TOWARDS A BIOPHYSICAL UNDERSTANDING OF OBSERVED PERFORMANCE OF EVAPORATION SUPPRESSANT FILMS APPLIED TO AGRICULTURAL WATER STORAGES – FIRST ANALYSES

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ABSTRACT
The potential utility of monomolecular layers ('monolayers') and other surface film materials for the reduction of open water evaporation has long been argued. However, outside the laboratory, trials to quantify the effectiveness of artificial surface films have produced highly variable results after application to water surfaces, whether natural water bodies or managed farm storages.

This paper briefly reviews the physical mechanisms involved in evaporation suppression and the biophysical literature on aquatic surface microlayers. The wide-ranging results from sixteen months of outdoor trough-scale and (simultaneous) replicated bucket-scale evaporation reduction trials are interpreted using biophysical measurements made on microlayer and immediate subsurface water samples taken from the experimental troughs.

When the prevailing environmental conditions and other ancillary measurements are taken into account, plausible hypotheses arise to account for at least some of the observed trial-to-trial differences in evaporation reduction and surface film performance. These results have implications for both small-scale trailing of evaporation suppressants and the deployment and management of artificial surface film materials on agricultural water storages.

Keywords: monolayers; surface films; natural microlayers; evaporation mitigation; farm dams

1. INTRODUCTION
Artificial hydrophobic compounds that form a surface layer at the interface of water and the atmosphere, when applied to a large body of water, are known to reduce evaporation. Materials demonstrated to have this property include both monomolecular layers ('monolayers') typically 2 nm thick, and thicker films comprising many hundreds of molecular layers, typically of order 1 μm thick. Naturally occurring surface films or microlayers (typically 0.1-1 μm thick), are commonly observed on water bodies, but lack the surface pressure required to reduce evaporative loss (Barnes 2008). Similarly, not all artificial monolayer compounds have the performance characteristics required to effectively reduce evaporative loss from agricultural water storages.

Outside the laboratory, trials to quantify the effectiveness of artificial surface films have produced highly variable results. The reasons for measurement difficulty and error are many and apply across natural water bodies and managed farm storages. Assessing the effectiveness and performance of artificial surface films must consider:
(i)   the prevailing atmospheric conditions (as characterised by radiation, temperature, relative humidity, rainfall and wind);
(ii)   the difficulties of making sufficiently accurate comparative water loss measurements, due in particular to dam seepage, and
(iii) the 'quality' of the water, and how various chemical compounds and consequent biological processes might interact with the applied surface film.

To avoid seepage loss and to provide replication, Morrison et al. (2008) undertook a series of outdoor trials over sixteen months at small scale (using multiple buckets and cattle troughs). In addition water Water quality factors were minimised by refilling the receptacles with potable

water from a mains supply; but again, quite variable results were obtained. This paper presents analyses the of Morrison et al. (2008) 'bucket and trough' results in the light of ancillary measurements and the physical mechanisms for evaporation suppression by surface films.

2 EVAPORATION SUPPRESSION MECHANISMS

The evaporation-suppressing surface films – monolayers, microlayers and others – achieve evaporation reduction by forming an effective physical barrier to the transfer of water vapour molecules from the water body to the atmosphere (Barnes and Gentle, 2005). However, not all surface films have this property and the material must exert a surface pressure of at least 15 mN/m over the open water surface for this evaporation suppression mechanism to operate (Barnes, 2008).

The immediate result of evaporation suppression by this mechanism alone is that the water surface will be warmer than it would otherwise have been. It follows that if the surface cover is broken for any reason – for example by wave action, inadequate material to cover the surface or degradation of the material over time – the resulting evaporation from the unprotected patches will actually be *higher* than it would otherwise have been without the film. Therefore the overall evaporation suppression performance observed, spanning covered and non-covered areas, will be downgraded significantly.

However, the raising of the water surface temperature argued above presumes that the radiant energy supplied to the water body (as the principal driver of evaporation) is unaffected by the surface film. For monolayers, typically a few nanometres thick, this is a reasonable presumption; but for films of say 100 nm to 1 µm thickness, interaction with incoming solar radiation is a possibility as the wavelengths in the visible spectrum span 0.4-0.7 µm. Clearly, significant reflection of energy by the surface film would enhance its evaporation-suppression performance.

Surface films will also provide some calming of the (millimetre-scale) capillary waves ('ripples'), reducing the near-surface atmospheric turbulence and water vapour transfer (Conover and Saylor, 2007). Although relatively minor, this evaporation suppression mechanism will apply whether or not the surface film meets the >15 mN/m surface pressure criterion, and it is likely that (with the exception of the lee shore) any evaporation suppression provided by natural microlayers is provided solely by this mechanism (Pittaway and van den Ancker, 2009).

3. 'BUCKET AND TROUGH' PERFORMANCE TRIALS

Because the evaluation of evaporation-reducing surface chemicals presents very major practical difficulties, evaluation at small scale offers the possibility of experimental control and replication. Morrison et al. (2008) report evaporation reduction trials conducted using shallow tanks, cattle troughs and arrays of buckets (having water surface areas of areas $78.5m^2$, $2.93m^2$ and $0.064m^2$ respectively) over sixteen months from January 2007 to April 2008. The apparatus at experimental site, the Agricultural Field Station on the Toowoomba campus of the University of Southern Queensland, is illustrated in Figure 1.

Three surface layer-forming chemicals were trialed, two in their commercially-available forms:
- 'Water$avr' – hexadecanol (cetyl alcohol), known to form a monolayer on a water surface, and supplied with hydrated lime dispersant;
- 'Aquatain' – a silicone based oil of unpublished composition; and
- an unspecified (pre-commercial) monolayer-forming material, hereafter labelled 'M', which was available only from December 2007.

Figure 1. Illustrating (a) four of the eight 1.2 kL cattle troughs and (b) twelve of the twenty-four 18 L buckets of the 'Bucket and Trough' performance trials (Morrison et al. 2008).

Each material was applied to the water surface of the troughs and buckets filled to a standard depth. Evaporative loss was determined by continuously logging at 15-minute time intervals (average of 1-minute measurements) using precision pressure sensitive transducers (PSTs) each with individual temperature compensation from simultaneous water temperature measurement at each transducer. All trials used municipal potable water to serve as a control over the same period of measurement. Automatic Weather Stations (AWS) were located adjacent to the trial site for collection of weather data. Product application rates ('dosage') and re-application intervals initially followed manufacturers' recommendations, but were increased three fold on the basis of preliminary results. In bucket array trials all treatments including control were replicated (4–8 times) in a randomised block design. The trough trials were conducted in parallel, with the PSTs inserted in one of each of the duplicated treatments.

Despite closely replicated trials and techniques to manage potential systematic error, there appeared to be considerable variability in the evaporation mitigation performance of all of these products. Change in water quality is considered unlikely to have contributed to the variability as potable water was used throughout the trials and receptacles were rigorously cleaned prior to the commencement of each trial.

4. BIOPHYSICAL ANALYSES and DISCUSSION
4.1 Methodology
The analyses presented here were restricted to the 'Phase 2' trials conducted from September 2008 to April 2009. These final six trials span the particularly variable weather experienced over these summer months. Trial length was typically two weeks, but this was occasionally truncated by poor weather or instrumentation failure. The monolayer-forming Material 'M' only became available from December 2007 and was therefore not available for the first two trials.

Clearly the changing weather conditions, both diurnally and trial-to-trial, imposed a different and constantly changing 'evaporative demand' on each of the water surfaces. Full analysis would therefore need to be undertaken with time increments of 15 minutes or shorter, and with particular regard for the changes in thermal energy storage in the water. However, analysis at a 'whole trial' scale, involving from 7 to 21 days of data, means that, to a first approximation, diurnal energy changes are cancelled out for whole-trial totals. To permit cross-trial comparison, the result for each treatment of each trial (i.e. cumulative evaporation) was standardised by dividing by the cumulative evaporation from the untreated trough or bucket (duplicated) designated the 'control', i.e. standardised with respect to the open (unprotected) water surface at the same spatial scale and with the same atmospheric exposure. The results from the six trials are then as shown in Figures 3(a) and (c), and these are analysed further with respect to the differing environmental conditions below.

However, other detailed data comparisons yielded two significant results: these are presented first as they impact on the differing evaporative demand analysis.

4.2 Product Limitations – Water$avr

Water quality measurements were undertaken for Trials 5 and 6 immediately after application of the two monolayer treatments (Water$avr and 'M') to investigate concern about the quantity of active constituent (hexadecanol) actually being applied with the Water$avr product. The surface interface of the tanks without the PST recorders was sampled for each treatment and control, using a Larsson plate sampler (Larsson et al 1974). Both hexadecanol and the unspecified monolayer 'M' are degraded by aquatic bacteria and hence the response of bacteria to the magnitude of the food supply can be assessed by the standard 5-day biochemical oxygen demand (BOD_5) test (for example, Sawyer et al., 2003). The results are set out in Table 1.

Table 1 Comparison of water quality data measured at the commencement of Trials 5 and 6 in which precise and equal volumes of product were applied. The measurements made were acidity (pH), electrical conductivity (EC) and standard 5-day biochemical oxygen demand (BOD_5).

Test \ Treatment	Trial #5, Day 0			Trial #6, Day 0		
	pH	EC [µS/m]	BOD_5 O_2 [mg/L]	pH	EC [µS/m]	BOD_5 O_2 [mg/L]
Control (open water)	7.9	794	2.8	8.2	1058	6.1
'Water$avr' (hexadecanol + hydrated lime)	10.2	830	**8.3**	10.9	984	**34.5**
Monolayer 'M'	8.1	918	29.7	8.3	1054	21.0

The results for 'M' in Table 1 indicate that the amount added in both Trials 5 and 6 induced a very similar response in the BOD_5 test. However, results for Water$avr are very different. Data for pH and electrical conductivity (EC) indicate that an equivalent amount of hydrated lime was applied, but the greatly different BOD_5 results, 8.3 mg/L versus 34.5 mg/L, indicate that much less hexadecanol had been added in Trial 5. The hydrated lime, comprising nominally 95%v/v of the product, is present as a 'filler', as an aide in applying larger volumes of product to the surface of large water storages. However on the much smaller scale used in these trials, the results indicate that the active constituent is not sufficiently well mixed to produce repeatable results.

4.3 Differences in Diurnal Temperature Variation

Bulk water temperature was measured on six of the buckets during the latter part of the final trial, Trial 6. As expected major diurnal variation was observed; however, when normalised against the diurnal variation of the open (untreated) water surface of the control bucket, significantly different performance was apparent for the three buckets having monolayer treatment (Water$avr and 'M') compared with the two buckets with Aquatain treatment. These results are shown in Figure 2.

For the monolayer treatments, the results of Figure 2 show a temperature difference of between +1.5 and +2.5°C at each peak, in the mid-afternoon, which is consistent with reduced evaporation. In clear contrast, the results for the Aquatain (silicone oil) treatments indicate that the surface temperature in these buckets tracks that of the control closely, and with little obvious diurnal variation. However, the evaporation performance results (Figure 3) indicate that Aquatain is also suppressing evaporation, but clearly doing so without the water surface heating up significantly compared to open water. A plausible explanation for this observation is that the **albedo** (the reflectance of the water surface to solar radiation) is increased by the presence of Aquatain; and as noted above, this is consistent with its thickness being of the same order as the wavelength of solar radiation.
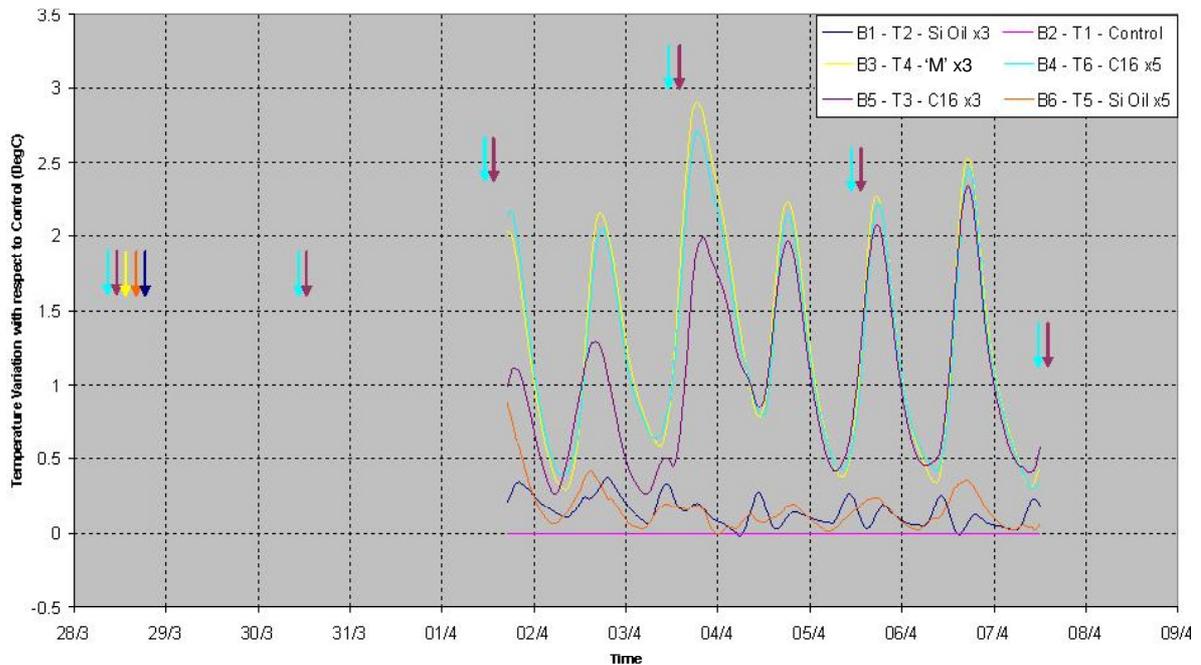
Figure 2. Smoothed diurnal bulk water temperature differences (four-hour moving average) over seven days for six buckets of Trial 6. Each record is shown as a difference with respect to the bulk water temperature of the control (bucket B2). At commencement in the afternoon of 01 April 2008, the six traces are (*in order from the top – material and dosage*): Water$avr x5; monolayer 'M' x3; Water$avr x3; Aquatain x5; Aquatain x5; control (= 0). Vertical arrows indicate initial product application (on 28 March) and subsequent re-application (Water$avr only) at two-day intervals.

4.4 Effect of Wind Stress

The disruptive effect of wind stress on monolayer films has long been known (Reiser 1969). In the recent laboratory 'wind tunnel' studies the products Water$avr, 'M' and Aquatain showed only limited resistance to the drag forces imposed by wind (McMahon et al. 2008). Of the three Aquatain was the most generally resistant to wind stress, and performance was independent of temperature. Of the two monolayers 'M' performed significantly better than Water$avr, but the performance of Water$avr was better at lower temperature.

The standardised evaporation performance results of Trials 1 to 6, both buckets and troughs, are set out in Figure 3 in order of increasing mean windspeed, which roughly double from calmest to windiest. In each barchart the utility of the surface film applied is indicated by the extent to which the ratio is less than unity: in Figure 3 these ratios are compared with both the prevailing distribution of windspeed and also temperature range and the general 'evaporative demand' (which integrates radiation exchange, humidity and windspeed).

Figure 3 shows there were cases where the ratio is greater than unity, indicating (slightly) enhanced evaporation. These results are not considered spurious: monolayers cause the uppermost millimetres of the water surface to be hotter than they would otherwise be, and broaching of the surface film by wind will result in increased evaporation (e.g. Trial3, 'M' at x1 dosage). For the three products, inspection of the results of Figure 3 indicates:

- for Water$avr, little discernable wind stress effect – but the uncertainty of the applied dose of its active ingredient (hexadecanol) – section 4.2 above – precludes any conclusion;

- for Aquatain, likewise little discernable wind stress effect in either buckets or troughs, suggesting some resilience to wind; however

- for monolayer 'M' with accurate x3 dosage, for both buckets and troughs, the results significantly improved average performance in rough proportion to lower average windspeed conditions – in sequence Trials 5, 4 and 6. In particular the monolayer 'M' results from Trial 6, again both buckets and troughs, indicate product performance closer to
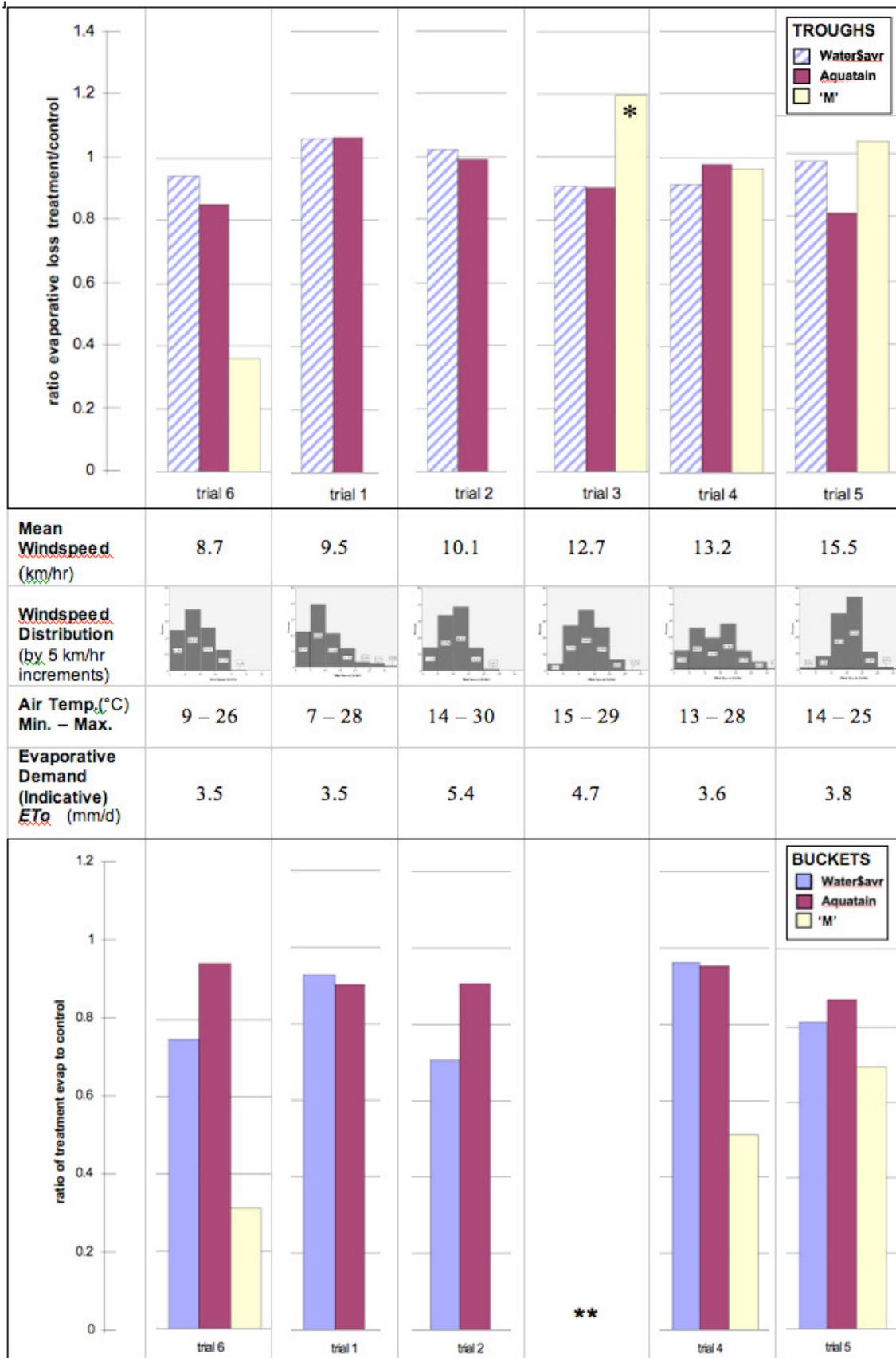
Figure 3. Comparison of the standardised evaporation results for Trials 1 to 6 ordered by increasing mean windspeed (*left to right*) for both troughs (*upper barchart*) and buckets (*lower barchart*) with associated average meteorological conditions. All products were applied at x3 dosage, except for the first trial with monolayer 'M' (Trial 3) which was at x1 dosage, (*indicated ∗*). The timing of Trial 3 troughs did not correspond to that of Trial 3 buckets and hence the latter results are not comparable and have been omitted (*indicated ∗∗*).

that routinely obtained in the laboratory, and despite a significant proportion of time during this trial with windspeeds in the ranges 10–15 and 15–20 km/hr.

In summary, the very consistent monolayer 'M' results, although few in number, underline the necessity of assessing product performance only with regard to the prevailing environmental conditions. Furthermore there are clearly times and conditions for which surface film deployment cannot provide any useful evaporation reduction.

4.5 Effect of Experimental Scale – Bucket versus Trough

Direct bucket–trough comparisons may be undertaken for five of the six trials presented in Figure 3 and the results are set out in Table 2. The mean of the bucket:trough ratios calculated is then a measure of the effect differing vessel size, but any such difference (i.e. having a ratio $\neq 1.0$) is significant only if it lies outside the range of its standard error.

Table 2. Comparison of five of the bucket trial and trough trial results of Figure 3, expressed as the ratio bucket:trough of the standardised evaporation results.

	Trial 6	Trial 1	Trial 2		Trial 4	Trial 5	MEAN ± Std.Error
Mean Windspeed (km/hr)	8.7	9.5	10.1		13.2	15.5	
Bucket:Trough Performance Ratio							
Water$avr	0.79	0.88	0.69		1.05	0.85	0.85 ± 0.05
Aquatain	1.11	0.85	0.92		0.98	1.03	0.98 ± 0.04
'M'	0.86	—	—		0.53	0.68	0.69 ± 0.08

The mean bucket:trough ratios indicate:

- for Water$avr –, as previously noted, the uncertainty of the applied dose of its active ingredient (hexadecanol) – section 4.2 above – precludes any conclusion;

- for Aquatain – clearly no significant difference between the performance of the product in buckets compared with troughs; however

- for monolayer 'M' (with accurate x3 dosage) – the result indicates significant difference in standardised evaporation according to size of trial vessel. Although a bucket:trough ratio of 0.69 is deduced, this is based on only a small number of results and cannot be considered definitive. However, consideration of the aerodynamics of each vessel and the fact that the 'lip' for the vessel will induce some additional turbulence (Figure 4), the relative sizes of the lip (100 mm for the buckets; 150 mm for the troughs) in relation to the vessel diameter, suggests relatively greater bluff-body turbulence in the smaller vessel and hence that evaporative demand might be enhanced at bucket scale.
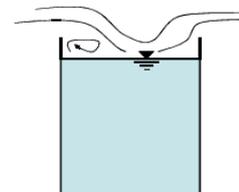

Figure 4. Possible wind profile over the buckets (flow left to right) – conceptual (reproduced from Morrison et al., 2008)

5. CONCLUSION

Trial-to-trial comparisons of repeated small-scale evaluations of evaporation-suppressing surface films (Morrison et al. 2008) have been undertaken in relation to prevailing environmental conditions. With ancilliary measurements, these analyses yield plausible hypotheses to account for at least some of the observed differences in evaporation reduction and surface film performance. It is concluded that:

1. for a commercial monolayer product which includes a bulking agent, trials undertaken at small scale (small surface area) can give misleading results because the actual rate of application of the active ingredient on small area surfaces may be uncertain;

2. there is a significant difference in water surface temperatures when evaporation is being impeded by a nanometre-thickness monolayer compared with that impeded by a micrometre-thickness film; and that this is consistent with a difference in the albedo caused by the thicker surface film;

3. over a trial of any significant duration (days) the distribution of windspeeds will have a major impact on apparent product performance and that this is not adequately represented either by average windspeed or cumulative evaporative demand; and

4. in small-surface-area trials, variations in apparent product performance can also be due to the size and configuration of the vessels used.

REFERENCES

Conover TA and Saylor JR (2007) Statistics of the surface temperature field of an air/water interface under air flow. *Exp Fluids* **43**, 509–524.

Barnes, G (2008). The potential for monolayers to reduce the evaporation of water from large water storages. *Agricultural Water Management*, **95**, 339-353.

Barnes, G.T., Gentle, I.R. (2005). *Interfacial Science: An Introduction*. Oxford University Press, Oxford.

Gladyshev, M. (2002). *Biophysics of the Surface Microlayer of Aquatic Ecosystems*. IWA Publishing London, United Kingdom.

Larsson K, Odham G and Sodergren A (1974) On lipid surface films on the sea 1: A simple method for sampling and studies of composition. Marine Chemistry **2**: 49-57.

McMahon C, Craig I, Turnbull, D, Schmidt E, and Hancock, N. (2008) *Laboratory Study of Wind Stress on Surface Film Materials, Trials, 2007-2008*. National Centre for Engineering in Agriculture, Technical Report 1002040/2, Toowoomba, Queensland, Australia. *Unpublished.*

Morrison P, Gill R, Symes T, Misra R, Craig I, Schmidt E, and Hancock, N. (2008) *Small Scale Evaporation Mitigation Trials, 2007-2008*. National Centre for Engineering in Agriculture, Technical Report 1002040/1, Toowoomba, Queensland, Australia. *Unpublished.*

Pittaway P and van den Ancker T (2009) Properties of natural microlayers on Australian freshwater storages and their potential to interact with artificial monolayers. *Submitted to* Marine and Freshwater Res.

Reiser, CO (1969). A system for controlling water evaporation, *Industrial and Engineering Chemical Research* 8, 63-69.

Sawyer, CN, McCarty, PL and Parkin, GF (2003). *Chemistry for Environmental Engineering and Science* (5th ed.) McGraw-Hill, New York.