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Sea-to-Air Transfer of Surface-Active Organic Compounds by Bursting Bubbles

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The bubble transport of natural surfactant materials from seawater to the air-water interface and to the air is investigated experimentally by a radiotracer test system. We have studied the rates at which four lipid materials of differing molecular structure are scavenged from artificial seawater and ejected into the atmosphere by air bubbles of various size distributions at differing airflow rates and bubbling times. We have found that the bubble transport to the air for all materials studied is linearly proportional to the quantity of material transported to the surface microlayer, and the constant of proportionality appears to be independent of the type of material but is a function of the airflow rate and bubble size. Small bubbles were found generally to be more effective in transporting surface-active organic compounds from seawater to the air.

1. INTRODUCTION

The exchange of particles between the ocean and atmosphere has been the subject of considerable research by oceanographers and meteorologists during the past several decades. Many studies have focused on the sea-air exchange of trace metals, viruses, and bacteria [*Duce and Hoffman*, 1976; *Liss and Slinn*, 1982; *Buat-Menard*, 1985]. Relatively few studies, however, have been directly concerned with the transport of surface-active organic components (surfactants) from the ocean water column to the atmosphere. This subject deserves more attention because surface-active organic material on sea salt particles may influence the oceanic production of condensation nuclei, and therefore the formation of rain, the evaporation of water from the sea, and the ocean-to-air flux of charged particles.

The presence of particulate and dissolved surface-active organic compounds, both at the sea surface and in the water column, has been found to be ubiquitous. However, the exact chemical composition and concentration of these compounds may vary greatly with geographic location, water depth, season, and the degree of terrigenous influence. A significant quantity of surfactant material transported to the atmosphere from the sea is mediated by bursting bubbles that are produced primarily from breaking waves and rain [*Blanchard*, 1964], and probably less substantially from biological and geochemical processes [*Blanchard and Woodcock*, 1957]. Bubbles ascending through the water column due to buoyancy forces are known to scavenge surface-active organic compounds and other materials (e.g., bacteria, viruses, and detritus) from the water [*Garrett*, 1967; *Detwiler*, 1979]. Upon reaching the surface, the bubbles burst and produce both jet and film droplets. A thorough review of previous laboratory studies by *Blanchard* [1989] has shown that while the top jet drop is approximately one-tenth the bubble diameter, the film drops are of much smaller sizes. As a result of the bubble-bursting process, a portion of the surfactant material adsorbed on the bubble surface will be ejected together with some seawater into the atmosphere. Also, a portion of the material accumulated in the surface microlayer by previous bubble scavenging will be ejected.

There have been a large number of studies on the atmospheric transport of bacteria and viruses by bursting bubbles, and their results may be applicable to some extent to the present study. *Blanchard and Syzdek* [1970] demonstrated in a laboratory experiment that the concentration of bacteria in jet droplets can be hundreds of times greater than in the main body of water. The enrichment factor, defined here as the ratio of the concentration of bacteria in droplets at the moment of their production relative to the concentration in the bulk water from which the drops originated, is a function of jet droplet (and thus bubble) size, the bubble rise distance (or bubble age, i.e., the length of time available for the bubble to scavenge bacteria), and the type of bacteria involved [*Blanchard*, 1989]. *Carlucci and Bezdek* [1972], however, have suggested that the enrichment of bacteria in jet droplets is derived largely from the surface microlayer itself instead of from the scavenging of bacteria by bubbles traveling through the water column. In later studies, *Bezdek and Carlucci* [1974] used a monomolecular layer of radioactive stearic acid to determine the transport to the atmosphere of surface liquid microlayers by bursting bubbles. They found that smaller droplets (diameters of 28–108 μm) are significantly more effective in removing organic surfactants from a seawater surface.

The sea-air exchange of surface-active organic material was first studied by *Blanchard* [1964, 1968]. He reported the presence of surface-active organic material on sea salt particles collected on thin platinum wires placed along the windward shore of Hawaii. The current paper investigates the rates at which four lipid materials of differing molecular structure are scavenged from artificial seawater and ejected into the atmosphere by air bubbles of various size distributions at differing airflow rates and bubbling times. The results obtained are the by-product of a series of laboratory experiments designed primarily to investigate the bubble transport of natural surfactant materials to the air-water interface [*Lindsley*, 1989; *Skop et al.*, 1989, 1991].

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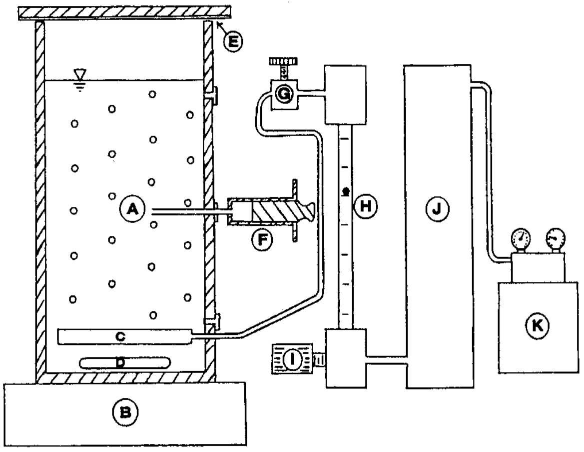

Fig. 1. Bubble test tank apparatus. Labeled components are as follows: A, artificial seawater with ^{14}C-labeled surfactant; B, magnetic stirrer; C, porous bubbling frit; D, magnetic stirring bar; E, cover and ejection collection filter; F, sampling syringe; G, airflow splitter and pressure dump valve; H, rotameter; I, airflow control valve; J, air drying and filtering container; K, air pump.

2. Experiments

2.1. *Test Tank and Seawater*

Experiments were conducted in an acrylic test tank (Figure 1). The tank had internal dimensions of 15.8 × 10.0 × 32.5 cm. The tank was filled with 3.5 L of artificial seawater, bringing the water level to 10 cm below the top of the container. An isotope injection port was located on one side of the tank at a depth of 10 cm below the water surface. The entire apparatus was placed on top of a magnetic stirrer, which allowed for mixing individual chemicals into the water column. The artificial seawater was prepared by mixing "Instant Ocean" (manufactured by Aquarium Systems, Mentor, Ohio) with doubly deionized-distilled water to make a salt mixture of approximately 35‰ salinity. This artificial seawater was filtered through glass wool and GF-D glass fiber and/or 0.45-μm Teflon filters before addition to the test tank. In order to remove surface-active organic contaminants, the tank and all glassware used in experiments were cleaned with methanol and distilled water. Other nonplastic surfaces were cleaned with methylene chloride and allowed to dry thoroughly before use. Salts were purified of potential organic impurities by multiple extractions with methylene chloride and subsequent drying at 40°C under nitrogen before dissolution.

2.2. *Bubble Generation Devices*

Two identical porous glass frits were mounted in plastic frames 2.5 cm from the tank bottom. Air bubbles were generated by flowing air (purified by activated carbon) through the frits and into the water column. The bubble rise distance through the water was thus 20 cm in all experiments. Three different mean airflow rates of 1.0, 2.0, and 4.0 mL min^{-1} cm^{-2} of water surface area were maintained. Three different frits of porosity designations D and C (manufactured by Ace Glass, Vineland, New Jersey) and AS-1 (our designation; manufactured by Penn Plax, Garden City, New York) were used. The bubble size distributions of each frit were predetermined by photographing the bubbles both near the bottom and top of the water column at various airflow rates. The bubble sizes produced were found to be relatively independent of measurement location and flow rate within the range of parameters studied here. Table 1 summarizes the number of bubbles counted and the mean value and standard deviation of the bubble diameters for each porosity frit.

TABLE 1. Bubble Size Distributions

Porosity Designation	No. of Bubbles Counted	Mean Diameter, μm	Standard Deviation, μm
AS–1	95	743	260
C	60	308	87
D	88	203	61

2.3. *Surfactants*

Four different surface-active materials, oleic acid, stearic acid, triolein, and cholesterol, were used to study the sea-to-air exchange process. These chemicals were radiolabeled with carbon 14, which emits low-energy beta particles (maximum energy level of 156 keV). Before each experiment, 6 μCi of radiolabeled surfactant was mixed with a calculated amount of otherwise identical, unlabeled surfactant to yield a total of 120 μg of material with an activity of 80,000 to 110,000 nuclear disintegrations per minute (dpm) per microgram. This mixture was then dissolved into 6 mL of methanol and thoroughly mixed to yield a final surfactant solution with a concentration of 20 μg mL^{-1}. After filling the tank with 3.5 L of artificial seawater, 3.5 mL of surfactant solution was injected into the center of the water column using a stainless steel needle attached to an all-glass syringe. The artificial seawater solution was then mixed with the magnetic stirrer for approximately 10 min. One-milliliter water samples were drawn at various depths immediately after mixing was completed and again 30 min later. From these samples, it was determined that the materials mixed uniformly throughout the water column of the test tank providing an initial concentration for the subsequent bubbling experiments of 20 μg L^{-1}.

Before experimental bubblings were initiated, a surface microlayer sampling device (described below) was used to remove small quantities of surface microlayer enrichment due to the mixing process. This mixing-induced surface microlayer film was found to be generally insignificant compared with that enrichment caused by bubbling during subsequent experiments. The surface blank value resulting from bulk water absorption was then determined by sampling the water surface immediately after the mixing-induced surface microlayer was removed. This blank value was considered as the zero base and was subtracted from all surface values of subsequent bubbling experiments.

2.4. *Surface and Air Sampling Methods and Scintillation Counting*

Water surface and air ejection film droplet collectors were made from Whatman 3 MM CHA grade chromatography paper. The surface collectors were mounted on acrylic holding frames, lowered into the tank, and touched to the water surface to collect scavenged and surface-accumulated materials. The pick-up efficiencies of surface microlayer samplings for each surfactant were predetermined by carefully sampling a water surface covered with known amounts of radiolabeled surfactant at known concentrations. The mean pickup efficiencies (88%, 86%, 62%, and 87% for oleic acid, stearic acid, triolein, and cholesterol, respectively) were later incorporated into surface microlayer sample determinations to obtain a calibrated surface microlayer concentration. The material ejected to the air at a height of 10 cm above the water surface by bursting bubbles was collected by similar Whatman 3 filters.

Each collection filter was divided into a grid of 16 rectangles. After experimental operations were completed, the surface and air collectors were allowed to dry and then cut into 16 sections. Eight sections were paired and placed into scintillation vials (two per vial) and filled with 10 mL of Aquasol scintillation fluid for subsequent isotope quantitation. A Beta-Trac 6895 scintillation counter was used to measure the radioactivity in each vial.

Three 35-μL samples of the radiolabeled surfactant–methanol mixture were deposited directly onto filter papers in filled scintillation vials to determine the absolute calibration count of disintegrations per minute per microgram for each surface-active material. This calibration constant was then used to convert the counts of all other vials from disintegrations per minute to micrograms of surfactant.

3. RESULTS AND DISCUSSION

The experiments that were conducted with different surfactant materials under various conditions of airflow rates, bubbling times, and bubble size distributions are listed in Table 2. Note that nitrogen was used instead of air as the bubbling gas for experiment OA05N. Because insignificant differences between results of experiments conducted with air and nitrogen were found [*Skop et al.*, 1991], we included results of this nitrogen test in our data analysis. To determine experimental variations, multiple tests were conducted under identical conditions. It was found that variations in bubble transport of surfactant materials from the water column to the water surface microlayer (denoted "surface transport") and to the air at 10-cm altitude (denoted "air transport") can be as large as 33% and 71%, respectively, from their mean values. Similarly large variations were also reported by H. Bezdek (private communication, 1989). The results presented below are all based on mean values of two or more experiments.

Plotted in Figure 2 is a time history for cumulative air transport utilizing oleic acid, stearic acid, cholesterol, and triolein as test materials. Each case plotted is for an airflow rate of 4.0 mL (min cm^2)$^{-1}$, a bubble size distribution generated by the D frit, an initial surfactant concentration of 20 μg L^{-1}, and sampling intervals of 30 s. It is clearly evident from Figure 2 that oleic acid was transported from the water column into the air at a rate much faster than was stearic acid. Stearic acid was, in turn, transported at a rate roughly twice that of triolein and 3 times that of cholesterol. Although the transport rate for triolein is slightly higher than that for cholesterol, the difference between them is not statistically significant. Also apparent from the data presented in Figure 2 is a decline in transport rate with increasing air bubbling time for all cases studied. This phenomenon is similar to that of the cumulative surface transport reported by *Skop et al.* [1991] and is due primarily to water column depletion of surfactant, as previously reported.

TABLE 2. Summary of Experimental Conditions

Test	Airflow Rate, mL (min cm^2)$^{-1}$	Sampling Time, s	Mean Bubble Diameter, μm
		Stedric Acid	
SA05	4.0	30, 60, 90, 120	203
SA06	4.0	30, 60, 90, 120	203
SA04B	1.0	30	203
SA04C	2.0	30	203
SA081	1.0	30	308
SA082	2.0	30	308
SA084T	4.0	30, 60, 90, 120	308
SA091	1.0	30	308
SA092	2.0	30	308
SA094T	4.0	30, 60, 90, 120	308
SA071	1.0	30	743
SA072	2.0	30	743
SA074T	4.0	30, 60, 90, 120	743
SA101	1.0	30	743
SA102	2.0	30	743
SA104T	4.0	30, 60, 90, 120	743
		Oleic Acid	
OA02	4.0	30, 60, 90, 120	203
OA04B	1.0	30, 60, 90, 120	203
OA05N	4.0	30, 60, 90, 120	203
OA071	1.0	30	203
OA072	2.0	30	203
OA074T	4.0	30, 60, 90, 120	203
OA081	1.0	30	743
OA082	2.0	30	743
OA084T	4.0	30, 60, 90, 120	743
OA091	1.0	30	743
OA092	2.0	30	743
OA094T	4.0	30, 60, 90, 120	743
OA101	1.0	30	308
OA102	2.0	30	308
OA104T	4.0	30, 60, 90, 120	308
OA111	1.0	30	308
OA112	2.0	30	308
OA114T	4.0	30, 60, 90, 120	308
OA130	1.0	30, 60, 90, 120	203
OA131	2.0	30, 60, 90, 120	203
		Triolein	
TO01	4.0	30, 60, 90, 120	203
TO02	4.0	30, 60, 90, 120	203
TO03B	1.0	30	203
TO03C	2.0	30	203
TO03D	4.0	30	203
		Cholesterol	
CH011	1.0	30	203
CH012	2.0	30	203
CH014T	4.0	30, 60, 90, 120	203
CH021	1.0	30	203
CH022	2.0	30	203
CH024T	4.0	30, 60, 90, 120	203

The cumulative surface and air transport of stearic acid at various bubbling times is plotted in Figures 3*a* and 3*b*, respectively, as a function of mean bubble diameter. The results are for an airflow rate of 4.0 mL (min cm^2)$^{-1}$. It is evident from these two figures that as the mean bubble diameter decreases, the amount of stearic acid transported to the water surface and to the air increases. The air transport increases with bubbling time at a higher relative rate than the surface transport, and this phenomenon is more pronounced for the case of the smallest bubble diameter studied. From a simple dimensional analysis, we assume that the amount of surfactant material (M) scavenged by bubbles

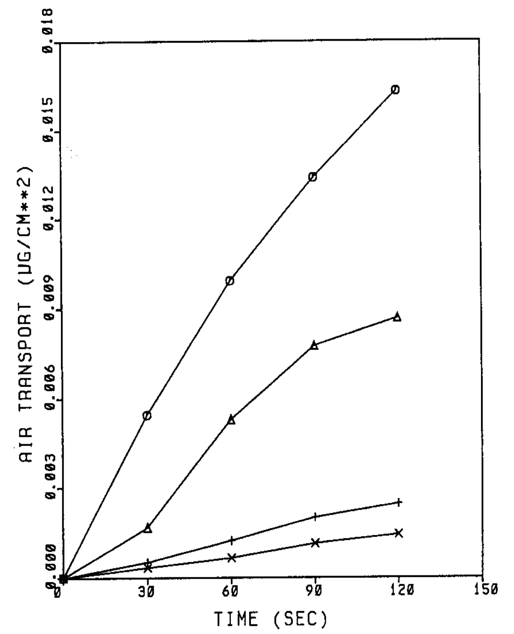

Fig. 2. Cumulative air transport versus time for oleic acid (circles), stearic acid (triangles), triolein (pluses), and cholesterol (crosses). Each case plotted is for an airflow rate of 4.0 mL (min cm^2)$^{-1}$, a bubble size distribution generated by the D frit, an initial surfactant concentration of 20 μg L^{-1} and sampling intervals of 30 s.

rising through the subsurface water is proportional in some power α to the number of bubbles (N) and the surface area A of each individual bubble, where α is possibly flow dependent and definitely surfactant dependent [*Skop et al.*, 1991]. For bubbles of two different diameters d_1 and d_2 but with the same airflow rate and initial surfactant concentration in the water,

$$\frac{M_2}{M_1} \approx \left[\frac{N_2}{N_1}\frac{A_2}{A_1}\right]^{\alpha} = \left[\frac{d_1^3}{d_2^3}\frac{d_2^2}{d_1^2}\right]^{\alpha} = \left[\frac{d_1}{d_2}\right]^{\alpha}$$

The amount of surfactant transport should be closely related to the bubble scavenging process, and this prediction is supported by the approximately inverse relationship between surface transport and mean bubble diameter (given constant total airflow rates) as depicted in Figure 3*a*. On the other hand, the process and mechanism by which surfactants are ejected into the air are more complicated. As is indicated from previous results of the sea-to-air transfer of bacteria [*Blanchard*, 1989], both the bubble scavenging process in the water column itself and the continuous enrichment in the air-water microlayer concentration at the seawater surface might contribute to the air ejection process of surfactants by bursting bubbles. The rapid increase of air transport at smaller bubble sizes shown in Figure 3*b* suggests that the effect of water surface microlayer enrichment may indeed be important.

The cumulative air transport of each surfactant material is plotted relative to total surface transport in Figure 4. These data represent results with the same bubble size distributions generated by the D frit and at three different airflow rates of 1.0, 2.0, and 4.0 mL (min cm^2)$^{-1}$. It is interesting to observe that all data points in Figure 4 tend to cluster toward three straight lines of differing slope, dependent only on airflow rate at the given mean bubble diameter. This finding appears to indicate that regardless of the type of surfactant material used in this study, the amount of surfactant ejected into the atmosphere is linearly proportional to the amount of surfactant transported to the surface microlayer. For a given mean bubble diameter, the slope is governed by the airflow rate. Slopes of the fitted straight lines in Figure 4 are listed in Table 3 as a function of airflow rate. For the same quantity of surfactant transported to the surface microlayer, more surfactant was found to be ejected into the atmosphere at a higher airflow rate. This should be intuitively evident, because at higher airflow rates, more bubbles are generated, thereby resulting in more jet droplets.

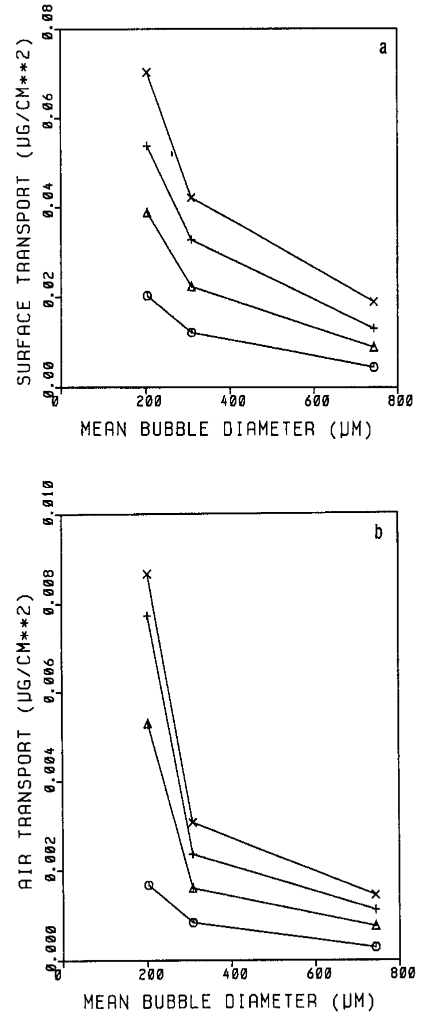

Fig. 3. Variations of cumulative (*a*) surface transport and (*b*) air transport for stearic acid with mean bubble diameter. The bubbling times are 30 s (circles), 60 s (triangles), 90 s (pluses), and 120 s (crosses). The results are for an airflow rate of 4.0 mL (min cm^2)$^{-1}$.

Plotted in Figure 5 is the cumulative air transport of oleic acid versus the cumulative transport to the surface microlayer. These are results under the same airflow rate of 4.0 mL (min cm^2)$^{-1}$ but different bubble size distributions generated by the D frit (d = 203 μm), the C frit (d = 308 μm), and the AS-1 frit (d = 743 μm), where d is the mean bubble diameter. Note that at each bubble size distribution, the air transport is linearly proportional to the surface

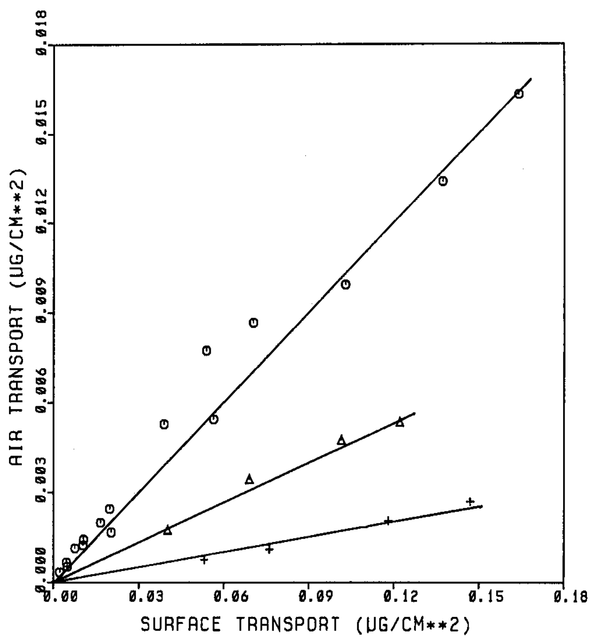

Fig. 4. Cumulative air transport versus surface transport for each surfactant at airflow rates of 1.0 (pluses), 2.0 (triangles), and 4.0 (circles) mL $(\text{min cm}^2)^{-1}$. The results are for the bubble size distribution generated by the D Frit.

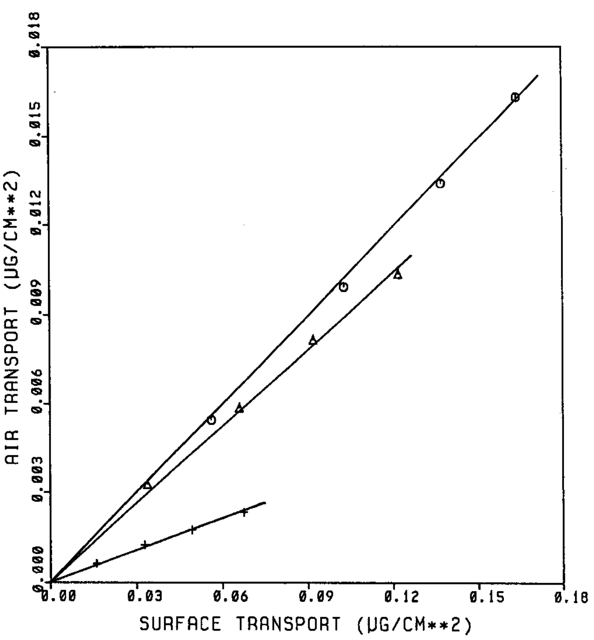

Fig. 5. Variations of cumulative air transport with surface transport for oleic acid. The mean bubble diameters are 203 μm (circles), 308 μm (triangles), and 743 μm (pluses). The results are for an airflow rate of 4.0 mL $(\text{min cm}^2)^{-1}$.

transport, and each case can be fitted with a straight line of different slope. The resultant slopes are also listed in Table 3. As the mean bubble diameter became smaller, the slope of the fitted straight line was found to be greater. These results suggest that small droplets (originating from the collapse of bubbles with a mean diameter of 203 μm) can transport organic materials more effectively from a seawater surface than can droplets derived from the collapse of larger bubbles. Similar results were reported by *Bezdek and Carlucci* [1974] using a preexisting surface microlayer and a different experimental technique.

4. Conclusions

The present work has examined experimentally the seawater-to-air transfer of surface-active organic compounds by bursting bubbles. We have found that the transport of surfactant from seawater to the air-water interface is closely related to the bubble-scavenging process, which is strongly dependent on the bubble flow field (i.e., the bubble size and density distribution and flow rate) and the chemical properties of the material being scavenged. It was found that oleic acid, stearic acid, triolein, and cholesterol were transported in decreasing order in direct relationship to their scavenging susceptibility. The ejection of surfactant materials to the atmosphere is a more complicated situation being dependent on the physics of direct bubble scavenging, pre-existing surface microlayer concentrations, and surface bursting processes. However, when the cumulative air transport at increasing bubbling times was plotted versus the cumulative surface transport, our results displayed a linear trend which is surfactant independent but flow dependent. Within the range of parameters studied, we have found that the ratio of air to surface transport is greater at higher airflow rates and smaller mean bubble diameters.

TABLE 3. Ratios of Air to Surface Transport as Functions of Airflow Rate and Mean Bubble Diameter

Airflow Rate, mL $(\text{min cm}^2)^{-1}$	Mean Bubble Diameter, μm	Air Transport/ Surface Transport
	Variable Airflow	
1.0	203	1.72×10^{-2}
2.0	203	4.56×10^{-2}
4.0	203	9.91×10^{-2}
	Variable Bubble Size	
4.0	203	9.91×10^{-2}
4.0	308	8.69×10^{-2}
4.0	743	3.52×10^{-2}

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