number could be produced a few seconds later when the bubbles resulting from the wave action had burst at the sea surface. A high-speed photographic study (KIENTZLER ET AL., 1954) confirmed the mechanism of the ejection of droplets from a breaking bubble (STUHLMAN 1932). The photographs indicate the manner in which small airborne droplets evolve from the vertical water jet which forms upon collapse of the bubble cavity. As seen in Fig. 1 and Fig. 2 the heights to which these droplets are ejected and their size is a function of the bubble diameter. The heights were

obtained with the use of a cathetometer and the bubble size determined from measurements of the buoyant force from a known number of bubbles collected in a small inverted glass hemisphere. The size of the ejected drops was determined by catching them on glass slides and exposing them to an atmosphere of known humidity. The resulting drop size could then be used to compute the sea salt content and thus the original size of the drop.

MASON (1954), MOORE and MASON (1954) and KNELMAN ET AL. (1954) found that the breaking of the bubble film produces small drops. It appears that the production of droplets by this mechanism is limited to the larger bubbles and any evaluation of their importance in modifying the salt particle spectrum over the sea must await an experimental study on the actual bubble spectrum. This point will be discussed later in the paper.

The foregoing work suggests that it is the breaking bubble at the sea surface that is responsible for the production of the atmospheric salt particles. In the next section the variation in bubble production by wave action and precipitation will be discussed.

2. Bubble Production at the Sea Surface

A. Wave Action

It is well known that increasing winds cause a proportionate increase in the production of "whitecaps" at the sea surface. These whitecaps produce bubbles in the sea which, when they break at the surface, produce airborne salt nuclei. Therefore a direct relation should exist between wind force and the concentration of airborne salt. This in fact has been found at deck levels by FOURNIER D'ALBE (1951), MOORE (1952) and at cloud levels by WOODCOCK (1953). Woodcock found that the weight concentration of sea salt at cloud base levels was increased by a factor of about ten when the wind force changed from three to seven.

It might be well to point out that in strong winds the effective area over which bubbles are breaking is appreciably greater than that covered by the obvious breaking wave. For a minute or more after the wave breaks the water in the immediate vicinity appears cloudy without the presence of a heavy foam patch on the surface. This cloudy appearance is caused by

the myriads of bubbles that are formed by the breaking wave. The persistence of the cloudy region signifies that the bubbles are small and thus slow in reaching the surface or that they have been carried far beneath the surface. Presumably the stronger the wind the more bubbles are produced and the deeper they are carried by the turbulent motions of the sea. Observation indicates that little or no coalescence occurs amongst the bubbles when they reach the surface. If this surface is clean the bubbles will break immediately. In the laboratory, experiments have been carried out by bubbling air through fine frits placed a few cm beneath the surface of the water. A rapid coalescence of bubbles occurs on the surface of fresh water but this is not observed in the case of sea water. Even though they are packed tightly at the surface the individual bubble bursts seem unaffected by the adjacent bubbles. It appears safe to assume that bubbles produced in the sea by wave action will in most cases burst individually at the sea surface and not coalesce.

The device that was used to determine the bubble spectrum produced by breaking waves consisted of a small ($9 \times 6 \times 2$ cm) box with one of the 9×6 cm sides transparent. A grid of lines was inscribed on this transparent side of the box, the opposite side being removable. Just prior to making a bubble count the box was completely filled with sea water and the removable side securely attached. The box was then placed, transparent side up, just beneath the sea surface in a region where breaking waves had left the sea cloudy with bubbles. The removable side (now the bottom) was slipped aside for a known time interval during which bubbles were free to rise into the box and become entrapped against the underside of the transparent top. The bottom was then securely attached to prevent leakage and the box removed from the water. Using a scale and a magnifying lens, the bubble spectrum, divided into appropriate size ranges, could be obtained.

A brief consideration of the energies involved showed that there was no danger of a flattening of the bubbles against the underside of the glass. For bubbles < 500 microns diameter the surface free energy is at least 400 times as great as the gravitational energy. Any bubble surface distortion, which must arise from the gravita-

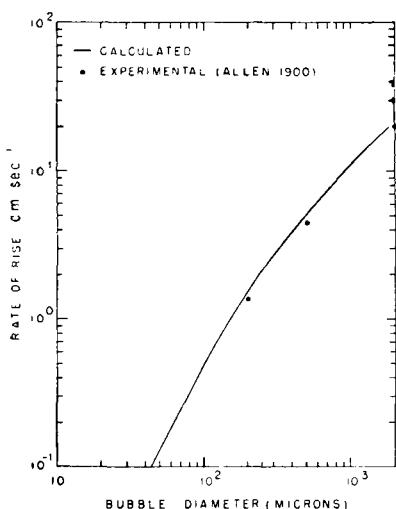


Fig. 3. The rate of rise of air bubbles in water. The calculated values are for sea water while the experimental ones are for fresh water.

tional energy, will be opposed by the surface free energy which, of course, tends to a minimum. It is apparent from the above considerations that the bubble surface distortion could not exceed 1/400 or 1/4 of one percent and thus the diameter will not undergo any significant change.

The bubble density or number per unit volume of water is easily obtained by dividing the number found in each size range by the area that was counted, the time of exposure and the rate of rise of the bubble in water. The size ranges were in 100 microns steps up to 500 microns. The rate of rise of the bubbles in each size range was assumed to be represented by the rising speed of the average sized bubble, with the exception of the first size range, where the representative rise speed was that for a 75 micron diameter bubble.

The rate of rise of bubbles in water may be calculated in the following manner. The general expression for the frictional retarding force is

$$f = 6 \pi n r v \left(\frac{C_d \cdot R}{24} \right) \quad (1)$$

where n is the viscosity of the water; r , the bubble radius; v , the velocity of rise; C_d , the drag coefficient; and R , the Reynolds number. This expression can be derived in a straightforward manner from Stokes' Law and the

fundamental relation between actual drag and impact drag. Now the buoyant force on the bubble is

$$f_b = 4/3 \pi r^3 g (\rho_w - \rho_a) \quad (2)$$

where g is the gravitational acceleration and ρ_w and ρ_a the density of sea water and air, respectively. At the terminal or steady state velocity of the bubble (2) must equal (1). By equating these expressions and then substituting for v in terms of the Reynolds number

$$v = \frac{nR}{2\rho_w r} \quad (3)$$

and letting $\rho_a \ll \rho_w$ we obtain

$$r^3 = \frac{9n^2}{4\rho_w^2 g} \frac{C_d R^2}{24} \quad (4)$$

C_d has been found to be a function of only the Reynolds number (GOLDSTEIN 1938) so, given any value of R , C_d may be obtained and (4) can be solved for r . With this value of r and R , (3) may be solved for the rate of rise v . In like manner a number of r versus v tabulations can be determined and a graph drawn. Figure 3 shows the calculated values plus some experimentally observed rise velocities (ALLEN, 1900). Allen's values were used for the bubble density calculations in this section while the calculated values outside of Allen's observations were used for the discussions in

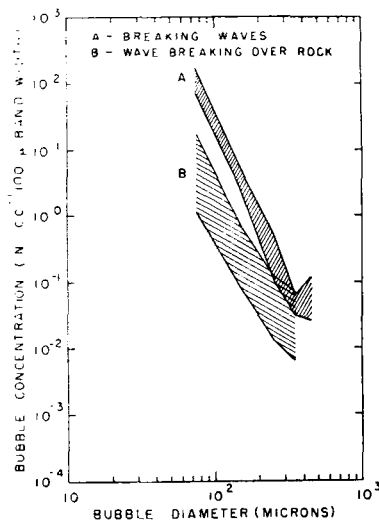


Fig. 4. The bubble concentration (cc^{-1} per 100 μ band width) in sea water produced by breaking waves or whitecaps.

the latter part of the paper. Stokes' law will apply for bubbles below about 110 microns diameter.

Figure 4 summarizes the experiments made on the bubble spectrum from breaking waves. All the experiments were carried out during the summer months on a beach near our laboratory where the water temperature was about 21° C. The hatched region A shows the limits of bubble density for six separate experiments conducted during a 2-hour interval at a time when fresh onshore winds were causing the waves to break about 15 meters from shore. The bubbles were obtained by wading some 5 meters out and exposing the sampling device already described for 2 seconds at a depth of about 10 cm. The measurements were made a few seconds after the breaking wave had passed. It was necessary to wait these few seconds to allow the relatively few bubbles of several mm diameter to rise to the surface. These large bubbles produced undesirable coalescence in the collecting box. It is realized that this method discriminates against the mm sized bubbles but they are present in far fewer numbers than the bubbles < 500 μ . The bubble spectrum in these experiments was determined out to a diameter of 750–1,500 microns but, as the size interval was 500 microns in this region, the values could not, without approximation, be plotted on Fig. 4. Had this been done the extension of region A and B would have continued with about the same slope as it has at present. Region B, an order of magnitude less than A, represents the spread of six determinations of the bubble spectrum found on the lee side of a rock over which the waves were breaking. The wind was not as strong as it was during the former measurements.

B. Snow

Among the natural sources of small bubbles in surface waters of the sea we have found that snowflake clusters are very significant. These bubbles, which are released as the snowflakes melt, are readily observed by allowing a snowflake to fall into a small beaker which is brimming full of sea water, and then quickly placing a clean glass cover-slip over the water in order to trap the bubbles. From fifty to several hundred bubbles were observed to rise and collect under the cover-slip as single flakes

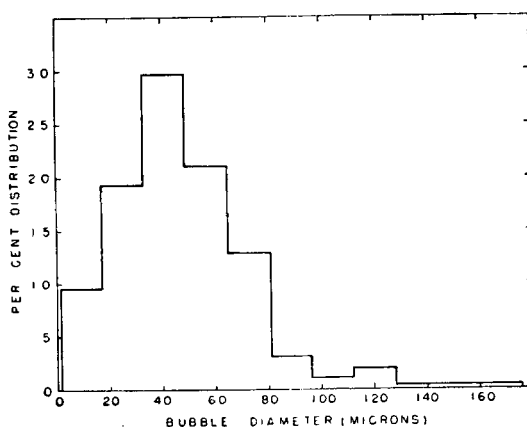


Fig. 5. The size distribution of bubbles, rising from a snowflake cluster melted in sea water.

melt. Figure 5 shows the size distribution of some three hundred of these bubbles, which were measured with a low-power microscope using an eyepiece micrometer.

While making these size measurements, which required perhaps 10 minutes, it was observed that bubbles smaller than about 30 μ diameter were slowly becoming smaller and that bubbles 50 μ or larger were growing. Thus the size distribution shown on Fig. 5 is only qualitatively correct, serving here only to emphasize the capabilities of snow in producing (or causing to be produced) a wide range of size among very small bubbles. Since, during the observation period, the small bubbles were becoming smaller and the large bubbles were becoming larger an increase in the size range with time occurred. This means that the initial bubble size distribution, present immediately after the flakes melted, was more limited in range than is shown in Fig. 5. The effects of time of immersion in altering a given initial bubble population depends upon a number of factors, such as depth of water, partial pressure of air in solution, etc. These and other factors are discussed at length in Section 3 of this paper.

C. Raindrops

The production of bubbles and nuclei by the impact of raindrops on the sea surface is a complex problem. It has been found that bubbles, produced directly and indirectly through the impact of raindrops, can produce

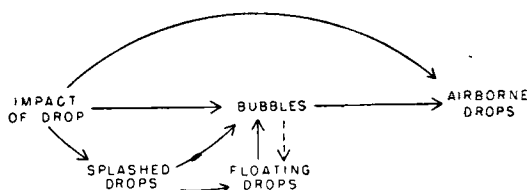


Fig. 6. A diagrammatic sketch of the methods of production of airborne drops by the impact of a fresh-water drop on a sea water surface. The dotted arrow indicates that floating drops are associated primarily with the collapse of the larger, less numerous bubbles.

nuclei. Before an attempt is made to describe these bubble-production methods in detail, and to show how they vary over the raindrop spectrum, it might be well to consider them in schematic form as shown in Fig. 6. It can be seen that the nuclei are produced either directly from the impact of the drop, or from bubbles produced as a result of the impact. The bubbles are produced by (1) direct impact of the raindrop on the sea surface, (2) splashed drops resulting from the impact, and (3) drops that momentarily remain floating on the sea surface.

Observations on the splashing of water and production of bubbles by simulated raindrops were made by visually observing, with suitable lighting, the behavior of freshwater drops on impact with a sea water surface. The drops were allowed to fall from a sufficient height to insure terminal velocity. The splashed drops and the smallest bubbles were easily visible in a parallel beam of light from a microscope lamp, using a suitable black velvet background. An estimate of the size of the bubbles and drops was made by applying Stokes' Law to the rate of rise and fall, respectively.

The direct production of bubbles by raindrops is a function of raindrop size. Small drops of the order of 0.4 mm diameter will produce 2 or 3 bubbles of about 50μ diameter that are carried only 1–3 mm beneath the surface. The production of bubbles increases rapidly with drop size as a 2.2 mm drop was observed to produce from 50–100 bubbles that were often carried down in a vortex ring to depths of 2–4 cm. The vast majority of these bubbles appeared to be under 50 microns diameter. On occasions it appeared that the vortex ring of bubbles formed not at the moment of impact of the drop with the water but at the

collapse of the water column that rises from the bottom of the impact cavity. This is quite plausible, for the remarkable photographic work of WORTHINGTON and COLE (1897) shows this water column, and they remark about the vortex ring that it forms upon collapse. They make no mention of bubbles in the vortex ring but they probably passed undetected as only the closest scrutiny will discover them. With increasing drop size an increase in number of bubbles was observed, although the bubble size was predominantly the same. Drops of 3 mm produced 100–200 bubbles while 4.7 mm drops produced an estimated 200–400 bubbles (see Fig. 7). The larger drops also produce several bubbles of about a mm diameter. With increasing drop size the vortex motion of the bubbles plus the depth of penetration decreased. The bubbles from drops of 4.7 mm were carried down less than 2 cm but eddy motions distributed bubble clusters some 3 cm horizontally. These bubbles would go rapidly into solution or grow depending upon whether the sea water was considerably under- or oversaturated, respectively. This, of course, will modify the bubble spectrum which in turn will affect the salt nuclei that are produced when the bubbles burst. This solubility effect of the bubbles is considered in some detail later in the paper.

The indirect production of bubbles by raindrops occurs when the drops produced by the splash of the raindrop fall back into the sea. As this method of bubble production depends

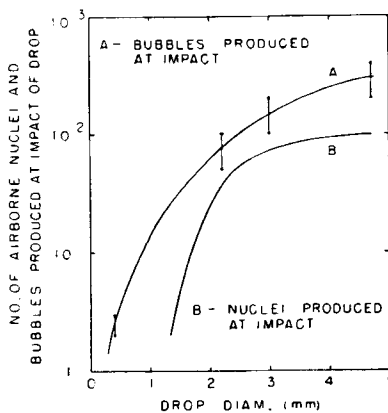


Fig. 7. Curve A represents the number of bubbles produced by the impact of a fresh-water drop on a sea water surface. Curve B represents the direct production of nuclei by the same drop at the moment of impact.

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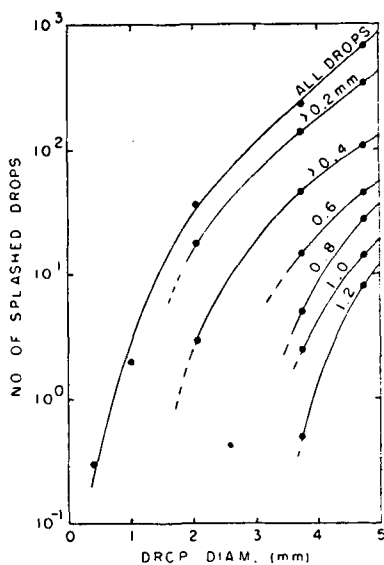


Fig. 8. The number of splashed drops $>$ the indicated size, that are produced by the impact of a fresh-water drop on a sea water surface. As these data were obtained with the aid of filter papers, splashed drops $<$ about 100 microns diameter and those remaining airborne (Curve B, Fig. 7) were not included.

entirely on the size and number of splashed drops it was necessary to determine the "splashed drop spectrum" over the range of raindrop size. This was done by catching the splashed drops on 60×90 cm squares of Whatman No. 1 filter paper. The "raindrops" and the sea water contained a sufficient amount of methylene blue dye to enable the splashed drops, at least down to about 100μ diameter, to be recorded as a blue spot on the filter paper. Tensiometer measurements showed that the blue dye did not significantly change the surface tension, consequently the character of the splash would not be expected to change. The relation of drop size to spot size on the filter paper was determined by letting drops of known size fall on the papers. A semi-disc of 10 cm diameter was cut from the center of the 90 cm edge of the filter paper and the paper then placed about 5 mm above the sea water surface and so positioned that the water drops would splash at the edge of the paper at the center of the semicircular opening. Only half of the splash was recorded so the final count of drops on the filter paper was multiplied by two. The splash from the largest drops extended out to about

50 cm from the point of impact of the drop with the water. The splash from four to six drops in each of three size categories from 2–5 mm was counted. Figure 8 presents the data in the form of a family of curves showing the total number of splashed drops larger than the indicated size. It can be seen that nearly half of the splashed drops are < 0.2 mm. A raindrop of 5 mm might be expected to produce nearly 900 drops of a size that is detected on the filter paper, of which only about 400 exceed 0.2 mm and only 12 exceed 1.2 mm. The splash from raindrops < 2 mm is probably mainly composed of drops < 0.4 mm. Drops < 1 mm produce, on the average, less than one splash drop. These last splash observations were made visually.

It now remains to determine just what this splash means in terms of bubble production. It might be expected that the bubble-producing ability of the splash drops would be a function of their velocity and the angle at which they enter the water. A larger number of combinations may be met with in the splash of a single large drop but fortunately a simplification enables us to make a reasonable estimate of the bubble production. The splash drops are observed to rise up to 40 cm from the water surface, a height sufficient to insure that drops up to 0.5 mm will nearly attain terminal velocity by the time they return to the water surface. Figure 8 indicates that all the splash drops from raindrops < 2 mm and about 80 percent from a 5 mm raindrop are < 0.5 mm. We might reasonably expect then that the splash drops could be considered as raindrops and, as discussed earlier in this section, each produce 2–3 bubbles of about 50μ diameter. On this basis the splash from a 2 mm raindrop might be expected to produce some 80 bubbles compared to over 2,000 for a 5 mm raindrop.

The third method of bubble production by raindrops falling into the sea is from "floating drops". These drops are similar to those that can be seen skimming across the surface of the water any time the water is violently agitated. As indicated in Fig. 6 the floating drops can be produced by both the splashed drops and the bubbles. Presumably the few that are produced by splashed drops are from drops that were not splashed to any great height while those produced by bubbles are presumably the lower, larger drops in the jet that is produced

when the bubble breaks. Observations on floating drops of about 2 mm diameter show that when they finally merge with the main body of water a thin column of bubbles is forced down several mm into the water. When these bubbles, perhaps 40 or more, fan out they are seen to be very small, perhaps $< 25 \mu$ diameter. Little can be said of the numbers or sizes of these floating drops that are produced by raindrops. It may be that rain produces relatively few compared to those that may be produced by breaking waves.

The airborne salt nuclei produced by direct impact of the raindrops with the water are nothing more than splashed drops that are, for the most part, small enough to remain airborne. Drops of 4.7 mm were observed to produce an estimated several hundred particles of $<$ about 50 microns diameter. At impact these particles seem to appear simultaneously within a region up to 4 cm above the water and some 10 cm from the point of impact. No doubt this is caused by the fact that the production mechanism of the particles gives them sufficient speed to escape detection by the eye until frictional retarding forces decrease their speed to the terminal value. This production mechanism appeared to be associated with the rapid formation and collapse of the large bubble that WORTHINGTON and COLE (1897) observed in their splash studies. In any event the ejection of the particles several cm above the surface increases the probability that they will remain airborne. Some of these particles were so small (< 10 microns) that a collection of them appeared and behaved like a small puff of smoke. There was no doubt that these would remain airborne, especially if the humidity were low over the water surface. The production of these minute splash drops was very much a function of drop size. A 2.4 mm drop produced perhaps 50–80 small particles while a 0.4 mm drop produced none that was visible to the naked eye (see Fig. 7).

D. Air Solubility Change in the Sea

The dissolved air content of the surface layers of the sea is usually at or near saturation and will vary from one season to the next. This seasonal change is presumably explained by the fact that the solubility of air in sea water is a function of temperature and also

that the production or utilization of oxygen by marine organisms will vary with the seasons. As the solubility of air is an inverse function of temperature it follows that, at saturation values, a maximum would be found near the end of the winter months when the water is at its lowest temperature and a minimum at the end of summer when the water is warmest. Consequently air should be given off by the sea during the spring and summer and absorbed during the winter. REDFIELD (1948), after an analysis of the seasonal variations of the oxygen distribution in the Gulf of Maine, concluded that about 3×10^5 cc of oxygen leaves the sea through a m^2 of sea surface during March–October and a similar amount re-enters during the winter and spring. It is logical to inquire as to how much of this oxygen might leave the sea in the form of bubbles. If we go to extremes and assume that it all comes out in the form of bubbles of 50 microns diameter we can compute the rather staggering number of $2,500 \text{ bubbles sec}^{-1} \text{ cm}^{-2}$ breaking at the sea surface. This certainly does not occur, as gaseous diffusion across the sea surface probably accounts for the greater part of the oxygen exchange in the normal course of events. However an intriguing question is whether bubble formation occurs in the sea after a short period of intense heating by an overlying warm air mass. If supersaturation by heating can keep ahead of the loss by gaseous diffusion to the air, and if sufficient nuclei for centers of bubble formation exist, there is a possibility that bubbles may form. Inasmuch as little or nothing is known of the interplay between these factors little more can be said.

Precipitation falling into the sea may, under certain conditions, bring about a supersaturation of the rain water—sea water mixture, even though both were only saturated initially. As the inverse relation between air solubility and temperature is not linear but in the form of a curve concave upward, it follows that the mixing of two initially saturated bodies of water at different temperatures will produce a supersaturated mixture. For example, consider raindrops which have essentially the wet bulb temperature (KINZLER and GUNN, 1951) and undoubtedly are saturated at that temperature. If raindrops, of a chlorinity essentially zero and saturated with air at 10°C , fall into saturated sea water ($\text{Cl} = 19 \text{‰}$) at 24°C and

mix such that the mixture is 90 percent sea water, the resulting supersaturation will be about 102 percent¹. Such supersaturations are probably not sufficient to cause bubble nucleation, but the rate of solution of the small bubbles produced by wave action and precipitation would be decreased. The important subject of the rates of solution of an air bubble as a function of saturation percentage will be discussed in the next section.

3. The Stability of Air Bubbles in Sea Water

The foregoing experiments have shown that whitecaps and all forms of precipitation particles are effective bubble producers. If these bubbles are produced in subsaturated water there is the possibility that a significant decrease in bubble diameter will be caused by the air within the bubble going into solution. On the other hand, if the water is sufficiently supersaturated many of the bubbles would be expected to grow. It will be clear shortly that for any supersaturation of sea water there exists a bubble size above which all bubbles will grow while those smaller than this size will go into solution. This modification of bubble size is clearly then a function of its initial size, the sea water saturation and the duration of existence of the bubble. Bubbles carried far beneath the surface will be subjected to gas diffusion across the bubble—water interface for considerably longer periods of time and are thus subject to greater change than those near the surface. Consequently it is very important that we obtain some knowledge of the effects of various solution times and rates on the bubble spectrum.

The calculations outlined here are an extension of those given by WYMAN ET AL (1952) and the reader should refer to these authors for a full understanding of the initial formulation. As a first approximation consider that due to the relative motion between the water and the bubble that the only gradient of dissolved gas that exists is across a thin shell with its inner surface at the air—water interface. Further assume that the air within the bubble consists of a single gas with a single diffusion constant and not primarily a mixture of

oxygen and nitrogen. The general gas law states:

$$n = \frac{1}{RT} \frac{4}{3} \pi r^3 p \quad (5)$$

when n is the number of moles of gas in the bubble; R , the gas constant; T , the absolute temperature; r , the radius of the bubble; and p , the pressure within the bubble. The pressure p is the hydrostatic plus the atmospheric pressure. The diffusion of air across the bubble surface can be expressed by Fick's law:

$$dn/dt = -\delta \, 4 \pi r^2 (p - p_0) \quad (6)$$

where p_0 is the partial pressure of the air in the bulk water and δ is a constant defined by: $\delta = \Delta \alpha / d$ where Δ is the diffusion constant of the air in the water; α , the solubility of the air in the water, and d , the thickness of the thin shell that is assumed to carry the diffusion gradient. It will be seen that this expression is necessary to convert $(p - p_0)$ in (6) into a concentration gradient as called for in Fick's law. If we differentiate (5) with respect to time and combine it with (6) we have:

$$dr/dt = -\delta \, RT \frac{(p - p_0)}{p} \quad (7)$$

This is the equation that was derived by WYMAN ET AL. (1952) and found to be in very good agreement with experiment. Experimentally they found that dr/dt at any given pressure was essentially constant, that it approached a limiting value at high pressures and it was essentially independent of temperature over the range 1—27° C. This is just what (7) predicts. As the water was always saturated with respect to air at one atmosphere, pressure p_0 is constant and dr/dt can be seen to approach a limiting value, $\delta \, RT$, at great depths. As the rate of solution is proportional to the absolute temperature dr/dt will change relatively little with the temperature range used in the experiments. With the experimental data one may compute the value of the term $\delta \, RT$ to be 10^{-4} cm sec⁻¹ and find that it is approximately constant at all depths. Equation (7) with this substitution combines both theory and experiment to describe the rate of solution of gas bubbles.

It should be noted in (7) that the total pressure p within the bubble is assumed to be only the hydrostatic plus atmospheric pressure

¹ This calculation was based on tables of air saturation as a function of temperature and chlorinity as given by MIYAKE (1951).

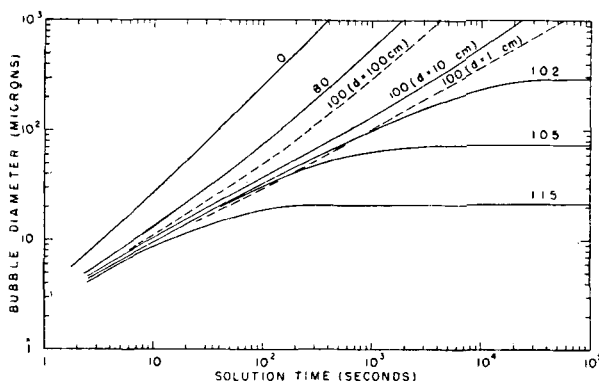


Fig. 9. The time of solution for a bubble in sea water at a depth of 10 cm. The family of curves represents various percentage saturations of air in sea water with respect to atmospheric pressure. The dashed lines show the solution times for bubbles at a depth of 1 and 100 cm in water saturated with air with respect to atmospheric pressure.

and no account is taken of the additional pressure $2\gamma/r$ due to surface tension effects (the surface tension of sea water γ is about 74 dynes cm^{-1}). This effect was negligible in the work of Wyman et al. where the bubbles were several mm in diameter but in the present case, where we must be concerned with bubbles < 100 microns, surface tension effects become of prime importance. If then we add the surface tension pressure term $2\gamma/r$ to the other pressure term p in (5) and (6) and solve simultaneously we obtain the general expression:

$$\int_0^t dt = -\frac{1}{3\delta RT} \int_{r^*}^r \frac{3pr + 4\gamma dr}{r(p - p_0) + 2\gamma} \quad (8)$$

which reduces to (7), as it should, if γ is set equal to zero. The solution of this integral is:

$$t = -\frac{(p - p_0)^{-1}}{3\delta RT} \left[3pr + \gamma \left\{ \frac{4(p - p_0) - 6p}{p - p_0} \right\} \ln \{ (p - p_0)r + 2\gamma \} \right]_{r^*}^r \quad (9)$$

Figure 9 was constructed from (9) and shows the solution times for bubbles in water of various degrees of saturation at a depth of 10 cm. The dashed lines show the solution times in water saturated at atmospheric pressures at depths of 1 and 100 cm. Note that within these depths there is little significant difference in solution times in saturated water

for bubbles $<$ about 40 microns diameter. The significance in Figure 9 would seem to be the equilibrium bubble diameters that are indicated at each value of supersaturation, below which all bubbles will, due to surface tension pressure effects, go into solution. Even at a supersaturation of 115 % all bubbles < 21 microns will be forced into solution. The value of this equilibrium diameter may be very important for if the majority of bubbles in a given bubble spectrum are $<$ this value, the bubbles themselves may be responsible for further increasing the supersaturation. As the supersaturation curves in Fig. 9 were constructed for a depth of 10 cm, it is of interest to determine how the equilibrium bubble diameters vary with depth as a function of supersaturation.

A bubble is at equilibrium with its surroundings when its total internal pressure, which is composed of the atmospheric, the hydrostatic and the surface tension pressures, is equal to the partial pressure of the gas in solution. As we are considering the case where the water is saturated at all depths with respect to atmospheric pressure, the partial pressure of the gas is $x A$, where x is the fractional value of the supersaturation and A is the atmospheric pressure. This is equated to the three components of the total internal pressure as given above to obtain

$$xA = A + d + \frac{2\gamma}{r} \quad (10)$$

where d is the hydrostatic pressure. Solving for r we find

$$r = \frac{2\gamma}{(x-1)A-d} \quad (11)$$

from which it is seen that for any supersaturation x there is a depth d beyond which all bubbles will go into solution. This depth is found by letting the denominator in (11) equal zero and solving for d . For supersaturations < 102 percent this depth is < 10 cm. At supersaturations > 102 percent (11) shows that for depths < 10 cm the critical radius, above which or below which bubbles grow or go into solution, is essentially constant for a given supersaturation and thus similar to the values indicated in Fig. 9. The time required for the bubbles to go into solution will decrease with depth in the range of 0–100 cm but probably not significantly so, judging from the curves for depth of 1 and 100 cm in Fig. 9.

4. Discussion

It will be of interest to examine the experimental data on the effectiveness of bubble production by breaking waves and precipitation in terms of the salt nuclei spectrum found in the atmosphere. The breaking wave is probably the most common method of production of airborne nuclei. With the data from Fig. 3 and Fig. 4 we can derive Table 1 which indicates the rate at which bubbles of various sizes rise to the surface $\text{cm}^{-2} \text{sec}^{-1}$. Assuming that only one of the 4 or 5 drops ejected from the breaking bubble remains airborne, column D of Table 1 can also represent the production rate of airborne nuclei from the sea surface shortly after a whitecap has formed. It would be unwise to attempt to compute the total production of nuclei from a breaking wave for we do not know to what depths the bubbles are carried and thus cannot say how long the concentration given in column B will be in existence. If the bubbles are all distributed uniformly to the same depth then the smallest ones will continue to break at the surface for the longest time. The production rate (column D) of about $34 \text{ cm}^{-2} \text{sec}^{-1}$ is comparable to the value of $40 \text{ cm}^{-2} \text{sec}^{-1}$ (for nuclei of mass $> 10^{-13}$ g) found by MOORE and MASON (1954) in laboratory tests. It would be well to

regard the similarity of these two values as probably fortuitous, and to accept it only as an agreement in order of magnitude. It is not clear as to whether bubbles were breaking over the entire area used in Moore and Mason's laboratory tests or only over a fraction of it. Also, it is not known how the present results will be affected by changes in wind force on the open sea. It is expected that increasing wind force will increase the numbers of bubbles in such a way that the slope of the curve in Fig. 4 will be essentially the same.

Table 1. An attempt to estimate the number of bubbles ($\text{cm}^{-2} \text{sec}^{-1}$) from a breaking wave. Columns B and C are obtained from Figs. 4 and 3, respectively. Column D is simply the product of B and C. Column E is obtained from D by assuming only 10 percent of the ocean active as a source bubbles.

A	B	C	D	E
Bubble diam. of center of size band (μ)	Bubbles cc^{-1} per 100 μ band width	Rise velocity cm sec^{-1}	Bubbles $\text{cm}^{-2} \text{sec}^{-1}$	Bubbles produced $\text{cm}^{-2} \text{sec}^{-1}$ assuming 10 % of sea active
75	100	0.3	30	3
150	3.6	0.9	3.24	0.32
250	0.25	1.9	0.47	0.047
350	0.05	2.95	0.15	0.015

Probably the most significant aspect of Table 1 is that the great majority of the bubbles are $< 200 \mu$. From Fig. 2 we see that these bubbles, upon bursting, could produce nuclei of the size found at the small end of the airborne sea-salt spectrum ($< \text{about } 10^{-10} \text{ g}$) by drops from the jets. MOORE and MASON (1954), with doubts as to the existence of bubbles $< \text{about } 500 \mu$ from whitecaps, have suggested that airborne salt nuclei $< 10^{-9} \text{ g}$ originate from the shattering of the film of the large bubbles. Inasmuch as the small bubbles do indeed exist it is likely that the mechanism by which the nuclei are produced is via the jet mechanism and not the bubble film. Observation (BLANCHARD 1954) shows that small bubbles ($< 50 \mu$) produce no droplets exceeding 1μ radius, other than those coming from the jet mechanism. MASON (1954) reports that bubbles of 0.5 to 3 mm give 100–200 droplets from the shattered film, with the largest having salt contents of about $2 \times 10^{-14} \text{ g}$. This weight is far less than the minimum of about 10^{-10} g that appears to provide the

nuclei for raindrop formation (WOODCOCK and BLANCHARD 1955).

The entire question as to the spectrum of bubbles that produce these large airborne nuclei and the exact method by which it is done may appear to be a trivial one. And it could well be so, if we were to assume that the properties of two drops of equal size, one produced by the jet mechanism and the other by the rupture of the bubble film, were the same. But this may not necessarily be so. It has been found (BLANCHARD 1955) that the droplets arising from the jet mechanism carry an appreciable electric charge that may contribute significantly to electrification processes in the atmosphere. Other considerations indicate that the droplets that are created by the jets may not be representative of the bulk sea water but of the surface film which may be contaminated. If droplets arising from the rupture of bubble films do not have the aforementioned properties they may play a different role in the precipitation process than those arising from the jet mechanism.

The production of bubbles by falling snow was found to be about $25 \text{ cm}^{-2} \text{ sec}^{-1}$ which, again assuming one airborne droplet per bursting bubble, gives a salt nuclei production rate of the same value. This is to be compared to the somewhat similar computed value of about 14 found for the nuclei production from bubbles produced by rain. The nuclei production by rain was estimated by carrying out the following steps, with each of the raindrop size distributions given by BLANCHARD (1953) and BEST (1950) for rain intensities of 20.8 and 25 mm hr⁻¹, respectively. Each distribution was divided into a number of intervals ($\leq 250 \mu$) and the number of drops striking the sea $\text{cm}^{-2} \text{ sec}^{-1}$ was computed. Then by using Fig. 7 and Fig. 8 one could compute the production rate of airborne nuclei from (a); bubbles produced directly by the drop, (b); impact of the drop and (c); bubbles produced by the drops $< 0.4 \text{ mm}$ that were splashed by the raindrops. It was found that the bubbles produced at impact were responsible for more than 80 percent of the total airborne nuclei and, even more surprising, Blanchard's rain distribution above (all drops $\leq 2.2 \text{ mm}$) produced about as many bubbles as did Best's (drops as large as 5 mm). It appears that the greater number of drops m^{-3} in the narrow

range distribution made up for the fact that larger drops produce more bubbles. These data indicate that a significant increase in the salt nuclei count might be found in atmospheric regions overlying the ocean through which rain or snow had fallen. The build up of airborne nuclei in such regions would be a function of the wind shear between sea level and the precipitation source and the duration of the precipitation.

The question as to the production of bubbles by the warming of the sea in the summer months or by the mixing of two saturated water masses at different temperatures will, as mentioned earlier, have to await more observations on the supersaturations of surface waters of the sea. The existence of supersaturations will depend, in some degree, on the absence of bubble nuclei. In the absence of these nuclei, which are thought to be gas particles surrounded by minute foreign materials in the water, the water may be highly supersaturated without the formation of bubbles (DEAN, 1944). The idea was recently advanced (FOX and HERZFELD, 1954) than minute bubbles in water, which are prevented from going into solution by the stabilizing action of an organic skin, will act as cavitation nuclei. They envisaged that this organic skin, probably produced by the disintegration of living organisms, acted as a mechanical barrier to the diffusion of gases. Upon cavitation the organic skin could be torn and bubble growth would follow. It seems probable that such bubble nuclei could exist in the oceans but their importance in bubble production in natural supersaturated waters is unknown.

From the calculations presented in Section 3 it appears that supersaturations in the surface layers of the sea can be produced by the small bubbles that are forced into solution by the increase in internal bubble pressure due to surface tension. Figure 9 indicates that supersaturation of at least 102 percent could occur if the bubbles are $< 300 \mu$ diameter. As the results of Section 2 show that a majority of the bubbles produced by natural processes are $< 300 \mu$, it is to be expected that a slight supersaturation of the surface waters would be produced. In particular, as the majority of the bubbles produced by snowflakes are $< 50 \mu$ diameter, it is expected that supersaturations of about 105 percent could be obtained. The

bubbling process will certainly produce supersaturations, as RAKESTRAW and EMMEL (1938) have measured nitrogen supersaturations of 102 percent in water that had been vigorously shaken with air and let stand until the bubbles were no longer visible.

If we assume that the usual saturation percentage at the sea surface is from 100 to 102, then in either case all bubbles $< 300 \mu$ will tend to go into solution and at rates, at least for the bubbles $< \text{about } 100 \mu$, that are nearly the same. The solution rates for the larger bubbles, though significantly different for 100 and 102 percent saturation, need not be considered, for the rate of rise of these bubbles will bring them to the surface long before any appreciable decrease in diameter has taken place. The small bubbles, with rates of rise of only a few tenths of a cm sec⁻¹, will require several hundred or only a few seconds to reach the surface depending on whether they rise from depths of about a meter or a few cm, respectively. In the former case the bubble may go entirely into solution while in the latter little change in size may be experienced. It appears then that the depth to which a small bubble is carried may be an important factor in controlling the final bubble size. This depth,

in turn, will be a function of the stability of the surface layers of the sea and the intensity of the mixing process. For example, we would expect very little downward mixing of bubbles produced by snow falling into a fairly calm sea. On the other hand, a great deal of downward mixing of bubbles from snow is to be expected in strong winds or when the surface waters are convectively unstable.

It is clear that many factors must be considered in order to make broad generalizations on the rate of nuclei production from naturally-produced breaking bubbles. Not only must we consider the various bubble producing mechanisms discussed in this paper, but we also must take into account the stability change of the surface layers of the sea as it varies geographically and with the seasons.

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REFERENCES

- ALIVERTI, G., and G. LOVERA, 1939: I fenomeni meteorologici sull'Oceano e il campo elettrico terrestre. *Atti della Reale Accademia delle Scienze di Torino* **74**, pp. 573—590.
- ALLEN, H. S., 1900: The motion of a sphere in a viscous fluid. *Phil. Mag.*, **50**, pp. 323—338.
- BEST, A. C., 1950: The size distribution of raindrops. *Quart. J. Roy. Met. Soc.*, **76**, pp. 16—36.
- BLANCHARD, D. C., 1953: Raindrop size-distribution in Hawaiian rains. *J. Met.*, **10**, pp. 457—473.
- 1955: Electrified droplets from the bursting of bubbles at an air—sea water interface. *Nature*, **175**, pp. 334—336.
- 1954: Bursting of bubbles at an air—water interface. *Nature* **173**, p. 1048.
- BOWEN, E. G., 1950: The formation of rain by coalescence. *Australian J. of Sci. Res.*, **3**, pp. 193—213.
- BOYCE, S. G., 1951: Source of atmospheric salts. *Science*, **113**, pp. 620—621.
- BYERS, H. R., 1955: Distribution in the atmosphere of certain particles capable of serving as condensation nuclei. *Proc. Conf. Physics of Cloud and Precip. Particles*, Woods Hole Ocean. Inst., Woods Hole, Mass. To be publ.
- COSTE, J. H., and H. L. WRIGHT, 1935: The nature of the nucleus in hygroscopic droplets. *Phil. Mag.*, **20**, pp. 209—234.
- Tellus IX (1957), 2
- CROZIER, W. D. and B. K. SEELY, 1950: Some techniques for sampling and identifying particulate matter in the air. *Proceeding of First National Air Pollution Symposium*, p. 45, Stanford, Calif., Stanford Press.
- DEAN, R. B., 1944: The formation of bubbles. *J. App. Physics* **15**, pp. 446—451.
- FOURNIER D'ALBE, E. M., 1951: Sur les embruns marins. *Bull. Inst. Oceanogr., Monaco*, **48**, No. 995, 7 pp.
- FOX, F. E. and K. F. HERZFELD, 1955: Gas bubbles with organic skins as cavitation nuclei. *J. Acoust. Soc. of Amer.* **26**, pp. 984—989.
- GOLDSTEIN, S., 1938: *Modern developments in fluid dynamics*. Vol. 1, p. 14. Oxford at the Clarendon Press.
- KIENTZLER, C. F., A. B. ARONS, D. C. BLANCHARD, and A. H. WOODCOCK, 1954: Photographic investigation of the projection of droplets by bubbles bursting at a water surface. *Tellus*, **6**, pp. 1—7.
- KINZER, G. D., and R. GUNN, 1951: The evaporation, temperature and thermal relaxation-time of freely falling waterdrops. *J. Met.*, **8**, pp. 71—83.
- KNELMAN, F., N. DOMBROWSKI, and D. M. NEWITT, 1954: Mechanism of the bursting of bubbles. *Nature* **173**, p. 261.
- KÖHLER, H., 1941: An experimental investigation on sea water nuclei. *Nova Acta reg. Soc. Sci. Upsaliensis*, ser. 4, **12**, No. 6, 55 pp.

- LUDLAM, F. H., 1951: The production of showers by the coalescence of cloud droplets. *Quart. J. Roy. Met. Soc.*, **77**, pp. 402—417.
- MASON, B. J., 1954: Bursting of bubbles at the surface of sea water. *Nature*, **174**, pp. 470—471.
- MIYAKE, Y., 1951: The possibility and the allowable limit of formation of air bubbles in the sea. *Papers in Meteorology and Geophysics*, **2**, pp. 95—101.
- MOORE, D. J., 1952: Measurements of condensation nuclei over the North Atlantic. *Quart. J. Roy. Met. Soc.*, **78**, pp. 596—602.
- MOORE, D. J., and B. J. MASON, 1954: The concentration, size distribution and production rate of large salt nuclei over the oceans. *Quart. J. Roy. Met. Soc.*, **80**, pp. 583—590.
- OWENS, J. S., 1926: Condensation of water from the air upon hygroscopic crystals. *Proc. Roy. Soc., London*, **A, 110**, pp. 738—752.
- RAKESTRAW, N. W., and W. M. EMMEL, 1938: The solubility of nitrogen and argon in sea water. *J. Phys. Chem.*, **42**, pp. 1211—1215.
- REDFIELD, A. C., 1948: The exchange of oxygen across the sea surface. *J. Mar. Res.*, **7**, pp. 347—361.
- STUHLMAN, O., 1932: The mechanics of effervescence. *Physics*, **2**, pp. 457—466.
- TWOMEY, S., 1955: The distribution of sea-salt nuclei in air over land. *J. Met.*, **12**, pp. 81—86.
- WOODCOCK, A. H., 1948: Note concerning human respiratory irritation associated with high concentrations of plankton and mass mortality of marine organisms. *J. Mar. Res.*, **7**, pp. 56—62.
- WOODCOCK, A. H., and MARY M. GIFFORD, 1949: Sampling atmospheric sea-salt nuclei over the ocean. *J. Mar. Res.*, **8**, pp. 177—197.
- WOODCOCK, A. H., 1952: Atmospheric salt particles and raindrops. *J. Met.*, **9**, pp. 200—212.
- 1953: Salt nuclei in marine air as a function of altitude and wind force. *J. Met.*, **10**, pp. 362—371.
- WOODCOCK, A. H. and D. C. BLANCHARD, 1955: Tests of the salt-nuclei hypothesis of rain formation. *Tellus*, **8**, pp. 437—448.
- WORTHINGTON, A. M., and R. S. COLE, 1897: Impact with a liquid surface, studied by the aid of instantaneous photography. *Phil. Trans.*, **189 A**, pp. 137—148.
- WRIGHT, H. L., 1940: Atmospheric opacity at Valentia. *Quart. J. Roy. Met. Soc.*, **66**, pp. 66—77.
- WYMAN, JR., J., P. F. SCHOLANDER, G. A. EDWARDS, and L. IRVING, 1952: On the stability of gas bubbles in sea water. *J. Mar. Res.*, **11**, pp. 47—62.