Technical Memorandum 7

Capacity of Waters in the Magela Creek System to Complex Copper and Cadmium

B.T. Hart and S.H.R. Davies

Supervising Scientist for
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CAPACITY OF WATERS IN THE MAGELA CREEK SYSTEM, NORTHERN TERRITORY, TO COMPLEX COPPER AND CADMIUM

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CONTENTS

TABLES

FIGURES

SUMMARY

Hart, B.T. and Davies, S.H.R. (1984). Capacity of waters in the Magela Creek system, Northern Territory, to complex copper and cadmium. Supervising Scientist for the Alligator Rivers Region, Tech. Mem. 7.

Two methods were used to determine the concentrations of copper-binding ligand (complexing capacity) and conditional formation constants for waters collected from the Magela Creek system, Northern Territory.

These data are particularly important in estimating the concentrations of toxic forms of copper that may result from particular effluent discharge strategies for the Ranger uranium operation.

An amperometric titration technique, employing differential pulse anodic stripping voltammetry at pH 6.0, was used to determine the copper-complexing capacity in water samples taken from five billabongs at the end of the 1979 dry season and from five sites in Magela Creek during the 1980 wet season. These results are discussed in detail and a number of management implications drawn from them.

An ion-exchange resin technique, employing Dowex 50WX8 at pH 7.0, was used to determined the copper-complexing capacity in three billabong waters collected during the 1979 dry season. The results are discussed and compared with those determined at the lower pH using the other technique. A preliminary study of the cadmium-complexing capacity using the ion-exchange resin technique is also reported.

1 INTRODUCTION

Trace metals may exist in a number of physico-chemical forms (speciation) in natural waters (Florence and Batley 1980; Forstner and Wittman 1979; Hart and Davies 1978). The speciation will be determined by factors such as pH, redox potential, and the types and concentrations of inorganic ligands such as hydroxide and bicarbonate, organic ligands such as fulvic acid, and colloidal matter present.

The 'bio-availability' of many trace metals is influenced by their speciation. Considerable evidence shows that the free ionic forms of several trace metals (e.g. copper, cadmium, lead and zinc) are the most toxic forms to phytoplankton (Sunda and Guillard 1976; Wong et al. 1978; Van den Berg et al. 1979; Gachter and Mares 1979; Gachter et al. 1978; Guy and Kean 1980), invertebrates (Andrew et al. 1977; Lake et al. 1979) and fish (Davies et al. 1976; Pagenkopf et al. 1974; Brown et al. 1974). Complexed forms appear to be non-toxic or at least considerably less toxic than the free metal ions.

Most natural waters have a capacity to reduce the toxicity of added trace metals (Sunda and Guillard 1976; Gachter et al. 1978; Andrew et al. 1977; Davies et al. 1976; Baccini and Suter 1979). This has been attributed to the complexation of the added metal by ligands present in the water and is generally referred to as the 'complexing capacity' of the water.

Since toxic trace metals may be added to the Magela Creek system as a result of the uranium mining and milling operations, it is of some importance to determine the capacity of these waters to complex any added trace metals. Such information will be important to the Supervising Scientist in establishing water quality standards for the operation.

This report contains the results of an investigation aimed at determining the copper-complexing capacity of waters from a number of billabongs at the end of the 1979 dry season and from the Magela Creek during the 1980 wet season. An amperometric titration technique was used to determine both the concentration of copper-binding ligand and the conditional formation constant in each water sample. An alternative technique, involving an ion exchange resin, was also investigated.

2 THEORY

When trace metal ions, such as copper, are added to natural water, they may become associated with the various inorganic and organic ligands (and colloids) as well as with suspended matter. In waters from which suspended matter has been removed, the total filterable metal concentration $[M_f]$ will be given by:

$$[M_f] = [M^{2+}] + [MI] + [ML] \qquad (1)$$

where: $[M^{2+}]$ = concentration of free metal ions

$[MI]$ = concentration of inorganic metal complexes

= $[MOH^+] + [M(OH)_2] + [MCO_3] + [M(CO_3)_2^{2-}] + \ldots$

and $[ML]$ = concentration of complexes with organic ligands and colloids.

When equilibrium has been established, the relation between the concentrations of ML and M^{2+} can be described by the equation:

$$[ML] = \frac{{}^*K\,[M^{2+}]\,[L_t]}{1 + {}^*K\,[M^{2+}]} \qquad (2)$$

where: $[L_t]$ = total concentration of metal-binding ligands (assuming one binding site per ligand molecule)

= $[L] + [ML]$

$[L]$ = concentration of free uncomplexed ligands

${}^*K$ = conditional formation constant for the reaction

$M^{2+} + L \rightleftharpoons ML$

= $[ML]/[M^{2+}]\,[L]$

Generally $[L_t]$ is referred to as the complexing capacity. However, to calculate the amount of metal complexed at a particular trace metal concentration it is also necessary to know the value of ${}^*K$, the conditional formation constant.

Methods that aim to measure $[L_t]$ and ${}^*K$ involve the titration of a natural water (from which suspended solids have been removed) by addition of known amounts of metal and, after a suitable equilibration time, measurement of the concentration of uncomplexed metal ion or a related quantity M', that will generally involve metal ion, metal-inorganic and perhaps weaker metal-organic complexes.

A typical titration curve is shown in Figure 1. The copper concentrations are derived from the peak currents measured by anodic stripping voltammetry (ASV) after additions of different amounts of copper. The curve is seen to have two distinct regions. For low amounts of added copper, the increase in [Cu'] is very small since most is complexed. However , when larger amounts of copper (in excess of $[L_t]$) have are added [Cu'] increases rapidly because the available binding ligands have all been complexed. For the curve to have a distinct 'break', the product ${}^*K\,[L_t]$ must be considerably greater than unity (Shuman and Woodward 1977; Hanck and Dillard 1977).

Of the methods commonly in use (see Hart (1980) for a full discussion) only the ion selective electrode (ISE) technique is a direct analytical probe for copper ions. With other methods, the concentration of free copper ion must be calculated. For example, anodic stripping voltammetry measures 'labile' copper from which the free copper ion concentration is then obtained by correction for any copper-inorganic species and labile copper-organic species.

Equation (2) may be rearranged into a more convenient form:

$$\frac{[Cu^{2+}]}{[CuL]} = \frac{[Cu^{2+}]}{[L_t]} + \frac{1}{{}^{*}K[L_t]} \qquad (3)$$

Thus a plot of $[Cu^{2+}]/[CuL]$ vs $[Cu^{2+}]$ should produce a straight line with slope = $1/[Lt]$ and intercept = $1/{}^{*}K[Lt]$ provided there is only one type of complexing ligand and only 1:1 complexes are formed (Van den Berg 1979).

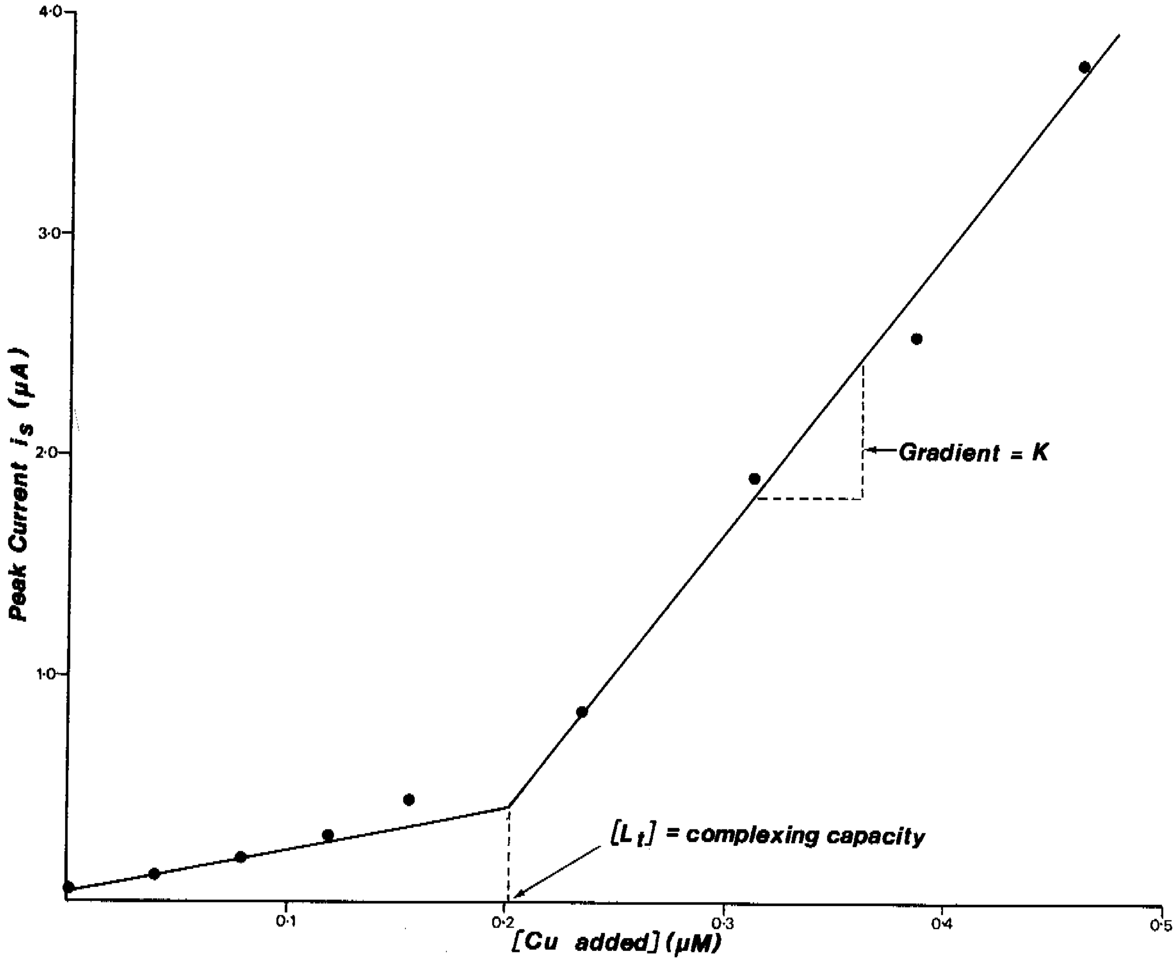

FIG. 1 AMPEROMETRIC TITRATION CURVE FOR COPPER ADDED TO FILTERED WATER COLLECTED FROM GULUNGUL BILLABONG (WEED BED).

3 AMPEROMETRIC TITRATION TECHNIQUE

3.1 Sampling and Analytical Procedures

Three water samples were taken from the middle of each billabong using acid-washed one-litre plastic bottles held approximately 10 cm below the water surface. One sample was used for general analysis and one for complexing capacity (CC) determinations on unfiltered water. The third was filtered (0.4 µm Nucleopore) as soon as possible (maximum delay 24 h) and used for CC determination. All filtration was done at the Jabiru laboratory of the Alligator Rivers Region Research Institute.

Determinations of complexing capacity were carried out in Melbourne. The delay between sampling and CC determination was up to 2 months, during which time samples were kept at 4°C in the dark.

The analytical procedure for determining complexing capacity adopted here is essentially that outlined by Shuman and Woodward (1977). Differential pulse anodic stripping voltammetry was used in the amperometric titration to determine the labile metal concentration. A PAR 174 polarographic analyser coupled with a hanging mercury drop working electrode was employed.

Deposition was carried out for 10 minutes at -0.6 V vs Ag/AgCl with the solution stirred for all but the last 15 seconds of the deposition time. The detailed procedure employed was as follows (for instrument settings see Hart and Davies (1978) p. 20):

20 mL of the sample was placed in the cell and 0.2 mL buffer (1 M sodium acetate adjusted to pH 6.05) was added. High purity nitrogen was bubbled through the sample for 10 minutes to remove oxygen and, during the analysis, was diverted over the top of the sample. After the voltammogram had been completed, the sample was spiked with copper solution and allowed to equilibrate for 10 minutes; nitrogen was bubbled through the solution during this time. The deposition and stripping steps were repeated.

This procedure was continued until sufficient data were obtained to draw a titration curve.

3.2 Treatment of Experimental Data

A peak stripping current i_s was determined at each concentration of added copper. The amperometic titration technique is based on the following assumptions (Shuman and Woodward 1977):

(i) The complex CuL does not contribute to the stripping current, i_s;

(ii) $i_s = \chi\,[Cu']$
where $[Cu'] = [Cu^{2+}] + [CuOH^{+}] + [Cu(OH)_2] + [CuCO_3] + [CuOAc^{+}]$;

At pH 6.0 with the acetate buffer used

$$[Cu'] = [Cu^{2+}] + [CuOAc^{+}]$$
$$= 2.41\ [Cu^{2+}]$$

(iii) at the start of the experiment $[L_t] > [Cu']$.

A computer program COMPCAP has been written to input the i_s and $[Cu^{2+}]$ data and produce the corresponding $[L_t]$ and log $^*K$ values. A listing of the program is given in Appendix A.

The steps in the program are as follows:

(i) plot i_s vs $[Cu_{added}]$ and use the upper straight line portion to calculate χ (see Fig. 1)

(ii) since $[Cu'] = i_s/\chi$, the calculated value of χ can now be used to calculate the value of $[Cu']$ corresponding to each value of $[Cu^{2+}]$

(iii) now

$$[Cu_{total}] = [Cu_{orig}] + [Cu_{added}]$$
$$= [Cu'] + [CuL]$$
$$= 2.41\ [Cu^{2+}] + [CuL]$$

(iv) the above relationships can now be used to calculate $[CuL]$ and hence to calculate the ratio $[Cu']/[CuL]$ or $[Cu^{2+}]/[CuL]$

(v) a plot of $[Cu^{2+}]/[CuL]$ vs $[Cu^{2+}]$ should produce a straight line with gradient $= 1/[L_t]$ and intercept $= 1/^*K[L_t]$

(vi) it was found necessary to place two constraints on the actual data plotted to avoid errors being too large. These were that:

$[CuL] > 0.01\ \mu M$, and that
$[Cu']/[CuL] < 5$

3.3 Results and Discussion

The amperometric titration technique was used to determine the copper complexing capacity and conditional formation constants at pH 6.0 for waters taken:

(a) during the 1979 dry season in late October and early November from five billabongs; Gulungul, Georgetown, Island, Leichhardt and Jabiluka (Fig.2).

(b) during the wet season in March 1980 from two locations in Gulungul Billabong and three locations in Magela Creek (Fig. 3).

All experimental data are recorded in Appendix B.

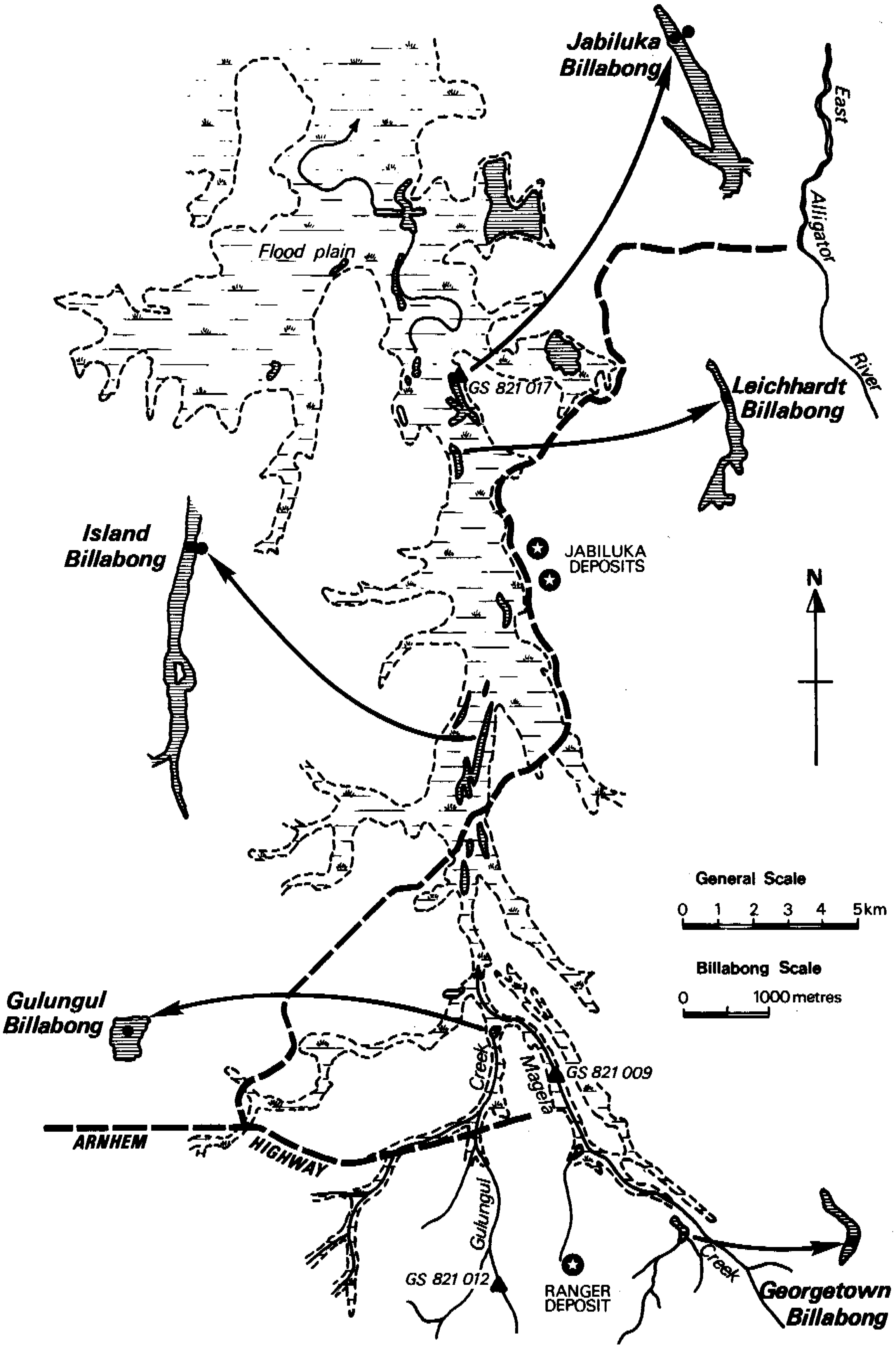

FIG. 2 SAMPLE LOCATIONS - DRY SEASON 1979

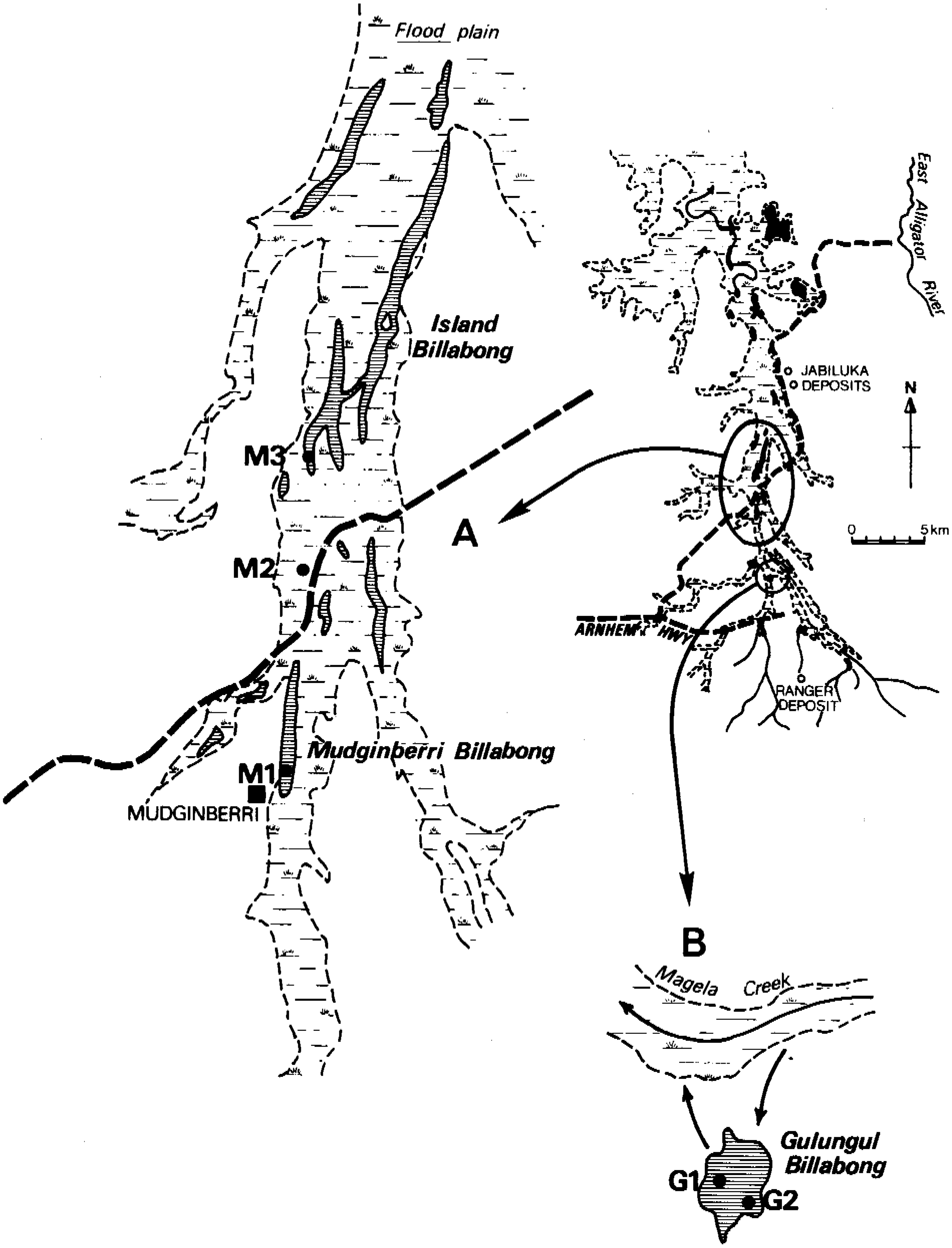

FIG. 3 SAMPLE LOCATIONS - WET SEASON 1980

TABLE 1 COPPER-COMPLEXING CAPACITIES AND FORMATION CONSTANTS AT pH 6.0 FOR WATER SAMPLES TAKEN DURING 1979 LATE-DRY SEASON[a]

Billabong	Date of Sampling	Filtered[b] or Unfiltered	$[L_t]$			$^*K$ x 10^{-7}	log $^*K$
			(μM)	(μgCu/L)	(μmol/mg DOC)		
Gulungul	25 Oct.	Filtered	0.46 ± 0.01	29.0	0.03	4.37 ± 0.48	7.6
		Filtered	0.434 ± 0.008	27.5	0.03	3.65 ± 0.24	7.5
Island	1 Nov.	Unfiltered	0.14 ± 0.01	9.1	0.01	7.1 ± 2.6	7.9
		Filtered	0.095 ± 0.009	6.0	0.01	18.8 ± 1.7	8.3
Jabiluka	4 Nov.	Unfiltered	0.236 ± 0.002	15.0	1.01	33.8 ± 1.3	8.5
		Filtered	0.067 ± 0.002	4.3	0.006	12.5 ± 9.1	8.1
Georgetown	29 Oct.	Filtered	0.24 ± 0.02	15.0	0.02	4.2 ± 1.2	7.6
Leichhardt	31 Oct.	Unfiltered	0.202 ± 0.005	12.8	-	11.8 ± 1.7	8.1
		Filtered	0.147 ± 0.007	9.3	-	9.3 ± 3.5	8.0

[a] Amperometric technique used

[b] Filtration through 0.45 μm Nucleopore filter

3.3.1 Dry season samples

Results for the copper-complexing capacity and formation constants are given in Table 1.

3.3.1.1 Gulungul Billabong

At the time of sampling, Gulungul Billabong was less than 1 metre deep and the water was acidic (pH 4.90), with high conductivity (236 µS/cm) and turbidity (suspended solids (SS) 1240 mg/L, turbidity 170 NTU). The dissolved organic carbon (DOC) level was also elevated (16.9 mg/L).

The copper concentration in unfiltered water taken from this billabong in November 1979 was: 7.4 µg/L (filterable (0.4 µm) 0.95 µg/L and ion-exchangeable 0.51 µg/L). The copper concentration increased almost eight-fold between July and November 1979, in July a value of 0.93 µg/L being recorded. The concentration of filterable copper increased by only a very small amount from 0.81 to 0.95 µg/L. At the end of the dry season, 54% of the filterable copper was in ion-exchangeable forms. We have no data to indicate the proportions at other times during the 1979 dry season but such data were being collected for two billabongs (Gulungul and Island) during the 1980 dry season.

Filtered waters (0.4 µm) from Gulungul Billabong contained the highest concentration of copper-binding ligands of any of the waters tested (Table 1). The formation constant at pH 6.0 (log $^{*}K$ = 7.5) indicated that strong copper complexes were formed. The two replicate samples (Table 1) showed very good agreement.

The concentration of copper-binding ligands and conditional formation constant can be used to calculate the speciation of copper added to this water. This was done for Gulungul Billabong using the experimentally determined parameters. The results are plotted in Figure 4 and indicate that, within the range of copper concentrations found naturally (0.001-0.01 µM = 0.06-0.6 µg/L), and for a water pH of 6.0, more than 94% would be complexed by the ligands present.

For comparative purposes the proportion of filterable copper complexed by water from Magela Creek during the wet season are also shown in Figure 4. This water would complex more than 90% of the copper up to concentrations of 0.01 µM. At higher concentrations than this, Gulungul Billabong water would be more effective at binding the copper.

3.3.1.2 Island Billabong

The quality of Island Billabong water did not change dramatically over the dry season; it remained almost neutral (pH 7.04) and clear (SS 7.1, turbidity 6.3 NTU) with a slightly elevated conductivity (42 µS/cm).

The copper concentration in unfiltered water taken from this billabong decreased slightly over the dry season (from 0.83 to 0.67 µg/L) while the filterable metal concentration remained almost constant (0.57 to 0.58 µg/L). The reason for this has not been determined.

The concentrations of copper-binding ligands in both filtered and unfiltered waters were low (Table 1). However, the copper complexes were more

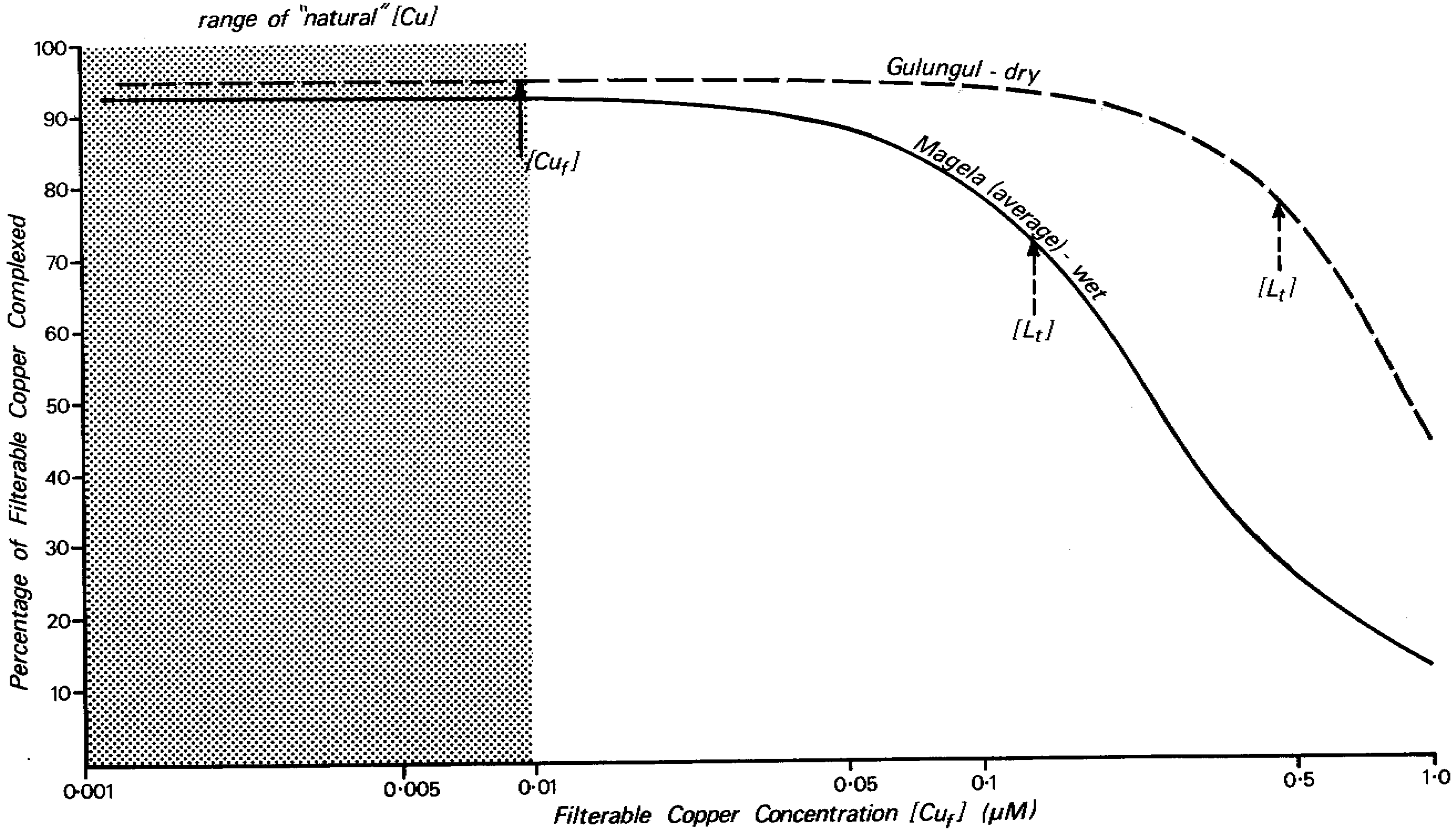

FIG. 4 FRACTION OF THE FILTERABLE COPPER CONCENTRATION COMPLEXED IN WATERS FROM:

— — — GULUNGUL BILLABONG DURING THE DRY SEASON

——— MAGELA CREEK DURING THE WET SEASON

stable than were those in Gulungul Billabong (compare log $^*K$ values). At natural copper concentrations, Island and Gulungul Billabong waters have approximately the same capacity to bind copper.

3.3.1.3 Jabiluka Billabong

As the dry season progresses this floodplain billabong becomes increasingly turbid. In November 1979 the suspended solids concentration was 240 mg/L and the turbidity 125 NTU. At that time the waters were slightly acidic (pH 6.52) with a DOC of 11 mg/L.

Copper concentration recorded in the late-dry season (November) was 9.0 μg/L (filterable 1.7 μg/L and ion-exchangeable 0.2 μg/L). The high copper concentration is no doubt a reflection of the increase in suspended solids concentration; the concentration of copper in the particulate matter was 30 μg/g.

The concentration of copper-binding ligands was 0.236 μM in the unfiltered sample (includes binding by the particulate matter) and 0.067 μM in the filtered sample. The higher value in the unfiltered sample indicates that the suspended material also has a capacity to complex copper. This suspended material in Jabiluka Billabong contained only 2% organic carbon by weight and was calculated to have a complexing capacity of 45 μg Cu/g SS.

The formation constant was 8.5 for the unfiltered sample and 8.1 for the filtered sample. Using the latter value we calculate that 88% of the copper present would be complexed.

3.3.1.4 Georgetown Billabong

By the end of the dry season, this backflow billabong had very high levels of suspended solids (3030 mg/L) mainly in the form of fine clays, and contained less than 0.4% organic carbon. The waters were acidic (pH 5.82) and had increased in conductivity from about 15 μS/cm to 63 μS/cm by the end of the dry season. The DOC concentration was 13.1 mg/L.

The copper concentration was relatively high (21.6 μg/L), the copper load being mostly associated with the suspended solids. The copper concentration of the suspended solids was calculated to be 7.1 μg/g. The filterable copper concentration was extremely low at 0.14 μg/L, being less than the mean concentration recorded in the previous wet season (0.2 μg/L). Some increase might have been expected owing to evaporative concentration.

Filtered water from this billabong was found to contain a quite high concentration of copper-binding ligands (0.24 μM). The formation constant was 7.6, the same as that obtained for Gulungul Billabong water. These data indicate that water from Georgetown Billabong will bind more than 90% of copper at concentrations below 0.01 μM.

3.3.1.5 Leichhardt Billabong

Although this billabong is situated on the flood plain (Fig. 2) it exhibits characteristics more like those of a channel billabong. At the end of the dry season Leichhardt Billabong water remained relatively clear (SS 7.3 mg/L; turbidity 29 NTU) and nearly neutral, although there was some increase in conductivity (114 μS/cm vs 15 μS/cm during the wet season). These data should be compared with those for Jabiluka - a typical floodplain billabong (Davies and Hart 1980).

All of the copper was present in filterable form at a concentration of 0.98 µg/L. This was approximately double the wet season concentration.

The concentrations of copper-binding ligands in unfiltered and filtered waters were similar to, but slightly higher than, those found in Island Billabong. The formation constants were similar for both billabongs. More than 93% of copper present in filtered waters would be complexed.

The copper adsorption capacity of the particulate matter from Leichhardt and Island Billabongs was similar (Island 400 µg Cu/g SS, Leichhardt 480 µg Cu/g SS) and was at least an order of magnitude greater than that of the suspended matter from Jabiluka Billabong. This significant difference between the sorption capacities of suspended matter from Island and Leichhardt Billabongs on the one hand, and from Jabiluka Billabong on the other is possibly due to the fact that in the first two billabongs suspended matter consisted mainly of phytoplankton and in the last it consisted of fine clays.

3.3.2 Wet season samples

Results for copper-complexing capacity and formation constants for five samples collected during the 1980 wet season are given in Table 2.

3.3.2.1 Gulungul Billabong

Two water samples were taken in March 1980 from Gulungul Billabong, one in open-water near the centre of the billabong (G1) and the other in weed beds closer to the shore (G2) (Fig. 3). The complexing capacity was determined at pH 6.0 on both filtered and unfiltered samples.

There were only minor differences in the qualities of water collected at the two sites. The pH, conductivity and DOC were similar (G1: pH 6.13, K 13.1 µS/cm, DOC 5.8 mg/L; G2: pH 6.38, K 11.3 µS/cm, DOC 6.6 mg/L). There was a slightly higher suspended solids concentration in the weed-bed sample (16.4 mg/L vs 10.4 mg/L) and, somewhat unexpectedly, the total organic carbon (TOC) in the open water was greater than in the weed bed (12.7 mg/L vs 7.0 mg/L).

The copper concentrations recorded at the two sites were quite different. In the open water samples the total copper concentration was 0.32 µg/L (filterable copper concentration 0.19 µg/L) while in the weed bed the copper concentration was 1.4 µg/L (filterable copper 0.29 µg/L).

The concentrations of copper-binding ligands in filtered and unfiltered samples from the open-water site were somewhat different, but concentrations in the weed-bed samples were similar (see Table 2). The log $^*K$ values were between 7.4 and 8.2.

The amount of copper bound per unit mass of DOC was quite low (0.02-0.03 µmol Cu/mg DOC).

TABLE 2 COPPER-COMPLEXING CAPACITIES AND FORMATION CONSTANTS AT pH 6.0 FOR WATER SAMPLES TAKEN DURING 1980 WET SEASON[a]

Billabong	Date of Sampling	Filtered[b] or Unfiltered	$[L_t]$ (μM)	$[L_t]$ (μgCu/L)	$[L_t]$ (μmol/mg DOC)	$^*K \times 10^{-7}$	log $^*K$
Corridor							
Mudginberri (M1)	3 March	Unfiltered	0.18 ± 0.11	11.4	0.03	5.1 ± 1.3	7.76
		Filtered	0.14 ± 0.03	9.1	0.03	3.6 ± 3.8	7.6
Flood plain (M2)	3 March	Unfiltered	0.081 ± 0.007	5.2	0.02	355 ± 175	9.6
		Filtered	0.068 ± 0.007	4.3	0.01	11.0 ± 12.9	8.0
Island (M3)	3 March	Unfiltered	0.16 ± 0.02	10.0	0.03	3.6 ± 1.6	7.6
		Filtered	0.14 ± 0.01	8.8	0.03	6.0 ± 3.2	7.8
Gulungul Billabong							
Open Water (G1)	1 March	Unfiltered	0.21 ± 0.02	13.3	0.02	2.4 ± 0.9	7.4
		Filtered	0.13 ± 0.01	8.1	0.02	7.0 ± 3.4	7.8
Weed Bed (G2)	1 March	Unfiltered	0.188 ± 0.004	11.9	0.03	6.3 ± 1.2	7.8
		Filtered	0.184 ± 0.009	11.7	0.03	14.8 ± 6.3	8.2

[a] Amperometric technique used

[b] Filtration through 0.45 μm Nucleopore filter

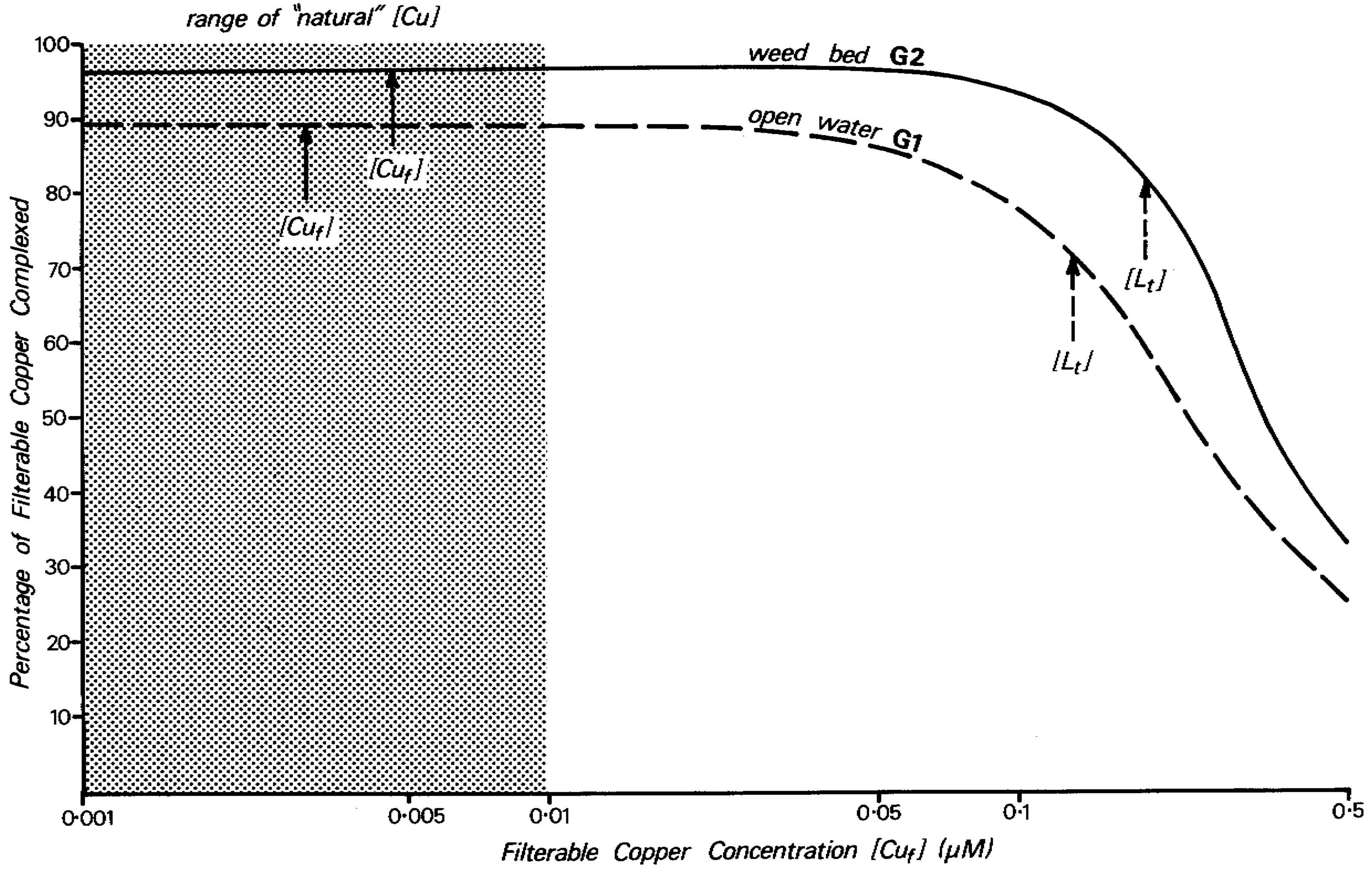

FIG. 5 FRACTION OF THE FILTERABLE COPPER COMPLEXED IN WATERS FROM GULUNGUL BILLABONG

Filtered water from the weed-bed sample had a slightly greater capacity to bind copper (Table 2; Fig. 5) than had the open-water sample. In this water, over 96% of the copper at 'natural' levels (less than 0.01 µM = 0.6 µg/L) would be bound. At higher concentrations (approaching 10 µg/L), the proportion would be a little less (approx. 85%). For an order of magnitude increase in total copper concentration above natural (i.e. 0.01 to 0.1 µM), the fraction in the ionic form would increase from 4% to approximately 15%; the ionic concentration, however, would increase almost forty times, from 0.0004 to 0.015 µM. Such a concentration could prove toxic to phytoplankton (Gachter and Mares 1979).

3.3.2.2 Magela Creek Water

Samples were taken from Magela Creek at three locations: at Mudginberri Billabong (M1), in the Mudginberri corridor flood plain just north of the crossing (M2) and Island Billabong (M3) (Fig. 3).

Generally the water quality was similar in each sample. However, a major change was noted in the suspended solids concentrations between the Mudginberri Billabong and the floodplain samples, which were approximately the same (12.8, 11.1 mg/L), and the Island Billabong sample where the level was very low (2.2 mg/L). This is possibly due to the 'filtering' effect of the water-flow through dense macrophytes upstream of the last sampling site. The TOC and DOC concentrations were very similar at all three locations (TOC 5.3 µg/L; DOC 4.6-5.0 µg/L).

The copper concentrations showed some variation. However, the mean values were very similar to those recorded in the previous wet season (0.38 ± 0.08 µg/L vs 1979 wet season 0.41 ± 0.16 µg/L; filterable 0.26 ± 0.11 µg/L vs 1979 wet season 0.30 ± 0.09 µg/L).

The concentrations of copper-binding ligands and log $^*K$ data are recorded in Table 2. There was little difference in concentrations of copper-binding ligands determined in filtered and unfiltered samples taken from Mudginberri and Island Billabongs. This makes it difficult to estimate the copper sorptive capacity of the particulate matter transported by Magela Creek during the wet season. Preliminary calculations suggest that this capacity could be similar to that found for particulate matter in Island and Leichhardt Billabongs (i.e. 400-500 µg Cu/g SS). This is a little surprising since it is considered that the major amount of this particulate matter is fine-grained sand (SiO_2) particles, which would have a low adsorptive capacity. This aspect will be further investigated during the 1980-81 wet season.

Essentially no difference was found in the copper-complexing capacity of filtered waters from Island and Mudginberri Billabongs. Both had concentrations of copper-binding ligands around 0.14 µM (9 µgCu/L) at pH 6.0. The sample collected from the flood plain contained approximately half this concentration (0.07 µM).

With the exception of the unfiltered sample taken from the flood plain, the log $^*K$ values were in the range 7.6 to 8.0 which is similar to values recorded in Gulungul Billabong during the wet and to those recorded in billabong waters during the dry season.

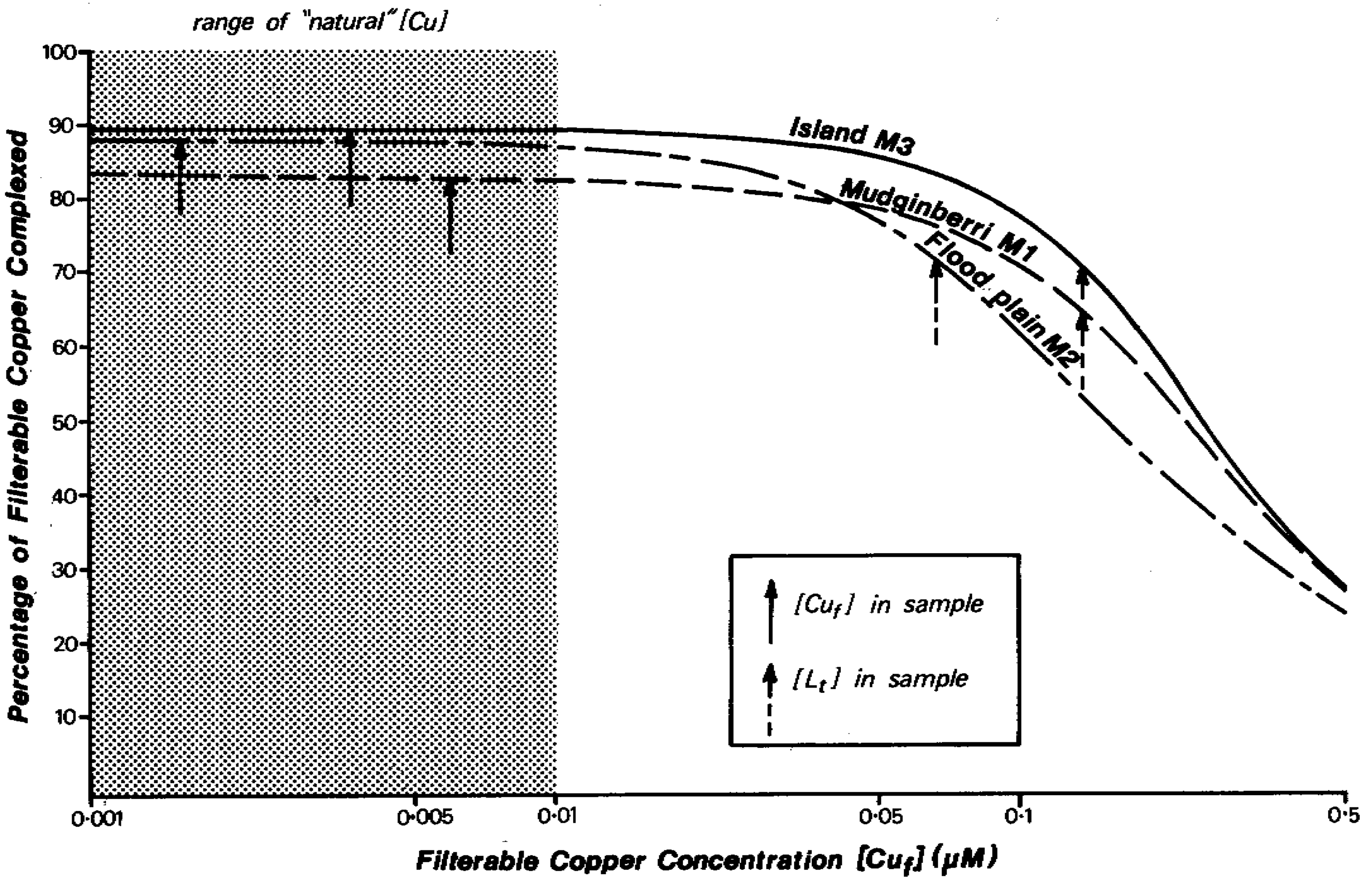

FIG. 6 FRACTION OF THE FILTERABLE COPPER COMPLEXED IN WATERS COLLECTED FROM MAGELA CREEK

The percentage of added copper complexed by these waters is shown in Figure 6. The values ranged between 83 and 89%, water collected at Mudginberri Billabong complexing the least amount.

3.4 Conclusions

3.4.1 Dry season samples

(a) The water quality in the five billabongs studied varied dramatically over the dry season.

(b) The concentrations of copper-binding ligands measured at pH 6.0 varied from a low value of 0.07 μM in filtered Jabiluka Billabong water to a high value of 0.45 μM in filtered Gulungul Billabong water; these values are equivalent to 4.3 and 29 μg Cu/L respectively.

(c) In each billabong tested the unfiltered sample had a higher concentration of copper-binding ligands than the filtered sample. This additional binding capacity resulted from the sorptive capacity of the particulate matter. There were marked differences however in this sorptive capacity, which appeared to depend upon the type of particulate material. For example, the highly organic particulate matter from Island and Leichhardt Billabongs had a much higher sorptive capacity than the more clayey particulate matter from Jabiluka Billabong.

(d) The concentration of copper-binding ligands was also measured as a function of the DOC in filtered waters. In the billabong waters tested, values ranged from 0.01 to 0.03 μmol Cu/mg DOC. These are very much lower than the 0.5 μmol/mg DOC reported by Baccini and Suter (1979) for Swiss lake waters.

(e) The error in the total ligand concentration as determined by the amperometric titration technique was generally satisfactory, ranging from 2% to 10%.

(f) The (log) formation constants determined at pH 6.0 ranged from 7.5 to 8.3 in filtered waters and from 7.9 to 8.5 in unfiltered waters. These are similar to the mean value of 8.2 obtained for Swiss lakes by Baccini and Suter (1979) after correction for pH differences using the relationship $\Delta \log {}^*K/\Delta pH = 1.0$.

(g) For copper concentrations of less than 0.01 μM (i.e. 'natural' concentration range) all waters collected during the dry season would, after filtration, complex more than 88% of the copper added. The capacity to complex copper was in the order:

Gulungul > Island > Leichhardt > Georgetown > Jabiluka.

3.4.2 Wet season samples

(a) There were only minor differences in the water qualities of samples taken at five sites in Magela Creek during the wet season.

(b) The extensive areas of macrophytes in the Mudginberri corridor were effective in 'filtering-out' suspended matter.

(c) The concentrations of copper-binding ligands in filtered waters were very similar, ranging from 0.07 to 0.18 µM. Interestingly, these two extremes were for samples taken in areas of dense macrophyte growth, the low value recorded on the flood plain and the high value in Gulungul Billabong.

There was little apparent difference in the concentrations of copper-binding ligands in filtered and unfiltered waters taken from the three Magela Creek sites. This was mainly due to the very low levels of suspended solids recorded at the time. Preliminary calculations suggest that the particulate matter transported by Magela Creek may have a copper sorptive capacity similar to that of the particulate matter in Island and Leichhardt Billabongs during the dry season. However, the errors associated with these calculations preclude drawing firm conclusions.

(d) In filtered waters concentrations of the copper-binding ligands as a function of DOC ranged from 0.01 to 0.03 µmol Cu/mg DOC. This range was almost identical to that found for filtered waters collected during the dry season.

(e) Values for log $^{*}K$ ranged from 7.6 to 8.2 for filtered waters and 7.4 to 7.8 for unfiltered waters. The very high value of 9.6 in filtered water from the flood plain was excluded from the latter range.

(f) The experimentally-derived values for the concentrations of copper-binding ligands and conditional formation constants are now available to enable the proportion of bound copper at any given concentration to be calculated. Data plotted in Figure 6 show that at 'natural' copper concentrations (less than 0.01 µM) and at pH 6.0, water from Magela creek will effectively bind up more than 80% of copper present.

(g) An aim of this research was to determine whether any major differences in complexing capacity existed between the wet and dry seasons. For filtered wet-season samples the mean values for the concentrations of copper-binding ligands and log $^{*}K$ were 0.13 µM and 7.9 respectively. The wet-season concentrations of copper-binding ligands were slightly less than, and the formation constants were the same as, the corresponding mean values obtained using all the dry season data. Exclusion of the result for Gulungul Billabong ($[L_t]$ 0.45 µM, log $^{*}K$ 7.6) gave mean values essentially the same for samples collected during both seasons (dry: $[L_t]$ 0.14 µM, log $^{*}K$ 8.0; wet: $[L_t]$ 0.13 µM, log $^{*}K$ 7.9).

The other major difference between the wet and dry seasons was the larger amount of suspended material present during the dry season, capable of binding any added heavy metals. By the end of the dry season the concentrations of suspended solids in backflow and floodplain billabongs can become very high. Evidence presented indicates the existence of two quite different qualities of suspended solids; in Island Billabong these are mainly organic while in Gulungul and Jabiluka they are mainly clays. These different solid materials also appear to have different abilities to complex added trace metals.

There is, however, a problem in defining rate of uptake. With the inorganic solids the process would be essentially physico-chemical adsorption, which occurs relatively rapidly. The organic solids, probably consisting of phytoplankton and bacteria, appear to take up more trace metal per unit weight than do inorganic solids, but we do not know the *rate* of uptake. It is, however, important to know this, since the experiments reported here all used a 10 minute equilibration time, and whether this equates to the natural situation, where equilibration times can be considerably longer, must be questioned.

4 ION-EXCHANGE RESIN TECHNIQUE

The ion-exchange method was adapted from the technique described by Van den Berg (1979) and Van den Berg and Kramer (1979). These workers measured the equilibrium distribution of added copper between the solution and MnO_2, the latter added as an ion exchanger. We have modified Van den Berg and Kramer's method by substituting the cation exchange resin Dowex 50WX8 for the MnO_2.

4.1 Analytical Procedure

4.1.1 Resin calibration

The cation exchange resin Dowex 50WX8 (20-50 mesh) in the sodium form, was calibrated by equilibrating a known weight of the resin with known concentration of a solution of the metal at constant pH and then determining the amount of metal adsorbed by the resin. In the experiments reported here the resin was calibrated at pH 7.0 for two metals, copper and cadmium.

Details of the procedure followed are: 100 ± 0.5 mg of the resin was added to a 50 mL aliquot of ultrapure water (Milli Q, UV irradiated for 6 hours in the presence of hydrogen peroxide (2 mL/L) in acid solution pH 3). The mixture was then spiked with 1 mL of buffer (0.5 M KNO_3, 0.05 M Na_2CO_3) which had previously been adjusted to pH 7.0 using nitric acid and further spiked with the metal (copper or cadmium) as nitrate. Checks showed that the final pH was within 0.15 units of that desired. The copper and cadmium solutions used for spiking were prepared from neutral salts and the pH of the stock solution (1000 mg/L) was adjusted to pH 2. Fresh spiking solutions were prepared daily from the stock solution.

The solutions were then equilibrated by shaking for 24 hours in a water bath set at 30°C. At the end of this time the supernatant was decanted and acidified with 100 μL of concentrated nitric acid (Suprapur). The concentration of copper or cadmium in the supernatant was determined by atomic absorption spectrophotometry (AAS) using a Varian AA375 with CBA 90 atomiser. The AAS operating conditions are given in Table 3.

4.1.2 Billabong samples

Experiments were conducted at pH 7.0 with filtered waters from Gulungul, Island and Jabiluka Billabongs; the copper-complexing capacity was determined for all three waters, but cadmium-complexing capacity only for Gulungul and Island.

TABLE 3 EXPERIMENTAL CONDITIONS USED FOR THE ATOMIC ABSORPTION SPECTROPHOTOMETER

Setting	Cd	Cu
Sample size (μL)	2 or 5	5
Wavelength (nm)	228.8	324.7
Hollow cathode setting	5	5
Background correction	on	on
Slit width (μm)	CRA	0.5
Instrument	AA 375/CRA 90/ASD	53
Peak height mode	yes	yes
N_2 flow setting	6	6
N_2 pressure (kPa)	150	150
CRA settings:		
Dry temp (°C)	110	110
Ash temp (°C)	450	700
Ash time (s)	30	20
Atomise temp (°C)	1300	2000
Ramp rate (°C/s)	400	800
Hold time (s)	3	2

A 500 mL aliquot of the sample was mixed with 10 mL of 0.5 M KNO_3/0.05 M Na_2CO_3 buffer and the pH adjusted to 7.0 using dilute nitric acid or sodium hydroxide. Not more than 2 mL was required to adjust the pH. The solution was stirred for 15 minutes and the pH readjusted if necessary.

Fifty mL aliquots of this solution were placed in polyethylene bottles containing 100 mg of Dowex resin and the mixtures spiked with known amounts of copper or cadmium solution. After equilibration (24 hours at 30°C) the samples were treated as described above in the calibration section.

4.2 Treatment of Experimental Results

For each copper spike added the experiment provided data on $[Cu_f]$ (copper in solution) and $[Cu_{ads}]$ (copper adsorbed to the resin).

The value of [Cu'] in equilibrium with each value of $[Cu_{ads}]$ was taken from the calibration curve.

Since $[Cu_f] = [Cu'] + [CuL]$,

then $[CuL] = [Cu_f] - [Cu']$

and this can be used to obtain values of [CuL] corresponding to each value of [Cu'].

At pH 7.0 $[Cu'] = [Cu^{2+}] + [CuOH^+] + [CuCO_3]$

$= 2.66\ [Cu^{2+}]$.

This relationship can be used to correct each [Cu'] to obtain the corresponding $[Cu_{ads}]$.

For cadmium, $[Cd'] = [Cd^{2+}]$ at pH 7.0

A plot of $[Cu^{2+}]/[CuL]$ vs $[Cu^{2+}]$ was then used to obtain the values of $[L_t]$ (= 1/gradient) and $^*K$ (= $1/[L_t]$ x intercept).

4.3 Results and Discussion

The ion-exchange technique was used to determine the complexing capacity and formation constants for copper in Gulungul, Island and Jabiluka Billabong samples and for cadmium in Gulungul and Island samples. All waters were collected at the end of the 1979 dry season (Oct-Nov). The results are given in Table 4. All relevant experimental data used to obtain these values are given in Appendix C.

4.3.1 Calibration

Details of the resin calibration procedure are given in Section 4.1.1. The calibration data are recorded in Appendix C and are also displayed graphically in Figures 7 and 8 for copper and cadmium respectively.

The calibration curve for copper was non-linear (Fig. 7). This may be due to the existence of two different copper-binding sites on the resin. The analysis of the calibration data (Fig. 9) gave two straight lines indicative of two binding sites, one with $\Gamma_{max} = 6.5 \times 10^{-8}$ mol Cu/g resin and $B = 3.8 \times 10^{8}$, and the other with $\Gamma_{max} = 2.0 \times 10^{-6}$ and $B = 3.3 \times 10^{6}$ (Γ_{max} is the maximum or limiting value of the number of moles of copper adsorbed per gram of resin, B is the binding constant equivalent to $^*K_{Cu\ Resin}$). With the experimental conditions used in this work, we calculate that the stronger sites could adsorb 0.13 μM copper and the weaker sites 4 μM copper.

Provided that the calibration curve is used to obtain values of [Cu'] from the known values of $[Cu_{ads}]$, the fact that the resin has two binding sites should not be of major concern.

The calibration curve for cadmium (Fig. 8) was linear and a least squares analysis of the data gave:

$$[Cd^{2+}] = 0.0894\,[Cd_{ads}] - 0.006 \qquad (r = 0.999)$$

where $[Cd^{2+}]$ and $[Cd_{ads}]$ are in μM.

In this case $[Cd'] = [Cd^{2+}]$ since at pH 7.0 the correction for $[CdOH^+]$ etc. was negligible.

4.3.2 Copper

Water from each billabong was found to bind copper very effectively, particularly at the low copper concentrations found naturally in the Magela system. Thus at concentrations of filterable copper up to 0.01 μM, over 96% would be complexed by ligands.

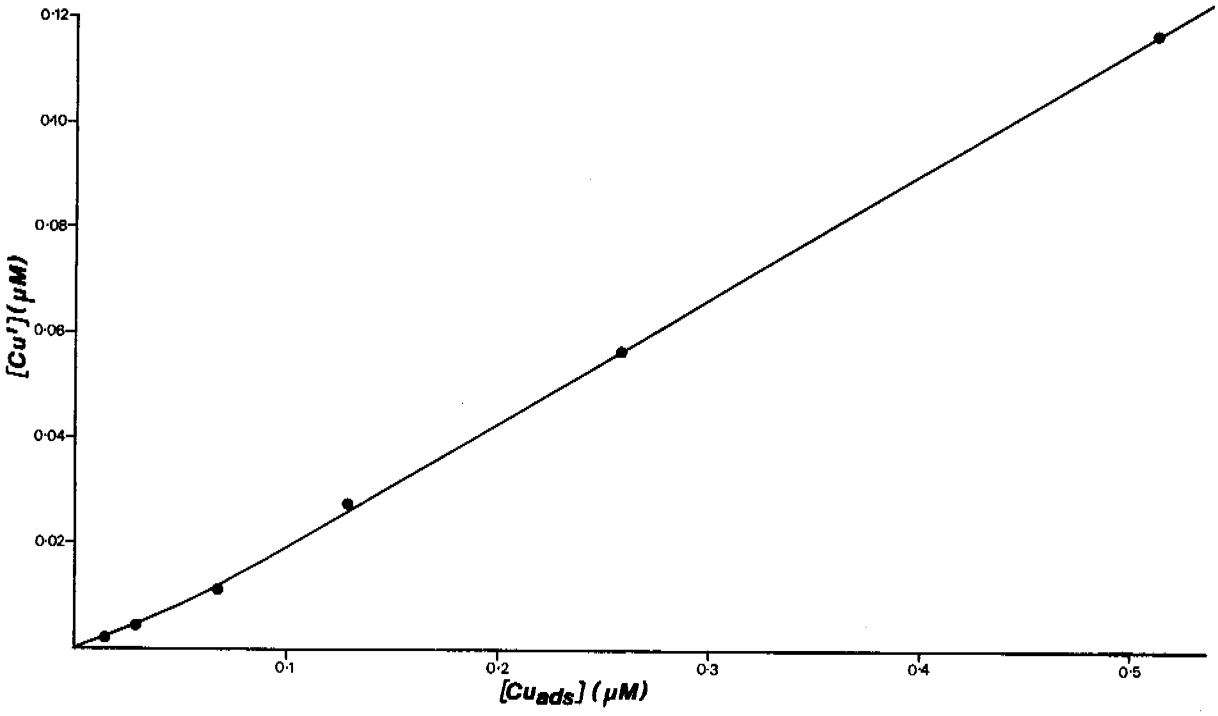

FIG. 7 CALIBRATION CURVE FOR COPPER WITH DOWEX ION EXCHANGE RESIN AT pH 7.0

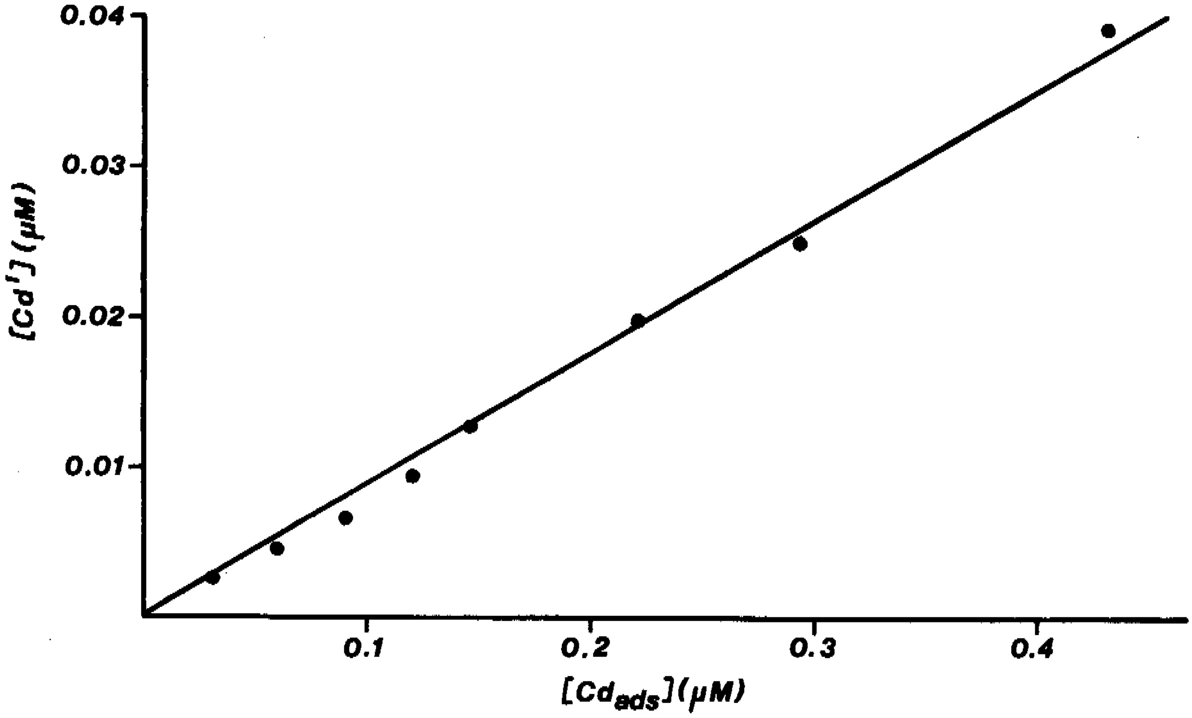

FIG. 8 CALIBRATION CURVE FOR CADMIUM WITH DOWEX ION EXCHANGE RESIN AT pH 7.0

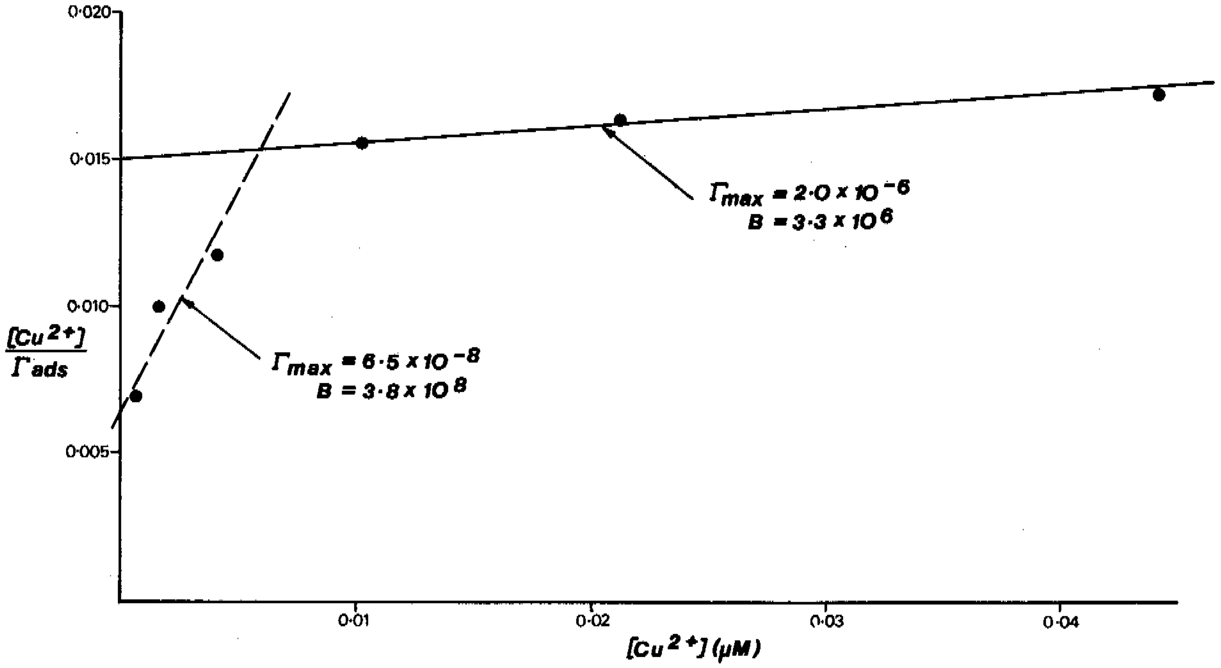

FIG. 9 PLOT TO DETERMINE THE BINDING CHARACTERISTICS OF COPPER WITH DOWEX ION EXCHANGE RESIN AT pH 7.0.

TABLE 4 COPPER-COMPLEXING CAPACITY AND CONDITIONAL FORMATION CONSTANTS, 1979 LATE-DRY SEASON.[a]

Metal	Date of Sampling	$[L_t]$ (µM)	$[L_t]$ (µg Cu/L)	$[L_t]$ (µmol/ mg DOC)	$^*K$ x 10^{-7}	log $^*K$	r[b]
<u>Copper</u>							
Gulungul	25 Oct.	0.15	9.5	0.01	66.9	8.8	0.998
Island	1 Nov.	0.18	11.4	0.02	17.6	8.3	0.977
Jabiluka	4 Nov.	0.29	18.4	0.03	67.3	8.8	0.999
<u>Cadmium</u>							
Gulungul	25 Oct.	0.017	1.9	0.001	28.6	8.5	0.999
Island	1 Nov.	0.044	4.9	0.005	24.3	8.4	0.941

[a] Ion-exchange technique used.
[b] Regression coefficient for $[M^{2+}]/[ML]$ vs $[M^{2+}]$
Filtered (0.45 µM Nucleopore) samples - pH 7.0

Very similar concentrations of copper-binding ligands were found in Gulungul and Island waters with slightly higher values recorded in Jabiluka. These are similar to the values obtained for these waters at the lower pH 6.0 using the amperometric technique (see Section 3.3.1).

The ligand concentrations calculated as µmol Cu/mg DOC, ranged from 0.01 in Gulungul to 0.03 in Jabiluka.

The copper formation constants were all quite high, ranging from 8.3 in Island Billabong to 8.8 in both Gulungul and Jabiluka Billabongs. Comparison with the values determined at the lower pH of 6.0 using the amperometric titration technique, showed very variable results. The differences in log $^*K$ were 0, 0.7 and 1.2 for Island, Jabiluka and Gulungul respectively. On the basis of work by Baccini and Suter (1979), one would expect a difference of approximately 1 unit in the log $^*K$ values determined by the two techniques, with the ion-exchange values being highest. This was found for Jabiluka and Gulungul Billabong waters. The result obtained for Island cannot be explained.

4.3.3 Cadmium

The concentration of cadmium-binding ligands in filtered Island Billabong water was found to be almost twice as high as that in Gulungul (0.044 vs 0.017 µM, Table 4). The formation constants for cadmium complexes were similar in both waters (log $^*K$: 8.4, 8.5). Allen et al. (1979) have also reported very similar results for cadmium complexation in filtered Lake Michigan water ($[L_t]$ 0.03 µM, log $^*K$ 7.9-8.1, pH approx. 8).

The concentrations of cadmium-binding ligands, expressed in terms of µmol Cd/mg DOC, were very low (0.001, 0.005) and were at least one order of magnitude less than for copper. The concentrations of cadmium-binding ligands were also one order less than for copper.

The strength of the cadmium complexes, given by the magnitude of log $^*K$, was surprisingly similar to that found for the copper complexes in these two waters. This was somewhat unexpected as one would generally expect the copper complexes to have higher formation constants than cadmium.

The experimentally derived $[L_t]$ and log $^*K$ data were used to calculate the proportion of the filterable cadmium in the 'natural' range below 0.0005 µM (less than 0.05 µg/L) that would be complexed at pH 7.0. Filtered Gulungul Billabong water would bind 82% of the cadmium and Island Billabong 91%.

4.4 Conclusions

(a) An ion-exchange resin technique based on the method of Van den Berg and Kramer (1979) was developed to determine the capacity of natural waters from the Magela Creek system to complex copper and cadmium. The method involves adding ionic copper or cadmium to a mixture of the natural water and the cation exchange resin Dowex 50WX8 (Van den Berg and Kramer use MnO_2), equilibrating and determining the distribution of metal between the solution and the resin.

(b) Evidence presented indicates that the resin may have two types of copper-binding sites. At pH 7.0, the stronger sites have a binding constant (B) of 3.8×10^8 and, with the experimental conditions used, could adsorb 0.13 μM added copper. The weaker sites have a binding constant of 3.3×10^6 and could adsorb up to 4.0 μM added copper.

(c) Copper-complexing capacity was determined for the waters of three billabongs, Gulungul, Island and Jabiluka. The concentration of copper-binding ligands ($[L_t]$) was similar in Gulungul and Island (0.15 and 0.18 μM respectively) but considerably higher in Jabiluka (0.29 μM). The logarithm of the conditional formation constants at pH 7.0 ranged between 8.3 and 8.8. At the natural copper concentration found in these billabongs (less than 0.01 μM), over 96% of the copper would be complexed at pH 7.0.

(d) The copper-complexing capacities calculated in terms of unit weight of dissolved organic carbon were very low (0.01 to 0.03 μmol Cu/mg DOC).

(e) The concentrations of cadmium-binding ligands in filtered billabong waters ranged from 0.02 to 0.04 μM. These are an order of magnitude lower than those for copper in the same waters, but are similar to that found for cadmium in Lake Michigan water (Allen et al. 1979). The logarithms of the conditional formation constants for cadmium ranged from 8.4 to 8.5. These are surprisingly high and are similar in magnitude to those found for copper. At the natural cadmium concentrations found in these billabongs (less than 0.05 μM), between 82 and 91% of the cadmium would be complexed.

5 MANAGEMENT IMPLICATIONS

It is now well accepted that ionic copper is the form most toxic to aquatic biota (Sunda and Guillard 1976; Guy and Kean 1980; Andrew et al. 1977; Brown et al. 1974; Davies et al. 1976). Complexed copper does not appear to be toxic.

The Swiss MELIMEX experiments, in which trace metals were added (over a period of one year) to water contained in plastic enclosures placed in Lake Baldegg, showed that the added metal load did not lead to an increase in copper-binding ligands (Baccini and Suter 1979), but did cause significant changes in the phytoplankton community (Gachter and Mares 1979). Baccini and Suter (1979) concluded that the biological availability of copper was dependent largely on the concentration of organic ligands and pH, and that the sorptive capacity of the biomass was related to the phytoplankton species present.

Certain algae, but not all (Swallow et al. 1978), are known to secrete organic compounds that are effective ligands for binding copper (Van den Berg et al. 1979; McKnight and Morel 1979). Van den Berg et al. (1979) found that three algal species produced quite different amounts of copper-binding ligands (*Anabaena* 6.73 μM (0.11 μmol/mg dry weight); *Navicula* 2.86 μM (0.036); *Scenedesmus* 0.66 μM (0.010)) over a growth period of ten days. When ligand concentrations and corresponding $^*K$ values were taken into account, a surprisingly similar concentration of copper ion was calculated to exist in each solution. It was suggested that this may be the threshold concentration of free copper ion at and below which algal species can survive, and that they achieve these levels by secreting complexing ligands.

In view of this finding we have calculated the free copper ion concentrations in each of the waters for which experimental data were obtained by the amperometric titration technique. It was assumed that the filterable concentration consisted only of copper ions and CuL complexes. Despite this over-simplification the data contained in Table 5 show the presence of remarkably similar copper concentrations in all waters tested. In all billabongs except Jabiluka, the free copper ion concentration ranged between 10^{-9} and 10^{-10} M at pH 6.0.

The pH in a number of billabongs is known to decrease over the dry season. Such a decrease could lead to more of the filterable copper being converted into the 'toxic' form as the following example indicates. If conditions at the end of the wet are pH = 6.0, $[L_t]$ = 0.13 μM and log $^*K$ = 7.9, and during the dry season the pH drops to 5.0 and log $^*K$ decreases by one unit to 6.9, calculations show that, in the range of filterable copper concentrations of up to 0.01 μM, more than 90% of the copper would be bound at the higher pH, but this would be reduced to only 50% at the lower pH.

The experiments reported here suggest that Magela Creek waters have a relatively large capacity to complex any added copper. This capacity is possibly as much as five times the level at which filterable copper is currently present.

The evidence available suggests that the Magela waters could sufficiently bind further small amounts of copper, so minimising any potential detrimental effects. However, the experiments reported here were only determined at one pH, and the effects of small reductions in pH on copper binding may well be significant, as the example above illustrates. Also it is possible that other mechanisms may result in copper, initially bound, being remobilised, or otherwise becoming biologically available.

Although Magela Creek waters appear to be effective in complexing copper at very low concentrations, it must be stressed that this complexing capacity would be quickly reduced if higher concentrations of copper were to be released to the system.

The above comments all relate to copper. The situation for other trace metals is not known.

In summary, the data reported here will enable the concentration of 'toxic' forms of copper in waters from the Magela Creek system to be estimated. The reality of this can then be examined experimentally. This capability will be particularly useful in predicting the concentrations of ionic copper that might result from particular effluent discharge policies applied to the mining and milling operations.

TABLE 5 CALCULATED[a] FREE COPPER ION CONCENTRATION AT PH 6.0 FOR EACH WATER TESTED.

Billabong		$[Cu_f]$ µM	$[Cu_f]$ µg/L	$[Cu^{2+}]$ x 10^{10} M
<u>Dry Season</u>				
Gulungul		0.015	0.95	8
Island		0.009	0.58	5
Jabiluka		0.027	1.7	29
Georgetown		0.002	0.14	2
Leichhardt		0.015	0.98	10
<u>Wet Season</u>				
<u>Magela</u>				
Mudginberri	M1	0.006	0.36	9
Flood plain	M2	<0.002	<0.10	2
Island	M3	0.003	0.24	4
<u>Gulungul</u>				
open water	G1	0.006	0.36	9
weed bed	G2	0.005	0.29	2

[a] The experimentally derived values for L_t and Log $^*K$ were used in the calculations.

There are a number of questions that still remain to be answered:

1. How well does the free copper ion concentration, calculated from the experimentally derived $[L_t]$ and log $^*K$ data, correspond to the biologically active component?

   Information will become available from the plastic enclosure experiments conducted during the 1980 dry season in Gulungul and Island Billabongs, and from the work being undertaken by Jill Chaney (University of Tasmania) on algal toxicity.

2. What are the short-term (daily) and long-term (seasonal) variations in the ionic copper concentrations and how are they influenced by changes in pH, suspended solids concentrations and phytoplankton and macrophyte populations?

   Information will become available from our study of Gulungul and Island Billabongs over the 1980 dry season.

3. If, as the evidence in this report suggests, the Magela waters have the capacity to reduce the concentrations at which ionic copper is present, what is the situation for other trace metals and which other metals are potentially the most dangerous?

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APPENDIX A

```
1 REM ****************************************************
2 REM
3 REM       PROGRAM COMPCAP
4 REM
5 REM ****************************************************
8 DIM CA(20),I(20),T(20),T1(20),CL(20),CT(20),CB(20),CN(20),X(20),Y(20)
10 INPUT"IS THE CALCULATED DATA TO GO TO LINE PRINTER (Y/N) : ";Z$
20 INPUT"CONTROL  :  1=DATA TO BE INPUT, 2=DATA ON DISC FILE : ";IN
30 ON IN GOTO 60   ,40
40 INPUT"DISC FILE NAME = ";Y$:OPEN"I",1,Y$:INPUT#1,R:FORI=1TOR:INPUT#1,CA(I):NE
XT:FORI=1TOR:INPUT#1,I(I):NEXT
50 GOTO70
60 CLS:S$=" ":GOSUB100
70 A5=0:GOSUB1500 :GOSUB1000 :GOSUB1040 :GOSUB1100 :PRINT@896,"";:GOSUB200  :GOS
UB500  :GOSUB600  :GOSUB700  :GOSUB3000 :END
100 INPUT"HOW MANY DATA SETS DO YOU HAVE";R:CLS
105 PRINT"TYPE IN DATA HIGHEST TO LOWEST CONCENTRATIONS"
110 PRINT"NUMBER          Cu ADDED         PEAK CURRENT"
120 PRINT"                 (uM)             (uA)"
130 FORN=1TOR:PRINTTAB(2);N;TAB(14);:INPUTCA(N):PRINTTAB(14);CHR$(27);S$:PRINTTA
B(35);CHR$(27);:INPUTI(N):PRINTTAB(35);CHR$(27);S$:NEXT
140 INPUT"DO YOU WISH TO MAKE A TEMPORARY DISC FILE OF THE DATA ";Z$:IF LEFT$(Z$
,1)="Y"GOTO145  ELSE RETURN
145 INPUT"NAME OF DISC FILE ";Y$
147 IFLEFT$(Z$,1)="Y" THEN LPRINT"THESE DATA ARE STORED ON DISC FILE NAMED ";Y$
150 OPEN"O",1,Y$:PRINT#1,R:FORI=1TOR:PRINT#1,CA(I):NEXT:FORI=1TOR:PRINT#1,I(I):N
EXT:CLOSE:RETURN
200 PRINT"RANGE OF VALUES TO BE USED IN THE REGRESSION ";R;" TO ";:INPUTR1
210 R2=R-R1+1:FORN=1TOR2:T(N)=CA(R1+N-1):T1(N)=I(R1+N-1):NEXT
220 RETURN
500 X1=0:X2=0:Y1=0:Y2=0:XY=0:TZ=0:YH=-1E38:YL=1E38:XH=-1E38:XL=1E38
505 A5=A5+1
510 N=0
515 FORJ=1TOR2:N=N+1:X1=X1+CA(J):Y1=Y1+I(J):X2=X2+CA(J)[2:Y2=Y2+I(J)[2:XY=XY+CA(
J)*I(J)
520 IFCA(J)>XHTHENXH=CA(J):IFCA(J)<XLTHENXL=CA(J):IFI(J)>YHTHENYH=I(J):IFI(J)<YL
THENYL=I(J)
525 NEXTJ
530 TM=(XY*N-Y1*X1)/(X2*N-X1*X1):TD=(Y1*X2-XY*X1)/(X2*N-X1*X1)
535 TA=XY-X1*Y1/N:TB=X2-X1*X1/N:TC=Y2-Y1[2/N:TC=Y2-Y1[2/N:TS=SQR(TB/N):TE=X1/N
540 TH=Y1/N:TT=SQR(TC/N):CLS:X1=X1/N:Y1=Y1/N
541 B=(XY-X1*Y1*N)/(X2-X1[2*N):A=(Y1-B*X1):S3=B/(Y2-(Y1*N)[2/N)*(XY-X1[2*N):C1=(
1/(N-1))*(XY-X1*Y1*N)
542 C2=C1/((Y2-(Y1*N)[2/N)/(N-1))[0.5:C2=C2/((X2-(X1*N)[2/N)/(N-1))[0.5
543 S4=((Y2-A*Y1*N-B*XY)/(N-2))[0.5:S2=S4/((X2-(X1*N)[2/N)[0.5):S1=(X2/(N*(X2-(X
1*N)[2/N)))[0.5*S4
545 TB=SQR(TB):TC=SQR(TC):RL=INT(1000*TA/(TB*TC)+0.5)/1000
550 PRINTTAB(12);"NUMBER OF PAIRS (N)  = ";N
555 PRINTTAB(12);"CORRELATION COEFFICIENT (R) = ";RL
560 PRINTTAB(12);"DEGREES OF FREEDOM (DF)     = ";N-2:PRINT
565 PRINTTAB(12);"SLOPE (M) OF REGRESSION LINE= ";TM
570 PRINTTAB(12);"Y INTERCEPT (B) FOR THE LINE= ";TD
575 IFLEFT$(Z$,1)="Y"GOTO 2000 ELSEGOTO580
580 RETURN
600 INPUT"Cu CONCENTRATION ORIGINALLY PRESENT (ug/L) = ";C1
605 C=C1/63.5
610 IF LEFT$(Z$,1)="N" GOTO620
615 LPRINT"
ORIGINAL Cu CONCENTRATION (ug/L) : ";C1
620 FORN=1TOR:CL(N)=I(N)/TM:CT(N)=CA(N)+C:CB(N)=CT(N)-CL(N):CN(N)=CL(N)/CB(N):NE
XT
625 IF LEFT$(Z$,1)="Y" GOSUB2200
630 L=0
635 FORN=1TOR:IFCB(N)<0.01 GOTO 640  ELSEIF CN(N)>5GOTO640  ELSEL=L+1:I(L)=CN(N)
:CA(L)=CL(N)
640 NEXT
645 R2=L
```

```
650 GOSUB500  :RETURN
700 CLS:PRINT"COMPLEXING CAPACITY (uM) = ";1/TM:PRINT"COMPLEXING CAPACITY (ug/L)
 = ";63.5/TM
710 KL=TM*10[6/TD:LO=LOG(KL)/2.303
720 PRINT"CONDITIONAL STABILITY CONSTANT (KL) = ";KL:PRINT"LOG KL = ";LO
725 PRINT"ERROR IN CONDITIONAL STAB. CONST. = ";(S1+S2)*KL
726 PRINT"ERROR IN COMPLEXING CAPACITY      = ";S1/TM
730 IFLEFT$(Z$,1)="Y"GOTO 2100 ELSEGOTO740
740 RETURN
1000 IFCA(R)<CA(1)THENFORI=1TOR:T(I)=CA(R+1-I):NEXT:ELSEFORI=1TOR:T(I)=CA(I):NEX
T
1010 PRINT"                                                          ":X(0)=0:X(
10)=T(R):FORN=1TO9:X(N)=X(N-1)+T(R)/10:NEXT
1020 IFI(R)>I(1)THENFORI=1TOR:T1(I)=I(R+1-I):NEXT:ELSEFORI=1TOR:T1(I)=I(I):NEXT
1030 Y(0)=T1(1):Y(6)=0:FORN=1TO5:Y(N)=Y(0)+N*(Y(6)-Y(0))/6:NEXT:RETURN
1040 REM ** PLOT ROUTINE **
1050 CLS:PRINT@781,"";:FORN=1TO10:PRINT"+----";:NEXT
1060 FORN=13TO653STEP128:PRINT@N,"+":PRINT@N+64,"!";:NEXT
1070 FORN=0TO9:PRINT@844+N*5,X(N):NEXT
1080 FORN=0TO6:IFY(N)<0.1ANDY(N)<>0,PRINT@5+N*128,USING"#.##[[[[";Y(N);:NEXT:ELS
EPRINT@5+N*128,USING"####.##";Y(N);:NEXT
1090 PRINT@448,"PEAK I";:PRINT@940,"Cu ADDED":RETURN
1100 FORN=1TOR:X=27+ABS(90*(T(N)-X(0))/(X(9)-X(0))):Y=(T1(R+1-N)-Y(0))/(Y(6)-Y(0
)):Y=37*Y:SET(X,Y):NEXT:RETURN
1500 IFIN=1 LPRINT"INPUT DATA SET" ELSE LPRINT"INPUT DATA SET ON DISC ";Y$
1510 LPRINT"NUMBER          Cu ADDED             PEAK CURRENT":LPRINT"
         (uM)                    (uA)"
1520 FORN=1TOR:LPRINTTAB(2)N;TAB(18)CA(N);TAB(41)I(N):NEXT
1530 RETURN
2000 LPRINT"
": IFA5=1 LPRINT"REGRESSION ON Cu ADDED AND PEAK CURRENT" ELSE LPRINT"REGRESSION
 OF CuLAB/CuBOUND VS CuLAB":LPRINTTAB(12);"NUMBER OF PAIRS (N) = ";N
2010 LPRINTTAB(12);"CORRELATION COEFFICIENT (R) = ";RL
2020 LPRINTTAB(12);"DEGREES OF FREEDOM   = ";N-2
2030 LPRINTTAB(12);"SLOPE OF REGRESSION LINE = ";TM
2040 LPRINTTAB(12);"Y INTERCEPT OF REGRESSION LINE = ";TD
2041 LPRINT"
 ERROR ANALYSIS"
2042 LPRINTTAB(12)"STANDARD ERROR OF INTERCEPT        = ";S1
2043 LPRINTTAB(12)"STANDARD ERROR OF SLOPE            = ";S2
2044 LPRINTTAB(12)"STANDARD ERROR OF ESTIMATE Y/X     = ";S4
2045 LPRINTTAB(12)"COEFFICIENT OF DETERMINATION       = ";S3
2046 LPRINTTAB(12)"COVARIENCE                         = ";C1
2047 LPRINTTAB(12)"CORRELATION COEFFICIENT            = ";C2
2050 RETURN
2100 LPRINT"
";"FINAL DATA
"TAB(12);"COMPLEXING CAPACITY (uM) = ";1/TM
2110 LPRINTTAB(12);"COMPLEXING CAPACITY (ug/L) = ";63.5/TM
2120 LPRINTTAB(12);"CONDITIONAL STABILITY CONSTANT (KL) = ";KL
2130 LPRINTTAB(12);"LOG KL                              = ";LO
2135 LPRINTTAB(12);"ERROR IN STABILITY CONSTANT         = ";(S1+S2)*KL
2136 LPRINTTAB(12);"ERROR IN COMPLEXING CAPACITY        = ";S1/TM
2140 RETURN
2200 LPRINT"NO.   Cu ADDED  PEAK CURRENT   Cu TOTAL   Cu LABILE   Cu BOUND    Cu
LAB/CuBOUND"
2210 FORN=1TOR:LPRINTUSING"  ##       #.###       #.###       #.###     #.###
  #.###       #.###";N,CA(N),I(N),CT(N),CL(N),CB(N),CN(N):NEXT
2220 RETURN
3000 PRINT"INPUT VALUES OF Cu LABILE (uM): END WITH 0"
3010 N=1
3020 INPUT CL(N):IFCL(N)=0GOTO3040

3030 N=N+1:GOTO3020
3040 FORI=1TON:CN(I)=TM*CL(I)+TD:CB(I)=CL(I)/CN(I):CT(I)=CL(I)+CB(I):NEXT
3045 LPRINT"
 CALCULATED DATA"
3050 LPRINT"NUMBER  Cu LABILE  Cu BOUND  Cu TOTAL"
3060 FORI=1TON-1:LPRINTUSING"  ##       #.###      #.###       #.###";I,CL(I),CB(I)
,CT(I):NEXT
3070 RETURN
```

APPENDIX B RAW DATA FROM AMPEROMETRIC TITRATION EXPERIMENTS

Table B.1 EXPERIMENTAL DATA FROM COPPER AMPEROMETRIC TITRATION OF BILLABONG SAMPLES TAKEN IN THE DRY SEASON 1979.

Gulungul				Island				Jabiluka			
Filtered/Run 1		Filtered/Run 2		Unfiltered		Filtered		Unfiltered		Filtered	
Cu_{added} (µM)	i_s (µA)	Cu_{added} (µM)	i_s (µA)	Cu_{added} (µM)	i_s (µA)	Cu_{added} (µM)	i_s (µA)	Cu_{added} (µM)	i_s (µA)	Cu_{added} (µM)	i_s (µA)
0.062	0.071	0.000	0.022	0.020	0.062	0.039	0.099	0.020	0.055	0.039	0.102
0.123	0.138	0.014	0.034	0.039	0.118	0.079	0.182	0.039	0.106	0.078	0.260
0.181	0.189	0.030	0.053	0.059	0.157	0.117	0.328	0.059	0.181	0.116	0.520
0.240	0.283	0.045	0.087	0.078	0.236	0.156	0.446	0.079	0.244	0.155	1.13
0.298	0.366	0.059	0.134	0.116	0.354	0.195	0.698	0.116	0.339	0.230	1.62
0.353	0.378	0.074	0.165	0.155	0.488	0.233	0.880	0.155	0.496	0.303	2.90
0.497	0.551	0.089	0.209	0.192	0.654	0.271	1.17	0.230	0.843	0.375	2.63
0.637	1.22	0.79	4.00	0.230	0.776	0.309	1.34	0.303	1.22	-	-
0.774	1.46	1.11	7.42	0.303	1.23	-	-	0.446	2.13	-	-
0.910	2.40	1.43	10.5	0.375	1.66	-	-	0.584	2.93	-	-
1.03	2.95	-	-	0.446	2.24	-	-	0.716	3.70	-	-
1.16	3.40	-	-	0.584	2.99	-	-	-	-	-	-
				0.716	4.03	-	-	-	-	-	-

Table B.1 ctd

Georgetown		Leichhardt			
Filtered		Unfiltered		Filtered	
Cu_{added} (µM)	i_s (µA)	Cu_{added} (µM)	i_s (µA)	Cu_{added} (µM)	i_s (µA)
0.00	0.039	0.020	0.039	0.000	0.052
0.073	0.129	0.039	0.063	0.039	0.102
0.146	0.201	0.078	0.134	0.079	0.181
0.218	0.303	0.116	0.228	0.117	0.252
0.360	0.567	0.144	0.299	0.156	0.378
0.500	0.992	0.230	0.583	0.195	0.453
0.637	0.32	0.303	0.890	0.233	0.756
0.771	1.75	0.375	1.43	0.271	0.803
-	-	0.446	1.82	0.347	1.21
-	-	0.716	3.74	0.422	1.58
-	-	-	-	-	-
-	-	-	-	-	-
-	-	-	-	-	-

Table B.2 EXPERIMENTAL DATA FROM AMPEROMETRIC TITRATION OF COPPER AND GULUNGUL BILLABONG SAMPLES TAKEN IN THE WET SEASON 1980

Cu$_{added}$ (µM)	Peak Current i_s (µA)			
	Site G1 - Open Water		Site G2 - Weed Bed	
	Unfiltered	Filtered	Unfiltered	Filtered
0.000	0.035	0.012	0.047	0.031
0.039	0.118	0.102	0.078	0.094
0.078	0.197	0.213	0.157	0.173
0.118	0.260	0.425	0.232	0.283
0.156	0.354	0.646	0.346	0.449
0.233	0.622	1.21	0.646	0.843
0.311	0.913	1.78	1.03	1.91
0.385	1.22	2.34	1.48	2.55
0.459	1.57	3.14	1.88	3.79
0.607	2.30	4.23	2.81	-
0.752	3.11	5.61	3.83	-
0.892	-	-	4.66	-

Table B.3 EXPERIMENTAL DATA FROM AMPEROMETRIC TITRATION OF COPPER AND MAGELA CREEK WATER TAKEN IN THE WET SEASON 1980

Cu$_{added}$ (μM)	Peak Current (i_s) (μA)					
	M1 - MUDGINBERRI		M2 - FLOODPLAIN		M3 - ISLAND	
	Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered
0.000	0.020	0.035	0.000	0.039	0.130	0.031
0.039	0.094	0.142	0.055	0.161	0.220	0.126
0.078	0.197	0.229	0.150	0.394	0.343	0.228
0.118	0.287	0.323	0.283	0.630	0.437	0.331
0.156	0.441	0.433	0.461	0.921	0.488	0.417
0.233	0.681	0.744	0.850	1.65	0.898	0.807
0.311	1.04	1.07	1.38	2.44	1.53	1.21
0.385	1.49	1.52	1.85	3.02	1.96	2.21
0.459	1.92	2.06	2.28		2.42	-
0.534	-	2.13	-	-	-	-
0.607	2.91	-	3.10	-	3.55	3.23
0.681	-	3.24	-	-	-	-
0.752	3.88	-	3.95	-	4.53	-
0.826	-	4.01	-	-	-	-
0.894	-	-	4.87	-	5.59	-

APPENDIX C RAW DATA FROM ION-EXCHANGE RESIN EXPERIMENTS

Table C.1 EXPERIMENTAL DATA USED TO DETERMINE COPPER-COMPLEXING CAPACITY AND FORMATION CONSTANTS IN BILLABONG WATER SAMPLES[a]

CALIBRATION		GULUNGUL		ISLAND		JABILUKA	
Cu_t[b]	Cu_f[b]	Cu_t	Cu_f	Cu_t	Cu_f	Cu_t	Cu_f
(all concentrations in µM)							
0.000[b]	0.0000[c]	0.0397	0.0380	0.0156	0.0129	0.0224	0.0200
0.016	0.0013	0.0475	0.0407	0.0310	0.0191	0.0374	0.0333
0.032	0.0036	0.0552	0.0445	0.0465	0.0318	0.0686	0.0562
0.079	0.0106	0.0707	0.0528	0.0774	0.0456	0.0992	0.0856
0.157	0.0268	0.117	0.0782	0.108	0.0635	0.177	0.158
0.315	0.0562	0.194	0.120	0.139	0.0765	0.331	0.290
0.630	0.117	0.349	0.181	0.170	0.0902	0.640	0.341
	0.658	0.238	0.324	0.141	0.950	0.405	
				0.634	0.247		

[a] Ion-exchange technique used

[b] Cu_t = total copper concentration

Cu_f = copper concentration after resin removed

[c] Results corrected for blank 0.23 µg/L = 0.0036 µM

Table C.2 EXPERIMENTAL DATA USED TO DETERMINE CADMIUM-COMPLEXING CAPACITY AND FORMATION CONSTANTS IN BILLABONG WATER SAMPLES [a]

Cd_t[b]	CALIBRATION Cd_f[b] (all concentrations in μM)			Cd_f(correct)
	Run 1	Run 2	Mean	
0.000	0.0000	0.0003	0.0002	0.0000
0.031	0.0028	0.0019	0.0024	0.0022
0.063	0.0044	0.0049	0.0047	0.0045
0.094	0.0069	0.0060	0.0065	0.0063
0.126	0.0093	0.0099	0.0096	0.0094
0.157	0.0120	0.0137	0.0129	0.0127
0.236	0.0189	0.0205	0.0197	0.0195
0.315	0.0221	0.0268	0.0245	0.0243
0.472	0.0363	0.0410	0.0387	0.0385

GULUNGUL		ISLAND	
Cd_t	Cd_f	Cd_t	Cd_f
0.0022	0.0004	0.0003	0.0003
0.0197	0.0039	0.0025	0.0015
0.0545	0.0104	0.0112	0.0057
0.0720	0.0146	0.0198	0.0079
0.0894	0.0167	0.0460	0.0136
0.177	0.0262	0.0913	0.0295
0.264	0.0352	0.177	0.0439
0.351	0.0423		

[a] Ion-exchange technique used

[b] Cd_t = total cadmium concentration

Cd_f = cadmium concentration after resin removed

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RESEARCH PUBLICATIONS

Research Reports (RR) and Technical Memoranda (TM)

TM1	Transport of trace metals in the Magela Creek system, Northern Territory. I. Concentrations and loads of iron, manganese, cadmium, copper, lead and zinc during flood periods in the 1978-1979 wet season. December 1981 (pb - 26 pp)	Hart, B.T., Davies, S.H.R, Thomas, P.A.
TM2	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.
TM3	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.
TM4	The foraging behaviour of herons and egrets on the Magela Creek flood plain, Northern Territory. March 1982 (pb, mf - 20 pp)	Recher, H.F. Holmes, R.T.
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