Photodegradation of Australian Freshwater Microlayers and the Implications for Potable Water Management

Stuckey, N.G.¹, Pittaway, P.A.¹, Larsen, K.²

¹National Centre for Engineering in Agriculture, Faculty of Engineering and Surveying, University of Southern Queensland, Toowoomba, Queensland, Australia 4350

² Faculty of Sciences, University of Southern Queensland, Toowoomba, Queensland, Australia 4350

Summary

Photodegradation has been known to break down toxic compounds in potable water storages as well as degrading pesticides and herbicides in agricultural water storages. In this study, the concentration and reactivity of humic substances (HS) present in natural microlayers on water storages in South East Queensland (SEQ) was investigated. Microlayer and subsurface samples were taken from eight water storages with dissolved organic carbon (DOC) used to quantify HS concentration. The E_2/E_3 ratio (ratio of absorbance at 250 nm to 365 nm) was used to indicate the molecular weight of DOC compounds, and absorbance at 253.7 nm and the permanganate index were used to compare the reactivity of humified DOC. The concentration of carbonyl compounds in the microlayer was also investigated as carbonyls are considered the most photoreactive functional group present in HS. Preliminary results indicate that the concentration of humic substances and their chemical reactivity in SEQ water storages are highly variable, reflecting the characteristics of the water catchments.

Keywords

Photodegradation, microlayer, monolayer, potable water, humic substances

Introduction

The photodegradation of freshwater microlayers has both advantages and disadvantages when it comes to implications for potable water management. Firstly the degradation of HS to smaller, more reactive compounds can be detrimental to potable water treatment, as these small molecular weight organic compounds can be toxic (e.g. hydrogen peroxide, Scully 1996). However, photodegradation can have a positive effect on potable water treatment. This is evident from the use of UV light as a disinfectant in the treatment of potable water for many years (Legriniet al. 1993).

Compounds in freshwater microlayers include naturally occurring and anthropogenic hydrophobic HS, including pesticides and artificial monolayers. Artificial monolayers have been applied to water storages and studied as an evaporation suppression method since the 1950's. However, they have shown varying field performance due to wind and wave action and varying half lives. The variation in half life is due to photo and microbial degradation, natural processes that may be substantially enriched in the microlayer relative to the immediate subsurface water.

The composition of microlayers on freshwater storages in Northern Europe have been studied for decades. Research in Australia is more recent, highlighting differences in microlayer and subsurface water composition associated with vegetation and climate (Pittaway and van den Ancker 2009). The hydrophobic, aromatic compounds concentrating within the microlayer strongly absorb ultraviolet light to produce photoreactive compounds, limiting the half-life of artificial monolayer products. Of the compounds found in the microlayer, those that have a lower molecular weight are considered the most reactive (Hessen and Tranvik 1998).

In this study the chemical reactivity and rate of photodegradation occurring within natural microlayers was investigated. Microlayer and subsurface water samples from eight storages located within SEQ were sampled in May 2010, with the concentration of DOC quantified using a Total Organic Carbon (TOC) analyzer. The E_2/E_3 ratio (absorbance at 250 nm and 365 nm) was used to indicate the molecular weight of aquatic HS. Absorbance at 253.7 nm and the permanganate index was used to quantify the concentration and reactivity of HS in the water samples.

Results

Results indicate that larger organic molecules derived from wooded catchments absorb UV light more strongly, and are more chemically reactive (higher permanganate index). Smaller molecules derived from a storage constructed on black vertisol soil within a cleared catchment absorbed less UV light, and were relatively unreactive (lower permanganate index). When UV absorbance was plotted against the permanganate index (all data standardised per unit DOC), results for the eight storages tested clustered into five groups (Figure 1), reflecting the attributes of the water catchments (Table 1).

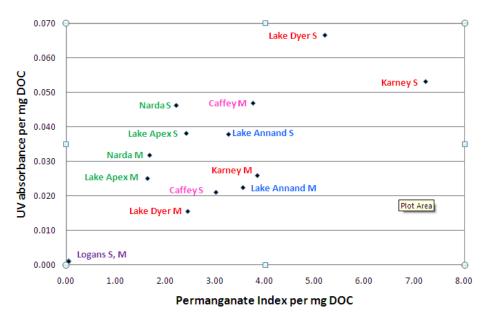


Figure Relationship 1. between UV absorbance and permanganate index (both standardized for DOC concentration). Storages with similar results to these two tests and similar relationships between microlayer and subsurface water have been grouped together, as shown by the different colours.

Table 1. Summary of results from testing carried out on water storages in SEQ. Colour coding of water storages in this table match those in Figure 1. UV absorbance was carried out at 253.7nm, and molecular size was inferred using the E_2/E_3 ratio with molecular size inversely proportional to the ratio.

Storage	Micro/ Subs	DOC mg/L	KMn Index / mg TOC	UV absorbance / mg TOC	E₂/E₃ Ratio	Storage Catchment Attributes
Logan's NW	М	2708	0.04	0.001	4.71	Black soil, grassy, very turbid
	S	2648	0.04	0.001	5.74	
Logan's SE	М	3083	0.04	0.001	5.28	Black soil, grassy, very turbid
	S	2775	0.04	0.001	5.48	
Narda Lagoon	М	41	1.67	0.032	4.05	Woodland, saw mill adjacent
	S	27	2.21	0.046	4.01	
Lake Apex	М	30	1.63	0.025	3.37	Woodland, runoff over grasses terrain
	S	19	2.41	0.038	3.52	
Caffey	М	16	3.84	0.026	3.68	Filled with bore water
	S	11	3.00	0.021	2.79	
Lake Annand	Μ	14	3.55	0.022	3.07	- Runoff primarily from roads
	S	6	3.26	0.038	2.48	
Kearneys Spring	М	6	3.75	0.047	2.49	Parkland, primary inflow from spring
	S	4	5.20	0.067	2.58	
Lake Dyer	М	15	2.44	0.016	3.14	Parkland, primary inflow pumped from creek
	S	3	7.22	0.053	2.47	

Preliminary Conclusions

Preliminary results indicate that water storages in SEQ differ substantially in the concentration and reactivity of DOC in subsurface and microlayer water samples. Differences in the chemical reactivity of the water samples reflect differences in the vegetation and management of the catchments. Results indicate/show that high molecular weight molecules, such as those derived from terrestrial vegetation, are more reactive than low molecular weight molecules which are derived from black soil.

Currently, an analytical method for the quantification of carbonyls in aqueous solutions is being developed to determine the amount of carbonyls present in a water sample. Controlled photodegradation experiments are being developed to quantify the rate and seasonality of photodegradation occurring in water samples from each of the storages. Results from these studies will be used to compare the resilience of artificial monolayer products to photodegradation, as a function of water quality.

References

Bureau of Meteorology, Australian Government. Commonwealth of Australia, 2010.

D. O. Hessen and L. J. Tranvik (1998) Aquatic Humic Substances: Ecology and Biogeochemistry. Springer, Germany.

N.M. Scully, DJ McQueen and D.R Lean (1996) Hydrogen Peroxide Formation: The interaction of ultraviolet radiation and dissolved organic carbon in lake waters along a 43-75°N gradient. Limnol Oceanogr 41(3), 540-548.

O. Legrini, E. Oliveros, and A. M. Braun (1993) Photochemical Processes for Water Treatment. Chem. Rev. 93, 671-69.

P.A. Pittaway, T.R. van den Ancker (2009) Microbial and Environmental Implications for use of Monolayers to Reduce Evaporative Loss from Water Storages. Technical Report, NCEA, University of Southern Queensland, Australia.