

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NRL Report 7897	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SURFACE-ACTIVE ORGANIC MATERIAL IN AIR OVER THE LIGURIAN SEA AND OVER THE EASTERN EQUATORIAL PACIFIC OCEAN	5. TYPE OF REPORT & PERIOD COVERED Interim report on one phase of a continuing NRL Problem.	
	6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) William R. Barger and William D. Garrett	8. CONTRACT OR GRANT NUMBER(s)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, D.C. 20375	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NRL Problem G02-03 RR 131-03-41-5907	
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research Arlington, Va. 22217	12. REPORT DATE June 30, 1975	
	13. NUMBER OF PAGES 20	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Air chemistry	Fog modification	Surface-active material
Air sampling	Marine fog	Surface chemistry
Condensation nuclei	Monomolecular films	Surface films
Fog chemistry	Sea fog	
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>Airborne particulate material was collected on glass-fiber filters with high-volume air samplers mounted aboard ships during July 1973 in the Ligurian Sea region of the Mediterranean Sea, and during February 1974 in the Pacific Ocean on a cruise from Panama to Ecuador via the Galapagos Islands. The filters were extracted with chloroform, and the lipid components of the extracts were converted to methyl esters for analysis by gas chromatography. Single fatty components in the range of 12 to 18 carbon atoms in length</p>		

20. Abstract (Continued)

varied up to a maximum concentration of 50 ng per cubic meter of air when expressed as methyl esters. For the Pacific samples, the concentration of total organic material extracted by chloroform ranged from 0.08 to 4.02 μg per cubic meter of air. In order to investigate the possibility of stabilization of fogs by organic chemical films, film pressure vs area isotherms were determined for the surface-active material recovered from each of the Pacific samples. There was not enough surface-film-forming material found to coat the droplets of a hypothetical fog in the sampled air, but enough material was found to entirely coat the nuclei associated with a fog. Therefore, the initial formation of a fog might be delayed because of a change in the wettability of the nuclei due to the surface film.

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SURFACE-ACTIVE ORGANIC MATERIAL IN AIR OVER THE LIGURIAN SEA AND OVER THE EASTERN EQUATORIAL PACIFIC OCEAN

INTRODUCTION

It has been known for 50 years that layers of certain surface-active organic chemicals one molecule thick can retard evaporation from water surfaces [1]. In 1955, Archer and La Mer [2] carried out a particularly detailed study of evaporation of water through fatty acid monolayers, which indicated that the rate of evaporation from a plane water surface could be decreased by a factor of 10,000. In the same study, it was also pointed out that the presence of a few percent of foreign molecules among the pure evaporation-retarding molecules could cause a large decrease in the evaporation resistance of the film. In the same year, R. S. Bradley [3] suggested that it was also possible to reduce the evaporation rate of water mists in an unsaturated atmosphere by a factor of 10,000 by coating the droplets with an insoluble monomolecular film. Because this mechanism of evaporation retardation may be significant in the formation and dispersion of fogs, it has been studied by many investigators over the past 20 years. Some have studied small groups of drops either freely falling or suspended on fine threads [4-9], whereas others have experimented on a larger scale with simulated fogs in a large chamber [10]. Field experiments have also been performed [11,12]. Hughes and Stampfer [13] have shown that certain surface-active chemicals can even enhance evaporation of water from suspended drops. All agree that surface films are capable of modifying the behavior of water drops suspended in air. A good review of the subject is contained in a recent report by Corrin, Connell, and Gero of Colorado State University [14]. Simultaneously with the studies of modification of droplet evaporation, research on the modification of evaporation of water from plane surfaces has also pressed forward because of the importance this subject has with regard to conserving water in reservoirs [15-17].

Since certain types of surface-active materials retard evaporation while others enhance it, the question of what happens in nature is immediately raised. To answer this question requires a detailed analysis of the surface-active material found in air. Earlier investigators pointed the way by suggesting that bubbles bursting at the surface of the sea provided the mechanism by which salt nuclei were transferred into marine air [18]. This same mechanism, of course, would also transfer any surface-active material from the sea into the air [19-21]. Early work on the analysis of the surface-active material found in sea slicks on the Bay of Panama [22] and more recent work in the Mediterranean [23] suggested what compounds to look for in marine air. Some of these materials were indeed found in air collected from a tower on the windward coast of the Island of Oahu, Hawaii [24]. Meanwhile, other investigators have steadily pursued the study of other kinds of organic material in air and have determined some of the types of compounds with which the surface-active materials are mixed [25-27].

This report describes a more sensitive chemical analysis of the surface-active material for individual components than was possible with the Hawaiian samples. The collections on which this report is based were made over the open ocean rather than from a tower. In addition, for the first time it was possible to determine the force-vs-area curves for the surface-active material associated with the particulates in marine air. A force-area curve describes the relationship between the area covered by a surface film and the change in surface tension of the liquid over which it is spread (film pressure).

Two groups of air samples which were collected on glass-fiber filters with a high-volume sampler mounted aboard ship are discussed. The first group was collected in the Ligurian Sea region of the Mediterranean Sea between July 17 and 29, 1973. Sampling times and locations for each sample plus the average windspeed, air temperature, and pressure are shown in Table 1. The cruise track for these sample collections is shown in Fig. 1. The

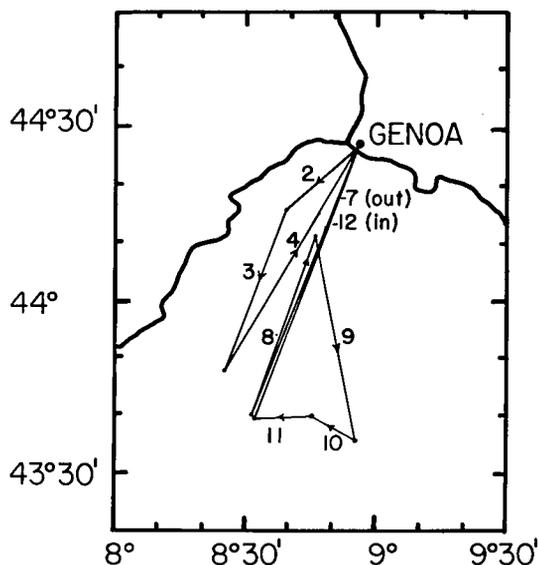


Fig. 1 — Surface track of ship used for taking Mediterranean air samples

second group of samples was collected in the Pacific Ocean with the same equipment between February 10 and 23, 1974, on a cruise from Panama to Ecuador via the Galapagos Islands. Sampling times and locations for each sample are given in Table 2, and the cruise track is shown in Fig. 2. The Pacific air samples were analyzed in greater detail than the Mediterranean samples and reflect the experience gained from working with the earlier Mediterranean collections.

Table 1
Mediterranean Air Samples, 1973

Sample Number	Sampling Period (Month-Day-Hour) (GMT + 2 Hr)	Beginning and Ending Locations	Air Volume Collected (m^3)	Avg Air Temp ($^{\circ}C$)	Avg Pressure (mb)	Avg Wind Velocity (knots)
M-2	7-17-1710 to 7-18-2000	44 $^{\circ}$ 25'N, 8 $^{\circ}$ 55'E to 44 $^{\circ}$ 15'N, 8 $^{\circ}$ 39'E	2735.4	24	1014	12
M-3	7-18-2015 to 7-19-1858	44 $^{\circ}$ 15'N 8 $^{\circ}$ 39'E to 43 $^{\circ}$ 48'N, 8 $^{\circ}$ 25'E	2315.8	24	1014	7
M-5	7-20-1648 to 7-21-1930	44 $^{\circ}$ 25'N 8 $^{\circ}$ 55'E to 44 $^{\circ}$ 25'N, 8 $^{\circ}$ 55'E	2721.8	—	—	—
M-6	7-21-1937 to 7-22-1807	44 $^{\circ}$ 25'N 8 $^{\circ}$ 55'E to 44 $^{\circ}$ 25'N, 8 $^{\circ}$ 55'E	2293.7	—	—	—
M-7	7-22-1808 to 7-23-1816	44 $^{\circ}$ 25'N 8 $^{\circ}$ 55'E to 43 $^{\circ}$ 39'N, 8 $^{\circ}$ 31'E	2460.2	24	1013	6
M-8	7-23-1830 to 7-24-1828	43 $^{\circ}$ 39'N 8 $^{\circ}$ 31'E to 44 $^{\circ}$ 11'N, 8 $^{\circ}$ 46'E	2443.2	24	1008	8
M-9	7-24-1829 to 7-25-1807	43 $^{\circ}$ 11'N 8 $^{\circ}$ 46'E to 43 $^{\circ}$ 36'N, 8 $^{\circ}$ 55'E	2409.2	22	1005	3
M-10	7-25-1808 to 7-26-1809	43 $^{\circ}$ 36'N 8 $^{\circ}$ 55'E to 43 $^{\circ}$ 39'N, 8 $^{\circ}$ 45'E	2448.3	22	1010	8
M-11	7-26-1810 to 7-27-1807	43 $^{\circ}$ 39'N 8 $^{\circ}$ 45'E to 43 $^{\circ}$ 39'N, 8 $^{\circ}$ 31'E	2441.4	23	1014	7
M-12	7-27-1808 to 7-29-1826	43 $^{\circ}$ 39'N 8 $^{\circ}$ 31'E to 44 $^{\circ}$ 25'N, 8 $^{\circ}$ 55'E	4923.8	21	1013	6

*Dash indicates data not available.

Table 2
Air Samples Taken Over the Eastern Equatorial Pacific Ocean, 1974

Sample Number	Sampling Period (Month-Day-Hour) (GMT - 6 Hr)	Beginning and Ending Locations	Air Volume Collected (m^3)	Avg Air Temp ($^{\circ}C$)	Avg Pressure (mb)	Avg Wind Velocity (knots)
P-1	2-10-1739 to 2-11-1607	8° 56'N, 79° 34'W to 6° 14'N, 82° 03'W	2290.3	28.6	1013	15.6
P-2	2-11-1610 to 2-12-1604	6° 14'N, 82° 03'W to 4° 45'N, 85° 26'W	2436.4	26.9	1011	1.3
P-3	2-12-1608 to 2-13-1619	4° 45'N, 85° 26'W to 2° 14'N, 89° 41'W	2473.8	26.5	1026	5.6
P-4	2-13-1622 to 2-14-1622	2° 14'N, 89° 41'W to 1° 15'S, 89° 09'W	2446.6	26.1	1009	11.3
P-5	2-14-1626 to 2-15-1915	1° 15'S, 89° 09'W to 1° 18'S, 90° 44'W	2733.7	26.5	1013	7.3
P-6	2-15-1917 to 2-16-1558	1° 18'S, 90° 44'W to 2° 35'S, 94° 15'W	2108.5	25.3	1012	10.2
P-7	2-16-1602 to 2-17-1602	2° 35'S, 94° 15'W to 0° 29'S, 93° 43'W	2446.6	25.8	1010	6.4
P-8	2-17-1606 to 2-18-1621	0° 29'S, 93° 43'W to 0° 28'S, 91° 13'W	2472.1	25.4	1011	7.5
P-9	2-18-1631 to 2-19-1602	0° 28'S, 91° 13'W to 0° 00'S, 88° 37'W	2397.3	25.4	1008	8.7
P-10	2-19-1606 to 2-20-1558	0° 00'S, 88° 37'W to 2° 38'S, 86° 05'W	2433.0	25.5	1008	10.3
P-11	2-20-1600 to 2-21-1612	2° 38'S, 86° 05'W to 2° 13'S, 83° 40'W	2467.0	24.1	1011	12.1
P-12	2-21-1615 to 2-22-1616	2° 13'S, 83° 40'W to 1° 27'S, 82° 04'W	2448.3	24.7	1009	8.3
P-13	2-22-1618 to 2-23-0928	1° 27'S, 82° 04'W to 1° 35'S, 81° 26'W	1953.9	24.5	1010	5.7

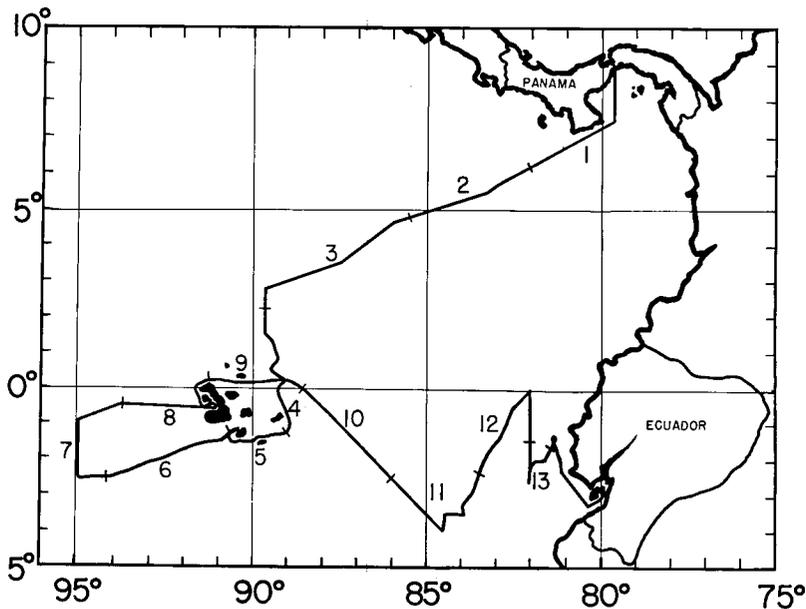


Fig. 2 — Surface track of ship used for taking Pacific air samples

ANALYTICAL CHEMISTRY

Collection and Treatment of Samples

Prior to each trip a batch of 8 x 10-in. glass-fiber filters was washed together in chloroform and dried at 100°C with the idea that even if all traces of organic material were not removed, the blanks should be more uniform. Filters were handled only with tongs. Aboard ship the air sampler was adjusted to pass 60 ft³ of air per minute (1.70 m³/min) through the filters. At the conclusion of the 24 hr sampling period, each filter was removed from the air sampler and sealed into a polyethylene bag for transport back to the laboratory. Filters used for blanks were also sealed into the polyethylene bags aboard ship and were transported and stored in the same manner as the sample filters.

In the laboratory the filters from the Mediterranean were extracted in Soxhlet apparatus for 2 hrs with 150 ml of freshly distilled chloroform, concentrated to about 30 ml and then poured through a small glass-fiber filter into a previously cleaned glass-stoppered bottle. Air filtered through a packed cotton column was used to evaporate the sample to dryness at room temperature. Fifteen ml of methyl alcohol was added to dissolve the residue and was then transferred to a 21-cm-long test tube with a 19/38 ground glass mouth. Four drops of concentrated HCl was then added to the solution. A condenser was inserted in the test tube's ground joint, and the solution was refluxed for 2 hr by heating it in a water bath held at 85°C [28]. The solution of methyl esters was then extracted three times with 10-ml portions of petroleum ether. The petroleum ether layers were drawn off with a syringe and evaporated to dryness in clean bottles.

Small test tubes were made by sealing the ends of glass eyedroppers in a flame and calibrating them with a scratch at 1/2 ml. The methyl esters were then taken up in 1 ml of carbon disulphide which had been previously passed through activated charcoal, and the solution was added to the eyedropper tubes. Approximately 0.5 ml of CS_2 was used to rinse the remaining traces of material into the eyedropper tube. The CS_2 was then evaporated to the 0.5 ml mark on the test tube, and the sample was ready for injection into the gas chromatograph.

A more complicated extraction procedure was used for the Pacific samples to study also the surface chemistry and total organic material extractable by chloroform. As before, the filters were extracted with 150 ml of freshly distilled chloroform in Soxhlet apparatus, reduced to about 30 ml by distillation of the chloroform, and poured through glass-fiber filters into acid-cleaned, glass-stoppered bottles for storage. Next, however, the solution was transferred to a 25-ml graduated cylinder and evaporated to exactly 10 ml. At this point the samples were divided in half by removing 5 ml with a pipet and transferring it to a preweighed 5-ml volumetric flask. The remaining 5 ml was poured into a 21-cm reaction tube as described earlier and evaporated to dryness at room temperature without using an airstream. Two ml of 10% BF_3 -methanol was added to the residue in each reaction tube. All tubes were placed together in a 100-ml beaker of water that was held at 75°C for 2 hr and then left to stand overnight. Three ml of petroleum ether were then added along with 1 ml of water, and the lower water-methanol layer was withdrawn with a long hypodermic needle. The petroleum ether layer was allowed to evaporate until only traces of water remained. One-half milliliter of CS_2 was added, and the solution was transferred to an eyedropper tube calibrated at 0.5 ml. One-half milliliter more of CS_2 was used to rinse the remainder into the tube. After the 1 ml of CS_2 solution was transferred to the eyedropper tube, any visible droplets of water were removed with a long hypodermic needle and discarded. The CS_2 solution of methyl esters was then evaporated to the 0.5-ml mark.

Gas Chromatographic Identification of Lipid Derivatives

A matched pair of 1/8-in.-diameter, 5-ft stainless steel columns packed with 10% EGSS-X on 100/120-mesh Gas Chrom P were prepared and installed in a Varian Aerograph Series 2700 gas chromatograph with dual flame ionization detectors. A Varian Aerograph Model 485 electronic digital integrator was used to determine peak areas. For the Mediterranean samples the columns were operated isothermally at 135°C with the detectors and injectors at 200°C. The carrier gas was helium, flowing at 25 ml/min. Hydrogen and air-flow rates were 30 and 300 ml/min, respectively. For the Pacific samples the same columns and apparatus were used. The only changes were in the temperatures. Column temperature was changed to 165°C, while the detectors were changed to 225°C and the injectors to 235°C. One microliter of the 0.5-ml solution of the methyl esters in CS_2 was injected into the chromatograph with a 5- μ l syringe. Quantities present in the samples were established by multiplying peak areas of unknowns by the mass per area determined by injection of a solution of standards of known concentration. The quantitative standard was prepared from NHI Reference Mixture D containing $C_{14:0}$, $C_{16:0}$, $C_{16:1}$, $C_{18:0}$, and $C_{18:1}$

methyl esters which was obtained from Supelco, Inc., Bellefonte, Pa. Results are shown in Table 3 and are corrected for blank filters that were carried through the entire transportation, storage, and extraction process. Since the methyl esters were identified by retention times alone, the retention indices are reported in order to indicate the degree of uncertainty in assigning given methyl esters to the unknown peaks. This method also permits the reporting of data in a comparable way from chromatographic columns operated under slightly different conditions. The numbers assigned in Table 3 to the standards were based on multiple injections of the standards throughout the series of analyses. The expression $x \pm y$ is used to describe the retention indices of the standards, where x is the average value and y is one-half of the range within which all the values fell.

Determination of Total Organic Material

In addition to gas chromatographic analyses for individual esters, the total amount of organic material extracted by chloroform was determined for each Pacific sample by evaporating the chloroform from the second half of the sample under vacuum and weighing the 5-ml volumetric flask plus residue. The value for the previously weighed flask was then subtracted to give the weight of organic material in half the air sampled. This value was doubled, and the value for the blank filter was subtracted from it to give the corrected value of organic material extractable by chloroform, reported in Table 3 as micrograms per cubic meter of air sampled.

Discussion of Analytical Results

In general, the total organic material extracted with chloroform from the Pacific samples in this study is less than the amount found in air sampled in Hawaii [24] and is in closer agreement with data taken in Bermuda by Hoffman and Duce [29] than the Hawaiian values are. The only sample from this group that is high is *P-1*, which was taken mostly near the coast of Panama after being started in the harbor. Perhaps the Hawaiian data indicate the presence of some material originating from the islands, whereas the Pacific data reflect the open-ocean condition to a greater extent. Table 3 indicates that generally the sixteen-carbon saturated fatty ester group, palmitate, is the most prominent individual lipid derivative present in the air samples, as was found in the Hawaiian air and in sea slicks collected from the Bay of Panama [22]. The maximum amount of any single methyl ester derivative found was approximately 50 ng of methyl palmitate per cubic meter of air in Mediterranean air samples 10 and 12. The Pacific samples, which were generally taken much farther from land, tend to contain less material than the samples from the Mediterranean. If the quantities of all the individual esters detected in the Pacific samples are added together and then divided by the sum of the total organic material values for all the Pacific samples, we see that the lipid derivatives constitute less than 4% of the total organic material extracted by chloroform. This, too, is in general agreement with data taken in Hawaii which indicated that 5 to 15% of the total organic material was made up of lipid derivatives.

Table 3
Methyl Esters Derived From Surface-Active Material in Marine Air
(Nanograms per Cubic Meter of Air at 25 °C ± 0.11 ng/m³)

Identification:*	12	13	13:1	14	15	16	16:1	17	18	18:1	Chloroform- Extractable Material††
R. I. Standards:†	—	—	—	1400±8	—	1600±8	1664±8	—	1800±7	1848±8	
R. I. Unknowns:†	1213±9	1299±4	1347±4	1407±4	1511±11	1604±4	1663±0	1719±14	1802±7	1855±10	(μg/m ³ of air at 25°C ±0.08μg/m ³)
Mediterranean Samples	M-2 0.5	--	—	1.2	—	34.8	—	—	9.9	—	
	M-3 —†	—	1.9	3.3	—	3.1	—	—	--	—	
	M-5 —	—	—	5.2	—	37.7	—	—	21.6	—	
	M-6 —	—	1.1	12.8	—	8.7	—	—	30.7	—	
	M-7 —	—	1.2	2.1	—	17.3	—	—	—	—	
	M-8 —	—	—	3.0	—	13.4	—	—	—	—	
	M-9 —	—	—	3.9	—	32.5	—	—	5.9	—	
	M-10 —	—	2.6	9.1	—	49.7	—	—	9.1	—	
	M-11 —	—	1.3	5.4	—	16.3	—	—	1.2	—	
	M-12 4.9	1.3	1.9	8.4	5.5	49.3	—	9.3	13.0	1.6	
Pacific Samples	P-1 8.6	—	—	19.5	17.6	38.3	10.7	—	14.9	13.9	4.02
	P-2 10.3	11.3	—	18.7	16.9	2.7	--	13.0	7.8	3.5	0.82
	P-3 5.1	8.4	—	11.0	8.6	11.7	—	4.2	1.8	0.8	0.24
	P-4 —	—	—	—	0.2	2.5	—	0.4	1.0	0.3	0.57
	P-5 1.6	1.1	—	2.1	0.6	4.6	—	0.8	0.9	—	0.59
	P-6 —	—	—	0.7	0.4	10.3	—	0.8	2.4	—	0.57
	P-7 —	—	—	—	—	3.1	0.1	0.7	0.2	0.2	0.16
	P-8 —	—	—	—	—	2.4	--	0.5	0.2	—	0.08
	P-9 —	—	—	0.9	--	4.2	—	—	0.3	0.1	0.50
	P-10 —	—	—	0.9	—	—	—	—	0.4	0.4	0.16
	P-11 —	—	—	0.3	—	1.2	—	—	0.3	0.8	0.24
	P-12 1.3	—	--	0.9	—	2.9	—	—	0.2	—	0.41
	P-13 —	—	—	0.5	—	3.0	—	—	0.5	—	0.51

*Number of carbon atoms in fatty acid group: Number of unsaturated sites.
†R. I. = Retention index.

‡Dash indicates values below detectable limit.
††Data not taken for Mediterranean samples.

SURFACE CHEMISTRY

Force-vs-Area Curves of Pacific Air Samples

To the residues from the half-samples used to determine total organics, chloroform was added again up to the 5-ml mark of the volumetric flasks, and a 0.150-ml aliquot of each solution was added to the surface of distilled water in a triangular tray to form a surface film from any surface-active material that was present. The film pressure vs area isotherms were determined for each sample by gradually compressing the surface film with a movable bar. Surface tension was monitored with a 1-cm² by 0.005-cm-thick Wilhelmy plate as the area was changed [30]. A detailed description of the apparatus appears in an earlier publication [31]. Areas corresponding to film pressures at 2-dyne/cm intervals were tabulated for the interval from 2 to 28 dyne/cm. The areas tabulated for the blank were then subtracted from the areas for the samples to give corrected values. These areas were in turn multiplied by the factor 1/0.015 to give the area that would be covered by the surface-active, film-forming material in the whole sample and then divided by the number of cubic meters of air sampled. The results are shown in Fig. 3 along with a curve of 1 μ g

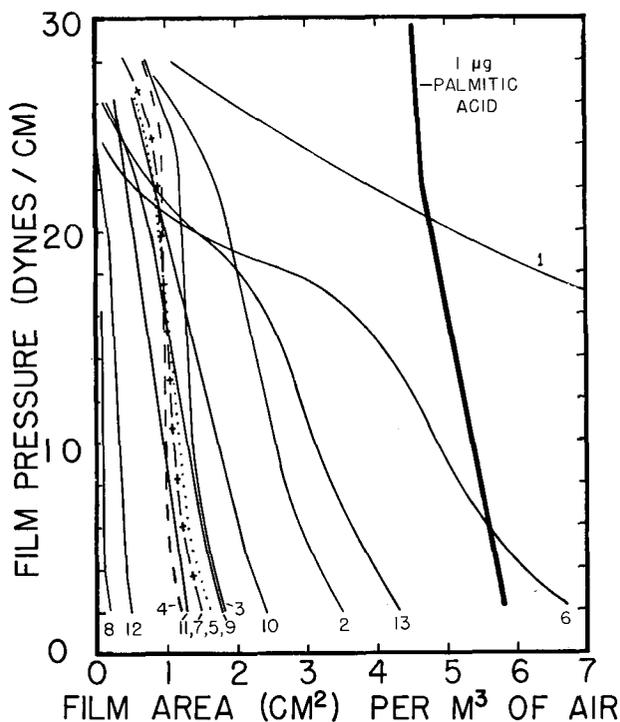


Fig. 3 — Force-vs-area curves for the surface-film forming material from the Pacific air samples normalized to the amount recovered from one cubic meter of air

of pure palmitic acid for comparison. This type of plot can be used to predict the amount of surface area of airborne droplets of a given size that could be covered by the film-forming material if this material were uniformly distributed throughout the cubic meter of air being considered. Using such a plot obviates the need to know the exact chemical composition of the film in order to predict its coverage.

The technique of constructing the final force—area curve by subtracting the force—area curve due to the blank must be accepted with caution, however, since this technique assumes that the blank material is additive with the sample material, and this may not be completely true. Also, in the data reported here, the areas due to the blanks were large in proportion to the areas due to the samples, so that errors may be significant if the two types of surface-active material differ greatly. However, if the two types of surface-active material are additive, the results will be correct. This technique should be considered only to give a first approximation until more data on the nature of surface-active material in air are available.

Relationship Between Total Organics and Force-vs-Area Curves

Each of the present series of samples required 24 hr of sampling time at an airflow rate of 60 ft³/min. However, it is often desired to take only short-duration samples, for instance, when sampling from aircraft. For several years we have been curious to see whether a good approximation of the total organic material extractable by chloroform from air samples could be estimated from force—area curves, since such curves can be obtained with extremely small samples. The curve for pure palmitic acid in Fig. 3, for example, was prepared from a total sample of 154 μg, and less material could have easily been used. To begin the study of the relationship of the force—area curves to total organics extractable by chloroform, a simple laboratory experiment was performed. The results of this experiment, used in conjunction with the data gathered from the Pacific air samples, suggest an approximate, general relationship between the mass of chloroform-extractable organic material present in an air sample and the area covered by the surface film formed from this material.

Since the gas chromatographic analysis of the surface-active material in the organic fraction of the air samples confirmed the earlier observation [24] that the palmitate group was the most prominent of the fatty substances present, force—area curves were determined for pure palmitic acid and for mixtures of palmitic acid and the straight-chain hydrocarbon eicosane, C₂₀H₄₂, to examine the effect of nonpolar materials on the shapes of force—area curves. Eicosane was chosen because its molecular weight is near that of palmitic acid. Very short-chain hydrocarbons would not be expected in the chloroform extracts because of losses due to evaporation either in nature or during the laboratory treatment of the samples.

In the laboratory each of a series of four force—area curves was generated by adding 0.035 ml of a mixture of a solution of 5.140-mg/ml eicosane and a solution of 5.144-mg/ml palmitic acid to the water surface in the same apparatus used for the force—area curves of the air sample extracts. The mixtures were in the following ratios of palmitic

acid to eicosane: 1:0, 1:1, 1:3, and 1:9, giving solutions of 100%, 50%, 25%, and 10% palmitic acid per total solute. Films spread on the water were compressed in the same manner as for the unknowns in the air samples. Measured areas were divided only by the amount of palmitic acid in the mixture in order to give the number of square centimeters covered by the film per microgram of palmitic acid in the solution. Results are shown in Fig. 4. If the area covered per microgram of palmitic acid is picked at the

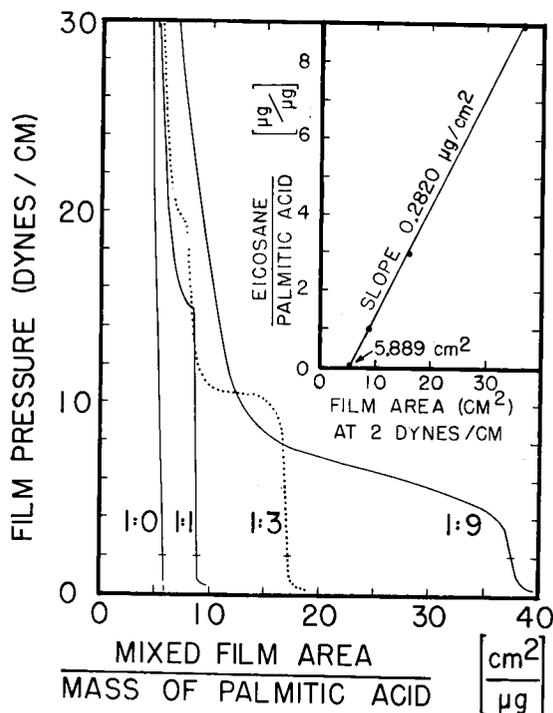


Fig. 4 — The effect of the nonpolar hydrocarbon eicosane on the shape of the force-area curve of palmitic acid

arbitrary low film pressure of 2 dyne/cm from each curve and plotted against the number of micrograms of eicosane added per microgram of palmitic acid, a straight line results (Fig. 4 inset). From the reciprocal of the slope of this line ($1/0.2820 \mu\text{g}/\text{cm}^2$) the effective change in area of the palmitic acid curve at 2 dyne/cm due to the hydrocarbon alone can be determined, and because the molecular weight is known in this particular case, the effective area per molecule of the hydrocarbon in the mixed monolayer can be found to be $16.6 \text{ \AA}^2/\text{molecule}$. However, from the work of many others [30] and from the curve for pure palmitic acid in Fig. 4, it is known that the minimum cross-sectional area of a hydrocarbon chain should be approximately 19 to $20 \text{ \AA}^2/\text{molecule}$. At a film pressure of 29.5 dyne/cm the palmitic acid curve in Fig. 4 indicates a coverage of $4.536 \text{ cm}^2/\mu\text{g}$, from which an area per molecule of $19.3 \text{ \AA}^2/\text{molecule}$ can be derived, since there are Avogadro's number of molecules per gram molecular weight.

Therefore, it must be concluded that the hydrocarbon part of the mixed film is present in greater thickness than just a single molecular layer even at the low film pressure of 2 dyne/cm. However, if the generally accepted value of minimum molecular area is divided by the effective area of eicosane in the mixed film (19.3/16.6), a factor of 1.16 is obtained which indicates that on the average there is only about 16% greater thickness than would be expected if all the hydrocarbon molecules were standing on end between the palmitic acid molecules whose heads are tied to the water surface by hydrogen bonding. Regardless of the orientation model that is postulated, the hydrocarbon must be tied to the surface by the surface-active molecules in the film, since perturbations in the force-area curves from the shape expected for pure palmitic acid are observed. Of primary significance in this report, however, is the interesting observation that the effect of the non-surface-active hydrocarbon is a linear function of the amount present at the low film pressure of 2 dyne/cm (Fig. 4 inset). This indicates that the total chloroform-extractable portion of the organic material from the air samples might be indicated by a force-area curve.

To test this hypothesis, the measured concentrations of chloroform-extractable organics from the Pacific air samples were compared to the film areas for the same samples at a film pressure of 2 dyne/cm. The data and results of a linear regression analysis are shown in Table 4. A correlation coefficient of 0.947 was found. The standard error of estimate or one standard deviation is $\pm 0.32 \mu\text{g}/\text{m}^3$. This is large compared to the average sample size of $0.68 \mu\text{g}/\text{m}^3$, but most likely reflects errors in weighing the evaporated samples coupled with deviations of the composition of the unknown films from the average composition or from the composition of the blank film. The slope of the derived line gives the empirically determined factor of $0.20 \mu\text{g}/\text{cm}^2$, relating the area covered by an average unknown spread film at 2 dyne/cm and the total organic material present in the air sample. In other words, an approximation of the total organic material present in a marine air sample may be made by collecting the sample on a filter, extracting with chloroform, determining the force-area curve, normalizing to the area covered per cubic meter of air, picking the area (cm^2) at 2 dyne/cm, and multiplying it by $0.20 \mu\text{g}/\text{cm}^2$ to give the total organics per cubic meter of air. Such an approach would be sensible, of course, only if the amount of organic material collected was too small to be accurately weighed by conventional methods, i.e. less than a milligram.

The empirically derived mass per unit area of $0.20 \mu\text{g}/\text{cm}^2$ for the film from an average marine air sample can be compared to the effective value of $0.28 \mu\text{g}/\text{cm}^2$ for the pure nonpolar hydrocarbon eicosane, and the value $0.17 \mu\text{g}/\text{cm}^2$ for the pure surface-active palmitic acid. The $0.28 \mu\text{g}/\text{cm}^2$ is from the slope of the line in the Fig. 4 inset, and the value $0.17 \mu\text{g}/\text{cm}^2$ is from the x -intercept of that line. If the empirically derived factor is compared to these two extremes, it is found to lie between them but is much closer to the value for the palmitic acid than to the value for the nonpolar hydrocarbon. Yet the gas chromatographic analysis indicated that only a very small portion (about 4%) of the total organic material was made up of the identified fatty substances. These two observations must be rationalized. Perhaps much of the chloroform-extractable material in the organic fraction is interacting with the surface-active fraction in such a way as to produce films which are very close to one molecule thick because the nonpolar materials are held at the

Table 4
 Concentrations of Organics in Air Predicted
 From Surface Film Data

Sample Number	Measured Concentration ($\mu\text{g}/\text{m}^3$)	Film Area at 2 dyne/cm (cm^2/m^3)	Predicted Concentration Using $0.20 \mu\text{g}/\text{cm}^2$
P-1	4.02	18.2	3.64
P-2	0.82	3.5	0.70
P-3	0.24	1.8	0.36
P-4	0.57	1.2	0.24
P-5	0.59	1.6	0.32
P-6	0.57	6.7	1.34
P-7	0.16	1.5	0.30
P-8	0.08	0.2	0.04
P-9	0.50	1.8	0.36
P-10	0.16	2.4	0.48
P-11	0.24	1.3	0.26
P-12	0.41	0.5	0.10
P-13	0.51	4.3	0.86
Mean	0.682	3.46	0.692
For $Y = A + BX$ where Y is the measured value			
A ($\mu\text{g}/\text{m}^3$)		- 0.0246	- 0.0246
B ($\mu\text{g}/\text{cm}^2$)		0.204	1.021
Correlation coefficient		0.947	0.947
Std. error of estimate ($\mu\text{g}/\text{m}^3$)		0.317	0.317

surface by interaction with the polar materials. It would be expected for the polar material to be made up of biologically produced high-molecular-weight components such as phospholipids, since the fatty derivatives examined in this report were probably split from larger compounds. The surface-active material must not be the major component because of the gas chromatographic results, but the nonpolar material must have less mass per unit area in the mixed film than that determined in the experiment with eicosane. This could perhaps be explained by hydrocarbons with shorter chains than eicosane being incorporated into the monolayer or by the presence of branched hydrocarbons between the surface-active molecules of the surface film. The model suggested is of large lipid molecules mixed with a wide range of molecular weights and shapes of hydrocarbons, plus other as yet unidentified compounds, making up the surface films associated with particulate material in the marine atmosphere. To confirm this model, much more work on the analytical chemistry of the organic fraction of the marine aerosol will have to be done.

Significance of the Data to Fog

What is the significance of these findings to the possibility of stabilization of fogs by natural films? First let us examine the characteristics of typical fogs and try to draw some conclusions. According to Jiusto [32], the drop size and concentration in fogs may be described by the first three lines in Table 5. The fourth line has been computed from the

Table 5
Fog Properties

Characteristic*	Radiation Fog (Inland)	Advection Fog (Coastal)
Average drop diameter	10 μm	20 μm
Typical drop size range	5-35 μm	7-65 μm
Drop concentration	200 cm^{-3}	40 cm^{-3}
Total drop surface area per m^3 air†	628 cm^2	502 cm^2
Nuclei diameter	0.08-0.8 μm	0.5 μm up
"Stabilized" drop diameter‡	0.4 μm	0.9 μm

*All items except 4 and 6 are data of Jiusto [32].

†Computed from 1 and 3.

‡Based on 0.2% coverage with a film that stops evaporation.

first two. An inspection of Fig. 3 shows that the amount of film coverage in one cubic meter of Pacific air seems in the majority of cases to cluster near the $1 cm^2$ value. In the case of coastal fogs this $1 cm^2$ of film area would be available to cover $503 cm^2$ of droplet surface area in each cubic meter of air, or about 0.2% of the area. Assuming that the film-forming material is evenly distributed and that it stops evaporation completely would lead to a final stabilized drop diameter of 0.9 μm for the coastal fog in Table 5 and a diameter of 0.4 μm for the inland fogs. These values are very close to the sizes of the

nuclei associated with the fogs reported in Table 5 by Jiusto [32], and therefore stabilization cannot be proven in this case. However, it appears that enough material is present to coat the nuclei and perhaps to slow the formation of fog because of a change in the wettability of the nuclei. An alternative interpretation can be made if it is assumed that the film-forming material is not evenly distributed, but resides only on 0.2% of the drops, retarding their evaporation in an unsaturated atmosphere. The reader is reminded, however, that the data in this report are for samples collected from clear air where no fog at all was present. A determination of the process that actually occurs requires additional experiments where fogs are collected and analyzed at least for the quantities of surface-film-forming materials that are available for coating the drops.

SUMMARY

Particulate material from 24-hr marine air samples was collected on glass-fiber filters in high-volume air samples operated aboard ship in the Mediterranean Sea and in the Pacific Ocean. The Mediterranean samples were analyzed by gas chromatography for methyl esters derived from the lipid portion of the organic material in the aerosol. Lipid material in the Pacific air samples was also determined, in addition to total organic material extractable by chloroform and the force-area curve for each sample. Total organic material extracted by chloroform ranged from 0.08 to 4.02 $\mu\text{g}/\text{m}^3$ of air, while the greatest concentration of any one methyl ester detected was 50 ng/m^3 of air. Methyl palmitate was found to be the most prominent ester detected, as was found in samples of Hawaiian air in a previous investigation. The sum of the methyl esters derived from the lipids was found to make up only about 4% of the total organics, which is also in general agreement with the Hawaiian findings. The film-forming material appears to be composed of a small amount of polar compounds diluted with a complex mixture of hydrocarbons and other unidentified compounds. The force-area curves indicated that enough film-forming material was present to cover completely the nuclei of a typical coastal fog. However, the amount of surface-active material found was only enough to cover about 0.2% of the surface area of fully formed fog. Therefore, evaporation retardation would not be likely to be significant in a fog formed in the particular parcels of air sampled in this study, but the initial formation of a fog in this air might be delayed because of a modification of the wettability of the nuclei by an encompassing coating of organic material.

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