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EFFECTS OF ORGANIC SURFACE FILMS ON EVAPORATION AND THERMAL STRUCTURE OF WATER IN FREE AND FORCED CONVECTION

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Abstract—Surface-active, film-forming compounds of the type which reduce evaporation (1-heptadecanol) and compounds which are not expected to affect evaporation (oleyl alcohol) were introduced on the surface of a 50 cm deep tank of water. Changes in heat flux and near-surface temperature structure were measured in 20°C and 28°C water with room temperature of 22°C and 30% relative humidity. Comparison with an earlier study by Jarvis indicates that the turbulence and surface renewal associated with deep water convection are important in mitigating the effects of surface-active compounds. A weak air flow (1 m s^{-1}) over the open tank resulted in dramatic changes in the frequency and amplitude of temperature fluctuations below the interface.

NOMENCLATURE

A,	amplitude of temperature spectra [°C];
c_p,	specific heat at constant pressure [J kg^{-1} °C^{-1}];
E,	evaporation rate [kg cm^{-2} s^{-1}];
f,	frequency [s^{-1}];
H,	sensible heat flux [J cm^{-2} s^{-1}];
k,	thermal conductivity of heat [J m^{-1} °C^{-1} s^{-1}];
K,	exchange coefficient for heat or moisture between the laboratory air and the air–water interface;
L,	latent heat of evaporation [J kg^{-1}];
q_a,	specific humidity of the air [kg m^{-3}];
q_s,	specific humidity for saturated air at temperature T_s[kg m^{-3}];
ST,	surface temperature;
T_a,	air temperature [°C];
T_b,	bulk water temperature [°C];
T_s,	interfacial surface temperature [°C];
T_{wb},	wet bulb temperature [°C];
ΔT,	deviation of surface temperature from bulk temperature, $T_s - T_b$.

Greek symbols

δ,	scaling depth;
γ,	surface tension [mN m^{-1}];
ρ,	density [kg m^{-3}];
σ, σ_T,	standard deviation of temperature fluctuations [°C].

INTRODUCTION

MONOMOLECULAR films have been applied to water reservoirs in the past in attempts to reduce evaporation. In particular cetyl alcohol (1-hexadecanol) was used extensively in studies by the U.S. Bureau of Reclamation, some results of which have been summarized [1]. The research reported here is related to a laboratory study by Jarvis [2], who measured the temperature at several depths in a water vessel as air of low relative humidity was blown over the surface at two speeds and with different surfactant compounds introduced on the surface during the experiments. He observed the change in surface temperature and in the temperature fluctuations, but did not measure evaporation rate or heat flux. Table 1 is a summary of Jarvis's findings with our interpretation of changes occurring in evaporation rate and in boundary layer thickness.

The practical use of these surfactant compounds to reduce evaporation from lakes and reservoirs was not always successful. The method of spreading the compound and the solvents used to disperse them modified the film coherence while surface waves and wind transport destroyed the films. The influences of circulation induced in the water by density differences and wind on evaporation retardation by monolayers are discussed in this paper. Limited success of programs to retard evaporation with organic films may be due in part to a misunderstanding of the forces involved, e.g. the author of ref. [2] says: "A rather surprising result was noted for monolayers of cetyl alcohol and stearic acid when the air flow was about 6 liters/minute at 55% relative humidity (where there was considerable convection and the surface temperature was initially the same as the bulk water). The presence of a cetyl alcohol monolayer (Fig. 7) decreased the surface temperature 0.2° to 0.3°C, even though it reduced the rate of evaporation." (The figure reference is to [2].)

Table 1. Results of the experiments of Jarvis [2] with surface active compounds on water

	Changes observed as compound was added	
Compound	Slow air flow rate (free convection)	Fast air flow rate (forced convection)
oleic acid	*ST* no change σ_T no change indicating no effect on *E*	*ST* decreased σ_T increased indicating little change in *E* but increase in δ
cetyl alcohol (1-hexadecanol)	*ST* increased σ_T decreased indicating *E* decreased	*ST* decreased σ_T increased indicating *E* not very much reduced (see comment in text) but increase in δ

This case corresponds to the lowest right hand box of Table 1, our interpretation being different from that of Jarvis. There is no evidence in the article that the evaporation was reduced very much, and from the reduction in the surface temperature and the increased temperature fluctuations, it is likely that evaporation remained large when the monolayer was applied under the condition of greater airflow.

Surfactant films on water may or may not reduce evaporation, but they all reduce the surface tension to some degree. This has the effect of increasing the stability and thickness of the water layer near the interface where molecular transfer of heat dominates. The surfactants, so to speak, *bind* this layer to the interface tending to make it less mobile. These two effects of surfactants will change the total heat flux and the stress transfer [3] respectively. As a consequence, thickness and the temperature structure of the interfacial boundary layer will also change [4]. The macroscale effects of these two properties are investigated in this report; the mechanisms occurring on the microscale are beyond the scope of this study.

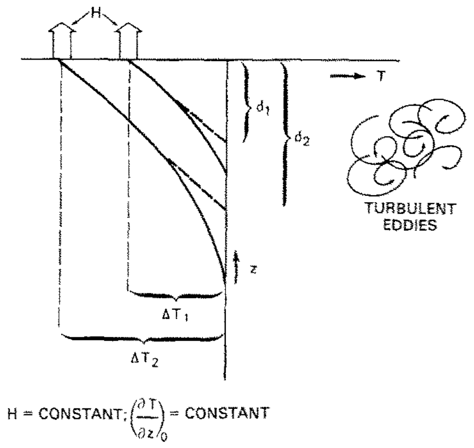

FIG. 1(a). Illustration of the relationship of surface temperature deviation, ΔT, and boundary layer scaling depth, δ, to heat flux under conditions of free convection.

In order to interpret Jarvis's observations and those to be presented here, one must have an understanding of how monomolecular surface films affect the heat flux and temperature structure of water, and a general understanding of how the temperature profile depends on heat flux and stirring of the water. The sketches in Fig. 1 illustrate some of these relationships for a clean water surface. In particular, the deviation of the surface temperature from that of deeper water, ΔT, depends on the heat flux and on the thickness of the interfacial boundary layer. This boundary layer is defined as the layer where molecular transfer dominates. A scaling depth of this layer, δ, is illustrated in Figs. 1(a) and 1(b). δ is an abstraction obtained by extending the temperature gradient, $\partial T/\partial z$, at the interface linearly to the temperature of the bulk water. Heat transferred to the interface by molecular conduction $[-k\,\partial T/\partial z]$, where k is molecular heat conductivity of water, balances the surface heat flux, which is externally determined by the

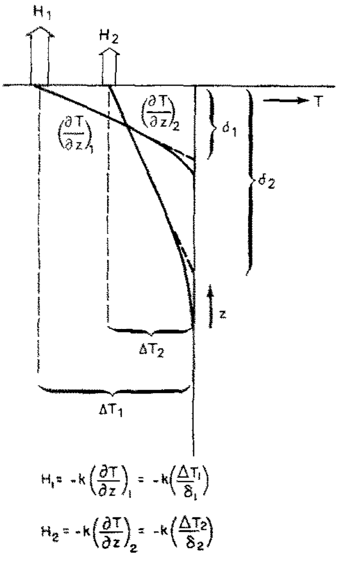

FIG. 1(b). Illustration of the effects of turbulent mixing in the water on the values of ΔT and δ for constant heat flux.

conditions on the air side of the interface. The linear gradient is an approximation. The true shape away from the interface is exponential or can be given in terms of error functions [5, 6].

Figure 1(a) illustrates what is known about the scaling depth, δ, and the value of ΔT for two values of heat flux under conditions of free convection in water with a clean surface [7, 8]. As heat flux increases, the temperature drop from the interior to the interface increases and the layer depth decreases. Thus, if we increase the heat flux by raising the water temperature, the ΔT becomes larger and as a consequence the standard deviation of temperature fluctuations, $\sigma_T(z)$, also increases, being proportional to heat flux (or to ΔT) in free convection [7]. The relative importance of gravity and surface tension forces (the Marangoni effect) on clean water in free convection were discussed in ref. [8].

Figure 1(b) illustrates how the mean temperature distribution changes as mechanical stirring of the water (by wind or other mechanisms) reduces the thickness of the boundary layer from δ_1 to δ_2, assuming that the upward heat flux at the air–water interface remains constant.

EXPERIMENTAL PROCEDURES

A rather large convection tank, 0.50 × 0.75 m cross-section, 0.50 m depth, has been used to study heat transfer and thermal structure in the boundary layer below an air–water interface in the past [7]. In later studies salt was added to the tank [9] and high frequency surface waves were produced [10]. Both of these additions resulted in substantial changes in heat flux and thermal structure. The effects are primarily originating at the interface, e.g. salt left behind in evaporation becomes concentrated immediately below the interface [11, 12] and surface waves create convergence and divergence zones at the interface influencing its structure [13, 14]. The present work employed the techniques of the previous studies with the only change being the addition of monomolecular films at the interface.

The convection tank was cleaned with detergent and rinsed repeatedly. It was then filled with water, which had passed through a carbon filter. At the top of the tank a coating of paraffin wax had been applied, and a movable barrier fitting tightly between the sides of the tank was pushed across the tank moving any surface film ahead of it. This film was then allowed to spill over the edge, the paraffin wax coating eliminating the possibility of adherence to the plexiglas walls. The cleanliness of the surface was then ascertained by measuring the surface tension with a du Nouy-ring 'interfacial tensiometer' (Kruss, W. Germany), which is an *in situ* device employing the ring (or du Nouy) method for evaluating surface tension. The swept water surface produced surface tension values consistent with clean water (e.g. 71.2 mN m^{-1} at a temperature of 30°C and 72.7 mN m^{-1} at 20.3°C).

The pure compounds listed in Table 2 were applied to the surface of the tank with a microsyringe, and the resulting surface tension of the film-covered surface was measured periodically during the course of each experiment. The liquid film-forming compounds, oleyl alcohol or methyl oleate, were added directly to the water surface in small quantities which were in excess of that required to form a complete monomolecular layer. The liquids spread spontaneously over the surface, and the excess liquid remained as an unspread droplet in equilibrium with the spread monomolecular layer. Under such self-regulating conditions, the surface tension remained constant during the experiment and is a measure of the equilibrium collapse pressure of the film. The solid 1-heptadecanol was added to the tank surface as a 1% solution in chloroform. The spread film of this material was compressed to its collapse pressure by moving the surface barrier a few cm. During the course of the experiments with 1-heptadecanol, the surface tension varied only a few tenths of a mN m^{-1}.

The monolayer-forming compounds selected for this study differ only slightly from those examined by Jarvis [2], and their physicochemical properties and effects on gas exchange and microscale hydrodynamics are expected to be nearly the same. 1-heptadecanol is a linear molecule capable of close packing in a homogeneous surface film. The tightly packed monolayer acts as a molecular barrier to the passage of gas (water) molecules [15], and because of strong intermolecular interactions, its film behaves like a rigid sheet with slow film spreading properties. The oleyl alcohol (9-octadecen-1-ol, *cis* isomer), on the other hand, is a more bulky molecule due to its permanently bent structure as a consequence of the *cis* double bond. Since its molecules have less coherence, films of oleyl alcohol are more fluid, spread much more readily than the linear 1-heptadecanol, and do not retard evaporation by a molecular barrier effect. Surface films of both compounds immobilize the air–water interface and modify its fluid properties (e.g. capillary wave

Table 2. Surface-active compounds applied to the convection tank

Name	Source	γ_1, Surface tension at 20°C (mN m^{-1})
Oleyl alcohol	The Hormel Institute freshly distilled	41.3
1-Heptadecanol, 99%	Lachat Chemicals	31.7
Methyl oleate, 98%	Lachat Chemicals	57.5

damping [16]). Methyl oleate (methyl ester of 9-octadecenoic acid, *cis* isomer) is similar in its properties to oleyl alcohol, except that its effect on surface tension is somewhat less.

Two types of experiments were performed. In the first, the changes in heat flux and surface temperature drop were measured as the compounds were applied. In the second, temperature fluctuations at various depths were measured before and after the application of the compounds. Both types of experiments were performed with 20°C water and with 28°C water, and in several cases the effect of a fan driven airflow over the tank corresponding to a $1\ \mathrm{m\,s^{-1}}$ wind was also measured. The temperature and humidity of the room were monitored with a ventilated Assman psychrometer. Both dry and wet bulb temperatures remained constant within ±0.3°C in all the experiments.

The heat flux was determined by calorimetry. A mercury-in-glass thermometer with 0.01°C marking was used to determine the temperature of the bulk fluid vs time. Corrections for heat losses through the walls are discussed in ref. [7]. The interface temperature was read with an infrared radiation thermometer (Barnes PRT5) to 0.1°C accuracy, and the fluctuating temperature in the water was measured with a resistance film probe (Thermosystems) using a precision bridge of in-house design [7]. The sensor is 15 μm in diameter and 1.2 mm long. It is positioned by a computer-controlled horizontal and vertical traverse mechanism [7]. The temperature data were recorded in digital form on magnetic tape using a computer (Raytheon 707), which was also used to calculate statistics and frequency spectra. Wind velocity was measured at the position of the water surface using a handheld anemometer (Hastings Air Meter). Unfortunately, time did not permit us to repeat each experiment or to perform all possible permutations. However, the consistency of the observed effects allows us to draw some general conclusions.

RESULTS

Heat flux and interfacial temperature

The effects of adding surfactant monolayers to the water surface on the heat flux and the ΔT (or the surface temperature) can be seen in Figs. 2 and 3. In Fig. 2 the tank is at a temperature close to the air temperature, so that any net heat loss is entirely due to evaporation. Initially, the heat flux is $55.6\ \mathrm{W\,m^{-2}}$ and $\Delta T = -0.3$°C. When 1-heptadecanol is added, the heat loss is approximately halved, but it does not vanish, ΔT is < 0.1°C. The tank surface was then cleaned and its cleanliness was tested by measuring the surface tension, after which oleyl alcohol was applied. With oleyl alcohol the net heat flux remains close to the value for the clean surface. It is actually a little larger. This may not be of statistical significance due to a combination of experimental error, effects of disturbance during cleaning, slight air movements, etc. The difference in ΔT between clean and oleyl alchol covered surface is also insignificant.

The $1\ \mathrm{m\,s^{-1}}$ wind was then made to blow over the tank. Note that the average heat flux in that whole period tripled, but no attempt was made to calculate the heat flux separately for clean and film covered surfaces. The ΔT is larger with wind indicating that the effect of an increase in heat flux dominates over the boundary layer thinning caused by the wind stress. From a differential form of the heat conduction equation we have

$$\Delta T \propto Q \cdot \delta. \qquad (1)$$

See also ref. [17].

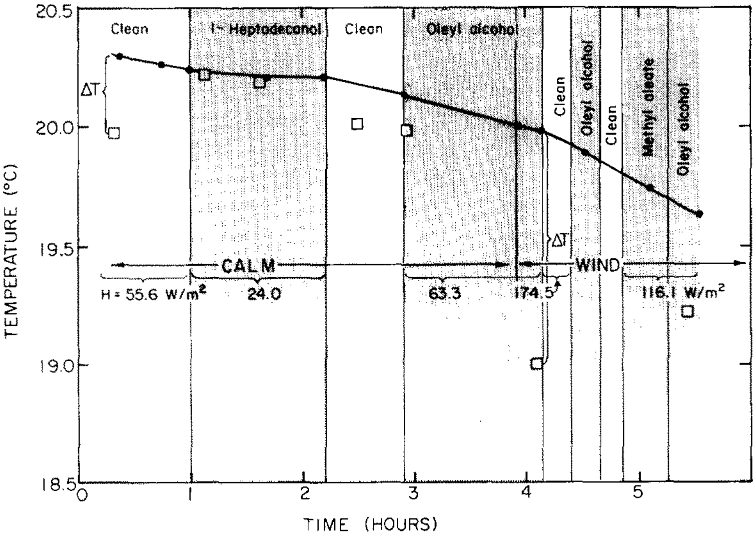

FIG. 2. Temperature vs time in the laboratory tank as film-forming compounds are added to the surface for calm or $1\ \mathrm{m\,s^{-1}}$ wind. Bulk water temperature was 20.3°C at the start. Psychrometric readings of the laboratory air gave $T_{\mathrm{dry\,bulb}} = 22.2$°C, $T_{\mathrm{wet\,bulb}} = 12.4$°C. —— bulk water temperature, □ interfacial temperature. Heat flux values apply to the linear portion of the bulk temperature curve immediately above.

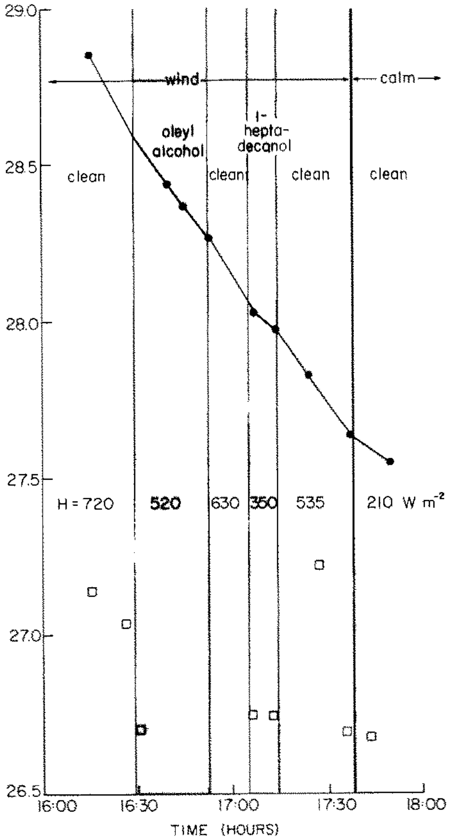

FIG. 3. Temperature vs time in the laboratory tank as compounds are added on the surface and wind of 1 m s^{-1} is superimposed. Bulk water temperature was 28.9°C at the start. Psychrometric readings of the laboratory air gave $T_{\text{dry bulb}} = 22.3^\circ\text{C}$, $T_{\text{wet bulb}} = 12.0^\circ\text{C}$. —— bulk water temperature, □ interfacial temperature. Heat flux values apply to the linear portion of the bulk temperature curve immediately above (not corrected for wall losses of the order of 10%).

Figure 3 illustrates the sequence of events when monolayers are imposed on 28°C water with 1 m s^{-1} wind blowing over it. Assuming a constant cooling of the tank between the two periods with a clean surface, one can estimate that the heat flux in the time period 16:29–16:50 in Fig. 3 would have been 675 W m^{-2} if the surface had remained clean. With the surface covered with oleyl alcohol, the heat flux was only 520 W m^{-2} which implies about a 20% reduction in evaporation rate. (Some of the heat flux is due to sensible heat transfer, which is not affected by the presence of surfactants.) 1-heptadecanol is again very effective, causing a reduction by about 50%. Reducing the wind speed from the low value of 1 m s^{-1} to calm on clean water reduces the heat flux by approximately the same amount. The ΔT values were large and variable. It is characteristic of convective conditions to produce large amplitude low frequency surface temperature variations. Nonetheless, when the surface temperature is averaged over 2 min, one can discern a tendency for the ΔT to be several tenths of a °C larger when a surfactant is present.

Temperature fluctuations below the surface

The resistance film probe in all experiments was positioned 2 mm below the surface at a central position in the tank. The depth can be determined quite accurately since the vertical stepper motor resolution corresponds to 12.5 μm. The interface is approached from above by manual stepping until the meniscus attaches itself to the probe. Then the computer is instructed to move the probe down 2 mm, which it performs by transmitting the required number of pulses. The choice of collecting time series rather than horizontal traverses was made because with monolayers on the surface, we wished to keep the interface undisturbed. Horizontal traverses across the tank were made to ascertain that our chosen location was representative of the average conditions. The film sensor was positioned at an angle to the vertical such that cold plumes descending from the interface would not travel along the probe mount axis. Data were recorded over a period of 11 min in each condition. Figure 4 is an example of a record obtained in 20°C water with a clean surface and with and without the 1 m s^{-1} wind blowing.

Second, third, and fourth moments of the temperature fluctuations were calculated for several compounds with and without 1 m s^{-1} wind (Fig. 5). The values of skewness and kurtosis are included in this figure, but not much significance should be attached to the absolute values of these higher moments. Oleyl alcohol on the surface and wind separately or together appear to increase standard deviation and skewness, while kurtosis is little affected by either. 1-heptadecanol, because of its ability to reduce evaporation in the calm condition, evidently reduces temperature fluctuations to nil.

When forming the ratio $\sigma_{\text{oleyl}}/\sigma_{\text{clean}}$ in the calm condition (σ being standard deviation of the temperature fluctuations), we find a ratio of approx. 1, while with the wind the ratio is 2–3. It appears that oleyl alcohol transmits the pressure fluctuations from the air more efficiently. However, traveling surface waves of any appreciable amplitude were not observed.

When the water temperature was raised to 28°C, the σ values in calm with or without compounds are all larger than in 20°C and independent of the surface condition. When the 1 m s^{-1} wind is imposed, the recorded values are up to 25% larger or smaller, which in the warm water case may be due to the large variability of the system.

Temporal scales

Frequency spectra of the temperature fluctuations were also calculated from the time series obtained at 2 mm depth with a sampling rate of 30 Hz. Records of 1024 values (33 s) were used with the Raytheon computer fast Fourier transform routine to produce a spectrum after a hanning filter [18] had been applied. Twenty individual spectra were than averaged together but no smoothing over spectral bands was applied. Since there is a slow temperature decrease as the tank

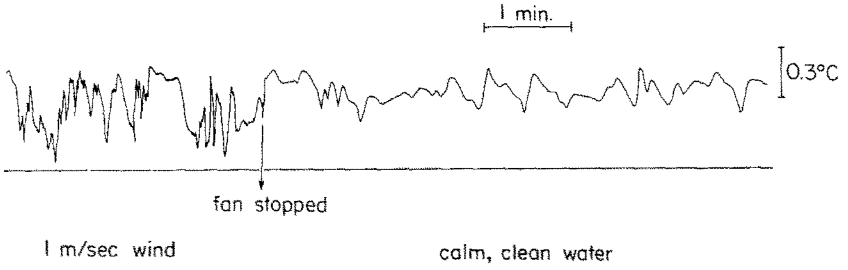

FIG. 4. Record of temperature fluctuations vs time measured at 2 mm depth in 20°C clean water.

cools, the effect of removing this trend was tested with indistinguishable results. The spectra presented here have been nondimensionalized with the variance σ^2 and frequency f. Thus, the ordinate is $fA^2/\sigma^2\Delta f$, where A is the spectral amplitude and Δf is spectral interval. Thus, differences between spectra below a clean water surface and below a surfactant covered one, or between spectra for calm and for 1 m s^{-1} wind, are not simply due to differences in mean heat flux. In order to demonstrate the representativeness of the spectral estimates, Fig. 6 shows two mean spectra produced from 16 and 20 individual spectra, respectively, in clean water and two with oleyl alcohol covered surface, both with the 1 m s^{-1} wind blowing.

The spectra will be examined for changes in temporal scales of the motion. These results can be compared to conclusions drawn for frequency spectra when the surface is calm versus when it is covered with 6 Hz waves [10].

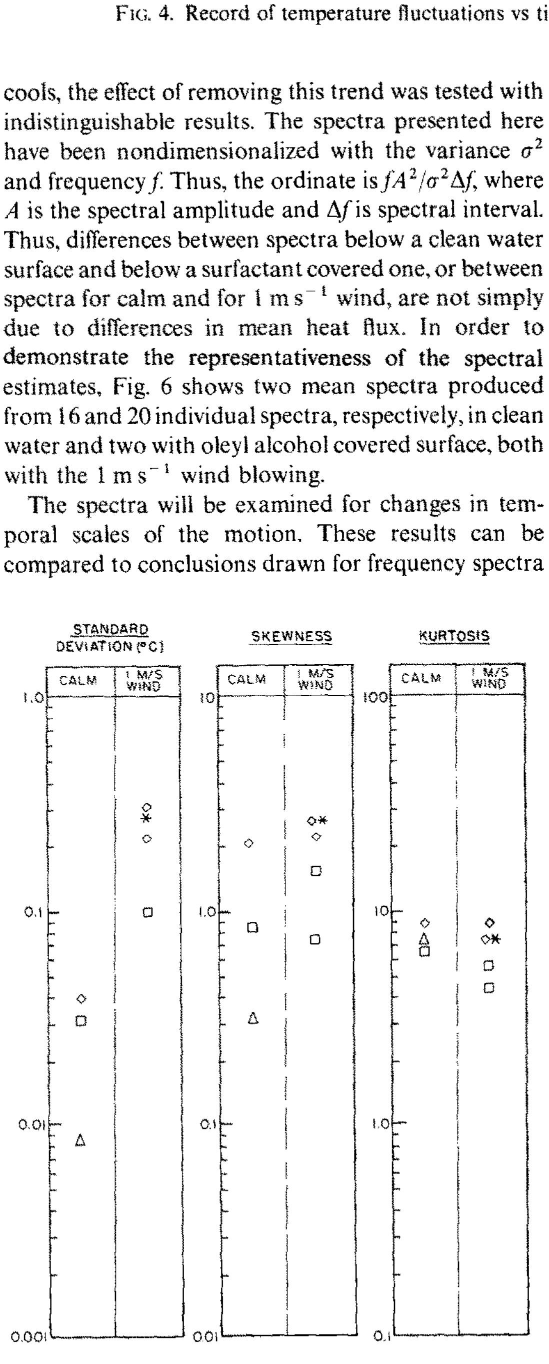

FIG. 5. Statistical moments calculated from time series obtained at 2 mm depth in 20° water for calm and 1 m s^{-1} wind. □ clean water, ◇ oleyl alcohol, △ 1-heptadecanol, × methyl oleate.

Spectra obtained with clean surface, with oleyl alcohol, and with 1-heptadecanol monolayers are seen in Fig. 7. The water was 20°C with no wind blowing. The large emphasis on frequencies >0.1 Hz in the case of 1-heptadecanol is due to the total variance in the denominator of the ordinate being small with this compound, i.e. one order of magnitude less than for clean water. A clean water surface and an oleyl alcohol covered one produce very similar spectra.

When the 1 m s^{-1} wind is superimposed (Fig. 8) we see that the general shape of the spectra is changed. A spectral peak due to the fan is seen at 2 Hz. In general, the spectra have most of their contributions (nondimensional amplitude $>10^{-2}$) at frequencies <1.0, 0.6 and 0.4 Hz, respectively, for clean, methyl oleate and oleyl alcohol, while it was much more evenly distributed without the wind. (Methyl oleate was used in this experiment to include a compound which has less surface activity and no molecular barrier to gas exchange.)

In 28°C water with a clean surface the difference between calm and wind is much less pronounced than in 20°C water. Figures 9(a) and 9(b) contrast these two cases. However, at 28°C the shape of the spectrum changes with wind in the same sense as in the 20°C case, i.e. to greater relative emphasis on the low frequencies. That the change is less implies that the buoyancy driven fluctuations are so great as to dominate over those introduced by a 1 m s^{-1} wind. The relative importance of buoyancy and forced convection cannot be quantified or generalized in these simple experiments, partly because the wind sets up large scale, low frequency motions in the tank, which are specific to the experimental setup.

A shift to lower frequencies with unstable stratification is typical also for a system as different as the turbulent atmospheric surface layer [19].

When surfactant monolayers are added to either a calm or wind disturbed tank at 28°C, the changes in spectral shape or total variance are minimal. At 20°C the net heat loss is solely due to evaporation since a small sensible heat flux into the tank would occur for $T_a = 22°C$. At 28°C, on the other hand, both sensible, H, and latent heat, LE, fluxes produce losses to the tank, about 15% being due to sensible heat flux, which

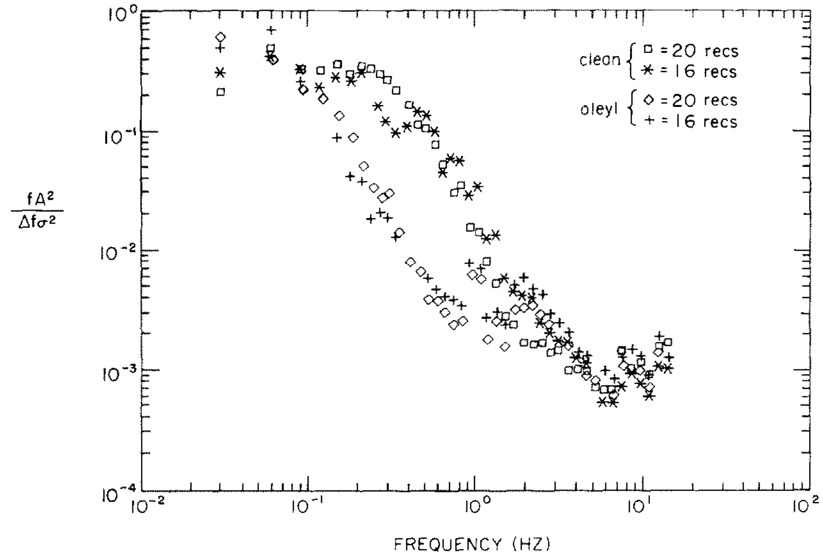

FIG. 6. Nondimensional spectra of temperature fluctuations at 2 mm depth in clean water: $H = 175\,\mathrm{W\,m^{-2}}$, $\gamma = 72.5\,\mathrm{mN\,m^{-1}}$, oleyl alcohol covered surface: $H = 155\,\mathrm{W\,m^{-2}}$, $\gamma = 40\,\mathrm{mN\,m^{-1}}$ (T_b 20°C, $T_{\mathrm{drybulb}} = 22.1°\mathrm{C}$, $T_{\mathrm{wetbulb}} = 12.8°\mathrm{C}$). The 1 m s^{-1} wind was blowing. For each condition there are two realizations, one averaged over 20, the other only 16 individual records. □ 20* 16 recs clean water, ◇ 20 + 16 recs oleyl alcohol.

is unaffected by the monolayers if T_s remains constant. The estimates of the relative importance of the two turbulent heat fluxes are obtained by forming the Bowen ratio, H/LE, and estimating H and LE by the so-called bulk method. One further assumes that the mechanisms for humidity and sensible heat transport in the atmosphere, represented by an exchange coefficient, K, are the same, viz.

$$\frac{H}{LE} = \frac{\rho c_p(T_s - T_a)K}{L\rho(q_s - q_a)K} \tag{2}$$

where the quantities on the RHS except K are known or were measured.

Heat exchange by infrared radiation would be directed into the tank for 20°C water and out of the tank for 28°C water and would be unaffected by monolayers. The relative importance of radiative and evaporative cooling cannot be determined without knowing the value of K. However, we can state that substantial heat loss occurs in the 28°C case even if evaporation is retarded, while this is not true for 20°C water. Since spectral shape and total variance of

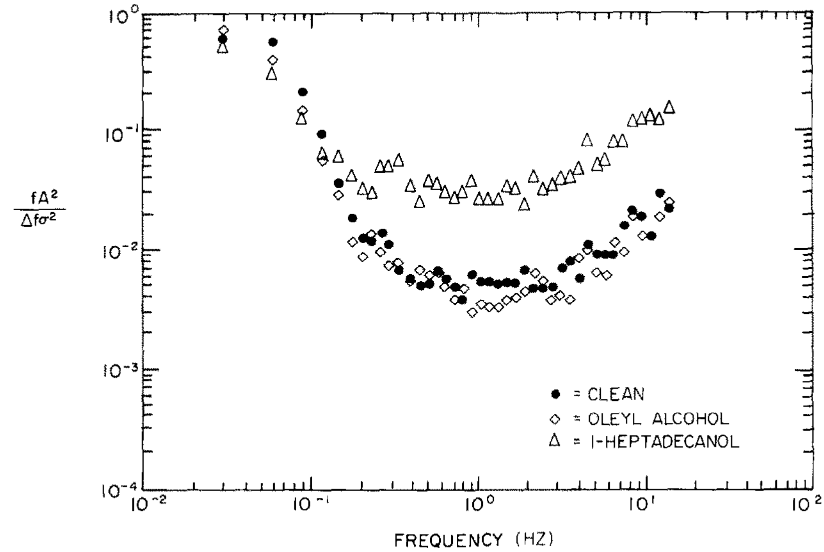

FIG. 7. Nondimensional frequency spectra of temperature at 2 mm depth in 20°C water, no wind. ● clean water $H = 56\,\mathrm{W\,m^{-2}}$, $\gamma = 72.7\,\mathrm{mN\,m^{-1}}$; ◇ oleyl alcohol $H = 44\,\mathrm{W\,m^{-2}}$, $\gamma = 41.3\,\mathrm{mN\,m^{-1}}$; Δ 1-heptadecanol $H = 24\,\mathrm{W\,m^{-2}}$, $\gamma = 31.7\,\mathrm{mN\,m^{-1}}$.

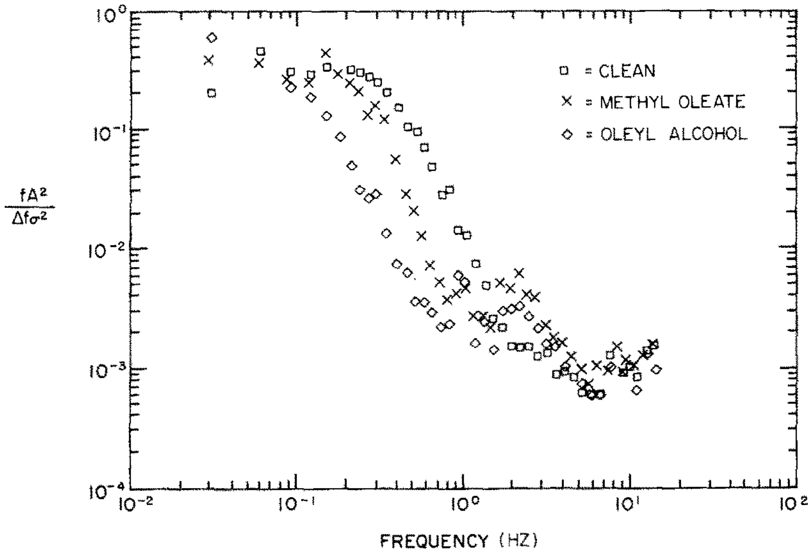

FIG. 8. Nondimensional frequency spectra of temperature fluctuations at 2 mm depth in water for 3 surface conditions with $1\,\mathrm{m\,s^{-1}}$ wind blowing. $T_{\mathrm{bulk}} = 19.8°\mathrm{C}$, $T_{\mathrm{drybulb}} = 21.8°\mathrm{C}$, $T_{\mathrm{wetbulb}} = 12.4°\mathrm{C}$. □ clean water $H = 175\,\mathrm{W\,m^{-2}}$, $\gamma = 72.7\,\mathrm{mN\,m^{-1}}$; × methyl oleate $H = 115\,\mathrm{W\,m^{-2}}$, $\gamma = 57.5\,\mathrm{mN\,m^{-1}}$; ◇ oleyl alcohol $H = 155\,\mathrm{W\,m^{-2}}$, $\gamma = 41.3\,\mathrm{mN\,m^{-1}}$.

temperature fluctuations are little affected by monolayers on 28°C water, it indicates that buoyancy driven motions mitigate the surfactant effects.

SUMMARY AND DISCUSSION

These simple but quantitative experiments on effects of surfactant monolayers on heat flux and on temperature structure and temperature fluctuations in the water have shown that the conditions within the bulk of the water itself are important, i.e. when buoyancy forces are large in the water, effects of surfactants are reduced. They also show that even a weak air flow, equivalent to a $1\,\mathrm{m\,s^{-1}}$ wind results in substantial changes. The heat flux becomes larger and the temperature spectrum shifts to lower frequencies. At 20°C these effects were modified by the surfactant monolayers while at 28°C the presence of surfactants was irrelevant both in the calm and the wind stirred condition.

Even though effects of the absolute temperature in regard to evaporation have been reported previously [20], they would not have included effects of the bulk dynamics of the water since only layers of water approx. 3 mm thick were studied in Petri dishes.

It appears from the present study that increased fluctuations and a drop in surface temperature obser-

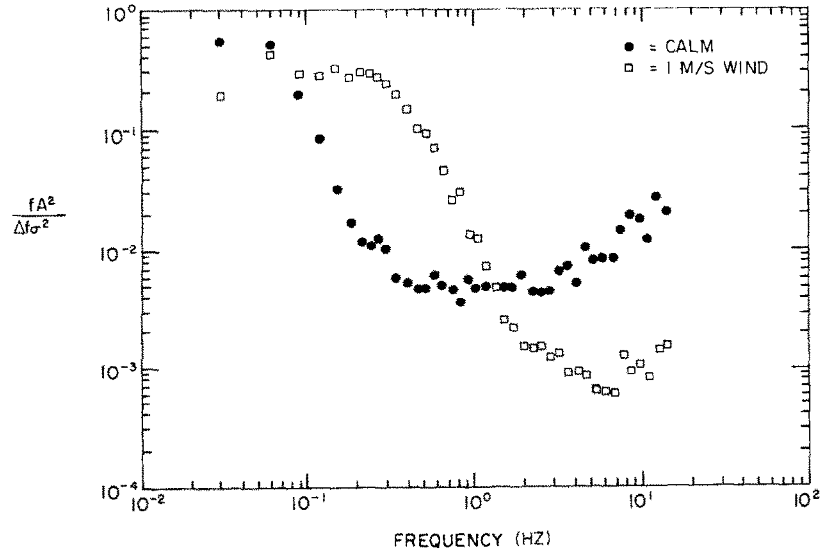

FIG. 9(a). Nondimensional frequency spectra of temperature in water at 2 mm depth. (a) 20°C water: ● calm, □ $1\,\mathrm{m\,s^{-1}}$ wind (b) 28°C water: ● calm, □ $1\,\mathrm{m\,s^{-1}}$ wind. $T_{\mathrm{drybulb\,cases}} \sim 22°\mathrm{C}$, $T_{\mathrm{wetbulb\,cases}} \sim 12°\mathrm{C}$.

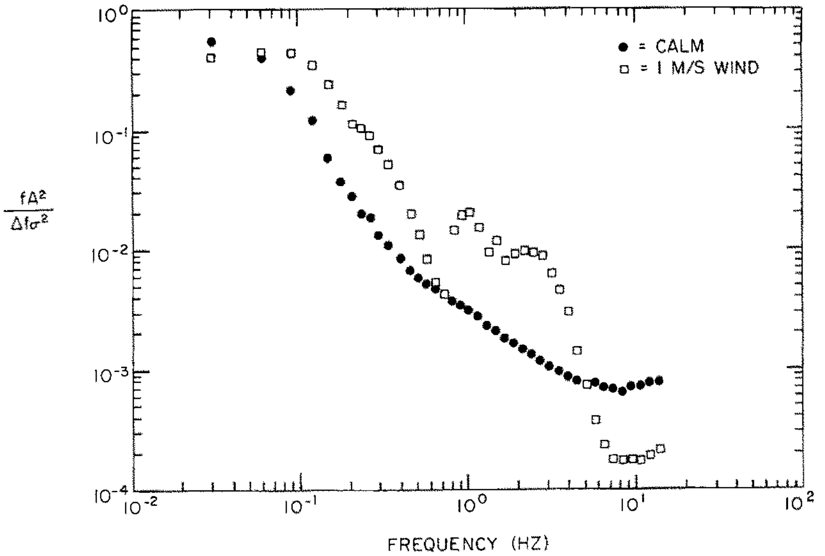

FIG. 9(b). Nondimensional frequency spectra of temperature in water at 2 mm depth, 28°C water, ● calm, □ 1 m s^{-1} wind. $T_{\text{dry bulb cases}}$ ~22°C, $T_{\text{wet bulb cases}}$ ~12°C.

ved in ref. [2], when a cetyl alcohol monolayer was applied with high flow rate of dry air, are not consistent with a statement that evaporation was retarded (at least it could not have been by very much). Even with a more rigid interface and therefore thicker boundary layer, a relatively large heat flux is required to maintain the surface temperature 0.4°C lower than the bulk. It is unlikely that the surface is completely coherent with a 'strong' airflow, but a certain reduction in mobility of the surface must be assumed to explain the drop in temperature, which requires a deeper layer with a steep temperature gradient. This is consistent with the larger temperature fluctuations, which can then be produced by vertical motions of the water past the temperature sensor. Our study of heat flux has shown that several monolayers reduce evaporation, but not so much as to eliminate ΔT.

One of us (KBK) has attempted to drive evaporation without airflow by establishing a water vapor density gradient through a porous metal lid a short distance < 1 mm above a water tank without success. T. Foster (personal communications) also told of problems when attempting to drive evaporation with a vacuum. It may well be that in both cases monolayers of surfactants were responsible for inhibiting evaporation (even though care had been taken to work with clean water). Even a weak airflow seems to mitigate the effects of the pure surfactants employed in this study.

The implication then is that the internal dynamics of a water body and the external conditions in the atmosphere above are as important as the chemical properties of a surfactant in affecting the evaporation rate.

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EFFETS DE FILMS SUPERFICIELS ORGANIQUES SUR L'EVAPORATION ET LE CHAMP THERMIQUE DE L'EAU EN CONVECTION NATURELLE OU FORCEE

Résumé—On introduit à la surface d'une masse d'eau de 50 cm de profondeur des agents du type qui réduit l'évaporation (1-heptadecanol) et des composés qui ne modifient pas l'évaporation (alcool oléique). Des changements de flux thermique et de champ de température au voisinage de la surface sont mesurés dans l'eau à 20°C et 28°C avec une température ambiante de 22°C et 30% d'humidité relative. Une comparaison avec une étude antérieure de Jarvis indique que la turbulence et le renouvellement de la surface associés a la convection en profondeur sont importants et affectent les effets des agents surfactifs. Une faible ventilation d'air (1 m s^{-1}) au dessus du réservoir provoque des changements considérables dans la fréquence et l'amplitude des fluctuations de température sous l'interface.

DER EINFLUSS VON ORGANISCHEN OBERFLÄCHENFILMEN AUF DIE VERDAMPFUNG UND DIE THERMISCHE STRUKTUR VON WASSER BEI FREIER UND ERZWUNGENER KONVEKTION

Zusammenfassung—Oberflächenaktive, filmbildende Verbindungen, die die Verdampfung behindern (Heptadekanol) und Verbindungen, von denen kein Einfluß auf die Verdampfung erwartet wird (ölhaltige Alkohole), werden auf die Oberfläche eines 50 cm tiefen Wassertanks aufgebracht. Die Veränderungen der Wärmestromdichte und des Temperaturprofils an der Oberfläche wurden in Wasser von 20 und 28°C bei Raumtemperaturen von 22°C und einer relativen Feuchte von 30% gemessen. Der Vergleich mit einer früheren Studie von Jarvis zeigte, daß Turbulenz und Oberflächenerneuerung, welche mit der Konvektion im tiefen Wasser zusammenhängen, wichting für die Milderung der Auswirkungen der oberflächenaktiven Verbindungen sind. Ein schwacher Luftstrom (1 m s^{-1}) über dem offenen Tank bewirkte eine drastische Änderung in der Frequenz und der Amplitude der Temperaturschwankungen unterhalb der Oberfläche.

ВЛИЯНИЕ ОРГАНИЧЕСКИХ ПОВЕРХНОСТНЫХ ПЛЕНОК НА ИСПАРЕНИЕ И ТЕРМИЧЕСКУЮ СТРУКТУРУ ВОДЫ ПРИ СВОБОДНОЙ И ВЫНУЖДЕННОЙ КОНВЕКЦИИ

Аннотация—Поверхностноактивные соединения, способные образовывать снижающие испарение пленки (типа 1-гептадеканол), и соединения, которые не оказывают влияния на испарение (масляный спирт), наносились на поверхность слоя воды глубиной 50 см. Проводились измерения величины теплового потока и структуры температуры у поверхности воды с температурой 20°С и 28°С при температуре окружающей среды в 22°С и относительной влажности 30%. Сравнение с ранее проведенным Джарвисом исследованием показывает, что турбулентность и обновление поверхности, обусловленные конвекцией в глубоком слое воды, значительно ослабляют роль поверхностноактивных соединений. Слабое течение воздуха (1 м $сек^{-1}$) над открытой поверхностью воды приводит к сильным изменениям частоты и амплитуды температурных колебаний под границей раздела фаз.