sealed lead-acid batteries, which were capable of 2–3 week's operation depending on the mode of operation.

However, there are additional constraints for the *in situ* monitoring of sea water, i.e. systems must be made more rugged and capable of being submersed to facilitate measurements at a particular point in the water column. In the late 1980s, the use of a submersible FIA system was reported to monitor silicate, sulfide, and nitrate concentrations in sea water that gave good correlation with laboratory techniques. The effects of extremes of temperature, pressure, and salinity on flow analysis and chemistries used in these systems have all been studied. During 1996 a submersible nitrate sensor based on FIA techniques was successfully tested in estuarine and coastal waters, over complete tidal cycles, and to depths of 40 m. Commercially available submersible FIA instruments permit laboratory FIA methods to be used *in situ*.

Other commercially available wet chemistry field instruments, which utilize the same basic proven chemistries as the CFA and FIA instruments, are available. For example, some instruments utilize rugged microprocessor-controlled syringe systems and a unique design of manifold for the collection of the sample, reagent addition, and colorimetric determination of the resultant colored species.

Field instruments enable a wide range of chemical determinations to be performed *in situ* and as the technology matures greater use of these will be made in the years to come.

See also

Harmful Phytoplankton Blooms. Nitrogen Isotopes in the Ocean.

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WHALES

See **BALEEN WHALES; SPERM WHALES AND BEAKED WHALES**

WHITECAPS AND FOAM

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Introduction

Oceanic whitecaps and sea foam are, respectively, the transient and semipermanent bubble aggregates that are found on the surface of the ocean when certain meteorological conditions prevail. These features are of sufficient size to be detectable by eye, and an individual whitecap or foam patch can readily be recorded using standard low-resolution photographic or video systems. When they are present in sufficient number on the sea surface they alter the general visual albedo, and microwave emissivity, of that surface, thus rendering their collective presence detectable by various satellite-borne instruments.

Almost all the bubbles that make up these structures were initially produced at the sea surface by breaking waves, and to understand the presence and distribution of whitecaps and foam patches it is necessary to first consider the genesis, and fate within the oceanic surface layer, of these bubbles. It will become apparent from the discussions contained in the following sections that the bubbles whose presence in great numbers is signaled by the appearance of whitecaps play a major role in the air–sea exchange of gases that are important in establishing our climate, and in the production of the sea-salt aerosol that contributes to the pool of cloud condensation nuclei in the atmosphere over the ocean. These same bubbles facilitate the sea-to-air transfer of heat and moisture, and scavenge from the bulk sea water and carry to the ocean surface various surfactant organic, and adhering inorganic, materials.

Spilling Wave Crests: Stage A Whitecaps

When a wave breaks in the more typical spilling mode, and even more so when a wave collapses in a plunging fashion, great numbers of bubbles are formed and constrained initially to a relatively small volume of water, typically extending beneath the surface a distance no greater than the height of the source wave and having lateral dimensions of only a few meters at most. Although these intense bubble clouds, often called alpha plumes, are individually often of convoluted shape, the concentration of bubbles in these alpha-plumes tends to decrease exponentially with depth, with an e-folding, or scale, depth that increases modestly from less than a meter to several meters, as the sea state increases in response to increasing wind speeds. The concentration of bubbles within an alpha-plume that has just been formed can be so great that the aggregate fraction of the water volume occupied by these bubbles, the void fraction in the terminology of the underwater acoustician, reaches 20% or even 30%. The size spectrum of the bubbles within such a plume is very broad, the bubbles present having radii ranging from several micrometers up to almost 10 mm (see **Figure 1**). Although there is no clear consensus on where the peak in the alpha-plume bubble number density spectrum lies, many authors would contend that it falls at a bubble radius of 50 µm or less. It has been suggested that the amplitude of this spectrum then falls off with increasing bubble radius in such a fashion that for over perhaps a decade of radius the total volume of the bubbles falling within a unit increment of size

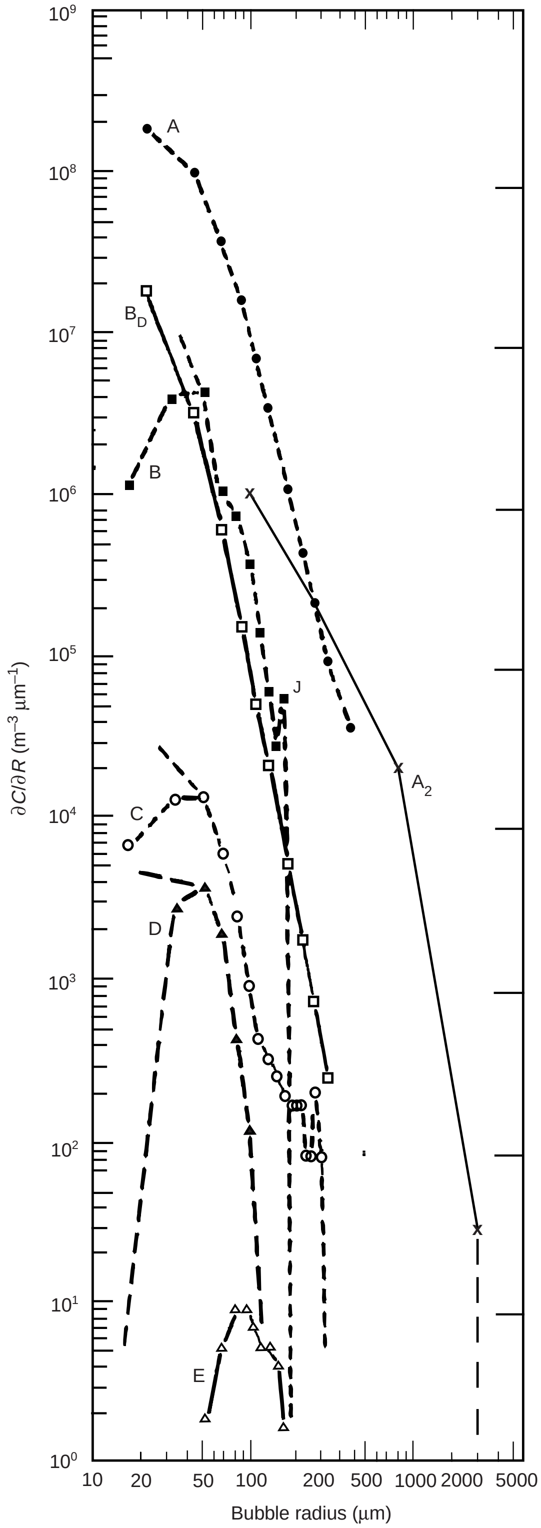

Figure 1 The number of bubbles per cubic meter of sea water, per micrometer bubble radius increment, as a function of bubble radius, as to be expected in (A) the alpha plume beneath a stage A whitecap, (B) the beta plume beneath a stage B whitecap, (C and D) in various portions of a gamma plume, and (E) the background, near-surface bubble layer. See Monahan and Van Patten (1989) for further details.

remains almost constant. It is thought that at even larger bubble radii this spectrum 'rolls off' even more rapidly, with less and less air being contained in those bubbles that fall in the larger and larger size 'bins', but there are as yet insufficient unambiguous observations to verify this contention.

The manifestation on the sea surface of an alpha-plume, the stage A whitecap, is the most readily detected category of whitecap or foam patch. Although bubbles on the surface in a stage A whitecap typically burst within a second of having arrived at the air–water interface, there is often a certain momentary 'packing' of bubbles, both vertically and laterally, on this surface, which results in this category of whitecap being truly white, with an albedo of about 0.5 which does not vary significantly over the entire visible portion of the electromagnetic spectrum. Since the visible albedo of the sea surface away from whitecaps is often 0.03–0.08, the average albedo of this surface will be noticeably increased when even a small fraction of the ocean surface is covered by spilling wave crests. Many of the satellite-borne passive microwave radiometers detect the electromagnetic emissions from the sea surface at wavelengths on the order of 10 mm. At such wavelengths a stage A whitecap is an almost perfect emitter, what in optics would be deemed a 'black body', while the rest of the sea surface at these wavelengths has a microwave emissivity on only 30% or 40%. Thus it only requires a small fraction of the ocean surface to be covered by stage A whitecaps for there to be a measurable increase in the apparent microwave brightness temperature of this surface.

An observer located within an alpha plume would observe, once the downward movement associated with the spilling event had been dissipated, a high level of small scale turbulence, and, superimposed on top of the rapid random motions caused by this turbulence, a clear upward movement of the larger bubbles. The reduction of gravitational potential energy associated with the upward motion of these big bubbles frees energy that then contributes to the mixing and turbulence within the plume, and this enhanced mixing, which extends to the very surface of the stage A whitecap, greatly increases the effective air–sea gas transfer coefficient, or 'piston velocity', associated with this whitecap, as compared to the gas transfer coefficient associated with the wind ruffled but whitecap-less adjacent portions of the ocean surface. These upward moving bubbles drag water along with them, and the resulting upward, buoyant, flow often induces two-dimensional, horizontal divergence at the surface; factors which also enhance the air–sea exchange of gases. Further, for gases that diffuse slowly through water, the fact that each bubble is a gas vacuole traveling from the body of the water to the air–sea interface can be an important consideration. These large bubbles, with their large cross-sectional areas and rapid rise velocities, are also important in the scavenging and transport to the sea surface of the various surface-active materials that are often present in high concentrations in the oceanic mixed layer.

Decaying Foam Patches: Stage B Whitecaps

Within seconds of a wave ceasing to break, the associated stage A whitecap has been transformed in a decaying foam patch, a stage B whitecap. As a consequence of the intense turbulence present in the alpha plume that had been present beneath the stage A whitecap, the initial lateral extent of the stage B whitecap (and of the top of the beta plume which is located beneath it) is typically considerably greater than that of a stage A whitecap, some would contend upwards of ten times greater. The greatest discrepancies in size between parent stage A whitecaps and the initial daughter stage B whitecaps occur in those cases where the wave crest spills persistently, or episodically, as it moves along over the sea surface leaving in its wake a long stage B whitecap, or a series of decaying foam patches with short distances between them. As was the case with the stage A whitecap, most of the bubbles that come to the surface in a stage B whitecap burst within a second of their arrival at the interface, and thus a stage B whitecap owes its existence, as did its precursor stage A whitecap, to the continuing arrival at the surface of new bubbles from the dependent bubble plume or cloud. The concentration of bubbles within the associated beta-plume is much smaller than it was in the alpha-plume that preceded it, for three reasons: (1) the plume has been diffused over a greater volume of sea water; (2) many of the large bubbles that were present in the precursor alpha plume have by now reached the sea surface and burst; and (3) most of the very smallest bubbles, those with radii of only a few micrometers, have gone into solution (see **Figure 1**). (The very smallest bubbles can dissolve even when the oceanic surface layer is saturated with respect to nitrogen and oxygen, because at a depth of even a meter they are subjected to significant additional hydrostatic pressure, and because with their small radii they experience a marked increase in internal pressure due to the influence of surface tension.) The stage B whitecap decays by being torn into tattered foam patches by the turbulence of the surface layer, and

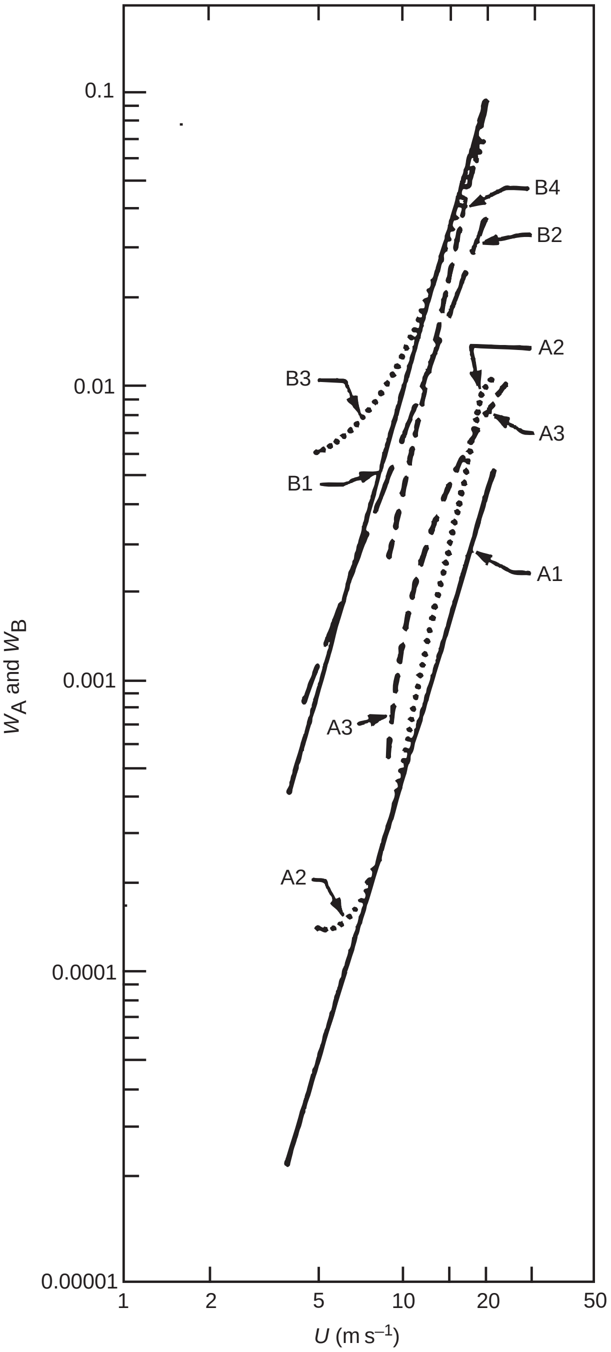

Figure 2 The fraction of the ocean surface covered by stage A (curves A1–A3) and stage B (curves B1–B4) whitecaps as a function of 10 m-elevation wind speed. See Monahan and Van Patten (1989) for further details.

by having these ever and ever smaller patches fading as the supply of bubbles from the associated portions of the beta-plume becomes exhausted. The cumulative effect of these factors is that the visually resolvable macroscopic area of a stage B whitecap decreases exponentially with time, with a characteristic e-folding time of 3–4 s. A stage B whitecap appears to the eye as a group of irregularly shaped pale blue, or green, areas clustered on the ocean surface. The visible albedo of a stage B whitecap is initially intermediate between that of a stage A whitecap and that of the ruffled sea surface, but within a few seconds its albedo approaches the low value associated with the wave-roughened sea surface. As a consequence of the relatively larger initial area of stage B whitecaps as compared to stage A whitecaps, and on account of the fact that the characteristic lifetime of a stage B whitecap is considerably greater than that of a stage A one, at any instant the fraction of the ocean surface covered by stage B whitecaps is typically at least an order of magnitude greater than the fraction covered by stage A whitecaps (see **Figure 2**).

The beta plume beneath each stage B whitecap is relatively rich in bubbles of intermediate size, with some investigators suggesting that the bubble number density spectrum for this plume has a peak at a bubble radius of about 50 μm (see **Figure 1**). When bubbles of this size burst at the surface in a whitecap they inject into the atmosphere droplets of several micrometers radius, called jet droplets, which contribute to the sea-to-air transfer of moisture and latent, and often sensible, heat. The rupture of the upper, exposed, hemisphere of these bubbles when they burst on the sea surface also produces smaller droplets, called film droplets, which constitute a significant fraction of the cloud condensation nuclei in the maritime troposphere. The largest bubbles produced by a breaking wave, most of which reach the surface in the stage A whitecap, are even more effective at generating these film droplets when they burst.

Because bubbles are relatively scarce within stage B whitecaps, these sea surface manifestations of beta plumes have visual albedos and microwave emissivities not greatly different from those of the adjacent, wind ruffled, surface, and are thus much more difficult to detect by remote sensing than are stage A whitecaps.

Wind-Dependence of Oceanic Whitecap Coverage

The frequency of wave breaking, and the average intensity of the individual breaking wave, both increase with increasing wind speed. The combined effect of these two factors is that the fraction of the sea surface covered at any moment by spilling wave crests, i.e. by stage A whitecaps, increases rapidly with strengthening wind speed. This can be seen from **Figure 2**, where the curves labeled A1, A2, etc. are summary descriptions of the dependence of stage A whitecap coverage on 10 m-elevation wind speed.

Curve A1, describing the most comprehensive set of stage A whitecap observations (actually a combination of four such sets), is described by eqn [1].

$$W_A = 3.16 \times 10^{-7} U^{3.2} \qquad [1]$$

where W_A is the fraction of the sea surface covered at any instant by spilling wave crests and U is the 10 m-elevation wind speed expressed in meters per second. Understandably, the fraction of the sea surface covered instantaneously by decaying foam patches, i.e. by stage B whitecaps, shows a similar strong dependence on wind speed. This can be seen from the steep slopes of the curves B1, B2, etc., on the log–log plot in **Figure 2**. Eqn [2] defines curve B1, which is a summary description of extensive observations, from both the Atlantic and Pacific Oceans, of stage B whitecap coverage made by several investigators.

$$W_B = 3.84 \times 10^{-6} U^{3.41} \qquad [2]$$

Here W_B represents the instantaneous fraction of the sea surface covered by decaying foam patches, and U is again the 10 m-elevation wind speed. The fact that for both categories of whitecap the fraction of the ocean surface occupied by these features varies with the wind speed raised to something slightly more than the third power, is consistent with the contention that whitecap coverage varies with the friction velocity (*see* **Heat and Momentum Fluxes at the Sea Surface** and **Wave Generation by Wind**) raised to the third power. It should be stressed that although whitecap coverage, both stage A and stage B, is most sensitive to wind speed, it also varies with the thermal stability of the lower marine atmospheric boundary layer, and with wind duration and fetch. Any factor that influences sea state will also affect whitecap coverage. For near-neutral atmospheric stability, oceanic whitecap coverage begins to be noticed when the 10 m-elevation wind speed reaches 3 or 4 m s^{-1}. (There is not a distinct threshold for the onset of whitecapping at a wind speed of 7 m s^{-1} as was contended in some of the early literature on this subject.)

Since whitecap coverage, particularly stage A coverage, is readily detectable from space, and given that whitecap coverage is very sensitive to wind speed, it is apparent that satellite observations of whitecap coverage can be routinely used to infer over-water wind speeds.

Stabilized Sea Foam

Many of the first bubbles to rise to the sea surface after a breaking wave has entrained air, not only scavenge organic material from the upper meter or so of the sea but also, as they reach the air–sea interface, accrue some of the organic material that is often found on that surface (not necessarily in the form of coherent slicks). As a consequence of accreting on their surface considerable dissolved, and other, organic material, such ‘early rising’ bubbles may become stabilized, and hence they may not break immediately, but rather persist on the ocean surface for protracted periods. If such a bubble has managed to coat its entire upper hemisphere with such surfactant material, the markedly reduced surface tension of its film ‘cap’ that results from this circumstance may enable this bubble to persist indefinitely at the air–water interface. Such bubbles are certainly present at the sea surface long enough to be winnowed into windrows, those distinctive, essentially downwind, foam and seaweed streaks that appears on the sea surface when a strong wind has been blowing consistently. Often organized convective motions are present in the upper layer of the ocean. Such Langmuir cells have associated with them lines of horizontal, two-dimensional, surface convergence and divergence, oriented for the most part downwind. When such Langmuir cells are present, stabilized bubbles will be drawn into the convergence zones, and since they are buoyant, they will remain to form fairly uniformly spaced foam lines on the sea surface marking the locations of such zones (**Figure 3**). It should be noted that the ‘late arriving’ bubbles, representing the vast majority of the bubbles rising within any alpha plume, do not persist on the air–sea interface for more than a second or so, even when the surface waters are quite organically rich.

The ability of bubbles to effectively scavenge surfactant organic matter from the bulk sea water and transport this material to the sea surface provides what has been described as an ‘organic memory’ to the upper mixed layer of the ocean. The more bubbles that have been injected into the upper layer of the ocean by breaking waves in the recent past, the more organic material has been brought to the sea surface and remains there. Although wave action is ‘a two way street’, in that the same waves which upon breaking produce the bubbles that carry organic material to the air–water interface also stir and mix the surface layer, none-the-less the net effect of high sea states is to alter the partition of organic matter between the bulk fluid and the interface in favor of the interface. This can be inferred from the observation that as a high wind event persists, more and more foam lines, containing more and more stabilized bubbles, appear on the ocean surface. In stormy conditions, such foam, or spume,

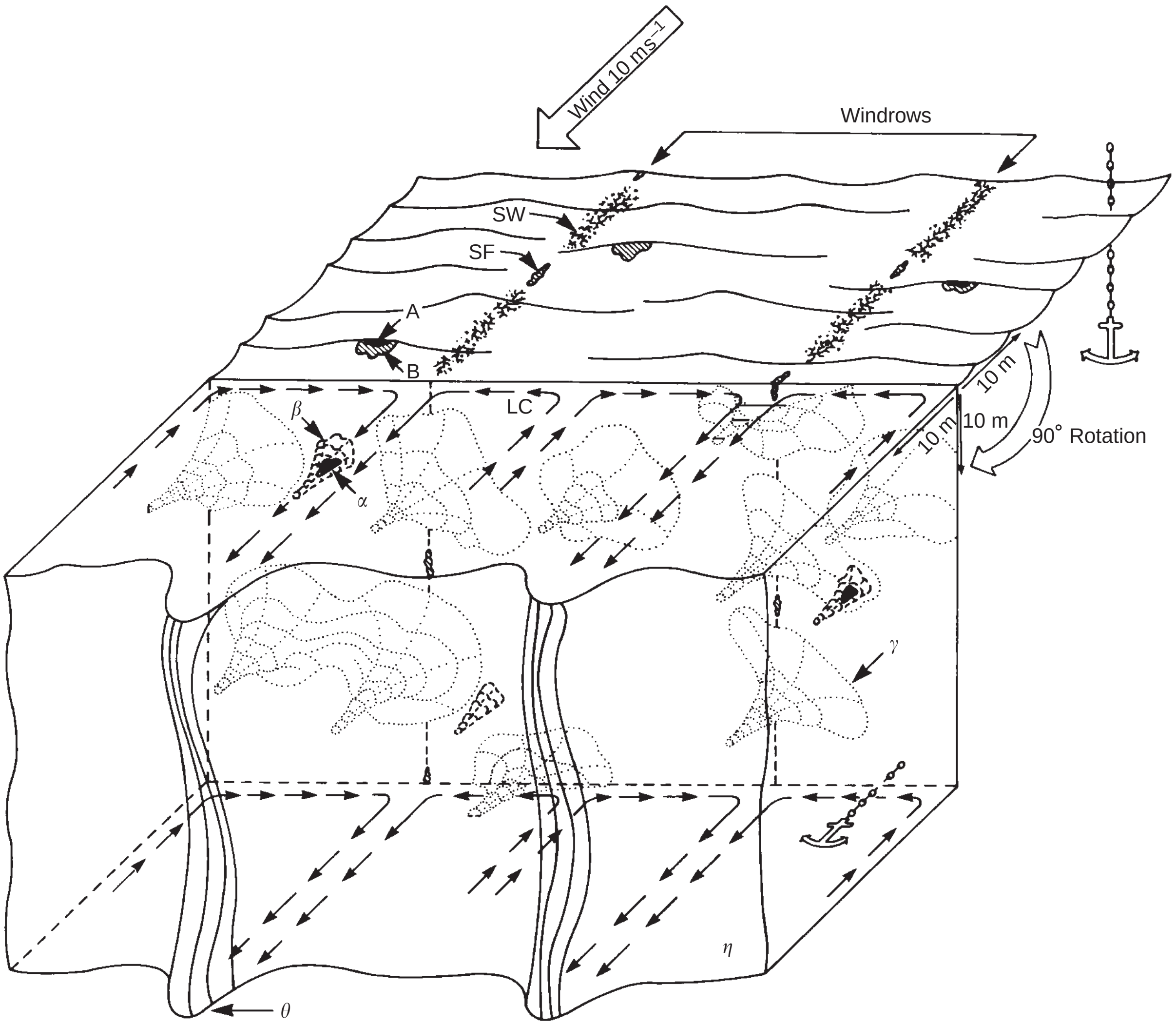

Figure 3 A view looking obliquely down at the sea surface showing stage A and stage B whitecaps, foam and spume lines, and simultaneously a view looking obliquely up toward the same sea surface showing the alpha and beta plumes associated with these whitecaps, the gamma plumes, and the near-surface bubble layer. The influence on these features of a classical Langmuir circulation, which is indicated by arrows, is depicted. A, Stage A whitecap; B, Stage B whitecap; SF, stabilized foam; SW, seaweed; LC, Langmuir circulation; α, plume of stage A whitecap; β, plume of stage B whitecap; γ, old (microbubble) plume; η, background bubble layer; θ, bubble curtain. From Monahan and Lu, 1990.

can be blown off the crests of waves, along with quite large drops of water, called 'spume drops', adding further to the indeterminacy that often prevails in such circumstances regarding the actual location of the air–water interface.

Not only do the above-mentioned Langmuir cells advent buoyant stabilized bubbles into the surface convergence zones, these same cells are believed to move the residual, long-lasting, gamma bubble plumes (those left after the dissipation of the beta plumes) into these same zones. (Alpha bubble plumes have readily detectable stage A whitecaps as their sea surface signatures, and the location of the beta plumes into which these alpha plumes decay can be determined from the position on the sea surface of their associated stage B whitecaps, but the large, diffuse, bubble-poor gamma plumes into which the beta plumes decay, have no apparent surface manifestation.) The influence of Langmuir cells on stabilized sea surface foam, on gamma plumes, and on the near surface layer that contains an ever sparser concentration of small bubbles, is depicted in **Figure 3**.

Global Implications

As can be seen from the curves in **Figure 2**, even at quite high wind speeds such as 15 m s^{-1} (33.5 miles

h^{-1}), only a small fraction of the sea surface is covered by stage B whitecaps (0.04 or 4%), and an even smaller fraction of that surface is covered by stage A whitecaps (0.002 or 0.2%). Yet the total area of all the world's oceans is very great ($3.61 \times 10^{14}\,m^2$), and as a consequence the total area of the global ocean covered by whitecaps at any instant is considerable. If a wind speed of $7\,m\,s^{-1}$ is taken as a representative value, then at any instant some $7.0 \times 10^{10}\,m^2$, i.e. some 70 000 km^2, of stage A whitecap area is present on the surface of the global ocean. Following from this, and including such additional information as the terminal rise velocity of bubbles, it can be deduced that some $7.2 \times 10^{11}\,m^2$, i.e. some 720 000 km^2 of individual bubble surface area are destroyed each second in all the stage A whitecaps present on the surface of all the oceans, and an equal area of bubble surface is being generated in the same interval. The vast amount of bubble surface area destroyed each second on the surface of all the world's oceans, and the great volume of water (some $2.5 \times 10^{11}\,m^3$) swept by all the bubbles that burst on the sea surface each second, have profound implications for the global rate of air–sea exchange of moisture, heat and gases. An additional preliminary calculation following along these lines, suggests that all the bubbles breaking on the sea surface each year collect some 2 Gt of carbon during their rise to the ocean surface.

See also

Heat and Momentum Fluxes at the Sea Surface. Wave Generation by Wind.

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WIND AND BUOYANCY-FORCED UPPER OCEAN

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Introduction

Forcing from winds, heating and cooling, and rainfall and evaporation, have a profound influence on the distribution of mass and momentum in the ocean. Although the effects from this wind and buoyancy forcing are ultimately felt throughout the entire ocean, the most immediate impact is in the surface mixed layer, the site of the active air–sea exchanges. The mixed layer is warmed by sunshine and cooled by radiation emitted from the surface and by latent heat loss due to evaporation (**Figure 1**). The mixed layer also tends to be cooled by sensible heat loss since the surface air temperature is generally cooler than the ocean surface. Evaporation and precipitation change the mixed layer salinity. These salinity and temperature changes define the ocean's surface buoyancy. As the surface loses buoyancy, the surface can become denser than the subsurface waters, causing convective overturning and