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Rates of sulphate removal in sulphate amended polyethylene enclosures in Georgetown Billabong

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Rates of Sulphate Removal in Sulphate Amended Polyethylene Enclosures placed in Georgetown Billabong

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Abstract

Keywords: sulphate removal; enclosures; sulphate-reducing bacteria; Georgetown billabong; wetland filters.

Two 9000 L cylindrical polyethylene cylinders (water-tanks) open at each end were placed in the deeper parts (1.5-1.8 m) of Georgetown billabong during the 1996 early dry season. One enclosure was amended with magnesium sulphate to approximately 5 mM to determine whether sulphate might be selectively removed and the other enclosure was used as a control (no sulphate added). The concentration of sulphate in the treated enclosure was chosen to match that in Retention Pond 2 so that the potential for using a natural billabong to polish sulphate from restricted release zone waters could be examined.

Sulphate was removed at the rate of 0.70–0.95 moles week^{-1}, which was equivalent to 0.13–0.18 moles week^{-1} m^{-2} and a half-time of between 147-204 days, but its removal did not appear to be selective compared with magnesium. The similar removal rate of sulphate and magnesium was attributed to a common rate limiting factor, with diffusion through sediment pore waters considered to be the most likely cause. In the latter part of the experiment, the enclosures were shaded in an attempt to increase carbon cycling and promote sulphate reduction but this had no appreciable effect on the rate of removal of sulphate.

Introduction

Ranger Uranium Mine (RUM) is situated about 230km east of Darwin on a lease excised from and completely surrounded by Kakadu National Park. The Park was designated a site of World Heritage significance by the Australian Federal Government in 1979 owing to the unique natural diversity occurring in this largely pristine area. The vegetation of the region is dominated by savanna and eucalypt woodland with large areas of natural wetland which are subjected to annual inundation. A Wet-Dry Tropics climate prevails consisting of two distinct seasons (Christian & Aldrick 1977). The Wet season which occurs from December to May is typified by hot humid conditions, and is punctuated by intermittent rain brought by monsoonal troughs and/or convective storms of varying severity that result in an average annual precipitation of around 1600 mm a^{-1}. In contrast, the Dry season (June-November) is typified by south-easterly winds which bring dry, cool conditions and very little rain.

The Ranger deposit was discovered in 1969 by the Electrolytic Zinc Co of Australasia Ltd and Peko-Wallsend Operations Ltd (Fox et al. 1977a). In 1972, sales contracts with two Japanese utilities received Government approval and in 1975 the Commonwealth Government set up the Ranger Uranium Mine Environmental Inquiry (Fox Inquiry) which negotiated a Memorandum

of Understanding between the concerned parties. In 1977, the final report of the Fox Inquiry was delivered and the Commonwealth Government announced its decision to allow mining and export of uranium to proceed provided strict environmental standards were implemented. In 1980, Energy Resources of Australia (ERA) was formed and the Commonwealth Government rescinded its ownership in the venture (Fox et al. 1977b).

Water Management

Water management at Ranger is crucial to determining off- and on-site impacts to people and ecosystems. Accordingly, mine waters are designated according to quality as either Restricted Release Zone (RRZ) water or non-RRZ water. RRZ water is used for ore processing and includes water from the tailings dam, plant and pit areas plus any rainfall that collects in these areas. It is stored in two retention ponds (RP), namely RP2 and RP3, and is utilised as either process water or as a dust suppressant to dampen haul roads and ore stock piles. Water is also removed from RP2 during the dry season and irrigated onto designated bushland to provide sufficient storage capacity before the onset of the next wet season. A portion of this RRZ water is also passed through a constructed wetland filter to reduce contaminant loadings prior to land application. Discharges of RRZ water into Magela Creek are allowed under strict conditions but to date none has been released since the commencement of operations at Ranger (Nisbet 1995). Non RRZ water is primarily composed of seepage and leachate from the waste-rock and very low grade ore stockpiles plus any runoff derived from their respective catchments. These waters are collected in two Retention Ponds, RP1 and RP4. Release of this water into the Magela creek system is allowed by regulatory authorities but, in the case of RP4 water, certain stringent conditions must be met (Fox et al 1977b).

Wetland Filter Treatment

Wetlands have a proven ability to remediate water contaminated from mining operations by their ability to transform and store pollutants. For example for acid mine drainage (AMD), these treatments usually involve removing dissolved iron and raising the pH before finally polishing the wastewater prior to release. Wieder (1992) tabulates data for five experimental wetlands designed to treat AMD, each of which was amended with a different organic substrate. In all cases Fe was removed from the water as it passed through the wetland although the efficiencies of removal varied from 22% using unamended peat to almost 80% for mushroom compost. Manganese removal efficiency was much less than Fe with the the most efficient substrate (mushroom compost) removing 25%. Eger (1994) also cites significant reductions in Cu, Ni, Co and Zn using organic amended wetland cells. In a study reported by Brodie (1990), AMD was treated using constructed wetland filters (CWF) with the objective of meeting US Environmental Protection Agency water quality guidelines. Iron removal normally exceeded 90% and manganese between 75–90%. The removal of the metals was usually accompanied by a pH increase.

In an effort to improve the quality of the RP2 water before its application to land, RUM have constructed an artificial wetland filter in the catchment of RP1. Originally, an experimental wetland was created composed of three cells of approximately 4000 m^3 separated by semi-permeable bunds utilizing overflow spillways (Jones & Raguso 1995b). Water flowed from the cells into a former clay borrow pit which acted as a sump. In 1994, a trial was conducted in which RRZ water was passed through the system. Its major findings were as follows (Nisbet 1995):

- sulphate concentration remained virtually constant (~700–800 mg L^{-1}) as water passed through the three cells but increased to 2000 mg L^{-1} in the central lake;

- uranium concentration was reduced markedly after passing through the wetland from 1000 $\mu g\ L^{-1}$ at the inlet to <50 $\mu g\ L^{-1}$ in the sump;
- magnesium concentration was unchanged by wetland filtration (200 $mg\ L^{-1}$)
- conductivity remained unchanged (1500 $\mu S\ cm^{-1}$);
- pH was lowered by approximately 0.5 unit from 7.5–8.0 at the inlet to 7.0–7.5 at the outlet.

The inability of conventional designs of CWFs to remove sulphate is not surprising. Work by Vile and Wieder (1993) and Stark et al (1994) have demonstrated poor sulphate removal although others such as Eger (1994) claim some success using a wetland design that encourages anaerobiosis from amendments of municipal compost. This inability to remove sulphate has prompted a series of investigations into how sulphate removal might be best achieved to remediate contaminated water on the Ranger leases.

It has been observed that a newly constructed wetland system does not imitate a natural wetland in terms of its physical properies and is therefore likely to differ also in ecological and/or chemical behaviour. In this respect, one the most important observations in relation to Jones & Raguso's (1995a) study was the absence of an unconsolidated layer of organic matter in the benthos and the consolidated nature of the clay bed. Hence the present study was undertaken to assess the feasibility of using a mature, natural billabong (Georgetown) to remove sulphate from RRZ water and to determine the rate which might be achieved.

Sulphate Reduction

When reviewing sulphate reduction rates obtained in studies, it is important to take into account the methods which were employed in these determinations. In most cases for natural water-bodies, the rate of reduction is measured using sediment cores injected with $^{35}SO_4^{2-}$ and the rate of $^{35}S^{2-}$ formation in the cores is then taken to be the rate of reduction. Up to 200 mmol $SO_4^{2-}\ m^{-2}\ d^{-1}$ can be reduced with little difference in rates shown for either marine, estuarine or freshwater systems (Urban et al 1994). Urban et al (1994) demonstrated that the rate of sulphate reduction was much higher than the rate of diffusion. The diffusive flux of sulphate only averaged 2% of the average rate of reduction, the implication being that sulphate reduction would not be significantly affected by the concentration of sulphate in water overlying sediment. They also verified this assertion by examining results quoted for other lake systems. Because the only other sources of sulphate available to maintain this high rate of reduction was from either the reoxidation of sulfide or a small contribution from the hydrolysis of sulphate esters leached from organic matter (<4%), Urban et al (1994) claim, by inference, that the rate of oxidation of reduced sulfur compounds must nearly equal the observed rate of sulphate reduction.

In natural, relatively unimpacted wetland systems (whether fresh, estuarine or marine) a steady state is achieved between the rates of oxidation and reduction of S and although the input of sulphate may vary from rainfall, run-off, or plant decomposition it would require new or abnormal processes to significantly change the direction and the cycle. In this respect, Bayley et al (1986) examined the implications of dry and wet S deposition on a freshwater lake in Ontario, Canada by applying sulfuric acid. In this four year study sulphate was removed from the water at the rate of 64%, 46%, 73% and 22% in successive years. However, annual input of sulphate was low ranging between 63– 97 meq $SO_4^{2-}\ m^{-2}\ y^{-1}$ which led to only small increments in SO_4^{2-} concentration of between 1.3–2.0 $mg\ L^{-1}$. Similarly, Castro and Dierberg (1987) measured background biogenic hydrogen sulfide emissions from wetlands in Florida and found a maximum rate of 0.272 $g\ S\ m^{-2}\ yr^{-1}$.

The process of sulphate removal by reduction in sediments is performed by sulphate-reducing bacteria (SRB) encompassing a diverse and ubiquitous group of anaerobic prokaryotes which collectively share the ability to utilise oxidised sulfur compounds generally and sulphate specifically as the terminal electron acceptor for respiratory oxidation of small organic molecules (Postgate 1984). Dissimilatory sulphate reduction performed by SRB, as opposed to the more usual assimilatory uptake effected by most microorganisms (including SRB) and plants, can lead to the consumption of sulphate at rates which are sufficiently high for the remediation of sulphate contaminated waste-water to take place (Maree 1990). In this way, sulphate is reduced to sulfide and precipitation normally takes place with iron(II) leading, initially, to the formation of ferrous monosulfide (FeS), the insoluble, metastable mineral mackinawite. Slow transformation of mackinawite to more refractory ferrous polysulfide mineral states such as pyrite (FeS_2) then occurs.

Georgetown Billabong

Georgetown has been described by Walker & Tyler (1984) as a backflow billabong, typically shallow with shelving banks containing clay or fine silt sediments. During the Dry season, influent flow to these billabongs ceases and they contract as a result of evaporation causing the macrophyte beds at the littoral to senesce. In turn, this leads to an increase in chemical oxygen demand and a reduction in macrophyte cover and water depth. Consequently, wind-induced turbulence can penetrate the sediment and resuspend fine sediments causing turbidity to rise to high levels (Walker & Tyler 1982).

Georgetown billabong is situated on a small tributary of Magela Creek and was formed by the deposition of a sandy levée bank from Magela Creek at its northern end during periods of high flow. Georgetown does however, have additional inflow from a small catchment at the southern end (Finlayson et al 1994) and, hence, direction of flow is dependent on the relative water levels of the two influents. If Magela Creek is in spate, water breaches the levee and flows from north to south but this situation can be reversed when backflow from the main creek diminishes and the small tributary at the southern end is the only source of input. The vegetation surrounding the billabong is dominated by *Melaleuca sp* whilst the littoral is dominated by the sedges *Eleocharis dulcis* and *Eleocharis sphacelata* up to a depth of 1.5 m (Finlayson et al 1994). Towards the Northern end of the billabong there is a small area of open water approximately 1.5–2 m deep where the enclosures were placed. The vegetation in this deeper water consists of the waterlily *Nymphaea violacea* and the free floating, submerged *Utricularia sp.*

Enclosures

Previous studies in tropical wetlands have shown that enclosures do not mirror billabongs in relation to the physico-chemical processes that occur (Hart et al 1984, 1985a,b; Noller et al 1989). For example, while some parameters such as temperature, pH and conductivity are similar, dissolved oxygen (DO) is not. In this regard, DO usually decreases with depth in confined water bodies as opposed to an open billabong due to lack of turbulent mixing. It is this confinement which favours stratification (Sanders 1985). Other artifacts of enclosures include restrictions in the lateral flow of particulates and dissolved nutrients; reduced rates of chemical cycling due to lack of mixing; and high sedimentation rates of particulates which allow light to penetrate the water column giving rise to increased primary production (Sanders 1985). In addition, enclosures show 'wall effects'. These include shading of the enclosed water, algal growth on the walls, and an increase in macrozooplankton which graze on food particles associated with periphytic growth on the walls of the enclosure (Liber 1994).

Therefore, enclosures are not likely to mimic physical, chemical and biological processes in billabongs at the micro-, or, in total, at the macro-scale. Nevertheless, despite these limitations their deployment can provide a cost effective means by which chemical and/or microbial transformations can be studied in billabongs under semi-controlled conditions.

Use of replication with enclosure experiments is a somewhat contentious issue. For example, Sanders (1985) lists several factors affecting the use of replicates including the fact that variability amongst replicate enclosures is usually a function of the enclosed volume. In this regard, whilst increasing the surface area of an enclosure will tend to make the enclosed body more representative of the whole water body, larger enclosures may contain more horizontal spatial heterogeneity. This, in turn, increases within-enclosure variability, demands more sampling stations within each enclosure thus defeating the original purpose of a lower cost non-replicated design, and may have the disadvantage in experimental design of not being able to quantify the variability within the whole water-body. Stephenson (1994) is of the opinion that where a simple 'fate study' is being performed, replication is unnecessary provided that the principal effect causing removal is non-variant in space. Consequently, the effects measured in a single enclosure cannot be concluded to be the response that will occur in the water-body as a whole. Rather, the behaviour inside an enclosure can only be regarded as one subset of possible responses.

Materials and Methods

Two 9,000 L green polyethylene watertanks (TeamPOLY SA; 2.57 m diameter x 1.89 m high) were prepared by cutting off their tops and bottoms. They were then immersed in Georgetown billabong on 11 July 1996 in approximately 1.6 m of water (about 50m east of the Georgetown billabong gauge board) and then hammered approximately 10 cm into the sediment in such a way as to effectively partition the water enclosed from the surrounding billabong water. After an initial settling period of 2 days, one of the enclosures (hereafter referred to as 'Enclosure 1') was spiked with around 10 kg $MgSO_4$ (reagent grade) to give a sulphate concentration similar to RP2 water of approximately 150 mg L^{-1} SO_4-S. The other enclosure (ie 'Enclosure 2') was left unamended as a control. In addition, approximately 200g NaBr was added to each enclosure as a conservative tracer to take account of leakage and evaporation. Each enclosure and the billabong water was then simultaneously sampled and thereafter weekly. After nine weeks the enclosures were covered with shade cloth (90%) to minimise entry of light to the system. This operation was performed to investigate the combined effects of reducing the activity of algae and possibly increasing the cycling of organic carbon to provide substrate for sulphate reducers.

In situ water parameters pH, temperature, conductivity and dissolved oxygen (DO) were measured at the surface and bottom of the enclosures and billabong using a *Hydrolab Datasonde 3* and then continuously from 11th October to 24th October in the surface and bottom waters of Enclosure 1. Water samples were taken weekly for the duration of the experiment between 09:00–09:40 h except on 11th September when sampling occured between 11:00–12:00 h. Georgetown billabong water was sampled from a zone approximately 10 m from the enclosures towards the middle of the billabong. Approximately 1 L of water was sampled from the surface (10 cm depth), middle and bottom (2 cm above the sediment-water interface) of each of the three treatments (ie Enclosures 1 and 2, and Georgetown billabong) from which 25mL was immediately filtered (<0.45 μm) and analysed for sulfide using methylene blue (Cline 1969). Turbidity was measured in the laboratory using a *Hach Model No. 18900*. In addition, 500 mL of each sample was filtered through Whatman GFC paper and the retained solids analysed for chlorophyll *a* (Eaton et al 1995). An unfiltered subsample was

retained for total N and P analyses by CSIRO Division of Coal and Energy Technology, Sydney. The remaining portion of sample was then passed through *Millipore* cellulose acetate (0.45 μm) and divided into subsamples prior to refrigeration (4°C) until analysis was performed. One subsample (~5mL) was used for the analyses of chloride, nitrate, sulphate and calcium by HPLC (*Waters Model 350*) with an *Alltech Wescan Anion-10 μm column* (4.6 mm id; 100 mm long) using EDTA as an eluent (leGras 1993). Finally a 100 ml subsample was used for total P and N analyses.

Results and Discussion

Trophic Status of Georgetown Billabong

The concentration of total soluble N and P over the period of the experiment is given in Table 1 (D Jones pers comm). Almost all the samples taken from the billabong and the enclosures contained a total P concentration which was below the detection limit (7 μg L^{-1}) for the method used, while total N, showed a range of 250–960 μg L^{-1}. Using the classification of Vollenweider (1968; cited in Walker & Tyler 1982), Georgetown billabong may be described as ultra-oligotrophic in terms of P and between oligo-mesotrophic and eutrophic in terms of N. This compares with <10 μg L^{-1} total P and 900–1600 μg L^{-1} total N for Georgetown billabong during the 1994 dry season (Jones & Raguso 1995a) which is in good agreement with the stated trophic status of this water body. However, Tyler and Walker (1982) found markedly different ranges of total P and N during the 1980 Dry season (July–October) of 142–559 μg L^{-1} and 995–3147 μg L^{-1} respectively. Accordingly, these high levels classified Georgetown as a hypereutrophic system. The reason for this change in trophic status is probably due in a large part to the elimination of feral buffalo from the region.

Table 1 Mean total soluble N and P (mg/L) in Georgetown billabong and the enclosures

	Georgetown billabong		Enclosure 1		Enclosure 2	
Date	Total N	Total P	Total N	Total P	Total N	Total P
17/7/96	0.353	<0.007–0.008	0.297	<0.007	0.458	<0.007
24/796	0.349	<0.007	0.259	<0.007	0.405	<0.007
21/8/96	0.460	<0.007–0.009	0.314	<0.007	0.332	<0.007
16/9/96	0.660	<0.007–0.014	0.750	<0.007–0.021	0.351	<0.007–0.014

pH

The pH of the water in Georgetown billabong during the experiment remained between 5.9 and 6.7 at both the surface and the bottom of the water column (Fig 1) and is in good agreement with published data (Walker & Tyler 1982; Jones & Raguso 1995a). Mean pH values are given in Table 2. There were no effects ($P>0.05$) on pH either within or between the billabong and enclosures and thus pH was neither influenced by an enclosure effect nor by the addition of magnesium sulphate.

An example of diurnal variation in pH in Enclosure 1 is shown (Fig 2) for a 12.5 day period immediately following installation of multi-probe recorders at 09.30 h on 11 October 1996. Marked diurnal variation occurred in the pH of both surface and bottom waters with

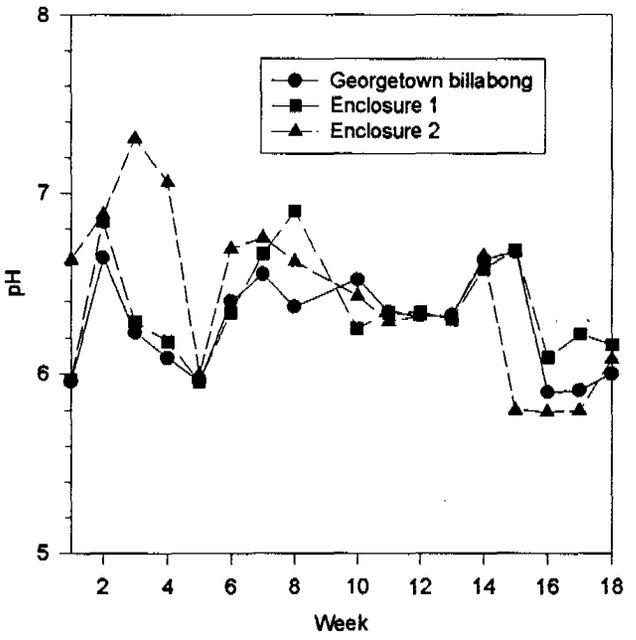


Figure 1 Mean weekly pH of waters in Georgetown billabong and the enclosures

Table 2 Mean (±SD) pH at the near surface and bottom of Georgetown billabong and the enclosures.

	Georgetown	Enclosure 1	Enclosure 2
Top	6.32 (0.28)	6.26 (0.29)	6.48 (0.52)
Bottom	6.26 (0.29)	6.46 (0.38)	6.38 (0.43)
Grand Mean	6.29 (0.28)	6.36 (0.35)	6.43 (0.47)

amplitudes of around 1–1.5 and 1 pH unit respectively. Over the whole data set which spanned 18 days, maximum pH was attained consistently in the surface water at 17.30 h compared with a less consistent maximum in bottom water between 13.30–16.30 h. Similarly, while a minimum pH was reached in surface water around 08.30 h, bottom water showed greater variability with minima occurring between 00.30–04.30 h.

The pattern to pH fluctuation reflects photosythesis and respiration cycles in the enclosure and, hence, match corresponding changes in the concentration of dissolved O_2 (see p 12). In surface water, where light is non-limiting to photosynthesis, the increase in pH from morning to mid-afternoon reflects the assimilation of dissolved CO_2. At depth, light is limiting so an increase in pH is less pronounced. However, this difference in rate of photosynthesis as a function of water depth which gives rise to a varying effect on pH, is tempered by convective mixing, caused by a temperature gradient (Fig 5), and by diffusion. The consumption of CO_2 during the photosynthesis cycle is in turn replaced by respiration and the release of CO_2. The dominance of respiration over photosynthesis will start earlier at depth than near the surface because of light limitation which may in part be influenced by shading. The relatively warmer water at the surface compared with the cooler water at depth (Fig 5) will subsequently lead to some convective mixing although the presence of a pH gradient (Fig 2) indicates that it is relatively ineffective.

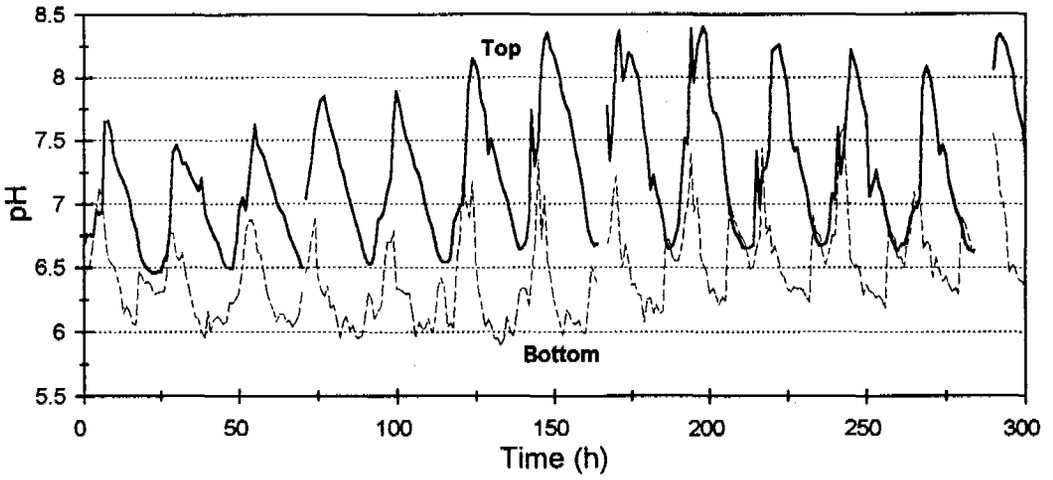


Figure 2 pH of surface and bottom waters in Enclosure 1 over a 300 h period from 11 October 1996

Conductivity

Changes in the conductivity of the treatments are shown in Figure 3. Since there were no significant differences ($P>0.05$) between surface and bottom waters within the billabong or each of the enclosures, data for each treatment was pooled and regressed against time. For each treatment, the trend in conductivity over time was approximately linear (Fig 3).

Conductivity in the open billabong increased in response to evaporation during the experiment (Fig 3) from 35 $\mu S\ cm^{-1}$ in July to 90 $\mu S\ cm^{-1}$ in November. Jones and Raguso (1995b) noted a similar conductivity during October 1994 (ie 92–136 $\mu S\ cm^{-1}$) in Georgetown billabong prior to the build-up to the wet season. Similarly, Walker and Tyler (1982) measured an increase in conductivity between July and October 1979 and 1980 from 30 to 90 $\mu S\ cm^{-1}$.

Enclosure 2, amended with sodium bromide as a conservative tracer, had an initial conductivity (ie 58 $\mu S\ cm^{-1}$) which was slightly higher than the open billabong. This difference increased over the experiment because of an enclosure effect due to the smaller surface area to volume ratio of the enclosure compared to the billabong which led to a lower rate of evaporation from the former. Whilst the conductivity of the open billabong increased by a factor of 2.7, the conductivity doubled in Enclosure 2. By adding magnesium sulphate to Enclosure 1, conductivity at the start of the experiment was approximately 770 $\mu S\ cm^{-1}$ and increased to near 1200 $\mu S\ cm^{-1}$ by the end experiment.

Temperature

Temperature, based on weekly readings, was unaffected ($P>0.5$) by either treatment or depth and averaged 26.1 °C. The trend in the temperature of surface and bottom waters for Georgetown billabong is shown in Figure 4 with a minimum of 22.5 °C reached in late August. Thereafter, temperature increased sharply to around 27 °C in September before establishing a plateau of 28–29 °C by the end of the experiment.

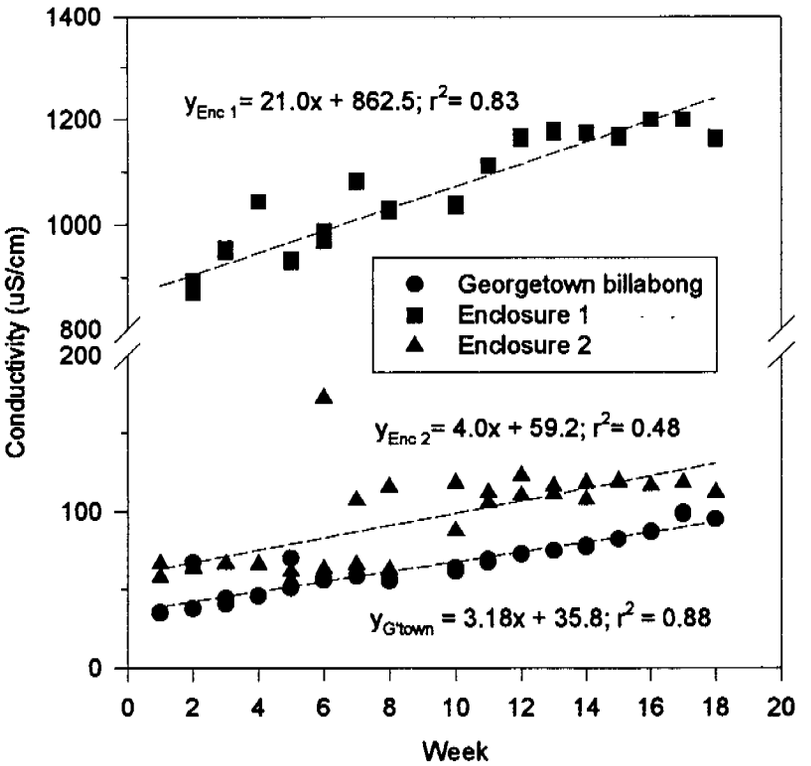


Figure 3 Changes in conductivity over time in Georgetown billabong and the enclosures

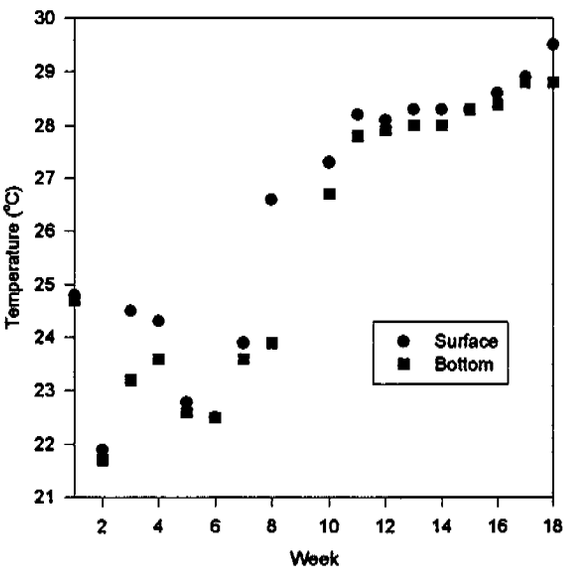


Figure 4 Temperature of surface and bottom waters in Georgetown billabong

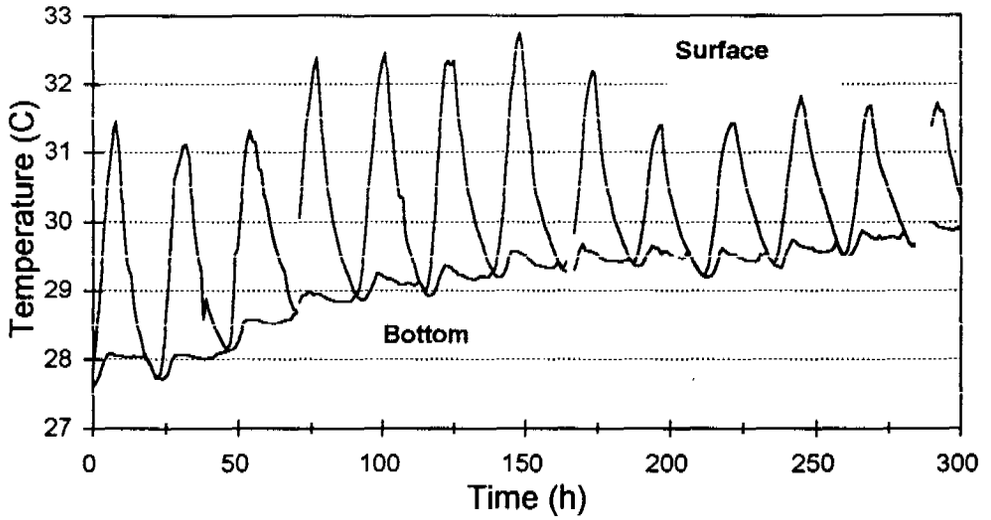


Figure 5 Temperature (°C) of surface and bottom waters in Enclosure 1 over a 300 h period from 11 October 1996

In situ monitoring of Enclosure 1 (Fig 5) provides strong evidence of a temperature gradient with distinct diurnal temperature change of >3 °C in surface water but a dampened diurnal response of around ±0.5 °C in bottom water. Maximum temperature in surface water was reached between 16.30–18.30 h. Minimum temperature in surface water was consistently recorded between 06.30–08.30 h at which time temperature matched that of bottom water suggesting that the gradient was periodically disrupted by convective mixing. During the 12.5 day period, the diurnal amplitude of temperature change in surface water varied in response to meteorological factors with little effect on bottom water. Overall, the mean daily temperature of both surface and bottom waters slowly increased as change between the dry and wet seasons took place.

Turbidity

Mean turbidity is given in Table 3. There were no differences ($P>0.05$) in turbidity between surface and bottom waters in any treatment. However, Enclosure 1 water had a lower ($P<0.002$) turbidity than either the open billabong or Enclosure 2.

Table 3 Mean (±SD) turbidity (NTU) at the near surface and bottom of Georgetown billabong and the enclosures.

	Georgetown	Enclosure 1	Enclosure 2
Top	80 (43)	7 (8)	69 (79)
Bottom	98 (47)	8 (10)	84 (108)
Grand Mean	89 (45)	7 (9)	76 (93)

Billabongs in the region have been observed to become more turbid as the Dry season progresses (Walker & Tyler 1984, Noller et al 1989, Jones & Raguso 1995b). This proved to be the case in the present study (Fig 6) and has been attributed (Walker & Tyler 1985) to the the senescence of aquatic macrophytes from evaporative flux and their resuspension from

sediment by wind-driven turbulence. In comparison, Enclosure 1 remained very clear throughout the experiment, probably due to the sheltering effect of the enclosed water from wind in conjunction with the flocculating effect that salt addition has on suspended matter. Enclosure 2 remained clear until the ninth week (Fig 6) when core samples were taken from inside the enclosure. During this operation, sediment was disturbed resulting in a dramatic increase in turbidity levels for the remainder of the experiment. A similar effect was shown in Enclosure 1 but because of the salt effect on flocculation, it was far less pronounced.

Chlorophyll *a*

Mean concentrations of chlorophyll *a* in suspended matter are given in Table 4. There were no significant differences ($P>0.05$) in mean chlorophyll *a* between surface and bottom waters in any single treatment or between surface waters of each treatment. However, there was a significant ($P<0.03$) effect of treatment on the chlorophyll *a* concentration in bottom water with Enclosure 1 containing a lower concentration than the open billabong but not Enclosure 2.

Over time (Fig 7), chlorophyll *a* increased in the open billabong reaching a maximum during late August–early October which coincided with the development of fresh south-westerlies (>50 km h^{-1}) and an increase in turbidity (Fig 6). Thereafter, chlorophyll *a* concentration fell to around 0.2 mg/L, corresponding to concentrations at the start of the experiment. A similar pattern but more pronounced maxima were shown in the enclosures. Interestingly, whilst a marginal effect on turbidity appeared to arise in Enclosure 1 from sampling disturbance in week 9 (Fig 6), both enclosures showed marked increases in chlorophyll *a* suggesting that although sediment quickly fell out of suspension in Enclosure 1, phytoplankton and algae brought into suspension had a longer residence time. However, it was surprising not to find that the greater clarity of the water in Enclosure 1 and the increased penetration of photosynthetically active radiation that would have resulted, did not encourage pelagic algal growth. In turn, this suggests that light was not the limiting factor to growth.

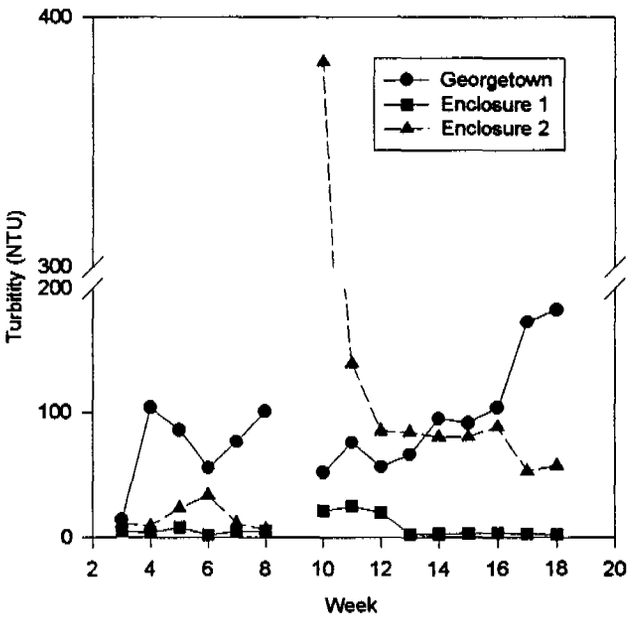


Figure 6 Mean turbidity of waters in Georgetown billabong and the enclosures

Table 4 Mean (±SD) chlorophyll *a* (mg/L) at the near surface and bottom of Georgetown billabong and the enclosures.

	Georgetown	Enclosure 1	Enclosure 2
Top	0.37 (0.27)	0.43 (0.70)	0.34 (0.43)
Bottom	0.31 (0.18)	0.15 (0.14)	0.24 (0.17)
Grand Mean	0.34 (0.23)	0.29 (0.51)	0.29 (0.33)

Dissolved Oxygen

Dissolved oxygen (DO) concentration in water is dependent upon its rate of exchange between the air-water interface, its consumption in biologically and chemically-mediated oxidation reactions, and its production from photosynthesis. Consequently, surface waters tend to be more oxygenated than water at depth and this pattern is well illustrated by the data presented in this study (Fig 8). In each of the three water bodies, levels of DO at the bottom of the profile were much lower ($P<0.001$) than at the surface (Table 5). In addition, the surface water in Enclosure 1 contained a higher ($P<0.05$) DO concentration than either the open billabong or Enclosure 2. Similarly, bottom water in Enclosure 1 contained almost three times the DO concentration than at the bottom of the billabong ($P<0.02$) but its concentration was not greater ($P>0.05$) than bottom water in Enclosure 2. For both surface and bottom waters, there was no statistically significant difference between DO levels in waters of the open billabong and Enclosure 2. The greater clarity of the water in Enclosure 1 (see above) would have allowed photosynthetically active radiation to penetrate the water column and reduced the importance of light limitation for algal growth. The fact that significantly greater pelagic growth was not demonstrated from weekly monitoring of chlorophyll *a* in Enclosure 1 suggests that it may have been epiphytic growth on the walls which was promoted.

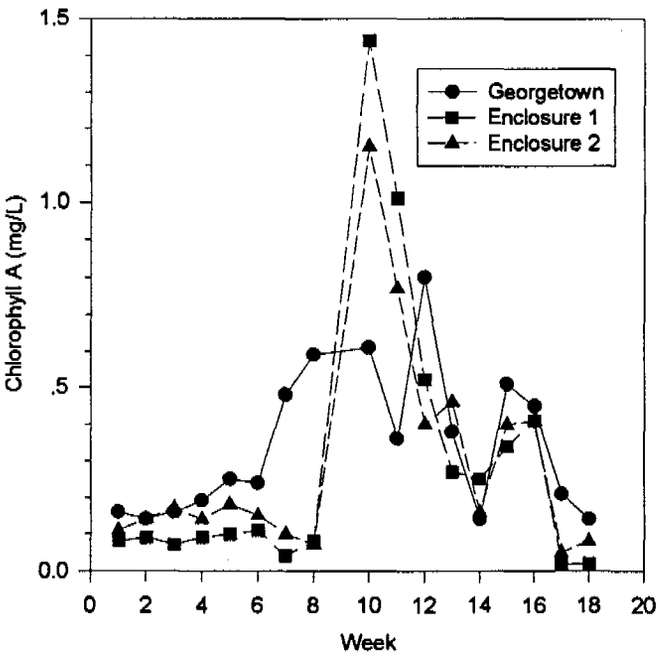


Figure 7 Mean chlorophyll *a* (mg/L) of waters in Georgetown billabong and the enclosures

Walker and Tyler (1984) found a range of between 10 and 20 % in the diurnal variation of the surface waters in the Dry season and this is in good agreement with diurnal cycles measured in this study. However, DO levels measured here tend to be slightly higher than their average saturation levels of 60% for surface waters in Georgetown billabong. (Fig 9) Our results do not support Walker and Tyler's (1984) assertion that 'DO levels scarcely change for some time after dawn' but rather that there is a steep increase following the diurnal low recorded at dawn. Jones and Raguso (1995a) only present data profiling the DO concentration at 14:00 hours on 8 July 1994. Their results show the presence of a weak oxycline between the depths of 0.6 and 1.6 m with surface DO levels of 5.4 mg L^{-1} declining to 1.4 mg L^{-1} at the water/sediment interface (ie 2.0 m depth). These levels are very similar to those determined in this study for Georgetown billabong in July (mean 5.1 to 1.7 mg L^{-1}).

Enclosure 1 behaved quite differently over time compared with the other treatments. While trends in DO were similar between the open billabong and Enclosure 2 and corresponded to a general decline in these waters, DO in Enclosure 1 steadily increased during the first 8 weeks of the experiment (Fig 8). In addition, the disturbance which occurred in week 9 from sampling resulted in a more pronounced and prolonged effect in Enclosure 1 compared with Enclosure 2. After disturbance in Enclosure 1, DO reached supersaturated concentrations suggesting that a limitation to algal growth, albeit temporary, had been removed. A possible explanation is that there was a nutrient limitation, which following disturbance of the sediment surface, resulted in increased nutrient availability. A similar effect on algal growth did not take place in Enclosure 2 perhaps because of light limitation.

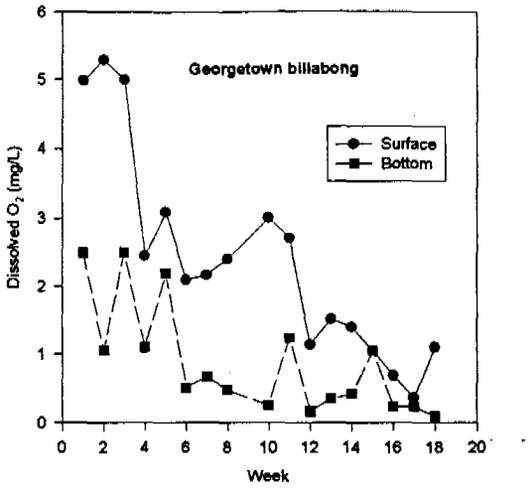
Dissolved oxygen showed marked diurnal variation in both surface and bottom waters but especially the latter (Fig 9). Over the monitoring period, diurnal variation in surface waters was around 2 mg/L compared with 4–6 mg O_2/L in bottom water which regularly became anoxic in early morning. Maxima in DO were attained in both waters between 14.30–16.30 h although minimum concentrations were reached in the bottom water (typically between 02.30–04.30 h) as much as 7 h before surface water (between 07.30–09.30 h).

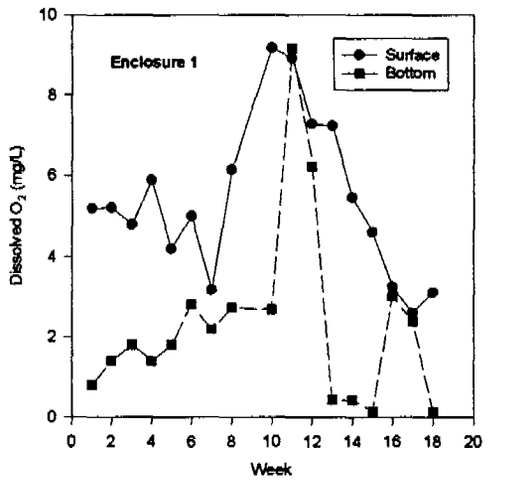
Table 5 Mean (±SD) dissolved O_2 (mg/L) at the near surface and bottom of Georgetown billabong and the enclosures.

	Georgetown	Enclosure 1	Enclosure 2
Top	2.38 (1.52)	5.36 (1.93)	3.47 (2.43)
Bottom	0.88 (0.81)	2.32 (2.29)	1.08 (1.03)
Grand Mean	1.63 (1.42)	3.84 (2.60)	2.28 (2.20)

Sulfide

Using the method of Cline (1969) sulphide can be detected visually under field conditions at concentrations as low as 1μM. During the experiment, sulfide was never detected in the water column of any of the treatments. If sulphate reduction had been stimulated by the addition of sulphate to Enclosure 1, there was no evidence that sulfide was leaving the system as hydrogen sulfide gas.





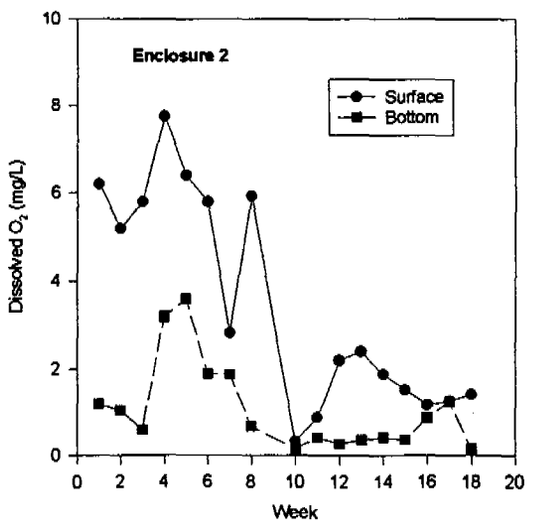


Figure 8 Dissolved O_2 (mg/L) in the surface and bottom waters of Georgetown billabong and the enclosures

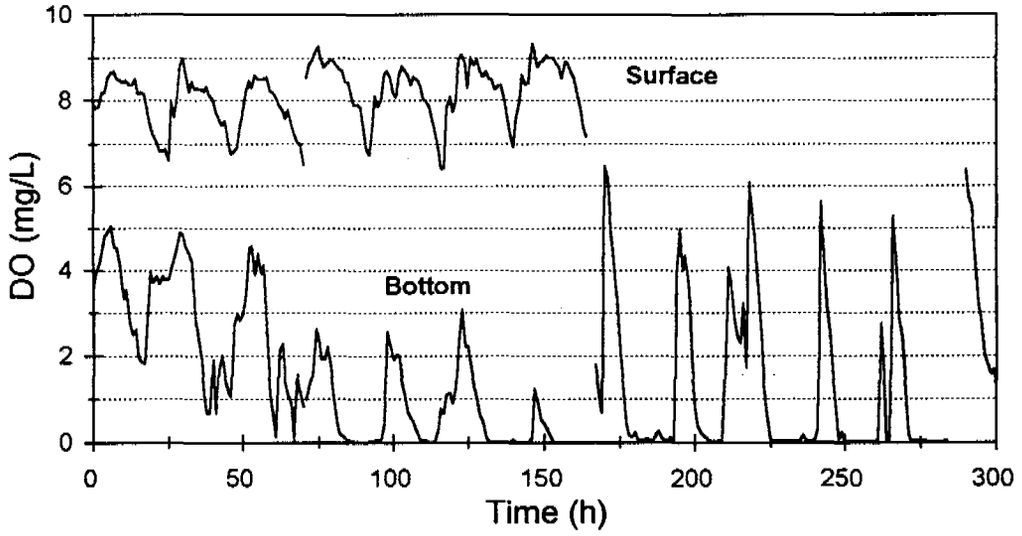


Figure 9 Dissolved O_2 concentration (mg/L) in surface and bottom waters of Enclosure 1 over a 300 h period from 11 October 1996

Estimating sulphate reduction

The concentration of solutes in the waters of the billabong and the enclosures were expected to change since the mass of dissolved matter is subject to dynamic equilibria which may be driven by chemical reactions, diffusion gradients and/or biological processes. In addition, the volume in which the solutes are contained does not remain constant. In this respect, the most obvious process to take into account in a mass balance is the evaporation of water and/or any exchange of waters that may occur between the enclosures and the open billabong. Hence, it was essential that a conservative tracer be used to determine whether sulphate was conserved. Bromide was chosen for this purpose because it is relatively inert in solution (ie is not adsorbed by particulates or sediment), is not normally present in measurable concentrations, and is not assimilated biologically to any marked degree. The ambient chloride concentration was also used as a surrogate conservative tracer for the same reasons.

To this end, sodium bromide was added to the enclosures. If processes inside both enclosures were similar, the concentration of bromide would be expected to vary similarly over time in each. The change in bromide concentration within each enclosure was approximately linear and in each case significantly ($P<0.01$) related to time (Fig 10). Although Br^- concentration increased three times as fast as in Enclosure 2 over the first 8 weeks of the experiment, there was no difference ($P>0.05$) in the slope of concentration over time between Enclosures 1 and 2. Even when the week 3 outlier in the Enclosure1 Br^- data was removed, there was no difference ($P>0.05$) in the slopes.

Chloride was also investigated as a tracer and it behaved similarly in both enclosures (ie there was no significant difference ($P>0.05$) between the rate of change of Cl^- in Enclosures 1 and 2), although little change occurred over the first 8 weeks (Fig 11). At week 9, there is a discontinuity in both data sets which was probably caused by disturbance of the enclosures during core sampling when water from the open billabong (whose chloride concentration at this time was higher than the chloride concentration in the enclosures) may have entered the enclosures. Correlation of the chloride data for Enclosures 1 and 2 provides a coefficient of

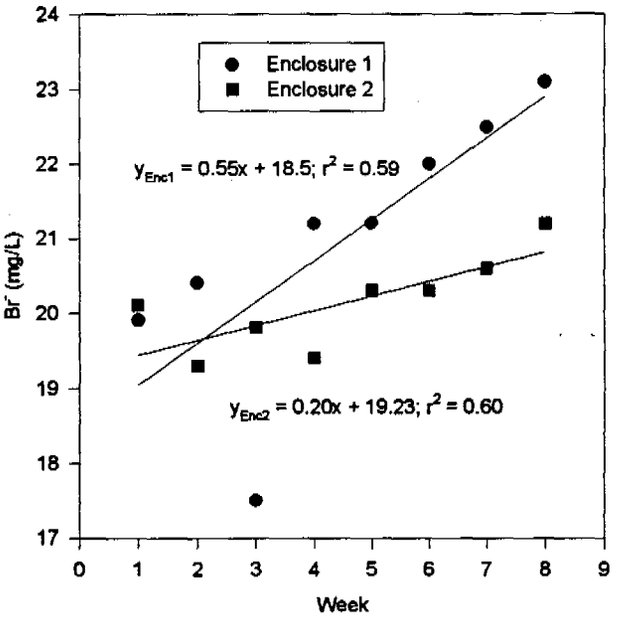


Figure 10 Changes in bromide concentration (mg/L) in the enclosures

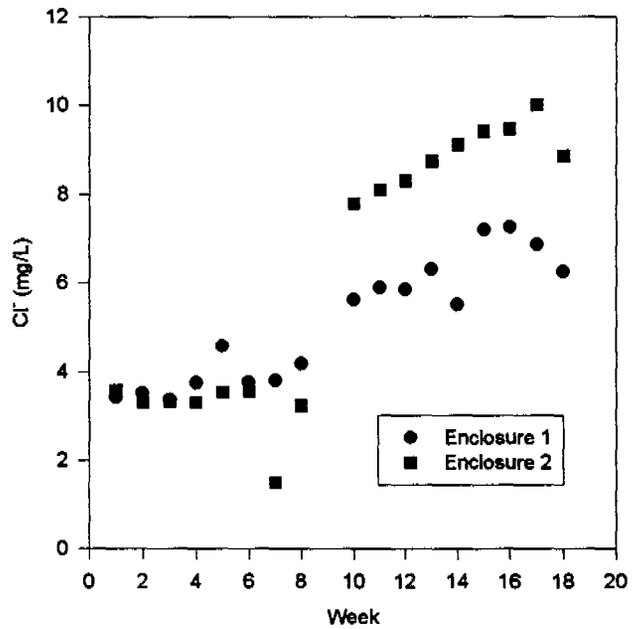


Figure 11 Changes in chloride concentration (mg/L) in the enclosures

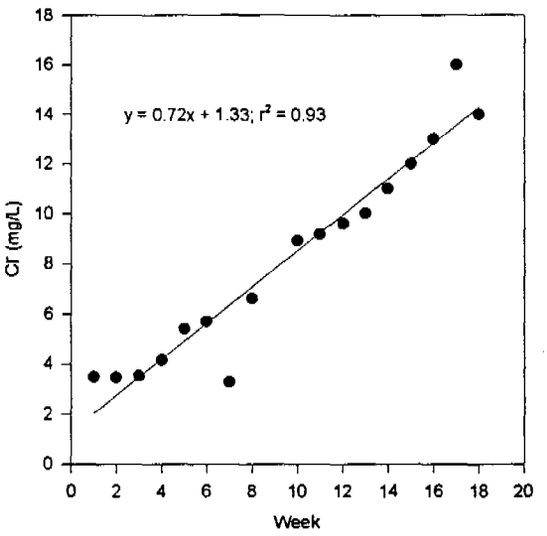


Figure 12 Changes in chloride concentration (mg/L) in Georgtown billabong

0.74 for the full data set and 0.94 if the outlier in the data set for Enclosure 1 at week 14 is omitted.

There are two potential problems with using chloride as a conservative tracer. First, the concentration of chloride in the open billabong (Fig 12) increased faster than in the enclosures (Fig 11) meaning that any ingress of billabong water would by implication increase the nominal rate of sulphate reduction calculated using chloride as a tracer. Second, because chloride was present at relatively low concentration in the enclosures this could give rise to errors in calculating sulphate reduction rate due to the imprecision of analytical measurement. In this respect, chloride concentration in Enclosure 1 rose from between 3 and 4 mg L^{-1} at the start to 10 mg L^{-1} at the end of the experiment. Hence, given that sulphate concentration in the amended enclosure was initially 456 mg L^{-1} (ie approximately 150 times the chloride concentration), even small errors in the determination of chloride resulting from sampling, contamination, or analysis could have an inordinately large effect on the calculation of sulphate removal.

Changes in mean sulphate concentration over time are shown for Enclosure 1 (Fig 13) and for Enclosure 2 and the open billabong (Fig 14). For each treatment, there were no differences ($P>0.05$) between surface and bottom waters in sulphate concentration. In addition, there was no evidence that sulphate amendment led to any discernable increase in the phosphate concentration of the water column from anion exchange as described by Caraco et al (1989).

Mass loss of sulphate from Enclosure 1 was calculated (Table 6) using both the Cl^- and Br^- data sets. Since the Br^- data only spanned the first 8 weeks of the experiment, a truncated Cl^- data set was used for comparison as well as the full data set (ie over 18 weeks). In the method employed, water volume in Enclosure 1 was estimated by accounting for changes in the ratio of measured Cl^- or Br^- to their initial values. The initial volume of water was assumed to be 8000 L and the mass of SO_4^{2-} was estimated from the measured SO_4^{2-} concentration. Mass of SO_4^{2-} was then regressed against time and the results are summarised in Table 7.

Rate of loss of sulphate from Enclosure 1 was 0.7 moles/week using the Br^- and truncated (ie Weeks 1–8) Cl^- data sets although in both cases the relationships between the mass of SO_4^{2-}

and time were not significant ($P>0.05$). When the full Cl^- data set was used, sulphate loss was linearly ($P<0.001$) related to time and was equivalent to 0.95 moles/week or 0.18 moles/week/m^2. The time for sulphate to reach half its initial concentration based on the derived relationships (Table 7) ranged from 147–204 days. However, it is probable that the minimum half-time of 147 days is an underestimation because of the non-conformity of the Cl^- data resulting from the effects of sampling within the enclosures during Week 9.

Loss of sulphate was calculated in a similar manner for Enclosure 2 and the open billabong (Table 8). In both cases, the decline in sulphate load with time was best described as curvelinear and sulphate mass was found to be significantly ($P<0.001$) related to the logarithm of time with half-times of 46 and 33 days respectively. The regressions of the Br^- and truncated Cl^- data sets against time for Enclosure 2 were not significant ($P>0.05$).

Any effect of the assimilation of sulphate by biota in Enclosure 2 and the billabong on sulphate mass, compared with Enclosure 1, is undoubtedly magified because of the relatively low sulphate concentrations. For example, Vymazel (1995) quotes K_S values (the concentration at which sulphate is absorbed at half the maximum rate) for algae ranging between 63 µM and 69 mM well above ambient sulphate concentrations in either Enclosure 2 or the billabong. Hence under the low sulphate loads of Enclosure 2 and the billabong, changes in sulphate concentration are likely to reflect algal growth rates and S demand to a much greater degree than Enclosure 1. However, whether the logarithmic form to the decline in sulphate mass in Enclosure 2 and the billabong is directly attributable to the population dynamics of algae (and/or other biota) and a decreasing demand for S in response to stress (ie declining water depth and increased turbidity) is not known.

There is some degree of uncertainity as to whether the decline in sulphate load from Enclosure 1 can be attributed (largely) to sulphate reduction. Some freshwater algae (eg *Nitella sp*) are known to be able to absorb sulphate luxuriously with uptake stimulated by light (Vymazel, 1995). However, although light level was promoted in Enclosure 1 and that it hosted epiphytic and pelagic algae, the net effect of biota on influencing sulphate load in Enclosure 1 was likely very small. For example, in the absence of data for algae but assuming a maximum quoted (Vymazel, 1995) uptake rate of sulphate for wetland plants of 65 g S m^{-2} y^{-1} (for *Lemna sp*), this equates to only 0.7 mol S m^{-2} per 18 weeks or 3.6 mol S per enclosure per 18 weeks and represents less than 20% of the S which was removed from Enclosure 1 over the duration of the experiment.

The pattern of sulphate concentration in Enclosure 1 was closely matched ($P<0.001$) by magnesium which is its principal co-ion (Fig 15). When the mass load of Mg^{2+} in Enclosure 1 was derived using the full Cl^- data set (as described above for sulphate) and regressed against time, the following relationship was defined (where $y = Mg^{2+}$ (mol) and x = week);

$$y = -1.05x + 42.93;\ r^2 = 0.6278\ (P<0.001)$$

Not surprisingly, the time for half the Mg^{2+} load to be removed (ie 143 days) closely matched that of sulphate (ie 147 days). Consequently, the same limiting factors determining the removal rate of sulphate were also acting on Mg^{2+}. In this respect, it is likely that an important rate limiting step to sulphate reduction is its diffusion in sediment to anaerobic zones. As the principal co-ion to sulphate, the diffusion rate of magnesium and hence its rate of removal from Enclosure 1 would be similarly affected. However, there is no corroborating evidence to suggest that sulphate was reduced and further *in situ* studies are required. If it is assumed that the decrease in mass load of sulphate from Enclosure 1 can be attributed to microbial reducers, then the rate at which it occurred took place too slowly to be of practical significance in terms of using unengineered, natural billabongs on the Ranger lease to polish RRZ water.

Table 6 Changes in the mass of SO_4^{2-} in Enclosure 1

	Concentration (µM)			Correction factor		Volume (L)		SO_4^{2-} (moles)	
Week	Cl^-	Br^-	SO_4^{2-}	Cl^-	Br^-	Cl^-	Br^-	Cl^-	Br^-
1	96.3	249.1	4767.5	1.00	1.00	8000.0	8000.0	38.1	38.1
2	98.9	255.3	4834.8	1.03	1.03	7790.0	7803.9	37.7	37.7
3	94.6	219.0	4841.3	0.98	0.88	8143.3	9097.1	39.4	44.0
4	105.7	265.3	5037.8	1.10	1.07	7287.5	7509.4	36.7	37.8
5	129.0	265.3	4914.6	1.34	1.07	5970.6	7509.4	29.3	36.9
6	105.6	275.3	5041.7	1.10	1.11	7294.0	7236.4	36.8	36.5
7	107.0	281.6	5302.1	1.11	1.13	7198.0	7075.6	38.2	37.5
8	117.9	289.1	4830.7	1.22	1.16	6536.7	6891.8	31.6	33.3
10	158.0		5904.0	1.64		4875.9		28.8	
11	165.7		5984.6	1.72		4650.0		27.8	
12	164.8		6099.0	1.71		4675.6		28.5	
13	177.5		6213.5	1.84		4341.6		27.0	
14	154.9		6177.1	1.61		4973.2		30.7	
15	202.8		6182.3	2.11		3798.9		23.5	
16	204.2		6062.5	2.12		3772.7		22.9	
17	193.0		6161.5	2.00		3993.0		24.6	
18	176.1		5458.3	1.83		4376.4		23.9	

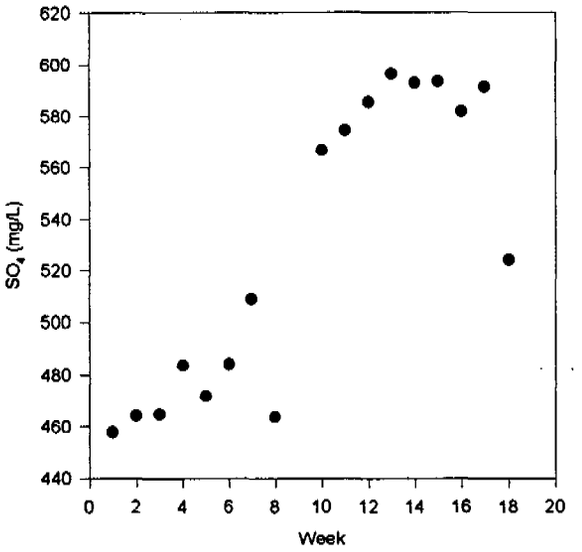


Figure 13 Sulphate concentration (mg/L) in Enclosure 1

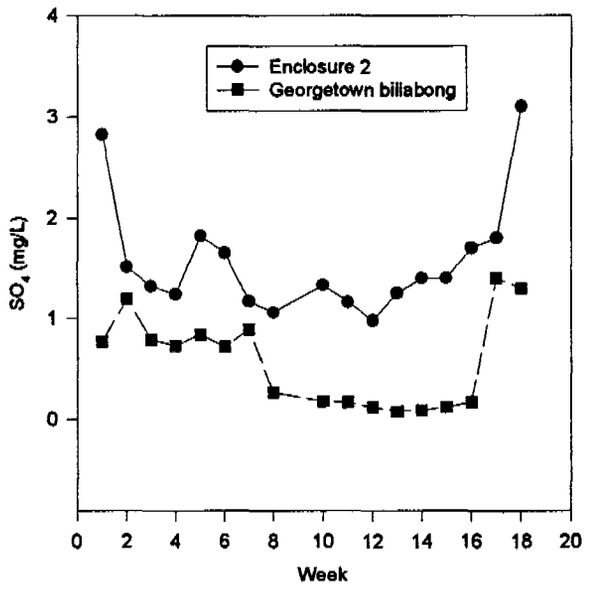


Figure 14 Sulphate concentration in Enclosure 2 and Georgetown billabong

Table 7 Predicted rate of change (mol/week) and initial mass (mol) of sulphate in Enclosure 1

Data set	Slope (mol/week)	Intercept (mol)	Explained variance (r^2)
Br^-	-0.70	40.88	0.3298 (NS)
Cl^- (truncated)	-0.70	39.12	0.2316 (NS)
Cl^- (full)	-0.95	39.99	0.8063 (P<0.001)

NS Not significant (P>0.05)

Table 8 Predicted rate of change (mol/ week) and initial mass of sulphate (mol) in Enclosure 2 and Georgetown billabong

Site	Data set	Slope (mol/ week)	Intercept (mol)	Explained variance (r^2)
Enclosure 2	Br^-	-0.013	0.19	0.4755 (NS)
	Cl^- (truncated)	-0.004	0.17	0.0441 (NS)
	Cl^- (full)	-0.0572[1]	0.2146[2]	0.5453 (P<0.001)
Billabong[3]	Cl^- (full)	-0.0303[1]	0.0933[2]	0.6081 (P<0.001)

[1]Slopes so marked have the units mol/ln week; [2]defined at week = 1; [3]regression based on a hypothetical cylinder of equivalent dimensions to the enclosures (ie at week 1, volume = 8000 L)

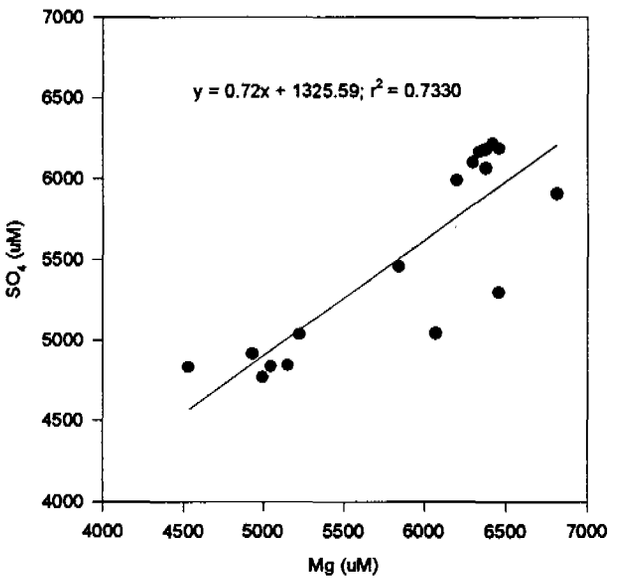


Figure 15 Relationship between sulphate and magnesium in the water of Enclosure 1

Conclusions

- The removal rate of sulphate in Enclosure 1 was between 0.70–0.95 moles $week^{-1}$ which was equivalent to 0.13–0.18 moles $week^{-1}$ m^{-2} and a half-time of between 147-204 days.
- There was no preferential loss of sulphate relative to magnesium. Rather the rate of change of the two ions appear to be the same suggesting that if sulphate was reduced, its loss was subject to the same rate limiting factor as for magnesium. This rate limiting factor is probably the diffusion of ions fom the water column into sediment pore water in response to a concentration gradient.
- Measured physico-chemical parameters for Georgetown billabong are in good general agreement with other studies except for the apparently large decrease in total soluble phosphorus and total nitrogen concentrations since the 1979-80 study conducted by Walker and Tyler (1982). This may have resulted from the removal of feral buffalo from Kakadu National Park..

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