

# Impact of Artificial Monolayers on Water Quality, Potable Water Treatment, Human Health and Lake Ecology

Pam Pittaway

November 2011



Urban Water Security Research Alliance  
Technical Report No. 57

Urban Water Security Research Alliance Technical Report ISSN 1836-5566 (Online)  
Urban Water Security Research Alliance Technical Report ISSN 1836-5558 (Print)

The Urban Water Security Research Alliance (UWSRA) is a \$50 million partnership over five years between the Queensland Government, CSIRO's Water for a Healthy Country Flagship, Griffith University and The University of Queensland. The Alliance has been formed to address South East Queensland's emerging urban water issues with a focus on water security and recycling. The program will bring new research capacity to South East Queensland tailored to tackling existing and anticipated future issues to inform the implementation of the Water Strategy.

For more information about the:

UWSRA - visit <http://www.urbanwateralliance.org.au/>  
Queensland Government - visit <http://www.qld.gov.au/>  
Water for a Healthy Country Flagship - visit [www.csiro.au/org/HealthyCountry.html](http://www.csiro.au/org/HealthyCountry.html)  
The University of Queensland - visit <http://www.uq.edu.au/>  
Griffith University - visit <http://www.griffith.edu.au/>

Enquiries should be addressed to:

The Urban Water Security Research Alliance  
PO Box 15087  
CITY EAST QLD 4002  
  
Ph: 07-3247 3005  
Email: Sharon.Wakem@qwc.qld.gov.au

Project Leader – Stewart Burn  
CSIRO Land and Water  
37 Graham Road  
HIGHETT VIC 3190  
Ph: 03-9252 6032  
Email: Stewart.Burn@csiro.au

Author: National Centre for Engineering in Agriculture, University of Southern Queensland

Pittaway, P. (2011). *Impact of Artificial Monolayers on Water Quality, Potable Water Treatment, Human Health and Lake Ecology*. Urban Water Security Research Alliance Technical Report No. 57.

### Copyright

© 2011 University of Southern Queensland. To the extent permitted by law, all rights are reserved and no part of this publication covered by copyright may be reproduced or copied in any form or by any means except with the written permission of University of Southern Queensland.

### Disclaimer

The partners in the UWSRA advise that the information contained in this publication comprises general statements based on scientific research and does not warrant or represent the accuracy, currency and completeness of any information or material in this publication. The reader is advised and needs to be aware that such information may be incomplete or unable to be used in any specific situation. No action shall be made in reliance on that information without seeking prior expert professional, scientific and technical advice. To the extent permitted by law, UWSRA (including its Partner's employees and consultants) excludes all liability to any person for any consequences, including but not limited to all losses, damages, costs, expenses and any other compensation, arising directly or indirectly from using this publication (in part or in whole) and any information or material contained in it.

### Cover Photograph:

Description: Agricultural landscape - preparing to sample the water column of Logan's Irrigation Storage, after sampling the natural microlayer during the calm of dawn.  
Photographer: Andrew Palmer  
© NCEA, USQ

## **ACKNOWLEDGEMENTS**

This research was undertaken by the University of Southern Queensland as part of the South East Queensland Urban Water Security Research Alliance, a scientific collaboration between the Queensland Government, CSIRO, The University of Queensland and Griffith University.

Particular thanks go to Andrew Palmer, Grant Beckett and Darren Morrow for assistance with the sampling, and to Vlad Matveev for his advice.

## FOREWORD

Water is fundamental to our quality of life, to economic growth and to the environment. With its booming economy and growing population, Australia's South East Queensland (SEQ) region faces increasing pressure on its water resources. These pressures are compounded by the impact of climate variability and accelerating climate change.

The Urban Water Security Research Alliance, through targeted, multidisciplinary research initiatives, has been formed to address the region's emerging urban water issues.

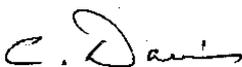
As the largest regionally focused urban water research program in Australia, the Alliance is focused on water security and recycling, but will align research where appropriate with other water research programs such as those of other SEQ water agencies, CSIRO's Water for a Healthy Country National Research Flagship, Water Quality Research Australia, eWater CRC and the Water Services Association of Australia (WSAA).

The Alliance is a partnership between the Queensland Government, CSIRO's Water for a Healthy Country National Research Flagship, The University of Queensland and Griffith University. It brings new research capacity to SEQ, tailored to tackling existing and anticipated future risks, assumptions and uncertainties facing water supply strategy. It is a \$50 million partnership over five years.

Alliance research is examining fundamental issues necessary to deliver the region's water needs, including:

- ensuring the reliability and safety of recycled water systems.
- advising on infrastructure and technology for the recycling of wastewater and stormwater.
- building scientific knowledge into the management of health and safety risks in the water supply system.
- increasing community confidence in the future of water supply.

This report is part of a series summarising the output from the Urban Water Security Research Alliance. All reports and additional information about the Alliance can be found at <http://www.urbanwateralliance.org.au/about.html>.



**Chris Davis**  
Chair, Urban Water Security Research Alliance

# CONTENTS

<b>Acknowledgements</b> .....	<b>i</b>
<b>Foreword</b> .....	<b>ii</b>
<b>Executive Summary</b> .....	<b>1</b>
<b>1. Introduction</b> .....	<b>3</b>
1.1. Water Security in South East Queensland .....	3
1.2. Surface Films as a Water Conservation Strategy .....	3
<b>2. Artificial Monolayers as a Strategy for Reducing Evaporative Loss</b> .....	<b>4</b>
2.1. Physics of the Evaporation Process .....	4
2.2. Energy Transfer at the Air/Water Interface and Capillary Waves .....	5
2.3. Temperature Differentials and the Thermal Boundary Layer in Water .....	6
2.4. Mechanisms for Reducing Evaporative Loss at the Molecular Level .....	6
2.5. Efficacy of Monolayers in Reducing Evaporative Loss .....	7
<b>3. Monolayers as a Technology for Reducing Evaporative loss</b> .....	<b>9</b>
3.1. History of Applying Monolayers as a Water Conservation Strategy .....	9
3.2. Accounting for the Inconsistency of Field Trial Results .....	10
3.3. Revisiting Monolayers as a Technology for Reducing Evaporative Loss .....	11
<b>4. The Biological, Chemical and Physical Properties of the Air/Water Interface</b> .....	<b>12</b>
4.1. The Air/Water Interface as a Microbial Environment .....	12
4.2. Temperature Differentials and Gaseous Exchange in the Air/Water Interface .....	12
<b>5. The Potential for Monolayers to Adversely Affect Natural Microlayer Processes and Water Quality</b> .....	<b>15</b>
5.1. Direct Impacts: Toxicity of the Active Ingredient .....	15
5.2. Indirect Impacts: Reduced Surface Tension .....	17
5.3. Indirect Impacts: Reduced Gaseous Diffusion .....	18
5.4. Indirect Impacts: Increased Water Temperature .....	20
5.5. Indirect Impacts: Adverse Impacts on Potable Water Treatment .....	22
<b>References</b> .....	<b>24</b>

## LIST OF FIGURES

Figure 1:	The direction of attractive forces between water molecules at the air/water interface, and within the bulk phase. Molecules at the surface have a higher free energy that induces the spontaneous contraction of the surface area, referred to as surface tension. Reproduced from Davies and Rideal (1963), Figure 1.1. ....	4
Figure 2:	The relationship between the area occupied per molecule (force-area isotherm), and the surface pressure exerted by the film. (a) refers to the gaseous phase, (b) the liquid-expanded phase, and (c) the liquid-condensed phase. Reproduced from Gladyshev (2002), Figure 4.3. ....	7
Figure 3:	Temperature profile of the laminar (zone 1), and intermediary (zone 2) zones that constitute the liquid thermal boundary layer located above the subsurface (zone 3) layer of a water body. The thickness of the liquid thermal boundary layer is greatest under wind speeds within the range of 1 to 10 m/sec., in the absence of forced convection. Reproduced from Gladyshev (2002), Figure 2.2. ....	13
Figure 4:	The resistances to evaporative loss that exist at the air/water interface. The gas phase resistance can be increased by increasing surface pressure and by increasing the vapour pressure (thick gas boundary layer). The interfacial resistance can be increased by reducing surface tension and by damping capillary waves. The liquid phase resistance can be increased by reducing the thermal gradient between the surface and subsurface temperature and/or by maintaining a warm surface film (thick liquid thermal boundary layer). Reproduced from Davies and Rideal (1963), Figure 7.1. ....	14
Figure 5:	Inhibition of the acidification of the growth medium of <i>Saccharomyces cerevisiae</i> by mid-chain length aliphatic alcohols disrupting cell membrane processes. The cut-off in biocidal activity is after a carbon chain length of 12 (C12). Reproduced from Kubo <i>et al.</i> (2003), Figure 2. ....	15
Figure 6:	The rate of biodegradation of linear (L) and branched (B) non-ionic surfactants, measured in a 5-day Biochemical Oxygen Demand test. AE refers to surfactants with carbon chain lengths of C12 to C15 and C13, synthesized using ethylene oxide (ethoxylated). NPE refers to a branched C9 ethoxylate. Reproduced from Kravetz <i>et al.</i> (1991), Figure 3. ....	16
Figure 7:	The comparative scales at which gravity waves, bulk thermal convection, capillary waves and boundary layer physics affect gaseous exchange and thermal convection at the air-water interface. At the millimeter scale, wind speed and the surface deviation temperature (thermal gradient) have a major impact on the diffusion of sparingly soluble gases such as oxygen, and of heat (section 4.2). ....	19

## EXECUTIVE SUMMARY

Water conservation strategies offer a feasible alternative to the unpopular commissioning of new reservoirs, and to the high infrastructure and running costs of desalination plants (McJannet *et al.*, 2008). Increasing temperatures and decreasing rainfall constrain the feasibility and profitability of the provision of potable water and irrigated agriculture. Of the estimated 7,000 GL of water stored in a million or so small on-farm storages (< 10 ha capacity), up to 20% may be lost to evaporation (Craig *et al.*, 2008). Strategies for reducing evaporative loss include physical floating covers, suspended physical covers, re-engineering the storage to reduce the surface to volume ratio, and applying an artificial monolayer. Of these options, only monolayer (a mono-molecular surface film) application is considered cost-effective for storages larger than 10 ha. The management of artificial monolayers to retard evaporative loss is an old concept (La Mer, 1962) that has not been adopted commercially due to extreme variability in field performance (Barnes, 2008). Recent research highlights deficiencies in the original products that in part account for variable field performance (Pittaway and van den Ancker, 2010b). The promise of improved field performance has encouraged managers of urban water utilities to consider monolayer application as part of their water conservation strategy (McJannet *et al.*, 2008). In contrast to privately owned farm irrigation storages, the adverse effects of monolayer application on the ecology and water quality of the storage must be considered, as well as the potential for monolayer compounds to adversely affect potable water treatment processes.

This literature review explores: the mechanisms by which artificial monolayers retard evaporative loss; how the application of an artificial monolayer may adversely affect the physical, chemical and biological processes that occur at the air/water interface; and the potential for monolayers to adversely affect aquatic food chains, potable water quality, and potable water treatment systems.

Relative to alternative technologies such as physical floating or suspended covers, or the application of thicker oil films, the adverse impact of monolayers on the survival and activity of aquatic flora and fauna is likely to be low (Craig *et al.*, 2008). However, the air-water interface (also referred to as the microlayer) where a monolayer exerts its effect is a physically, chemically and biologically dynamic habitat vital to the survival of many aquatic organisms (Norkrans, 1980). The most extensive study of the impact of a monolayer on water quality was by Wixson (1966), using a mixture of the fatty alcohols hexadecanol and octadecanol. Non-filamentous algae appeared to decrease in abundance over the first 15 days, but recovered to population densities above a control by the end of the trial. Bacterial populations increased over the duration of the trial as they degraded the monolayer, producing few if any byproducts. The most detailed study on the impact of an artificial monolayer on aquatic invertebrates was by Wiltzius (1967), using floating cages. The author concluded that the duration of a monolayer in the condensed state was limited by the speed and occurrence of prevailing winds, and by the economics of product application. The monolayer product was only likely to be applied over summer, when water demand and evaporative losses were highest. Many aquatic insect species emerged outside this treatment window, limiting the potential for adverse impacts on the aquatic food chain.

To evaporate, a water molecule must first overcome the transport resistance of the liquid phase (liquid thermal boundary layer), and adsorb at the surface (Davies and Rideal, 1963). Once adsorbed, the molecule must overcome interfacial resistance, vapourising from molecules at the surface into the gaseous phase (gaseous boundary layer). A condensed monolayer retards evaporative loss by increasing transport resistance in both the liquid thermal and the gaseous boundary layers by calming capillary waves and by compressing the extended hydrophobic tails. Natural surface films also calm capillary waves, but the chemical structures of natural aquatic humic compounds are too heterogeneous to affect transport resistance in the gaseous boundary layer. Winds above 6 m sec<sup>-1</sup> and wave action readily disrupt a condensed artificial monolayer, with the potential to re-form the monolayer once calm conditions prevail.

Monolayers that suppress evaporative loss reduce latent heat loss and oxygen diffusion whenever prevailing micrometeorological conditions operate at a scale that is equivalent to the thickness of the liquid thermal boundary layer (Wells *et al.*, 2009). Whenever the scale is larger (for example thermal stability associated with warm surface films and stratification, or thermal instability associated with

wind and wave-breaking processes), the presence of a condensed monolayer has no significant impact on gaseous exchange and heat flux. Therefore, the adverse impact of a monolayer in reducing gaseous exchange and latent heat loss are transient, and not cumulative.

Potential hazards to potable water quality in surface water storages include: the concentration of major ions (salinity and hardness) and the pH of the water; turbidity; the presence of potentially pathogenic bacteria, viruses and protozoa; naturally occurring organics and anthropogenic volatile and non-volatile organics; and the presence of metals and radionuclides (Nadebaum *et al.*, 2004). Artificial monolayer compounds are anthropogenic, non-volatile organic molecules. Classed as linear, saturated insoluble non-ionic surfactants, monolayer compounds are considered non-toxic (Dorn *et al.*, 1993). Therefore, only emulsified monolayer compounds are likely to enter the potable water supply, as most reservoir off-take pipes are located well below the surface. The compatibility of monolayer compounds with long-chain polymers used in the pre-treatment of potable water indicates that most monolayer compounds will be removed during flocculation and coagulation. The concentration of monolayer compounds in the water after pre-treatment and filtration should be very low, posing little risk to disinfection treatment processes such as chlorination, ozone and ultraviolet disinfection. Unbranched, non-ionic surfactants break down completely after a relatively short exposure to ozone, posing less of a risk than unsaturated, quaternary ammonium surfactants.

These results indicate that the currently available long-chain, saturated fatty alcohols and glycol monoalkyl ethers formulated as artificial monolayers are unlikely to affect the quality of municipal potable water, the efficacy of potable water treatment systems, or the ecology of surface water reservoirs. Both classes of monolayer compounds are biodegradable, being susceptible to microbial degradation and/or photodegradation. Their similarity to naturally occurring surface films and ease of disruption suggests that monolayers have little impact on the activity and survival of aquatic animals. Indeed, the biodegradability of saturated fatty alcohol and glycol monoalkyl ether monolayers must be taken into consideration when matching a monolayer product with the quality of water in the storage to ensure the product persists for long enough to reduce evaporative loss.

To provide the cost-effectiveness necessary for the technology to be commercially viable, automated dosing systems will be required to ensure monolayer product is only dispensed when prevailing meteorological conditions are conducive to the formation of a condensed monolayer. Unlike floating covers or other physical water conservation strategies, monolayer application can be intermittent, biodegrading within hours to ensure any adverse impacts on aquatic ecology are minimal.

# 1. INTRODUCTION

## 1.1. Water Security in South East Queensland

The recent drought in South East Queensland (SEQ) resulted in historically low water levels in the major reservoirs supplying potable water to urban populations, necessitating the imposition of stringent water restrictions (Water Services Association of Australia, 2010). Summer rains in 2009/2010 replenished most water storages, but concerns about longer-term urban water security remain. Climate variability and change and the increasing population density in SEQ will continue to place constraints on the capacity of existing reservoirs to supply sufficient potable water. Water conservation strategies offer a feasible alternative to the unpopular commissioning of new reservoirs, and to the high infrastructure and running costs of desalination plants (McJannet *et al.*, 2008).

Water security has been a key issue for broadacre agricultural irrigators for many years. Increasing temperatures and decreasing rainfall constrain the feasibility and profitability of irrigated agriculture both now, and into the future. Of the estimated 7,000 GL of water stored in a million or so small on-farm storages (< 10 ha capacity), up to 20% may be lost to evaporation (Craig *et al.*, 2008). This estimate is based on an evaporation rate of 2 m per year, and an average farm dam depth of 5 m maintained for 50% of the year. Strategies for reducing evaporative loss from farm dams include physical floating covers, suspended physical covers, re-engineering the storage to reduce the surface to volume ratio, and applying an artificial monolayer. Of these options, only monolayer (a monomolecular surface film) application was considered cost-effective for storages larger than 10 ha.

## 1.2. Surface Films as a Water Conservation Strategy

The management of surface films applied to water storages to retard evaporative loss is an old concept (La Mer, 1962). In practice, the economic and environmental costs of applying a formulation to the thickness required to retard evaporative loss limited application to laboratory studies. The exception was when the formulation was based on an organic molecule containing a hydrophilic polar anchor and a hydrophobic tail, with adjacent tails packing together to form a condensed surface film only one molecule thick (a monolayer). The hydroxyl functional group in alcohols is an example, which in combination with non-polar, hydrophobic hydrocarbons, form molecules termed amphiphiles (Greek for loving both, in this case, water and oil). Short-chain amphiphilic alcohols (for example methanol, ethanol and propanol) are water-soluble, whereas longer-chain alcohols (chain length of 16 carbons or greater: C16) spread to form an insoluble monolayer over the water surface.

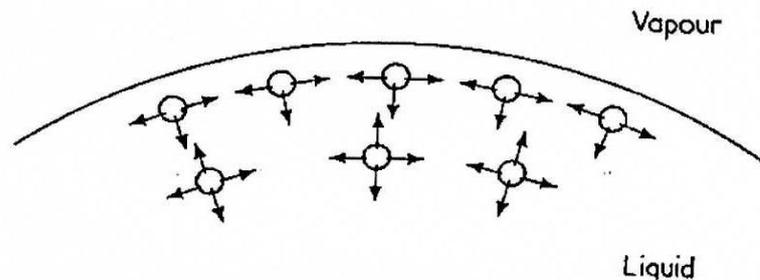
In clean water trials, the three most commonly used monolayer compounds - hexadecanol, octadecanol and 2-(octadecyloxy)ethanol - effectively reduced evaporative loss by as much as 40% (Barnes, 2008). However, the technology was not widely adopted, due to the extreme variability in monolayer performance encountered in field trials (McJannet *et al.*, 2008; Frenkiel, 1965). Recent research highlights deficiencies in the original products that in part account for variable field performance (Barnes, 2008; Pittaway and van den Ancker 2010b). These include product susceptibility to sublimation and microbial degradation, monolayer film susceptibility to physical disruption, and deficiencies in the technology used to apply the compounds. The development of new, more resilient artificial monolayer products and improved application strategies has the potential to improve the reliability of field performance, improving the likelihood of commercial adoption.

The promise of improved field performance has encouraged managers of urban water utilities to consider monolayer application as part of their water conservation strategy (McJannet *et al.*, 2008). However, in contrast to privately owned farm irrigation storages, the adverse effects of monolayer application on the ecology and water quality of the storage must be considered, as well as the potential for monolayer compounds to adversely affect potable water treatment processes. In this literature review, the mechanisms by which artificial monolayers retard evaporative loss will be described, to explore how the application of an artificial monolayer may adversely affect the physical, chemical and biological processes that occur at the air/water interface. The physical, chemical and biological properties of the three industry standard monolayer compounds (hexadecanol, octadecanol, 2-(octadecyloxy)ethanol) will be evaluated to assess the potential for monolayers to adversely affect aquatic food chains, potable water quality, and potable water treatment systems.

## 2. ARTIFICIAL MONOLAYERS AS A STRATEGY FOR REDUCING EVAPORATIVE LOSS

### 2.1. Physics of the Evaporation Process

The physical interactions between molecules in the liquid phase impart very specific properties at the interface between a liquid and a gas, or the liquid and a second, immiscible liquid (e.g. Davies and Rideal, 1963). In pure water, the net attraction between water molecules is greatest in the bulk water. However, at the air-water interface, molecules at the surface are not in force-equilibrium and have a higher Helmholtz free energy. At constant temperature and volume, the Helmholtz free energy is equal to the surface tension of water (72.8 mN/m). Surface tension arises from the imbalance of the forces acting on water molecules at the surface (Figure 1), tending to pull surface water molecules into the bulk phase to minimise surface area (Barnes and Gentle, 2008). This surface tension is exploited by different life phases of many aquatic invertebrates. Surface tension supports the weight of adult water striders, the air tubes of some aquatic larvae enabling them to respire, and the weight of female mosquitoes, midges, dragonflies and mayflies, enabling them to oviposit eggs onto and/or into submerged vegetation (Ross *et al.*, 1982).



**Figure 1:** The direction of attractive forces between water molecules at the air/water interface, and within the bulk phase. Molecules at the surface have a higher free energy that induces the spontaneous contraction of the surface area, referred to as surface tension. Reproduced from Davies and Rideal (1963), Figure 1.1.

The mass transfer of molecules across the gas-liquid interface into the air is referred to as evaporation. To evaporate from the liquid phase, a molecule must overcome a series of transport resistances (Davies and Rideal, 1963):

- liquid phase resistance;
- interfacial resistance; and
- gas phase resistance.

In the liquid phase, a molecule must first overcome the transport resistance of the liquid phase, to adsorb to the surface (Davies and Rideal, 1963). Once adsorbed, the molecule must overcome interfacial resistance (including surface tension), vapourising from molecules at the surface into the gaseous phase (evaporation). From the kinetic theory of materials (above absolute zero), all liquids and solids have a tendency to evaporate into the gaseous phase, and all gases have a tendency to condense back into the liquid phase. However, no net evaporation will occur if the gas pressure is equal to the vapour pressure at the temperature of the liquid surface. If the vapour pressure is reduced (for example by the continuous transport of vapour molecules away from the surface by wind), the gas phase resistance is less, resulting in higher rates of evaporation. The reduction in the gas phase resistance is due to the increase in the driving force of transport, in this case the wind.

Using thermodynamic principles, the maximum evaporation rate for an open water surface at atmospheric pressure exposed to dry air at high wind speed can be calculated (Eames *et al.*, 1997). To achieve this maximum rate, the temperature of the water must be constant, and the vapour pressure must be minimal. Under such conditions at a water temperature of 20°C, the theoretical evaporation rate is 9 m/hr, implying that many lakes and seas should evaporate completely within a matter of hours (Jones, 1992). However, maximum rates of evaporative loss recorded for terrestrial and marine water bodies are 5 to 6 orders of magnitude less (e.g. for a temperate lake 50 cm/yr, and a tropical sea 2 m/yr). The theoretical evaporation rate only reduces by about two orders of magnitude if the vapour pressure is increased and the air is very humid, conditions that increase the gas phase transport resistance. This discrepancy between theoretical and observed evaporation rates indicates that, at or near the surface, other phenomena must affect the transport resistance of water molecules moving from the liquid phase to the gas phase.

The evaporation coefficient defines the interfacial resistance to evaporation, and is calculated by dividing the experimentally measured evaporation rate by the theoretical maximum rate for the same micrometeorological conditions (Eames, 1997). Reasons for accepting an evaporation coefficient for water of less than unity include molecular collisions in the diffusion sublayer adjacent to any static boundary in an airflow (boundary layer fluid mechanics, Davies and Rideal, 1963). The thickness of this gas boundary layer is dependent on the friction properties of the static surface as well as the velocity of the bulk air, operating at a micrometre scale. At this scale, the highly efficient (and therefore low resistance) process of ‘fully forced’ turbulent transport cannot develop. In the absence of turbulence, the water vapour pressure within the gas boundary layer will be close to saturation, and the transport of water molecules will be governed by the physics of diffusion. Unless this layer is mechanically disturbed, the transport resistance (the concentration gradient normal to the surface) is very high, despite the relative thinness of the gas boundary layer.

A diffusion sublayer also exists in the liquid phase. The thickness of the layer immediately below the vapour/liquid interface is determined by the temperature difference between the surface and the immediate subsurface water, the upward heat flux, the kinematic viscosity, density and thermal conductivity of water, and the shearing stress in the air above the water (Jones, 1992). A low evaporation coefficient for water may indicate a significant thermal resistance to heat transfer in the liquid adjacent to the surface (Eames *et al.*, 1997). Interphase molecular transfer is linked to heat transfer from the liquid adjacent to the interface (the liquid thermal boundary layer), not the amount of heat available in the bulk liquid. A large temperature gradient may develop in the liquid thermal boundary layer when evaporation is high and the resistance to heat transfer is low (a thin liquid thermal boundary layer). In the ocean, the estimated thickness of the liquid thermal boundary layer under light winds is between 4 and 0.25 mm, reducing to 0.25 to 0.1 mm for strong winds (Wu, 1971a). The liquid thermal boundary layer may be mechanically disrupted by wave-breaking, but is rapidly restored by the undulating motion of turbulent flow.

In summary, for evaporation to occur, water molecules in the liquid phase must diffuse across the liquid thermal boundary layer. Water molecules must then adsorb at the surface, to vaporise within the gas boundary layer. Molecules must diffuse across the gas boundary layer without condensing. In the gas phase, molecules are transported via convection to the edge of the gas boundary layer (Davies and Rideal, 1963). Despite the relative thinness of both diffusion boundary layers, the resistance imposed on the transport of water molecules across the air/water interface as influenced by micrometeorological conditions and the presence of impurities is sufficient to explain the discrepancy between theoretical and observed maximum evaporation rates (Jones, 1992; Eames *et al.*, 1997). Beyond the gas boundary layer, air turbulence (wind) is the key driver of evaporative loss. Within the liquid thermal boundary layer, the temperature of the top row of water molecules at the surface determines the vapour pressure, driving evaporation (Barnes, 1986).

## **2.2. Energy Transfer at the Air/Water Interface and Capillary Waves**

Both energy (heat) and mass are transferred when water molecules evaporate (Jones, 1992). The removal of heat at the surface lowers the temperature, raising the surface tension/free energy of water at the surface above the free energy of the bulk water. Surface tension-driven convection is produced,

with surface molecules moving downward in a circular motion to produce natural convective circulation at the micrometre scale (Wu, 1971b). Under evaporative convection, the cooler surface water produced by latent heat loss is less buoyant than the warmer bulk liquid, descending in cold thermal plumes (Gladyshev, 2002). This thermal motion induces capillary waves, effectively roughening the surface of the fluid. The surface roughness induces spontaneous breaks in thin fluid films, allowing processes such as the coalescence of a droplet into the liquid to occur (Aarts *et al.*, 2004).

The impact of capillary waves reduces the thickness of the liquid thermal boundary layer, by inducing fluctuations in the local position of the surface (Duque *et al.*, 2008). The high surface tension of water and the orderly nature of molecules in the bulk phase stabilise molecules within the liquid thermal boundary layer (adsorption), extending the molecular residence time. More water molecules reach the interface, enhancing the potential for diffusion into the gas boundary layer. In the presence of capillary waves, the thickness of the liquid boundary layer is reduced, enhancing evaporative loss. Capillary waves also enhance gaseous diffusion and heat transfer by increasing the interfacial area and the interfacial flux (Hopfinger and Das, 2009).

### **2.3. Temperature Differentials and the Thermal Boundary Layer in Water**

The difference between the air and water temperature and the wind speed affect the dynamics of the natural convective circulation by changing the temperature gradient within the liquid thermal boundary layer (Gladyshev, 2002). Cold surface films produce downward cellular convection, whereas warm surface films are gravitationally stable. The transfer of heat through a cold surface film is much greater, due to the descent of convective thermals and the formation of capillary waves reducing the thickness of the liquid thermal boundary layer. In the absence of wind under typical room humidity of 21% and with the air temperature greater than the water temperature, evaporative cooling produces a cold surface film. If evaporation is suppressed by increasing the relative humidity to 88%, a cold surface film will only occur if the air temperature is less than the water temperature. The thermal stability of a warm surface film increases the resistance to interfacial heat transfer, reducing the evaporation coefficient (Eames *et al.*, 1997).

The liquid boundary layer under a warm surface film is an order of magnitude thicker than that of a cold film, with warm film boundaries extending 60 to 80 mm immediately below the surface (Gladyshev, 2002). In the ocean, the surface temperature is generally cooler than the subsurface, with the estimated boundary layer no thicker than 4 mm (Wu, 1971a). The thickness of the liquid thermal boundary layer is critical for the exchange of oxygen and carbon dioxide, and other gases that are poorly soluble in water. The oxygen concentration in the gaseous boundary layer under most micrometeorological conditions is high and constant, whereas concentrations in the liquid thermal boundary layer depend on the rate of molecular diffusion. If the liquid thermal boundary layer is thick, the rate of oxygen diffusion into the water will be substantially reduced (Gladyshev, 2002).

### **2.4. Mechanisms for Reducing Evaporative Loss at the Molecular Level**

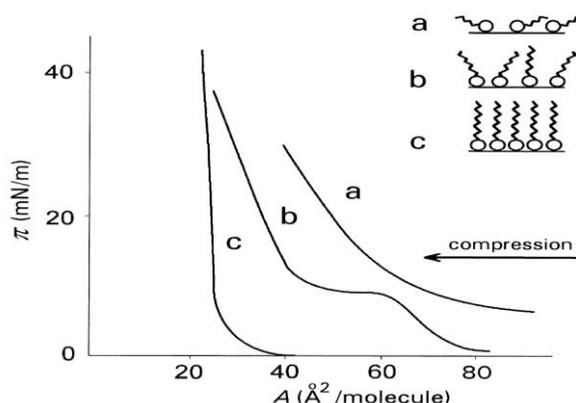
The rate of evaporative loss is highest when the transportation of water molecules from the bulk phase into the liquid thermal boundary layer, from the liquid thermal boundary layer into the gaseous boundary layer, and from the gaseous boundary layer into the air flow is rapid. Transport from the gaseous boundary layer into the airflow is determined by the wind shear (Wu, 1971b). In the presence of capillary waves, the surface roughness of the water increases, increasing the wind shear. If the formation of capillary waves is suppressed, the wind shear will decrease, allowing the vapour pressure at the water surface to increase. As the vapour pressure increases, the rate of condensation will also increase, reducing evaporative loss. Capillary waves can be suppressed by reducing the surface tension of water, and by reducing convective circulation.

Surface tension can be reduced if a second, immiscible liquid is added to water (Davies and Rideal, 1963). If the immiscible molecules are amphiphiles, the hydrophilic head of the molecule will adsorb at the air-water interface, with the hydrophobic tails escaping into the gaseous boundary layer. This

oriented, uni-molecular thick layer is referred to as a monolayer. The tendency for the molecules to adsorb at the interface (the laminar layer or surface skin) may reduce surface tension. The drop in surface tension from 72 mN/m for pure water to the lower equilibrium associated with the adsorption of an artificial monolayer, is equal to the surface pressure exerted by the packed monolayer molecules comprising the surface film. In the absence of forced convection in either the gas or the liquid phases, this change in surface tension is sufficient to inhibit the formation of capillary waves (Saylor and Handler, 1999), damping fluid motion (Saylor *et al.*, 2000a).

The compound used in experiments by Saylor *et al.* (2000a) was oleyl alcohol, a monolayer that dampens capillary waves by increasing surface viscosity, without reducing evaporative loss. The surfactant properties of oleyl alcohol inhibited natural convection in the water, thereby increasing the thickness of the liquid thermal boundary layer (Saylor *et al.*, 2000a). The increased thickness of the liquid thermal boundary layer was sufficient to reduce gaseous exchange in the water (Saylor and Handler, 1999), but evaporative convection at the air interface was relatively unaffected. These results suggest that, at the molecular level, damping capillary waves alone is insufficient to substantially retard evaporative loss.

Oleyl alcohol is an unsaturated fatty alcohol with the chemical formula of  $C_{18}H_{36}O$ , classed as a non-ionic surfactant. Octadecanol is also a C18 fatty alcohol, but unlike oleyl alcohol, is classed as a saturated non-ionic surfactant. However, for surface chemists the term ‘surfactant’ is reserved for water soluble amphiphiles. Oleyl alcohol is water soluble, whereas hexadecanol, octadecanol and other saturated long-chain amphiphiles are insoluble. Amphiphiles consisting of saturated carbon chains are more likely to pack together tightly, forming a complex, rigid film immediately above the air/water interface (Davies and Rideal, 1963). In combination with the damping of capillary waves, the presence of an ordered, closely packed long-chain molecular barrier may increase the thickness of both the liquid thermal and the gaseous boundary layers, reducing evaporative loss (Figure 2). The calculated area occupied per molecule of linear, saturated amphiphile indicates that the high surface pressures exerted by monolayers capable of retarding evaporative loss corresponds to the orderly, tight packing of the molecules (Barnes and Gentle, 2008).



**Figure 2:** The relationship between the area occupied per molecule (force-area isotherm), and the surface pressure exerted by the film. (a) refers to the gaseous phase, (b) the liquid-expanded phase, and (c) the liquid-condensed phase. Reproduced from Gladyshev (2002), Figure 4.3.

## 2.5. Efficacy of Monolayers in Reducing Evaporative Loss

The effectiveness of saturated, long-chain amphiphiles in reducing evaporative loss is correlated with an increase in specific resistance as the monolayer is laterally compressed (Barnes and Gentle, 2005). Monolayers of linear amphiphiles may exist in four phases: solid, liquid-condensed, liquid-expanded, and gaseous (Figure 2). Monolayers in the liquid-condensed and solid phases pack most tightly, whereas, in the liquid-expanded phase, the hydrophobic chains lack the regularity to pack, occupying

twice the molecular area. In the gaseous phase, the molecules are widely separated, occupying up to 40 times the molecular area of a condensed monolayer. Within a condensed monolayer, the long-chain molecules are parallel, fully extended, and closely packed. The head groups interact with water molecules and each other, and the hydrocarbon chains interact with adjacent hydrocarbon chains. However, if impurities such as non-homologous amphiphilic hydrocarbons are added, for example cholesterol, the evaporative resistance of the monolayer may reduce substantially. The impurities occupy the spaces between the ordered clusters of monolayer molecules, producing large holes. The efficiency of the monolayer in retarding evaporation can be reduced by 90 to 99%, if as little as 1% of the area of the monolayer is occupied by holes (Barnes and La Mer, 1962).

To be effective in retarding evaporative loss, the surface area of the water must be substantially covered by the film, or the monolayer must be initially compressed by wind or wave action (Barnes and La Mer, 1962). Spontaneous spreading is essential for film coverage during application and for 'self-repair' after turbulence or other disturbances disrupt the monolayer film. Chain lengths of the order of C<sub>18</sub> and above are more effective in retarding evaporative loss, but spread more slowly than molecules of shorter chain length. If a mixture of a short- with a long-chain saturated fatty alcohol is made (homologous amphiphiles), it is possible to achieve spreading and to maintain high evaporation resistance. Fatty alcohols with chain lengths of C<sub>16</sub> and less will spread spontaneously, and will readily mix with longer chain compounds. Under pressure, the longer chain amphiphiles squeeze out the shorter chain molecules, re-establishing the ordered, tightly packed monolayer structure required to reduce evaporative loss. The shorter chain compounds may be lost to the system via evaporation from the surface, or via dissolution in the bulk water below the monolayer.

### 3. MONOLAYERS AS A TECHNOLOGY FOR REDUCING EVAPORATIVE LOSS

#### 3.1. History of Applying Monolayers as a Water Conservation Strategy

Ancient Greeks utilised the capacity of oil to smooth a rough sea (Gladyshev, 2002) and, at the turn of the 20<sup>th</sup> century, the French applied oil to water to reduce the formation of fog (Frenkiel, 1965). However, it was not until the end of the 19<sup>th</sup> century that experiments were conducted to investigate the compressibility of amphiphiles and their impact on surface tension. Langmuir developed the first experimental method (the Langmuir Trough) for measuring the pressure of a surface film produced from pure chemical compounds. Surface pressure was defined as the difference between the surface tension of pure water, and that of the water sample with a film covering the surface. Langmuir also established the relationship between the surface pressure induced by applying an artificial film, and the specific area occupied per amphiphilic molecule (Barnes and Gentle, 2005).

The focus on monolayer materials occurred in the 1950s and 1960s, when researchers found that molecularly oriented monomolecular films reduced evaporative loss more effectively than a much thicker, disorganized film of oil. Multi-molecular oil films were easily damaged by wind, rain and dust, and once broken did not reform (Frenkiel, 1965). Multi-molecular oil films must also be thick enough to reflect the physical properties of the bulk compound (one to 100 microns thick), yet thin enough to remain buoyant.

The first monolayer compounds to be investigated in detail were long-chain, saturated fatty acids, terminating in a hydrophilic carboxyl group (La Mer, 1962). In the liquid-condensed phase, increasing the length of the hydrophobic alkyl chain increased the surface pressure from 12 to 40 dynes/cm (12 to 40 mN/m). The efficacy of fatty acid monolayers in reducing evaporative loss varied linearly with an increase in chain length up to the C<sub>20</sub> acid, substantially reducing evaporative loss below that of a clean water surface. The energy of activation required to separate two adjacent carboxyl groups increased with an increase in chain length from C<sub>16</sub> to C<sub>20</sub> by 300 calories. Provided the monolayer was initially spread with sufficient pressure to exclude impurities, the reduction in the rate of evaporation was independent of the surface pressure in the range of 10 to 24 dynes/cm (mN/m: Rosano and La Mer, 1956). Resistance to evaporative loss was highest for monolayer films that resisted compression. The authors concluded that the resistance to evaporation depended on the cohesive forces between the hydrocarbon tails of monolayer molecules resisting compression (Barnes and La Mer, 1962).

During the 1950s and 1960s, field trials were undertaken on water storages to test the feasibility of using artificial monolayers to conserve water. Early trials indicated that monolayers with ester or acid head groups interacted with water chemistry to form a rigid layer that lacked the spontaneous spreading and self-sealing properties required for film maintenance and repair (Frenkiel, 1965). Only the non-ionic, saturated alcohols with a chain length greater than 12 were capable of self-sealing and maintaining the liquid-condensed film required to retard evaporative loss. The higher the chain length, the greater the specific resistance of the monolayer film for a given surface pressure. A problem with the fatty alcohols was that, as the temperature increased above 20<sup>o</sup>C, the performance of the compound in reducing evaporative loss declined. Measurements conducted at a standard surface pressure of 35mN/m and temperatures of 5, 20 and 40<sup>o</sup>C for myristyl (C<sub>14</sub>OH), cetyl (C<sub>16</sub>OH) and stearyl (C<sub>18</sub>OH) alcohols indicated that the reduction in performance was due to the sublimation of the fatty alcohols (Brookes and Alexander, 1960). The rate of sublimation reduced as the carbon chain length increased. The experiment was repeated with the unsaturated, compressible monolayer compound oleyl alcohol, where loss was due to solution in the water, not sublimation. The authors concluded that, for the saturated alcohols, the removal of one OH group from the aqueous boundary layer and 14 CH<sub>2</sub> groups from the gaseous boundary layer was most likely to occur as vapourisation. The introduction of a double bond (as in the monolayer compound oleyl alcohol) rendered the monolayer more prone to loss via solution in the aqueous phase.

For evaporative control under warmer conditions, saturated fatty alcohols with carbon chain lengths of 18 and 20 were tested (Frenkiel, 1965). However, increasing chain length reduced the capacity of the compound to spontaneously spread. Researchers investigated the potential to reduce the rate of sublimation in long-chain alkyl compounds by replacing the hydrophilic head group with a compound that interacted more strongly with the water phase (Deo *et al.*, 1961). Laboratory trials indicated that the new class of monolayer compounds, the glycol monoalkyl ethers spread spontaneously, produced a high surface pressure, resisted compression, and were less prone to sublimation than their fatty alcohol chain-length counterparts. However, despite advances in the physical chemistry of the compounds, monolayer technology was not widely adopted at the commercial scale, due to a lack of consistent performance under field conditions (Barnes, 2008).

### 3.2. Accounting for the Inconsistency of Field Trial Results

The compounds most commonly applied during field trials were the C16 alkyl fatty alcohol hexadecanol (cetyl alcohol, C<sub>16</sub>OH), and the C18 alkyl fatty alcohol octadecanol (stearyl alcohol C<sub>18</sub>OH). Rates of application were calculated on the area occupied per molecule in the liquid-condensed state, applying sufficient product to produce a uniform film one molecule thick across the surface (Barnes 2008). One explanation for poor performance was that the methods used for application failed to produce a spontaneously spreading film, with the compound clumping in islands, failing to produce a liquid-condensed film. In more recent trials, results have indicated that a liquid-condensed film characterised by a high surface pressure will only result if the application is between 3 and 5 times greater than the calculated monomolecular application rate (Hancock *et al.*, 2011). Applications greater than 5 times the monomolecular rate show no improvement in reducing evaporative loss. Calculating a monomolecular application rate assumes that the water surface is planar. However, the generation of capillary waves (refer section 2.2) increases surface roughness, necessitating higher application rates for full surface coverage and film compression.

A second explanation for the inconsistency of field trials involves the meteorological conditions under which the trials were conducted (Frenkiel, 1965). Wind is a key factor, with mild winds assisting full monolayer coverage, but winds greater than 5 to 10 km/hr. (2 to 4 m/sec) progressively decrease coverage over time. Automatic dispensing overcame this problem, but the cost of dispensers and reliability of operation limited their use. Even in the absence of wind, under conditions that should favour the formation of a liquid-condensed film, inconsistent results were obtained. The inconsistent results are likely to reflect the microclimatic conditions that prevailed during the trials. Accurately measuring the rate of evaporation from a water surface in field trials is technically challenging (McJannet *et al.*, 2008). In the majority of laboratory and field trials, the performance of a monolayer is measured as the volume of water lost from a receptacle covered with a monolayer, subtracted from the volume lost from an equivalent storage with a clean water surface. In the laboratory, standardising the key drivers of evaporative loss, water and air temperature, and relative humidity, is possible. In the field, these parameters vary diurnally (Gladyshev, 2002), affecting the repeatability of results obtained on monolayer performance.

Monolayers exert their effect at the molecular level by damping capillary waves, and by increasing the thickness of the liquid thermal boundary layer and the gaseous boundary layer (refer section 2.3). At the mm scale, the increase in resistance immediately above and below the water extends the ‘thickness’ of both boundary layers. Microclimatic conditions that reduce evaporative loss (for example high relative humidity in the absence of wind and/or a warm surface film) also increase the resistance of both boundary layers, at a scale that is larger than the impact of a monolayer (Gladyshev, 2002). Winds consistently above 4 m/sec and turbulence in the bulk water will also have a far greater impact on the rate of evaporation than the presence of a liquid-condensed monolayer. Consistent results on monolayer performance can only be obtained if data is partitioned into time intervals when the key driver most likely to affect evaporative loss is the composition of the surface film (Hancock *et al.*, 2011).

The final factor affecting the consistency of field results is the impact of water quality. The stability of insoluble monolayers of low molecular weight and high molecular weight monolayers with a fatty acid terminal group is affected by changes in pH and electrolyte concentration (Binks, 1991). High molecular weight, alkyl fatty alcohols and glycol monoalkyl ethers remain stable (Frenkiel, 1965).

However, liquid-condensed films of long-chain fatty alcohols are prone to physical disruption from non-homologous amphiphiles (refer section 2.4). In laboratory studies, extensive precautions are taken to exclude such impurities (Barnes and La Mer, 1965). Amphiphiles commonly exist in the natural environment, concentrating at the air/water interface of water bodies to produce a natural surface film (a microlayer). Natural surface films have very similar properties to artificial monolayer compounds and, as impurities, may disrupt the physical structure of the film, increasing the rate of evaporative loss (Pittaway and van den Ancker 2010a).

The thin layer of water and associated organic film bordered on the upper surface by the air interface and on the lower surface by the water interface is referred to by biologists as a microlayer. Microbes occupying the microlayer are referred to as neuston, as distinct from plankton occupying the bulk water (Gladyshev, 2002). Bacteria, fungi, organic matter, nitrogen, phosphorus and trace elements are concentrated within the microlayer of fresh-water bodies at levels substantially higher than in bulk water (Hatcher and Parker, 1974; Munster *et al.*, 1998). The hydrophobic organic materials responsible for the formation of microlayers include long-chain acids and hydrocarbons (Meyers and Kawka, 1982), which are structurally very similar to C<sub>16</sub>OH and C<sub>18</sub>OH monolayer compounds.

In water bodies with well-developed microlayers, the population of microbial species capable of utilising saturated and unsaturated lipids such as C<sub>16</sub> palmitic acid is likely to be very high (Norkrans, 1980). Early laboratory trials indicated that common freshwater bacteria in the genera *Pseudomonas* and *Flavobacterium* readily degrade hexadecanol monolayers (Chang *et al.*, 1962), reducing surface pressure and therefore the integrity of the film. It is therefore not surprising that, in some field trials, researchers attributed loss of monolayer function to microbial degradation (Vines, 1962). In more recent laboratory studies, the resilience of monolayer compounds to bacterial attack was shown to increase with increasing chain length, and with the substitution of the hydrophilic alcohol terminal group with a glycol ether group (Pittaway *et al.*, 2010b). The fatty alcohol C<sub>18</sub>OH was more resilient than the C<sub>16</sub>OH compound, with the half-life of the compound increasing from two days to more than four days. The C<sub>18</sub>E1 monolayer was even more resilient, with very little compound lost over the four-day duration of the trial.

### 3.3. Revisiting Monolayers as a Technology for Reducing Evaporative Loss

The development of improved monolayer compounds with a greater resilience to sublimation, wind, and microbial degradation has rekindled interest in monolayers as a strategy for conserving water (Barnes, 2008). The development of an autonomous application system, programmed to apply monolayer under specific environmental conditions at pre-determined rates, has also improved the commercial feasibility of the technology (Brink *et al.*, 2010). Unlike thicker, multilayered oil films, the application rate of monolayer compounds is much lower, producing a much thinner barrier at the air/water interface (refer section 3.2). The spontaneous spreading and re-spreading properties of the film allow for film recovery after physical disruption from raindrop impact, wind, waves, aquatic plants and animals, or boats.

Compared to alternative technologies, such as physical floating or suspended covers, or the application of thicker oil films, the adverse impact of monolayers on the survival and activity of aquatic flora and fauna is likely to be low (Craig *et al.*, 2008). The effect of surface films on processes such as gas diffusion and thermal convection varies with both the thickness and the chemical composition of the film. For example, increasing the thickness of a petroleum film from 2.5 to 40-50 nm decreased the ratio of the oxygen transfer coefficient on clean versus film water by a factor of 2.5 (Gladyshev, 2002). By contrast, an artificial monolayer mixture of octadecanol and hexadecanol decreased the oxygen transfer coefficient from 0.64 cm/h to 0.43 cm/h, a ratio reduction of only 1.4. The chemical composition of the monolayer may also affect its biochemical properties. The potential for monolayers to adversely affect the ecology of reservoirs supplying potable water to urban populations is a key issue that must be resolved, before the technology can be deployed by water managers.

## 4. THE BIOLOGICAL, CHEMICAL AND PHYSICAL PROPERTIES OF THE AIR/WATER INTERFACE

### 4.1. The Air/Water Interface as a Microbial Environment

The air/water interface, or microlayer, has a thickness associated with surface tension (laminar layer), the gaseous boundary layer, and the liquid thermal boundary layer (refer section 2). The thickness of the microlayer varies with micrometeorological conditions, at a millimetre scale. Within the microlayer, naturally occurring hydrophobic molecules concentrate, increasing the concentration of dissolved organic carbon, nitrogen, and minerals above that of the immediate subsurface water (enrichment: Norkrans, 1980). Early quantitative studies indicate that natural films commonly occurring on water bodies such as lakes and ponds induce surface pressures exceeding  $30 \text{ dynes cm}^{-1}$  (Goldacre 1940). Later studies indicate that the thickness of these natural films varies from 100 to  $500 \mu\text{m}$  (Munster *et al.*, 1998).

The hydrophobic, dissolved organic matter originates from the breakdown of waxy, terrestrial leaf and bark litter, from humified peat fragments, from animals, aquatic heterotrophic bacteria, and from metabolites produced by photosynthesising phytoplankton (Norkrans, 1980). The chemical composition of microlayer films reflects the relative proportions of different source materials (Meyers and Kawka, 1982). Carbon chains of C22 to C28 derived from waxy alkanes and aliphatic alcohols predominate if inputs are largely leaf and bark litter, whereas C12 to C18 straight-chain acids predominate if algal metabolites are the main input. The presence of double bonds, side-branches, and aromatic rings attached to hydrocarbon chains impedes the formation of a liquid-condensed surface film (refer section 2.4). Accordingly, the surface pressure and molecular packing imparted by natural surface films is generally less than that required to retard evaporative loss (Gladyshev, 2002). At the margins of water storages, wind or wave action compresses the natural films but the effect is generally localised and insufficient to retard evaporative loss.

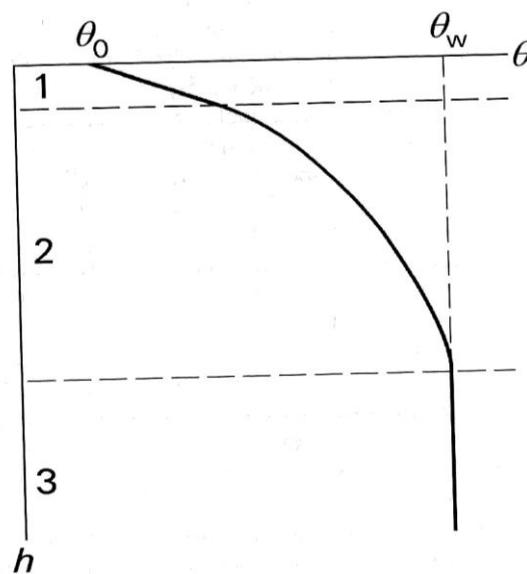
To utilise these natural microlayer compounds, bacteria must be sufficiently hydrophobic to attach to the compounds (Dahlback *et al.*, 1981) and, after attachment, biosurfactants must be produced to emulsify the hydrocarbons and for de-adhesion (Neu, 1996). The physiological capabilities necessary for microbes to exploit organic materials within the microlayer differentiate microlayer populations from planktonic populations in the bulk water (Gladyshev, 2002). Photochemical processes that occur within the microlayer also differentiate this region from the bulk water. Chromophores, compounds concentrating in the microlayer, include aromatic rings that absorb ultraviolet light (Norkrans, 1980). These chromophores become photochemically reactive, producing low molecular weight organic acids that are more readily metabolised by microlayer bacteria (Brinkmann *et al.*, 2003). The synergy between photochemical and microbial degradation is responsible for the 'cleansing' properties of natural microlayers (Baier, 1972).

### 4.2. Temperature Differentials and Gaseous Exchange in the Air/Water Interface

At the millimetre scale, the difference in temperature between the laminar layer and the subphase (surface deviation temperature) affects the thickness of the liquid thermal boundary layer (Gladyshev, 2002). The temperature of a surface film undergoing evaporative loss will invariably be lower than the bulk water, due to the cooling effect of energy being transferred into the gaseous phase during evaporation (refer section 2.1). A laminar layer exists immediately below the water surface where heat is conducted at the molecular level, causing a linear decrease in temperature with depth (zone 1 in Figure 3). Immediately below the laminar layer (the intermediate layer), the temperature decreases exponentially (zone 2 in Figure 3) to the uniform temperature of the turbulent diffusion layer (subsurface water). Zones 1 and 2 are collectively referred to as the liquid thermal boundary (or skin) layer (Katsaros, 1980, Wells *et al.*, 2009). Measurements of heat transfer at sea indicate that the thickness of the laminar layer can range from 0.2 to 3.0 mm, with the total liquid thermal boundary layer producing a skin thickness of 8 to 9 mm (Gladyshev, 2002). However, this relationship only holds if the wind speed 10 m above the water surface is within the range of 1 to 10 m/sec. Under

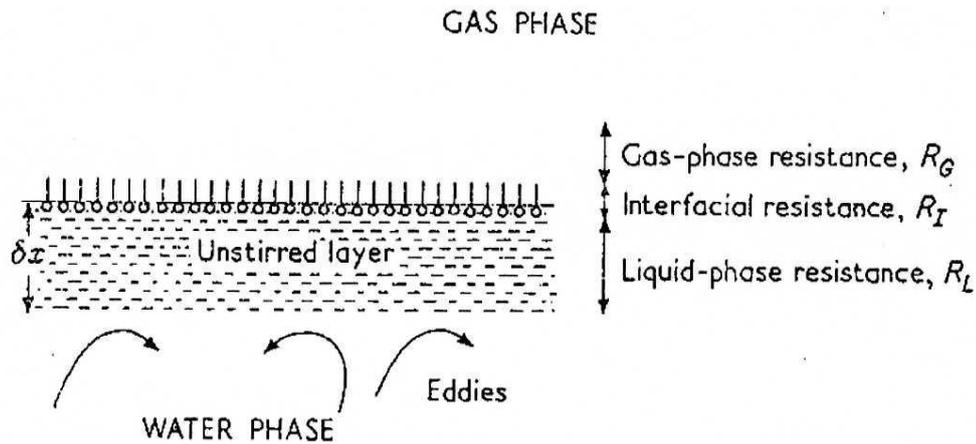
forced convection, turbulent eddies minimise the thickness of the liquid thermal boundary layer by replacing the colder water within the intermediate region with bulk, subsurface water (Katsaros, 1980).

The heat flux within the liquid thermal boundary layer of water is a function of radiation (incoming radiation minus the radiation emitted from the water surface), convection (the exchange of kinetic energy between water molecules), and evaporation. In practice, cold films occur more than 80% of the time (Gladyshev 2002) due to the latent heat flux of evaporation. However, under low wind speeds, high humidity and low solar radiation (low evaporative demand), it is possible to generate a warm surface film. Over a diurnal cycle, the heat flux of the surface film on a water storage may vary from positive to negative, directly affecting the resistance to interfacial heat transfer. At water temperatures above 4°C, water molecules in a cold surface film are less buoyant than molecules in the warmer sub-phase. A micro-convection current is generated as the cold water descends (turbulent eddies or Rayleigh-Benard convection, Wells *et al.*, 2009), reducing the thickness of the liquid thermal boundary layer (Figure 4).



**Figure 3:** Temperature profile of the laminar (zone 1), and intermediary (zone 2) zones that constitute the liquid thermal boundary layer located above the subsurface (zone 3) layer of a water body. The thickness of the liquid thermal boundary layer is greatest under wind speeds within the range of 1 to 10 m/sec., in the absence of forced convection. Reproduced from Gladyshev (2002), Figure 2.2.

The frequency of the micro-convection current depends on the difference between the temperature of the surface and subsurface of the water (surface deviation temperature). If the surface deviation temperature is small or if the surface film is warm, the film becomes gravitationally stable, increasing the thickness of the liquid thermal boundary layer. In laboratory studies, inducing a cold film on a water sample increased the oxygen transfer rate from 0.759 cm/hr to 1.17 cm/hr (Gladyshev, 2002). The oxygen transfer coefficient decreased from 0.414 cm/hr to 0.234 cm/hr when the differential of a warm surface film increased from 1.5°C to 3.5°C above the temperature of the sub-phase.



**Figure 4:** The resistances to evaporative loss that exist at the air/water interface. The gas phase resistance can be increased by increasing surface pressure and by increasing the vapour pressure (thick gas boundary layer). The interfacial resistance can be increased by reducing surface tension and by damping capillary waves. The liquid phase resistance can be increased by reducing the thermal gradient between the surface and subsurface temperature and/or by maintaining a warm surface film (thick liquid thermal boundary layer). Reproduced from Davies and Rideal (1963), Figure 7.1.

In summary, the presence of a surface film can affect the dynamics of the air/water interface (microlayer) in several different ways:

1. reducing the surface area for gaseous exchange by damping capillary waves (increasing the thickness of the liquid thermal boundary layer and therefore the resistance to interfacial transport (Figure 4);
2. reducing the convective heat flux by reducing the surface deviation temperature (increasing the thickness of the liquid thermal boundary layer); and
3. reducing evaporative loss by increasing surface pressure and vapour pressure, and therefore the gas phase transport resistance (increasing the thickness of the gas boundary layer).

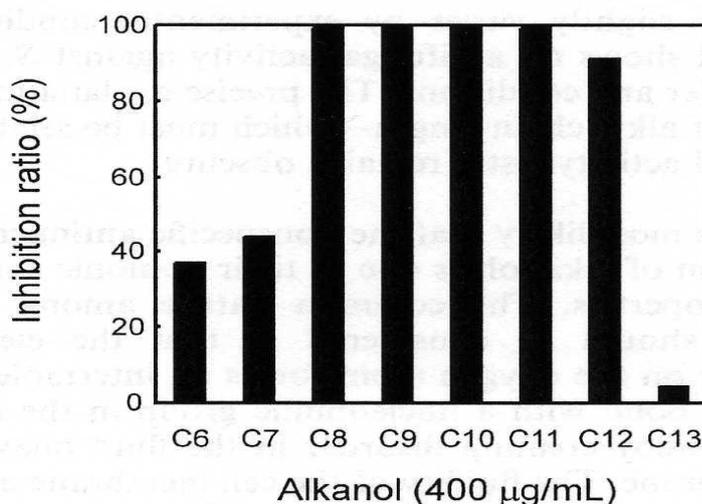
All natural surface films are capable of damping capillary waves, and may reduce the convective heat flux. However, most natural films lack the precise molecular packing required to retard evaporative loss (refer section 4.1). Moreover, the influence of natural surface films on physical processes at the air/water interface is limited by the prevailing micro-meteorological conditions. Once the wind speed exceeds 3 to 5 m/s, wind and wave-breaking processes are the primary factors determining rates of gaseous exchange and heat flux (Gladyshev, 2002). In the absence of wind, an increase in the thickness of the liquid thermal boundary layer associated with a warm surface film, or an increase in the thickness of the gaseous boundary layer associated with high relative humidity, have a far greater impact on microlayer processes than the properties of the surface film. These results highlight the fact that the impact of an artificial monolayer on heat and gas transfer processes at the air/water interface will depend on the interaction between incoming radiation (air and water heat flux), wind speed and wave action, vapour pressure deficits and the properties of natural surface films.

## 5. THE POTENTIAL FOR MONOLAYERS TO ADVERSELY AFFECT NATURAL MICROLAYER PROCESSES AND WATER QUALITY

### 5.1. Direct Impacts: Toxicity of the Active Ingredient

Primary aliphatic alcohols with chain lengths from C9 to C12 kill microorganisms and aquatic insect larvae by disrupting membranes and membrane biochemical processes (Kubo *et al.*, 2003; Hammond and Kubo, 1999; Mohr *et al.*, 2005). The anaesthetic effect responsible for the biocidal properties cuts out as the carbon chain length increases from C11 to C15. This toxic property is common to other linear, non-ionic surfactants such as the alkyl ethoxylates (Lewis, 1991). As chain length increases from C9 to C12, the acute toxicity of linear surfactants increases (Dorn *et al.*, 1993). The cut-off from C12 to C13 is dramatic, with very little activity in aliphatic alcohols with chain lengths exceeding C13 (Kubo *et al.*, 2003) (Figure 5).

Early studies also indicated that long-chain alkanes and alkanols promoted the development of tumors when applied in combination with the carcinogen 7, 12-dimethylbenz anthracene (Sice, 1966). Alkane and aliphatic alcohols with carbon chain lengths from C6 to C20 were applied to the skin of laboratory mice, in combination with the carcinogen and alone. When applied alone, no tumors were observed. The compounds decanol, dodecane and tetradecane (carbon chain lengths of C10, C12 and C13 respectively) were the most potent, indicating that the compounds increased the uptake of the carcinogen by modifying cell membranes.

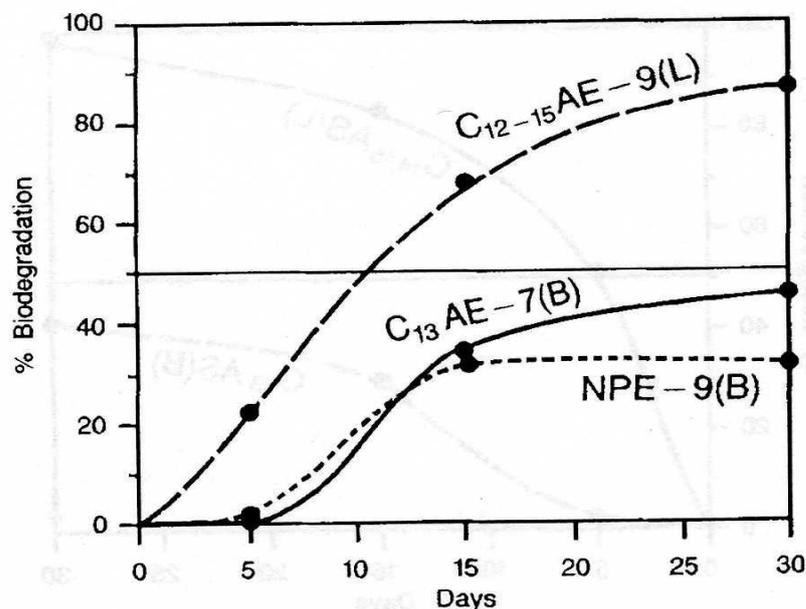


**Figure 5:** Inhibition of the acidification of the growth medium of *Saccharomyces cerevisiae* by mid-chain length aliphatic alcohols disrupting cell membrane processes. The cut-off in biocidal activity is after a carbon chain length of 12 (C12). Reproduced from Kubo *et al.* (2003), Figure 2.

Branched non-ionic surfactants are not as acutely toxic as linear non-ionic surfactants with the same chain length (Dorn *et al.*, 1993; Krogh *et al.*, 2003). Highly-branched surfactants lack the ability to closely pack at the air/water interface, reducing the ability of the surfactants to adsorb and penetrate biological membranes (Rosen *et al.*, 2001). However, branched surfactants biodegrade more slowly (Figure 6), and produce more potentially toxic metabolites. Treated effluent derived from highly-branched non-ionic surfactants tends to be more surface-active and more toxic to aquatic organisms than effluent derived from linear or less-branched non-ionic surfactants (Kravetz *et al.*, 1991). Aromatic, ethoxylated surfactants are more toxic than aliphatic surfactants (Patoczka and Pulliam, 1990).

Studies analysing the intermediate metabolites produced from the degradation of hexadecanol (C<sub>16</sub>OH) and octadecanol (C<sub>18</sub>OH) indicate that straight-chain compounds are preferentially utilised by bacteria, producing few metabolites (Langley, 1970). The soluble, gelatinous material observed at the surface,

acting as a binder between hexadecanol particles (Langley, 1970; Ludzack and Ettinger, 1957), was most likely biosurfactant produced by bacteria attaching to and metabolising the hydrophobic monolayer compounds (refer section 4.1).



**Figure 6:** The rate of biodegradation of linear (L) and branched (B) non-ionic surfactants, measured in a 5-day Biochemical Oxygen Demand test. AE refers to surfactants with carbon chain lengths of C12 to C15 and C13, synthesized using ethylene oxide (ethoxylated). NPE refers to a branched C9 ethoxylate. Reproduced from Kravetz *et al.* (1991), Figure 3.

Of the three surfactant classes (cationic, anionic and non-ionic), non-ionic surfactants are considered the most environmentally safe (Lewis, 1991). Monolayer compounds capable of suppressing evaporative loss have carbon chain lengths of C16 and above, are linear, and whilst classed as non-ionic surfactants, are insoluble in water (Barnes, 2008). The chain length of the most commonly used monolayer compounds hexadecanol (C<sub>16</sub>OH), octadecanol (C<sub>18</sub>OH) and 2-(octadecyloxy) ethanol (C<sub>18</sub>E1) is above the cut-off point for biocidal, linear non-ionic surfactants, indicating that they lack the acute toxicity characteristic of the lower chain compounds. As a linear compound, hexadecanol is also readily degraded by aquatic organisms (Langley, 1970). Concern was expressed by some scientists that the vulnerability of hexadecanol to bacterial degradation may limit the commercial feasibility of the technology (Silvey, 1960; Chang *et al.*, 1962). More recent laboratory studies indicate that increasing the carbon chain length from C16 to C18, and changing the chemistry of the hydrophilic portion, increases the environmental resilience of the monolayer (Pittaway and van den Ancker, 2010b).

Bacteria naturally produce lipid storage compounds that are very similar to the long-chain fatty alcohols (Kadouri *et al.*, 2005). Biosynthesis and degradation of these compounds is cyclic, using long-chain fatty alcohols and fatty acids as precursors. Long-chain fatty acids and alcohols are also widespread in plant species, and may constitute from 2 to 70% of the cuticular wax composition of grasses (Dove and Mayes, 1991). In Australia, leaf and bark litter are the most common organic substrates available for aquatic organisms (Bunn, 1986). In freshwater storages, the chemical constituents of natural microlayers include saturated and unsaturated even-numbered carbon chain lengths of C12 to C 22, with the linear, saturated C16 compound palmitic acid the most common (Norkrans, 1980). The concentration of short-chain fatty acids and alcohols is higher in the immediate subsurface water than in the microlayer, suggesting that they have been forced out due to competitive adsorptive processes (refer to Section 2.4). The physical and chemical properties of these naturally derived, long-chain surfactants are very similar to the properties of artificial monolayers, explaining why C16 compounds such as hexadecanol are so readily degraded in aquatic environments. Naturally

occurring microlayer compounds have the potential to adversely interact with artificial monolayers in three ways (Pittaway and van den Ancker, 2010b):

- As microbial substrates favouring the growth of microbes pre-adapted to degrade long-chain amphiphiles such as artificial monolayer compounds;
- As non-homologous amphiphilic hydrocarbons disrupting the orderly packing and/or forming holes in artificial monolayer films; and
- As chemically reactive humus-like compounds increasing photodegradation.

The impact of water quality on the half-life of monolayer molecules and on the integrity of the condensed surface film may indeed be greater than the impact of the monolayer on water quality.

Field trials undertaken with pure formulations of hexadecanol and octadecanol confirm that the fatty alcohol compounds are not directly toxic to aquatic animals (Wiltzius, 1967). However, if lower chain-length alcohols are mixed with the active ingredient to improve the rate of spreading (refer section 2.4), acute toxicity to aquatic organisms may be observed. These results indicate that chemical compounds formulated with the active monolayer ingredient need to be tested for toxicity. For example, in recent tank-scale trials, the pH of the microlayer water sample increased from 7.9 to 10.2 after the application of a commercial formulation of hexadecanol incorporating hydrated lime as a 'filler' (Pittaway and van den Ancker, 2010b). The pH returned to that of the control within four days, but immediately after application, the elevated pH had the potential to adversely affect organisms that interact with or reside within the microlayer.

## 5.2. Indirect Impacts: Reduced Surface Tension

The most extensive examination of the effect of monolayers on water quality was undertaken by Wixson (1966), using a mixture of the compounds hexadecanol and octadecanol. No reference was made to any pre-existing microlayer observed on the lake. The study was conducted in North America, over a period of 30 days. Relative to the clean water surface, applying the monolayer reduced oxygen diffusion by 10 to 15%. However, this effect varied with the timing of measurements, and over the duration of the trial. The author was concerned that the decrease in surface tension that occurred after applying the monolayer caused some filamentous algae to sink. Non-filamentous algae appeared to decrease in abundance over the first 15 days, but recovered to population densities above the control by the end of the trial. Bacterial populations increased over the duration of the trial, as they utilised the monolayer compounds as a metabolic substrate. No significant effects of the monolayer on the fish species *Gambusia affinis* and *Fundulus notatus* were observed.

Surface tension is a very important property of water, utilised by many aquatic animals. Surface tension is the phenomenon of water molecules at the air-water interface contracting, increasing the force per unit length, pulling surface water molecules into the bulk phase (refer section 2.1). This induces an elasticity that enables small, winged insects to stride across the surface, small aquatic larvae and pupae to position their breathing siphons above the laminar layer, for emerging adult insects to escape from their submerged pupal cases, and for winged adult insects to alight on the surface to attach eggs to emergent aquatic vegetation (ovipositing). The most detailed studies on the impact of an artificial monolayer on aquatic invertebrates was conducted by Wiltzius (1967), using floating cages.

Surface pressure is the drop in surface tension from 72 mN/m to the lower equilibrium associated with the presence of amphiphilic compounds at the water surface (refer section 2.1). Natural microlayers can reduce surface tension if the molecules are sufficiently homogeneous to form a liquid-condensed film when compressed. In visible marine slicks comprised mainly of algal metabolites, surface pressures ranging from 0.5 to 35 mN/m have been recorded (Gladyshev, 2002). These surface pressures reduce surface tension from 72 mN/m to 71.5 and 37 mN/m respectively. Localised reductions in surface tension in freshwater storages may result in drownings of aquatic pupae, larvae and adult insects that depend on surface tension. However, as the generation mortality of insects is typically above 80%, these losses may not be ecologically significant (Ross *et al.*, 1982).

The concern with artificial monolayers is that the drop in surface tension across a water surface will be more extensive and more uniform, imparting a greater impact on aquatic microlayer specialists than the localised effects of natural surface films. In the study undertaken by Wiltzius (1967), a condensed monolayer of mixtures of the C<sub>16</sub> and C<sub>18</sub> fatty alcohols was maintained for 2 months over the summer period, on College Lake in Colorado, USA. A series of floating cages was constructed to compare the emergence of adult insects from the natural water surface or from water treated with monolayer, using a randomised block design. However, no observations were made on the presence of a natural microlayer, and no data is available on the surface pressure of treated and untreated surface films within the floating cages.

The most commonly encountered emergent aquatic insects were midges, with 15 species identified. The reduction in surface tension significantly reduced adult midge emergence by 47% (Wiltzius, 1967). Midge species with larger pupae, respiring via horns or trumpets (one functioning spiracle or propneustic) were most badly affected. A controlled laboratory experiment, using one midge species that has no spiracles (apneustic) but respire through filaments, indicated that reduced emergence was not only due to larval and pupal suffocation, but also due to the inability of the emerging adults to escape from the water. The test species *Tendipes riparius* suffered an emergence reduction of 54%. A laboratory study on the propneustic *Aedes* mosquito larvae indicated that increasing the proportion of longer chain fatty acids in the monolayer preparation increased pupal mortality from 69 to 97%. These effects were attributed to the decrease in surface tension associated with increasing the chain length of the monolayer formulation from C16 to C18 or C20. In the laboratory, surface tension reduced from the normal clean water value of 72 dynes cm<sup>-1</sup> to between 30.8 and 38.4 dynes cm<sup>-1</sup> (equivalent to surface pressures of 0 mN m<sup>-1</sup> and 41.2 to 33.6 mN m<sup>-1</sup> respectively). The higher pupal mortality was not reflected in the larval mortality, suggesting that the greater body mass of the pupae was more adversely affected by the reduction in surface tension. The drowning rate of Gerrid water striders also increased as the proportion of higher chain length fatty alcohol increased in the formulation, progressively reducing surface tension.

None of the fish species either observed in the lake or used in the laboratory trials suffered any adverse effects. There was some concern that the surfactant properties of the monolayer films may adversely affect the plumage of water birds (Wiltzius, 1967). Experiments with detached mallard duck breast feathers indicated that the presence of the monolayer increased the rate at which the feathers sank. However, the evaporative loss of the films adhering to ducks in flight should reduce the potential for any adverse impacts, and the natural preening behaviour of water birds should restore the water repellency of their plumage. Ingestion of the monolayer compounds during preening or feeding should not adversely affect aquatic animals as the industry standard monolayer products, the long chain fatty alcohols, are not directly toxic (refer to section 5.1).

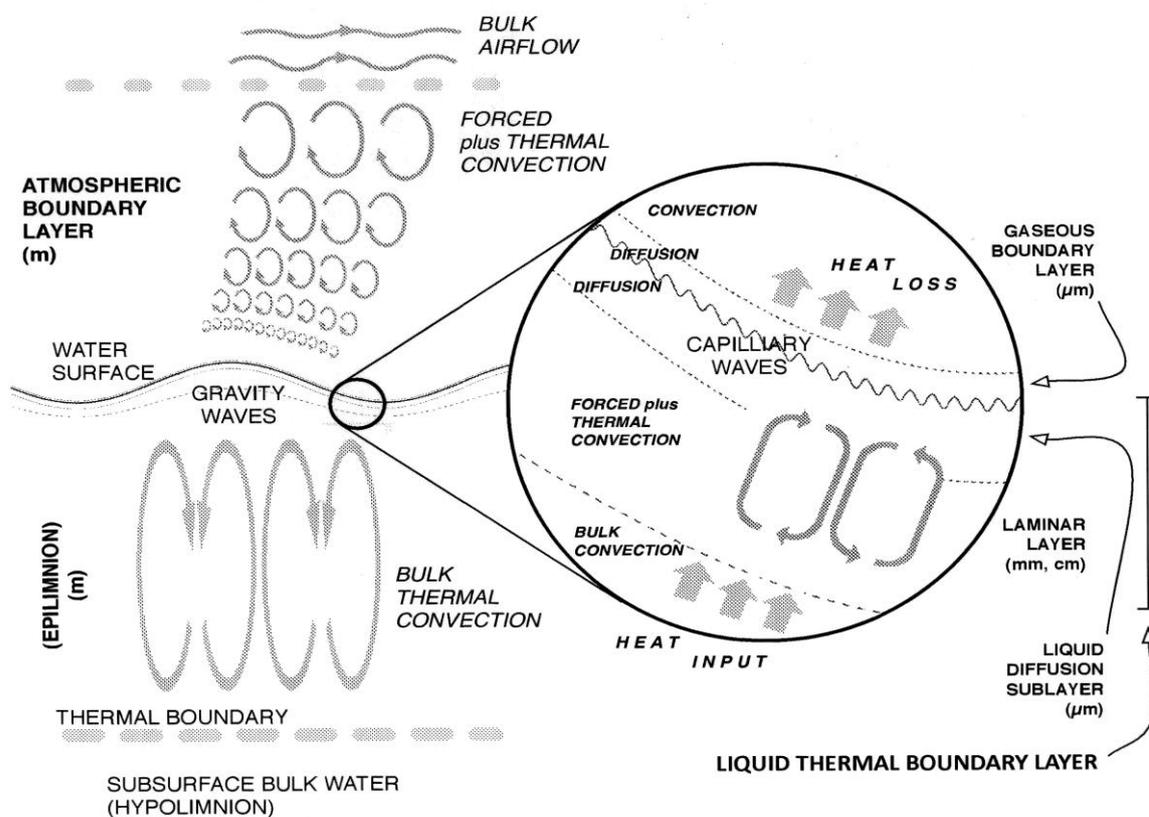
The author concluded that the only potentially adverse impact of the monolayers was on aquatic insects. However, the duration of the monolayers in the condensed state was limited by the speed and occurrence of prevailing winds, and by the economics of product application. The monolayer formulation was only likely to be applied over summer, when water demand and evaporative losses were highest. Many aquatic insect species emerged outside this treatment window, limiting the potential for adverse impacts on the aquatic food chain. Most of the midges commonly inhabiting lakes managed for irrigation and/or potable water have their peak emergence timed with spring and autumn lake circulations. Wiltzius (1967) also noted that the dissolved oxygen concentration in the treated pens at College Lake were on average 0.7 mg/L lower than untreated pens.

### **5.3. Indirect Impacts: Reduced Gaseous Diffusion**

The air/water exchange of soluble gases such as water vapour is controlled by the gaseous boundary layer, whereas the exchange of sparingly soluble gases such as carbon dioxide, oxygen, nitrogenous gases and sulfur dioxide is controlled by the liquid thermal boundary layer (Gladyshev, 2002; refer to section 4.2). The application of an artificial monolayer increases the transport resistance at the molecular level in both the gaseous and the liquid thermal boundary layers, and must therefore reduce gaseous exchange. In laboratory experiments, the diffusion layer  $\delta$  and the transfer coefficient  $K$  range from 0.015 mm and 47.5 cm/h with intensive stirring, to 2.76 mm and 0.26 cm/h without stirring.

Values for  $\delta$  in the range of 0.01 to 0.06 mm and  $K$  values of 15.0 cm/h have been reported for the Pacific Ocean, and a  $\delta$  value of 0.3 mm was reported for a small forest lake.

Within the liquid thermal boundary layer at the molecular level, the physical phenomena that regulate oxygen diffusion also regulate thermal conductivity (Gladyshev, 2002). Therefore, wind speed and the surface deviation temperature (thermal gradient) between the surface and the liquid thermal boundary layer will have a major impact on the diffusion of sparingly soluble gases such as oxygen (Figure 7). At wind speeds of less than 2 or 3 m/s, when the water is smooth and free convection occurs, the surface deviation temperature (thermal gradient) will influence  $K$  to a much greater degree than wind speed. The relationship between wind speed and  $K$  is strong and linear between 2 or 3 m/s and 6 or 7 m/s due to the forced convection induced by ripple and wave action (Gladyshev, 2002). At speeds of greater than 7 m/s the dependence of  $K$  on wind speed increases steeply. The performance of artificial long chain fatty alcohol monolayers in retarding evaporative loss is also fundamentally a function of wind speed (Barnes, 2008).



**Figure 7:** The comparative scales at which gravity waves, bulk thermal convection, capillary waves and boundary layer physics affect gaseous exchange and thermal convection at the air-water interface. At the millimeter scale, wind speed and the surface deviation temperature (thermal gradient) have a major impact on the diffusion of sparingly soluble gases such as oxygen, and of heat (section 4.2).

Under calm conditions, or with wind speeds of less than 2 or 3 m/s, the impact of the monolayer on  $K$  will depend on the surface deviation temperature (Gladyshev, 2002). If the water surface is warm relative to the subsurface, the thermal stability of the liquid thermal boundary layer will increase  $\delta$  way beyond the equivalent thickness induced by the presence of a condensed monolayer (Katsaros and Garrett, 1982; refer to section 4.2). In the presence or absence of an applied monolayer, aquatic organisms in water storages experiencing warm surface films diurnally and/or seasonally must adapt to the low oxygen concentrations associated with the low  $K$  values. The impact of a monolayer on reducing the dissolved oxygen concentration of the water will be greatest when wind speed is within the range of 2 or 3 m/s and 6 or 7 m/s, when the presence of a condensed monolayer is the single most important determinant of  $K$  and  $\delta$  (Gladyshev, 2002).

In laboratory experiments, the application of a hexadecanol monolayer reduced evaporative loss by 25% on stirred or unstirred water, whilst the oxygen transfer rate remained unaffected within the range of 0.3 to 0.7 cm/h (Linton and Sutherland, 1958). However, when a jet of air was blown across the surface (19 L/min), the presence of the monolayer reduced the oxygen transfer coefficient by 40%. The authors calculated that under the influence of a light breeze, the oxygen concentration in a water storage that was initially at 90% saturation would only reduce to 80% saturation after the application of a condensed monolayer. However, once the wind speed increased above 6 or 7 m/s, turbulence has a far greater impact on the oxygen transfer rate than the presence of a monolayer (Gladyshev, 2002). Indeed, above 6 or 7 m/s most monolayer films would be disrupted, reforming only once calmer conditions prevailed (Barnes, 2008).

Thus, while several studies report reductions in the dissolved oxygen concentration (eg Wixson, 1966; Frenkiel, 1965), or a reduction in ammonia gas emissions (Simpson *et al.*, 1988) after the application of a monolayer, the impact of the monolayer on gaseous exchange changes with the prevailing micrometeorological conditions. Monolayers that suppress evaporative loss will reduce oxygen diffusion whenever prevailing micrometeorological conditions operate at a scale that is equivalent to the thickness of the liquid thermal boundary layer (Wells *et al.*, 2009). However, whenever the scale is larger than the thickness of the thermal boundary layer (for example thermal stability associated with warm surface films and stratification, or thermal instability associated with wind and wave-breaking processes), the presence of a condensed monolayer has no significant impact on gaseous exchange and heat flux.

#### **5.4. Indirect Impacts: Increased Water Temperature**

The formation of a condensed monolayer on the water surface reduces the cooling effect associated with evaporative loss and capillary waves (refer section 2.2). Experimentally, the impact of a condensed monolayer in retarding evaporative loss is proportional to the rise in temperature of the water surface (Jarvis *et al.*, 1962; Bartholic *et al.*, 1967). Several authors have expressed concern that the increase in water temperature associated with the application of a condensed monolayer may adversely affect water quality by reducing the dissolved oxygen concentration (Parker and Barsom, 1970) and by increasing the risk of algal blooms (McJannet, 2008). However, if the scale of the impact of an artificial monolayer is taken into consideration, these risks may not be as great as they initially appear.

In the case of the Jarvis *et al.* (1962) experiments, the depth of water had to be limited to produce the proportional response between surface temperature and surface pressure induced by applying long chain fatty alcohol monolayers of increasing chain length. Under the laboratory conditions of the assay, limiting the water depth to 0.4 cm, maintaining the temperature of the water 7°C lower than the ambient air temperature, and maintaining an atmosphere of low relative humidity was necessary to achieve the relationship between surface temperature and surface pressure. A cold surface film would have prevailed under these conditions, with the presence of the monolayer reducing evaporative loss by increasing the thickness of both the gas and liquid thermal boundary layers (Figure 7; refer to section 4.2). Retarding evaporation reduces latent heat loss, implying that the water surface covered with a condensed monolayer should always heat up relative to a clean water surface.

The presence of the monolayer stabilises the surface film by increasing the resistance to interfacial heat transfer (Gladyshev, 2002). However, the magnitude of the difference between the surface and subsurface water temperature (surface deviation temperature) for a film-covered and a clean water surface is dependent on the heat flux from the water surface to the air. Under a positive, downward heat flux (air is warmer than the water, as in the Jarvis *et al.*, 1962 experiments), the presence of a monolayer retards heat transfer downwards (film-covered surface is warmer than the clean water surface). Under a negative, upward convective heat flux (air is colder than the water), the presence of a monolayer retards heat transfer upwards (film-covered surface is cooler than the clean water surface). Varying the drivers of evaporative loss, such as relative humidity, also changes the magnitude of the surface deviation temperature.

For example, in the Jarvis *et al.* (1962) experiments the temperature of the hexadecanol-covered water surface at a depth of 0-2 mm with a humidity of 0%, increased by 0.4°C above that of a clean water surface. Increasing the humidity to 55% reduced the temperature of the monolayer-covered surface film below that of a clean surface by 0.2 to 0.3°C. At 55% relative humidity the role of evaporation in the heat balance is much lower for the clean water surface (less latent heat loss), with the direction of the heat flux determined by the magnitude of the difference between the temperature of the air and the water (Gladyshev, 2002). For a clean water surface, the latent heat loss associated with evaporation will induce a cold surface film if the air temperature is warmer than the water temperature. Restricting the depth of the water to 0-2 cm inhibits the descent of cold thermals, limiting the change in the thickness of the liquid thermal boundary layer normally associated with a cold surface film (Katsaros, 1980; refer section 4.2). At 88% relative humidity (no latent heat loss), a cold surface film will only occur if the air temperature is lower than the water temperature. Increasing relative humidity to 55% reduced the thermal gradient in the liquid thermal boundary layer of the clean water (increasing the interfacial heat transfer resistance), but the interfacial heat transfer resistance of the monolayer-covered water remained the same. The relative difference in the surface deviation temperature of the clean water and the monolayer-covered water is dependent on the difference between the air and water temperature. In the absence of latent heat loss (high relative humidity) and convective heat loss (no descending thermals) and with the air temperature higher than the water temperature (a cold surface film), it is possible for a monolayer-covered surface to be cooler than a clean water surface, as observed by Jarvis *et al.* (1962).

The application of both saturated and unsaturated monolayer compounds retards heat conductance to a similar degree (Barnes and Hunter, 1982), indicating that the presence of a natural microlayer may also have the same effect. The interfacial heat transfer resistance induced by a monolayer operates in a dual fashion, to reduce heat loss when the water temperature is greater than the air temperature, and to reduce heat gain when the air temperature is greater than the water temperature (Gladyshev, 2002). In nature, the surface deviation temperature varies diurnally, with the dual effect of a condensed monolayer on heat conductance cancelling out any surface-heating effects associated with the reduction in evaporation during the day. Moreover, micrometeorological processes such as a thermally stable warm surface film formed in the absence of wind, or turbulence associated with wind and wave action, or rainfall, are effective at a much greater scale (Saylor, 2003), limiting the potential for artificial monolayers to adversely affect the limnology of water storages.

Biological activity, such as the formation of algal blooms, also increases surface temperature, presumably by increasing the thickness of the liquid thermal boundary layer (Katsaros, 1980). Phytoplankton produce free fatty acids, with saturated, straight-chain C16 (palmitic acid) and C18 (stearic acid) fatty acids the most common (Gladyshev, 2002; refer to section 4.1). In sufficient purity and quantity, these fatty acids damp capillary waves and increase surface pressure, increasing the thickness of the liquid thermal boundary layer in exactly the same way as the application of an artificial monolayer (refer section 2.4). Algal blooms in Australia were observed as early as 1878 by European colonists recording the occurrence of a blue-green algal bloom on Lake Alexandrina in South Australia (Queensland Water Quality Taskforce, 1992), and are a natural feature of many freshwater systems.

Natural reservoirs such as blocked drainage lines and back-swamps are a rare feature of the natural topography in Queensland (Stanton, 1975). Freshwater impoundments are comparatively recent in origin, built by local communities to improve the reliability of a water supply in a highly variable climate. During 1991 and 1992, algal blooms were reported from 17 Queensland water storages, with the majority located within the Southeast corner of the state (Queensland Water Quality Taskforce, 1992). Therefore, within a relatively short time-frame, aquatic organisms have adapted to changes in surface pressure, temperature and gaseous diffusion associated with the outbreak of algal blooms in artificially constructed water storages. The adaptive changes evident within these freshwater ecosystems should also enable aquatic organisms to adapt to similar changes induced by the application of an artificial monolayer to reduce evaporative loss.

It is possible that an increase in microlayer temperature and the thickness of the liquid thermal boundary layer induced by the application of an artificial monolayer may favour the activity of blue-green algae (Cyanobacteria). Cyanobacteria are considered 'summer species', capable of rapid growth

under calm conditions (Zohary and Breen, 1989). Unlike other phytoplankton, Cyanobacteria vary their position in the water column by regulating air pressure in a gas vacuole. Positive buoyancy allows Cyanobacteria to stabilise their location within the water column, overcoming barriers such as a thick liquid thermal boundary layer. Blue-green algae are also the phytoplankton group most commonly associated with toxic algal blooms (Queensland Water Quality Taskforce, 1992). The Water Quality Taskforce concluded that the prevention of blue-green algal outbreaks in aquatic systems in Australia (in the absence of an applied artificial monolayer) was extremely unlikely. An integrated approach including nutrient control, biological control, algicide application, physical control and water treatment was recommended, a strategy that will also limit any adverse algal impacts associated with the application of an artificial monolayer.

## **5.5. Indirect Impacts: Adverse Impacts on Potable Water Treatment**

Potable or safe drinking water must be free from pathogenic organisms and toxic compounds (Gardner *et al.*, 2008), and aesthetically must have minimal colour, turbidity or odour (Bennett and Drikas, 1993). Water treatment processes vary with the nature of the water source, and the impurities that must be removed (Stevenson, 2003). Surface sources (lakes, reservoirs and rivers) typically require more treatment than groundwater sources (wells and bores), and are the most common source of potable water in SEQ. The Australian Drinking Water Guidelines require water utilities to implement management systems that account for six operational principles (Gardner *et al.*, 2008):

1. The greatest risk to consumers of drinking water is pathogenic micro-organisms. Protection of water sources and treatment are of paramount importance and must never be compromised.
2. The drinking water system must have, and continuously maintain, robust multiple barriers appropriate to the level of potential contamination facing the raw water supply.
3. Any sudden or extreme change in water quality flow or environmental conditions (e.g. extreme rainfall or flooding) should arouse suspicion that drinking water might become contaminated.
4. System operators must be able to respond quickly and effectively to adverse monitoring signals.
5. System operators must maintain a personal sense of responsibility and dedication to providing consumers with safe water, and should never ignore a consumer complaint about water quality.
6. Ensuring drinking water safety and quality requires the application of a considered risk management approach.

Potential hazards to potable water quality likely to be present in surface water include the concentration of major ions (salinity and hardness) and the pH of the water, turbidity, the presence of potentially pathogenic bacteria, viruses and protozoa, naturally occurring organics and anthropogenic volatile and non-volatile organics, and the presence of metals and radionuclides (Nadebaum *et al.*, 2004). Artificial monolayer compounds are anthropogenic, non-volatile organics. Classed as linear, saturated non-ionic surfactants, monolayer compounds are considered non-toxic (Dorn *et al.*, 1993; and section 5.1). In aquatic systems, fatty alcohol monolayer compounds degrade to produce few if any byproducts (Wixson, 1966; Langley, 1970).

Indirectly, regular applications of artificial monolayers may increase the population of aquatic bacteria utilising the compound as a substrate (Wixson, 1966). In the liquid-condensed form, monolayers increase the thickness of the liquid thermal boundary layer, favouring the activity of cyanobacteria (section 5.4). Hazards associated with cyanobacterial 'algal' blooms include toxins, odour, colour and taints, and filter blocking (Nadebaum *et al.*, 2004). Algal blooms occur more commonly under calm conditions that favour stratification, conditions that operate at a much larger scale than the millimetre 'calming' scale of a condensed monolayer (Figure 7; and sections 5.3 and 5.4). Repeat application of an artificial monolayer is therefore unlikely to increase the frequency of algal blooms on a reservoir. On the contrary, repeat monolayer application should improve water quality by conserving more water in the storage, reducing the likelihood of excessive drawdown (Nadebaum *et al.*, 2004).

An increase in cyanobacteria or heterotrophic bacteria may adversely affect potable water treatment systems by blocking sand filters (Nadebaum *et al.*, 2004). Potable water treatment systems in SEQ commonly include pre-treatment with coagulation/flocculation (Gardner *et al.*, 2008) to reduce the concentration of suspended particles below 2–3 mg/L (Stevensen, 2003). Under higher loading rates, the solids collect in the voids within the sand filter medium. Once the shear stress on the coated sand grains exceeds the limit for deposition, wormhole-like channels perforate the clogged layer. The filtrate quality progressively deteriorates as the channels emerge from the bottom of the sand filter. Coagulation involves the aggregation of finer, suspended particles into larger flocs, removed from the water by either sedimentation or filtration. In SEQ, after 20 to 30 minutes of mixing, the water is retained in a sedimentation tank for several hours to allow the floc to settle under gravity (Gardner *et al.*, 2008). Clean water is skimmed from the top, and flows into high-rate sand filters.

Coagulation and flocculation occur within a mixing tank, often with the addition of either aluminium sulfate (alum) and/or synthetic organic polymers (Gardner *et al.*, 2008). Polymers vary in molecular weight from  $10^4$  to  $10^6$  daltons, may be linear or branched, and may be cationic, anionic or non-ionic (Ebeling *et al.*, 2010). Particles suspended in water are negatively charged. Polymers act by neutralising the charge, forming bridges between particles. Under van der Waals force, the particles aggregate into dense, closely packed flocs that rapidly settle under gravity. Long-chain polymers enhance the flocculation process by attaching at relatively few sites on individual particles, leaving longer chain segments and loops free to attach to other particles. In Australia, the polymers recommended for use in potable water treatment are limited to anionic polyacrylamides, poly aluminium chlorides and silica sulfates, and cationic polydiallyldimethylammonium chlorides (NHMRC, 2004).

Only emulsified artificial monolayer compounds are likely to enter the potable water supply as most reservoir off-take pipes are located well below the surface. However, as non-ionic surfactants, the currently available artificial monolayer compounds are chemically compatible with the anionic and cationic polymers recommended for coagulation and flocculation (NHMRC, 2004). Moreover, the presence of non-ionic surfactants is an advantage in potable water treatment systems using membrane filtration, as adsorbed surfactants enhance fouling resistance and protect cellulose acetate and polyamide membranes from degradation (Wilbert, 1997; Leiknes, 2009).

The compatibility of monolayer compounds with long-chain polymers used in the pre-treatment of potable water indicates that most monolayer compounds will sediment out following flocculation and coagulation. The concentration of monolayer compounds in the water after pre-treatment and filtration should be very low, posing little risk to disinfection treatment processes such as chlorination, ozone and ultraviolet disinfection. The ozonation of some surfactants may lead to the formation of byproducts that are more toxic than the parent compound (Delanghe *et al.*, 1991). However, unbranched, non-ionic surfactants break down completely after a relatively short exposure to ozone, posing less of a risk than unsaturated, quaternary ammonium surfactants. These results indicate that the currently available long-chain, saturated fatty alcohols and glycol monoalkyl ethers formulated as artificial monolayers, are unlikely to affect the quality of municipal potable water, or the efficacy of potable water treatment systems.

## REFERENCES

- Aarts, D., Schmidt, A., and Lekkerkerker, H., 2004, Direct visual observation of thermal capillary waves. *Science* 304, 847-850.
- Baier, R., 1970, Surface quality assessment of natural water bodies. Proceedings 13<sup>th</sup> Conference of Great Lakes Research pp 114-127. *International Association of Great Lakes Research*.
- Barnes, G., 1986, The effects of monolayers on the evaporation of liquids. *Advances in Colloid and Interface Science* 25, 89-200.
- Barnes, G., 2008, The potential for monolayers to reduce the evaporation of water from large water storages. *Agricultural Water Management*, 95, 339-53.
- Barnes, G., and Gentle, I., 2005, *Interfacial Science*. Oxford University Press, Oxford UK.
- Barnes, G., and Hunter, D., 1982, Heat conduction during the measurement of the evaporation resistances of monolayers. *Journal of Colloid and Interfacial Science* 88, 437-443.
- Barnes, G., and La Mer, V., 1962, The evaporative resistances of monolayers of long-chain acids and alcohols and their mixtures. Pp 9-33 in *Retardation of Evaporation by Monolayers*. Ed V La Mer Academic Press London UK.
- Bartholic, J., Runkles, J., and Stenmark, E., 1967, Effects of a monolayer on reservoir temperature and evaporation. *Water Resources Research* 3, 173-179.
- Bennett, L., and Drikas, M., 1993, The evaluation of colour in natural waters. *Water Research* 27, 1209-1218.
- Binks, B., 1991, Insoluble monolayers of weakly ionizing low molecular mass materials and their deposition to form Langmuir-Blodgett multilayers. *Advances in Colloid and Interface Science* 34, 343-32.
- Brink, G., Wandel, A., Pittaway, P., Hancock, N., and Pather, S., 2010, A universal design framework for installation, planning and operational management of evaporation-suppressing films on agricultural reservoirs. *Proceedings of the International Conference in Agricultural Engineering*, Clermont-Ferrand, France September 6-8 2010.
- Brinkman, T., Horsch, P., Sartorius, D., and Frimmel, F., 2003, Photoformation of low-molecular-weight organic acids from brown water dissolved organic matter. *Environmental Science and Technology* 37, 4190-4198.
- Brooks, J., and Alexander, A., 1960, Losses by Evaporation and solution from monolayers of long-chain aliphatic alcohols. Volume 1V section B pp 196-201 in the *Third International Congress of Surface Activity*, Cologne, Germany.
- Chang, S., McClanahan, M., and Kabler, P., 1962, Effect of bacterial decomposition of hexadecanol and octadecanol in monolayer films on the suppression of evaporation loss of water. In *Retardation of Evaporation by Monolayers: Transport Processes*. Ed Le Mer V Academic Press, Berkeley Square, London UK.
- Craig, I., 2008, Loss of storage water through evaporation with particular reference to arid and semi-arid zone pastoralism in Australia. Desert Knowledge CRC Working Paper 19, *The WaterSmart™ Literature Reviews*. Desert Knowledge CRC, Alice Springs.
- Dahlback, B., Hermansson, M., Kjelleberg, S., and Norkrans, B., 1981, The hydrophobicity of bacteria – an important factor in their initial adhesion at the air-water interface. *Archives of Microbiology* 128, 267-270.
- Davies, J., and Rideal, E., 1963, *Interfacial Phenomena*. 2<sup>nd</sup> Edition, Academic Press, London UK
- Delanghe, B., Mekras, C., and Graham, N., 1991, Aqueous ozonation of surfactants: A review. *Ozone Science and Engineering* 13, 639-673.
- Deo, A., Kulkarni, S., Gharpurey, M., and Biswas, A., 1961, Rate of spreading and equilibrium spreading pressure of the monolayers of n-fatty alcohols and n-alkoxy ethanols. *Journal of Physical Chemistry* 66, 1361-1362.
- Dorn, P., Salanitro, J., Evans, S., and Kravetz, L., 1993 Assessing the aquatic hazard of some branched and linear non-ionic surfactants by biodegradation and toxicity. *Environmental Toxicology and Chemistry* 17, 1751-1762.
- Duque, D., Tarazona, P., and Chacon, E., 2008, Diffusion at the liquid-vapour interface. *Journal of Chemical Physics* 128, 134704-1 to 134704-10.
- Eames, I., Marr, N., and Sabir, H., 1997, The evaporation coefficient of water: a review. *International Journal of Heat and Mass Transfer* 40, 2963-2973.
- Ebeling, J., Rishel, K., and Sibrell, P., 2010, Screening and evaluation of polymers as flocculation aids for the treatment of aquacultural effluents [www.aseanfood.info/Articles/11014941.pdf](http://www.aseanfood.info/Articles/11014941.pdf) accessed 21/12/2010.
- Frenkiel, J., 1965, Evaporation reduction: physical and chemical principles and review of experiments. *Arid Zone Research* 27, *Evaporation Reduction*, UNESCO, Paris.

- Gardner, T., Yeates, C., and Shaw, R., 2008, Purified Recycled Water for Drinking: The Technical Issues. *Queensland Water Commission*, Brisbane Qld, Australia.
- Gladyshev, M., 2002, *Biophysics of the Surface Microlayer of Aquatic Ecosystems*. IWA Publishing London, United Kingdom.
- Goldacre, R., 1949, Surface films on natural bodies of water. *Journal of Animal Ecology* 18(1), 36-39.
- Hammond, D., and Kubo, I., 1999, Structure-activity relationship of aliphatic alcohols as mosquito larvicides with novel findings regarding their mode of action. *Bioorganic and Medicinal Chemistry* 7, 271-278.
- Hancock, N., Pittaway, P., and Symes, T., 2011, Towards a biophysical understanding of observed performance of evaporation suppressant films applied to agricultural water storages – first analyses. *Australian Journal of Multidisciplinary Engineering*.
- Hatcher, R., and Parker, B., 1974, Microbiological and chemical enrichment of freshwater-surface microlayers relative to the bulk-subsurface water. *Canadian Journal of Microbiology* 20, 1051-57.
- Hopfinger, E., and Das, S., 2009, Mass transfer enhancement by capillary waves at a liquid-vapour interface. *Experiments in Fluids* 46, 597-605.
- Hostmark, O., and Teigland, S., 2009, Role of water activity of liquid in controlling evaporation rate of low-viscosity liquids. *Drying Technology* 27, 1152-1155.
- Jarvis, N., Timmons, C., and Zisman, W., 1962, The effect of monomolecular films on the surface temperature of water. Pp 41-58 in *Retardation of Evaporation by Monolayers*. Ed V La Mer, Academic Press, London UK.
- Jones, F., 1992, *Evaporation of Water with Emphasis on Application and Measurements*. Lewis Publishers, Chelsea Michigan USA.
- Kadour, i D., Jurkevitch, E., Okon, Y., and Castr-Sowinski, S., 2005, Ecological and agricultural significance of bacterial polyhydroxyalkanoates. *Critical Reviews in Microbiology* 31, 55-67.
- Katsaros, K., 1980, The aqueous thermal boundary layer. *Boundary-Layer Meteorology* 18, 107-127.
- Katsaros, K., and Garrett, W., 1982, Effects of organic surface films on evaporation and thermal structure of water in free and forced convection. *International Journal of Heat and Mass Transfer* 25, 1661-1670.
- Kravetz, L., Salanitro, J., Dorn, P., and Guin, K., 1991, Influence of hydrophobe type and extent of branching on environmental response factors of non-ionic surfactants. *Journal of the American Oil Chemistry Society* 68, 610-618.
- Krogh, K., Halling-Sorensen, B., Mogensen, B., and Vejrup, K., 2003, Environmental properties and effects of non-ionic surfactant adjuvants in pesticides: a review. *Chemosphere* 50, 871-901.
- Kubo, I., Fujita, T., Kubo, A., and Fujita, K., 2003, Modes of antifungal action of Aliphatic alcohols against *Saccharomyces cerevisiae*. *Bioorganic and Medicinal Chemistry* 11, 1117-1122.
- La Mer, V., 1962, Preface. Pp vii-xiii in *Retardation of Evaporation by Monolayers*. Ed V La Mer Academic Press, London UK.
- Leiknes, T., 2009, The effect of coupling coagulation and flocculation with membrane filtration in water treatment: A review. *Journal of Environmental Sciences* 21:,8-12.
- Lewis, M., 1991, Chronic and sublethal toxicities of surfactants to aquatic animals: a review and risk assessment. *Water Research* 25, 101-113.
- Linton, M., and Sutherland, K., 1958, The solution of oxygen through a monolayer. *Australian Journal of Applied Science* 9, 18-23.
- Ludzack, F., and Ettinger, M., 1957, Biological oxidation of hexadecanol under laboratory conditions. *Journal of the American Waterworks Association* 49, 849-858.
- McJannet, D., Cook, F., Knight J. and Burn, S., 2008, Evaporation reduction by monolayers: overview, modelling and effectiveness. CSIRO: Water for a Healthy Country National Research Flagship. Urban Water Security Research Alliance Technical Report No. 6.
- MacRitchie, F., 1969, Evaporation retardation by monolayers. *Science* 163, 929-931.
- Meyers, P., and Kawka, O., 1982, Fractionation of hydrophobic organic materials in surface microlayers. *Journal of Great Lakes Research* 8, 288-98.
- Mohr, J., Gribble, G., Lin, S., Eckenhoff, R., and Cantor, R., 2005, Anaesthetic potency of two novel synthetic polyhydric alkanols longer than the n-alkanol cutoff: evidence for a bilayer-mediated mechanism of anaesthesia? *Journal of Medical Chemistry* 48, 4172-4176.
- Munster, U., Heikkinen, E., and Knulst, J., 1998, Nutrient composition, microbial biomass and activity at the air-water interface of small boreal forest lakes. *Hydrobiologia* 363, 261-70.
- Nadebaum, P., Chapman, M., Morden, R., and Rizak, S., 2004, *A Guide to hazard Identification and Risk Assessment for Drinking Water Supplies*. Research Report 11, Cooperative Research Centre for Water Quality and Treatment April 2004.
- Neu, T., 1996, Significance of bacterial surface-active compounds in the interaction of bacteria with surfaces. *Microbiological Reviews* 60, 151-166.

- NHMRC 2004, *Australian Drinking Water Guidelines*. National Health and Medical Research Council, and Natural Resource Management Ministerial Council. Canberra, Australia.
- Norkrans, B., 1980, Surface microlayers in aquatic environments. *Advances in Microbial Ecology* 4, 51-85.
- Parker, B., and Barsom, G., 1970, Biological and chemical significance of surface microlayers in aquatic ecosystems. *Bioscience* 20, 87-93.
- Patoczka, J., and Pulliam, G., 1990, Biodegradation and secondary effluent toxicity of ethoxylated surfactants. *Water Research* 24, 965-972.
- Pittaway, P., and van den Ancker, T., 2010a, Properties of natural microlayers on Australian freshwater storages and their potential to interact with artificial monolayers. *Marine and Freshwater Research* 61, 1083-1091.
- Pittaway, P., and van den Ancker, T., 2010b, *Microbial and Environmental Implications for use of Monolayers to Reduce Evaporative Loss from Water Storages*. Technical Report 07/10. Cooperative Research Centre for Irrigation Futures. IF Technologies Ltd. 978 0 9808674 7 3.
- Queensland Water Quality Task Force, 1992, *Freshwater Algal Blooms in Queensland*. Volume 1 Main Report, October 1992. Chairman D Connell, Queensland Water Quality Taskforce, Government of Queensland, Brisbane.
- Rosano, H., and La Mer, V., 1956, The rate of evaporation of water through monolayers of esters, acids and alcohols. *Journal of Physical Chemistry* 60, 348-353.
- Rosen, M., Fang, L., Morrall, S., and Versteeg, D., 2001, The relationship between the interfacial properties of surfactants and their toxicity to aquatic organisms. *Environmental Science and Technology* 35, 954-959.
- Ross, H., Ross, C., and Ross, J., 1982, *A Textbook of Entomology* 4<sup>th</sup> Edition. John Wiley & Sons, New York USA.
- Saylor, J., 2003, The fate of soluble and insoluble surfactant monolayers subjected to drop impacts. *Experiments in Fluids* 34, 540-547.
- Saylor, J., and Handler, R., 1999, Capillary wave gas exchange in the presence of surfactants. *Experiments in Fluids* 27, 332-338.
- Saylor, J., Smith, G., and Flack, K., 2000a, The effect of a surfactant monolayer on the temperature field of a water surface undergoing evaporation. *International Journal of Heat and Mass Transfer* 43, 3073-86.
- Saylor, J., Szeri, A., and Foulks, G., 2000b, Measurement of surfactant properties using a circular capillary wave field. *Experiments in Fluids* 29, 509-518.
- Sice, J., 1966, Tumor-promoting activity of n-alkanes and 1-alkanols. *Toxicology and Applied Pharmacology* 9, 70-74.
- Silvey, J., 1960, Physical, chemical and biologic effects of hexadecanol on Lake Hefner, 1958. *Journal of the American Waterworks Association* 52, 791-802.
- Simpson, J., Muirhead, W., Bowmer, K., Cap, G., and Freney, J., 1988, Control of gaseous nitrogen losses from urea applied to flooded rice soils. *Fertilizer Research* 18, 31-47.
- Stanton, J., 1975, *A preliminary assessment of wetlands in Queensland*. CSIRO Division of Land Use Research Technical Memorandum 75/10. CSIRO, Canberra. 52pp.
- Stevenson, D., 2003, A review of current and developing potable water treatment processes. Proceedings of the Institute of Mechanical Engineers 217 part E *Journal of Process Mechanical Engineering*, 11-23.
- Vines, R., 1962, Evaporation Control: A Method of Treating Large Water Storages. Pp 137-160 In *Retardation of Evaporation by Monolayers*. Ed V La Mer, Academic Press London UK.
- Water Services Association of Australia, 2010, Water Restrictions and Storage Levels. [www.wsaa.asn.au/media/Facts/Pages/default.aspx](http://www.wsaa.asn.au/media/Facts/Pages/default.aspx) accessed 30/05/2010
- Wells, A., Cenedese, C., Farrar, T. and Zappa, C., 2009, Variations in ocean surface temperature due to near-surface flow: Straining the Cool Skin Layer. *Journal of Physical Oceanography* 39, 2685-2710.
- Wilbert, M., 1997, *Enhancement of Membrane Fouling Resistance through Surface Modification*. Water Treatment Technology Program Report 22. United States Department of the Interior, Bureau of Reclamation, Denver Colorado USA.
- Wiltzius, W., 1967, *Effects of monolayers on insects, fish, and wildlife: a reservoir evaporation reduction study*. Research Report 7, Water Resources Technical Publication, United States Department of the Interior, Bureau of Reclamation, Washington DC USA.
- Wixson, B., 1966, *Studies on the ecological impact of evaporation retardation monolayers*. Texas Water Resources Institute technical report 6. Texas A & M University.
- Wu, Jin, 1971a, An estimation of oceanic thermal-sublayer thickness. *Journal of Physical Oceanography* 1: 284-286.
- Wu, Jin, 1971b, Evaporation retardation by monolayers: Another mechanism. *Science* 174, 283-85.
- Zorahy, T., and Breen, C., 1989, Environmental factors favouring the formation of *Microcystis aeruginosa* hyperscums in a hypertrophic lake. *Hydrobiologia* 178, 179-192.

# Urban Water Security Research Alliance

