

RESEARCH ARTICLE

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Key Points:

- A surfactant effect in whitecap foam evolution is identifiable and largely confined to the decay stage
- A whitecap foam area stabilization factor (Θ) is defined to quantify this surfactant imprint
- Field and laboratory values of Θ show overlapping values

Supporting Information:

- Supporting Information S1
- Figure S1
- Figure S2
- Figure S3
- Figure S4
- Figure S5
- Figure S6
- Figure S7

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On the imprint of surfactant-driven stabilization of laboratory breaking wave foam with comparison to oceanic whitecaps

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Abstract Surfactants are ubiquitous in the global oceans: they help form the materially-distinct sea surface microlayer (SML) across which global ocean-atmosphere exchanges take place, and they reside on the surfaces of bubbles and whitecap foam cells prolonging their lifetime thus altering ocean albedo. Despite their importance, the occurrence, spatial distribution, and composition of surfactants within the upper ocean and the SML remains under-characterized during conditions of vigorous wave breaking when in-situ sampling methods are difficult to implement. Additionally, no quantitative framework exists to evaluate the importance of surfactant activity on ocean whitecap foam coverage estimates. Here we use individual laboratory breaking waves generated in filtered seawater and seawater with added soluble surfactant to identify the imprint of surfactant activity in whitecap foam evolution. The data show a distinct surfactant imprint in the decay phase of foam evolution. The area-time-integral of foam evolution is used to develop a time-varying stabilization function, $\phi(t)$ and a stabilization factor, Θ , which can be used to identify and quantify the extent of this surfactant imprint for individual breaking waves. The approach is then applied to wind-driven oceanic whitecaps, and the laboratory and ocean Θ distributions overlap. It is proposed that whitecap foam evolution may be used to determine the occurrence and extent of oceanic surfactant activity to complement traditional in-situ techniques and extend measurement capabilities to more severe sea states occurring at wind speeds in excess of about 10 m/s. The analysis procedure also provides a framework to assess surfactant-driven variability within and between whitecap coverage data sets.

Plain Language Summary The foam patches made by breaking waves, also known as “whitecaps”, are an important source of marine sea spray, which impacts weather and climate through the formation of cloud drops and ice. Sea spray chemistry depends on the chemistry of the whitecap that makes it. This chemistry is poorly understood, especially during storms when whitecaps are most prevalent but chemistry measurements are also the most difficult. In this article, we show that foam chemistry affects the persistence of laboratory whitecaps: the more surfactant a whitecap contains, the longer it persists. This effect has enabled us to develop a remote sensing tool to detect the presence of chemistry in whitecaps by analyzing a time-series of photographs of the foam. We have applied the technique to an existing set of whitecap images, and get reasonable values for implied surfactant concentrations in the ocean but validation of the technique in the field will have to await simultaneous measurement of whitecaps and sea surface chemistry. If validated, the new remote sensing tool will provide the first large-scale observations of ocean surface chemistry and its variation in space and time on wind-driven seas.

1. Introduction

Naturally occurring oceanic surfactants are organic molecules with both hydrophobic and hydrophilic end members that are thought to be primarily of biological origin [Garrett, 1967a]. Because of their amphiphilic nature, they preferentially reside at air-water boundaries such as the air-sea interface, and the surfaces of bubbles. Surfactants near the sea surface play important roles in the Earth's climate system by modulating the physics and chemistry of the upper ocean and sea surface microlayer (SML), increasing the drag force acting on a bubble as it rises through the water column, and prolonging the lifetime of foam cells at the water surface [e.g., Garrett, 1967b, 1967c; Clift et al., 1978; Jähne et al., 1984; Ternes and Berg, 1984;

Henry, 2010]. Here, the term “foam cell” refers to a bubble which resides at the water surface and may (or may not) be packed adjacent to other floating bubbles.

The accumulation and enrichment of surfactants within the upper 1 mm or so of the ocean gives rise to the physically, chemically, and biologically distinct SML. Consequently, the SML represents an important interface at the ocean-surface which helps regulate global biogeochemical cycles and climate-related processes by altering the production and composition of marine sea spray aerosol (SSA) particles, modifying the air-sea transfer of gas, impacting the evolution of the wave spectrum, and by providing a habitat to a distinct marine ecosystem known as the neuston [e.g., Ermakov *et al.*, 2006; Upstill-Goddard, 2006; Russell *et al.*, 2010; Salter *et al.*, 2011; Cunliffe *et al.*, 2013].

Identifying the occurrence, distribution, and composition of the SML, its relation to the physical and chemical properties of the underlying water column, and establishing best practices for doing so, remains an active area of research [Cunliffe and Wurl, 2014]. The SML is typically sampled using in-situ methods encompassing a variety of techniques, each with their own merit, focus, and application [e.g., Garrett, 1965; Harvey, 1966; Harvey and Burzell, 1972; Shinki *et al.*, 2012]. Remote sensing techniques, both direct and indirect, have also been explored to monitor aggregations of surface active materials, which manifest as sea surface slicks [e.g., Cox and Munk, 1954; Cini *et al.*, 1983; Romano, 1996; Gade *et al.*, 2006, and references therein]. However, as sea states become more severe and wave breaking becomes more frequent, sea slicks tend to disperse, and many manual SML sampling techniques become increasingly difficult to implement in a reliable, repeatable and useful manner [Cunliffe *et al.*, 2013]. A practical upper wind speed limit on many in-situ sampling methods is about 10 m/s [Cunliffe and Wurl, 2014].

Bubbles traveling through a liquid will scavenge surface active material which naturally adsorbs onto the air-water interface at the bubble surface [Stefan and Szeri, 1999]. The rate of adsorption is dependent on the concentration of surfactant present, as well as the type of surface active material and the bubble size [e.g., Sam *et al.*, 1996]. Bubble scavenging is a key physical process influencing the cycling of surfactants in the upper ocean [Cunliffe *et al.*, 2013], and rising bubble plumes generated by breaking waves are thought to be an important mechanism in the formation of the SML [Wurl *et al.*, 2011]. Furthermore, field evidence exists of the vertical transport of surface active material by rising bubbles generated by the ocean-going vessels, highlighting the important role of bubble scavenging in oceanic surfactant transport [Milgram *et al.*, 1993].

At the water surface, the lifetime of an individual foam cell is related to the initial thickness of its thin film cap, the rate at which fluid drains from this film cap, and the critical thickness of the film cap at the point of rupture. In the absence of surfactants, formation to rupture occurs on timescales on the order of milliseconds [Henry, 2010]. However, in the presence of surfactants, gradients in surfactant concentration within the film cap give rise to gradients in surface tension. Consequently, Marangoni forces arise that act to oppose the gravity-driven film drainage, and may also affect the critical thickness at which rupture occurs. The net effect is an increase in lifetime of a foam cell over and above that expected in water free from surfactant. Previous experimental studies have shown that between values of about 20–36 PSU, salinity has no appreciable effect on foam stability [Peltzer and Griffin, 1988]. Foam stability is also likely to be somewhat dependent on water temperature as thin film fluid drainage rates are inversely proportional to fluid viscosity [Manev and Nguyen, 2005].

The stabilization of ocean foam by natural surfactants has long been known [e.g., Langmuir, 1938; Stommel, 1951; Wilson, 1959; Monahan, 1971; Ross and Cardone, 1974; Monahan and Lu, 1990; Holthuijsen *et al.*, 2012]. Historical data sets of oceanic whitecap coverage (W) show orders of magnitude scatter when parameterized with wind speed [Anguelova and Webster, 2006]. While some of this variation is driven by variation in wind stress, wave development, wave energy dissipation, and image processing methodologies [Monahan, 1971; Callaghan *et al.*, 2008a, 2008b, 2016; Goddijn-Murphy *et al.*, 2011; Schwendeman and Thomson, 2015], given what is known about the effects of surfactants on small-scale fluid dynamics and thin film stability [e.g., Henry, 2010], it is likely that variations in water chemistry have also contributed to the observed variability. This potential surfactant effect was noted by Monahan [1971]. However, almost nothing is known about how large the effects of surfactants on whitecap coverage variability may be. Since whitecap coverage is used as a proxy for estimating bubble-mediated exchange processes such as sea spray aerosol flux and air-sea gas exchange [Monahan *et al.*, 1982; Woolf, 1997; Callaghan, 2013; Goddijn-Murphy *et al.*, 2016],

variations in W that are driven by water chemistry, as opposed to air entrainment, need to be understood and explicitly accounted for in order to improve parameterizations of bubble-mediated processes.

Here we present a study of the effects of surfactants on the evolution of foam generated by breaking waves in a wave channel at the Hydraulics Laboratory of the Scripps Institution of Oceanography (SIO). The experiments were conducted using filtered seawater with and without the addition of the soluble surfactant Triton X-100 (hereafter TX-100). The data show that the decay phase of foam area evolution is sensitive to the presence of surfactants over oceanographically relevant concentrations, whereas the initial foam area growth phase appears largely independent of the added surfactant. This characteristic behavior is exploited and quantified through the development and use of a stabilization function, which is based on the integral of the foam area over time. Furthermore, a parameter we are calling the stabilization factor is defined and used to quantify the level of foam stabilization. These foam stabilization metrics are applied to time series of foam area evolution for over 500 oceanic whitecaps and the results compared to the laboratory data. Identifying a distinctive behavior in foam area evolution provides a framework to assess variations in W driven by surfactants, and could be used as the basis of a remote sensing technique to identify the occurrence, spatial extent and temporal variability of surfactant activity in the upper ocean and SML.

2. Materials and Methods

Experiments were carried out using seawater in a 33 m long glass channel (0.5 m wide, 0.6 m water depth) equipped with a programmable flap-type wave paddle (see also *Callaghan et al.*, [2013, hereinafter CDS13] and *Callaghan et al.* [2016]).

2.1. Laboratory Breaking Wave Generation

Wave groups of specific spectral bandwidth, amplitude, and slope were generated using a technique that exploits the dispersion of surface gravity water waves [Longuet-Higgins, 1974]. All wave components were generated simultaneously, and their phases were chosen to “focus” the wave group energy at a specified position along the channel, x_f , at a specific time t_f . The spectral components and their amplitudes within each wave group were chosen to generate breaking waves ranging from gently spilling to strongly plunging. The wave groups are characterized in terms of a maximum linear slope, $S = \sum_{i=1}^N a_i k_i$, where a_i and k_i are the amplitude and wavenumber of the i th spectral component out of a total of N components. Values of S were varied between 0.332 and 0.465, and further details may be found in CDS13. The repeatability of wave packet generation was around 2% in water surface elevation time series, $\eta(t)$, and 3% in wave packet energy measured at the upstream wave gauge, E_u (see supporting information Figures S1 and S2).

2.2. Water Type

Filtered seawater pumped from 300 m offshore of La Jolla Shores, adjacent to SIO, was used, and experiments were carried out with two water types, simply termed “filtered” and “surfactant.” For the filtered experiments, the seawater remained unmodified after filling the channel, whereas for the surfactant experiments, sufficient soluble surfactant TX-100 was added to achieve a concentration of 0.2 mg L⁻¹. This is believed to represent conditions of medium ocean productivity [Wurl et al., 2011]. The seawater surface tension was measured with a Wilhelmy Plate tensiometer (Kruss, model K11) which reported values of 73(±0.5) mN m⁻¹ and 70(±0.5) mN m⁻¹, for the filtered and surfactant experiments, respectively. These values correspond to film pressures of approximately 1(±0.5) and 4(±0.5) mN m⁻¹, respectively. Water temperature and salinity remained relatively stable at 15.5(± 1) °C and 33.5(± 0.1) PSU, respectively, throughout both experiments.

For the purposes of the study, data generated in the filtered seawater experiment are considered to be representative of “clean” or “surfactant-minimized” conditions. In effect, the filtered seawater experiments act as a control where water chemistry is not expected to dominate the physical evolution of the breaking wave two-phase flow and subsequent foam evolution. In practice, the filtered seawater contained some unquantified level of naturally occurring surfactants, which likely had some foam stabilization effect. Indeed, when performing experiments on this scale, it is practically impossible to obtain water entirely free from surfactants. However, the measured surface tension of ~73 mN m⁻¹, coupled with the foam observations presented in Figure 1 (compare images in Figures 1a and 1c) and those presented later, suggests that

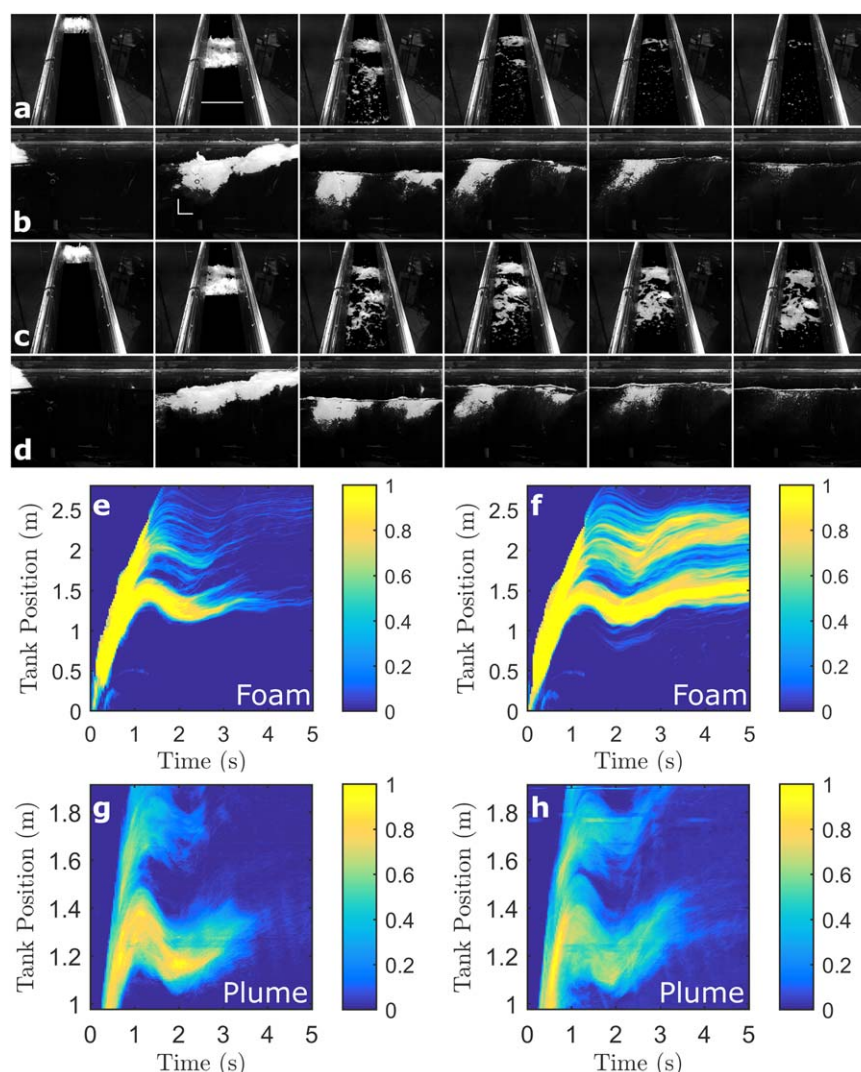


Figure 1. (a–h) Figures 1a and 1b, respectively, show images of the evolving foam patch and bubble plume for a single wave breaking in the filtered seawater experiments. Figures 1c and 1d show foam and bubble plume evolution in the surfactant experiment, respectively, generated by a breaking wave with the same spectral content as that shown in Figures 1a and 1b. The horizontal white line in Figure 1a is 44 cm in scale, the effective width of the channel. The vertical and horizontal white lines in Figure 1b are 10 cm in scale. All horizontally adjacent images are separated in time by 2/3 s. Figures 1e and 1f show the across channel fractional foam coverage as a function of time and distance along the wave channel for the breaking waves shown in Figures 1a and 1c, respectively. Figures 1g and 1h show the normalized maximum bubble plume depth as a function of time and distance along the wave channel for the breaking wave in Figures 1b and 1d, respectively.

overall surfactant-driven foam stabilization was sufficiently low in the filtered experiments to provide reference values for surfactant-minimized foam area evolution.

The addition of TX-100 resulted in differences of $\sim 4\%$, $\sim 3\%$ and $\sim 11\%$ in maximum surface elevation, $\eta_{\max}$, upstream wave packet energy, E_u , and energy dissipation ΔE_T , respectively, between the filtered and surfactant seawater experiments. This is discussed in detail in the supporting information and supporting information Figures S1 and S2. Further specific details on the seawater filtration method, the addition of TX-100 to the wave channel, the repeatability of the wave generation process, and the effect of the added TX-100 on water surface elevation time series and wave packet energy are detailed in the supporting information.

2.3. Foam and Bubble Plume Imaging

The evolving whitecap foam area and bubble plume cross-sectional area generated by wave breaking were recorded with a pair of time-synchronized downward- and sideward-looking 1 megapixel IDT Motion Pro X digital cameras operated at 30 Hz (hereafter termed foam and plume cameras, respectively). A schematic of

the experimental configuration can be seen in Figure 1 of CDS13. The mean camera pixel resolutions respectively were 2 mm and 0.7 mm for the foam and plume cameras, which were determined following procedures outlined in *Lippmann and Holman* [1989] and *Bouquet* [2006]. The broadband scattering of light by bubbles and foam allows the use of an intensity threshold to separate them from background water.

3. Results and Discussion

A series of 10 breaking waves with varying slope and spectral bandwidth were generated in both the filtered and surfactant experiments, resulting in 20 breaking waves for study. This gives a total of 10 pairs of breaking waves such that each member of a pair had the same initial spectral content, but was generated in seawater with markedly different water chemistry due to the addition of TX-100. The basic premise is that by generating breaking waves with the same initial spectral content, but in seawater with different surfactant loadings, any measured differences in foam and plume evolution, during and after breaking, between the filtered and surfactant seawater experiments may be primarily attributed to surfactant effects.

Figures 1a and 1b show the evolving whitecap foam area and coincident sub-surface bubble plume cross-sectional area for a breaking wave in the filtered seawater experiment. Figures 1c and 1d show the companion breaking wave foam and bubble plume evolution from the surfactant seawater experiment. These images were used to measure the evolving foam area and sub-surface bubble plume cross-sectional area, shown in Figures 1e–1h. For the filtered and surfactant experiments, respectively, Figures 1e and 1f show the across-channel fractional foam coverage along the wave channel as a function of time from initial breaking. The total foam area in each across-channel row of pixels was calculated and divided by the across-channel area in that row of pixels, so a value of 1 corresponds to complete across-channel foam cover. By adopting this approach, the foam area data in each 2-D image were compressed into a single vector of normalized foam areas for a specific time, which were then stacked in time to produce Figures 1e and 1f. The corresponding evolving bubble plume cross-sectional area is shown in Figures 1g and 1h. Here, the plume penetration depth measured within each column of image pixels has been normalized by the maximum plume depth, and a similar time stacking procedure carried out. Figure 1 shows the physical link between the whitecap foam observed from above the water surface and the corresponding bubble plume beneath the water surface that feeds it. Superposed on these features are the periodic water elevation and orbital velocity patterns characteristic of progressive water waves, which decay with time because of the finite duration of the wave groups employed here.

3.1. Brief Review of CDS13

An initial report of the results from these experiments was given in CDS13, and the salient points are summarized here. In the filtered seawater experiments, when surfactant effects are minimized, the surface whitecap persists for only as long as it is supplied by a sufficient, optically detectable, upward flux of sub-surface bubbles (Figures 1a, 1b, 1e, and 1g). CDS13 demonstrated a largely 1:1 relationship between the characteristic whitecap decay and bubble plume degassing times (see their Figure 8), and this regime of foam decay was termed “bubble-plume controlled.” In the surfactant experiments, the foam persisted for longer times (see Figures 1c and 1f), and was still present after the measured sub-surface plume had practically disappeared (Figure 1h). This regime of foam decay was termed “surfactant stabilized.” In this regime, a strong relationship between characteristic foam and plume decay times is still present, but foam decay times were approximately 3 times longer than the plume decay times.

3.2. General Description of Laboratory Foam Area Evolution

Figure 2a shows the evolution of foam area from a representative pair of breaking waves generated with the same initial spectral content, but in filtered (black line) and surfactant (red line) seawater. During the initial stages of breaking, air is entrained and the whitecap foam area, $A(t)$, increases quickly in time. Thereafter, a peak in foam area (A_o) is reached and the foam area decays. The peak foam area, A_o , marks the point when foam generation and decay processes are in equilibrium, and its time of occurrence is denoted t_{A_o} . This timescale is used to decompose the foam area evolution into a growth phase and a decay phase. Several previous studies have exploited the peak foam area to characterize the decay phase of foam evolution, both in the laboratory and the field [e.g., *Monahan et al.*, 1982; *Nolan*, 1988; *Sharkov*, 2007; *Anguelova and Huq*, 2012].

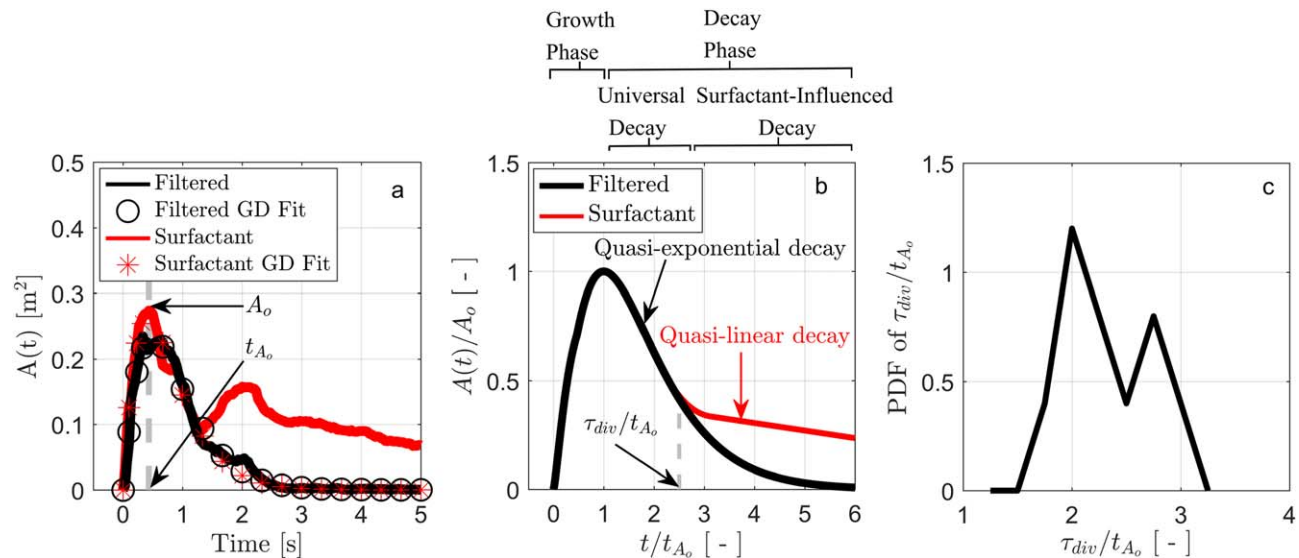


Figure 2. (a) The evolution of foam area from a pair of breaking waves generated with the same spectral input to the wave paddle, but in the filtered seawater (black line) and surfactant (red line) experiments. The black circles and red asterisks represent foam evolution as a result of fitting the growth-decay function (equation (1)) over a restricted range of times (see text for details). The vertical, dashed grey line marks the time of occurrence of the maximum foam area. (b) The idealized conceptual model of foam area evolution. Foam evolution is divided into a growth and decay phase, with the latter further subdivided into universal decay and surfactant-influenced decay. The black line represents foam area evolution expected when surfactants have a minimal effect, with the red line indicating a measureable surfactant-driven stabilization effect. A divergence timescale, τ_{div} , is defined to be the point at which these two foam area time-series become measurably different. Time is normalized by the time to maximum foam area, t_{A_o} . (c) The probability density function of the ratio of the divergence timescale to the maximum foam area time (τ_{div}/t_{A_o}) for the 10 pairs of breaking waves studied.

During the foam area growth phase, and for the first second or so into the decay phase, the evolution of the foam area for both seawater types is similar (Figure 2a). The growth rate and magnitude of the evolving foam area is similar for both breaking waves, although A_o is slightly larger in the surfactant seawater case. This small difference may be due to a surfactant effect, but may also be due to natural variability associated with slightly different initial conditions in the wave channel prior to each breaking wave. No systematic differences in growth phase foam area evolution were found for breaking wave pairs across the two water types (see supporting information Figure S3).

After 1–2 s into the decay phase, the two time series in Figure 2a diverge. In filtered seawater, the foam area decay is approximately exponential throughout, whereas in the surfactant case the decay transitions from approximately exponential to approximately linear after an initial, temporary rise. The temporary rise is indicative of the staggered injection of air observed in laboratory and oceanic breaking waves [Callaghan, 2013; Deane et al., 2016], coupled with the effects of surfactant-driven stabilization. A single whitecap may result from several impingements of the breaking wave crest on the underlying water surface, and each impingement may generate distinct foam strips and bubble plumes as the breaking crest propagates forward [see also Deane and Stokes, 2002, Figure 2; Thorpe, 2005, Figure 9.8b; Callaghan, 2013, Figure 1; Lim et al., 2015, Figure 5]. As air is lost through buoyancy, these degassing bubble plumes generate bubble-laden buoyancy-driven flows that replenish the surface whitecap, before diverging at the water surface and transporting existing surface foam radially outward. When foam is sufficiently stabilized, this can lead to the rise in the foam area seen in the surfactant experiments and to a lesser extent in the filtered experiments.

The divergence of the filtered and surfactant foam area time series is present across all the breaking waves studied in CDS13. This divergence is indicative of the effects of surfactants which stabilize the thin fluid films in the foam against rupture. A second timescale (τ_{div}) is therefore introduced to identify the time at which the filtered and surfactant foam area time series diverge for a pair of breaking waves with the same spectral content. The black circles and red asterisks in Figure 2a show the temporal evolution of foam area as given by a simple growth-decay function for the filtered and surfactant water types, respectively. The formulation and application of this function is designed to capture the effects of foam area evolution, free from the stabilizing effects of surfactants, and it is described in detail in §3.4 below. For present purposes,

foam area time series from the filtered seawater and TX-100 surfactant seawater experiments will be denoted $A_{\text{FILT}}(t)$ and $A_{\text{TX}}(t)$, respectively.

3.3. A Conceptual Model of Foam Area Evolution

An idealized conceptual model of foam evolution, motivated by the laboratory data, is presented which describes the effects of surfactant-driven stabilization on foam evolution. Figure 2b shows the conceptual model for filtered and surfactant seawater foam evolution where the foam area has been normalized by A_o , and time normalized by t_{A_o} . The black line represents idealized growth and decay of foam area in surfactant-free conditions, whereas the red line shows the expected foam area evolution when surfactant concentrations are sufficient to have a measurable effect on foam evolution. The conceptual model divides whitecap evolution into growth and decay phases separated at $t/t_{A_o} = 1$.

The decay phase is further subdivided into a “universal” decay phase followed by a “surfactant-influenced” decay phase, the two phases diverging at the normalized divergence time, $\tau_{\text{div}}/t_{A_o} = 2.5$ (Figure 2b). During the universal decay phase, surfactant-driven foam stabilization does not produce a measureable effect on the decay of foam area at the TX-100 concentration levels studied, and both filtered and surfactant seawater foam decay quasi-exponentially. This stage of decay is primarily controlled by the degassing of the sub-surface bubble plume [Callaghan *et al.*, 2013]. After the scaled divergence time ($\tau_{\text{div}}/t_{A_o}$) in Figure 2b, the filtered seawater foam area continues to decay quasi-exponentially, indicative of buoyancy-driven bubble plume degassing. However, in the surfactant-influenced example, the quasi-exponential decay transitions to a quasi-linear decay. At this stage, both bubble plume degassing and surfactant-driven stabilization play a role in the observed foam decay, but the latter process is expected to dominate.

In summary, air entrainment and bubble plume formation are expected to dominate during the growth phases of foam area evolution, and the universal phase of foam decay is expected to be dominated by bubble plume degassing. Thereafter, at times $t \geq (2-3)t_{A_o}$, both plume degassing and surfactant-driven stabilization will control the foam decay rate, and the observed foam area evolution will result from a combination of these physical and chemical regimes.

3.4. The Foam Area Growth-Decay Function

It is desirable to describe foam area growth and decay with a mathematical model that captures the physics of air entrainment, bubble plume formation, and foam evolution in the presence and absence of surfactants. This is not currently available to us, and to proceed, a pragmatic approach is adopted to describe foam area evolution when bubble plume evolution dominates foam growth and decay in the absence of surfactants (black curve, Figure 2b).

As for previous studies on evolving air fraction and two-phase flow in breaking waves [e.g., Lamarre and Melville, 1991; Blenkinsopp and Chaplin, 2007; Lim *et al.*, 2015], the evolution of foam area from breaking waves in the filtered seawater experiments is well-described by a growth-decay (GD) function of the form:

$$A_{\text{GD}}(t) = c_0 t^n \exp(-t/c_1), \quad (1)$$

where c_0 , c_1 and n are constants determined from a least mean squares fit to the data.

A least mean squares fit of equation (1) to the filtered seawater foam time series, $A_{\text{FILT}}(t)$, (open, black circles in Figure 2a) yields the term $A_{\text{GD,FILT}}(t)$ with fit coefficients $c_0 = 2.01(\pm 0.16)$, $n = 1.25(\pm 0.05)$, and $c_1 = 0.39(\pm 0.01)$, and a squared correlation coefficient $r^2 = 0.99$ (all $\pm$ values in parentheses represent 95% confidence intervals of the preceding mean value, except where otherwise stated). Fitting the GD function to the surfactant foam area, $A_{\text{TX}}(t)$ (red asterisks in Figure 2a), but over a limited time range that only includes times in the universal decay phase before $t = \tau_{\text{div}}$, results in the term $A_{\text{GD,TX}}(t)$ with fit coefficients of $c_0 = 2.06(\pm 0.47)$, $n = 1.10(\pm 0.12)$, and $c_1 = 0.38(\pm 0.04)$. The magnitude and trend of the GD function fit to the surfactant foam area using this restricted time range is almost indistinguishable from the evolution of filtered foam evolution (black line). The root mean square (rms) difference between the two fits (black circles and red asterisks) is 0.01 m^2 or about 4% of A_o for this event. This is comparable in magnitude to the rms difference between the filtered GD fit and the filtered data, which is 0.006 m^2 , or about 2.5% of A_o .

These results are representative of the entire data set and reinforce the idea that the primary effects of surfactant-driven stabilization on foam evolution are limited to times greater than τ_{div} . A GD function fit to

the foam data based on its behavior during the growth and decay phase prior to τ_{div} provides a baseline estimate of what the expected foam evolution would be in the absence of stabilization effects.

The divergence time τ_{div} (see Figure 2b) is easily determined in the laboratory data by comparing the filtered and surfactant foam time series for the same focused wave groups (see Figure 2a). This has been done for all breaking wave pairs and a probability density function (PDF) of the scaled divergence time $\tau_{\text{div}}/t_{A_0}$ is shown in Figure 2c. The majority of values lie in the range $1.5t_{A_0}$ to $3t_{A_0}$, which provides sufficient time to estimate the expected foam decay in the absence of surfactants by fitting the GD function over times $t \leq \tau_{\text{div}}$. Any departure from this assumed behavior after τ_{div} is proposed to be an indication of foam stabilization.

The transition from universal to surfactant-influenced decay at $t \geq \tau_{\text{div}}$ represents an important shift in the underlying foam decay regime. We speculate that this transition may reflect a competition between destabilizing buoyancy-driven bubble sorting and stabilizing surfactant effects within the evolving whitecap. For instance, during the universal decay phase, large bubbles (radius greater than about 0.7 mm) rise to the surface and may coalesce with existing foam cells leading to larger, rapidly deforming foam cells not effectively stabilized by Marangoni forces and which therefore rupture on short timescales. During the surfactant-influenced decay, the whitecap foam is replenished by smaller and more slowly rising bubbles, which are more effectively stabilized by Marangoni forces thereby prolonging foam cell lifetime.

In any case, identifying τ_{div} in the signature of individual breaking wave whitecaps establishes a starting point for the quantification of surfactant-driven stabilization in whitecap foam evolution.

3.5. The Foam Area-Time-Integral, $\chi(t)$, and Stabilization Function, $\phi(t)$

Having identified and described the conceptual phases of foam evolution, we now introduce the foam area-time-integral, $\chi(t)$, and the foam stabilization function $\phi(t)$, which itself is based on χ . The area-time-integral has some useful properties: it asymptotes to a stable value with increasing time, and is sensitive to the stabilization of foam by surfactants. It has units of $\text{m}^2 \cdot \text{s}$ and is defined for a foam area time series as

$$\chi(t) = \int_0^t A(t') dt' \quad (2)$$

where $A(t)=0$ at $t=0$ and t' is a dummy variable of integration.

Figure 3a shows the area-time-integral from the filtered, $\chi_{\text{FILT}}(t)$, and the TX-100 surfactant experiments, $\chi_{\text{TX}}(t)$, plotted as a function of time scaled by τ_{div} . The area-time-integrals $\chi_{\text{FILT}}(t)$ and $\chi_{\text{TX}}(t)$ are calculated from equation (2) using the foam area time series $A_{\text{FILT}}(t)$ and $A_{\text{TX}}(t)$, respectively. Also shown are the area-time-integrals $\chi_{\text{GD,FILT}}(t)$ and $\chi_{\text{GD,TX}}(t)$ calculated from $A_{\text{GD,FILT}}(t)$ (black circles) and $A_{\text{GD,TX}}(t)$, respectively.

The area-time-integrals $\chi_{\text{FILT}}(t)$ (black line) and $\chi_{\text{TX}}(t)$ (red line) are almost indistinguishable for times $t/\tau_{\text{div}} \leq 1$. However, for times $t/\tau_{\text{div}} > 1$, the curves rapidly diverge and approach asymptotic values of approximately $0.25 \text{ m}^2 \text{ s}$ and $0.75 \text{ m}^2 \text{ s}$ for the filtered and surfactant foam data, respectively, with the latter clearly showing the imprint of surfactant-driven foam stabilization (see also supporting information Figure S4 for further examples). The area-time-integrals $\chi_{\text{GD,FILT}}(t)$ (black circles) and $\chi_{\text{GD,TX}}(t)$ (red asterisks) also both follow the data-derived integrals closely for times $t/\tau_{\text{div}} \leq 1$. This is to be expected for $\chi_{\text{GD,FILT}}(t)$, since it is determined from $A_{\text{FILT}}(t)$ of the filtered seawater experiments. The fact that $\chi_{\text{GD,TX}}(t)$ also follows $\chi_{\text{FILT}}(t)$ indicates that it is insensitive to the presence of surfactants in $A_{\text{TX}}(t)$. This is the result of fitting equation (1) over the restricted time range $t/\tau_{\text{div}} \leq 1$, and extrapolating to later times to calculate $A_{\text{GD,TX}}$, as outlined in §3.3 above. At later times, $\chi_{\text{GD,FILT}}(t)$ and $\chi_{\text{GD,TX}}(t)$ follow the trend and magnitude of $\chi_{\text{FILT}}(t)$ only, indicating they do not exhibit behavior associated with foam stabilization as is evident in $\chi_{\text{TX}}(t)$ (red curve in Figure 3a). These laboratory data therefore suggest that surfactant-driven foam stabilization imprint can be effectively removed upon the correct identification of the divergence timescale, τ_{div} , in conjunction with applying the simple growth-decay function (equation (1)) as described in §3.4.

Having defined the area-time-integral above, and shown that it can capture a surfactant-driven stabilization signal in a foam area time series, a stabilization function $\phi(t)$ is now introduced which compares area-time-integrals from two foam area time series. The stabilization function is defined by equation (3), and is based on the normalized difference between an observed area-time-integral χ_{OBS} and some reference area-time-integral χ_{REF} :

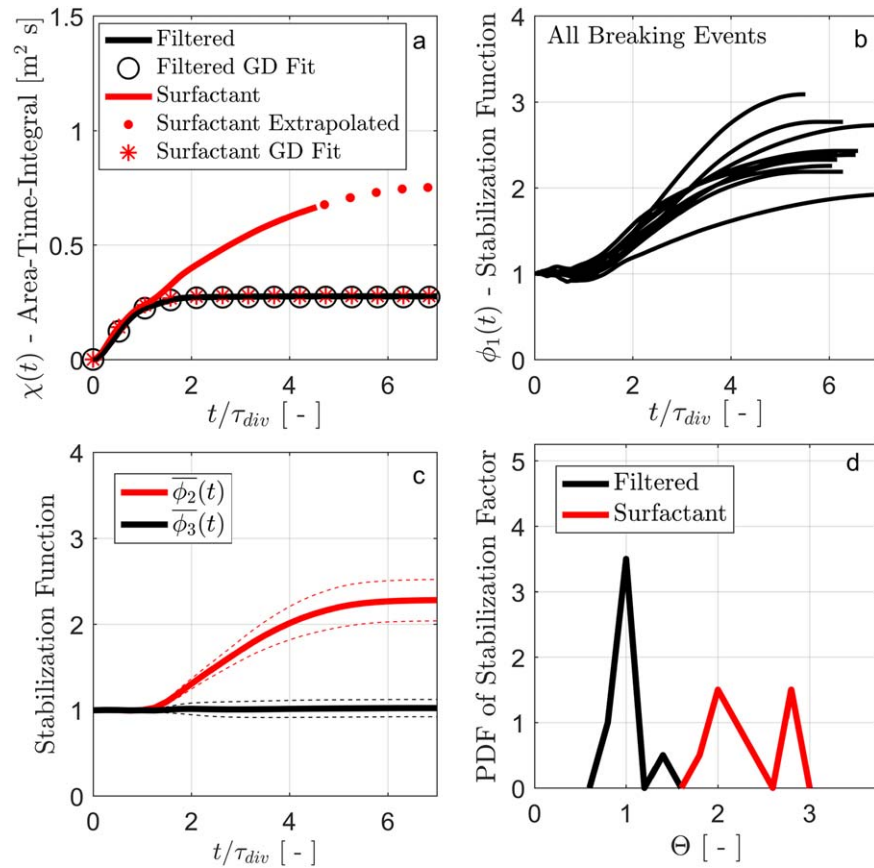


Figure 3. (a) The area-time-integral as a function of normalized time corresponding to the data and GD function fits shown in Figure 2a. The red dots result from a linear extrapolation of the evolving foam area to 0 for times greater than the last recorded image. (b) The stabilization function ϕ_1 for all 10 breaking waves in the surfactant experiment. (c) Mean value of the stabilization functions for all breaking waves in filtered ($\phi_3(t)$, black line) and surfactant ($\phi_2(t)$, red line) seawater experiments. Dashed lines represent 95% confidence intervals on mean values. (d). The PDF of the stabilization factor Θ for the filtered (black line) and surfactant (red line) seawater experiments.

$$\phi(t) = 1 + \frac{\chi_{OBS}(t) - \chi_{REF}(t)}{\chi_{REF}(\infty)} \quad (3)$$

The normalizing factor is the asymptotic limit of the reference foam area time series, $\chi_{REF}(\infty) = \lim_{t \rightarrow \infty} \chi_{REF}(t)$. If the observed time series is unaffected by surfactants, then χ_{OBS} should be equal to χ_{REF} , and the stabilization function has a value of unity at all times. Because the area-time-integral $\chi(t)$ has a well-defined asymptotic limit, the stabilization function also has a well-defined asymptotic limit called the stabilization factor, which is discussed in §3.6. To re-state, by choosing a form for χ_{REF} that is free from the influence of surfactants, any surfactant effect present in χ_{OBS} can be identified with the stabilization function, $\phi(t)$, and then quantified with the stabilization factor. The choice of χ_{REF} and the calculation of $\Theta = \lim_{t \rightarrow \infty} \phi(t)$ are discussed below in §3.5.1 and §3.6, respectively.

3.5.1. Choice of χ_{REF} in $\phi(t)$

To determine the stabilization function for a breaking wave with a particular χ_{OBS} , the reference function χ_{REF} used in equation (3) must be an area-time-integral calculated from a foam area time series unaffected by surfactants. It should also be from a breaking wave of similar scale and spectral content to that used to calculate χ_{OBS} . To evaluate the role of surfactant-driven stabilization in foam evolution for the present data set, two reasonable choices for χ_{REF} are as follows.

Firstly, for a given pair of foam area time series from the filtered and surfactant experiments, χ_{FILT} is used as χ_{REF} in equation (3). χ_{FILT} is taken to be representative of the surfactant-free baseline foam evolution expected for the corresponding breaking wave in the surfactant seawater experiments. Using χ_{TX} as χ_{OBS} in equation (3), along with χ_{FILT} as χ_{REF} , allows the stabilization function to be determined for foam evolution

Table 1. Variations of the Stabilization Function $\phi(t)$ Equation (3), With Corresponding Values of χ_{OBS} and χ_{REF}

$\phi(t)$	χ_{OBS}	χ_{REF}
$\phi_1(t)$	χ_{TX}	χ_{FILT}
$\phi_2(t)$	χ_{TX}	$\chi_{GD,TX}$
$\phi_3(t)$	χ_{FILT}	$\chi_{GD,FILT}$

in the surfactant experiments. For the specific choices of $\chi_{OBS} = \chi_{TX}$ and $\chi_{REF} = \chi_{FILT}$, the stabilization function is denoted $\phi_1(t)$. A list of all variations of $\phi(t)$, along with the area-time-integrals used for χ_{OBS} and χ_{REF} to derive them, is given in Table 1.

The second approach is to use $\chi_{GD,TX}$ for χ_{REF} in equation (3) (see section 3.4), where $\chi_{GD,TX}$ is deter-

mined from $A_{GD,TX}(t)$. For the example above, $\chi_{GD,TX}$ would take the place of χ_{FILT} . The combination of $\chi_{OBS} = \chi_{TX}$ and $\chi_{REF} = \chi_{GD,TX}$ provides an additional approach to evaluate the stabilizing surfactant effects on foam evolution. In this case, the stabilization function is denoted $\phi_2(t)$ (see Table 1).

3.5.2. Evaluating $\phi(t)$

The existence of an initial stage of foam area evolution unaffected by surfactants is quite fortuitous and has important implications for quantifying any surfactant effects on foam evolution from wind-driven oceanic whitecaps (see section 4 below). For example, unlike with laboratory experiments, in a field application, the choice $\chi_{REF} = \chi_{GD}$ is necessary because pairs of breaking waves with identical scale and spectral content cannot be deterministically reproduced in the open ocean in water with different underlying chemistry properties. The choice of $\chi_{REF} = \chi_{GD}$, however, unavoidably introduces an additional degree of uncertainty into the value of the stabilization function. This degree of uncertainty can be analyzed here with the available laboratory data, and the results are discussed in the following section.

Values of $\phi_1(t)$ for all 10 breaking wave pairs are shown in Figure 3b. For times $t \leq \tau_{div}$, which cover the foam area growth phase and universal-decay phase, $\phi_1(t)$ has a value that is approximately unity indicating little difference in observed foam evolution between the filtered and surfactant experiments. For $t > \tau_{div}$, however, values of $\phi_1(t)$ grow larger than 1 clearly highlighting the surfactant-driven stabilization effect. With increasing time, $\phi_1(t)$ approaches its asymptotic limit, which has a value of $2.5(\pm 0.2)$ when averaged over all 10 breaking wave pairs. This indicates that, on average, a TX-100 concentration of 0.2 mg L^{-1} in the wave channel resulted in approximately 2.5 times more integrated foam area when compared to the filtered seawater experiments.

Because $A_{GD,TX}(t)$ and $\chi_{GD,TX}(t)$ are based upon an extrapolation of $A(t)$ for times $t > \tau_{div}$, the evaluation of $\phi_2(t)$ contains additional uncertainty related to the efficacy of equation (1) to predict the behavior of foam evolution free from surfactant effects. It is therefore meaningful to (i) evaluate the trend and magnitude of $\phi_2(t)$ with reference to $\phi_1(t)$, and to (ii) compute a third stabilization function, $\phi_3(t)$, for the filtered seawater data which uses $\chi_{OBS} = \chi_{FILT}$ and $\chi_{REF} = \chi_{GD,FILT}$ (see Table 1). $\chi_{GD,FILT}$ is calculated from $A_{GD,FILT}(t)$ by applying equation (1) over the restricted time period $t \leq \tau_{div}$, as was done for $A_{GD,TX}(t)$. If $\chi_{GD,FILT}$ and $\chi_{GD,TX}$ provide an adequate reference area-time-integral for surfactant-free foam evolution, the trend and magnitude of $\phi_2(t)$ should be similar to $\phi_1(t)$, and the magnitude of $\phi_3(t)$ should be ≈ 1 for all times.

The ensemble average over all breaking waves of $\phi_2(t)$ and $\phi_3(t)$, denoted $\overline{\phi_2}(t)$ and $\overline{\phi_3}(t)$ respectively, are shown in Figure 3c. For case (ii) above, the value of $\overline{\phi_3}(t)$ is approximately unity at all times, as shown by the black curve in Figure 3c. Evidently, $\chi_{GD,FILT}$ adequately captures the trend and magnitude of the measured foam decay in the filtered seawater experiments. For case (i) above, the ensemble average stabilization function $\overline{\phi_2}(t)$ (red curve, Figure 3c) deviates significantly from unity at times $t > \tau_{div}$, demonstrating that the foam stabilization function is sensitive to surfactant-driven stabilization effects when they are present. Furthermore, it can be seen that $\overline{\phi_2}(t)$ asymptotes to a value of ~ 2.5 , which is in good agreement with the ensemble average value of all the $\phi_1(t)$ curves in Figure 3b, given earlier. This suggests that $\chi_{GD,FILT}$ can provide an adequate estimate of the expected baseline foam area evolution in the absence of stabilizing surfactant effects, even when it is determined from a foam area time series that is affected by surfactants.

3.6. The Stabilization Factor, Θ

Taken together, these two results suggest that stabilization functions of the form $\phi_2(t)$ or $\phi_3(t)$ can be reliably used to identify and quantify foam stabilization effects when no comparable surfactant-free foam area time series is available. This result has important implications for field applications of the stabilization function discussed in §4.

A useful metric for foam stabilization is the asymptotic limit of the stabilization function $\phi(t)$:

$$\Theta = \lim_{t \rightarrow \infty} \phi(t), \quad (4)$$

which is called the stabilization factor. When surfactant effects are minimal, $\Theta \approx 1$, whereas $\Theta > 1$ indicates a measurable degree of foam stabilization. Moreover, as an asymptotic limit, it is insensitive to the total duration of the whitecap signature. Probability density functions of Θ for the filtered and seawater experiments are shown in Figure 3d. There is a clear separation between the distributions of stabilization factors of filtered and surfactant experiments. The stabilization factors from the filtered experiments exhibit a narrow distribution centered at unity, with a mean value of $1.02(\pm 0.1)$. However, the stabilization factors from the surfactant experiments are slightly broader in distribution, with most of the values lying in the range 2 – 3, with an overall mean value of $\Theta = 2.28(\pm 0.39)$. The larger range of stabilization factor values in the surfactant experiments may reflect spatio-temporal variations in concentrations of TX-100 throughout the wave channel, or reflect complex dynamics associated with SML disruption and repair.

4. Application to Oceanic Whitecaps

The analysis of oceanic whitecaps in intermediate to deep-water presented here is based on an experiment (SPACE08) conducted in October–November of 2008 from the Martha’s Vineyard Coastal Observatory Air Sea Interaction Tower (ASIT), 3 km south of Martha’s Vineyard, using a 5 megapixel camera operating at 3 – 6 fps and mounted 23 m above the mean sea surface. A full description of the experiment and data set can be found in *Callaghan et al.* [2012]. One of the notable features of the data set is that the area-weighted, mean foam decay time observed on different days varied by over a factor of between observations (from 1.4 s to 4.8 s), indicating that some environmental parameter controlling foam lifetime also varied.

4.1. Oceanic Whitecap Evolution

The evolution of a typical oceanic whitecap is shown in a series of sea surface images (cropped from larger images) in Figure 4, and the associated foam area time series is shown in Figure 4. The x-axes show time, and time scaled by the divergence time τ_{div} , the choice of which is discussed in detail further below. The inset plot shows the area-time-integral for the measured whitecap data (χ_{obs} , red line), and for its corresponding GD fit (χ_{GD} , black line), for comparison to Figure 3a. The whitecap evolution has features similar to the laboratory breaking waves depicted in Figures 1 and 2a. An initial growth phase, consistent with active air entrainment by the breaking wave, is followed by a quasi-exponential decay that transitions to a quasi-linear decay, similar to the laboratory observations (Figure 2a).

During the growth phase (Figures 4a and 4b), distinctive discrete foam strips and bubble plumes generated from individual injection events formed during breaking can be seen behind the leading edge of the breaking wave. Characteristically, the primary orientation of the breaking wave crest, as well as the collective orientation of these smaller foam strips and bubble plume structures, lies almost perpendicular to the direction of breaking. Figure 4c shows the whitecap at the point when (i) active breaking has stopped (as deduced from successive images of the advancing breaking wave), (ii) air is likely no longer being entrained, and (iii) the whitecap area is diminishing rapidly (Figure 4g). Furthermore, the discrete surface foam features readily seen in Figures 4a and 4b have begun to lose their distinctive structure as the sub-surface bubble plumes degas, larger bubbles rise upward, and entrained air is lost through buoyancy.

As depicted in Figures 4d–4f, the whitecap is in a decay phase that is quantitatively and qualitatively different from the preceding universal-decay phase, which occurs at approximately $0.5 \leq t/\tau_{div} \leq 1$. Consistent with the laboratory data, the decay of whitecap area after the universal decay phase is more gradual than the preceding decay, and the decay rate shows a quasi-linear trend in marked contrast with the initial quasi-exponential decay. The visual appearance of the remaining surface foam has also changed markedly. As well as being much reduced in surface area, the distinctive plume structures characteristic of active breaking are no longer present. Instead, the remaining foam has taken on a “streaky” appearance which is elongated in a direction parallel to the direction of wave breaking, and the prevailing wind. These features are not present in the laboratory data, and are therefore likely due to direct or indirect interaction between the foam at the surface and the wind shear stress, as well as the continuous underlying wave straining. Similar foam streaks can be observed in *Thorpe* [2005, Figures 9.8e and 9.8f]. We hypothesize that the evolution of the whitecap in Figures 4a–4f is exhibiting the same kind of foam stabilization effects due to naturally

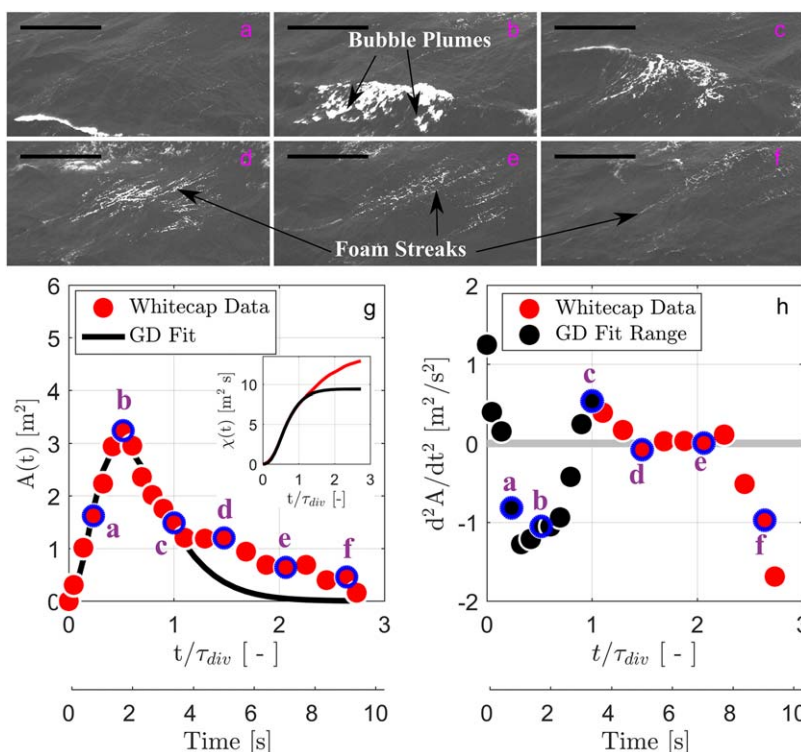


Figure 4. (a–h) Figures 4a–4f show the evolving whitecap, with corresponding measured foam areas highlighted in Figure 4g. The horizontal black line represents a scale of 5 m. The images have been cropped from larger images to focus on the whitecap event in question. Figure 4g shows the evolving whitecap area. Also shown is the GD function fit to the data over times $t \leq \tau_{div}$, and extrapolated to later times. Time is normalized by the divergence time, τ_{div} (see text for details on the evaluation method of τ_{div}). The figure inset shows the evolving area-time-integral of the data and GD function fit with time normalized by τ_{div} . Figure 4h shows the smoothed second temporal derivative of the whitecap foam area. The filled black circles show the range of times over which the GD function was fitted to produce the black curves in Figure 4g. The data points highlighted by the blue circles correspond to the images shown in Figures 4a–4f.

occurring ocean surfactants that are observed in the laboratory experiments of CDS13, but which were due to the addition of TX-100.

4.2. Estimating the Divergence Timescale, τ_{div}

Determining the stabilization factor for oceanic whitecaps requires that the divergence timescale, τ_{div} , be identified. In the laboratory, the identification of τ_{div} is straightforward because each surfactant-influenced breaking wave has a matching filtered seawater conjugate, providing a surfactant-free proxy for the foam area time series. No such proxy exists for the field data, and a reliable, robust and objective method to estimate τ_{div} for oceanic whitecaps needs to be established. Identification of τ_{div} for the oceanic whitecaps studied here is achieved as follows.

The time-evolving whitecap area data are first smoothed with a running linear smoothing function of length $t = t_{A_0}$, after which the second temporal derivative of foam area (d^2A/dt^2) is calculated (see Figure 4h). The divergence time is then chosen to be the first peak in d^2A/dt^2 after the first zero up-crossing. This zero up-crossing marks the inflection point, or change in curvature, of d^2A/dt^2 as $A(t)$ enters the latter stages of foam area decay, and the next occurring peak represents a local maximum after this point. Thereafter, the value of d^2A/dt^2 fluctuates around 0 indicating a quasi-linear decay superimposed upon background variability. Using this value of τ_{div} to specify a fit range, the GD function (equation (1)) is fitted to the measured foam area data, as was done with the laboratory data. The resulting GD fit is plotted as the black line in Figure 4g. For times $t/\tau_{div} \leq 1$, during the growth phase and universal decay phase, the GD fit agrees well with the data. For times $t/\tau_{div} > 1$, during what we propose is the surfactant-influenced decay phase, the data and GD function fit diverge in a manner similar to the surfactant-influenced laboratory data.

An alternative method to estimate τ_{div} is to use the occurrence of the first zero up-crossing of d^2A/dt^2 , which by definition leads to slightly smaller values of τ_{div} . A sensitivity test on the dependence of Θ on the

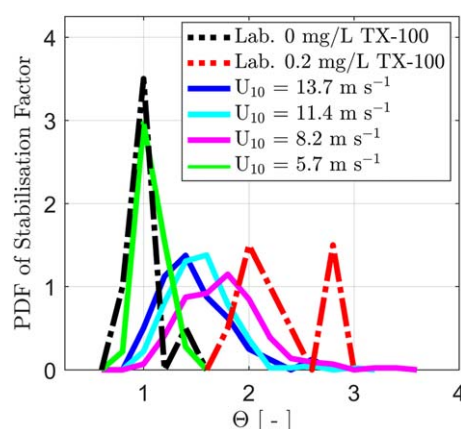


Figure 5. Probability density functions of the stabilization factor, Θ , for the two laboratory experiments (filtered, dashed black line; surfactant, dashed red line), and for oceanic whitecaps taken from 4 different time periods, but measured at the same location from the Air-Sea Interaction Tower at the Martha's Vineyard Coastal Observatory. These time periods are equivalent to those in Callaghan *et al.* [2012] and Callaghan [2013].

points fall. For the field data, ensemble average values of Θ , (and associated standard deviation in parentheses) are $1.48 (\pm 0.35)$, $1.54 (\pm 0.29)$, $1.76 (\pm 0.38)$, and $1.07 (\pm 0.13)$ for periods with mean wind speed of 13.7 m s^{-1} , 11.4 m s^{-1} , 8.2 m s^{-1} , and 5.7 m s^{-1} , respectively. For comparison, the equivalent mean and standard deviation values of Θ for the filtered and surfactant laboratory data are $1.02 (\pm 0.16)$, and $2.28 (\pm 0.39)$, respectively. It is important to note that we do not have measurements of biological activity at the ASIT that may have affected the surfactant concentration and composition during the observation periods.

Field data taken at the lowest wind speed (green line, Figure 5) show a very similar distribution to the data from the filtered seawater experiments, with a single, well-defined and narrow peak at $\Theta = 1$. The implication is that the measured whitecap foam decay during this period shows the same minor effects of stabilization observed in filtered seawater from La Jolla Shores Beach. At the two intermediate wind speeds, the distribution of Θ is broader, with the majority of values lying in the range $1 \leq \Theta \leq 2.5$. The observation period with highest wind speed condition (blue curve in Figure 5) immediately followed the period with lowest mean wind speed (green curve in Figure 5), and was characterized by a rapid increase in wind speed over a period of about 1 h. Therefore, it was very much a transition period representing highly non-stationary forcing conditions in contrast to the three other time periods during which the meteorological conditions were relatively stable. The distribution of Θ values for this high wind speed period generally lies above that from the preceding low wind speed period.

It is difficult to say definitively why field measurements of Θ from the low wind speed period were broadly similar to results from the filtered seawater experiments, while Θ values at higher wind speeds were closer to the surfactant-added experiment. Without a detailed chemical characterization of the surfactants in the upper ocean and SML during SPACE08 and the laboratory experiments, only speculation is possible. Therefore we limit the degree of speculation here, but remark that a possible reason may be related to the ratio of insoluble to soluble surfactants within the SML.

Laboratory experiments by Garrett [1967c] showed that mixtures of soluble and insoluble surfactants in natural seawater led to more stable bubbles at a water surface when compared to artificial solutions with single insoluble surfactant components only. Processes that affect this ratio may also be important to bubble and foam lifetime, in addition to absolute surfactant concentration. The cumulative effect of continued surface compression and dilation, characteristic of a wavy, but unbroken surface, can lead to the displacement of soluble surfactant components from the SML into the bulk water [Bock and Frew, 1993]. Therefore, the Θ value measured during the low wind speed period, may reflect a higher ratio of insoluble to soluble surfactant components within the SML. Indeed, as unbroken water surfaces age, more hydrophilic surfactants can be pushed into the bulk water, leaving a higher proportion of more hydrophobic, insoluble surfactants in

specific choice of τ_{div} is given in section S.5 and supporting information Figure S7, and suggests that there is only a small difference between the two resulting estimates of Θ .

4.3. Oceanic Values of the Stabilization Factor, Θ

Having established a procedure for calculating τ_{div} for the field data, values of the stabilization factor, Θ , for oceanic whitecaps can be calculated and compared to the laboratory values. Figure 5 shows PDFs for the laboratory data of CDS13, as well as for 4 sets of oceanic whitecaps taken during SPACE08 at different time periods. These time periods are the same as those referred to in Callaghan *et al.* [2012], and Callaghan [2013], and we refer the reader to those papers for full details of the wave and wind conditions for these periods.

The combined laboratory and field data sets of Θ show an encouraging range of overlap. The laboratory data from the filtered and surfactant seawater experiments are seen to provide lower and upper bounds to the combined data set, within which the majority of field data

the SML. As wave breaking scale and frequency increase with higher wind forcing, this solubility ratio of components within the SML is likely to change, with soluble surfactants able to more readily adsorb onto the air-water interface than less-mobile insoluble films [Garrett, 1967c]. This could increase the relative abundance of soluble surfactants within the SML, leading to greater bubble and foam stability. Indeed, the transition to larger Θ values between the low wind speed regime and high wind speed regime over a short ~ 1 h time period may be indicative of such temporal heterogeneity in SML composition driven by breaking waves and bubble scavenging.

The laboratory data can provide a first-order interpretation of the field values of the stabilization factor in terms of equivalent concentration of TX-100 (TX_{eq}). To achieve this, a simple linear relationship between the TX-100 concentration used in the experiments, (namely 0 mg L^{-1} and 0.2 mg L^{-1} for the filtered and surfactant experiments respectively) and the relevant mean value of the stabilization factor (namely 1.02 and 2.28 for the filtered and surfactant experiments respectively) has been assumed giving the relationship $TX_{eq} = 0.16(\Theta - 1)$. Following this approach values of TX_{eq} for the SPACE08 Θ data range between 0 and 0.4 mg L^{-1} . We do not have the necessary ground truth data to validate these estimates, and they are therefore speculative by nature. Moreover, a dedicated field campaign would be needed to compare the calibrated stabilization factor values to results of surfactant activity derived from established voltammetry methods. Therefore, this simple approach must be considered preliminary, with further laboratory and field validation required. Nevertheless, it is instructive to place these preliminary estimates in the context of field measurements of surfactant activity from the upper ocean and surface microlayer, which are also reported in equivalent concentrations of TX-100. For example, recent relevant measurements have been made by Pereira *et al.* [2016] along an offshore coastal transect in the North Sea, off the North East coast of England. Surfactant activity was found to vary 5-fold between 0.08 mg L^{-1} and 0.38 mg L^{-1} seasonally, and to vary by a factor of 2 spatially along a single 20 km transect, with values typically increasing with increasing proximity to the coast. Similar values of equivalent concentration of TX-100 have been reported by [Wurl *et al.*, 2011] at coastal and open ocean sites.

5. Relevance to the Remote Sensing of Breaking Wave Energy Dissipation

A connection between the abundance of whitecap foam at the ocean surface and energy dissipation by breaking waves has long been postulated [e.g., Ross and Cardone, 1974; Wu, 1979; Kraan *et al.*, 1996; Hwang and Sletten, 2008; Scanlon *et al.*, 2016]. However, because surfactant-driven foam stabilization can have a measurable influence on foam abundance, understanding the temporal and spatial evolution of foam from individual breaking waves is required to correctly interpret measured foam coverage in terms of breaking wave energy dissipation. Indeed, the oceanic values of the stabilization factor presented in Figure 5 provide preliminary evidence of a measurable foam stabilization signal and what the magnitude of this effect may be.

Callaghan *et al.* [2016] report a novel remote sensing technique (the volume-time-integral technique) to estimate the energy dissipated by individual breaking waves using the spatial and temporal evolution of the breaking wave's whitecap foam. Their experimental data showed a linear relationship between total breaking wave energy dissipation measured in Joules, and the evolving two-phase flow volume integrated in time during the whitecap area growth phase. These findings are consistent with the idea that turbulence within breaking waves that exceed a minimum scale saturates and total energy dissipated by the air entraining, two-phase flow, is proportional to flow volume [Deane *et al.*, 2016].

Two key parameters are required to estimate breaking wave energy dissipation for whitecaps using the volume-time-integral technique: the whitecap foam area-time-integral during the whitecap growth phase and an integral measure of the bubble plume penetration depth, $\hat{z}_{p,\infty}$ (see the discussion following equation (6) and Figure 3a in Callaghan *et al.* [2016]). Two dimensional images of evolving foam can be easily used to calculate the area-time-integral during the whitecap area growth phase. The laboratory data presented here indicate that this phase of whitecap area evolution does not show the same sensitivity to the presence of surfactants as for the latter stages of foam decay (see supporting information Figure S3).

In cases where surfactant effects on foam decay are not significant, $\hat{z}_{p,\infty}$ can be parameterized in terms of the foam decay time τ_{decay} , where

$$\tau_{\text{decay}} = \frac{1}{A_o} \int_{t_{A_o}}^{\infty} A(t) dt \quad (5)$$

In cases where surfactants measurably influence foam decay (i.e., see Figures 1c and 5), the stabilizing effects of the surfactant must be removed before an accurate estimate of $\hat{z}_{p,\infty}$ can be obtained from τ_{decay} . Given a measured foam area time series with a surfactant imprint, $A_{\text{TX}}(t)$, an expected surfactant-free value of τ_{decay} can be estimated by generating a “clean-water” equivalent foam area time series, $A_{\text{GD,TX}}(t)$ which is then substituted into equation (5).

The effectiveness of this approach can be evaluated by comparing the relationship between bubble plume depth and foam decay times derived from the laboratory time series $A_{\text{FILT}}(t)$, $A_{\text{TX}}(t)$, and $A_{\text{GD,TX}}(t)$. The results are shown in Figure 6 where the relationships between foam decay time and two different measures of bubble plume penetration depth are presented. In Figure 6a, the asymptotic value of the area-weighted mean bubble plume penetration depth, $\hat{z}_{p,\infty}$, is used. This is defined in *Callaghan et al.* [2016] as

$$\hat{z}_{p,\infty} = \int_0^{\infty} A(t) z_p(t) dt / \int_0^{\infty} A(t) dt. \quad (6)$$

In Figure 6b, the maximum value of the mean bubble plume penetration depth, $\bar{z}_p$, is used which is defined as

$$\bar{z}_p = \max \{ \bar{z}_{p,t} \}, \quad (7a)$$

where

$$\bar{z}_{p,t} = \frac{1}{M} \sum_{j=1}^M z_{p,j,t}, \quad (7b)$$

is calculated at every time step in the bubble plume evolution as measured using the sideward-looking plume camera, and the index j represents a particular column out of the M columns of pixels in an image of the bubble plume. We refer the reader to sections 4.1 and 6 in *Callaghan et al.* [2016] for further information.

The open black circles in both plots of Figure 6 show the relationship between τ_{decay} and each specific measure of z_p for the breaking waves generated in the filtered seawater experiment. Also shown are the power law relationships between foam decay times and bubble plume penetration depth derived from least mean squares fits to the data. These power law relationships are reproduced from *Callaghan et al.* [2016] as

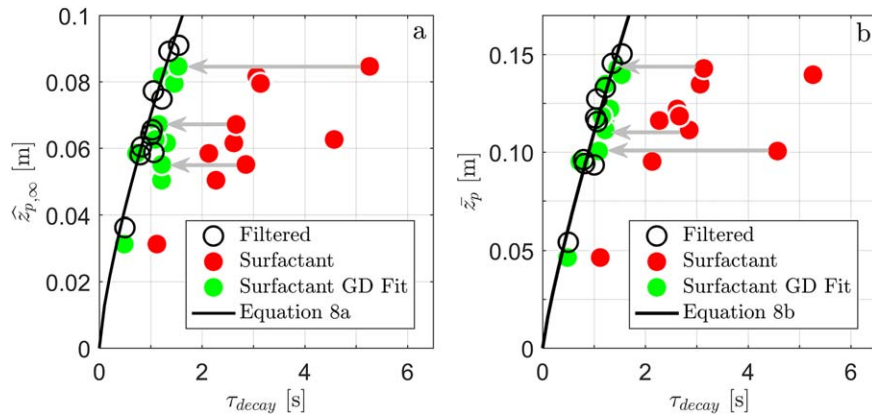


Figure 6. (a) The relationship between foam decay times and the area-weighted mean bubble plume penetration depth for the filtered data (black circles), the surfactant data (red dots), and the GD fit to the surfactant data (green dots). (b) The relationship between whitecap decay times and mean bubble plume penetration depth for the filtered data (black circles), the surfactant data (red dots), and the GD fit to the surfactant data (green dots). The grey arrows in each plot highlight the magnitude of the reduction in τ_{decay} for several particular breaking waves, when the surfactant imprint is removed.

$$\hat{z}_{p,\infty} = 0.07(\pm 0.01)\tau_{\text{decay}}^{0.74(\pm 0.15)}, \quad (8a)$$

and

$$\bar{z}_p = 0.11(\pm 0.01)\tau_{\text{decay}}^{0.84(\pm 0.11)}, \quad (8b)$$

with correlation coefficients of $r^2=0.88$ and $r^2=0.94$, respectively. In each case, a strong relationship between foam decay time and bubble plume depth is evident, with relatively little scatter in the experimental data.

The red dots in Figure 6 indicate that surfactant-driven foam stabilization leads to relatively larger values of τ_{decay} when compared to clean-water, or surfactant-minimized, conditions. Not removing the effect of surfactant-driven stabilization would lead to inaccurate estimates of each measure of bubble plume depth. However, by following the procedure outlined above, a clean-water surfactant-minimized equivalent foam decay time can be estimated, effectively removing the surfactant imprint. The result of this removal procedure is demonstrated with the green dots in Figures 6a and 6b, respectively. The magnitude of the reduction in τ_{decay} is highlighted by the arrows in Figure 6 for several breaking waves. These new values of τ_{decay} lie closely to equations (8a) and (8b), respectively, and align with the filtered seawater data points.

6. Conclusions

At the outset, it was postulated that finding evidence of surfactant activity in the evolution of the foam area of individual whitecaps may provide a remote sensing technique to identify the occurrence, spatial extent and temporal variability of surfactant activity in the upper ocean and the surface microlayer. It was also suggested that doing so would provide a framework within which any contribution from surfactants to foam stabilization, and hence measures of whitecap coverage, could be quantified.

Analysis of data from laboratory experiments using the surfactant TX-100 demonstrate an unambiguous stabilization effect on foam evolution in 2-D laboratory breaking waves. The stabilizing effect of surfactant on the surface foam was found to begin at timescales of about 1.5–3 times the time of maximum foam area, t_{A_0} . No systematic surfactant-driven stabilization effect was observed in the growth phase of whitecap foam area evolution. Further work using 3-D breaking waves, and a wider range of surfactants should be carried out in future experiments.

A set of analytical tools has been developed to identify, quantify, and understand the evolution of the stabilizing effects of surfactants on whitecap foam. A stabilization factor, Θ , has been defined which can be calculated using digital images of whitecap foam evolution. The analysis concepts have been applied to the time series of over 500 wind-driven 3D oceanic whitecaps to calculate field values of the stabilization factor. Distributions of Θ for laboratory and field data show an encouraging level of overlap, suggesting some similarities between the laboratory experiments and the ocean data. Moreover, when Θ is interpreted in terms of concentration of TX-100, the foam-derived values fall within the range of recent in-situ field measurements of surfactant activity in the surface microlayer and upper ocean, although these values are speculative and further laboratory and field work is needed to provide a robust calibration of Θ in terms of surfactant activity.

Within the constraints of idealized laboratory experiments, the new concepts, metrics and ideas encapsulated within the foam area-time-integral (χ), the divergence time (τ_{div}), the stabilization function (ϕ) and the stabilization factor (Θ), and how they are combined and implemented, provides a framework for identifying and evaluating foam stabilization effects in oceanic whitecap foam. Indeed, adopting a whitecap-by-whitecap based analysis of field data could provide a wealth of previously-unexplored information on foam stabilization effects. Moreover, application of the ideas presented here to whitecap image data sets has enormous potential to help in the interpretation of scatter within and between whitecap coverage data sets that may be driven by variations in water chemistry. This would provide an additional framework relevant to the interpretation and use of whitecap coverage data sets to parameterize bubble-mediated processes such as air-sea gas exchange and aerosol production flux, as well as correctly interpreting whitecap coverage for estimates of breaking wave energy dissipation. Finally, a method for recovering a surfactant-free foam area decay timescale from a surfactant-influenced foam area time series has been developed.

This has important implications for estimating bubble plume penetration depth from foam area decay time-scales, and ultimately, for the remote sensing of individual breaking wave energy dissipation values using whitecap foam signatures.

In the global oceans there are myriad naturally occurring surfactants, with a wide spectrum of solubilities, diffusivities, and concentrations, both within the surface microlayer and the upper ocean, where they are scavenged and transported upward by rising bubbles. There are presently no studies of whitecap foam evolution from breaking waves, either in the laboratory or ocean, that are complemented by a complete chemical characterization of natural surfactants present, along with their foam stabilization effects. Indeed, while the tools developed here are useful for investigating variability in foam evolution, it must be acknowledged that inferences drawn from experiments using only TX-100 have inherent limitations. For example, it is natural to ask how surfactant imprints in foam area evolution may change in the presence of surfactants of different characteristics and when the surfactant loading on the inner and outer surfaces of bubbles and foam cells are different. Additionally, it is not yet known what the relative importance of surfactants in the bulk water or the SML is for bubble and foam cell lifetime. Until further investigation, it remains to be proven how the estimated values of equivalent TX-100 concentration presented here compare to those commonly derived from well-established voltammetry techniques [e.g., *Salter et al.*, 2011]. Clearly, further work is needed to better interpret ocean whitecap foam evolution for the identification of surfactant activity, and to achieve a more robust quantitative relationship between the two variables, but the initial data presented here demonstrate that such an approach may be feasible.

The framework outlined here has been explicitly developed using digital cameras operating in the visible part of the electromagnetic spectrum. However, sub-surface bubble-plume formation and surface whitecap foam evolution can also be observed using underwater acoustics, infra-red digital cameras, hyper-spectral radiometers, and satellite-based microwave radiometers [e.g., *Jessup et al.*, 1997; *Deane and Stokes*, 2002; *Angelova and Gaiser*, 2011; *Salisbury et al.*, 2013; *Potter et al.*, 2015; *Randolph et al.*, 2017]. Each remote sensing technique offers a unique observation of bubble and whitecap foam evolution, with associated advantages and disadvantages. Dedicated laboratory and field campaigns that employ a range of these observational approaches simultaneously could provide a more complete evaluation of the physical and chemical processes relevant to breaking waves, and may lead to more accurate models and parameterizations of breaking waves, whitecap foam evolution, and bubble-mediated processes.

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