Technical Memorandum 13

Fate of Heavy Metals in the Magela Creek System, Northern Australia

I. Experiments with plastic enclosures placed in Island Billabong during the 1980 Dry Season: heavy metals

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Hart, B.T., Jones, M.J. and Bek, P. (1985). Fate of heavy metals in the Magela Creek System, northern Australia. I. Experiments with plastic enclosures placed in Island Billabong during the 1980 Dry Season: Heavy Metals. Supervising Scientist for the Alligator Rivers Region, Technical Memorandum 13.

Two 5 m diameter plastic enclosures were used to isolate parts of Island Billabong so that the processes operating to remove added metals from the water column could be studied. The metals manganese, cadmium, copper, lead and zinc were added to one enclosure; the other enclosure was kept as a control. The changes in metal concentrations were monitored over a six-week period from 6 November 1980. Additionally, an analytical scheme was applied that allowed the total concentration of each metal to be divided into three operationally defined fractions: particulate, ion-exchangeable, and non-ion-exchangeable.

Where valid comparisons could be made, the behaviour of the metals in the enclosure differed from their behaviour in the billabong. Some reasons for these differences have been advanced. The differences, while significant at the very low concentrations found naturally in Island Billabong waters, are not expected to influence the usefulness of the enclosures in providing information on the behaviour of higher concentrations of heavy metals added to this system.

All of the metals added to the enclosure were found to be quite removed from the water column over a period of days. For example, after fifteen days, in excess of 65% of each metal had been removed, presumably to the sediments and the epiphytic growth that had built up on the walls of the enclosure. Study of the changes in the speciation of the added metals provided considerable insight into the mechanisms by which these metals are removed from the water column. The main pathways for the removal of each metal are discussed. The behaviour of manganese is believed to have significantly influenced the rapid removal of the other metals. We have postulated that particulate, and possibly also colloidal, forms of MnO_x are formed by the slow oxidation of manganese(II), and that it was these colloidal and particulate surfaces that influenced the behaviour of the other added metals.

1 INTRODUCTION

A number of workers have used plastic enclosures to isolate part of a marine or freshwater system so that the influence of added metals on the biota, particularly phytoplankton and zooplankton, might be studied (Reeve et al. 1976; CEPEX 1977; Maeda and Tanaka 1977; Gachter 1979; Hart et al. 1985a; Brunskill et al. 1980; Marshall and Mellinger 1980; Hunt and Smith 1980; Kerrison et al. 1980). Enclosure experiments are field experiments, so the results should reflect more closely the changes occurring in the natural system than do laboratory-based experiments. They are also more controllable than full-scale field experiments.

In November 1980, two 5 m diameter plastic enclosures were placed in Island Billabong and a mixture of the metals manganese, copper, lead, zinc and cadmium was added to one. The billabong and enclosures were monitored over a six-week period. The changes in the concentrations of the added metals are discussed in this report. The changes in limnology and phytoplankton populations are discussed in detail by Hart et al. (1985b), but will be summarised here briefly.

Little change occurred in the chemical limnology of the billabong during the period of the experiment (Hart et al. 1985b), but the suspended solids concentration and turbidity increased, with maximum values recorded in early December, when a diatom bloom was observed.

Temperature, dissolved oxygen (DO) and pH profiles were measured regularly and on the basis of temperature and DO, the behaviour of the control enclosure was very similar to the billabong. However, major differences were observed in the mean pH values recorded in the two systems; the pH in the billabong decreased from around 6 to 5, while in the enclosure it was always above 6 (pH 6.2 to 6.9).

Initially, both Island Billabong and the control enclosure were dominated by the diatom *Eunotia zasuminensis* and during the first fifteen days of the study the cell numbers and species composition in both remained similar. Between Day 15 and the end of the study, quite different cell numbers and species composition were observed in the billabong and in the control enclosure. Cell numbers in the control enclosure stayed approximately constant over this period but there were changes in the species composition; the diatom *Eunotia zasuminensis* became increasingly dominant. An algal bloom was observed in the billabong around Day 29, possibly due to an influx of nutrients brought in by a small amount of rain which fell around this time. This bloom mainly consisted of two species, *Eunotia zasuminensis* and the euglenoid *Trachelomonas oblonga*.

The added heavy metals had a very significant effect on both the phytoplankton numbers and the species composition in the metal-loaded enclosure. A very rapid decrease in the algal cell numbers was observed, particularly in the first three days of the experiment. Most affected was the diatom *Eunotia zasuminensis*, whose numbers were reduced by over two orders of magnitude in the first fifteen days. Interestingly, in the period after Day 15 the cell numbers in the metal-loaded enclosure were considerably higher than in the control and were almost the same as in the billabong.

2 METHODS

2.1 Enclosures

Two 5 m cylindrical enclosures were constructed from 1 mm nylon-reinforced polyethylene film. Each enclosure had an inflatable ring sealed around the top of the polyethylene curtain to prevent the enclosure from sinking and pockets around the bottom in which sand was placed for anchorage.

To install an enclosure in the billabong, the float was inflated and sand was added to the bottom pockets, the curtain was gathered and tied to the float, and the enclosure was floated out to the required position. When the required position had been reached, the curtain was released and the sand pockets were pushed into the sediments to ensure an effective seal. Scuba divers assisted in these operations.

2.2 Addition of Heavy Metals

A mixture of the metals was added to one enclosure and the other was kept as a control. The following amounts of metals (in mg) were added to the metal-loaded enclosure to produce initial concentrations approximately ten times the Wet Season levels reported by Hart and Davies (1982): manganese 10 650, cadmium 49.1, copper 599, lead 88.4 and zinc 1910. The metals were added on 6 November 1980 (Day 1). The metals were added by pouring the concentrated solution onto the surface waters of the enclosure at several points. An attempt was made to mix the solution of metals with the water of the enclosure by stirring with an oar.

2.3 Sampling and Speciation of Heavy Metals

Eight sets of samples were taken from the billabong and each enclosure between 6 November and 4 December 1980. On the morning of each sampling day, samples were taken (from just below the surface) in acid-washed 1 L polyethylene bottles. They were immediately taken back to the laboratory where they were processed according to the scheme outlined in Figure 1. Approximately 500 mL of the water sample was acidified (5 mL conc. HNO_3/L) and used to determine the 'total' metal (M_t) concentration. A further 500 mL was filtered through an acid-washed 0.1 µm Nuclepore filter: 200 mL of the filtrate was acidified and used to determine the 'filterable' metal (M_f) concentration; another 200 mL was added to a 250 mL acid-washed polyethylene bottle containing 0.5 g Chelex-100 resin (Na form) and the supernatant solution analysed for 'non-ion-exchangeable' metal (M_n) concentration.

From these fractions, three physico-chemical forms were defined:

(i) Particulate metal ($M_p = M_t - M_f$): the fraction associated with particulate matter greater than 0.1 µm in size.

(ii) Non-ion-exchangeable metal (M_n): fraction containing forms that are less than 0.1 µm in size and are not ion-exchangeable with Chelex resin.

(iii) Ion-exchangeable metal ($M_{ie} = M_f - M_n$): fraction containing forms that are less than 0.1 µm in size and are are ion-exchangeable with Chelex resin.

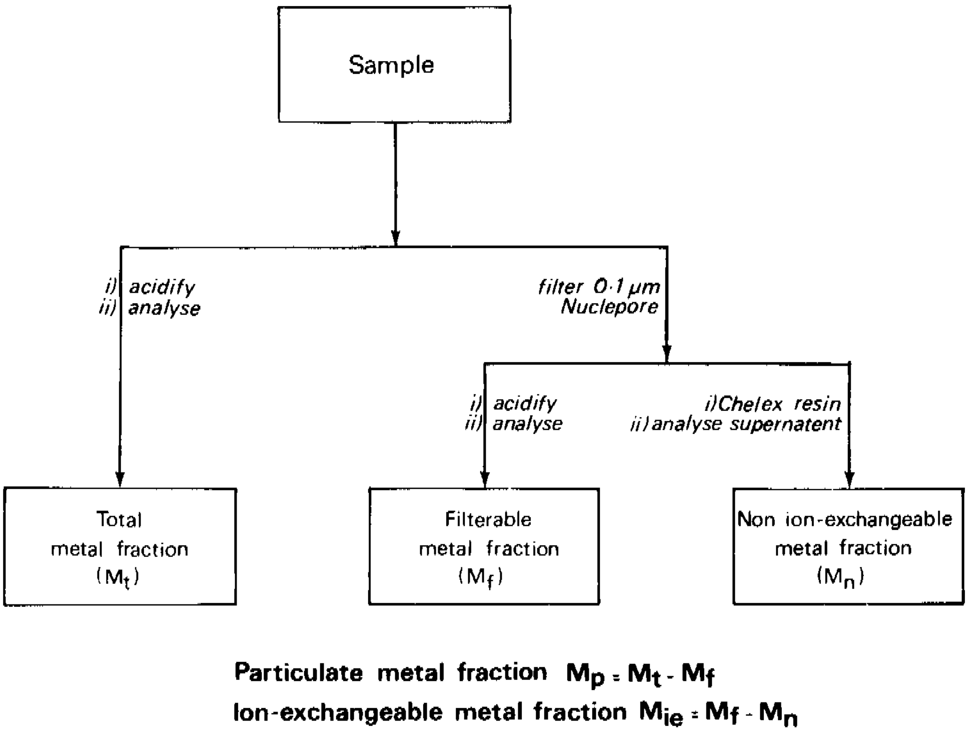

FIGURE 1 ANALYTICAL SCHEME USED TO SEPARATE HEAVY METAL SPECIES.

2.4 Analytical Methods

All samples for metal analysis were digested by boiling the acidified solutions for 10 minutes. Manganese was determined either by flame atomic absorption spectroscopy (AAS) or graphite furnace AAS, using a Varian Techtron CRA-90 carbon rod atomiser. Cadmium, copper, lead and zinc were determined using anodic stripping voltammetry (PAR 174 with hanging mercury drop electrode). In each case, calibration was achieved by using the method of standard additions. The precision of repeat analysis (as relative standard error) was: Mn (flame) 6%; Mn (furnace) 10%; Cu 3%; Pb 5%; and Zn 6%.

3 RESULTS

A summary of the total, filterable and non-ion-exchangeable metal concentrations is given in Table 1; the actual results are shown in Figures 2 to 6 and are tabulated in the Appendix. Figures 2 to 6 also show the theoretical total concentrations of the metals in the metal-loaded enclosure, assumming complete mixing and no losses. These lines were derived by dividing the amount of added metal by the volume of water in the enclosure, taking evaporation over the period into account.

TABLE 1 SUMMARY OF THE CONCENTRATIONS OF HEAVY METAL FRACTIONS IN ISLAND BILLABONG AND THE ENCLOSURES.

All concentrations are in µg/L; where values were less than the detection limit, $\bar{x}$ and σ were calculated assuming they were equal to the detection limit. M_t = total metal concentration; M_f = filterable metal concentration; M_n = non-ion-exchangeable metal concentration.

Site	Fraction	Mn	Cu	Pb	Zn	Cd
Island Billabong	M_t	43 - 110	0.4 - 1.7	<0.2 - 0.9	1.6 - 11	<0.24
	$\bar{x}$	70	0.8	0.5	4.2	-
	σ	23	0.4	0.2	3.2	-
	M_f	8.4 - 110	<0.2 - 1.4	<0.2 - 0.4	1.3 - 4.5	<0.25
	$\bar{x}$	52	0.6	0.3	2.5	-
	σ	31	0.5	0.1	1.1	-
	M_n	<0.5 - 8.2	<0.2 - 0.6	<0.2 - 0.4	<0.2 - 2.3	<0.25
	$\bar{x}$	2.2	0.3	0.2	0.6	-
	σ	3.0	0.2	0.1	0.7	-
Control Enclosure	M_t	26 - 43	<0.1 - 1.3	0.2 - 0.9	3.5 - 16	<0.25
	$\bar{x}$	33	0.8	0.5	9.5	-
	σ	6	0.3	0.3	4.2	-
	M_f	0.8 - 15	<0.2 - 0.8	<0.2 - 0.3	3.2 - 15	<0.25
	$\bar{x}$	7.7	0.4	0.2	9.1	-
	σ	5.4	0.2	0.0	4.0	-
	M_n	<0.5 - 14	<0.2 - 0.4	<0.2 - 0.2	<0.2 - 3.5	<0.25
	$\bar{x}$	2.6	0.2	0.2	1.0	-
	σ	4.7	0.1	0.0	1.2	-
Metal-loaded Enclosure	M_t	76 - 1020	1.9 - 42	0.8 - 7.6	11 - 180	<0.25 - 3.8
	$\bar{x}$	370	12	2.7	57	1.3
	σ	310	13	2.2	55	1.2
	M_f	13 - 990	0.4 - 26	<0.2 - 2.6	10 - 170	<0.25 - 3.5
	$\bar{x}$	310	6.9	0.9	51	1.2
	σ	309	7.9	0.7	52	1.1
	M_n	<0.5 - 360	<0.2 - 4.3	<0.2 - 0.6	0.4 - 28	<0.25 - 0.44
	$\bar{x}$	110	1.3	0.3	12	0.27
	σ	140	1.6	0.2	13	0.07

3.1 Manganese

Billabong and control enclosure. In the billabong, both the total and filterable manganese concentrations increased three- to fourfold over the study period; the total manganese increased from around 43 µg/L to 110 µg/L and the filterable manganese from 8.4 µg/L to 107 µg/L. The increases can be attributed to an increase in ion-exchangeable manganese (i.e. the difference between the filterable and non-ion-exchangeable concentrations - Fig. 2a). With the exception of Day 15, most (63-96%) of the manganese in the billabong was in ion-exchangeable forms with small amounts in particulate forms. On Day 15, almost 90% of the manganese was in particulate forms. Over the study period very little of the manganese was in non-ion-exchangeable forms.

The behaviour of manganese in the control enclosure was significantly different from its behaviour in the billabong. First, the total manganese concentration remained constant (33 ± 6 µg/L), with perhaps some evidence of a trend towards slightly lower concentrations around the middle of the study period (Fig. 2b). Second, most of the manganese in the control enclosure was in particulate forms (although a small amount was in ion-exchangeable forms initially), whereas in the billabong most of the manganese was in ion-exchangeable forms.

Metal-loaded enclosure. As there was inadequate initial mixing, the concentration of manganese in the surface water was very high (Fig. 2c) immediately after the solution of metals had been added. From Day 2 to Day 15 there was a continual decrease in the total and filterable manganese concentrations. The total manganese concentration was not reduced to the concentration expected, assuming complete mixing, until about Day 8. By Day 15 the total manganese concentration had decreased to about 100 µg/L and remained at this level until the end of the study.

The proportion of total manganese that was in filterable forms also decreased by Day 15. There was an obvious change in the speciation of manganese between Day 15 and the end of the study. On Day 15 almost all the manganese was in particulate forms, but over the next fourteen days these were converted to filterable forms which were mostly ion-exchangeable. This trend was very similar to that in the billabong.

The concentration of non-ion-exchangeable manganese was also found to undergo considerable change over the study period. On Day 1 the concentration was quite high (approx 350 µg/L), but it fell almost to zero by Day 2. Between Day 2 and Day 6 the concentration increased to a maximum of almost 240 µg/L, and then decreased again to around zero by Day 15 and remained very low until the end of the study (Fig. 2c).

3.2 Copper

Billabong and control enclosure. The mean total copper concentration in both the billabong and the control enclosure was 0.8 µg/L. In the billabong, there was considerable variation in the concentrations of all forms of copper measured (Fig. 3a); particulate, non-ion-exchangeable and ion-exchangeable forms all dominated the copper speciation at different times, but based on the mean data (Table 1), copper was approximately equally distributed over the three forms during the study. In the control enclosure the total copper concentrations seemed to increase (by 25% to

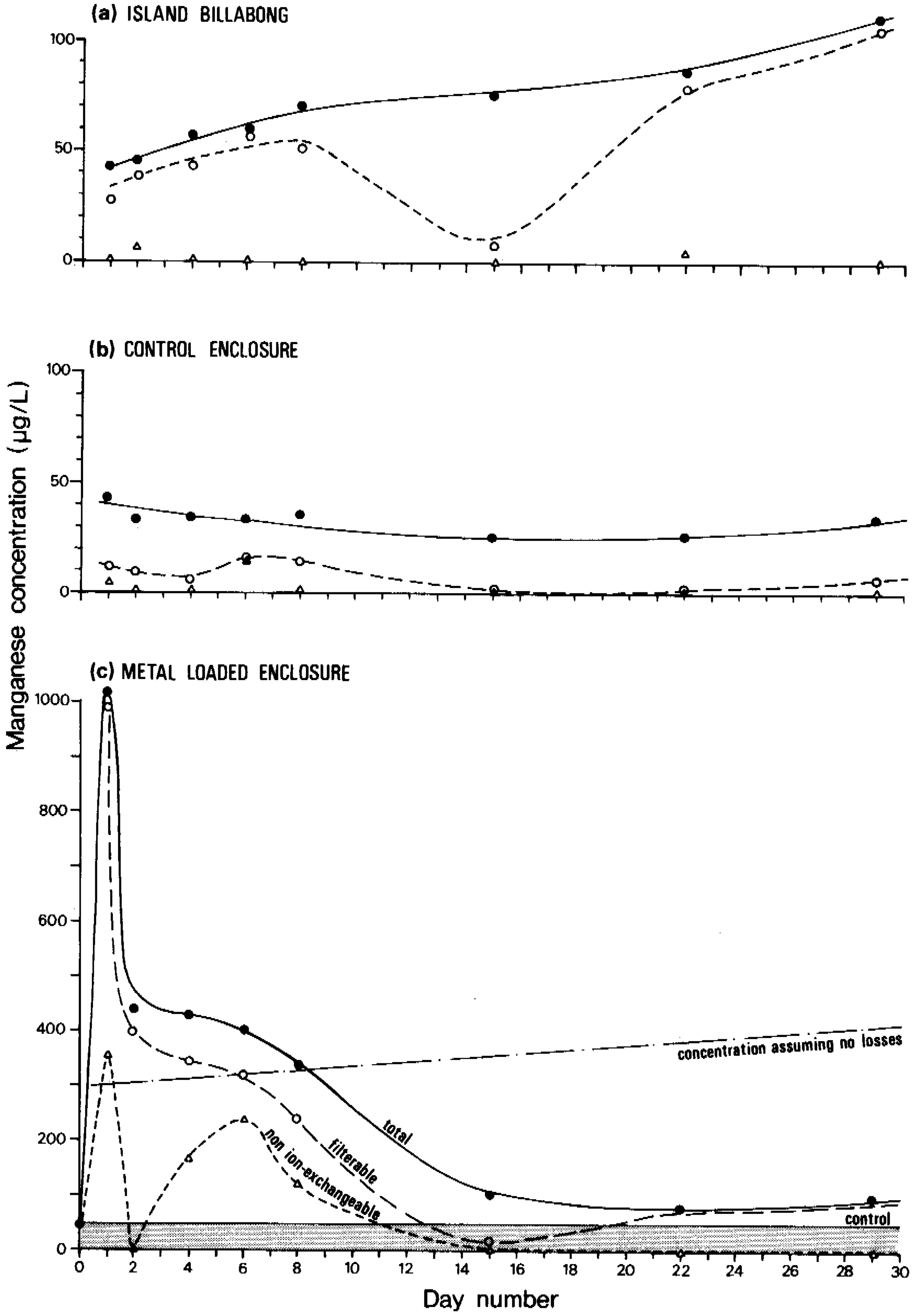

FIGURE 2 VARIATIONS IN TOTAL, FILTERABLE AND NON-ION-EXCHANGEABLE MANGANESE CONCENTRATIONS IN (A) ISLAND BILLABONG, (B) THE CONTROL ENCLOSURE AND (C) THE METAL-LOADED ENCLOSURE.

30%) towards the end of the study (Fig. 3b). As the filterable and non-ion-exchangeable copper concentrations in the control enclosure were generally less than 0.2 μg/L, the detection limit of the analytical method, it is not possible to make meaningful statements about the speciation.

Metal-loaded enclosure. The initial reduction in the copper (and lead) concentrations appeared to be very much more rapid than for the other metals. The total copper concentration was reduced to the initial concentration expected, assuming complete mixing, after two days (Fig. 3c). By Day 2, most of the copper was in ion-exchangeable forms (84%) with a small amount in particulate forms (13%); only about 3% was in non-ion-exchangeable forms. Between Day 2 and Day 6, the total copper concentration remained essentially constant (15 to 13 μg/L) but the filterable copper concentration was reduced by half (13 to 6.4 μg/L). With the exception of the data for Day 6, there is a trend showing an increase in the non-ion-exchangeable copper concentration and a reduction in the ion-exchangeable copper concentration (Fig. 9). The analytical result for the non-ion-exchangeable copper concentration in the surface-water sample on Day 6 is thought to be incorrect. This conclusion is supported by the following: (i) a sample taken at 1.5 m depth had total and filterable copper concentrations similar to the surface sample, but a very much higher concentration of non-ion-exchangeable copper (Cu_t 12 μg/L; Cu_f 5.5 μg/L; Cu_n 3.0 μg/L); (ii) the speciation of manganese, zinc and cadmium was very similar in the surface and bottom samples (Appendix Table A3).

A further decrease in the total and filterable copper concentrations was observed between Day 6 and Day 15. The non-ion-exchangeable copper concentration also decreased over this period to very low levels (Fig. 3c) so that by Day 15 almost all the copper was in particulate forms (83%). Thus, with the reservation about the Day 6 result, the behaviour of copper between Day 6 and Day 15 was similar to that of manganese. After Day 15, the total copper concentration showed an increase (Day 22) and then a decrease (Day 29) to 1.9 μg/L - a value over three times higher than in the control enclosure and nearly twice as high as in the billabong. The increase at Day 22 was due to an increase in the non-ion-exchangeable copper concentration.

3.3 Lead

Billabong and control enclosure. In the billabong the total lead concentrations tended to decrease over time (Fig. 4a). The proportion of the total lead that was in filterable forms was variable, ranging from less than 25% to 91%. The non-ion-exchangeable fraction was very low on all occasions except for Day 29 when all the lead was in this form. The total lead concentration in the control enclosure showed a steady increase during the study period; this was the opposite of the trend observed in the billabong. Throughout the study, the lead in the control enclosure was predominantly in particulate forms (Fig. 4b).

Metal-loaded enclosure. There was a rapid decrease in the concentration of the added lead, so that within ten to fifteen days the concentrations were similar to those in the billabong and control enclosure. The initial, very high concentration of lead was reduced to below the calculated initial value in approximately three days; this was similar to

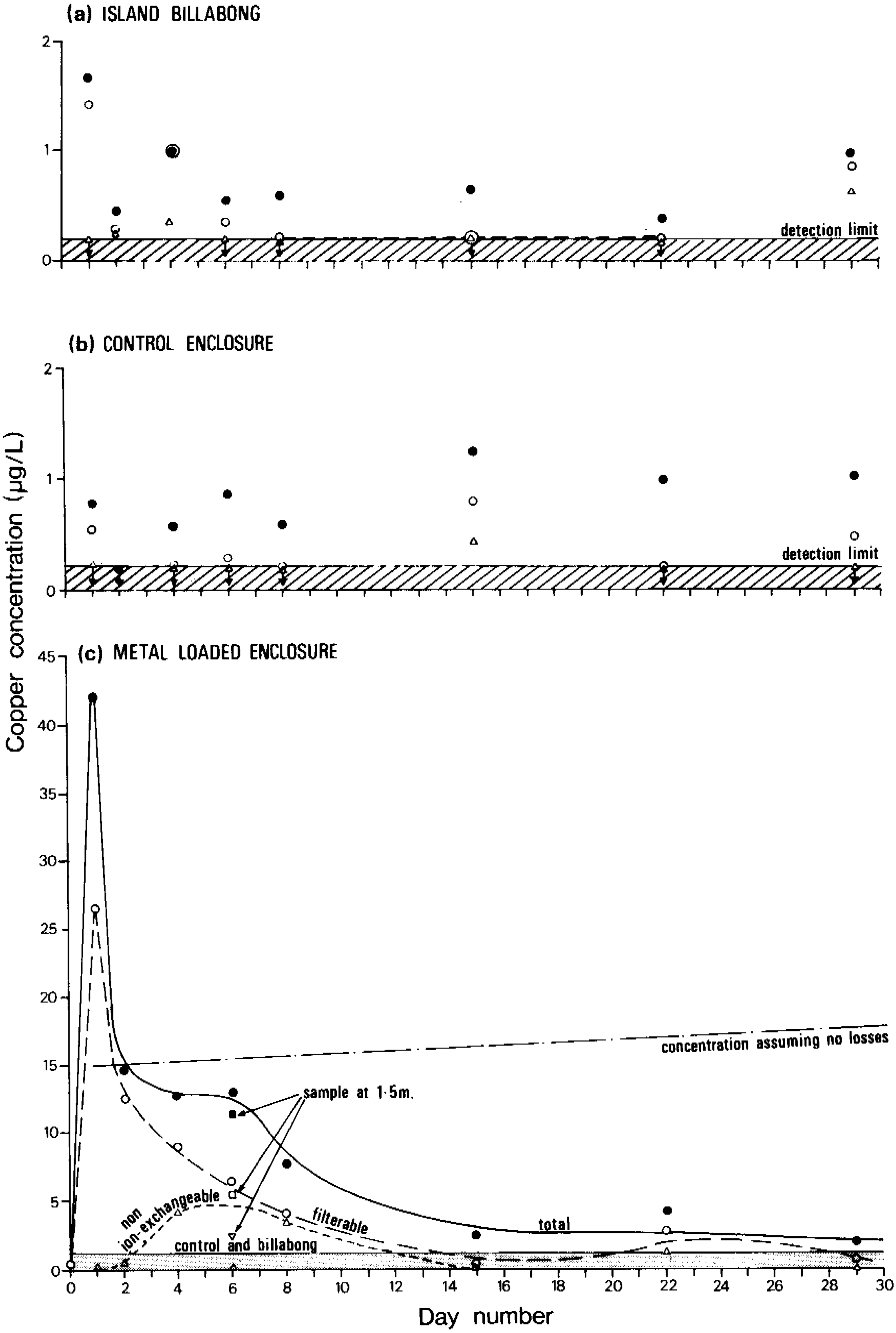

FIGURE 3 VARIATIONS IN TOTAL, FILTERABLE AND NON-ION-EXCHANGEABLE COPPER CONCENTRATIONS IN (A) ISLAND BILLABONG, (B) THE CONTROL ENCLOSURE AND (C) THE METAL-LOADED ENCLOSURE.

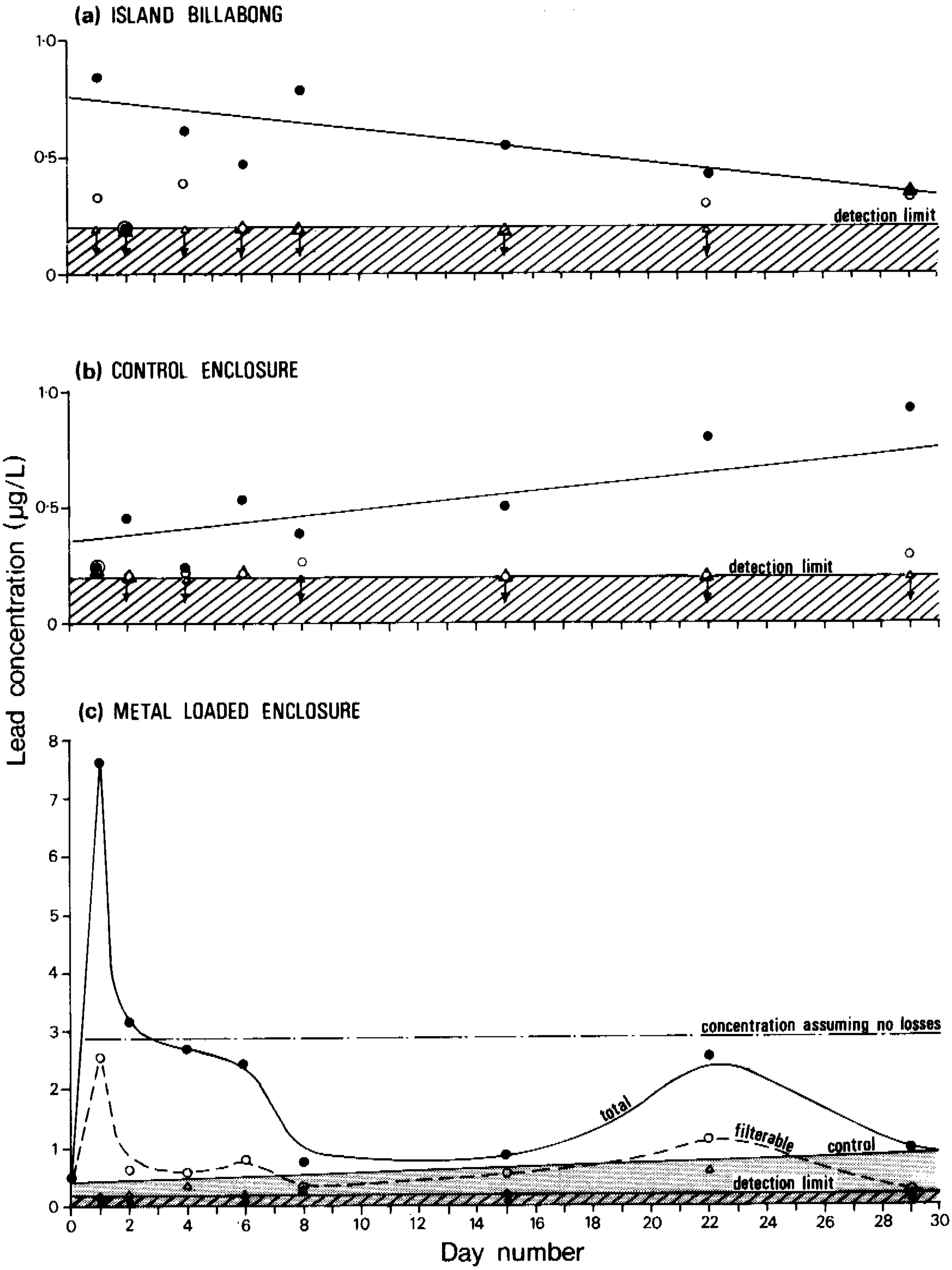

FIGURE 4 VARIATIONS IN TOTAL, FILTERABLE AND NON-ION-EXCHANGEABLE LEAD CONCENTRATIONS IN (A) ISLAND BILLABONG, (B) THE CONTROL ENCLOSURE AND (C) THE METAL-LOADED ENCLOSURE.

the behaviour of copper, but different from manganese, zinc and cadmium which took seven to eight days to fall below the calcluated initial values.

By Day 2, most (80%) of the lead in was particulate forms (Fig. 4c) and the reduction in concentration with time was mainly due to a reduction in these particulate forms. The small filterable fraction consisted mainly of ion-exchangeable forms. A further, albeit small, reduction in the total lead concentration (3.2 to 2.5 µg/L) occurred between Day 2 and Day 6. At the same time there was a very small increase in the filterable lead concentration, primarily due to an increase in the ion-exchangeable lead fraction; at Day 6, 51% of the lead was in particulate forms and 47% was in ion-exchangeable forms. Between Day 6 and Day 15 there was a rapid reduction in the lead concentration to less than 1 µg/L; at Day 15 the speciation was 39% particulate, over 39% ion-exchangeable and less than 22% non-ion-exchangeable. The reduction in the total lead concentration between Day 6 and Day 15 was a result of a decrease in the particulate fraction. Between Day 15 and Day 22, the total lead concentration increased; there was a large increase in the particulate fraction and a small change in the non-ion-exchangeable fraction (Fig. 4c).

3.4 Zinc

Billabong and control enclosure. In the billabong, there was some evidence of an increase (from 2 µg/L to 11 µg/L) in the total zinc concentration over the study period (Fig. 5a). The most noticeable increase occurred between Day 22 and Day 29 (6.1 to 11 µg/L), when the particulate zinc concentration approximately doubled. The filterable zinc concentration increased approximately twofold over the study period. Almost all the filterable zinc was in ion-exchangeable forms (Fig. 5a). Although the speciation of zinc varied considerably throughout the study, particulate and ion-exchangeable forms seemed to dominate.

In the control enclosure there were much higher concentrations of total and filterable zinc than in the billabong (Table 1). This was particularly so in the first few days of the experiment and may have been due to the release of zinc from the enclosure curtain. Both the total and filterable zinc concentrations showed considerable variability over the study period. The zinc was mainly in ion-exchangeable forms.

Metal-loaded enclosure. The behaviour of zinc in the metal-loaded enclosure was similar to that of manganese and cadmium. The total zinc concentration decreased quite rapidly (two to threefold) in the first day. From then until Day 15 there was a further decrease from approximately 80 µg/L to 20 µg/L which was followed by a less rapid decrease to around 10 µg/L (approx. the same as in the billabong) by the end of the study. The total zinc was not reduced to the calculated initial concentration until around Day 8; this is similar to the behaviour of manganese but different from lead and copper where this was achieved by Day 2 or 3.

In the initial period (Day 2), zinc speciation was dominated by ion-exchangeable forms (84%) (Fig. 5c). Between Day 2 and Day 6, the behaviour of zinc was similar to manganese; the total zinc concentration dropped (from 80 µg/L to 63 µg/L), the particulate zinc concentration stayed constant (Day 2: 12 µg/L; Day 6: 13 µg/L), but the proportion of

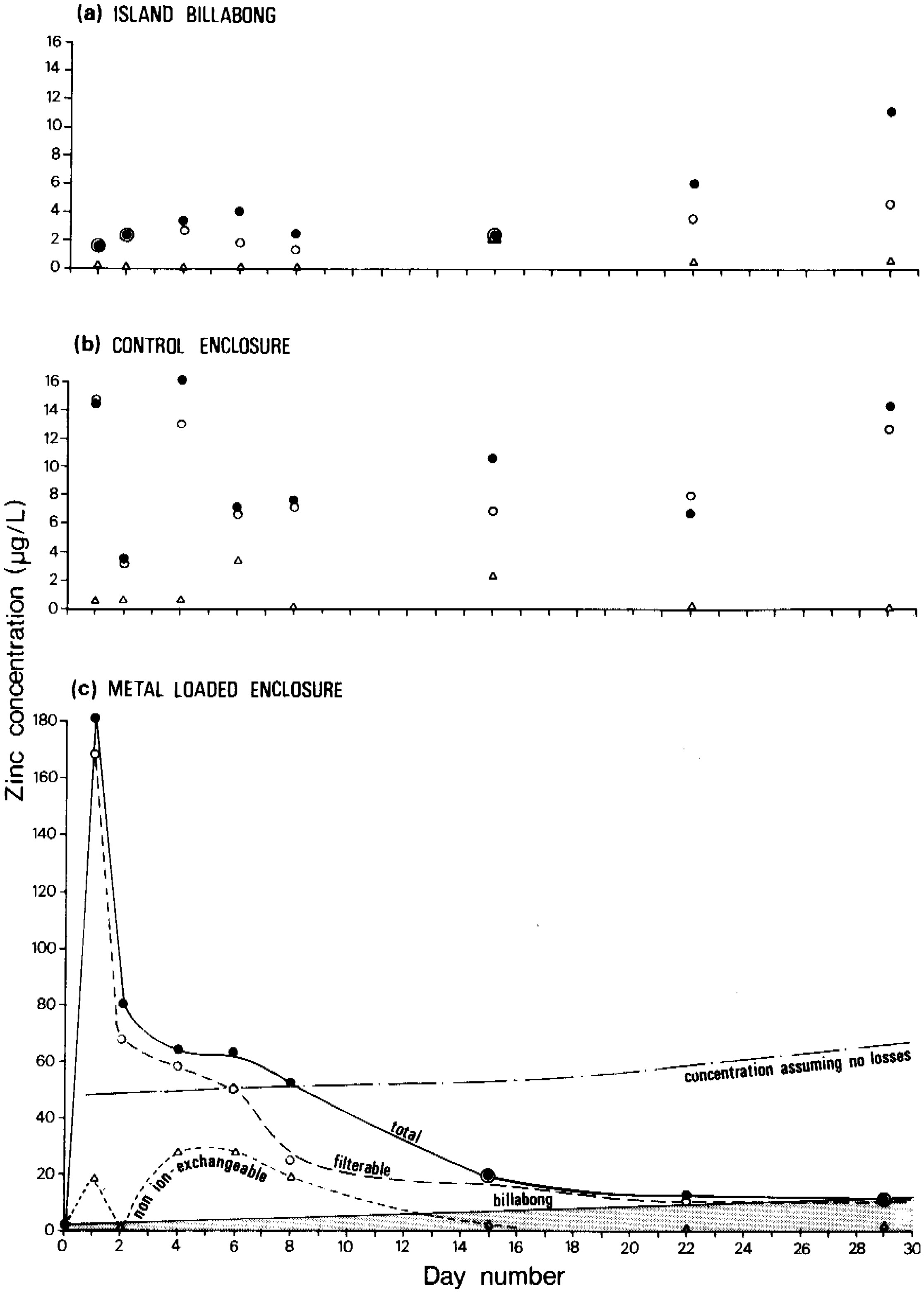

FIGURE 5 VARIATIONS IN TOTAL, FILTERABLE AND NON-ION-EXCHANGEABLE ZINC CONCENTRATIONS IN (A) ISLAND BILLABONG, (B) THE CONTROL ENCLOSURE AND (C) THE METAL-LOADED ENCLOSURE.

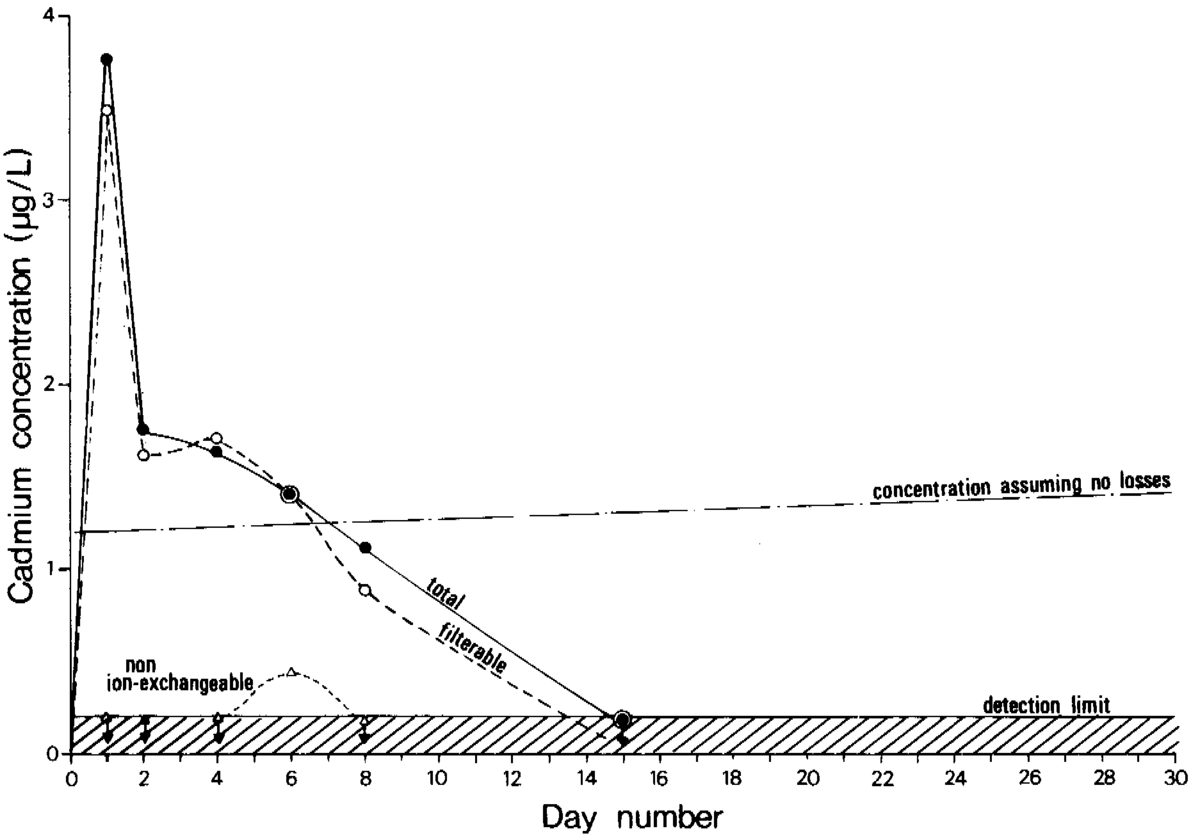

FIGURE 6 VARIATIONS IN TOTAL, FILTERABLE AND NON-ION-EXCHANGEABLE CADMIUM CONCENTRATIONS IN THE METAL-LOADED ENCLOSURE.

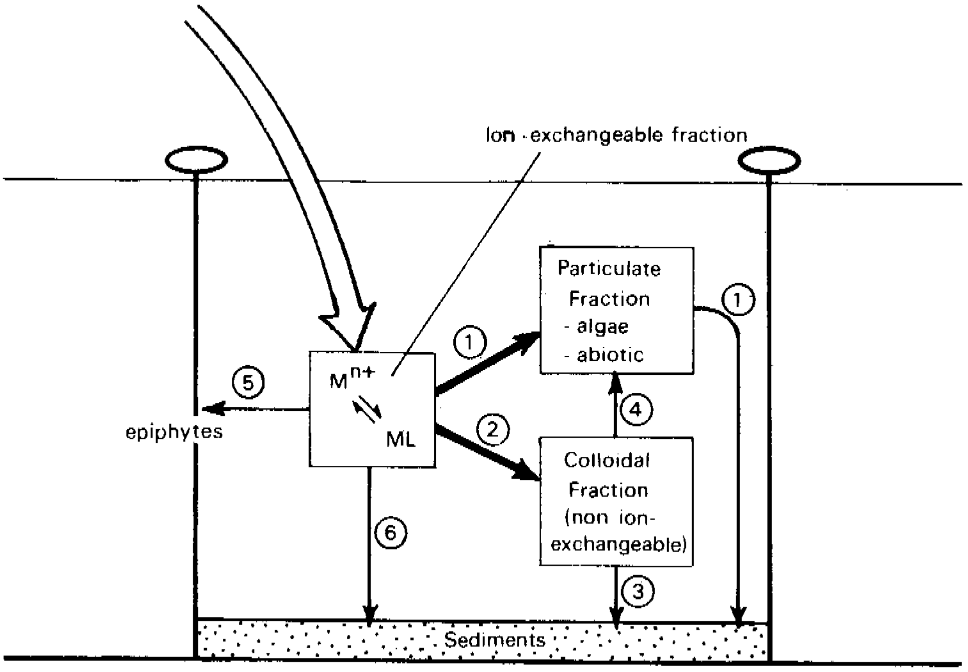

FIGURE 7 THE FOUR MAJOR HEAVY METAL COMPARTMENTS IN THE METAL-LOADED ENCLOSURE AND THE MAIN PATHWAYS BY WHICH THE METALS ARE REMOVED FROM THE WATER COLUMN.

the zinc in non-ion-exchangeable forms increased markedly (from less than 0.5% of the total on Day 2 to 45% of the total on Day 6) (Fig. 5c).

Between Day 6 and Day 15, the total zinc concentration reduced further to 19 µg/L; both non-ion-exchangeable and particulate concentrations decreased. By Day 15, the zinc was almost all in ion-exchangeable forms and stayed in this form to the end of the study even though there was a further reduction in the total zinc concentration (19 µg/L to 11 µg/L) over this period. Although zinc and manganese behaved similarly over the first fifteen days, the speciation of these two metals was quite different from Day 15; manganese was essentially all in particulate forms and zinc was all in ion-exchangeable forms.

3.5 Cadmium

Billabong and control enclosure. All concentrations of cadmium were below the detection limit of 0.25 µg/L.

Metal-loaded enclosure. The total cadmium concentration decreased rapidly between Day 1 and Day 2 and was reduced to the calculated initial concentration by around Day 7 (Fig. 6). This was similar to the behaviour of manganese and zinc. By Day 15, the concentration had reduced to less than 0.25 µg/L. During the study period, essentially all the cadmium was in ion-exchangeable forms; the only exception was on Day 6, when some 31% of the cadmium was in non-ion-exchangeable forms.

4 DISCUSSION

4.1 Changes in Metal Speciation

4.1.1 General background

Metals may be present in natural waters in a number of physico-chemical forms, including:

(i) free metal ions (M^{2+});

(ii) simple inorganic complexes (e.g. MOH^+, $M(OH)_2$, MCO_3) - the concentration of these species will be low in Island Billabong water because of the low pH (5.0-6.2) and low alkalinity (approx. 3 mg/L as $CaCO_3$);

(iii) dissolved metal-organic complexes (M-L) - the concentrations of dissolved organic carbon are reasonably high in Island Billabong waters (5-25 mg/L) and complexes with fulvic acids are expected to be important (particularly in the case of copper and lead);

(iv) metal-colloid complexes (M-Coll) - little is known of these complexes, but they are thought to form by sorption of the metal onto organic colloids or inorganic colloids which have a surface coating of organic matter;

(v) metal-algal complexes (M-Alg) - formed by the active or passive association of the metal with algae and,

(vi) metal-particulate matter complexes (M-Partic) - formed by association of the metal with non-algal particulate matter.

As outlined in the Methods section, our fractionation scheme permits the total metal concentration to be divided into three broad categories:

(i) ion-exchangeable metal fraction (M_{ie}) - this will include free metal ions, inorganic complexes and most of the dissolved organic complexes (those that are ion-exchangeable with Chelex resin);

(ii) non-ion-exchangeable metal fraction (M_n) - this will consist mainly of M-Coll species;

(iii) particulate metal fraction (M_p) - this will consist of M-Alg and M-Partic forms.

To facilitate later discussion on the processes operating to remove added metals from the metal-loaded enclosure, we will assume that the metals are distributed over four main compartments within the enclosure (Fig. 7); these are the (i) ion-exchangeable or 'dissolved' fraction, (ii) non-ion-exchangeable or 'colloidal' fraction, (iii) particulate fraction, and (iv) sediments and epiphytes. Also shown in Figure 7 are a number of potentially important pathways for the removal of the added metals. These are:

Path 1 - direct association with algal or non-algal particulate matter followed by sedimentation. The association of metals with algae may result in their death and it is possible that some decomposition of these algae, leading to release of metals back to the water column, could occur.

Path 2 - complexation of the metal ions by colloidal (organic) matter to produce non-ion-exchangeable forms.

Path 3 - agglomeration of this non-ion-exchangeable colloidal matter to form larger particles which settle out of the water column.

Path 4 - association of the colloid-bound metals with existing particulate matter, followed by sedimentation.

Path 5 - association of the metal ions with epiphytic growth on the walls of the enclosure.

Path 6 - direct sorption of the metal ions by the sediments.

From the experimental data obtained for each metal, some tentative assessment of the major pathway of removal likely to operate in Island Billabong has been made.

4.1.2 Billabong and control enclosure

If the enclosures are to be used to simulate the behaviour of the billabong, the changes in metal speciation should be similar in both. The changes observed in the billabong and the control enclosure are now discussed.

4.1.2.1 Manganese

Manganese appeared to behave quite differently in the control enclosure and the billabong (Fig. 2). In the control enclosure, the total manganese concentration remained approximately constant (33 ± 6 μg/L), and the predominant fraction was particulate manganese (around 75% of the total). By contrast, the total manganese concentration in the billabong increased three to fourfold over the study period, from 43 μg/L to 110 μg/L. Most of this increase can be attributed to an increase in ion-exchangeable manganese, the form which dominated (around 75% of the total) the speciation of manganese in the billabong.

A number of possible reasons can be advanced to explain the increased manganese concentration observed in the billabong. Evapo-concentration would have caused an increase in concentration, but this has been calculated to be small and approximately the same in both systems (around 5-7 μg/L). Another possibility is related to the significant differences in algal numbers in the control enclosure and the billabong, particularly around Day 29 when an algal bloom was observed in the billabong, but not in the control enclosure (Hart et al. 1985b). If the manganese content of the algae were high, this would have contributed to the increased total manganese concentration found in the billabong. However, it seems unlikely that this mechanism was important since the algal-associated manganese would have increased the particulate fraction and not the ion-exchangeable fraction as was observed. Another possibity is the release of manganese from sediments or particulate matter. Davison (1981) has shown that, in the anoxic hypolimnion of a lake, manganese can be readily liberated from settling particulate matter. However, there was no evidence that Island Billabong was anoxic for any length of time during this study and if manganese was released, it must have been due to a different mechanism. The change in pH in the billabong, from around 6 to about 5 over the study period, could have caused some release of sediment- or particulate-bound manganese. The pH in the control enclosure remained more constant, and above 6, over the study period (Hart et al. 1985).

These data show clearly that the behaviour of manganese in the control enclosure did not simulate its behaviour in the billabong. The reasons for the differences are not known.

4.1.2.2 Copper

The mean total copper concentrations in the control enclosure and in the billabong were the same and quite low (0.8 μg/L). No discernible trend was observed in the total copper concentration, although there was considerable variation in the copper speciation in both systems (Fig. 3). Since many of the filterable and non-ion-exchangeable copper concentrations were less than 0.2 μg/L, the detection limit of the analytical method, it is difficult to make meaningful statements about the speciation. However, based on the mean data from Table 1, the copper in the billabong was approximately equally distributed over all three fractions, while in the control enclosure particulate forms made up approximately 50% of the total, ion-exchangeable forms around 20% and non-ion-exchangeable forms around 30%.

Despite the variability, the data suggest that the behaviour of copper in the control enclosure was different from its behaviour in the billabong.

4.1.2.3 Lead

The mean total lead concentrations in the billabong and the control enclosure were the same and quite low (0.5 µg/L). In the billabong, there was a trend towards lower total lead concentrations over the study period, while in the control enclosure the opposite trend was observed (Fig. 4). In both systems, particulate forms of lead predominated. Because many of the filterable and non-ion-exchangeable lead concentrations were below the 0.2 µg/L detection limit, it is not possible to comment on the relative proportions of ion-exchangeable and non-ion-exchangeable forms.

These data show that the control enclosure does not simulate the billabong. Although the mean concentration of total lead was the same in both systems, the speciation and behaviour was quite different.

4.1.2.4 Zinc

Very significant differences were observed in the mean total zinc concentrations in the control enclosure (9.5 µg/L) and in the billabong (4.2 µg/L) (Table 1). The much higher concentrations in the control enclosure may have been a result of zinc leached from the enclosure material. This is supported by the fact that most of the zinc in the enclosure was in ion-exchangeable forms. In the billabong, zinc was almost equally distributed between particulate and ion-exchangeable forms with a small amount in non-ion-exchangeable forms.

In the billabong, there was an increase (from 2 to 11 µg/L) in the total zinc concentration over the study period (Fig. 5). The large increase that occurred between Day 22 and Day 29 (6.1 to 11 µg/L) was probably caused by the large increase in algal numbers around this time. The twofold increase in the filterable zinc concentration was possibly due to a combination of evapo-concentration and the release of zinc from sediments and particulate matter due to the lower pH; the pH fell from around 6 to 5 by the end of the study. Although the speciation of zinc varied considerably throughout the study, particulate and ion-exchangeable forms dominated in the billabong.

4.1.2.5 Cadmium

In both the control enclosure and the billabong, all concentrations of cadmium were below the detection limit of 0.25 µg/L. This precludes any discussion of the speciation.

4.1.2.6 Summary

The concentrations of all the metals were found to be very low in both the billabong and the control enclosure and this made speciation studies quite difficult. On a number of days, the concentrations of the various fractions were below the analytical detection limit and comparisons could not be made between the two systems. Where comparisons could reasonably be made, it seemed that the behaviour of the metals in the enclosure was different from their behaviour in the billabong. Some reasons for these differences have been advanced. No comparisons of the behaviour of zinc could be made, since the enclosure walls are suspected to have released a significant amount of zinc into the water column.

The conclusion at this stage must be that the metals studied do not appear to behave in the same manner in the enclosures as in the billabong. These differences, while significant at the very low concentrations found naturally in Island Billabong waters, are not expected to influence the usefulness of the enclosures in providing information on the behaviour of higher concentrations of metals added to this system.

4.1.3 Metal-loaded enclosure

Variations in the concentrations of the ion-exchangeable, non-ion-exchangeable and particulate fractions of the added metals are shown in Figure 8. The distribution of each metal over the four major components of the system is shown in Figure 9. As a result of inadequate initial mixing, the added metals were not evenly distributed through the water column, for at least a few days after their addition; so it was necessary to make certain assumptions when estimating the quantities of the metals in each compartment at Days 2 and 6. Manganese was assumed to act conservatively (i.e. no loss occurs) over the first six days. With this assumption, the total manganese concentrations observed in the surface waters of the metal-loaded enclosure were calculated to overestimate the total amount of manganese added by a factor of 1.4 on Day 2 and 1.3 on Day 6. These two factors were then used to scale down the concentration of all the other metals.

4.1.3.1 Manganese

Manganese ions added to natural waters will, after equilibration, be present in a number of forms including free manganese ions (Mn^{2+}), simple inorganic complexes ($MnOH^+$, $MnCO_3$), organic complexes, and complexes with colloidal and particulate matter. In addition to these, Mn(II) may also be oxidised to MnO_x forms (Wilson 1980; Stumm and Morgan 1981; Hem 1981). There have been a number of studies on the oxidation process in natural waters and the process is known to be autocatalysed (i.e. catalysed by the presence of MnO_x) (Stumm and Morgan 1981). The rate is increased by the presence of other surfaces such as clays, solid organic matter and FeOOH, which apparently adsorb the Mn(II) and assist with the oxidation (Coughlin and Matsui 1976; Wilson 1980), but it is slower if dissolved organic matter is present, presumably because such organics complex some Mn(II) and reduce the concentration of free Mn(II) (Wilson 1980). The autocatalytic rate equation given by Stumm and Morgan (1981) is:

$$
\begin{aligned}
-\,d[Mn(II)]/dt &= k_0\,[Mn(II)] + k\,[Mn(II)]\,[MnO_x] \\
&= (k_0 + k'[OH]^2 p_{O_2}\,[MnO_x])\,[Mn(II)]
\end{aligned}
$$

where k_0 = first order rate constant; k = autocatalytic rate constant;
p_{O_2} = partial pressure of oxygen.

Recent work by Diem and Stumm (1984) suggests that this rate law may only be applicable to solutions that are initially oversaturated with respect to $MnCO_3$ or $Mn(OH)_2$. They found that in homogeneous solutions, not oversaturated with respect to $MnCO_3$ or $Mn(OH)_2$ and free of catalysts, Mn(II) remains unoxidised for several years.

Application of the autocatalytic rate equation (using the values published by Stumm and Morgan (1981) for the various constants) to the waters of Island Billabong and the enclosures indicates that at natural pH (around 7) it would take about 2000 days to reduce by half an Mn(II) concentration of 400 μg/L. However, more recent studies have shown that the rates of oxidation of Mn(II) in natural waters are orders of magnitude faster than in synthetic solution (Nealson and Ford 1980; Sung and Morgan 1981; Chepnik et al. 1982; Emerson et al. 1982; Burdige and Kepkay 1983; Hart and Jones 1984). The difference is generally ascribed to very efficient surface catalysis or bacterial mediation.

Recent work by Hart and Jones (1984) showed that Mn(II) added to unfiltered Island Billabong water at pH 7 was significantly reduced in concentration in a few days. No reduction in concentration occurred in filtered Island Billabong water. Hart and Jones (1984) attributed the reduction in concentration in the unfiltered water to oxidation of the Mn(II) catalysed by bacteria.

One would expect manganese ions added to Island Billabong water to undergo a number of competitive reactions which would include complexation with organic and inorganic ligands in solution, oxidation to MnO_x catalysed by particulate matter and bacteria, and interaction with algal cells or abiotic particulate matter.

The changes in manganese concentrations with time (Fig. 2), together with the changes in the amounts in each major compartment (Fig. 9), indicate that 65% to 70% of the added manganese was rapidly removed from the metal-loaded enclosure (in about fifteen days). The changes that occurred in the concentrations of the three main forms of manganese are discussed below and are shown in Figure 9.

There was a gradual build-up in the concentration of particulate manganese over the first ten days (to around 100 μg/L), followed by a decrease almost to zero about Day 22 (Fig. 8). Particulate manganese can be in a number of different forms:

(i) manganese associated with algae,

(ii) an MnO_x coating formed on existing particulate matter by the oxidation of Mn(II), perhaps catalysed by the particulate matter or by associated bacteria (Emerson et al. 1982; Hart and Jones 1984),

(iii) colloidal, organic or MnO_x complexes that have either agglomerated to form larger particles or become associated with existing particulate matter, and

(iv) manganese associated with other (abiotic) particulate matter, excluding (ii) and (iii).

The first of these possibilities seems unlikely; there was a significant reduction in the concentrations of algae (Fig. 10) without a corresponding reduction in the total manganese concentration. In fact, between Days 2 and 6 the total manganese concentration remained constant. The gradual increase in the concentration of particulate manganese supports the third and fourth possibilities. We postulate that the particulate forms of manganese were probably a mixture of MnO_x coatings, Mn(II) adsorbed to particulate surfaces, and Mn-organic colloids that had become associated with the particulate surfaces. The influence of the oxide-coated surfaces on the speciation of the other metals will be discussed later.

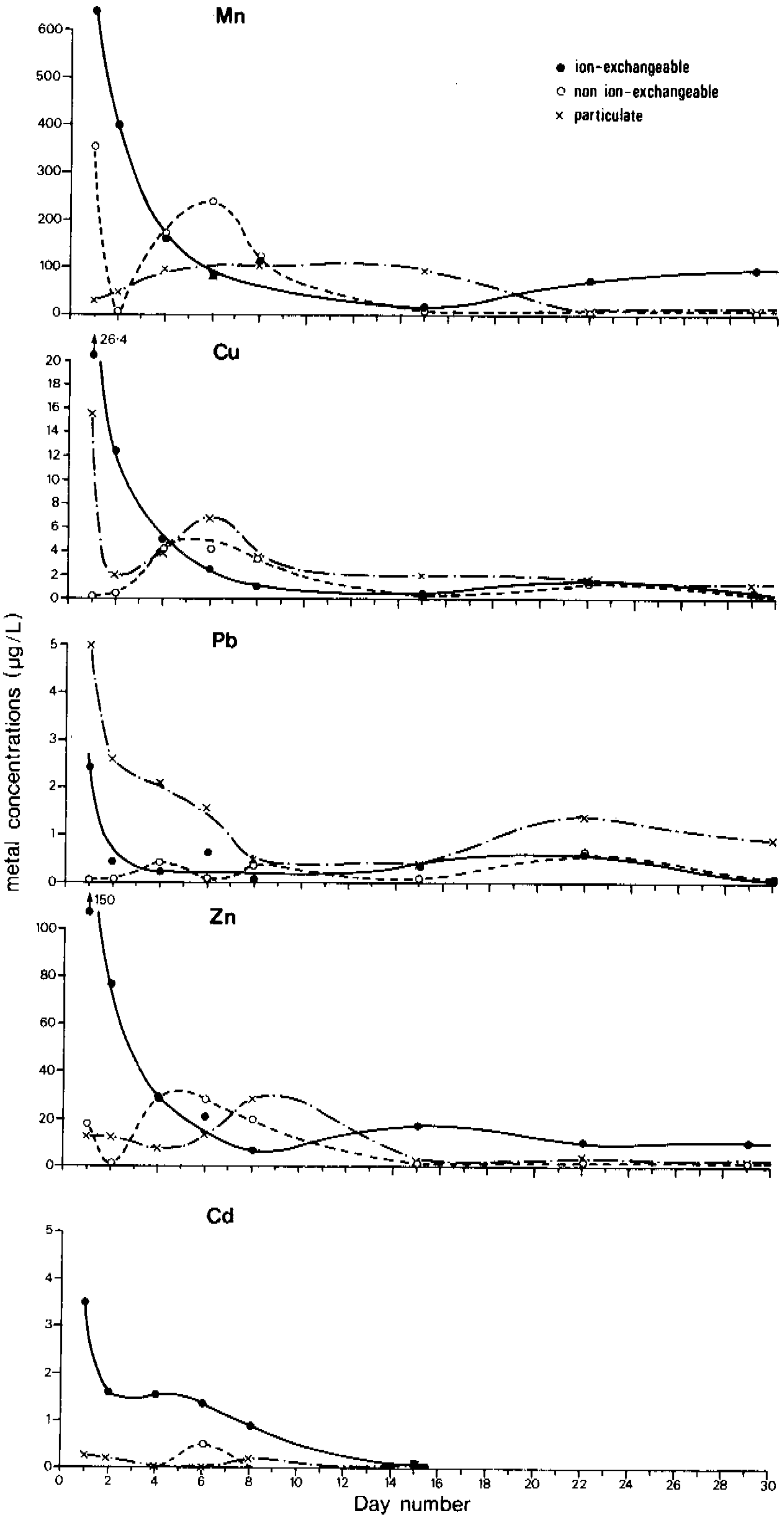

FIGURE 8 VARIATIONS IN THE CONCENTRATIONS OF THE ION-EXCHANGEABLE, NON-ION-EXCHANGEABLE AND PARTICULATE FRACTIONS OF MANGANESE, COPPER, LEAD, ZINC AND CADMIUM IN THE METAL-LOADED ENCLOSURE.

Initially, from Day 1 to Day 2, there was a very rapid decrease in the concentrations of both the ion-exchangeable and non-ion-exchangeable forms. Most of this change was due to mixing, rather than to any major changes in speciation. Between days 2 and 6, the total manganese concentration remained relatively constant while the ion-exchangeable manganese concentration decreased markedly from around 400 µg/L to less than 100 µg/L, the non-ion-exchangeable fraction increased from 1.3 µg/L to around 240 µg/L, the particulate fraction also increased but to a lesser extent (Fig. 8). This strongly suggests that, during this four day period, the ion-exchangeable forms were being converted into non-ion-exchangeable forms, and to a lesser extent to particulate forms.

The non-ion-exchangeable manganese could have been formed by either of two processes:

(i) a slow complexation of Mn(II) by organic colloids to form strong Mn-organic complexes that are not ion-exchangeable with Chelex-100. Little is known about the rates of formation of manganese-colloidal complexes. The strong Mn-organic complexes may not have been formed directly from Mn(II) and organic ligands, since it is possible that a two step process, in which the Mn(II) is initially rapidly complexed by ligands that form weak complexes (say Mn-L) and then these complexes are converted slowly into more stable complexes (Mn-Coll), was involved, i.e.

$$Mn^{2+} \xrightarrow{\text{L, fast}} \text{Mn-L} \xrightarrow{\text{Colloid, slow}} \text{Mn-Coll}$$

(ii) the formation of MnO_x colloids by the oxidation of Mn(II) ions. At the near neutral pH of the enclosed water it seems likely that, if oxidation did occur, it would have been catalysed by bacteria.

$$Mn^{2+} \xrightarrow{\text{oxidation, slow}} MnO_x \text{ (colloidal)}$$

During the first four or five days the amount of manganese in particulate forms also increased. This could have been due to the direct oxidation of Mn(II) onto the particulate surfaces or the association of colloidal forms of manganese with the particulates.

Between Days 6 and 15, there was a substantial decrease in the total manganese concentration, from 410 µg/L to 100 µg/L, due mainly to a reduction in the non-ion-exchangeable fraction (Fig. 8). There was also a substantial reduction in the ion-exchangeable fraction from 85 µg/L to around 13 µg/L. The particulate manganese concentration changed little during this period (Fig. 8). On Day 15, 87% of the manganese was in particulate forms and 13% in ion-exchangeable forms.

The reduction in the concentration of non-ion-exchangeable manganese may have been due to its association with existing particulate matter which then settled from the water column, or simply to agglomeration of the colloids to form larger particles which could also settle out. This hypothesis may be represented by the following equation:

$$\text{Mn-Coll} \longrightarrow \text{Mn-Coll-particulates} \longrightarrow \text{settle out}$$

$$\text{Mn-Coll} \longrightarrow \text{agglomerate} \longrightarrow \text{settle out}$$

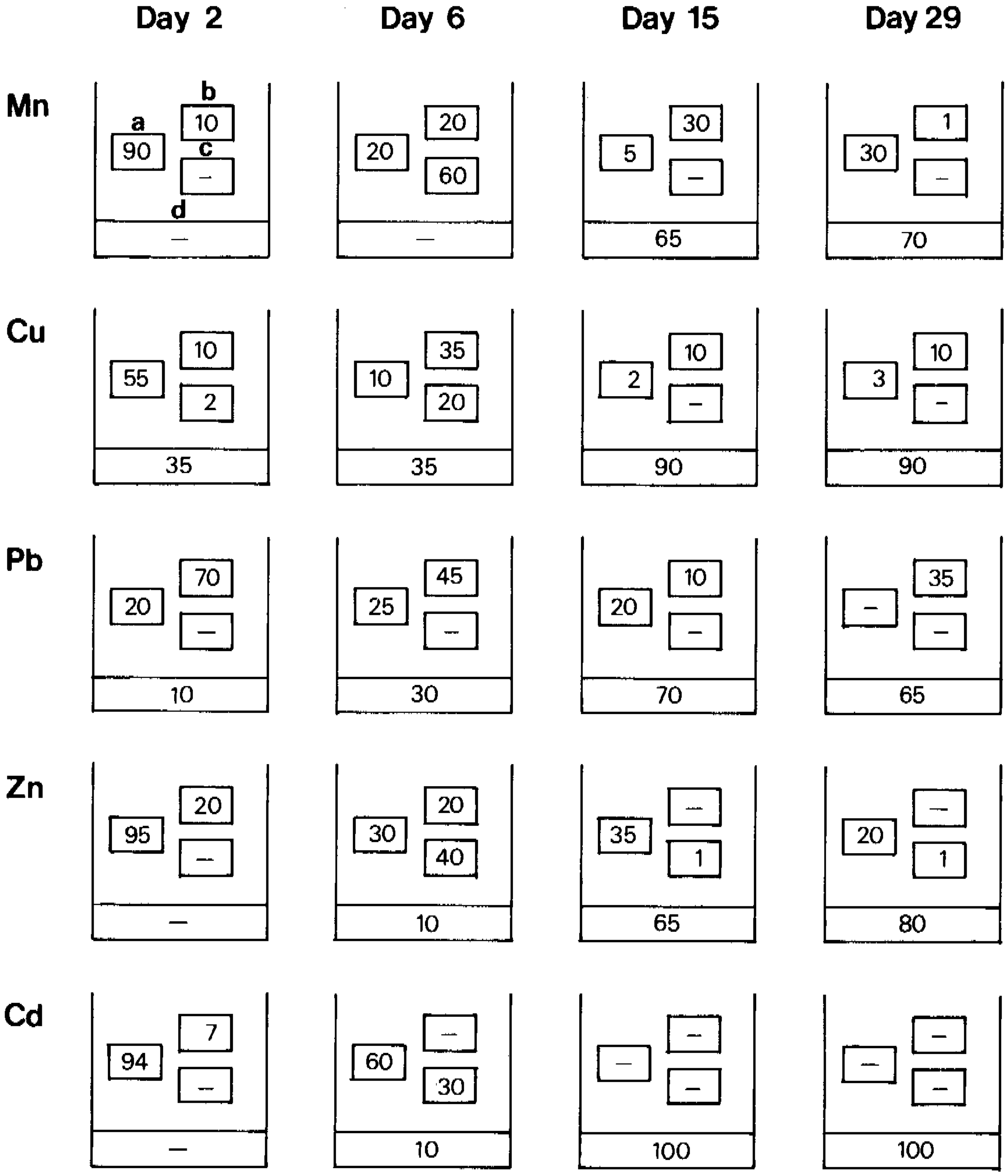

FIGURE 9 PERCENTAGE OF THE TOTAL AMOUNT OF ADDED METAL PRESENT IN EACH OF THE FOUR COMPARTMENTS (A) ION-EXCHANGEABLE, (B) PARTICULATE, (C) NON-ION-EXCHANGEABLE AND (D) SEDIMENTS AND EPIPHYTES.

It is difficult to obtain information on this mechanism, since the relative changes in the measured quanitities, Mn_n = Mn-Coll and Mn_p, will depend greatly on the relative rates of formation of Mn-Coll and Mn-Coll-particulate forms. Also, we cannot exclude the possibility that some Mn(II) was oxidised to MnO_x on the surface of the particulates during this period.

Although the total Mn concentration remained relatively constant between Day 15 and the end of the study, there were significant changes in the speciation, with particulate-associated Mn being transformed into ion-exchangeable forms. The particulate-associated Mn could have existed in two forms: (i) as Mn(II) adsorbed to algae or other particulate matter, or (ii) as MnO_x coated particles (> 0.1 µm in size). If the manganese was associated with algae, it is difficult to see how it could have been released in ion-exchangeable forms without major changes in the algal population. Such changes were not observed during this period (Fig. 10). It is more likely that the Mn was released from the particulate surfaces by the 0.6 unit drop in pH (from about 6.0 to 5.4) over this period. The other possibility, that particulate-associated MnO_x was converted into Mn^{2+}, an ion-exchangeable form of Mn, would have required the existence of reducing conditions in the enclosure for a short period of time. Since our sampling was done weekly during this period of the study, it is possible that such reducing conditions did exist but were not recorded.

Main removal mechanisms (Fig. 9). These experiments make it possible to draw a number of conclusions regarding the fate of manganese ions discharged into Island Billabong. The data indicate that added Mn(II) ions would be rapidly removed from the water column, probably to the sediments. After fifteen days, 65% to 70% of the added manganese had been removed from the water column. The removal mechanism is speculative at this stage, but seems to involve a relatively slow process in which Mn(II) is converted into non-ion-exchangeable forms, which either agglomerate (colloidal MnO_x) or associate (organic complexes) with existing particulate matter, followed by loss of these larger particles to the sediments. It is possible that some oxidation of Mn(II) directly on the surface of the particulate matter (perhaps catalysed by bacteria) also occurs. Manganese-algal interactions do not seem to play a significant part in the removal of manganese. The main removal mechanisms are summarised below:

$$Mn^{2+} \longrightarrow \text{Mn-Coll} \longrightarrow \text{Mn-Coll-particulate} \longrightarrow \text{settle out}$$

$$Mn^{2+} \longrightarrow \text{Mn-Coll} \longrightarrow \text{agglomerate} \longrightarrow \text{settle out}$$

4.1.3.2 Copper

The aqueous chemistry of copper has been reviewed recently by Leckie and Davis (1979), Nriagu (1980), Florence (1982) and Hart (1982). In natural waters copper is present in a number of different forms, including (i) free copper ions and simple inorganic complexes, (ii) copper-organic complexes, (iii) copper-colloid complexes, (iv) copper-particulate complexes, (v) copper-algal complexes. Copper has a marked tendency to form strong complexes with natural organic ligands. For example, in Magela Creek water, which is very soft, slightly acidic (pH approx. 6) and has a DOC concentration of around 5 mg/L, Hart and Davies (1981c) estimated that over 90% of the 0.3 µg/L of filterable copper would be bound to natural organic matter. In hard waters and in those with high pH's, hydroxy- and carbonato-complexes can be more important.

In a study of copper speciation in Australian freshwaters, Florence (1977) found that between 32% and 54% of the filterable copper in Woronora Reservoir was non-ion-exchangeable and was associated with organic colloids. In Tarago Reservoir, in which the water was slightly acidic and low in both dissolved salts and dissolved organic carbon, some 20% to 50% of the filterable copper was non-ion-exchangeable (Hart and Davies 1981b). Hart and Davies (1977) found that, at low flow, approximately 25% of the filterable copper in the Yarra River was non-ion-exchangeable.

In the present study there was a very significant reduction in the total copper concentration on the first day (Fig. 3). The reduction is thought to be due partly to mixing of the added metal solution and partly to the rapid interaction of the added Cu(II) ions with algae, and their subsequent settling out. The ratio of total metal concentration on Day 1 to the concentration on Day 2 supports the theory that copper and lead are removed more rapidly than can be explained by simple mixing through the water column: the ratio was lower for copper (0.35) and lead (0.41) than for zinc, manganese and cadmium (0.44, 0.44 and 0.56 respectively). In the absence of other removal mechanisms, one would expect the relative decrease in concentration, due to mixing, to be the same for all the added metals.

If it is assumed that between Days 1 and 2 (i) mixing resulted in the copper concentration being reduced by a factor of 0.44 and (ii) the rest of the observed reduction in concentration (4 μg/L, 35% of the added copper) was due to association with algae which then sedimented, then the 1.3×10^6 cells/L lost between Days 1 and 2 (Fig. 10) would have contained around 3×10^{-6}μg Cu/cell. This concentration seems excessive when compared with other published values. For example, Klotz (1981) reported concentrations over ten times less than the above for algae (*Chlorella*, *Scenedesmus* and *Chlamydomonas*) taken from a copper-polluted river in Connecticut. A plausible explanation may be that part of the 4 μg/L copper was removed by uptake by epiphytes that had started to grow on the enclosure walls.

Between Days 2 and 6, the ion-exchangeable copper concentration decreased dramatically from 12 μg/L to 2.5 μg/L and at the same time the non-ion-exchangeable and particulate copper concentrations both increased (Fig. 8). These changes were similar to those observed for manganese, although, for copper the particulate fraction seemed to be more important at Day 6. During this four day period the total copper concentration remained approximately constant. This suggests that after the initial loss of copper there was a redistribution of ion-exchangeable forms into non-ion-exchangeable and particulate forms. Unfortunately, our speciation scheme only gives information on the general form of the copper without any specific detail about the bonding. Equilibrium calculations indicate that the ion-exchangeable copper would probably mainly consist of Cu-fulvic complexes, with small amounts of $CuOH^+$ and free copper ions.

Thus, to explain the changes in copper speciation between Days 2 and 6 it is necessary to consider the possible changes in the Cu-fulvic complexes which would give particulate and non-ion-exchangeable forms. The increase in the particulate copper could have arisen from a slow reaction between (organic) particulate matter and Cu-fulvic complexes, or by association

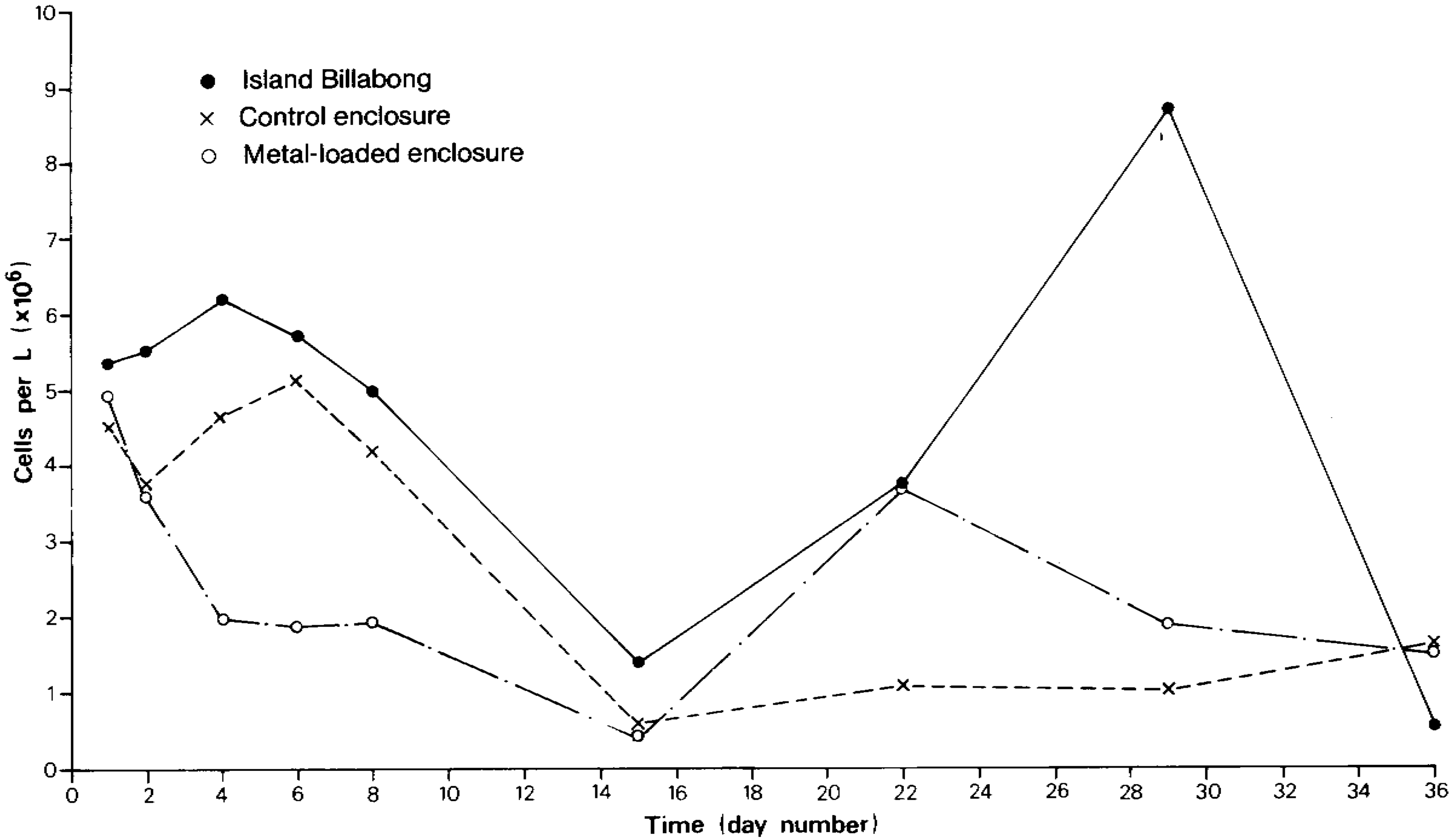

FIGURE 10 ALGAL CELL CONCENTRATIONS IN ISLAND BILLABONG, THE CONTROL ENCLOSURE AND THE METAL-LOADED ENCLOSURE (FROM HART ET AL. 1985b).

with MnO_x-coated particulate matter (it was postulated in the preceding section that such surfaces may be produced by the catalysed oxidation of Mn(II)). Certainly it is well known that copper is readily adsorbed to MnO_x surfaces (Van den Berg 1982). The similarity in the behaviour of copper and manganese during this four day period suggests that the same mechanism may operate in the formation of both the non-ion-exchangeable copper and manganese. We postulate that the non-ion-exchangeable copper could be formed by either of two mechanisms:

(i) a slow reaction between Cu-fulvate complexes (ion-exchangeable) and existing colloidal matter;

(ii) a reaction between Cu-fulvate complexes and slowly forming MnO_x colloids.

These may be represented as:

$$\text{(i)}\quad Cu^{2+} \xrightarrow{\text{fast}} \text{Cu-L} \xrightarrow{\text{slow}} \text{Cu-L-Coll (or Cu-Coll)}$$

$$\text{(ii)}\quad Cu^{2+} \xrightarrow{\qquad} \text{Cu-L} \xrightarrow{MnO_x} \text{Cu-L-}MnO_x \text{ or } (\text{Cu-}MnO_x)$$

Gachter and Mares (1979) in their MELIMEX experiments found that copper exhibited a much higher affinity to macromolecular or colloidal substances than did cadmium, zinc or lead. In these experiments, colloidal matter was defined as being material that passed through a 0.45 µm membrane filter but was retained by an Amicon UM 2 ultrafilter. Further, they found that the ratio of colloidal to ultrafiltered copper (and lead) was higher in the metal-loaded enclosures than in the control, although considerable variation in the above ratio was noted in both enclosures. They concluded that, with time, the complex-forming substances varied in composition and that the types of ligands were different in the metal-loaded and control enclosures.

Recently Van den Berg (1982) and Hirose et al. (1982) have shown that small concentrations (2×10^{-8} - 2×10^{-7} M) of very strong copper-binding ligands are present in seawater. If similar organic ligands are present in Island Billabong waters, we estimate that their log conditional stability constants at pH 6 would be around 8 to 10, which is sufficiently large to produce complexes that would not be broken up by the Chelex resin.

Between Days 6 and 15 the concentration of all copper fractions decreased; the particulate fraction possibly because of sedimentation and the colloidal fraction either by association with existing particulate matter or by agglomeration to form larger particles, that then settled out. The fact that the ion-exchangeable fraction further decreased in concentration over this period suggests that additional reactions occurred between these forms and the particulate and colloidal forms. By Day 15 almost 90% of the copper had been removed from the water column to the sediments (and the epiphytes on the enclosure wall). The 10% left in the water column was mainly in particulate forms. The copper speciation changed little between Day 15 and the end of the study.

Main removal mechanisms (Fig. 9). The added ionic copper appeared to be very rapidly taken up by the phytoplankton. Some 35% of the copper was lost to the sediments in the first day. After this initial, rapid loss, most of the copper in the water column was in ion-exchangeable forms, probably as Cu-fulvate complexes; a small amount was also associated with the particulate matter. Over the next four days most of the ion-exchangeable copper was converted into almost equal amounts of particulate and non-ion-exchangeable forms. Over the next nine days to Day 15 most of the copper in the water column was removed to the sediments, in the case of the non-ion-exchangeable forms possibly by agglomeration to form larger particles or by association with existing particulate matter which settled out. The little which remained in the water column was in particulate forms. Between Day 15 and the end of the study there was little further change in the speciation. The main removal mechanisms for copper are summarised below:

(i) $Cu^{2+} \longrightarrow \text{Cu-algae} \longrightarrow \text{settle out (rapid)}$

(ii) $Cu^{2+} \longrightarrow \text{Cu-L} \longrightarrow \text{Cu-particulate } (MnO_x \text{ coated}) \longrightarrow \text{settle out}$

$Cu^{2+} \longrightarrow \text{Cu-L} \longrightarrow \text{Cu-Coll} \longrightarrow \text{Cu-Coll-particulate} \longrightarrow \text{settle out}$

4.1.3.3 Lead

The aqueous chemistry of lead has not been studied as extensively as that of many other metals (Laxen and Harrison 1977; Demayo et al. 1980; Florence and Batley 1980; Florence 1982; Hart 1982). In freshwaters, lead has been found to exist in the free ionic form (Pb^{2+}), as simple inorganic complexes (particularly $PbCO_3$), as lead-organic complexes (e.g. Pb-fulvate) and in colloidal and particulate forms (Florence and Batley 1980). A number of studies have shown the importance of lead hydroxy-carbonate and lead-organic forms, but in Island Billabong waters lead hydroxy-carbonate is not expected to be important in the speciation of lead because the alkalinity is so low. Lead has been shown to have a strong affinity for both particulate and dissolved organic matter (Ferguson and Bubula 1974; Buffle et al. 1977) and these complexes are almost as strong as those formed between copper and natural organic matter. Considerable amounts of lead can be bound to inorganic and organic colloids, and association with inorganic colloids is generally considered more important than it is for copper (Florence and Batley 1980; Laxen and Harrison 1977; Benes et al. 1979).

There have been some studies of lead speciation in Australian freshwaters. Florence (1977) found that approximately 70% of the filterable lead in Woronora Reservoir water was ion-exchangeable, both inorganic and organic colloidal species being important, and Hart and Davies (1981a) reported that 60% to 65% of the filterable lead in Yarra River water was ion-exchangeable. In a study of two small freshwater streams in the United Kingdom, Laxen and Harrison (1981) found that less than 40% of the filterable lead was ion-exhcnageable, a result which is much lower than those reported above for Australian waters.

In the experiments reported here, the speciation of lead in the metal-loaded enclosure was markedly different from the other metals. Initially, lead seemed to behave similarly to copper: the concentration was rapidly reduced, probably by association with algae that died and settled out of the water column to the sediments and by Day 2 some 70% of the lead was in particulate forms and 10% had been lost from the water column (Fig. 8). In this same period considerably more copper was removed from the water column, suggesting that copper probably reacts with the algae faster than lead does. This is also indicated by the ratio of the total metal concentration on Day 1 to that on Day 2 (Cu 0.35, Pb 0.41).

After Day 2, the lead was primarily associated with particulate matter and the most significant change to Day 15 was the reduction in this fraction (Fig. 8). By Day 15 around 70% of the lead had been removed from the water column (Fig. 9). The dominance of particulate over colloidal or ion-exchangeable forms of lead may be related to the rate at which the complexes are formed. Batley and Florence (1976) reported that ionic lead, added to filtered seawater, equilibrated very slowly with the existing pool of lead; only 20% to 50% of the added lead had exchanged after three days.

The form of the particulate lead is not known but lead has a strong affinity for solid organic matter (Ferguson and Bubula 1974) and the most likely possibilities are association of lead with abiotic particulate matter (organic or MnO_x-coated) or algae. It is possible to make some tentative estimates of the relative importance of lead-algal and lead-MnO_x particulate interactions, and for this purpose the data for Day 4 will be used. On Day 4, the particulate MnO_x concentration was around 2×10^{-6} M and the corresponding total algal ligand concentration was around 2×10^{-8} M (the former was calculated assuming all the particulate manganese was MnO_x and the latter was calculated assuming the total algal ligand concentration was 1×10^{-14} M/cell - see Baccini and Suter 1979). Baccini and Suter (1979) assumed that the log K for copper-algal associations was around 6 to 7 (water pH was 8). A corresponding figure for lead in Island Billabong water would be about 4 or 5. There is little information on the value of log K for Pb-MnO_x complexes, but by comparison with the data for Cu-MnO_x complexes (see Van den Berg 1982), a representative figure would be 5. When these figures are used it is relatively simple to show that Pb-MnO_x complexes would dominate over lead-algal complexes, provided equilibrium was established. In the early stages of the experiment very little particulate MnO_x would have been present in the water column because the oxidation process is relatively slow at these low pHs; therefore lead-organic, and to a lesser extent lead-algal, interactions would have dominated.

Main removal mechanisms (Fig. 9). The added ionic lead rapidly became associated with the particulate phase. The main mechanism for the removal of lead from the water column was by association with the particulate phase and sedimentation of this material. If MnO_x-coated particulates were formed, as has previously been suggested, ionic lead would become associated with these in preference to algae. The lead did not appear to form non-ion-exchangeable species as did each of the other metals. This may simply be related to the faster rate of association of lead with the particulate matter. The main removal mechanism for lead is summarised below:

$$Pb^{2+} \longrightarrow \text{Pb-particulate } (MnO_x\text{-coated}) \longrightarrow \text{settling out}$$

4.1.3.4 Zinc

In the aquatic environment zinc is a relatively mobile element. In natural waters it may exist as the simple hydrated ion (Zn^{2+}), as inorganic complexes (e.g. $ZnCO_3$, $ZnOH^+$), as organic complexes (e.g. Zn-fulvate) or adsorbed to inorganic or organic colloids or particulates (Florence 1980, 1982). Florence (1980) found that organic complexes seem to be less important in the speciation of zinc than of copper, lead and mercury, although in some waters an appreciable proportion of the filterable zinc may be bound in colloidal organic forms (Benes and Steines 1975; Blutstein and Smith 1978; Hart and Davies 1981a). In three Australian freshwaters (Woronora Reservoir (Florence 1977), Lake Tarli Karng and Tarago Reservoir (Hart and Davies 1981b)), in excess of 80% of the filterable zinc was found to be in ion-exchangeable forms.

In the experiments reported here, there was some suggestion that some zinc was leached from the enclosure walls into the water column. The amount was around 450 mg or approximately 25% of the added amount. Zinc also appeared to be leached from the walls of the control enclosure.

The behaviour of zinc in the metal-loaded enclosure was in many respects similar to that of manganese (Fig. 8). For example, there was an initial rapid decrease in concentration due mainly to mixing of the added metal solution with the total water column; this appeared to take around seven or eight days to complete. The association of the added ionic zinc with algae appeared to be less important than for copper and lead. The initial speciation of zinc was dominated by ion-exchangeable forms, with only a small amount in particulate forms and none in non-ion-exchangeable forms. This observation may have been influenced by the release of ion-exchangeable forms of zinc from the enclosure material.

By Day 6 a considerable amount of the ion-exchangeable zinc had been converted into non-ion-exchangeable forms, and there was evidence that some zinc had been lost to the sediments (Fig. 9). This behaviour was very similar to that of manganese, and we speculate that over this four day period the ion-exchangeable zinc became associated with colloidal matter to produce non-ion-exchangeable complexes as manganese had done. The time taken for these forms to reach maximum concentration also supports this hypothesis.

The peak in the concentration of particulate zinc occurred some four days after that of ion-exchangeable zinc. This could be attributed to slow agglomeration of non-ion-exchangeable forms to produce particles, or to a slow rate of association of the non-ion-exchangeable forms with existing particulate matter.

By Day 15 all the non-ion-exchangeable and particulate zinc had been lost to the sediments. Calculations suggest that some 65% of the added zinc was removed from the water column by this time, however, this value is probably in error because leaching of zinc from the enclosure walls is suspected to have maintained an artificially high zinc concentration in the water column. The large amount of ion-exchangeable zinc remaining in the water column until the end of the study was also due to leaching from the enclosure walls. The same behaviour was observed in the control enclosure.

Main removal mechanisms (Fig. 9). The behaviour of zinc added to Island Billabong water followed closely that of manganese, and this suggests that the behaviour of zinc was strongly influenced by association with colloidal matter, as we have suggested for manganese. Calculation of the amount of the added zinc removed from the water column is difficult because of the suspected leakage of zinc from the enclosure walls. Despite this, it appears that most of the zinc was removed from the water column by the end of the experiment. Removal was mainly by association of ion-exchangeable zinc with colloidal matter which then either agglomerated to form particles or became associated with existing particles, which then settled out. The main removal mechanisms for zinc are summarised below:

$$Zn^{2+} \longrightarrow \text{Zn-particulate} \longrightarrow \text{settle out}$$

$$Zn^{2+} \longrightarrow \text{Zn-Coll} \longrightarrow \text{Zn-Coll-particulate} \longrightarrow \text{settle out}$$

4.1.3.5 Cadmium

Cadmium, like zinc, is quite a mobile metal in the aquatic environment. In natural waters it will exist predominantly in the form of free metal ions (Cd^{2+}) and simple inorganic complexes (e.g. $CdOH^{+}$, $CdCO_3$) (Florence 1982). Cadmium seems to be less likely to form organic complexes than do copper and lead (Florence 1980). There is some evidence that cadmium forms complexes with colloidal matter in some natural waters. For example, Hart and Davies (1981a) found that around 75% of the filterable cadmium in the freshwater section of the Yarra River was ion-exchangeable and the remainder was bound to colloidal matter. The colloidally bound cadmium was removed, probably by coagulation, in the estuarine part of the river. In two Australian reservoirs (Woronora Reservoir (Florence 1977) and Tarago Reservoir (Hart and Davies 1981b)), in excess of 80% of the filterable cadmium was found to be ion-exchangeable.

In the experiments reported here, the total cadmium concentration decreased rapidly between Day 1 and Day 2, mainly due to a marked reduction in the concentration of ion-exchangeable cadmium. This was similar to the other metals and was probably mainly due to mixing. The total cadmium concentration was not reduced to the calculated initial concentration until around Day 7 (Fig. 6); manganese and zinc behaved similarly. During the study period, ion-exchangeable forms dominated the cadmium speciation. The rather constant concentration of ion-exchangeable cadmium between Days 2 and 6 suggests that little additional mixing or interaction with colloidal or particulate matter occurred. Some non-ion-exchangeable forms of cadmium were observed by Day 6 (31% of the total), but these were rapidly removed from the water column. The rapid removal of ion-exchangeable cadmium observed between Days 6 and 15 may have resulted from direct sorption by sediments after complete mixing of the added cadmium with the water column. By Day 15, the concentrations of all forms of cadmium were below the analytical detection limit.

Main removal mechanism (Fig. 9). Essentially all the cadmium was lost from the water column in fifteen days. Over this period ion-exchangeable forms dominated the speciation of cadmium. The major mechanism by which cadmium was lost from the water column seems to be either direct uptake by epiphytes growing on the enclosure walls or uptake by bottom sediments. Around Day 6 there was some evidence that a small amount of the cadmium had been converted to non-ion-exchangeable forms and that these had become associated with particulate matter which then settled out of the water column.

$$\mathrm{Cd}^{2+} \longrightarrow \text{Cd-epiphytes}$$

$$\mathrm{Cd}^{2+} \longrightarrow \text{Cd-sediments}$$

5 CONCLUSIONS

Comparison of the behaviour of the metals, at natural concentrations, in the billabong and the control enclosure was difficult as all metal concentrations were very low and this imposed significant problems for the speciation studies undertaken. In fact, on a number of occasions the concentrations of the various metal fractions were below the analytical detection limits, and comparisons between the two systems could not be made. However, where such comparisons could reasonably be made, the behaviour of the metals in the enclosure was different from that in the billabong. Some reasons for these differences have been advanced. Comparisons of the behaviour of zinc were particularly difficult as the enclosure walls appeared to release a significant amount of zinc into the water column.

The conclusion at this stage must be that the metals studied do not behave in exactly the same manner in the enclosures as in the billabong. The differences, while significant at the very low concentrations found naturally in Island Billabong waters, are not expected to influence the usefulness of the enclosures in providing information on the behaviour of higher concentrations of metals added to this system.

All five metals added to the metal-loaded enclosure were found to be quite rapidly removed from the water column. For example, after fifteen days over 65% of each metal had been removed, presumably to the sediments and to the epiphytic growth that had built up on the walls of the enclosure. Study of the changes in the speciation of the added metals provided considerable insight into the mechanisms by which these metals are removed from the water column. The main removal pathways for each metal are shown in Figure 11.

The behaviour of manganese is believed to have significantly influenced the rapid removal of the other metals. We have postulated that particulate, and possibly also colloidal, forms of MnO_x are formed by the slow oxidation of Mn(II), and that these colloidal and particulate surfaces influenced the behaviour of the other added metals. Hart and Jones (1984) have shown that unfiltered Island Billabong waters at neutral pH, oxidation of Mn(II) occurs in a few days. They suggest that this oxidation is catalysed by bacteria.

Around 65% to 70% of the manganese added to the metal-loaded enclosure was removed from the water column in fifteen days. Removal appears to be by conversion of Mn(II) into non-ion-exchangeable forms, a relatively slow

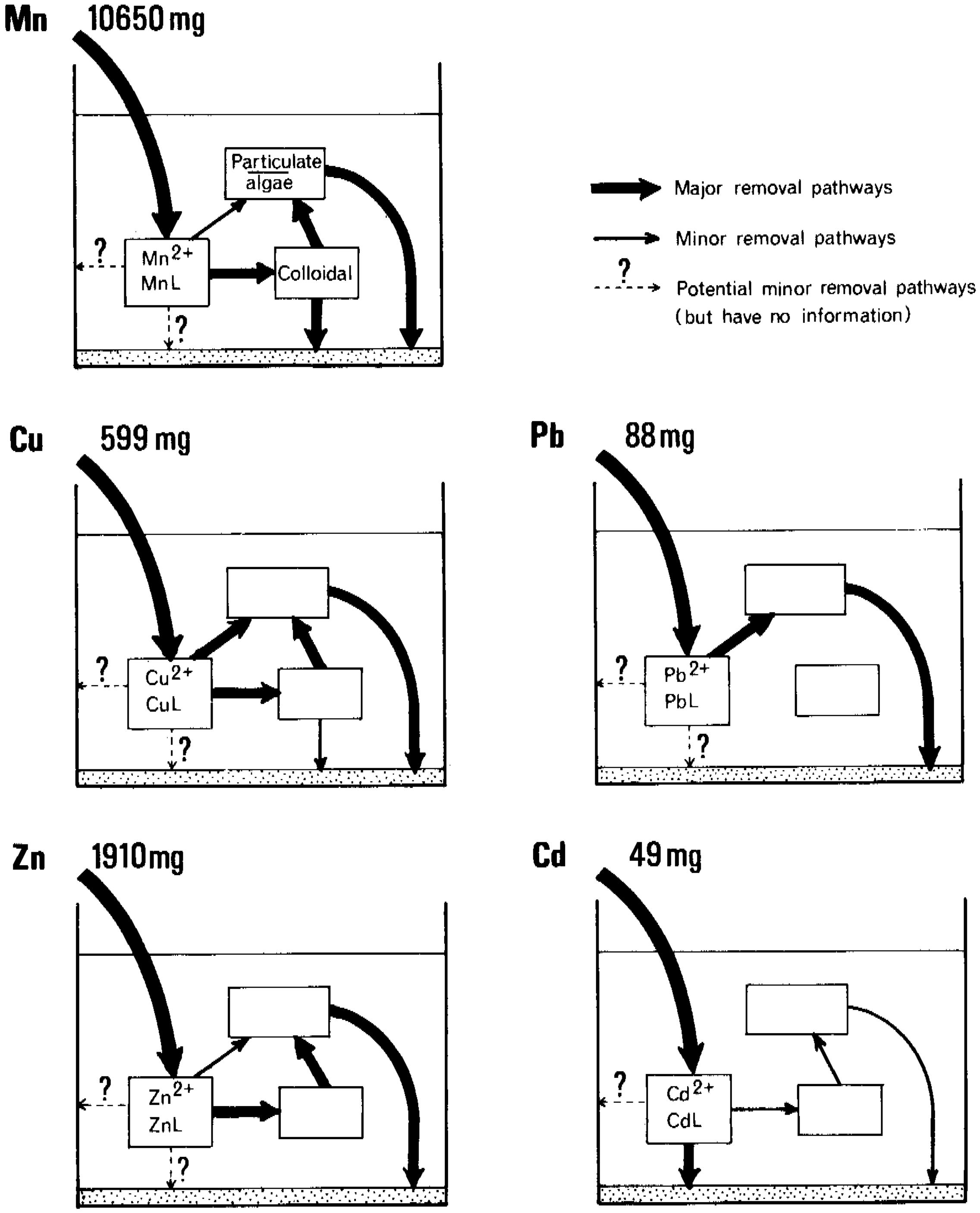

FIGURE 11 MAJOR PATHWAYS BY WHICH EACH OF THE FIVE METALS IS REMOVED FROM THE WATER COLUMN IN THE METAL-LOADED ENCLOSURE.

process, followed by agglomeration of these non-ion-exchangeable forms or their association with existing particulate matter, and the subsequent loss of these larger particles to the sediments. Some oxidation of Mn(II) directly on the surface of the particulate matter also appeared to occur. Manganese-algal interactions do not seem to play a significant part in the removal of manganese.

Part of the added ionic copper was very rapidly taken up by the phytoplankton and about 35% was lost to the sediments in the first day, probably by sedimentation of the algae killed by the copper (Hart et al. 1985b). After this initial loss, most of the copper in the water column was in ion-exchangeable forms, probably as Cu-fulvate complexes; a small amount was also associated with the particulate matter. Over the following four days most of the ion-exchangeable copper was converted into almost equal amounts of particulate and non-ion-exchangeable forms and by Day 15, almost all the copper added to the water column had been transferred to the sediments. Thus, after the initial uptake of copper by the algae, this metal is removed from the water column via two main pathways: (i) by association with particulate matter (probably coated with MnO_x) which subsequently settle out, and (ii) by the formation of non-ion-exchangeable (colloidal) forms (either Cu(II) or Cu-fulvates associated with MnO_x colloids) which agglomerate to form larger particles that settle out of the water column.

The behaviour of zinc closely followed that of manganese and this suggests that it was strongly influenced by association with colloidal MnO_x. Interpretation of the amount of the added zinc removed from the water column is difficult, as extra zinc was almost certainly released from the enclosure walls. Despite this, it appears that most of the zinc was removed from the water column by the end of the experiment, mainly by association of ion-exchangeable zinc with colloidal matter which then either agglomerated to form particles or became associated with existing particles, and then settled out.

The added cadmium was lost from the metal-loaded enclosure in fifteen days. Over this period ion-exchangeable forms dominated the speciation. The major mechanism by which cadmium was lost from the water column seems to have been direct uptake either by sediments or by epiphytes growing on the walls of the enclosure.

The added lead seemed to behave quite differently to the other metals. Soon after it was added to the enclosure, most of it became associated with the particulate phase. Sedimentation of this particulate matter was the main mechanism by which lead was removed from the water column. Calculations confirm that lead would become associated with MnO_x coated particulate matter in preference to association with algae. The lead did not appear to form non-ion-exchangeable species as did each of the other metals; this may simply be related to the faster rate at which lead becomes associated with the particulate matter.

A further series of experiments, using three enclosures, were undertaken during the 1981 Dry Season. Copper was added to one, a mixture of manganese and zinc to another and the third was kept as a control. The results will be published in the near future.

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APPENDIX

Concentrations of total, filterable and non-ion-exchangeable metal in Island Billabong, the control enclosure and the metal-loaded enclosure.

TABLE A1 CONCENTRATIONS OF METALS IN FRACTIONS OF SURFACE SAMPLES FROM ISLAND BILLABONG.

M_t = total metal; M_f = filterable metal; M_n = non-ion-exchangeable metal. All concentrations in µg/L.

Date	Fraction	Mn	Cu	Pb	Zn	Cd
6.xi.80	M_t	43	1.7	0.85	1.6	<0.25
	M_f	27	1.4	0.33	1.6	<0.25
	M_n	<0.5	<0.20	<0.20	<0.34	<0.25
7.xi.80	M_t	47	0.40	<0.20	2.4	<0.25
	M_f	40	0.27	<0.20	2.4	<0.25
	M_n	8.2	0.26	<0.20	<0.20	<0.25
9.xi.80	M_t	59	1.0	0.61	3.4	<0.25
	M_f	43	1.0	0.39	2.7	<0.25
	M_n	1.2	0.35	<0.20	0.21	<0.25
11.xi.80	M_t	61	0.54	0.49	4.1	<0.25
	M_f	57	0.36	<0.20	1.7	<0.25
	M_n	0.6	<0.20	<0.20	<0.20	<0.25
13.xi.80	M_t	71	0.60	0.79	2.4	<0.25
	M_f	50	0.20	<0.20	1.3	<0.25
	M_n	<0.5	<0.20	<0.20	<0.20	<0.25
20.xi.80	M_t	77	0.64	0.55	2.4	<0.25
	M_f	8.4	<0.20	<0.20	2.5	<0.25
	M_n	<0.5	<0.20	<0.20	2.3	<0.25
27.xi.80	M_t	87	0.40	0.41	6.1	<0.25
	M_f	80	<0.20	0.29	3.5	<0.25
	M_n	5.3	<0.20	<0.20	0.46	<0.25
4.xii.80	M_t	110	0.98	0.35	11.23	<0.25
	M_f	100	0.84	0.32	4.5	<0.25
	M_n	<0.5	0.64	0.37	0.53	<0.25

TABLE A2 CONCENTRATIONS OF METALS IN FRACTIONS OF SURFACE SAMPLES FROM THE CONTROL ENCLOSURE.

M_t = total metal; M_f = filterable metal; M_n = non-ion-exchangeable metal. All concentrations in µg/L.

Date	Fraction	Mn	Cu	Pb	Zn	Cd
6.xi.80	M_t	43	0.79	0.24	15	<0.25
	M_f	11	0.55	0.23	15	<0.25
	M_n	3.3	<0.20	0.24	0.45	<0.25
7.xi.80	M_t	3.3	<0.20	0.46	3.5	<0.25
	M_f	8.3	<0.20	<0.20	3.2	<0.25
	M_n	<0.5	<0.20	<0.20	0.68	<0.25
9.xi.80	M_t	34	0.58	0.23	16	<0.25
	M_f	5.4	<0.20	<0.20	13	<0.25
	M_n	<0.5	<0.20	<0.20	0.64	<0.25
11.xi.80	M_t	33	0.86	0.54	7.2	<0.25
	M_f	15	0.28	0.20	6.7	<0.25
	M_n	14	<0.20	0.22	3.5	<0.25
13.xi.80	M_t	34	0.59	0.38	7.7	<0.25
	M_f	14	<0.20	0.26	7.2	<0.25
	M_n	<0.5	<0.20	<0.20	<0.20	<0.25
20.xi.80	M_t	26	1.3	0.50	11	<0.25
	M_f	0.8	0.82	<0.20	7	<0.25
	M_n	<0.5	0.44	<0.20	2.3	<0.25
27.xi.80	M_t	26	1.0	0.81	6.8	<0.25
	M_f	1.1	<0.20	<0.20	8.1	<0.25
	M_n	0.8	<0.20	<0.20	<0.20	<0.25
4.xii.80	M_t	33	1.0	0.92	4	<0.25
	M_f	6.2	0.48	0.28	13	<0.25
	M_n	<0.5	<0.20	<0.20	<0.20	<0.25

TABLE A3 CONCENTRATIONS OF METALS IN FRACTIONS OF SURFACE SAMPLES FROM THE METAL-LOADED ENCLOSURE.

M_t = total metal; M_f = filterable metal; M_n = non-ion-exchangeable metal. All concentrations in µg/L.

Date	Fraction	Mn	Cu	Pb	Zn	Cd
6.xi.80	M_t	1020	42	7.6	180	3.8
	M_f	990	26	2.6	170	3.5
	M_n	360	<0.20	<0.20	18	<0.25
7.xi.80	M_t	450	15	3.2	80	1.8
	M_f	400	13	0.63	68	1.6
	M_n	1.3	0.41	<0.20	0.38	<0.25
9.xi.80	M_t	430	13	2.7	64	1.7
	M_f	340	9.1	0.57	58	1.7
	M_n	170	4.3	0.37	28	<0.25
11.xi.80	M_t	410	13	2.5	63	1.4
	M_f	320	6.4	0.82	50	1.4
	M_n	240	<0.20	<0.20	28	0.44
13.xi.80	M_t	350	7.9	0.75	53	1.1
	M_f	240	4.3	0.37	25	0.89
	M_n	130	3.4	0.35	19	<0.25
20.xi.80	M_t	100	2.5	0.90	19	<0.25
	M_f	13	0.43	0.55	19	<0.25
	M_n	<0.5	<0.20	<0.20	0.70	<0.25
27.xi.80	M_t	76	4.4	2.6	13	<0.25
	M_f	76	2.9	1.2	10	<0.25
	M_n	1.2	1.3	0.63	0.37	<0.25
4.xii.80	M_t	100	1.9	0.97	11	<0.25
	M_f	97	0.56	<0.20	11	<0.25
	M_n	<0.5	<0.20	<0.20	0.77	<0.25

TABLE A4 CONCENTRATIONS OF METALS IN FRACTIONS OF SAMPLES TAKEN AT 1.5 m DEPTH FROM ISLAND BILLABONG, THE CONTROL ENCLOSURE AND THE METAL-LOADED ENCLOSURE.

M_t = total metal; M_f = filterable metal; M_n = non-ion-exchangeable metal. All concentrations are in µg/L.

Site	Date	Fraction	Mn	Cu	Pb	Zn	Cd
Island Billabong	6.xi.80	M_t	48	0.65	0.44	1.2	<0.25
		M_f	31	<0.20	0.40	0.89	<0.25
		M_n	3.6	<0.20	<0.20	0.2	<0.25
	11.xi.80	M_t	70	1.1	1.8	3.7	<0.25
		M_f	64	0.72	0.51	1.6	<0.25
		M_n	<0.5	0.32	<0.20	<0.20	<0.25
Control Enclosure	6.xi.80	M_t	47	0.57	0.80	9.9	<0.25
		M_f	6.4	<0.20	<0.20	3.2	<0.25
		M_n	<0.5	<0.20	<0.20	2.0	<0.25
	11.xi.80	M_t	41	0.87	4.1	9.1	<0.25
		M_f	11	0.56	0.31	4.3	<0.25
		M_n	<0.5	0.30	<0.20	0.68	<0.25
Metal-loaded Enclosure	6.xi.80	M_t	62	1.5	0.81	8.4	<0.25
		M_f	2.5	0.94	0.21	7.4	<0.25
		M_n	<0.5	0.95	0.20	1.8	<0.25
	11.xi.80	M_t	410	12	1.7	68	1.3
		M_f	240	5.5	<0.20	59	1
		M_n	140	3	<0.20	25	0.65

SUPERVISING SCIENTIST FOR THE ALLIGATOR RIVERS REGION

RESEARCH PUBLICATIONS

Research Reports (RR) and Technical Memoranda (TM)

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TM 2	Transport of trace metals in the Magela Creek system, Northern Territory. II. Trace metals in the Magela Creek billabongs at the end of the 1978 dry season. December 1981 (pb - 23 pp)	Davies, S.H.R., Hart, B.T.
TM 3	Transport of trace metals in the Magela Creek system, Northern Territory. III. Billabong sediments. December 1981 (pb - 23 pp)	Thomas, P.A., Davies, S.H.R., Hart, B.T.
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