

Reduction of Evaporation of Natural Water Samples by Monomolecular Films

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A capacidade de filmes monomoleculares de álcoois graxos em reduzir a evaporação de amostras naturais de água, coletadas em dois reservatórios de São Paulo (Guarapiranga e Billings), foi estudada em laboratório. As reduções da evaporação foram determinadas diretamente, medindo-se o volume de água evaporado dos recipientes de teste após certo tempo. Filmes mistos de hexadecanol e octadecanol apresentaram alto potencial de redução da evaporação (até 57%) e persistência na superfície da água, por cerca de 48 horas. Uma breve discussão sobre a melhor eficiência desses filmes mistos na redução da evaporação de água é também apresentada.

The ability of monomolecular films of fatty alcohols in reducing evaporation of natural water samples collected from two reservoirs in São Paulo (Guarapiranga and Billings) was studied in the laboratory. Evaporation reductions were determined directly by measuring the volume of water evaporated from the test recipients after a certain period of time. Mixed films of hexadecanol and octadecanol showed high potential of evaporation reduction (up to 57%) and persistence on the water surface of *ca.* 48 hours. A brief discussion on the better efficiency of these mixed films in reducing water evaporation is also presented.

Keywords: water, evaporation, fatty alcohols, monomolecular films, surface tension

Introduction

Water is the most precious natural resource available to mankind. Most of our usable fresh water is retained in lakes and reservoirs, but this type of storage allows for the greatest loss of water by evaporation. The increasing demand for municipal and industrial fresh water, and the current increase in the global temperature indicate that it is necessary to employ techniques for reducing evaporation aiming at the conservation of water supplies.

It has been known for a long time that monomolecular films of certain surfactants can retard water evaporation.¹ This seems to be the only viable technology for reducing the evaporative losses of water from reservoirs.² For many years, important studies in laboratory scale were carried out in order to identify the optimal substances and conditions for reducing water evaporation.³⁻⁵ Among the surfactants tested, biodegradable fatty alcohols of low toxicity presented the highest resistance to water evaporation, especially 1-hexadecanol and 1-

octadecanol.² The first field experiment was conducted in Australia in the beginning of the 50's, and the obtained evaporation reductions of 30% called attention of many research groups and governments around the world.^{6,7} In the following decades, several experimental and theoretical works were published, and the main conclusions were collected in a review published in 1986.⁸

Although the spreading of a monomolecular film on the surface of a reservoir has been considered as an alternative technology for fresh water conservation by the United Nations Environment Programme, only a few investigations on this subject have been reported in the last years.⁹ Among the most recent works on this subject, it is worth to mention the use of soluble surfactants, which showed little influence on evaporation reduction.¹⁰ New methods for accurately measuring evaporation reduction have also been developed, and may be useful for investigating details of the mechanisms behind the effect of monolayers on water evaporation.^{11,12} Other works have focused attention on the influence of mixed films on evaporation reduction, and showed that the evaporation resistance of films of a pure fatty alcohol can be decreased or increased by adding small amounts of other surfactants, the latter

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effect being ascribed to the less defective structure of the mixed films studied.¹³⁻¹⁵

A common feature of all laboratory investigations on evaporation reduction is the use of pure water, usually deionized and bidistilled. The general concern that leads to this practice is related to the possible contaminations on the water surface that would eventually change the properties of the films and then interfere with the results, which is valid. On the other hand, since the studied films are to be applied on the surface of real reservoirs, it is also important to verify the efficiency of such films in reducing evaporation of natural water samples. Even knowing that changes in composition may occur in the course of the experiments due to isolation of the collected samples from the environment, such studies would yield more realistic results related to the potential of evaporation reduction and the persistence of the films on the water surface, which are desirable to be known before applications in the field.

Bearing this in mind, we have verified the potential of monomolecular films of fatty alcohols in reducing the evaporation of water samples collected from the reservoirs Guarapiranga and Billings, both located in the South Region of São Paulo. Mixed films of hexadecanol and octadecanol presented higher potential of evaporation reduction than films of the pure surfactants, and the persistence on the water surface was estimated to be 48 hours. The better efficiency of the mixed films in reducing water evaporation is also discussed.

Experimental

Volumes of 5 L of water samples were collected from the Guarapiranga (SL: 23°40'27", WL: 46°43'40") and Billings (SL: 23°46'09", WL: 46°29'50,2") reservoirs using disposable plastic bottles, according to the procedures recommended by the Standard Methods.¹⁶ The samples were kept in ice during transport to the laboratory, and all necessary material was previously prepared so that the experiments started immediately after arriving at the lab. For each water sample, independent evaporation reduction experiments were performed using identical Petri dishes (diameter 9 cm) and round shallow trays (diameter 31 cm) initially filled with 20 and 2000 mL, respectively. The test recipients were left exposed to the air at the same conditions of temperature, relative humidity and air circulation for intervals of 22 h (Petri dishes) and 72 h (trays). Evaporation reductions (ER) were estimated by comparing the differences in the water volume evaporated from the recipients (V_{evap}) with and without a film (control) at the end of the experiments. This simple and direct method has been used before with tap water, and the results obtained

are in good agreement with the literature.¹⁷⁻¹⁹ For the experiments presented here, the uncertainty in the measurements of the water volume remaining in the recipients (using Pasteur pipettes and graduated cylinders) was less than 3%. Fatty alcohols as hexadecanol (99%) and octadecanol (95%) were purchased from Aldrich and used without further purification. Monomolecular films of pure hexadecanol (C_{16}), pure octadecanol (C_{18}) and mixtures of 1:9 and 2:8 (m:m) of C_{16} and C_{18} ($C_{16}:C_{18}$) were formed on the surface of the samples by depositing small volumes of chloroform solutions (8 mmol L^{-1}) from a microsyringe (Hamilton) until saturation of the surface was observed (formation of stable lenses). Surface tension (γ) was measured by the ring method using a Du Noüy tensiometer (Fischer Scientific, model 21). At the beginning of the experiments with Petri dishes, the value of γ was determined for each sample. In the experiments with trays, small volumes of the solution of $C_{16}:C_{18}$ were replaced periodically to verify the changes in the film stability (spreading or lens formation) due to biodegradation. The samples contained no suspended material visible to the naked eye, and no changes in turbidity were observed at the end of the experiments. In order to study the efficiency of mixed films of fatty alcohols, small crystals of hexadecanol and octadecanol were placed on the surface of water (MilliQ) on a Petri dish and γ was monitored as a function of time.

Results and Discussion

During sampling at Guarapiranga reservoir the presence of certain species of algae on the water surface was noticed, which gave this sample a slight green color, not observed in the sample collected at Billings. In order to check other possible surface contaminations, γ was measured before monolayer deposition. No difference in γ was found among the values for the samples and those obtained for tap and deionized and bidistilled water (73 mN m^{-1} , at 20°C), probably indicating no previous contamination by surfactants. After monolayer deposition until saturation of the surface, the lower value of 50 mN m^{-1} was found in the samples from both reservoirs when covered with a $C_{16}:C_{18}$ film (1:9). Monolayers of pure C_{16} and C_{18} yielded the same value of 53 mN m^{-1} for both water samples.

Tables 1 and 2 show the results of experiments with Petri dishes initially filled with 20 mL of each sample. After 22 hours, it was observed that, for the Guarapiranga samples, the highest evaporation reduction of 38.5% was obtained with the mixture of $C_{16}:C_{18}$, whereas for the Billings samples the same value of 35.8% was obtained with the mixed film and with a pure octadecanol film (Table

Table 1. Volume of water evaporated from Petri dishes (V_{evap}) and percentage of evaporation reduction (ER) for samples from the reservoirs Guarapiranga and Billings covered with films of C_{16} , C_{18} and $C_{16}:C_{18}$ (1:9). The initial volume of water in the dishes was 20 mL

Sample		Guarapiranga		Billings	
Dish	Film	V_{evap} (mL)	ER (%)	V_{evap} (mL)	ER (%)
1 (Control)	No Film	13.0	-	18.7	-
2	C_{16}	10.0	23.0	14.8	20.8
3	C_{18}	9.2	29.2	12.0	35.8
4	$C_{16}:C_{18}$	8.0	38.5	12.0	35.8

1). Different reasons could be responsible for this, as the formation of the monolayer at the moment of deposition, the homogeneity of the surfactant solutions or even small changes in the air circulation around the test recipients. Thus, in order to confirm the high efficiency of mixed films in reducing water evaporation, the sample collected from Billings reservoir (apparently less contaminated) was chosen for another experiment using films of $C_{16}:C_{18}$ in the proportions of 2:8 and 1:9 (Table 2).

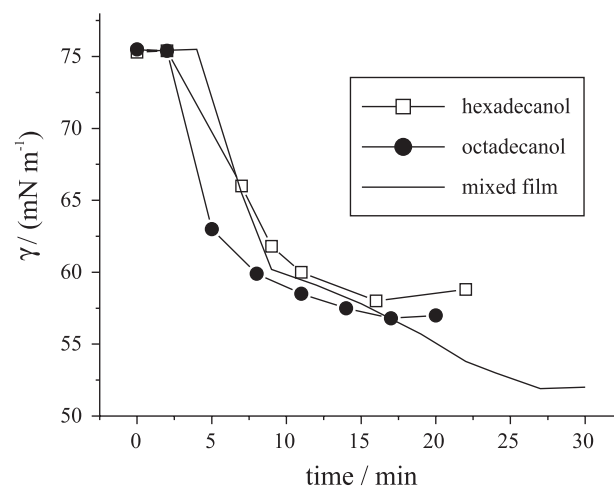
Table 2. Volume of water evaporated from Petri dishes (V_{evap}) and percentage of evaporation reduction (ER) for samples from Billings reservoir covered with mixed films of $C_{16}:C_{18}$ containing 2:8 and 1:9 of C_{16} and C_{18} . The initial volume of water was 20 mL

Dish	Film	V_{evap} (mL)	ER (%)
1 (Control)	No Film	13.0	-
2	$C_{16}:C_{18}$ (2:8)	7.0	46.1
3	$C_{16}:C_{18}$ (1:9)	5.6	57.0

Surprisingly, the results presented in Table 2 showed even higher values of evaporation reduction (46.1 and 57%). The differences in the values of evaporation reduction presented in Tables 1 and 2 (and especially in those obtained with the mixture $C_{16}:C_{18}$, 1:9) indicate that large fluctuations may occur when the films are deposited on natural water samples. This might be due to variations in the composition of the samples in each test recipient as a consequence of the poor homogeneity of the natural sample tested. On the other hand, these results confirm that mixed films of $C_{16}:C_{18}$ have a high potential for reducing water evaporation. The following considerations are related to this particular feature of these mixed films.

It is well known that C_{18} films can reduce water evaporation better than C_{16} films, but higher evaporation reductions for $C_{16}:C_{18}$ mixed films when compared to films of the pure components would not be expected. The higher resistance of mixed films to evaporation was reported by Barnes and La Mer using pure water.²⁰ These authors found that mixed films of fatty alcohols showed higher resistance to water evaporation at surface pressures below 15 mN m^{-1} . In the present experiments, however, the value of 50 mN m^{-1} for γ obtained with the water surface of both samples saturated by a film of $C_{16}:C_{18}$, (1:9) corresponds to a surface pressure of 23 mN m^{-1} , a value a little higher than that

reported previously.²⁰ An explanation for both the present result with mixed films and that reported by Barnes and La Mer may be the synergistic effect observed in mixtures of hexadecanol and octadecanol, which leads to a larger decrease in γ due to the formation of a more condensed film than those of the pure alcohols.²⁰ An example of this property is shown in Figure 1, where the results of three experiments with pure and mixed films are plotted together.

**Figure 1.** Decrease in surface tension (γ) as a function of time for monomolecular films of hexadecanol, octadecanol, and a mixture (1:9) spread from small crystals (~ 2 mm in diameter) deposited on the water surface. (Obs.: the total mass deposited on the water surface for each case was 0.0059 g for C_{16} , 0.0054 g for C_{18} and 0.0059 g for the mixed film).

The curves in Figure 1 show the final value for γ of water when the films are in equilibrium with the crystals deposited on the surface, that is, the equilibrium spreading pressure (ESP). It is well known that films of fatty alcohols are able to decrease γ of water by nearly 40 units (high ESP), and the values obtained from Figure 1 showed high deviation from the expected ones (16.5, 18.5, and 23.5 mN m^{-1} for pure C_{16} , pure C_{18} and the mixture, respectively). However, it is also recognized that films of fatty alcohols spread from solid particles may be affected by factors such as the perimeter of the crystals in contact with water, the historic of the solid sample (*i.e.*, previous melting), aging, and the possible formation of hydrates, leading to values of ESP much lower than 40 mN m^{-1} .²¹⁻²³ In the experiment of Figure 1, the small crystals of the alcohols were used as

received without previous melting or mixing. Nevertheless, when crystals from both pure alcohols were deposited on the water surface ("mixed film" curve) the decrease in γ was nearly 6 units lower than those obtained with the deposition of crystals of the pure alcohols alone. The final values of γ do not represent the ESP of these films, but indicate the formation of a more condensed monolayer on the water surface. Although not totally conclusive with respect to the mechanism behind the observed effect, the results indicate that mixed films of $C_{16}:C_{18}$ may present higher evaporation reductions in a larger range of surface pressures (up to $\sim 23 \text{ mN m}^{-1}$ instead of 15 mN m^{-1} or below), and that the potential of such mixed films in reducing water evaporation may be greater than previously assumed.

The experiments carried out on shallow trays were also used to test the persistence of the film on the water surface. The results presented in Tables 3 and 4 were all obtained with a mixed film of $C_{16}:C_{18}$ in the proportion of 1:9. From Table 3, the highest evaporation reduction (19.2%) was observed with the sample from Billings reservoir, which may be ascribed to the fact that this sample was less polluted than the other. This was confirmed when the persistence of the film was checked by periodically depositing small volumes of the surfactant solution on the surface of the samples in the course of the experiment. The initial volumes of the $C_{16}:C_{18}$ solution added were 66 and 68 μL for the samples from Guarapiranga and Billings, respectively. Subsequent additions of smaller volumes were made every 24 h, and the observed results are shown in Table 4.

The formation of a lens on the water surface indicates that the surface is still saturated by the film previously deposited, which remains in equilibrium with the lens. Despite the fact that different volumes were added, it is clearly seen in Table 4 that saturation of the surface of the Guarapiranga samples was maintained for 48 h (two

additions), with the film spreading completely on the last day of experiment (after 72 h), whereas for the Billings sample the repeated observation of lenses on the surface indicated that it was kept nearly saturated during the three days of experiment, with the film presenting longer stability. Knowing that films of fatty alcohols biodegrade quickly by biochemical oxidation and that the Guarapiranga samples were more polluted, it is reasonable to assume that the film degraded faster in this sample than in the other.²⁴ For the samples used in this study, the results in Table 4 also suggest that the proper interval for replacing the film would be around 48 h.

Conclusions

Mixed films of hexadecanol and octadecanol presented high potential for reducing evaporation of the natural water samples studied and persistence of *ca.* 48 hours on the water surface. The larger evaporation reductions obtained with such films is ascribed to a synergistic effect between the surfactants, which leads to the formation of a more condensed film on the water surface. Since experiments with natural water samples can provide more realistic results, the previous knowledge of the potential of evaporation reduction and the persistence of the films on the surface of the reservoir to be treated may also be useful to estimate the costs for the application of this technology.

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Table 3. Volume of water evaporated from shallow trays (V_{evap}) and percentage of evaporation reduction (ER) for samples from the reservoirs Guarapiranga and Billings covered with a film of $C_{16}:C_{18}$ (1:9). The initial volume of water in the trays was 2000 mL

Sample		Guarapiranga		Billings	
Dish	Film	V_{evap} (mL)	ER (%)	V_{evap} (mL)	ER (%)
1 (Control)	No Film	590	-	563	-
2	$C_{16}:C_{18}$	500	15.2	455	19.2

Table 4. Effect observed after periodic deposition of small volumes of a solution of $C_{16}:C_{18}$ (1:9) on the surface of the water samples in the trays (a microsyringe of 10 μL was used)

Sample	Guarapiranga			Billings		
	3	3	15	6	10	4
Observed Effect	Stable Lenses	Stable Lenses	Complete Spreading	Stable Lenses	Unstable Lenses	Stable Lenses

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