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Spreading rate and dispersion behavior of evaporation-suppressant monolayer on open water surfaces: Part 1 – at zero wind stress

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Abstract
Effective evaporation suppression by a monolayer film is largely dependent on the maintenance of that film over as much of the water surface as practically possible. Hence, an autonomous system capable of adaptive re-application of monolayer according to the prevailing wind conditions in order to satisfy this requirement is highly desirable. Key to the design and functioning of a system of this nature is a fundamental understanding of the spatial movement/distribution characteristics of the monolayer material. To ‘bridge’ between centimeter-scale, clean room laboratory experimentation (e.g. with a Petri dish) and field conditions (i.e. hectare-scale open water storages), the spreading rate and dispersion behavior of different application quantities of octadecanol monolayer (in water-emulsion) was investigated on 0.3 m, 2 m and 6 m diameter laboratory water tanks under zero wind stress. A standard formula for spreading is shown to be applicable to ‘bulk’ monolayer from a center point on circular, open water surfaces of scale 0.3 m, 2 m and 6 m diameter. Under still conditions, monolayer spread (as expected) in a uniform circular pattern outwards, centered on the point of application. ‘Bulk’ application involved the placement of enough material to form layers 1×, 3× or 6× monomolecular. Hitherto this has not been demonstrated with either these ‘overdosed’ (3×, 6×) material quantities or at these scales, scales which come closer to those required for monolayer application for the evaporation mitigation of practical open water storages. An empirical relationship for spreading rate has been developed as a function of both time and storage size.

Highlights:
- Monolayer experiments with no wind produce spreading coefficients and spreading exponents
- A robust model for spread has a low sensitivity to the spreading exponent value
- Empirical formula for spreading coefficient as a function of storage size is determined

Keywords: Monolayer, Evaporation reduction, Spreading rate, Dam storage size
1 Introduction

In Australia, the efficient use of stored agricultural water is critical as the population pressure and the variability in annual rainfall increase. One attractive and cost effective technique for reducing evaporation from larger open water reservoirs (>10 ha) is the use of a monomolecular film [Barnes, 2008]. Much of the monolayer-based evaporation mitigation research was undertaken in the 1950s, 60s and 70s and centered on the use of the spreading insoluble fatty alcohols, hexadecanol (C\textsubscript{16}H\textsubscript{33}OH) and octadecanol (C\textsubscript{18}H\textsubscript{37}OH) (for example Frenkiel [1965] and Brown [1988]). Many researchers from this era have reported highly variable field performance results (from 0–43% efficiency, summarized by McJannet et al. [2008]), which undoubtedly contributed to the lack of their commercial adoption in the subsequent decades. However, drought and near-drought conditions over much of southern Australia in the last decade have encouraged research into improving monolayer performance [Craig et al., 2007].

Effective evaporation suppression of water by a monomolecular film is fundamentally dependent on the maintenance of that film over the great majority of the water surface. In the laboratory under controlled conditions complete cover can easily be established; however, in the field under natural weather conditions, this is very difficult to both achieve and maintain. Across all the readily-available publications to date reporting the in-field performance of monolayer, it would be nearly impossible to find one that does not make reference to the deleterious effects of wind. Wind is the principal factor negatively affecting the persistence of monolayer on the water surface [Crow, 1963]. Wind increases film volatilization, surface drift downwind, and beaching on the lee shore, while also generating waves, which can break-up or submerge the film [Fitzgerald and Vines, 1963; Frenkiel, 1965; Reiser, 1969].

Vines [1962] reported that wind-induced drift of a monolayer film across the water surface starts to occur at wind speeds of around 3.2 km/h. McArthur [1962] and Crow and Mitchell [1975] report similar values. Above this threshold wind speed, it is generally agreed that a monolayer film will drift downwind at a speed of about 3.5(±0.7)% of the wind speed (e.g. Hale and Mitchell [1997]). The general approach to maintaining a continuous film cover during wind speeds greater than 3.2 km/h has been to apply monolayer continuously at a rate equal to that at which it is removed [Frenkiel, 1965; Crow, 1963; Reiser, 1969]. However, even a ‘constant’ wind is highly dynamic and, of course, varies from location to location and in both speed and direction. Also, periods of calm (defined here as wind speeds < 3.2 km/h) may persist for hours or even days. Therefore, an effective monolayer application system should be capable of non-continuous application during periods of calm and also continuous application during periods of wind [Brink et al., 2011].

Central to the design of the application system and appropriate application strategies is knowledge of the spatial distribution of monolayer applied to the water surface; and in turn this requires a fundamental understanding of the characteristics of monolayer movement under different wind conditions. Thus, in order to characterize monolayer movement, it is necessary to achieve this for both low wind conditions, < 3.2 km/h, and for a range of wind conditions > 3.2 km/h.

Using octadecanol (in water-emulsion) as a benchmark monolayer material, this paper reports experimental results with zero wind stress at a range of scales (using laboratory water tanks of diameter 0.3 m, 2 m and 6 m); and a companion paper [Brink et al., 2016] reports experimental results for a range of windspeeds (at the 6m diameter tank scale). The present methodology was designed to ‘bridge’ between centimeter-scale, clean room laboratory experimentation (e.g. a Petri dish and Langmuir trough) and the desired field conditions, i.e. on
extensive open water storages, where experimentation is particularly challenging, principally due to lack of environmental control. By this means the validity of extrapolation of the results to field (hectare) scale is argued.

2 Background

During low wind conditions, there would be little if any influence by the wind on monolayer movement, therefore, rate of coverage will largely be dictated by the natural spreading rate of the monolayer. As monolayer molecules are amphiphilic (each has a hydrophobic part and hydrophilic part), they anchor themselves to the water surface causing a decrease in surface tension (e.g. Barnes and Gentle [2011]). When a monolayer-forming material is first placed on the water it creates a surface tension gradient between the film-forming material and the water surface causing rapid initial spreading [Myers, 1992]. This phenomenon of fluid flow caused by surface tension gradients is known as Marangoni flow [Jensen, 1995; Dussaud and Trojan, 1998; Tarasov et. al., 2006; Berg, 2009]. Marangoni flow is typically a very rapid transport process whose speed is controlled by the initial spreading force per unit length [Davies and Rideal, 1961]:

\[
S = \gamma_{\text{w/a}} - (\gamma_{\text{ml/a}} + \gamma_{\text{ml/w}})
\]

where \(\gamma_{\text{w/a}}, \gamma_{\text{ml/a}}\) and \(\gamma_{\text{ml/w}}\) represent the surface tensions of the water/air, monolayer/air and monolayer/water interfaces respectively. The greater the value of \(S\), the greater the driving forces causing spreading [Saylor and Barnes, 1971].

Many researchers from the field of surface chemistry measure spreading rate in terms of relative changes in surface tension using surface tensiometers; however, this does not provide a direct measurement of spreading rate [Hale and Mitchell, 1997]. More recently, engineering researchers have been concerned with the dynamics of spreading of monomolecular films in industry and science, as they provide an interesting transport mechanism for technological processes [Berg, 2009]. In this field, spreading at the air-water interface is measured according to the speed of advance of the leading edge (edge between clean and monolayer covered water surface), which is usually identified experimentally using small tracer particles (such as talcum powder).

The spreading dynamics at the air-water interface of a deep liquid (which we are exclusively dealing with in this paper) are different to those for a thin liquid [Berg, 2009]. A simple force balance first proposed by Fay [1969] determines the advance of the leading edge of a thin film spreading on a deep liquid in the surface-tension regime. Fay [1969] and Dussaud and Trojan [1998] reasoned that the force per unit length driving the spreading process is the spreading force, which is opposed by the viscous drag force exerted on the film by the subsurface boundary layer.

The full theory for spreading is complicated and in most cases full solutions are numerical [Jensen, 1995; Chebbi, 2001 and Berg, 2009]. However, Dussaud and Trojan [1998] show that where the spreading film is non-volatile, immiscible in water, has a constant concentration source and is expanding radially on deep water, the leading edge position is given by:

\[
d(t) = K \left( \frac{S^{1/2}}{(\mu \rho)^{1/2}} \right) t^*
\]
where \(d(t)\) is the distance travelled by the leading edge, \(K\) is the spreading coefficient, \(\mu\) is the dynamic viscosity of water, \(\rho\) is the density of water, \(S\) is the spreading force, \(t\) is the elapsed time since monolayer first touched the water surface, and \(n\) is the scaling exponent.

The value of the scaling exponent \(n\) has been determined numerically by Foda and Cox [1980] and Jensen [1995] to be 0.75, and verified experimentally by Camp and Berg [1987], Dussaud and Troian [1998] and Tarasov et al. [2006] to be 0.75±0.01. The value of 0.75 has mathematical appeal, since it renders \(K\) dimensionless in eq. (2). The implication from these results is that the exponent may be universal for all non-volatile immiscible films (for an infinite source of monolayer). However, for volatile and/or miscible films, or a finite source spreading other than radially, this exponent has found to be lower [Dussaud and Troian, 1998].

Berg [2009] reported that the spreading coefficient \(K\) is 1.1547 for an axisymmetric geometry, which is in excellent agreement with Chebbi [2001], who calculated \(K\) to be 1.15 through numerical analysis. However, Camp [1985] reported values in the range of 0.67 to 1.06 while Dussaud and Troian [1998] reported values of 0.87 or 0.88 for silicone.

Following Dussaud and Troian [1998], \(K\) can be calculated from empirical data using:

\[
K = \frac{(\mu \rho)^{1/4}}{S^{1/2}} k_D
\]  

in which \(k_D\) is determined from a power-law fit to experimental data:

\[
d(t) = k_D t^n
\]  

Berg [2009] reported that the spreading dynamics of the leading edge of a monolayer is generally modeled by eq. (4).

Of the relevant studies found in literature, all were conducted on small surface areas (< 3 m\(^2\)) and over very short time spans (< 5 s) [Camp and Berg, 1987; Dussaud and Troian, 1998; Tarasov et al., 2006; Berg, 2009]. As noted, this has motivated the objective of the present study to measure the spreading rate of octadecanol at different scales over different time durations (i.e. spreading periods) and compare with the spreading rates predicted using eqs. (3) and (4). To the best of our knowledge a spreading coefficient for octadecanol has not previously been reported, despite this material being used extensively in evaporation mitigation research. In addition, the value of the spreading exponent must also be confirmed for octadecanol (when applied as a monolayer-water emulsion) to validate extrapolation to full-scale water storages.

3 Materials and Methods

3.1 Monolayer material and application amounts

Octadecanol in a volatile solution was not considered suitable as the use of volatile solvents on many water storages is undesirable due to both cost and environmental concerns [Barnes, 2008]. Hence a monolayer-water emulsion of 4% 1-octadecanol (C\(_{18}\)H\(_{37}\)OH) (purity grade ≥ 99% GC), 1% Brij® 78 (comprising polyoxyethylene (20) stearyl ether, C\(_{18}\)H\(_{37}\)(OCH\(_2\)CH\(_2\))\(_{20}\)OH), and Milli-Q water (18.2 MΩ cm resistivity), was made by melting the alcohol (octadecanol) and emulsifier (Brij 78) together and then adding hot water (at approximately 70°C) while stirring, and the emulsion was then allowed to cool with continued stirring [Herzig et al, 2011]. The emulsion was observed to be stable for at least 6 months (i.e. no separation of the octadecanol and water) and displayed improved spreading ability (Figure 1)
and evaporative resistance compared to octadecanol in powder form (Table 1). (For the remainder of this paper the abbreviation C18OH is used to indicate octadecanol deployed using Brij 78.)

As the monolayer application requirement in the field will be different for different size reservoirs it is necessary to determine the effect of different application amounts on spreading rate. In addition, application rates greater than the theoretical value required for still water are necessary in order to compensate for material losses due to volatilization and/or submergence (Vines, 1962; Frenkiel, 1965; Reiser, 1969; Crow and Mitchell, 1975) as well as the increased surface area due to both gravity and capillary waves. Denoting the theoretical (still water) value for monomolecular layer formation as ‘1×’ (= 2.3 mg/m² for the C18OH monolayer-water emulsion, [Herzig et al., 2011]), the surface pressure required to reach equilibrium surface pressure was measured for three different application amounts: 1×, 3× and 6×, as set out in Table 1. Surface pressure was measured using a Wilhelmy plate cut from Whatman 1 Chr chromatography paper, attached to a NIMA force sensor (NIMA Technologies, Coventry, UK) using the standard procedure (Barnes et al., 1980). Corresponding evaporation resistances were measured using a modified Langmuir-Schaefer method [Barnes et al., 1980].

**Figure 1 (Single Column).** Comparison of surface pressure as a function of time for octadecanol (C18OH) in a powder form, C18OH+Brij78 (the monolayer-water emulsion used in this study) and Brij78 in solution with water. All surface pressures were measured in a PTFE Langmuir trough with a NIMA force sensor.
Table 1. Surface pressures and evaporative resistances measured for C$_{18}$OH monolayer-water emulsion at different application amounts, including a comparative measurement for C$_{18}$OH powder at a 6× application amount. A single monolayer requires 2.3 mg/m$^2$ of emulsion.

<table>
<thead>
<tr>
<th>No. of Monolayers Applied</th>
<th>Monolayer Form:</th>
<th>Π (equilibrium surface pressure) [mN/m]</th>
<th>Evaporative Resistance [s cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>Emulsion</td>
<td>0</td>
<td>n/a</td>
</tr>
<tr>
<td>1</td>
<td>Emulsion</td>
<td>~13</td>
<td>n/a</td>
</tr>
<tr>
<td>3</td>
<td>Emulsion</td>
<td>~41</td>
<td>n/a</td>
</tr>
<tr>
<td>6</td>
<td>Emulsion</td>
<td>~44</td>
<td>5.0</td>
</tr>
<tr>
<td>6</td>
<td>Powder</td>
<td>~35</td>
<td>4.6</td>
</tr>
</tbody>
</table>

3.2 Measurement of the initial spreading force

The initial spreading force $S$ for the monolayer-water emulsion was determined by measurement of the force balance on a custom-built PTFE Langmuir trough and barrier.

An immiscible film-forming material (octadecanol, dissolved in hexane) was applied to the water surface of the trough, compressed by the barrier to a high surface pressure. Once compressed, a drop of the monolayer-water emulsion was placed on top and the barrier was then moved backwards, decreasing the surface pressure. Surface pressure measurements taken during this process indicated that the drop started to spread at a surface pressure of 14±1 mN/m (at a water temperature of 23°C): this was taken to be the initial spreading force.

3.3 Experimentation with 0.3 m diameter tank

Experiments were conducted in a round polypropylene plastic bin, 0.3 m in diameter and 0.37 m deep, which was lined with a black polythene plastic bin liner sheeting. This improved the visual contrast between talcum powder and monolayer during measurements, and also allowed the bin liner and water to be replaced for every spreading test, negating the need to clean the water surface of residual surfactant. This procedure, with the assumption that the surface pressure of the clean tap water was < 4 mN/m, avoided the need to measure the initial surface pressure with indicator oils (which would have required sacrifice of a substantial portion of the surface area). A measuring tape was also suspended across the top of the tank for calibrating the digital rulers used during video analysis (similar to that for the 2 m diameter cattle trough, Figure 2).

For each test the water was left for an hour to settle before applying monolayer and all replicate tests for each application amount were run on the same day to minimize temperature differences – water temperature is known to affect the spreading rate of monolayer [McArthur, 1962]. Temperature variation within each set of replicates was measured to be less than 1°C.
Polyethylene cattle trough, diameter 2.0 m, used for spreading rate tests. Each has a measuring tape that is suspended across the top of the trough for calibrating the digital rulers used during video analysis.

Figure 2 (Single Column). (a) Talcum powder application (prior to monolayer application) to visualize the spreading characteristics of the monolayer on the water surface; and (b) monolayer spreading in a circular pattern as identified by the talcum powder collecting around the edges of the spreading front (both shown here for the 6 m diameter tank).

Prior to monolayer application the water surface was dusted with a very thin layer of Sigma-Aldrich ‘Technical Talc’ powder (following Davies and Rideal [1963], Lange and Huhnerfuss [1978] and Hale and Mitchell [1997]). Although O’Brien et al. [1975] reported that the use of talcum powder underestimated spreading rates of oleic acid by < 10% compared to rates measured using thermistors, Hale and Mitchell [1997] stated that measurement error in his study accounted for much of this difference. During this study, the layer of talcum powder applied to the water surface was kept as thin as practically possible in order to minimize any potential errors imposed by its use. A hand-held ‘Gilmour’ pesticide duster proved to be an effective method for applying a very fine layer of talc to the water surface (Figure 3). The temperature of the top 10 mm of water was also measured before the application of monolayer with a K-type thermocouple and Lutron TM-905 digital thermometer.
Monolayer was applied from approximately 15 mm above the water surface in the middle of the tank by hand with a micropipette. All spreading rate tests were recorded with a Canon Digital IXUS 80IS digital video camera mounted above the center of the tank from a wall bracket. Video (Figure 4) was recorded at 30 frames per second and at a resolution of 640 × 480 pixels, and manually analyzed frame-by-frame (using Adobe Flash software) (following Mitchell et al. [1995]). The spreading front and time were measured relative to the first point of contact of monolayer with the water surface.

Monolayer surface pressures were measured 20 minutes after application using a range of calibrated indicator oils, each comprising a different proportion of dodecanol (C_{12}H_{25}OH) in mineral oil such that it spreads at a specific water/monolayer surface pressure. The range used spanned 4 mN/m to 22 mN/m in 1 mN/m steps, plus 24, 28, 32 and 34 mN/m.

Figure 4 (2 Column). Screen shots of video analysis in Adobe Flash (2 m diameter tank shown); (a) first point of contact at $t = 0$ seconds (no monolayer has been applied yet); (b), (c), and (d) radii of the monolayer at 5 s, 10 s and 15 s seconds after application respectively.

3.4 Experimentation with 2 m diameter tank

The second set of experiments was conducted similarly in a round polyethylene plastic cattle trough, 2 m in diameter and 0.7 m deep. This had a black polythene plastic sheet fixed to the bottom of the tank, again to improve the contrast between talcum powder (used for visualizing the monolayer on the water surface) and monolayer while a measuring tape was suspended across the top of the tank and fixed on opposing sides of the tank rim (Figure 2). The measuring tape was secured such that the middle of the tape intersected the middle of the tank. The water level was always kept below the height of the measuring tape so it did not touch the water surface.
The tank was filled with tap water until overflowing and until the water surface was thoroughly cleaned of impurities and residual monolayer. When the surface appeared clean, the water interfacial surface pressure was tested with calibrated indicator oils. If the water surface was measured to be < 4 mN/m, the cleaning process was stopped, but again only after all of the indicator oil was allowed to overflow over the edge of the tank. Three hours’ settlement time was allowed for each measurement, thereby reducing the influence of water currents set up during the cleaning process (following Hale and Mitchell [1997]). Again, in order to minimize the effect of temperature, as water temperature was not regulated, replicates for each application amount were all run on the same day. Temperature variation was contained to 2°C within all sets of replicates.

Again, as monolayer is not visible to the human eye, an empirical method of determining if the water surface was clean of monolayer was necessary [Timblin et al., 1962; Grundy, 1962; McArthur, 1962]. A very thin layer of Sigma-Aldrich ‘Technical Talc’ powder was also applied to the water surface before application of monolayer using the method described in Section 3.2. The temperature of the top 10 mm of water was also measured before the application. Monolayer was then applied from approximately 15 mm above the water surface in the middle of the tank by hand with a calibrated medical syringe. After 20 minutes of monolayer application, the interfacial surface pressure was again checked with the indicator oils. All spreading rate tests were recorded with the same digital camera and analyzed in the same manner as described in Section 3.3.

3.5 Experimentation with 6 m diameter tank

The third and final set of experiments was conducted similarly in a round water tank, 6 m in diameter and 0.3 m deep, fitted with an impervious black polyethylene (PE) liner. Two thick strips of cloth tape, (silver in color) with ruler markings every 100 mm, were fixed to the liner in a criss-cross pattern with the intersection point of the strips of tape in the center point of the liner (Figure 5).

The tank was filled with tap water until overflowing. As in the 2 m diameter trough tests, before every test the water surface was thoroughly cleaned of impurities and residual monolayer by overflowing. However, because of the larger area, repeated scraping was performed over the water surface to the overflowing edge of the tank with a 5 m long, 90 mm diameter polyethylene (PE) pipe (typically for 45 minutes) again until the water interfacial surface pressure was measured to be < 4 mN/m (measured in a portion of the water surface sectioned off with the PE pipe so that the oil was contained and subsequently flushed over the edge of the tank to remove it). Again, after cleaning, the water was left for three hours to settle. Because the water temperature was not regulated during testing, replicates for each application amount were all run on the same day to minimize temperature variations. At this scale, with a much greater diameter-to-depth ratio for the water body, the water temperature variation could be contained to 1°C within all sets of replicates.

Talcum powder was again applied to the water surface before monolayer application by the same method detailed in Section 3.3 and the temperature of the top 10 mm of water measured before the application of monolayer. Monolayer was then applied at the center of the tank using a calibrated medical syringe operated ‘remotely’ at the end of a 3 m long, 25 mm diameter aluminum pole (Figure 5-inset). Monolayer application was delivered at approximately 20 mm above the water surface.
The 6 m diameter water tank (lined with a black polyethylene liner) used for spreading rate tests. Monolayer is being applied with a calibrated medical syringe fixed to the end of a 3 m long aluminum tube for reach. Another aluminum tube, inside the larger diameter aluminum tube, is used to push down on the syringe plunger to apply monolayer.

The interfacial surface pressure was again checked 20 mins after the application of monolayer using the calibrated indicator oils. All spreading rate tests were recorded with a Logitech Webcam Pro 9000 digital camera suspended from the roof 5.5 m above the center of the tank. Video was recorded at 25 fps and at a resolution of 960×720 pixels, and likewise manually analyzed.

4 Results

At each experimental scale (0.3 m, 2 m and 6 m) the spreading rate results are only valid up to the time when the proximity of the edge of the tank starts to affect the spreading rate. It was observed for all three tanks that the spreading rate would drop to zero abruptly when the edge of the monolayer was close to the edge (e.g. Figure 6), at radial distances of approximately 110 mm, 700 mm and 2600 mm respectively. Hence data were regarded as valid for the first 1 s, 10 s and 55 s for the 0.3 m, 2 m and 6 m tanks respectively.
Figure 6 (Single Column). Diameter versus time for monolayer spreading on the 2 m and 6 m diameter tanks. As is visible in both tanks, the monolayer spreads until nearing the edge of the tank whereupon the spreading rate drops to zero.

As the monolayer spreads such that the leading edge was clearly close to a perfect circle every time, the radius was repeatedly measured from the first point of contact of monolayer with the water surface to the leading edge in a single direction for operational convenience. However, the validity of the perfect circle assumption was quantified at each tank scale by simultaneously measuring the spreading front radius in four orthogonal directions outwards from the first point of monolayer application. The average variation was 1.3%, 1.3% and 2.0% for the 0.3 m, 2 m and 6 m diameter tanks respectively.

Three replicate tests were carried out for each application amount to ensure reproducibility. The data from the three replicates for each application amount was then averaged and plotted for radius versus time. The results from the 0.3 m, 2 m and 6 m diameter tanks are shown in Figure 7. For the 2 m and 6 m tanks the average uncertainty was 3% and 5% respectively across the three replicate experiments for each; this compares with the uncertainty of ≤ 2% arising from the simple technique of radius estimation.
Figure 7 (Single Column). The leading edge radius versus time for application of monolayer placed at the center of each tank (at time = 0). At each timestep the error bars represent the mean and standard deviation of five replicate experiments. (a) 0.3 m tank with 6× application only; the average standard deviation is 0.0045 m; (b) 2 m tank with three different application amounts (1×, 3× and 6×); (c) 6 m tank with three different application amounts (1×, 3× and 6×).
The power law eq. (4) was used to fit each set of replicate tests and the results, plus the calculated spreading coefficients eq. (3), are set out in Table 2. As noted in Section 2.3, the initial spreading force $S$ for the octadecanol+Brij78 monolayer-water emulsion used in this study was determined to be $14\pm 1$ mN/m (at a water temperature of 23°C).

Finally, to inform comparison across size scales and the possible effect of application amount, a direct comparison was performed in which the same quantity of monolayer, 7.0 mg/m², was applied to the larger two tanks, namely 2 m and 6 m. (The 0.3 m tank was omitted because its small diameter limited the validity of the open-water spreading beyond a few seconds.) Water temperatures were 19°C and 23°C respectively. The results are shown in Figure 8 and discussed below.

Table 2. Summary of monolayer quantities applied and water temperatures during testing, including the constants and exponents derived from the 0.3 m, 2 m and 6 m tank results.

<table>
<thead>
<tr>
<th>No. of Monolayers</th>
<th>Monolayer Quantity [mg]</th>
<th>Water Temp. [°C]</th>
<th>Fitted factor eq. (4) $k_D$</th>
<th>Fitted exponent eq. (4) $n$</th>
<th>Eq.(4) fit quality $R^2$</th>
<th>Spreading Coefficient eq. (3) $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 m Diameter Tank:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.1</td>
<td>23</td>
<td>0.108</td>
<td>0.769</td>
<td>0.9999</td>
<td>0.898</td>
</tr>
<tr>
<td>2 m Diameter Tank:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>7.0</td>
<td>19</td>
<td>0.107</td>
<td>0.788</td>
<td>0.998</td>
<td>0.907</td>
</tr>
<tr>
<td>3</td>
<td>20.0</td>
<td>18</td>
<td>0.105</td>
<td>0.825</td>
<td>0.994</td>
<td>0.896</td>
</tr>
<tr>
<td>6</td>
<td>40.0</td>
<td>18</td>
<td>0.103</td>
<td>0.849</td>
<td>0.998</td>
<td>0.881</td>
</tr>
<tr>
<td>Mean (± std. error):</td>
<td>0.105 (±0.001)</td>
<td>0.821 (±0.018)</td>
<td>0.895 (±0.008)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 m Diameter Tank:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>60.8</td>
<td>19</td>
<td>0.133</td>
<td>0.733</td>
<td>0.9996</td>
<td>1.134</td>
</tr>
<tr>
<td>3</td>
<td>182.4</td>
<td>18</td>
<td>0.138</td>
<td>0.742</td>
<td>0.9999</td>
<td>1.160</td>
</tr>
<tr>
<td>6</td>
<td>364.6</td>
<td>19</td>
<td>0.144</td>
<td>0.735</td>
<td>0.9997</td>
<td>1.207</td>
</tr>
<tr>
<td>Mean (± std. error):</td>
<td>0.138 (±0.003)</td>
<td>0.736 (±0.003)</td>
<td>1.167 (±0.021)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 8 (Single Column). Comparison of radius increase over the first 10 s for a 3x application on the 2 m and 6 m diameter tanks. Each line represents the average, and the error bars indicate the standard deviation, for three replicates. (The experimental artifact at 3.5 s for the 6 m tank is not considered significant.)

5 Analysis and Discussion

5.1 Comparison with theoretical parameters

The theoretical spreading curve according to eq. (2) using the Chebbi [2001] values of $K = 1.15$ and the spreading exponent $n = 0.75$ is plotted as the upper curve in Figures 9–11 for each size of tank. This theoretical curve is compared directly with the empirical data; and also with eq. (2) using the appropriate empirically derived $K$ and $n$ values and spreading exponents (Table 2) for the 6x application. This last curve was added to assess the quality of fit as a precursor to extrapolation across experimental scales (below).

In all calculations, spreading force $S$ was taken to be 14 mN/m, and the values for dynamic viscosity and density of water were calculated using the average water temperature recorded for 6x application at their respective tank scale. It can be seen that the theoretical curve over-predicts the experimental results for the smaller tanks, although this over-prediction diminishes with increasing tank size, so that it is a reasonably-good model for the 6 m tank.
**Figure 9 (Single Column).** Spreading front radius versus time for the 0.3 m diameter tank. The plots are, respectively, the measured data; eq. (2) with $K = 1.15$ and $n = 0.75$ (Berg and Chebbi values); and eq. (2) with $K$ and $n$ values from Table 2 for the measured data.

**Figure 10 (Single Column).** Spreading front radius versus time for the 2 m diameter tank at a 6x monolayer application. The three plots were derived as per Figure 9.
5.2 Comparison and reconciliation across different experimental scales

The duration of the spreading observed for the 0.3 m, 2 m and 6 m tanks was 1 s, 10 s and 55 s respectively (Figures 9–11). To facilitate comparison, and exploration of the implications for extrapolation to field scale, the three empirical curves were compared directly by extrapolation of each curve out to 100 s duration as shown in Figure 12.
Figure 12 (Single Column). Comparison of the predicted spreading front radius versus time derived from the three different tanks scales by extrapolation to 100 s duration via eq. (2). The dashed lines are extrapolations using the empirically-derived $K$ and $n$ values (Table 2) for the 6× application. The solid lines are extrapolations using the empirically-derived $K$ values for $n = 0.75$ (Table 3).

Figure 12 indicates that the predicted spreading radii diverge, as might be expected, especially for the 0.3 m tank results which involve a 100-fold extrapolation. The predictions for the 2 m and 6 m tanks also diverge at extended times (after approximately 30 s), and the extrapolations to 100 s do not differ monotonically with experimental scale (0.3 m–2 m–6 m) as might have been expected. Whilst the 6 m tank produced higher values than the 2 m tank for the 10 s that the latter was measured, the value of $n$ was significantly higher for the intermediate tank size, which produces the much higher extrapolation at 100 s. Clearly such extrapolation is heavily dependent on the value of the spreading exponent $n$, and Dussaud and Troian [1998] noted that the 0.75 value for non-volatile systems is not always reproducible.

A final comparison was made. The standard value of $n = 0.75$ was used to perform curve-fits of the data from the three tanks, thereby determining values of $K$ for each. This procedure does not produce least-squares curve fits, because the error between the function and the data is not minimized; however, it is the most rigorous method to compare values of $K$ for the different tank sizes. The results are listed in Table 3 and visualized in Fig. 12, from which it is apparent that the quality of fit is not significantly degraded and the behavior is monotonic with respect to tank size. The resulting relationship between $k_D$ and tank diameter $D$ is:

$$k_D = 0.114D^{0.0683}$$

with an $R^2$-value of 0.9942. This relationship provides a means of extrapolating the behavior of the monolayer to full-size dams.
Table 3. Curve-fits for the 0.3 m, 2 m and 6 m tank results for n = 0.75.

<table>
<thead>
<tr>
<th>Tank Diameter (m)</th>
<th>No. of Monolayers</th>
<th>Fitted factor eq. (4) $k_D$</th>
<th>Exponent eq. (4) $n$</th>
<th>Fit quality $R^2$</th>
<th>Spreading Coefficient eq. (3) $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>6</td>
<td>0.105</td>
<td>0.75</td>
<td>0.9970</td>
<td>0.873</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>0.118</td>
<td>0.75</td>
<td>0.9845</td>
<td>1.009</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>0.130</td>
<td>0.75</td>
<td>0.9964</td>
<td>1.090</td>
</tr>
</tbody>
</table>

6 Conclusions

It has been demonstrated that the formula of Dussaud and Troian [1998] and others, eq. (2), is applicable to the spreading of ‘bulk’ monolayer from a center point on a circular, open water surface of scale 0.3 m, 2 m and 6 m diameter. As expected, under still conditions, monolayer spreads in a uniform circular pattern outwards centered on the point of application. ‘Bulk’ application involved the placement of enough material to form layers which were 1×, 3× or 6× the monomolecular density. Hitherto this has not been demonstrated with these ‘overdosed’ material quantities and at these scales which come closer to those required for monolayer application for the evaporation mitigation of practical (hectare-scale) open water storages.

However, although characteristically similar across the three experimental scales, replicated results showed that the spreading rate varied slightly but significantly between the different scales and different dosage rates (1×, 3× and 6×), resulting in slightly different fitted values of the spreading coefficient $K$ and spreading exponent $n$. The reason for this discrepancy can principally be explained by the sensitivity of the value of $n$ to the data. When curve-fits of the data were produced using the generally accepted value of $n = 0.75$ (which was up to 13% lower than the value obtained from a least-squares curve-fit), the quality of the fit was not significantly reduced and a physical trend for $K$ was obtained. So while the value of $n$ is very sensitive to the data collected, modeling of the data using a standard value of $n = 0.75$ (with a value of $K$ determined by using $n = 0.75$), is not very sensitive to the data collected. It is therefore plausible that any debate in the literature regarding the “appropriate” value of $n$ is unproductive.

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References


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Highlights:

- Monolayer experiments with no wind produce spreading coefficients and spreading exponents
- A robust model for spread has a low sensitivity to the spreading exponent value
- Empirical formula for spreading coefficient as a function of storage size is determined