Technical Memorandum 12

Use of Plastic Enclosures in Determining the Effects of Heavy Metals Added to Gulungul Billabong

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ABSTRACT

Hart, B.T., Jones, M.J. and Bek, P. (1985). Use of plastic enclosures in determining the effects of heavy metals added to Gulungul Billabong. Supervising Scientist for the Alligator Rivers Region, Technical Memorandum 12.

Plastic enclosures placed in Gulungul Billabong were used to investigate the behaviour of heavy metals added to billabong waters. One metre diameter enclosures were apparently too small because they did not simulate the dissolved oxygen profiles observed in the billabong. Three metre diameter enclosures were better, showing dissolved oxygen and temperature profiles which were similar to those in the billabong.

Heavy metals added to one of the large enclosures caused observable changes in the algal populations. There was, however, considerable uncertainty about which changes were brought about by the added metals and which were due to natural causes.

The added heavy metals, manganese, zinc and copper, were all rapidly lost from the water column to the sediments. The manganese was reduced to ambient levels in approximately 10-15 days while the zinc and copper concentrations were reduced less rapidly but were near ambient concentrations by the end of the four-week study. The loss of heavy metals was mainly by association of the added ionic metal with particulate matter, which then settled out.

1 INTRODUCTION

A major problem with laboratory-based experiments designed to determine the behaviour and toxicity of heavy metals in a water body is the extrapolation of the results to the field situation. A better method may be to isolate part of the water body by means of a plastic or rubber enclosure, then add the metals to this isolated water and monitor any changes.

Several experiments using enclosures to study the effects of added nutrients or heavy metals have been carried out in different parts of the world. Lund (1972) and Lack and Lund (1974) were probably the first to exploit the use of enclosures, called Lund tubes, to study phytoplankton populations in Blelham Tarn in the English Lakes District. In Switzerland the MELIMEX experiments used enclosures to determine the effects of adding heavy metals continuously over a period of time (Gachter 1979). In Canada, enclosures have been used in lake acidification studies (Schindler et al. 1980) and to observe the chemical and biological processes which affect oxidation and reduction of arsenic (Brunskill et al. 1980), the uptake of radiocarbon by algae (Bower and McCorkle 1980) and the influence of cadmium on zooplankton and periphyton (Marshall and Mellinger 1980). Kerrison et al. (1980) also used small enclosures in an Italian lake to study the effect of cadmium on zooplankton and phytoplankton populations.

A number of enclosure experiments have also been run in the marine environment. One of the most comprehensive was the CEPEX experiment conducted in Saanich Inlet, British Columbia (CEPEX 1977; Reeve et al. 1976). Hunt and Smith (1980) have reported enclosure experiments conducted in Narragansett Bay in which the long-term response and variability of iron, copper, cadmium and lead was studied. In Japan, Maeda and Tanaka (1977) studied the behaviour of zinc and copper in coastal seawater isolated by plastic enclosures.

During August 1980 four plastic enclosures, of two sizes, were placed in Gulungul Billabong, a mixture of heavy metals was added to one enclosure of each size and the enclosures were monitored over a four-week period. The results of these experiments are discussed in this report.

2 METHODS

2.1 Enclosures

Four cylindrical enclosures were constructed from 1 mm green PVC film; two were 1 m diameter and two were 3 m diameter. Each enclosure was equipped with an inflatable ring for flotation and pockets around the bottom in which sand was placed for anchorage. A diagram of an enclosure is given in Figure 1.

To install an enclosure in the billabong, the float was inflated, sand was added to the bottom pockets and the whole floated out to the required position. At this stage the curtain was gathered and tied to the float. When the required position was reached, the curtain was released, and the sand pockets were pushed into the sediments to ensure an effective seal.

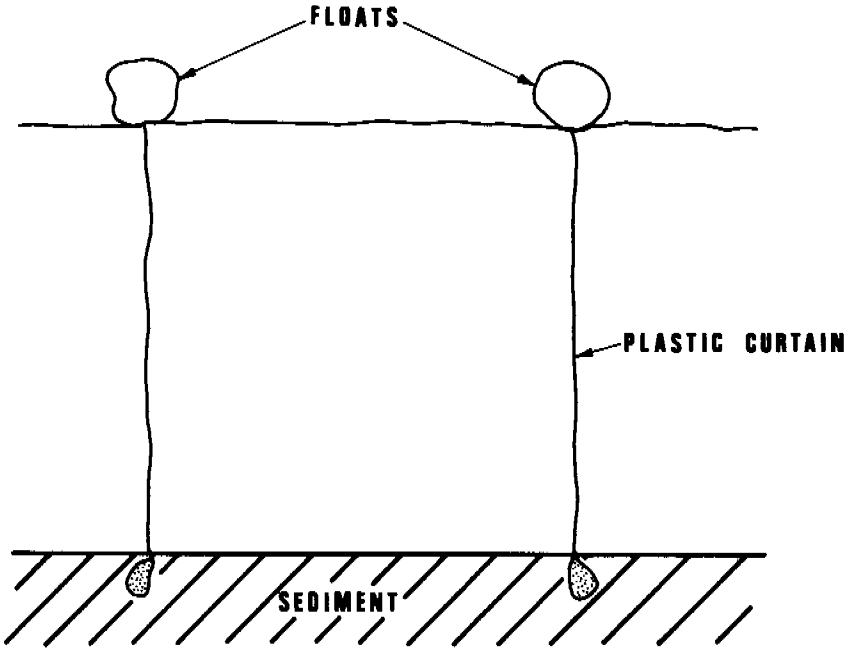

FIGURE 1 DESIGN OF THE PLASTIC ENCLOSURES.

Three problems were encountered. One of the 3 m enclosures had a faulty seal in the float which prevented it from being inflated. Buoyancy was achieved by cutting the float and inserting foam styrene strips. All future enclosures will have the top float constructed as a series of compartments so that if a leak develops the enclosure will still float, and only the faulty compartment will need to be repaired. The second problem concerned the 1 m enclosures whose floating rings would not remain in circular configurations but buckled into narrow oval shapes. To overcome this the floats were fixed into an approximate square shape with plastic rods taped to their tops. Thirdly, the bottom sediments were disturbed while pushing the enclosure curtains into the sediment. This caused an increase in the turbidity of the enclosed water which was only slightly reduced after two days settling. At this stage it was decided to pump the turbid water out and replace it with surface water from the billabong.

2.2 Addition of Heavy Metals

A mixture of metals was added to one enclosure of each size and the other was used as a control. The enclosures were labelled as follows:

1 - 1 m diameter, control
2 - 1 m diameter, metal-loaded
3 - 3 m diameter, control
4 - 3 m diameter, metal-loaded

The following amounts of heavy metals (in mg) were added to enclosures 2 and 4 to produce initial concentrations approximately ten times the Wet Season levels reported by Hart et al. (1979):

	Mn	Cu	Zn
2	63.5	3.2	22.1
4	565.6	28.3	198.0

2.3 Monitoring Program

After the metals had been added to the enclosures *in situ* monitoring of the temperature and concentration of dissolved oxygen (DO) was undertaken in each enclosure and in the billabong. Depth profiles of temperature and DO were determined each morning and evening on days 1-5 and 8, 14 and 21 (Day 1 was 26.8.80). Measurements were made at 10 cm intervals from the surface to the bottom (90 cm). Results are shown in Figure 2.

During the first two days of monitoring the DO probe was allowed to get too close to the sediments, resulting in a marked increase in water turbidity in the enclosures. This problem was avoided on the other monitoring days.

Water samples were taken on the morning of each monitoring day and analysed for turbidity, suspended solids, conductivity, alkalinity, and sodium, potassium, calcium, magnesium, chloride and sulphate concentrations. Results are given in Table 1.

On the morning of each sampling day, samples were taken in acid-washed 1 L polyethylene bottles from just below the surface. They were immediately taken back to the laboratory for processing. Approximately 500 mL was filtered through an acid-washed 0.4 µm Nuclepore filter; 200 mL of the filtrate was acidified and used to determine the 'filterable' metal concentration, another 200 mL was added to a 250 mL acid-washed polyethylene bottle containing 0.5 g Chelex-100 resin (sodium form) and analysed for 'ion-exchangeable' metal concentration. Approximately 500 mL of the unfiltered water was acidified (with 5 mL conc. HNO_3/L) and used to determine the 'total' metal concentration.

2.4 Analytical Methods

All general water quality parameters were determined using methods described by APHA (1975). Manganese was determined either by flame AAS or flameless AAS using a Varian Techtron CRA-90 atomiser. Copper and zinc were determined using anodic stripping voltammetry. In each case, calibration was achieved by using the method of standard additions.

2.5 Collection and Counting of Algae

A separate, 200 mL, surface water sample was collected for identification and counting of algal species. The samples were preserved with formalin.

The counting method was based on Steel (1969). Millipore filters (0.45 µm) were placed in a Swinnex holder and a small volume of well shaken sample was passed through using a syringe. Filters were then placed on microscope slides to dry at room temperature. Immersion oil was dropped on the filters to render them clear and a cover slip was placed on top.

A Zeiss microscope with phase contrast optics was used for counting the algae. Routine magnification was x160, with higher magnification used to check small specimens or clarify identification. Field by field counting was performed until either 500 of the most common species had been enumerated, or 25% of the total field area had been counted.

Difficulty was experienced in counting *Microcystis aeruginosa* because these form irregular clumps. Humphries (Dept. Zoology, ANU, pers. comm.) has reported a method for separating these cells to facilitate counting, but this was not used in the present study. A qualitative assessment of the abundance of *Microcystis aeruginosa* is given in Table 3.

Species identification was assisted by reference to the lists of algal species found in the Magela Creek region by Ling and Tyler (1985).

TABLE 1 GENERAL WATER QUALITY OF SURFACE WATER SAMPLES.

Date	Sample[a]	SS (mg/L)	pH	Conduct. (µS/cm)	[Cl] (mg/L)	$[SO_4]$ (mg/L)	Alkalinity (mg/L $CaCO_3$)
3.9.80	B	15	6.66	54.2	13.7	0.50	14.5
	1	460	6.76	342[b]	18.2	0.32	276[b]
	2	340	6.75	65.6	15.7	0.36	21.4
	3	28	7.16	54.9	14.2	0.18	19.2
	4	62	6.80	59.1	13.9	0.20	11.5
9.9.80	B[c]	25	6.59	62.3	14.2	0.52	11.1
	1	620	5.89	60.6	19.4	0.34	9.6
	2	165	6.51	78.1	15.6	0.37	29.6
	3	25	6.57	66.9	15.6	0.19	17.2
	4	48	6.60	73.3	14.8	0.21	15.4
16.9.80	B[d]	34	6.57	63.9	15.9	0.63	11.7
	1	106	6.20	63.8	16.0	0.52	11.3
	2	21	6.57	84.4	17.1	0.19	28.1
	3	40	7.06	67.1	15.2	0.23	16.9
	4	16	6.55	73.1	15.6	0.19	18.7

	Turbidity (NTU)				
Date	B	1	2	3	4
26.8.80	10	34	102	72	68
27.8.80	10	134	300	90	145
29.8.80	12	135	330	85	130
3.9.80	18	35[b]	1500	34	82
9.9.80	23	120	130	43	78
16.9.80	28	46	44	51	57

[a] B = Billabong; 1 = Enclosure 1; 2 = Enclosure 2;
3 = Enclosure 3; 4 = Enclosure 4.

[b] Results suspect.

[c] Na 9.0 mg/L, K 2.3 mg/L, Ca 0.69 mg/L, Mg 0.88 mg/L.

[d] Na 10.3 mg/L, K 2.7 mg/L, Ca 1.25 mg/L, Mg 0.97 mg/L.

3 RESULTS AND DISCUSSION

3.1 Simulation of the Billabong by the Enclosures

If the enclosures are to be used to obtain information on the response of the billabong to various perturbations, they must first be shown to behave like the billabong. We assessed this by comparing the temperature and dissolved oxygen (DO) profiles in the billabong and in the two control enclosures. Some caution must be exercised in these comparisons, particularly for the first week of the experiment, as the turbidity in the enclosures was much higher than in the billabong (Fig. 5).

A number of trends are apparent and these are discussed below.

3.1.1 Billabong

Each morning, temperature was essentially constant over depth and ranged between 25° and 27°C. During the day the surface layer heated up and the late afternoon surface water temperature varied between 28.5° and 32°C. The type of temperature profile that developed during the day appeared to depend primarily upon whether there was any wind mixing of the water column. On some days (e.g. Days 5 and 21) there was a distinct stratification (Fig. 2).

In the mornings the concentrations of DO were essentially the same at all depths. The absolute concentrations were mostly between 3 and 5 mg/L and appeared to be related to the photosynthetic activity (and hence DO concentration) during the previous day. The concentrations of DO also depended upon the time they were measured. Most were measured at around 0800 h (sunrise 0630 h), but the high values recorded on Days 14 and 21 were measured later in the morning (1000 h and 0930 h respectively).

In the late afternoon the DO concentrations at the surface ranged between 5.0 and 8.4 mg/L (Fig. 2) depending upon the day. There was clear evidence of elevated DO concentrations in the top 25 to 60 cm of the water column on a number of days (e.g. Days 4, 5 and 21). The profile measured on Day 14 is difficult to explain. Here the DO was greatest (greater than 10 mg/L) at depths below 0.5 m; in the surface 10 cm the DO was still elevated (8.0 mg/L) but was less than at depth.

3.1.2 Enclosures 1 and 2

The two 1 m diameter enclosures were unfortunately very turbid in the early part of the study (Table 1). The reasons for this have been explained previously. Because of the powerful overriding effects of turbidity on the other parameters, it is not possible to ascribe any of the differences between these two enclosures to the effects of the added heavy metals. However, it is of some use to determine whether these small enclosures simulate the behaviour of the billabong.

Temperature profiles in the two enclosures were similar on most morning and evening sampling occasions. During the day the water temperature in the two enclosures increased by 1° to 2°C depending upon the day (Fig. 3).

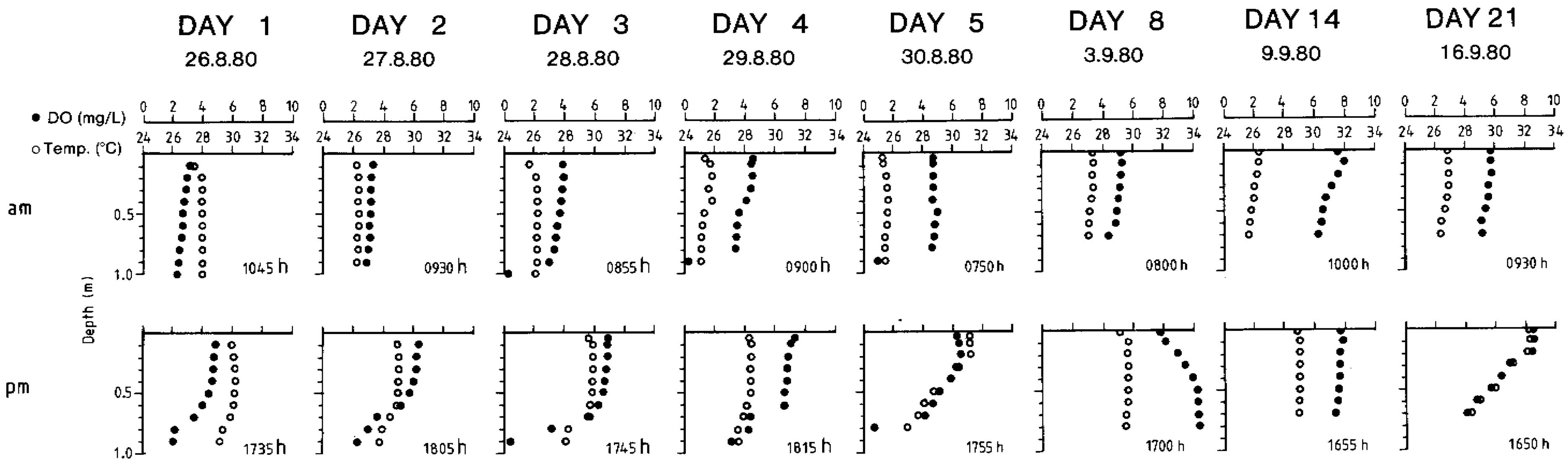

FIGURE 2 DISSOLVED OXYGEN AND TEMPERATURE PROFILES IN GULUNGUL BILLABONG.

DO was extremely low in the two enclosures at each morning measurement; concentrations were mostly less than 1 mg/L. These low dissolved oxygen concentrations probably resulted from reduced photosynthesis due to the shading effect of the suspended solids and the enclosure itself. Four days after the enclosures were put into the billabong, 30 to 50 small catfish were found dead in enclosure 1. This was probably a consequence of the low concentrations of DO. Considering the procedure followed in installing the enclosures we are mystified as to how any fish would have been present in the enclosure.

Although primary production undoubtedly occurred during the day it was insufficient to raise the DO above 3 mg/L until about Day 14 of the experiment. There was some evidence that by the third week of the experiment some primary production was occurring in the surface waters of enclosure 2 (Fig. 3); by this time the turbidity had fallen to levels similar to those in the other enclosures (Table 1).

Visual observation indicated that there was a very small algal population present in these two enclosures (Tables 2 and 3).

Our conclusion is that the 1 m diameter enclosures are too small to effectively simulate the behaviour of the billabong. This conclusion must remain a little tentative because of the turbidity problem experienced.

3.1.3 Enclosure 3

The results obtained for this enclosure, the control 3 m diameter enclosure, are shown in Figure 4.

The temperature profiles in enclosure 3 were similar to those in the billabong. This was true for both the morning and evening sampling occasions (Fig. 4). The difference in turbidity between this enclosure and the billabong (Fig. 5) did not appear to significantly influence the temperature profiles.

In the early morning, the DO profiles in this enclosure were similar to those in the billabong; DO concentrations were reasonably constant at all depths. The absolute values were around 2 to 3 mg/L and were some 1 to 2 mg/L lower than the corresponding concentrations recorded in the billabong. This possibly reflects the reduced primary production in this enclosure due to the reduced light penetration caused by its higher turbidity.

By late afternoon, the DO concentrations in the surface waters were elevated but not to the extent noted in the billabong. Thus on Day 2 the surface DO in the billabong was 6.8 mg/L and in enclosure 3 it was 5.7 mg/L. The depth of the euphotic zone was greater in the billabong than in the enclosure (Fig. 4). This effect was also noticeable on days 4, 5, and 14.

After three weeks the dissolved oxygen profiles in enclosure 3 were similar to those in the billabong. This may indicate that a time span of roughly three weeks is required for the enclosures to adjust after they have been installed.

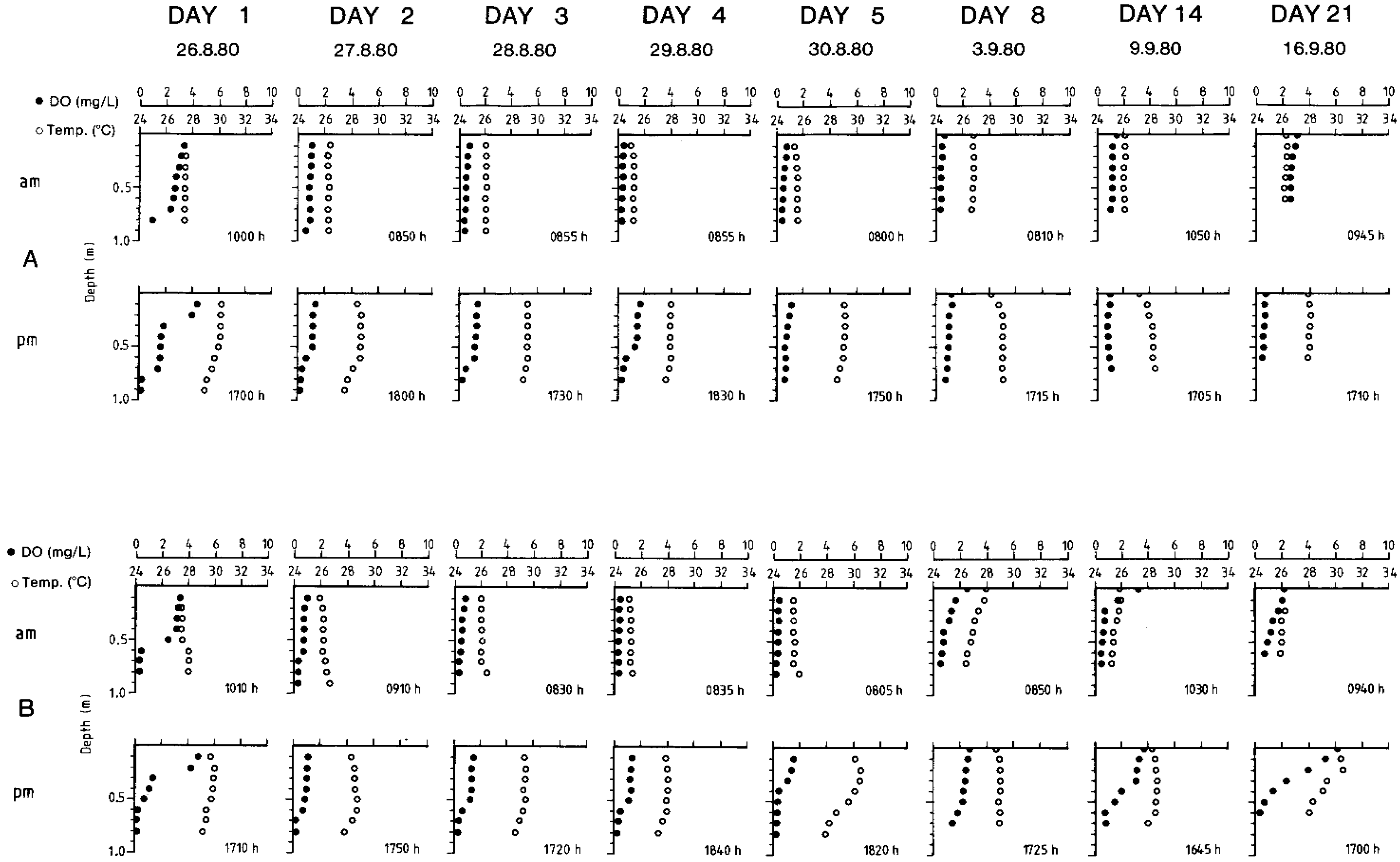

FIGURE 3 DISSOLVED OXYGEN AND TEMPERATURE PROFILES IN (A) ENCLOSURE 1 AND (B) ENCLOSURE 2.

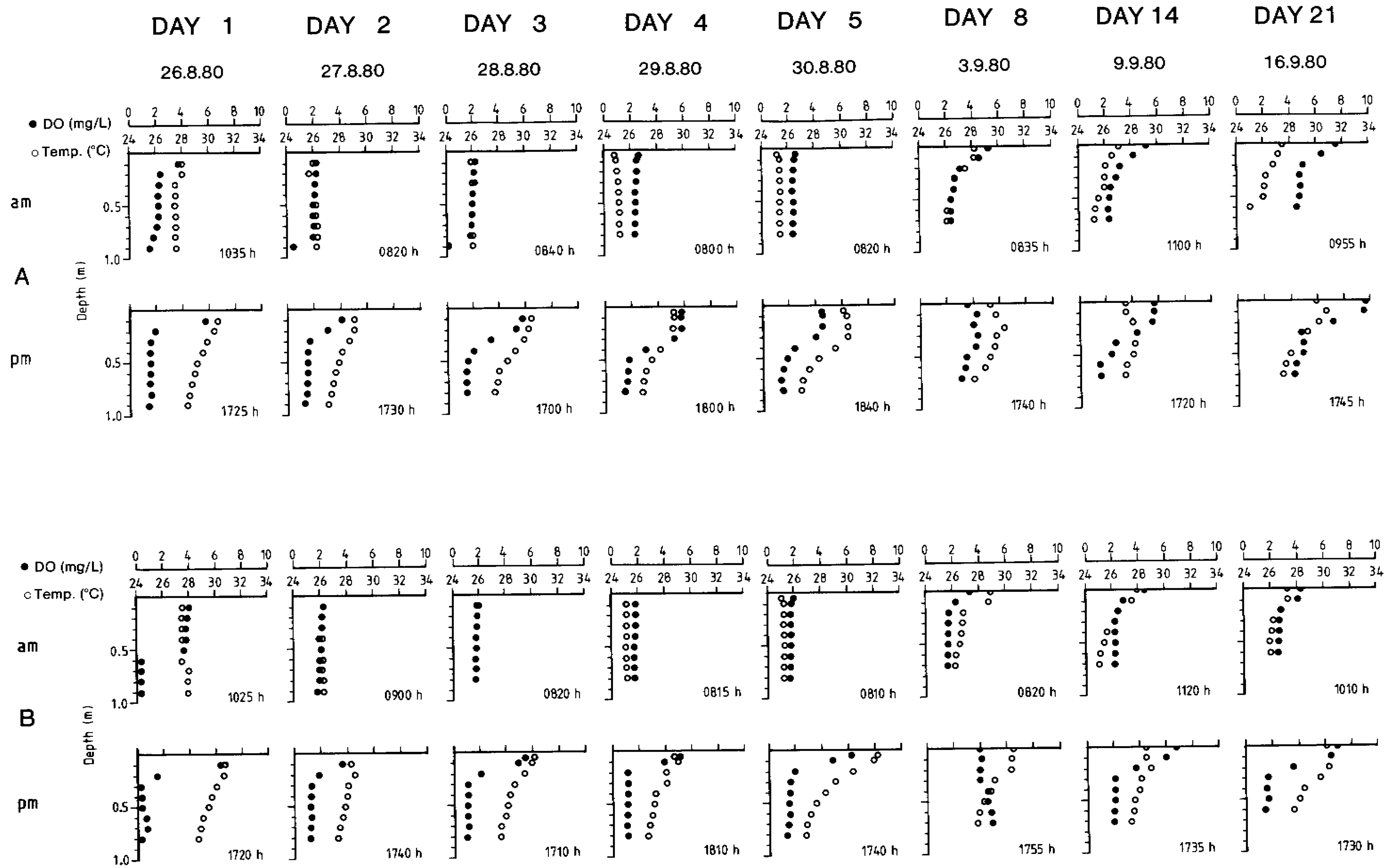

FIGURE 4 DISSOLVED OXYGEN AND TEMPERATURE PROFILES IN (A) ENCLOSURE 3 AND (B) ENCLOSURE 4.

TABLE 2 VISUAL OBSERVATIONS OF ALGAE PRESENT IN GULUNGUL BILLABONG AND ENCLOSURES.

Date	Time	Billabong	Enclosure 3	Enclosure 4	Enclosure 1	Enclosure 2
29.8.80	0855	Green algal scum, thick in places	Green algal scum, approx. one half as thick as in billabong	Some algae but very much less than in 3 and billabong	No algae	No algae
30.8.80	0745 - 0815	Algae - less than 29.8.80	Algae	Little algae	No algae	No algae
30.8.80	1730 - 1830	Algae	Algae	Small amount algae	No algae; small fish at surface (anoxia)	No algae, no fish
3.9.80	0800 - 0840	Algal windrows	Algae	No visible algae	Dead catfish (~50)	No visible algae, no catfish
9.9.80	1000 - 1120	Algae, large clumps	Algae, ~ same as billabong	Quite different to 3 and billa., insect pupae	Turbid, bad smell	Turbid, no visible algae, insect pupae
16.9.80	0920 - 1010	Algae, thick	Algae	No algae	Blue-green algae present	One dead catfish, no algae

Our conclusion at this stage is that the 3 m diameter enclosures simulate the behaviour of the billabong quite well. The temperature profiles were very similar and the small discrepancy is explainable by the differences in turbidity. The DO behaviour in the enclosure was a little different from that in the billabong, as the euphotic zone was shallower in the enclosure leading to lower DO concentrations in the early morning. These differences are probably partly a consequence of the differences in turbidity. In future experiments we will test the hypothesis that a period of three weeks is needed for these enclosures to 'acclimatise'.

3.2 Influence of Heavy Metals Added to Enclosure 4

3.2.1 Temperature and dissolved oxygen

The temperature and DO results for this enclosure are difficult to interpret because of the high turbidity and high concentrations of suspended solids in the first week of the experiment. The temperature profiles were similar to those in enclosure 3. The DO profiles were different, but it was not possible to determine whether the differences were due to lower productivity in enclosure 4 as a result of the toxicity of the added heavy metals or as a result of the higher turbidity in this enclosure.

3.2.2 Algal populations

Visual observation of the algae present in the two large enclosures suggested marked differences; there were considerably fewer algae in enclosure No 4. These observations are summarised in Table 2.

Quantitative data on species and total numbers of algae are given in Table 3. The dominant alga in the billabong and in all enclosures was *Trachelomonas oblonga.* This species is very common in all billabongs in the Magela Creek system. *Anabaena flos-aquae, Eunotia zasuminensis* and *Mallomonas splendens* were also present in reasonably large numbers in the billabong.

Over the period of the experiment the numbers of *Trachelomonas oblonga* decreased significantly in control enclosure 3, while *Anabaena flos-aquae*, the other dominant species, increased. Three days after the addition of the metals, enclosure 4 showed an almost complete absence of algae, although *Trachelomonas oblonga* persisted during the first three days.

3.2.3 Concentrations of heavy metals

The relative changes in the concentrations of heavy metals over the duration of the experiment were similar for each of the three metals (Table 4, Fig. 6). Very high concentrations were observed immediately after the metals had been added, followed by a steady decrease over time to concentrations very close to the control. Because the added metal was not immediately mixed with the total enclosure volume, high initial concentrations were recorded on Day 1.

Reductions in concentrations were expected as the heavy metals were mixed and diluted. However, in all cases the reduction was greater than that expected from mixing alone. For each heavy metal we have calculated the expected concentration change assuming complete mixing and no losses;

TABLE 3 ALGAL SPECIES AND NUMBERS[a] IN GULUNGUL BILLABONG AND ENCLOSURES.

Species	Billabong				Enclosure 1 (control)			Enclosure 2 (metal-loaded)			Enclosure 3 (control)				Enclosure 4 (metal-loaded)		
	Day[b]				Day[b]			Day[b]			Day[b]				Day[b,c]		
	0	1	3	28	0	1	3	0	1	3	0	1	3	28	0	1	3
EUGLENOPHYCEAE:																	
Trachelomonas oblonga	90	94	100	43	291	175	169	218	216	188	364	115	167	17	353	112	230
CHRYSOPHYCEAE:																	
Mallomonas splendens	16	6	10	7	25	19	32	21	36	37	13	-	5	-	5	-	-
Mallomonas sp.	-	-	9	-	-	5	-	-	-	5	-	-	7	-	11	-	-
BACILLARIOPHYCEAE;																	
Eunotia zasuminensis	36	18	16	-	53	5	15	16	6	-	7	6	6	-	-	-	-
Eunotia sp. 1	5	-	17	-	-	5	-	-	-	-	-	-	-	13[d]	-	-	-
Eunotia sp. 2	-	-	-	-	-	6	-	-	-	-	-	-	-	10[d]	-	-	-
Eunotia sp. 3	-	-	-	-	-	-	-	-	-	-	-	-	-	10[d]	-	-	-
Melosira granulata	-	-	6	-	-	6	-	5	8	-	-	-	-	7[d]	-	-	-
Gomphonema	6	-	-	-	-	-	-	-	-	-	-	-	-	-	12	-	-
Pinnularia	-	-	5	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MYXOPHYCEAE:																	
Anabaena flos-aquae	51	27	51	123	23	18	8	13	10	2	24	20	28	60	18	15	-
Microcystis aeruginosa[e]		-	-	A	-	-	-	-	-	-	A	P	Ab	P	A	Ab	Ab
CHLOROPHYCEAE:																	
Actinastrum sp.	12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

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[a] Cells/mL. Only counts of 5 cells/mL or greater have been included.

[b] Day 0 = 26.8.80, Day 1 = 27.8.80, Day 3 = 29.8.80, Day 28 = 23.9.80.

[c] Cell numbers too low on day 28 for significant count, water very turbid. Species present: *Trachelomonas oblonga* and *Mallomonas* sp.

[d] We suspect the high diatom numbers to be a result of the enclosure wall being knocked before sampling. *Eunotia* sp. are usually attached, not planktonic. (J. Kessel, pers. comm.).

[e] Cell numbers not counted because of clumping, A = abundant, P = present, Ab = absent.

these are shown in Figure 6. The slight increase in this predicted concentration results from the volume change in the enclosure over the period of the experiment.

Within the accuracy of the experiment, we found that essentially all the metal added to the enclosure was lost from the water column. The mechanism for removal was probably rapid association of the added metal with suspended matter (particulate and colloidal) followed by rapid settling out of the suspended matter taking the sorbed metals with it. As noted previously the concentrations of suspended matter in the enclosures were initially very high due to the stirring up of bottom sediments. Thus the suspended matter would be expected to have characteristics similar to the bottom sediments. Previous work (Thomas and Hart 1984) has shown that billabong sediments can very effectively take up added heavy metals.

Hesslein et al. (1980) have studied the behaviour of radioisotopes added to whole lakes in Canada. They found the loss of zinc, mercury, iron and cobalt from the water column fitted well an exponential relationship of the form:

$$C_t = C_0 \, e^{-kt}$$

where C_0, C_t = metal concentrations at time 0 and t respectively,
k = first order rate constant,
t = time.

The values they obtained for k (d^{-1}) were: for Zn 0.03, for Hg 0.05, for Fe 0.04 and for Co 0.04.

There seems little point in attempting to fit our data to such a relationship, since in the first few days the metals added to the enclosure were not homogeneously mixed and the reduction in heavy metal concentrations was due to a combination of dilution by mixing and losses from the water column by sorption and sedimentation processes. In future experiments greater care will be taken to ensure adequate initial mixing.

We now comment on the changes observed in each metal over the study period.

3.2.3.1 Manganese

The forms of manganese varied considerably in both the billabong and control enclosure (Table 4). Mean values and standard errors for total, filterable and non-ion-exchangeable manganese concentrations are given in Table 5. The total manganese concentrations in the billabong and enclosure 3 remained relatively constant at 36-44 µg/L, but the speciation of manganese changed. Initially, approximately 75% was in filterable forms with most of this tightly bound (non-ion-exchangeable), but by the end of the study period, most (90%) of the total manganese was in particulate forms. The reason for this change is not known.

The changes in concentrations of manganese in the metal-loaded enclosure were dramatic (Fig. 6). After 15-16 days the concentrations of total and filterable metal were back to ambient levels as represented by the levels in the control enclosure and in the billabong. During that period essen-

TABLE 4 CONCENTRATIONS OF MANGANESE, ZINC AND COPPER IN GULUNGUL BILLABONG AND ENCLOSURES 3 AND 4.

All concentrations in µg/L. Values in brackets were obtained using carbon rod atomiser.
t = total, f = filterable, n = non-ion-exchangeable.

Date	Form	Billabong			Enclosure 3			Enclosure 4		
		Mn	Zn	Cu	Mn	Zn^a	Cu	Mn	Zn	Cu
26.8.80 (before metal added)	t	44.9	9.0	26.4 (31.6)	44.6	13.1	2.3	38.1	11.7	2.7
	f	24.8	8.2	14.7 (15.1)	33.5	6.2	1.8	35.4	5.3	2.1
	n	23.1	0.7	0.3	33.5	6.6	1.6	32.7	4.7	0.8
26.8.80 (after metal added)	t	-	-	-	-	-	-	235.0	80.0	12.7 (14.3)
	f	-	-	-	-	-	-	155.0	37.4	4.3
	n	-	-	-	-	-	-	150.9	26.2	0.9
27.8.80	t	33.4	6.2	4.0	49.2	7.6	1.6	152.3	42.6	17.8 (21.6)
	f	26.5 (27.6)	5.5	1.5	23.1	4.1	1.6	141.3	28.0	3.9
	n	3.3	1.7	0.4	13.8	0.9	0.1	122.3	24.8	0.7
29.8.80	t	30.0	9.3	4.7	47.6	10.3	1.5	171.3	33.7	5.5
	f	17.5	9.0	3.5	31.8	9.3	1.0	81.5	16.4	2.3
	n	0.4	1.6	<0.1	28.2	1.4	<0.1	59.8	4.8	0.1
3.9.80	t	43.3	7.7	11.5 (10.5)	47.6	11.0	2.4	59.8	26.6	6.4
	f	12.9	3.5	7.5	21.4	6.5	1.0	55.9	15.9	3.4
	n	0.7	2.0	1.0	0.7	1.9	<0.1	54.2	12.2	<0.1
9.9.80	t	69.6	8.0	3.1	41.5	14.4	1.4	62.5	24.8	6.2
	f	1.5	6.9	3.0	1.5	5.9	1.0	3.3	8.8	1.7
	n	0.8	2.2	1.2	0.6	2.8	1.1	<0.8	1.7	0.7
16.9.80	t	38.4	4.3	3.6	29.2	11.5	1.6 (1.5)	32.7	17.3	3.8
	f	2.1	4.0	2.5	0.5	6.3	2.7 (2.5)	1.0	10.1	3.1
	n	0.5	2.5	1.1	0.2	0.5	0.5	<0.8	1.1	1.4
23.9.80	t	35.1	12.6	6.0	50.8	13.8	3.4	31.3	11.3	3.8
	f	2.8	4.8	1.7 (4.1)	2.7	9.1	2.8	17.4	8.8	2.6
	n	0.8	1.9	0.5	0.4	4.4	0.3	0.8	3.5	1.7

[a] Total metal concentration obtained using flame AAS.

tially all the added manganese was lost from the water column, presumably to the sediments. It seems that the added ionic manganese rapidly becomes associated with colloidal and particulate matter, even on Day 1 there was little manganese in ion-exchangeable forms.

Over the first 10 days or so, when most of the loss occurred, the most significant reduction was in the filterable manganese concentration which was almost all in non-ion-exchangeable forms. The absolute concentration of particulate bound manganese remained relatively constant over the study period (30-40 µg/L). The mechanism by which manganese was lost possibly involved sedimentation of particulate manganese which was kept at a relatively constant concentration by coagulation of colloidal filterable manganese.

3.2.3.2 Zinc

The concentrations of zinc in the control enclosure and the billabong were very much less variable than the concentrations of manganese (Table 4). The mean total zinc concentration was around 10 µg/L and the mean filterable concentration around 6.5 µg/L (Table 5). Approximately 60% to 70% of the filterable zinc was ion-exchangeable.

The reduction, over time, in the concentration of zinc in the metal-loaded enclosure was not as noticeable as the reduction in the concentration of manganese (Fig. 6). Only by the end of the four-week study period were the concentrations of total and filterable zinc reduced to about the same level as the concentrations in the control enclosure and the billabong. In the first 10-15 days the drop in the total zinc concentration was mainly due to loss of filterable zinc, while in the latter period of the study the main loss was particulate zinc.

There was little change in the absolute concentration of ion-exchangeable zinc over the period (Fig. 6). Most of the change in the filterable zinc concentration was due to loss of bound forms (possibly colloidal). At the end of the study period approximately 60% to 90% of the filterable zinc was ion-exchangeable.

TABLE 5 MEAN HEAVY METAL CONCENTRATIONS IN GULUNGUL BILLABONG AND ENCLOSURE 3.

Form	Billabong			Enclosure 3		
	Mn[a]	Zn[a]	Cu[a]	Mn[a]	Zn[a]	Cu[a]
total	42.1 (13.1)	8.2 (2.6)	5.5 (3.1)	44.4 (7.3)	11.7 (2.3)	2.0 (0.7)
filterable	12.6 (10.8)	6.0 (2.1)	3.3 (2.2)	16.4 (14.5)	6.8 (1.8)	1.7 (0.8)
non-ion-exchangeable	4.2 (8.4)	1.8 (0.6)	0.7 (0.4)	11.1 (14.5)	2.6 (2.2)	0.5 (0.6)

[a] Mean concentration in µg/L, standard error is given in parentheses; n = 7 except for Cu in Gulungul Billabong, where n = 6.

3.2.3.3 Copper

Some unexpectedly high concentrations of copper were recorded for the billabong (Table 4). This was particularly so for the sample taken on Day 1 when the values were higher than in the metal-loaded enclosure. Because of the uncertainty in these figures, they have not been considered in the following discussion.

In the control enclosure the total copper concentrations remained reasonably constant at around 2 µg/L. The concentrations of filterable copper also remained constant and were approximately 85% of the total. There was some evidence that the concentration of filterable copper was increasing towards the end of the experiment (Table 4). Taken over the whole study period, approximately 70% of the filterable copper was ion-exchangeable; but it varied from 100% near the middle of the period to 0% to 20% towards the end.

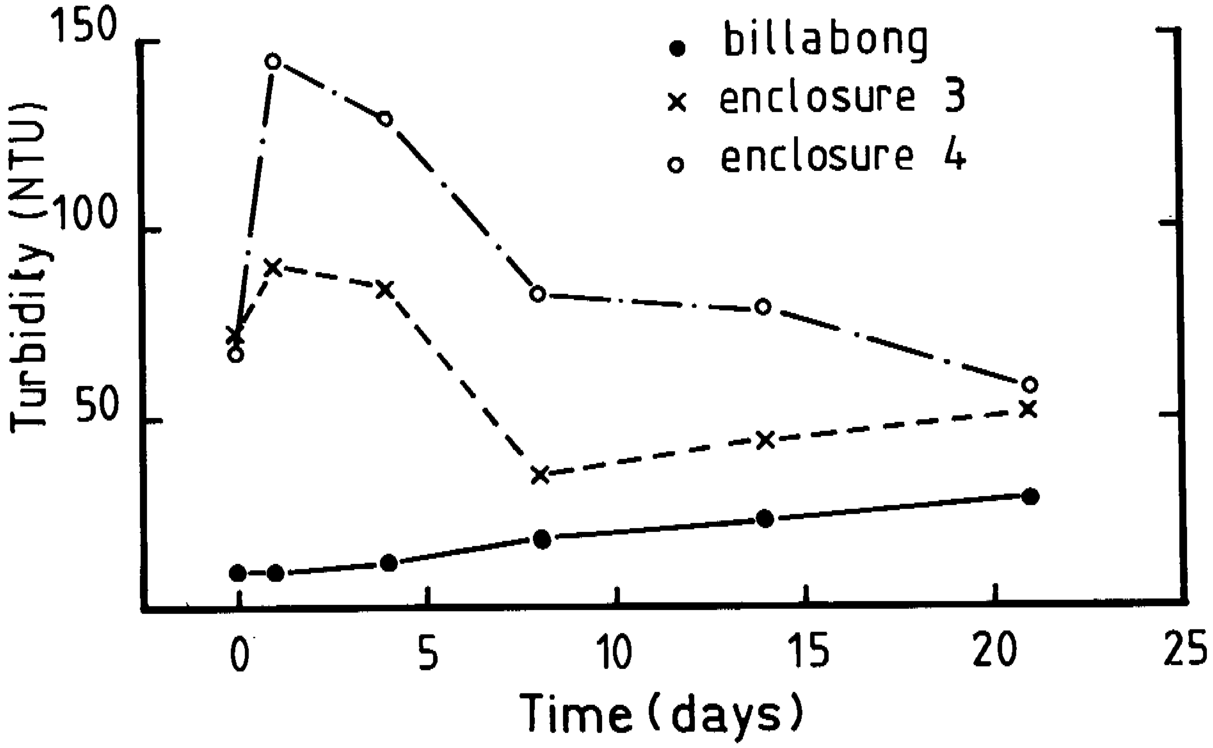
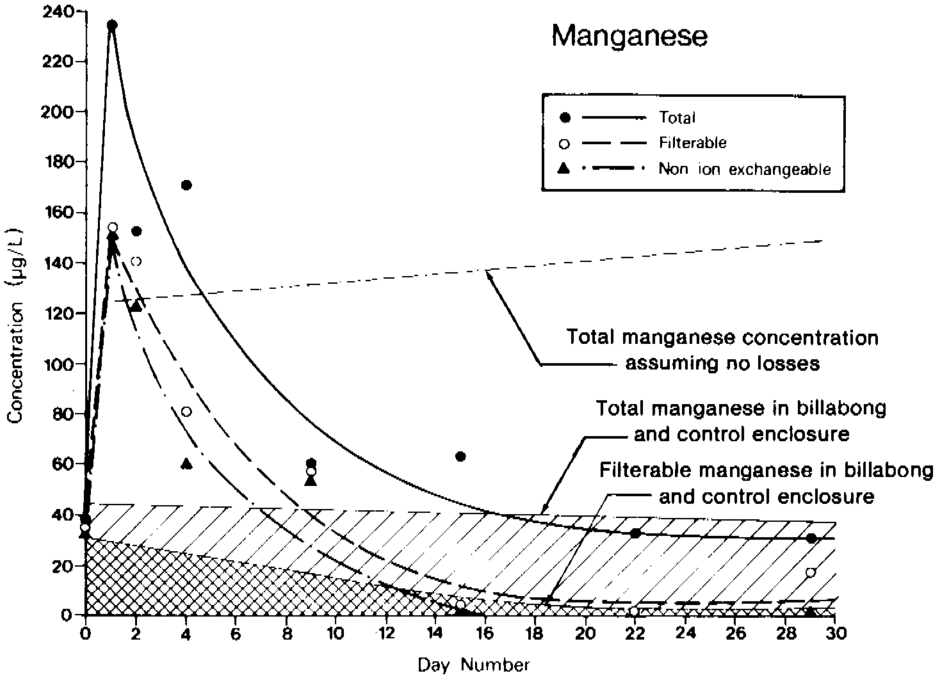
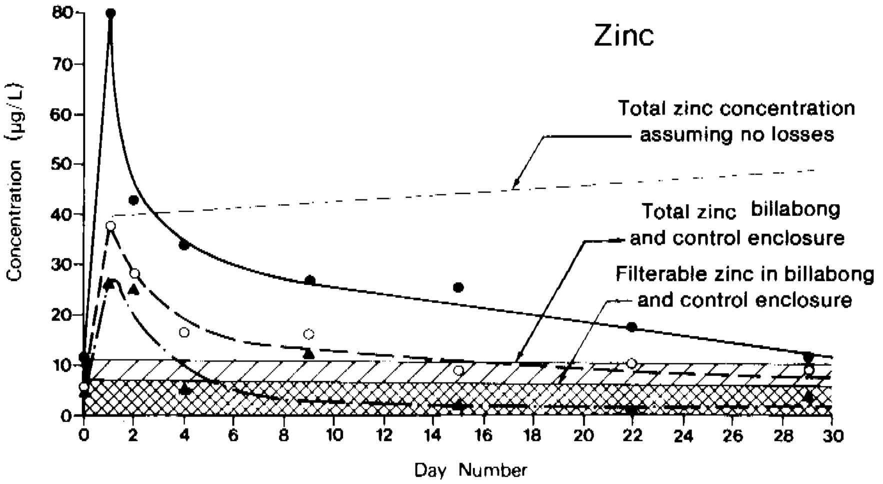
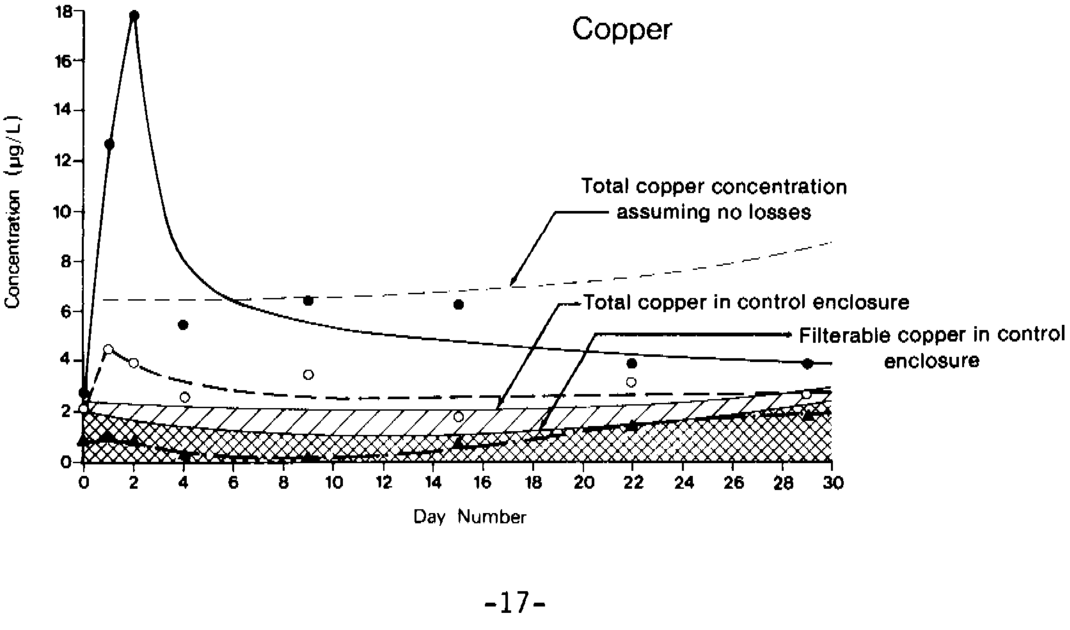


FIGURE 5 TURBIDITY IN GULUNGUL BILLABONG AND ENCLOSURES 3 AND 4.

FIGURE 6 (FACING PAGE) CHANGES IN TOTAL, FILTERABLE, AND NON-ION-EXCHANGEABLE CONCENTRATIONS OF MANGANESE, ZINC AND COPPER IN ENCLOSURE 4. TOTAL AND FILTERABLE METAL CONCENTRATIONS IN THE BILLABONG AND THE CONTROL ENCLOSURE ARE ALSO SHOWN.


Manganese
Total
Filterable
Non ion exchangeable
Total manganese concentration assuming no losses
Total manganese in billabong and control enclosure
Filterable manganese in billabong and control enclosure
Concentration (µg/L)
0
20
40
60
80
100
120
140
160
180
200
220
240
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Day Number


Zinc
Total zinc concentration assuming no losses
Total zinc billabong and control enclosure
Filterable zinc in billabong and control enclosure
Concentration (µg/L)
0
10
20
30
40
50
60
70
80
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Day Number


Copper
Total copper concentration assuming no losses
Total copper in control enclosure
Filterable copper in control enclosure
Concentration (µg/L)
0
2
4
6
8
10
12
14
16
18
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
Day Number

Although there was considerable loss of copper from the water column in the metal-loaded enclosure, the total and filterable copper concentrations had not returned to ambient levels at the end of the four-week study period (Fig. 6). During this period the filterable copper concentration changed little (4.3 to 2.6 µg/L). It is apparent that over time a large proportion of the filterable copper became bound into forms not available to the Chelex resin (Fig. 6). Thus 9 days after the metal had been added almost all the filterable copper was ion-exchangeable (3.4 µg/L), but after 29 days only 35% (0.9 µg/L) was ion-exchangeable.

Initially the bulk (70% to 80%) of the ionic copper added to enclosure 4 was very rapidly associated with the particulate matter and the major reduction of copper in the water column was due to loss of particulate copper (Fig. 6). From this experiment it appears that, in Gulungul Billabong, ionic copper is very rapidly associated with particulate matter but becomes associated with the colloidal matter slowly.

4 SUMMARY AND CONCLUSIONS

In August 1980 four plastic enclosures (two 1 m diameter, two 3 m diameter) were placed in Gulungul Billabong, a mixture of heavy metals was added to one enclosure of each size and the changes were monitored in all enclosures and the billabong over a four-week period.

Unfortunately, the sediments at the bottom of each enclosure were disturbed during installation and again during the first two days by the dissolved oxygen meter. This increased the turbidity which undoubtedly had an effect on the parameters monitored.

The dissolved oxygen and temperature profiles in the enclosures were compared with those in the billabong to assess how closely the enclosures simulated the billabong. The profiles were measured in the early morning and the late afternoon. The profiles in the 1 m enclosures rapidly deviated from those in the billabong; particularly noticeable were the very low DO levels that developed in these enclosures. Although the elevated turbidity in the small enclosures no doubt influenced their behaviour, we believe they were too small to effectively simulate the behaviour of the billabong. On the other hand the 3 m enclosures had temperature and dissolved oxygen profiles that were very similar to those in the billabong. The small differences between these enclosures and the billabong can probably be explained by the differences in turbidity.

The behaviour of three heavy metals, manganese, zinc and copper, was studied. Total, filterable and ion-exchangeable concentrations were determined at intervals during the study period. All three metals showed the same general behaviour with time. In the metal-loaded 3 m enclosure there was an initial large increase in concentration after the addition of the metals, followed by a rapid decrease in concentration to levels approximating those in the control enclosure and the billabong. Manganese reached ambient concentrations within approximately 15 days; zinc and copper, however, were reduced to near ambient levels only by the end of the four-week study period and hence are potentially more mobile than manganese. The main mechanism for the loss of heavy metals appeared to be association with particulate matter, which then sedimented out.

The increased concentrations of suspended matter in the enclosures undoubtedly had an influence on the results. With normal suspended solids levels we expect that the metals would have stayed in the water column for considerably longer. The effect of this possibility on the biota is not known.

The algal flora in the metal-loaded enclosure was noticeably different from that in the control enclosure and the billabong. Initially the dominant algal species in the billabong and enclosures was *Trachelomonas oblonga*. *Anabaena flos-aquae*, *Eunotia zasuminensis* and *Mallomonas splendens* were also present in the billabong. Three days after the solution of metals was added, enclosure 4 showed an almost complete absence of algae apart from *Trachelomonas oblonga*, which suggests that the heavy metals were toxic to virtually all the phytoplankton species present. There were also differences between the algal floras in the control enclosure and the billabong. At this stage it is not possible to decide which changes were due to the toxicity of the metals and which were natural changes.

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