Reports

Evaporation Retardation by Monolayers: Another Mechanism

Abstract. *The effects on evaporation rates of the suppression of small waves by monolayers, which heretofore have been neglected, are considered to be a major mechanism for retarding evaporation under wind.*

In order to conserve water to meet the ever-increasing demand, it is necessary to suppress the rate of evaporation from lakes and reservoirs. The idea of applying a film of oil to retard evaporation is very old, but more recently some special substances have been used, which spread spontaneously on water to produce a film one molecule thick, the so-called monolayer. All related work on this aspect of the problem has been categorized as the "retardation of evaporation by monolayers" (*1*).

Evaporation involves several transport processes. They may be classified as follows:

1) Transport below the interface (convective circulation): A continuous exchange exists between the water molecules in the bulk and in the surface. This convective circulation near the interface is induced by evaporation cooling.

2) Transport across the interface (vaporization): Because of a net input of thermal energy to the water, the free energy of the water molecules increases, enabling some molecules to escape from the interface.

3) Transport above but near the interface (diffusion): The vapor near the interface is transported away from the interface through molecular or eddy diffusion.

4) Transport far above the interface (convection): Through diffusion the vapor reaches the edge of the boundary layer and is carried away by the airflow.

Fundamental studies in laboratories on the retardation of evaporation by monolayers have been concerned primarily with the effect of the chemical structure of the film, since it is directly related to the most relevant process (vaporization). During these studies, the other transport conditions described above were held constant and the effects of the other variables, such as the volume of the air layer and any motion in the air, were reduced to a minimum. This kind of experiment, in which an attempt has been made to relate the rate of evaporation to the state of compression of film, has also been adopted to evaluate the retardant for engineering applications (*1*). The other transport processes, convective circulation, diffusion, and convection, have not been considered (*2*) to be directly affected by monolayers.

In addition to providing resistance to evaporation, the film on the water surface also suppresses ripples generated by the wind (*3, 4*), a natural variable. Recent studies on wind-wave interactions (*5*) have demonstrated that ripples constitute the dynamic roughness of the wind-disturbed water surface and that the wind shear is closely related to the surface roughness. In other words, the wind structure over the natural body of water is governed to a large extent by ripples riding on top of long waves. If these ripples are suppressed by the film, the consequent change in the wind structure should directly affect the diffusion and convection of vapor from the water surface. I point out here that this last effect may be significant enough to constitute the major mechanism responsible for evaporation retardation by monolayers in the field.

Continued vaporization from a free water surface causes a continued increase in the vapor pressure in the air just above the surface; the rate of vaporization therefore decreases while the rate of condensation increases. When the air is saturated with vapor, the molecules cross the interface in both directions at the same rate. Undoubtedly, there exists a gradient of vapor distribution above the surface. The saturation occurs only very close to the surface. It is then obvious that the rate of evaporation depends on the transport of vapor along the gradient away from the surface, or

$$E = -\rho k_{\mathrm{w}} \frac{dq}{dz} \tag{1}$$

where E is the rate of evaporation, ρ is the mass density of moist air, k_{w} is the vapor transfer coefficient, q is the specific humidity, and z is the elevation. The specific humidity, the mass of water per unit mass of moist air, is proportional to the vapor pressure e and the ambient atmospheric pressure p (*6*),

$$q \approx \frac{e}{p} \tag{2}$$

Substituting Eq. 2 into Eq. 1, we have

$$E \approx k_{\mathrm{w}} \frac{\rho}{p} \frac{de}{dz} \tag{3}$$

The transport is a molecular process when there is no air motion or when the airflow is laminar. In the field, however, wind is generally present and turbulent, having an eddy viscosity k_{m} expressed as

$$k_{\mathrm{m}} = \frac{u_*^2}{(du/dz)} \tag{4}$$

where u_* is the shear velocity of the wind and u is the wind velocity at an elevation z above the mean water surface. Adopting Eq. 4 and further considering that the velocity gradient within a turbulent boundary layer is proportional to the shear velocity, we have from Eq. 3

$$E \approx \frac{k_{\mathrm{w}}}{k_{\mathrm{m}}} \frac{\rho u_*}{p} \frac{de}{dz} \tag{5}$$

If we adopt Reynolds' analogy (*6*) in which one assumes that the transport of vapor is the same as that of momentum, we have

$$E \approx \frac{\rho u_*}{p} \frac{de}{dz} \tag{6}$$

For a steady turbulent wind blowing over a large natural body of water, the parameters ρ, p, and de/dz are not very different for various wind velocities. The evaporation rate is therefore proportional to the shear velocity of the wind.

For engineering use or field measurement, the shear velocity of the wind and the distribution of vapor pressure are not measured; another form of Eq. 6, the so-called Dalton's law, has generally been used (6):

$$E = (a + bu)\ (e_s - e) \qquad (7)$$

where a and b are experimentally determined coefficients, u and e are the wind velocity and vapor pressure, respectively, measured at a certain elevation from the water surface, and e_s is the saturated vapor pressure. The constant a is added to take care of the case without wind. Most laboratory and field data have been compiled and correlated with this formula. The evaporation data is most commonly related to the wind velocity instead of the shear velocity.

The effects of an artificial slick upon the wind boundary layer over the sea surface have been studied recently (*4*). The sea slick was generated by a spontaneous spreading of the film-forming chemical, oleyl alcohol (9-octadecen-1-ol, the *cis* isomer). Vertical wind profiles were measured for the clean sea surface and for the surface with a sea slick, and were found to follow the logarithmic profile

$$\frac{u}{u_*} = \frac{1}{\kappa} \ln\left(\frac{z}{z_0}\right) \qquad (8)$$

where κ is the Karman constant and z_0 is the roughness length. Values of z_0 calculated from the measured profile are reproduced in Fig. 1.

It may be seen in Fig. 1 that, as the wind velocity increases from 1 to 4 m/sec, the roughness length increases sharply. This sharp increase is due to the rapid growth of small waves in this region, and the transition of the wind boundary layer from smooth to rough presumably takes place within this range of wind velocity (*7*). For the present purpose, it is sufficient to say that the stem of the roughness growth with the wind velocity for the clean sea surface is clearly demonstrated. During the passage of the slick, a monolayer, the small waves were observed (*4*) to be damped and the roughness length, as expected (*5*), changes drastically (see Fig. 1). The transition of the wind boundary layer was delayed to a higher wind velocity, as the stem of the roughness growth shifted to wind velocities between 5 and 7 m/sec. Below this velocity range, the surface is smooth; above this velocity range, the roughness length with the sea slick is comparable with that for the clean surface. The latter effect is probably due to the disruption of the surface film by wind. If this is true, an upper limit of the wind velocity may be imposed on the application of monolayers for the retardation of evaporation.

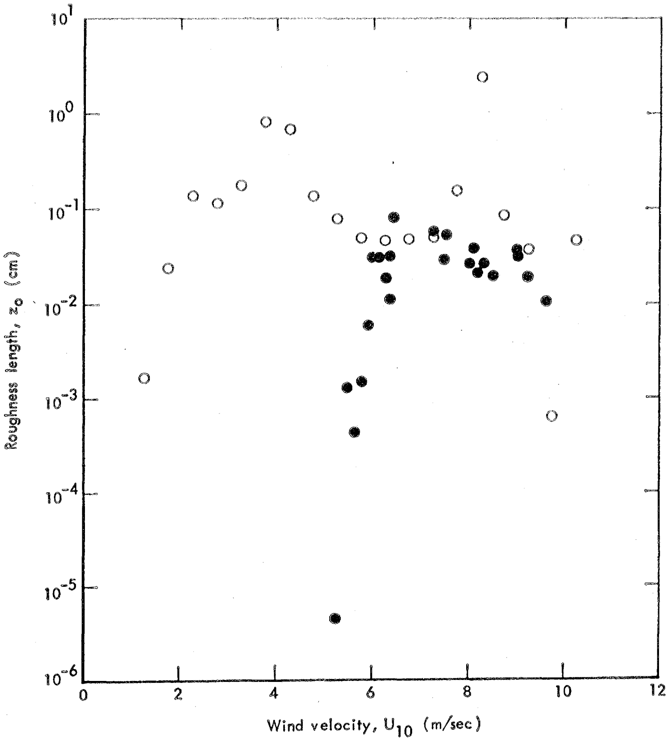
The shear velocity of the wind calculated from the roughness length for both cases, with and without sea slick, are shown in Fig. 2. Because of the limitations of the data, it is hard to compare the shear velocity for the same wind velocity, but it is clear that before the disruption of the monolayer, for the same shear velocity, the wind velocity for the surface with a sea slick is about twice that for the clean surface. My discussion of the implications of these results (see below) will be limited to low wind velocities less than those needed to cause the disruption of the surface film.

A summary of results from more significant field studies was compiled by La Mer and Healy (*2*). Most results were obtained under the same wind conditions for cases with and without monolayers; the same wind condition was specified as under comparable wind velocities. It was shown (*2*) that the application of monolayers cut down the evaporation by about one-third.

As discussed above, in order to have the same shear velocity, the wind velocity for the surface with a sea slick must be twice as great as that for the clean surface. Because the wind stress coefficient c varies rather weakly with the wind velocity u, for the same wind velocity, the shear velocity,

$$u_* = \sqrt{c}\ u$$

for the surface with a sea slick is therefore about one-half of that for the



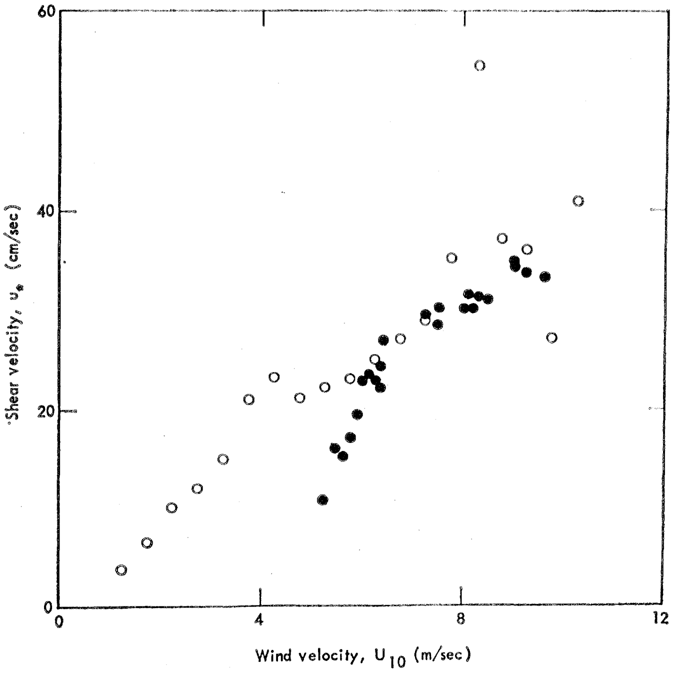


Fig. 1 (left). Comparison of surface roughness over a sea slick and over a clean surface [from (*4*)]. (Open circles) Clean surface; (solid circles) sea slick. [Courtesy of the American Meteorological Society, Boston, Massachusetts] Fig. 2 (right). Comparison of wind shear velocities measured over a sea slick and over a clean surface. (Open circles) Clean surface; (solid circles) sea slick.

clean surface. Consequently, the comparison of the rate of evaporation for cases with and without monolayers on the basis of comparable wind velocities was actually obtained under quite different wind shear velocities. Since the wind shear velocity, rather than the wind velocity, is believed to be the governing parameter for evaporation, and since the difference in the wind shear velocity is great enough to account for the claimed reduction, I conjecture that the retardation of evaporation due to monolayers in the field under turbulent wind may actually be due to the wave-damping effects of these layers.

Note added in proof: A note (*8*) on the effect of the wave-suppressing characteristics of macromolecular films in retarding evaporation appeared after this report was submitted for review. The mechanism proposed herein is, nevertheless, entirely different from that suggested by Garrett. He considered that the wave suppression acts to diminish the area of the water surface in contact with air. On the other hand, I consider that the wave suppression alters the wind structure. In other words, Garrett's interpretation is based on geometry, an area change of the air-water interface, whereas my interpretation is based on dynamics, a change of transport processes above the air-water interface.

JIN WU

Hydronautics, Incorporated,
Pindell School Road,
Laurel, Maryland 20810

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Methyl Mercury and Inorganic Mercury Collection by a Selective Chelating Resin

Abstract. *A commercially available chelating resin selectively and quantitatively collects methyl mercuric and inorganic mercuric forms of mercury to the exclusion of all other metals studied, except the noble metals. Both forms of mercury can be collected from* pH *1 to 9. Collected mercury is readily eluted with a slightly acid, 5 percent solution of thiourea, and the resin can be reused for many cycles. Selectivity,* pH *effects, capacity, and elution characteristics of the resin are described. A resin-loaded paper composed of 50 percent resin and 50 percent cellulose shows properties similar to those of the loose resin.*

The purpose of this report is to summarize available tests on a chelating resin, Ionac SRXL (*1*), which should provide new opportunities for analysis and for recovery of mercury from industrial and natural aqueous solutions. Previous studies have shown that the resin is highly selective for gold and platinum metals, but its usefulness for mercury had not been considered (*2–4*). My results indicate that the resin has a high affinity for dissolved mercury in both the methyl mercury and the inorganic forms.

Koster and Schmuckler, original developers of the resin (*2*), explain the selectivity for noble metals by stating that it will ". . . bind only ions with the d^8 electronic configuration forming square planar complexes. . . ." They further explain that the resin has redox properties because of double bonds, enabling it to collect a species such as Pt^{4+} which is reduced to the Pt^{2+} and then bound as a square planar complex. The mechanism for Hg^{2+} and CH_3Hg^+ collection has yet to be determined.

The properties of SRXL resin were studied in two ways. Data were obtained with resin as received from the manufacturer and with resin-loaded paper, consisting of 50 percent SRXL resin (− 325 mesh) and 50 percent cellulose (*4*). Comparisons were made between the resin behavior in a column and its behavior in the resin paper. All solutions were prepared with reagent-grade chemicals, and tracer studies were performed with the ^{203}Hg radioactive isotope and a NaI(Tl) detector.

Selective collection of noble metals, especially gold, from solutions containing high concentrations of more common metals has been reported (*2–4*). I have found also that the resin quantitatively collects dissolved mercury as methyl mercury or as inorganic mercury from solutions of high common metal concentration. A column of resin, 30 by 15 mm, quantitatively collected 100 μg of Hg^{2+} from 250 ml of chloride solutions of iron, nickel, copper, and zinc in amounts up to 10 g/liter. Radioactive ^{203}Hg was used to determine the completeness of collection (Table 1).

Selectivity tests for mercury in the CH_3HgCl, $HgCl_2$, and $Hg(NO_3)_2$ forms were conducted by filtering solutions containing a mercury salt mixed with various metals through paper disks (3.5 cm in diameter) containing SRXL resin; the solution was passed six times through each disk. The disks were rinsed with dilute HCl solution, dried, and analyzed by fluorescent x-ray spectrography. From solutions containing Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Hg^{2+} or CH_3Hg^+, only the mercury was detected on the disks; the instrument conditions were sensitive to less than 5 μg for any one of the metals. Neutron activation analysis of SRXL paper disks which were used to collect gold from solutions containing nitrate or chloride salts of metals failed to show any common metal collection (*4*).

Comparisons with another resin, Chelex 100, reported to have a high affinity for Hg^{2+}, show that the Chelex 100 resin fails to collect the methyl mercury form although it does quantitatively collect Hg^{2+}. A paper specially prepared (H. Reeve Angel & Co.) with the Chelex 100 resin, was compared chromatographically with the SRXL

Table 1. Mercury ion (Hg^{2+}) collection from solutions of high metal concentration.

Conc. of Fe, Ni, Cu, and Zn mixture (g/liter)	^{203}Hg (count/min)*			Hg collected (%)
	Before	After	Background	
0.5	5202	217	224	~ 100
1.0	5318	214	213	~ 100
5.0	5498	225	209	~ 100
10.0	5510	225	209	~ 100

* Average of four or more 1-minute counts.