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To cite this article: M. A. Lund & D. S. Ryder (1997) Can artificially generated gilvin (g440m^{-1} , Gelbstoff) be used as a tool for lake restoration?, SIL Proceedings, 1922-2010, 26:2, 731-735, DOI: [10.1080/03680770.1995.11900812](https://doi.org/10.1080/03680770.1995.11900812)

To link to this article: <https://doi.org/10.1080/03680770.1995.11900812>



Published online: 01 Dec 2017.



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Can artificially generated gilvin ($\text{g}440\text{m}^{-1}$, Gelbstoff) be used as a tool for lake restoration?

M. A. Lund and D. S. Ryder

Introduction

Gilvin is the term given to coloured humic substances occurring in aquatic systems at concentrations sufficient to effect the attenuation of photosynthetically available radiation (sensu KIRK 1986). The colour is imparted by high concentrations of these substances released from organic matter during decomposition; consisting of a soluble labile component (fulvic acid), a soluble refractory component (humic acid) and an insoluble component (humins) (KIRK 1986). It is generally accepted that the heterogeneous nature of the compounds forming gilvin make its chemistry and biology complex and somewhat unpredictable.

The Swan Coastal Plain (SCP) of Western Australia contains numerous wetlands that are, or are believed to have been dystrophic (with gilvin levels up to $265\text{g}440\text{m}^{-1}$, WRIGLEY et al. 1988). The SCP is a series of parallel dunes bordered by the Indian Ocean to the west and the Darling Scarp to the east. In the interdunal depressions the water table becomes exposed as chains of wetlands. The oldest dune system (Bassendean system) is closest to the Scarp and consists of leached sands containing little calcium carbonate. The next two systems (Spearwood and Quindalup) are younger, less leached and generally contain limestone. Work by WRIGLEY et al. (1988) found most dystrophic wetlands on Bassendean sands or on other non-limestone sands. Calcium and other divalent cations are thought to enhance the natural coagulation and precipitation of humic substances (PETERSON 1989).

The presence of high concentrations of dissolved humic substances (DHS) can have a significant effect on aquatic productivity by altering the physical or chemical environment, modifying autotrophic primary production or by acting as a direct carbon source for bacteria, algae and plants in the form of dissolved organic carbon (JONES 1992). It generally effects primary production through the fixation of trace metals or phosphate, inhibition of enzymes, absorption of light or lowering the ambient pH (JACKSON & HECKY 1980). There are many recorded cases

on the SCP of low primary productivity in hyper-eutrophic coloured wetlands, suggesting that the artificial staining of wetlands may be useful as a means of controlling algal productivity, without the need to tackle the often more complicated problem of nutrient control.

The aim of this study is to examine the release of gilvin from decomposing vegetation in a range of calcium carbonate concentrations and determine its effectiveness as a tool to control algal blooms in both *in vitro* and *in situ* conditions.

Methodology

Experiment 1

To test the effectiveness of artificially generated gilvin as a tool for controlling algal blooms, six enclosures that isolated a column of water (1.7m^3) from the surrounding lake (see LUND 1992) were established in an eutrophic wetland (Lake Monger; $32^{\circ}4'S$ $115^{\circ}20'E$). To three randomly chosen enclosures, 500g of dry *Eucalyptus marginata* leaves were added to raise gilvin levels by 40 units in 14 days. The enclosures and the lake were sampled every 3–4 days over 3 weeks in the summer of 1990/91. On each occasion, the dissolved oxygen (DO), pH and conductivity of each enclosure was measured. A water sample was also taken for determination of soluble reactive phosphorus (SRP), chlorophyll *a* (Chl*a*), alkalinity, gilvin and the E4/E6 ratio. The methods followed those in; APHA (1989) for SRP and alkalinity, MORAN & PORATH (1980) for Chl*a*, and WRIGLEY et al. (1988) for gilvin and the E4/E6 ratio.

Experiment 2

A laboratory experiment was used to evaluate the role of CaCO_3 (as high and low alkalinity) in limiting gilvin production. Twelve treatments, each replicated 3 times were established randomly in 14 L plastic buckets containing 10 L of water (as specified below) at 20°C .

High alkalinity (>100 mg CaCO₃ L⁻¹)

Lake Monger water
Artificial

3 × *E. rudis*
3 × *E. rudis*

3 × *B. articulata*
3 × *B. articulata*

3 × Control
3 × Control

Low alkalinity (<60 mg CaCO₃ L⁻¹)

Hyde Park Lake* water
Tapwater

3 × *E. rudis*
3 × *E. rudis*

3 × *B. articulata*
3 × *B. articulata*

3 × Control
3 × Control

* Hyde Park Lake (31°56'S 115°51'E) a clear (gilvin <2 g 440 m⁻¹) eutrophic wetland

Each treatment contained either no leaves (controls), or dry senescent leaves of *Baumea articulata* (200 g) or *Eucalyptus rudis* (23 g). All lake water was sieved (63 µm mesh) before use. Artificial high alkalinity water was created by dissolving 100 g CaCO₃ and 10 g CaO in 40 L of tap water overnight. The solution was then filtered (Whatman® GF/C) and diluted to give an alkalinity of 140 mg CaCO₃ L⁻¹. Each treatment was sampled on 3 occasions over the 2 weeks of the experiment. Water samples were taken for determination of alkalinity, and after filtering (Sartorius® acetate) for gilvin, and E4/E6 ratio as per above methods. The pH, conductivity and DO were measured in situ.

Experiment 3

This experiment aimed to test the level of gilvin needed to control algal blooms produced in a series of 12 outdoor tanks (1.4 m³) formed by adding an initial inoculum of concentrated algal cells (from a nearby wetland) and subsequently adding 8.5 g of commercial fertiliser (Aquasol®) at strategic intervals. Once the blooms were established, treatments were randomly assigned to each tank so that replicates included a range of algal biomass, estimated by turbidity. The mass of *E. rudis* leaves needed to produce gilvin concentrations of 0, 20, 35 and 52 g 440 m⁻¹ after 2 weeks was calculated to produce the following treatments, no leaves (control), 730 g, 1300 g and 1900 g of leaves, with 3 replicates per treatment. Tanks were sampled on 3 occasions over a 2 week period. On each occasion pH, conductivity and DO were measured and samples were taken for determination of CHLa, SRP, gilvin and E4/E6 ratio as per previous methods.

Results and discussion

In a preliminary trial, gilvin was successfully produced in the laboratory at predictable rates from a variety of common wetland plant species (*Eucalyptus marginata* 876 g440 m⁻¹, *E. rudis* 237 g440 m⁻¹, *B. articulata* 17 g440 m⁻¹, from 10g of senescent leaves in 1.5l of distilled water over 2 weeks). Based on these results experiment 1 was undertaken in Lake Monger, a eutrophic lake previously studied by LUND

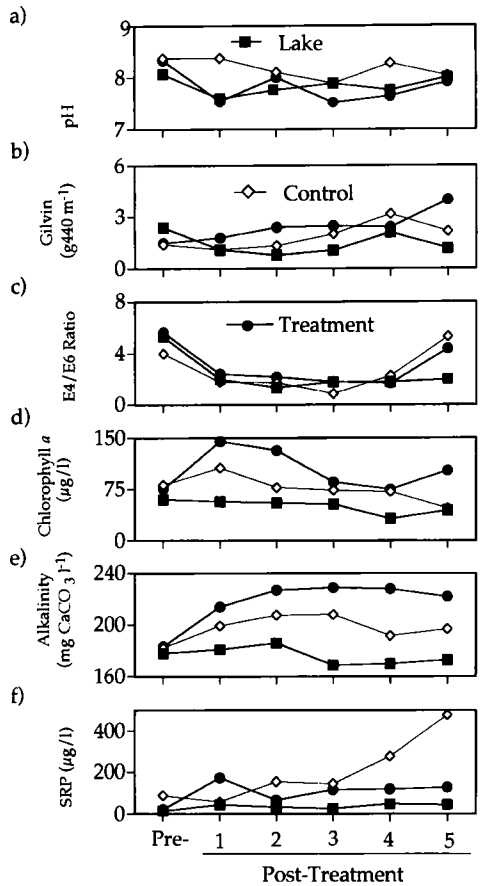


Fig. 1. Mean values for a) pH, b) Gilvin, c) E4/E6 ratio, d) Chlorophyll a, e) Alkalinity, and f) Soluble reactive phosphorus for treatments in Experiment 1 over time.

(1992). The lake is located on a limestone aquifer and is not strongly coloured (<3 g440 m⁻¹), but anecdotal evidence suggests that the water may have been more coloured in the past. Alkalinity and CHLa (Fig. 1) increased in the treatment enclosures, but were not significantly

($P < 0.05$) different to the lake or controls (Repeated measures ANOVA). There was no significant ($P < 0.05$) difference between the treatment and control for gilvin, E4/E6 ratio or pH. The major effect of the enclosure itself (i.e. lake vs. control) was to promote release of SRP from the sediments with an associated rise in CHLa, pH, and DO.

Suspecting that high alkalinity (i.e. Ca^{2+} ions) may be responsible for the low gilvin levels in experiment 1 (as per PETERSON 1989), an in vitro experiment was designed to test this hypothesis. Experiment 2 used *E. rudis* and *B. articulata* as they represent flora commonly found around wetlands on the SCP. The presence of Ca^{2+} ions did not appear to affect the release of gilvin, with the highest levels being recorded in the high alkalinity and lake water treatments (Fig. 2). A potential problem with in vitro experiments to elucidate DHS interactions is that the range of potential interactions

that may occur are limited compared to the field. The continued rise of gilvin levels in experiment 2 despite the high alkalinity may be a result of a finite supply of ions (which would not be encountered in the field) limiting the precipitation of DHS. The high level of gilvin produced in lake water treatments may reflect the presence of a diverse and abundant microbial community enhancing the decomposition process. The E4/E6 ratio is designed to indicate the relative importance of humic and fulvic acids (KONONOVA 1966), with higher values reflecting a higher fulvic acid component. The E4/E6 ratio in the low alkalinity treatments increased over time and declined in high alkalinity treatments. One conclusion is that the ionic composition of the high alkalinity water preferentially precipitates the lower molecular weight fulvic acids released during decomposition. The resultant gilvin levels may be a result of increased humic acid concentrations, as VISSER (1984) found that humic acids, while contributing a small component of DHS can contribute 75% of the colour.

Experiment 3 examined what level of gilvin was necessary to control an established algal bloom. DAVIS et al. (1993) classified SCP wetlands as dystrophic only where gilvin levels exceeded $52 \text{ g}440 \text{ m}^{-1}$. We decided to investigate whether lower gilvin levels may be sufficient to control algal blooms. In the tanks, gilvin levels increased slowly with little difference between medium and high treatments, whereas in the low treatment gilvin levels declined after week 1 (Fig. 3). The E4/E6 ratio increased in all enclosures in proportion to the treatment. Mean CHLa declined in all treatments except the controls where it increased. CHLa levels were however extremely variable between replicates. The high values of mean CHLa in the high treatment result from one replicate with a bloom 3 or 4 times greater than the other replicates. If this replicate is ignored the mean CHLa actually increases slightly. In all treatments phaeophytin increased with time indicating a decline in the health of the algae present due to DHS.

The presence of DHS has the potential to control algal blooms, however they appear less effective under highly eutrophic conditions. This may be due to rapid consumption of fulvic acids by biota commonly associated with highly eutrophic waters (DE HAAN 1992). The addition of leaves to Lake Monger enclosures saw

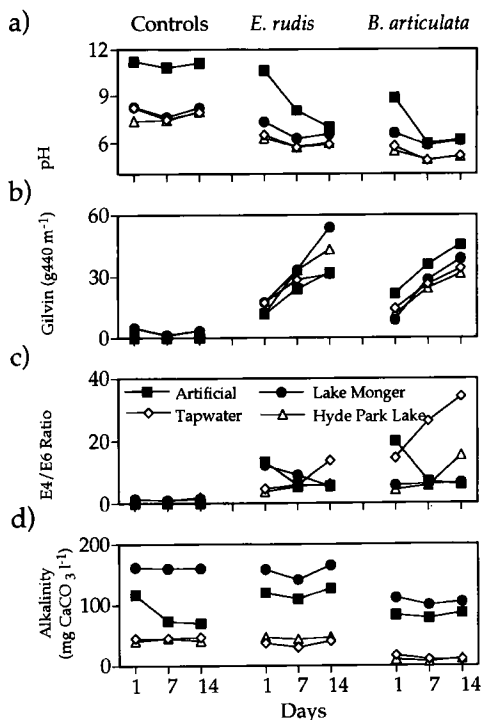


Fig. 2. Mean values of a) pH, b) Gilvin, c) E4/E6 ratio, and d) Alkalinity for treatments in Experiment 2 over time for controls, *Eucalyptus rudis* and *Baumea articulata*.

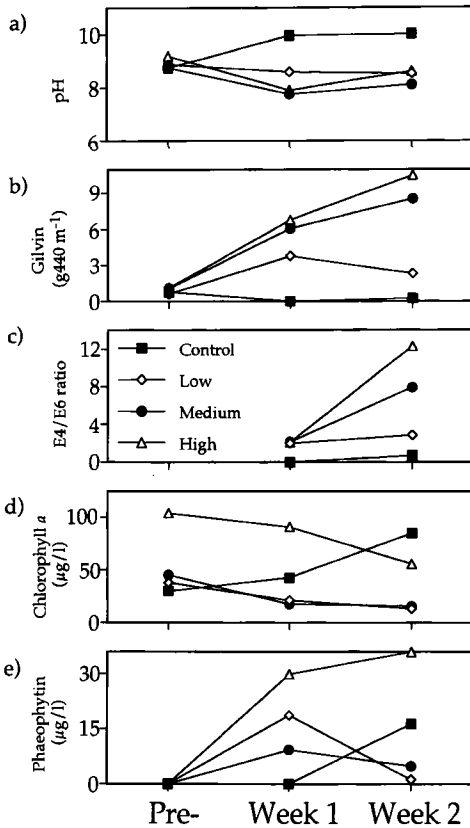


Fig. 3. Mean values for a) pH, b) Gilvin, c) E4/E6 ratio, d) Chlorophyll *a* and e) Phaeophytin in Experiment 3 over time.

an immediate increase in CHL_a, indicating that the system may have been carbon limited. This was reflected in a decrease in the E4/E6 ratio to background lake levels indicating that the labile component of the DHS was utilised by the biota. While the gilvin levels produced in experiment 3 were well below those expected (based on experiment 2), they were well above those found in the in situ enclosures. The in situ enclosures probably have replenishable sources of ions responsible for the precipitation of DHS components released during decomposition, as well as more abundant biota to utilise that carbon resource. The photodegradation of biologically refractory DHS into lower molecular weight, biologically labile organic carbon has been found to be an important step in the deg-

radation of humic substances (KIEBER 1989). This process may be responsible for an increase in the labile component in the field trials. These results suggest that the ionic composition of Lake Monger removing DHS from suspension, the effects of ultraviolet radiation and biodegradation of DHS may have contributed to the lack of staining in the in situ enclosures.

Conclusion

In lakes such as Lake Monger which are highly eutrophic and have a high alkalinity, the difficulty in producing gilvin in situ from leaves is such that it does not appear to be a useful tool for lake restoration. In lakes with low alkalinity, artificially producing gilvin may be a simple method for reducing algal biomass, although this requires further investigation. An alternative avenue of future research is to isolate the chelating agents within the DHS and synthesise these to control algal blooms (see WILSON 1991).

Acknowledgements

The authors wish to thank Edith Cowan University for providing infrastructure and funding for the project. One author (DSR) is funded by an Australian Postgraduate Research Award.

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Authors' address:

M. A. LUND and D. S. RYDER, Centre for Ecosystem Management, Edith Cowan University, Joondalup Drive, Joondalup, WA 6027, Australia.