Photodegradation of Dissolved Organic Matter: The Impact on Monolayers

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Evaporation Loss

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Varying Field Performance of Monolayers

- Monolayers reduce evaporation by $\leq 60\%$
- Some field trials 0% reduction
- Field results extreme day to day variability (10-40%)
Factors Affecting Field Performance of Monolayers

- Mechanical disruption of monolayer film
  - Wind
  - Waves
  - Beaching
  - Introduction of impurities
- Volatilization
- Dissolution into subsurface
- Microbial degradation
- Photodegradation
  - Direct
  - Indirect
Impact of the Microlayer on Monolayers?

High conc. DOM

(100 to 500 μm thick)

Norkrans 1980 Advances in Microbial Ecol 4 pp51-85
Photodegradation of Monolayers

- Monolayer compounds may undergo photochemical reaction
  - Direct photolysis = chemical change due to photon absorption by chromophores in molecule
  - Indirect photolysis = reaction initiated by chromophore light absorption in other molecules
Structure of Monolayer Compounds Studied

Hexadecanol – (C\textsubscript{16}OH)  
\( \text{C}_{16}\text{H}_{34}\text{O} \)

Octadecanol – (C\textsubscript{18}OH)  
\( \text{C}_{18}\text{H}_{38}\text{O} \)

2-octadecoxyethanol – (C\textsubscript{18}E\textsubscript{1})  
\( \text{C}_{20}\text{H}_{42}\text{O}_{2} \)
Direct Photodegradation of Monolayers

- Monolayer applied to distilled water
- Volatilization = samples placed in the dark
- Direct photodegradation = samples irradiated
- Monolayer loss measured as reduction in evaporative saving

<table>
<thead>
<tr>
<th></th>
<th>Volatilization</th>
<th>Direct Photodegradation</th>
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</thead>
<tbody>
<tr>
<td>Hexadecanol (C₁₆OH)</td>
<td>22.8%</td>
<td>23%</td>
</tr>
<tr>
<td>Octadecanol (C₁₈OH)</td>
<td>18.6%</td>
<td>18.8%</td>
</tr>
<tr>
<td>2-Octadecoxyethanol (C₁₈E₁)</td>
<td>14.2%</td>
<td>14.3%</td>
</tr>
</tbody>
</table>
Water Bodies Monitored for this Study

a - Kearneys Spring, b - Lake Annand, c - Caffey Dam, d - Lake Apex, e – Logan’s Dam, f – Lake Dyer, g - Narda Lagoon, h - Pittaway Pond
Water Bodies Selected for this Study

Kearneys Spring
Lake Annand
Caffey Dam
Lake Apex
Logan’s Dam
Lake Dyer
Narda Lagoon
Pittaway Pond

Turbid Brown Water  Clear Water  Brown Water  Black Water
Indirect Photodegradation of Monolayers

• Monolayers **DO NOT** undergo direct photodegradation
• Reactive species in water degrade monolayers
  – e.g. LMWC \(^1\text{O}_2\), \(^3\text{O}_2\), ·OH
• DOM photochemical reactions produce reactive species
• Photodegradation of monolayers **IS INDIRECT**
Photoreactivity of Water Bodies

- Photoreactive DOM produces reactive species
- Reactive species produce higher rates of photodegradation of monolayers
- DOM quality and quantity varies within water bodies
Photoreactivity of Water Bodies

- Indirect photolysis > > in more reactive water bodies
- Pesticide degradation = index of indirect photolysis (natural cleansing)
- Pentachlorophenol for my study
- << half-life >> photoreactive the water body
Photoreactivity of Water Bodies – PCP Half-lives

Time (Minutes)

Karney  Annand  Caffey  Apex  Logans  Dyer  Narda  Pittaway  Distilled
Photochemical Properties of DOM

• Several tests investigated
  – DOC
  – UV Absorbance (253.7 nm)
  – Aromaticity (UV Abs 280 nm)
  – Permanganate Index
  – Molecular Size (E$_2$/E$_3$ Ratio)
  – IR spectroscopy

• Relationship with photoreactivity?
Relationship with Photodegradation

Standardized UV Abs (253.7 nm)

Standardized KMn

Standardized UV Abs (280 nm)

$E_2/E_3$ Ratio
Grouping of Permanganate Index Results

Group 1
High Reactivity
KMn ≤ 3.37

Group 2
Moderate Reactivity
3.37 ≥ KMn ≤ 4.46

Group 3
Low Reactivity
KMn ≥ 4.46

Graph showing the distribution of Permanganate Index results with three groups:
- Group 1: High Reactivity (KMn ≤ 3.37)
- Group 2: Moderate Reactivity (3.37 ≥ KMn ≤ 4.46)
- Group 3: Low Reactivity (KMn ≥ 4.46)
Photoreactivity of Water Bodies

Group 1
High Reactivity
KMn ≤ 3.37
(Apex, Narda, Pittaway)

Group 2
Moderate Reactivity
3.37 ≥ KMn ≤ 4.46
(Annand, Logans)

Group 3
Low Reactivity
KMn ≥ 4.46
(Kearney, Caffey, Dyer)
Monolayer Half-lives – Wet Season

- C16OH
- C18OH
- C18E1

Monolayer Half-life (Hours)

- Clear Water
- Brown Water
- Turbid Brown Water
- Black Water
- Distilled Water
Monolayer Performance Specifications

- $C_{16}OH$ not suitable, volatilization too great
- $C_{18}OH$ – suitable for clear and coloured water (Annand, Apex, Logan’s, Narda, Pittaway)
- $C_{18}E_{1}$ – restricted for use on clear water only (Kearney, Caffey, Dyer)
- Monolayer selection may change with season
Urban Water Security Research Alliance

THANK YOU

www.urbanwateralliance.org.au