



Technical Memorandum 24

The determination of zinc in Magela Creek water

C.A.A. LeGras and B.N. Noller

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the Alligator Rivers Region

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ABSTRACT

Christopher A.A. LeGras & Barry N. Noller (1989). The determination of zinc in Magela Creek water. Technical Memorandum 24, Supervising Scientist for the Alligator Rivers Region.

Water from Magela Creek was sampled on 19 occasions at a location approximately 150 m downstream from the outflow of Georgetown Billabong during March-April 1986. Water was also sampled from two sites at Bowerbird Billabong, about 20 km upstream from Georgetown billabong. Samples were analysed for the total of all labile forms of zinc, operationally defined here as that portion of the metal mobilised by acidification of unfiltered samples to 0.1% (1 mL/L) with nitric acid giving a final pH of 1-2. This is regarded generally as the fraction of zinc most available to biota. A rigorous sampling and analytical procedure to minimise contamination by extraneous zinc is described. The concentration of zinc in Magela Creek water varied from 87-121 ng/L at Bowerbird Billabong and 196-738 ng/L at the site below Georgetown. At this site there was a positive correlation between zinc concentration and turbidity except during the flood event which occurred during the sampling period.

These data are compared with the statistically derived interim receiving water standard for zinc, and with acute lethal toxicity data on zinc for some Magela Creek fish species.

1 INTRODUCTION

1.1 Water release standards

Uranium mining in the Alligator Rivers Region (Fig. 1) is being carried out in an area of exceptional environmental value - it includes Kakadu National Park, most of which is included on the World Heritage List, and much of the Region has been inscribed on the Register of the National Estate. In recognition of the uniqueness of this environment, control measures have been formulated to ensure that a high level of environment protection is maintained.

The high variability of annual rainfall and its seasonal nature in a monsoonal climate give rise to special considerations in the design of water management systems at mine sites. In years of extremely high rainfall it may be necessary, unless significant interruption to the mining schedule is accepted, to discharge mine water into the surface water system. A discharge control regime based upon toxicological testing of effluent water is currently being developed but, prior to finalisation of protocols and incorporation in authorisations, the control regime adopted has been based upon receiving water standards for a number of the most significant chemical constituents and variables. For some of these constituents the standard has been based, in the absence of suitable elemental toxicological data, upon the observed natural variability of the constituent in the surface water of the Region.

Zinc is one of the constituents for which this procedure was followed in formulating appropriate receiving water standards for discharge of waste water from the Ranger uranium mine into the nearby Magela Creek. In 1985 an interim receiving water standard for zinc of 17 $\mu\text{g/L}$ was recommended by the Office of the Supervising Scientist (Brown et al. 1985). This figure had been based on 1978-84 concentration data for gauging stations (GS) 8210009 and GS8210028 provided by the Northern Territory Water Resources Division (n.d.). These data, together with the data for Mudginberri Billabong, are reproduced here as Table A1. (The locations of the sampling sites are shown in Fig. 1.) Less extensive concentration data for zinc in Magela Creek water are given in Hart et al. (1981; 1982), Davies & Hart (1981). Unfortunately, these data were collected when there was little appreciation of the likely magnitude of zinc concentrations in Magela Creek, and probably limited acknowledgment of the ease with which contamination with this metal can occur during sample collection and analysis. More recently, Hart et al. (1986) have reported zinc concentrations almost a factor of 10 lower than found in the previous studies ($0.8 \pm 0.9 \mu\text{g/L}$ vs $7 \pm 9 \mu\text{g/L}$). Recommended interim receiving water standards were reduced to 1.7 $\mu\text{g/L}$ on the basis of these results (Supervising Scientist 1986).

As Hart et al. (1986) were sampling during flood events, when heavy metal concentrations are known to increase (Hart et al. 1987), their zinc values also are almost certainly higher and more variable than the true values.

The present study is concerned with the acquisition of reliable concentration data for zinc which could be used to re-evaluate the receiving water standard for Magela Creek.

1.2 Present study

Important components in the acquisition of reliable data are sampling and analytical protocols which are sufficiently rigorous and which contain suitable internal checks to minimise risk of zinc contamination and to detect it when present. The method developed for the present investigation has four main features:

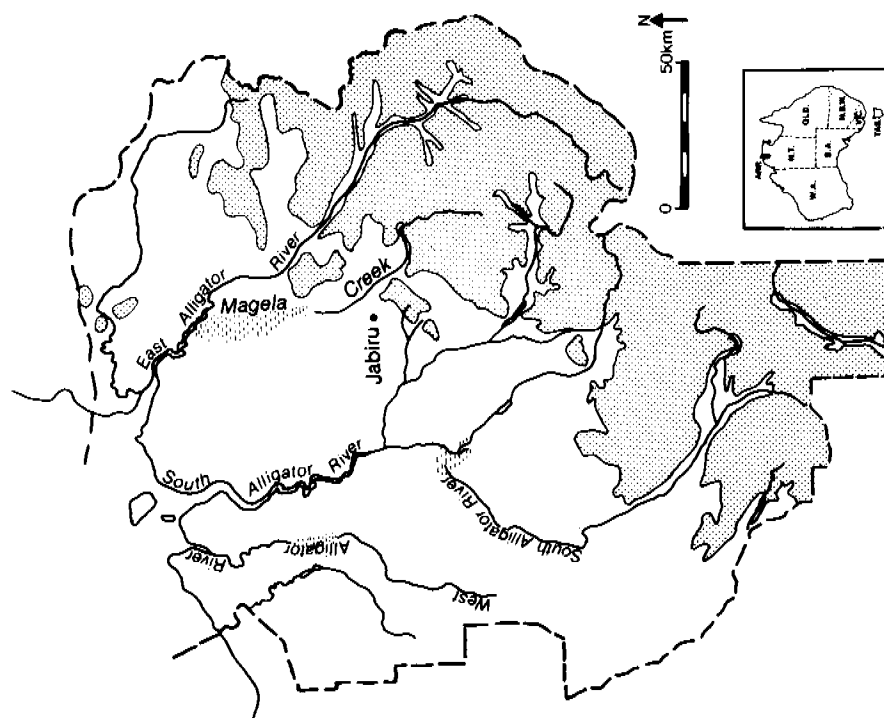
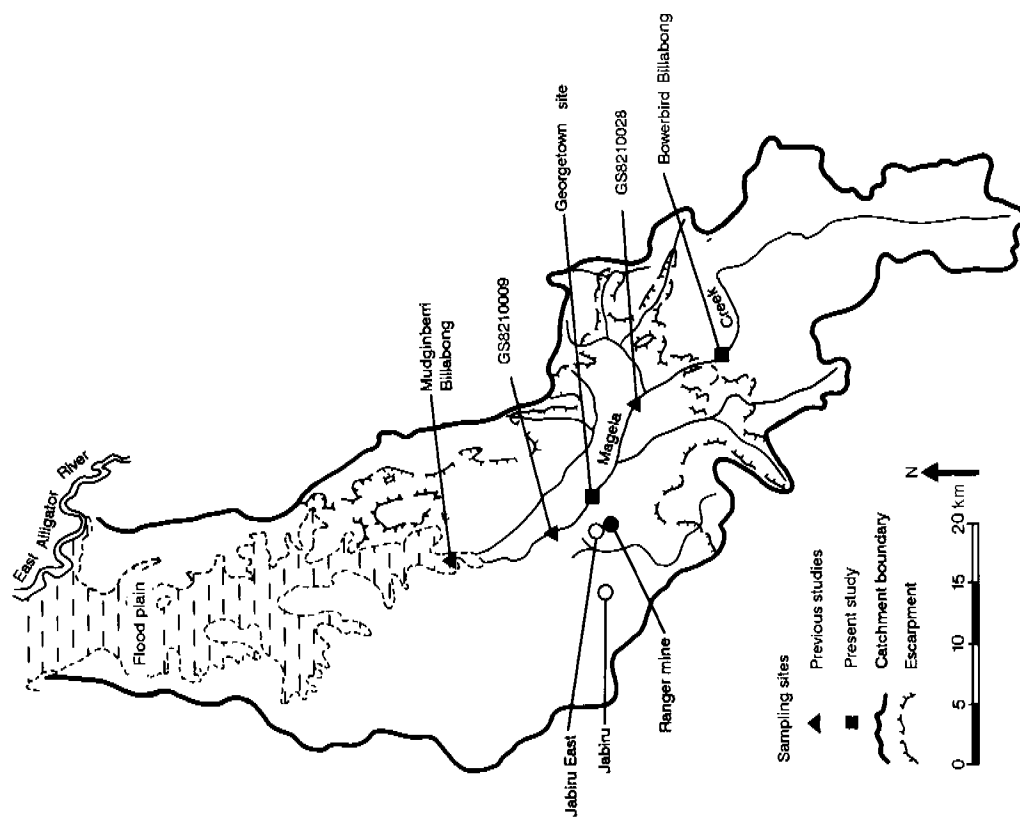


Figure 1. The Alligator Rivers Region and the Magela Creek catchment showing the location of the sampling sites

- i) each 'blank' and 'sample' bottle was filled with high purity water (Millipore Super-Q grade) and the zinc concentration in this water was determined prior to use of the sample bottle for collection of water in the field;
- ii) all bottles, including blanks, were transported inside sealed plastic bags, placed inside an airtight plastic box;
- iii) all manipulations of samples and blanks were carried out inside an all-plastic laminar-flow work station, equipped with a high efficiency particulate air filter (AS 1387, 1976); and
- iv) high purity water stored in a Teflon bottle in the laminar-flow workstation was determined for zinc every day.

2 METHODS

2.1 Water sampling sites

Water samples were collected from two sites over a period of about one month during the 1986 Wet season. The Georgetown site (Fig. 1), which is downstream of the outflow from Georgetown Billabong and 150 m upstream from the NT Water Resources Division Sampling Section 1A (Fig. 2), was sampled 19 times. In contrast, Bowerbird Billabong was sampled only once at each of two locations. The Georgetown site was selected because it is near the discharge pipe from which any authorised release of water from the Ranger uranium mine would occur. Data from this site therefore describe zinc concentrations and their variability in a potential mixing zone. Bowerbird Billabong was selected because it is in the headwaters of the creek and is largely free from anthropogenic effects.

2.2 Sample collection

Ten 120 mL Nalgene polyethylene bottles (Cat. No. 2002-0004), 5 for blanks and 5 for samples, were used for each day's collection from the Georgetown site. Five blank bottles and twenty sample bottles were used for the Bowerbird site. Each had been soaked for several days in 10% HNO_3 and was washed copiously with Millipore Super-Q water (conductivity $< 1 \mu\text{S}$) and left filled with this water. (All surfaces with which samples would come into contact during analysis had initially been washed with Decon 90 detergent, water, 10% HNO_3 and water.) The water in each bottle was then analysed for zinc to confirm the thoroughness of the washing, as was the 10% Aristar HNO_3 used to acidify blanks and samples. The concentration of zinc in the 10% HNO_3 was $440 \pm 170 \text{ ng/L}$ ($n = 20$), well within the certified maximum concentration of the metal in the undiluted acid, $10 \mu\text{g/L}$. The blank and sample bottles were sealed in separate zip-top polyethylene bags, which were placed in an airtight plastic box. This box contained a pair of plastic gloves and was transported to the field inside a larger plastic bag.

Creek water from the Georgetown site was sampled by wading into the westernmost channel of Magela Creek to a water depth of about 30 cm and collecting five bottles of water using gloved hands, the sampling point being upstream of the person taking the sample. Each bottle was rinsed thoroughly with creek water before sampling by completely refilling from just below the surface. The bottles were recapped and resealed as before. The same procedure was used at the Bowerbird sites except that sampling was performed from the bank.

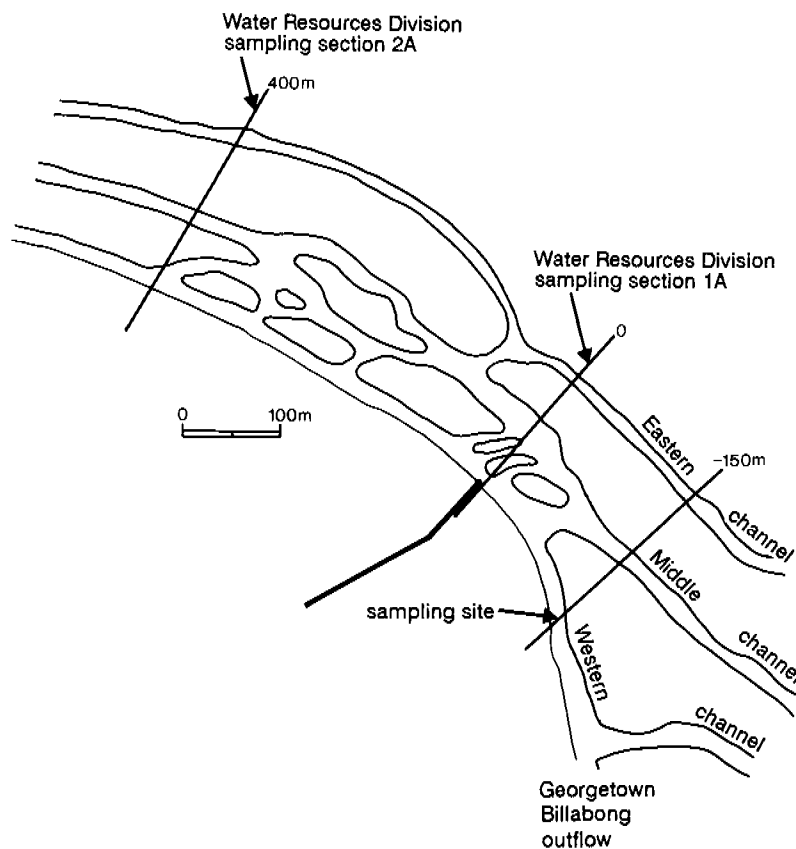


Figure 2. Location of the Georgetown sampling site

2.3 Analytical procedure

At the laboratory the box and bags were opened in a room protected from external contamination (clean laboratory) and the capped sample and blank bottles transferred immediately to the laminar-flow work station. The work station contained the following items for the duration of the investigation: high purity water contained in Teflon bottles for rinsing; a Teflon wash-bottle; concentrated Aristar HNO_3 ; 10% Aristar HNO_3 ; a Nalgene polyethylene bottle calibrated to 100 mL ('the calibrated bottle'); an Oxford 1 mL dispensing pipette; acid-soaked pipette tips; control water (0.1% HNO_3 in high purity water); a slightly sticky cloth for cleaning the laminar-flow work station and a pair of lint free clean-room gloves. USEPA standard waters and calibration standards were diluted from stock solutions as required and stored in the laminar-flow work station. A paper surgical cap, dacron coat and plastic overshoes were worn while working in the clean laboratory.

The volume of water in each sample and blank bottle was adjusted to 100 mL by visual comparison with the calibrated bottle and an aliquot of the discarded portion of the sample from one bottle used to measure turbidity, about 45 minutes after sample collection using a Hach Model 2100A Turbidimeter. The remaining volume was acidified with 1 mL of 10% HNO_3 . The acidified bottles were stored undisturbed to allow suspended matter to settle for 1 to 7 days, depending on the turbidity of the sample. Where zinc determinations were

performed on turbid samples, results for zinc concentration were high and non-reproducible, even when background correction was used. This extra observed concentration, typically 200-600 ng/L, was attributed to the presence of zinc in the mineralogical component of the suspended solids. To test the plausibility of this attribution, a calculation was made using the value found by Hart (1987b) for residual (that is, matrix) zinc in stream sediments (23 $\mu\text{g/g}$) and the mean concentration of suspended solids, 13 mg/L (Hart 1987a). This calculation yields a concentration of zinc from the mineral matrix of the suspended solids of 300 ng/L. Similarly, the mean concentration of zinc in 16 associated groups of rock samples of the Cahill Formation (Ferguson & Winer 1980), 44 $\mu\text{g/g}$, gives an analogous concentration of zinc from the mineral matrix of 570 ng/L. Therefore, it is reasonable to assume that the extra observed concentration of zinc originates in the mineral matrix of suspended solids. The effect is not observed if suspended matter is allowed to settle. No attempt was made to filter samples because previous experience has shown this to be a frequent and unpredictable source of contamination (B.N. Noller, unpublished results). For the present investigation it was considered that filtration would add little to an appreciation of the speciation of labile zinc, because relatively little zinc is present in the particulate fraction at the pH of the samples when collected.

Solutions from duplicate blank cups and triplicate sample cups were determined (average of five readings) for zinc by graphite furnace atomic absorption spectroscopy using a Perkin-Elmer 5000 spectrophotometer, HGA500 graphite furnace and AS40 autosampler housed in the clean laboratory. For the determination of the metal, acid-soaked 2 mL polystyrene cups were washed under a rapid jet of high purity water in the clean laboratory, transferred to the laminar-flow work station, rinsed with two aliquots of supernatant blank or sample solution using the dispensing pipette, loaded with about 1.5 mL of blank or sample solution and placed in the carousel of the autosampler. Zinc was determined in calibration standards, reference waters, control water, blanks and samples by direct calibration according to the spectrophotometer and furnace programs detailed in Tables A2 and A3. The reference waters used were USEPA Trace Metal samples 2 and 6 diluted 1:100 and 1:1000 respectively. The results for these determinations, and those for the control water are presented in Table 1. Zinc determinations for USNBS Standard Reference Material 1643a (trace metals in water) performed between 21.12.82 and 22.1.85 under comparable conditions to the present ones yielded $67 \pm 8 \mu\text{g/L}$ for 91 determinations (Certificate Value $72 \pm 4 \mu\text{g/L}$). These NBS data increase confidence in the present methodology, and hence results.

2.4 Concentrations of zinc and sources of contamination in blanks

The method of blank evaluation was as follows. It was recognised that there were two intrinsic sources of zinc in sample blanks: the flushing system of the AS40 autosampler and the Aristar HNO_3 used for acidification. Zinc concentrations were determined by a linear comparison of peak heights of solutions with the peak height of the calibration standard (1 $\mu\text{g/L}$ Zn). These experiments were performed with an electrodeless discharge lamp as radiation source, which has a more intense but less stable emission than the hollow cathode lamp used subsequently. In this way the concentration of zinc in high purity water was determined to be $8.0 \pm 2.4 \text{ ng/L}$ ($n = 40$), interpreted as the contribution from the flushing system. The zinc concentration in a 0.1% HNO_3 solution in Super-Q water was $14 \pm 1.7 \text{ ng/L}$ ($n = 6$).

For the main study, the smallest peak for any blank run, comprising 5 determinations of each of 2 cups for each of 5 bottles (50 determinations in all), was arbitrarily assigned as 14 ng/L. Other blank concentrations were calculated by direct comparison with this value.

Table 1. Concentrations of zinc in control water and reference waters

Date	Control water ^a (ng/L)	US EPATM2 ^b (µg/L)	US EPATM6 ^c (µg/L)
18.3.86	20 ± 4.0 (n = 3)		422 ± 4.0 (n = 3)
19.3.86	23 ± 10.0 (n = 3)		415 ± 6.0 (n = 3)
20.3.86	29 ± 11.0 (n = 3)		467 ± 8.0 (n = 3)
21.3.86	20 ± 4.0 (n = 3)		452 ± 9.0 (n = 3)
24.3.86	19 ± 3.0 (n = 3)	77.6 ± 0.9 (n = 3)	437 ± 32.0 (n = 3)
25.3.86	20 ± 4.0 (n = 3)	78.0 ± 1.1 (n = 3)	
26.3.86	51 ± 23.0 (n = 3)	79.0 ± 0.2 (n = 3)	
27.3.86	59 ± 15.0 (n = 3)	71.8 ± 0.8 (n = 3)	
1.4.86	49 ± 16.0 (n = 3)	85 ± 10 (n = 6)	
2.4.86	38 ± 4.0 (n = 3)	77.0 ± 0.3 (n = 3)	
3.4.86	69 ± 21.0 (n = 3)	80.0 ± 1.2 (n = 3)	
4.4.86	25 ± 5.0 (n = 3)	76.7 ± 0.7 (n = 3)	
10.4.86 (1150 h)	45 ± 15.0 (n = 3)	77.3 ± 0.1 (n = 3)	
10.4.86 (1615 h)			
11.4.86 (1145 h)	34 ± 6.0 (n = 3)	83.8 ± 1.8 (n = 6)	
11.4.86 (1730 h)			
14.4.86		84.6 ± 2.2 (n = 3)	
15.4.86		85.9 ± 2.0 (n = 6)	
16.4.86		84.8 ± 0.7 (n = 3)	
Mean ± SD	36 ± 19 (n = 42)	81 ± 5.5 (n = 48)	439 ± 24 (n = 15)
Certified Values		79 ± 8.0	396 ± 44

^a0.1% HNO₃ stored in clean-air station; ^bdetermined at a dilution of 1:100; ^cdetermined at a dilution of 1:1000

Only two instances of gross contamination of blanks were encountered during the investigation. On 26.3.86, 1 of 5 blanks and on 27.3.86, 4 of 5 blanks contained zinc in the concentration range 500-850 ng/L, even though the initial determination of unacidified water in the blank bottles apparently showed none. However, a careful re-examination of the peak heights for the unacidified bottles subsequently found to be contaminated showed that the concentration of zinc was near 20 ng/L compared with approximately 8 ng/L for all others. The contamination was attributed to the mobilisation by acid of zinc from resin fines present in the Millipore Super-Q water after changing the ion-exchange resin cartridges on 24.3.86. The contamination was prevented on subsequent days by ensuring that the small but consistent increase in zinc concentration in the unacidified bottles was absent by carefully examining peak heights before sample collection.

3 RESULTS AND DISCUSSION

The average turbidity at the Georgetown site over the study period was 7.7 ± 3 NTU (n = 19). The average concentration of zinc in the blanks for that site was 31 ± 20 ng/L (n = 19) and in the samples 307 ± 149 ng/L (n = 19). All errors quoted are one standard deviation of the mean. These data, and those for Bowerbird Billabong are detailed in Table 2. The concentrations for individual bottles are recorded in Table A4. A graph of zinc concentration as a function of turbidity is presented as Fig. 3.

Table 2. Summary of zinc concentrations in blanks and in Magela Creek samples, and of turbidity and stream flow

Date	Turbidity (NTU)	Stream flow ^a (m ³ /s)	Zinc \pm SD (ng/L)	
			Blanks	Samples
Georgetown site				
18.3.86	1.5	2.3	30 \pm 7.0 (n = 5)	196 \pm 17.0 (n = 5)
19.3.86	53.0	3.0	25 \pm 2.0 (n = 5)	738 \pm 82.0 (n = 5)
20.3.87	6.4	2.3	31 \pm 5.0 (n = 5)	305 \pm 16.0 (n = 3)
21.3.86	3.0	2.3	42 \pm 6.0 (n = 5)	244 \pm 10.0 (n = 5)
24.3.86	1.0	1.7	111 \pm 7.0 (n = 5)	207 \pm 13.0 (n = 5)
25.3.86	4.3	3.2	22 \pm 4.0 (n = 5)	342 \pm 22.0 (n = 5)
26.3.86	7.9	2.6	35 \pm 20.0 (n = 4)	450 \pm 17.0 (n = 4)
27.3.86	4.3	2.2	21 (n = 1)	272 \pm 20 (n = 5)
1.4.86	4.8	3.0	33 \pm 9.0 (n = 5)	223 \pm 6.0 (n = 3)
2.4.86	3.5	2.7	27 \pm 6.0 (n = 5)	232 \pm 10.0 (n = 5)
3.4.87	2.7	2.3	21 \pm 2.0 (n = 5)	232 \pm 11.0 (n = 5)
4.4.86	2.3	2.3	24 \pm 4.0 (n = 5)	203 \pm 22.0 (n = 5)
10.4.86 (1150 h)	13.0	50	35 \pm 10.0 (n = 5)	651 \pm 16.0 (n = 5)
10.4.86 (1615 h)	5.5	55	21 \pm 2.0 (n = 5)	292 \pm 20.0 (n = 5)
11.4.86 (1145 h)	8.7	19	24 \pm 4.0 (n = 5)	239 \pm 23.0 (n = 4)
11.4.86 (1730 h)	10.0	13	24 \pm 5.0 (n = 5)	290 \pm 20.0 (n = 5)
14.4.86	6.5	7.0	24 \pm 6.0 (n = 5)	239 \pm 19.0 (n = 5)
15.4.86	4.6	4.6	24 \pm 4.0 (n = 5)	222 \pm 4.0 (n = 5)
16.4.86	3.8	3.3	22 \pm 3.0 (n = 5)	255 \pm 17.0 (n = 5)
Mean \pm SD			31 \pm 20 (n = 19)	307 \pm 149 (n = 19)
Bowerbird Billabong (15.4.86)				
Billabong (upstream)			23 \pm 4.0 (n = 5)	121 \pm 28 (n = 9)
Billabong outflow				86 \pm 8 (n = 10)

^aCalculated from data supplied by Ranger Uranium Mines Pty Ltd

3.1 The physico-chemical nature of labile zinc

Zinc(II) usually forms six bonds to other ions or molecules, with a resultant stereochemistry which is roughly octahedral. Hence the zinc ion, Zn^{2+} , is really the hexaaquazinc(II) ion, $\text{Zn}(\text{H}_2\text{O})_6^{2+}$. Substitution of water molecules by other ligands is not usually favoured for this metal because the d^{10} electronic structure confers no ligand-field stabilisation energy on ligand replacement (Cotton & Wilkinson 1980). Therefore, the only impetus to reaction in solution is the possibility of stronger covalent bonds (an enthalpic effect). In aqueous solution this effect is reduced or eliminated by the numerical preponderance of water molecules (an entropic effect). Consequently, complexation of Zn^{2+} at the concentrations present at the Georgetown site ($\approx 10^{-8}$ M) with natural inorganic ligands such as hydrogencarbonate or chloride ions ($\approx 10^{-4}$ M; Hart et al. 1987) would probably be negligible.

Zinc does not form strong complexes with humic acids. Guy & Chakrabarti (1976) showed that, below pH 5.5, all zinc in a humic acid solution passed through a dialysis membrane, while at pH 7 only 45% was dialysable. This accords with the x-ray crystal structure of zinc with a humic acid model compound (Cariati et al. 1983). The organic compound acted as a counterion rather than a ligand. Kragten (1978) documents the stability of many zinc complexes as a function of pH. Except where polydentate chelates are formed, zinc carboxylate complexes are weak. Therefore it may be reasonably assumed that a negligible quantity of zinc will be bound to humic compounds in Magela Creek.

At the pH of the Georgetown site during the study period, 5.31 ± 0.25 (Noller & Hunt 1987), hydrolysis of the $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ ion ($\text{pK}_a = 9.17$; Kragten 1978) would be negligible, as would the concentrations of more hydrolysed species, such as $\text{Zn}(\text{OH})_2$ and ZnO , unless the latter were present in metastable form from the weathering of rocks.

We therefore conclude that essentially all soluble zinc was present as the $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ ion.

The proportion of zinc which is associated with particulate matter in freshwaters is variable but in most cases is near 50% of the total. Hart et al. (1985a,b) found that for Gulungul and Island billabongs in the Magela system, the proportion of zinc exchangeable with Chelex-100 (and assumed therefore not to be associated with particulates), determined from $0.1 \mu\text{m}$ filtrates, averaged 51% ($\text{pH} \approx 6$) and 45% ($\text{pH} 5-6$) of total zinc, respectively, with higher values of particulate-associated zinc occurring with increased concentrations of suspended solids. Other values for Chelex-100 exchangeable zinc in freshwaters are: 34% (Figura & McDuffie 1977); 50% (Hart & Davies 1977) and 100% (Florence 1977). The latter study, on waters described as unpolluted and soft, most closely parallels the present investigation.

It is probable that most of the particulate-associated zinc is adsorbed onto oxide/oxy-hydroxide particles ($\text{Fe}(\text{III})$ and $\text{Mn}(\text{III})/(\text{IV})$). Benjamin & Leckie (1981) have observed that absorption of Zn^{2+} onto freshly precipitated, amorphous iron oxyhydroxide is negligible below pH 5 but that virtually all available zinc is bound to an excess of this material at pH 7. The 'hydrated ferric oxide' particles in Magela Creek would probably be much less efficient at adsorbing Zn^{2+} than this because:

- i) they would not have the same surface activity as freshly precipitated material, and
- ii) they are thought to be at least partly covered with natural organic material (Thomas & Hart 1984; Hart 1987b) which, as explained earlier, would not be expected to complex with zinc at the prevailing pH values. The ability of high-valence oxides of manganese to adsorb zinc is not certain. These oxides exert a greater inductive effect than ferric oxides, so uncovered oxides of Mn should adsorb Zn the more strongly. However, natural organic material should also adsorb more strongly to Mn oxides and this, coupled with the much higher concentration of Fe oxides compared with Mn oxides (NT Water Resources Division, 1987), suggests that Mn oxides may not adsorb significant amounts of Zn at the pH of the creek during sample collection.

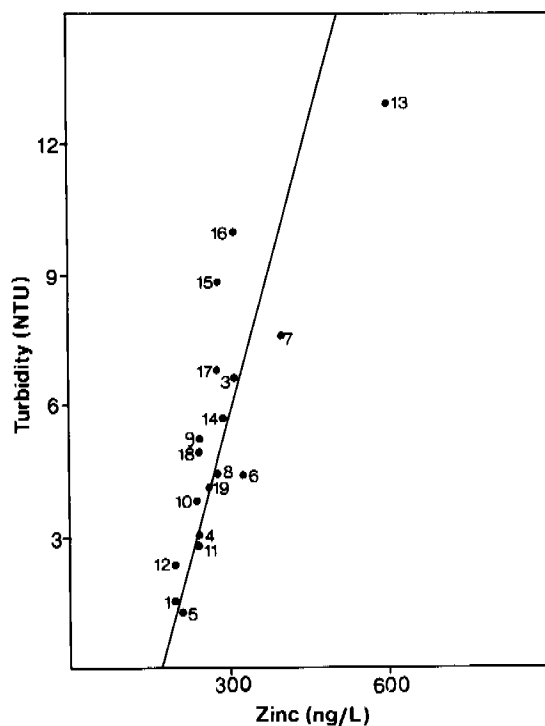


Figure 3. Concentration of zinc as a function of turbidity in samples from the Georgetown site
The turbidity of sample 2 (19.3.86) is off-scale and has not been included

Zinc may be bound to clay particles either by adsorption to hydroxyl groups, which is the principal mode for kaolinites and illites, or by cation exchange with the supplementary ions of minerals which have undergone isomorphous replacement, which is the principal mode for montmorillonites (Pickering 1980). Kaolinite is the most common clay mineral in the Magela Creek system, both in suspended sediments (Thomas & Hart 1984) and soil profiles (Chartres et al. 1988), with illite also being present.

However, although both kaolinite and illite can adsorb significant quantities of zinc (up to approximately 5 g/kg clay near pH 5; Pickering 1980), it is not thought that this occurs in Magela Creek because:

- i) both calcium and magnesium, which are present in the creek at concentrations about 1000 times that of zinc, generally compete efficiently with zinc for clay adsorption sites, even at equimolar proportions (Pickering 1980), and,
- ii) clay particles are almost certainly coated with organic material, in similar manner to the oxyhydroxides described above (Thomas & Hart 1984; Hart 1987b).

A third category of particle-associated zinc which may be present in the collected samples is that contained in living microorganisms. There are no data for zinc in Magela Creek phytoplankton but an estimate of the possible maximum derived from this source can be made as follows: the concentration of zinc in a *Microcystis* bloom sampled from RP2 in 1985 was 25 µg/g dry mass (Noller et al. 1987). The concentration of zinc in RP2 is higher than that in Magela Creek and therefore the value of 25 µg/g is regarded here as representing the maximum concentration of zinc that might be present in phytoplankton in the samples collected. This concentration can be used to calculate two estimates of the potential maximum zinc contribution from this source. (It is assumed that phytoplankton constitute the dominant microorganisms in Magela Creek.)

The first estimate uses data for total organic carbon (TOC). The mean TOC for Mudginberri Billabong, GS8210009 and GS8210028 for March and April 1979-1981 (n = 18) was 3.1 ± 0.5 mg/L (NT Water Resources Division, n.d.). It has been calculated, for one North American lake water, that approximately 8% of the TOC resides in the protoplasm of living phytoplankton (Saunders 1977). On this basis the concentration of carbon in Mudginberri Billabong attributable to phytoplankton is:

$$3.1 \text{ mg/L} \times 0.08 = 0.25 \text{ mg/L}$$

Stumm & Morgan (1981) report the chemical formula for the dry mass of algal protoplasm as being $\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P}$. Therefore, the dry mass of phytoplankton is approximately 36% carbon, and the dry-mass concentration of phytoplankton is:

$$0.25 \text{ mg/L} \div 0.36 = 0.69 \text{ mg/L dry mass phytoplankton.}$$

If the concentration of zinc in phytoplankton is 25 µg/g dry mass the zinc concentration from this source in Magela Creek is:

$$25 \text{ µg/g} \times 0.69 \text{ mg/L} = 17 \text{ ng/L zinc.}$$

The second estimate uses data for chlorophyll *a* concentration in water. The mean chlorophyll *a* concentration for Mudginberri Billabong, GS8210009 and GS8210028 at the times specified above for TOC was 1.4 ± 2.4 µg/L. Kirk (1983) reports a phytoplankton carbon:chlorophyll *a* ratio of 90:1 for nutrient-deficient surface waters. An estimate of the concentration of carbon due to phytoplankton can therefore be calculated thus:

$$90 \times 1.4 \text{ µg/L} = 130 \text{ µg/L.}$$

This can be converted to the dry mass of phytoplankton using the carbon content of algal protoplasm:

$$0.13 \text{ mg/L} \div 0.36 = 0.36 \text{ mg/L dry mass phytoplankton.}$$

Using 25 $\mu\text{g/g}$ as the dry-mass concentration of zinc in phytoplankton, the zinc concentration in Magela Creek water is:

$$25 \text{ } \mu\text{g/g} \times 0.36 \text{ mg/L} = 9 \text{ ng/L zinc.}$$

This value would be a maximum concentration because some of the measured chlorophyll *a* may be extracellular.

The calculation of zinc concentration in phytoplankton as between 9 ng/L and 17 ng/L using two different estimates increases confidence that any contribution of zinc from phytoplankton is a very small proportion of total measured zinc. This result is important because it is uncertain whether zinc originally incorporated in living protoplasm was liberated and therefore determined using the sample preparation procedure described earlier. The calculations above show that it is very probably less than the blank concentration, and therefore negligible.

It is concluded that acidification of the samples to 0.1% with HNO_3 (pH 1-2) mobilises all significant sources of zinc into solution except that fraction bound in the mineral matrix of the sediments. This 'residual' zinc would not be taken up by biota in the short-to-medium term and therefore is not included in the labile component of total zinc which is the subject of the present study.

3.2 Present results and comparison with other data

The results of the present investigation have two major features:

- i) the measured concentration of zinc in the creek is consistently at the lower end of the ranges found in previous studies. Some total zinc concentrations from previous studies are shown in Table 3. They show, in general, a declining trend in measured total zinc concentrations in that portion of the creek upstream of the Mudginberri Corridor. This suggests that previous determinations of zinc may have contained errors. The present results show a further decline; they are believed to be reliable because of the rigour with which contamination was minimised, and the satisfactory results for internal checks such as pre-collection monitoring and the determination of zinc in control waters.
- ii) the concentration of labile zinc in samples correlates with turbidity except for the four samples collected during the flood event which occurred in the sampling period. Linear regression of zinc concentrations against turbidity, with and without the flood event samples, yielded the following results:

$$\begin{array}{llll} [\text{Zn}^{2+}] = 16T + 180 & (n = 19) & \text{corr.} = 0.82 & (P < 0.001) \\ [\text{Zn}^{2+}] = 12T + 200 & (n = 15) & \text{corr.} = 0.92 & (P < 0.001) \end{array}$$

This correlation was not expected because previous work shows that very little labile zinc is associated with that fraction of the suspended load ($> 0.4 \mu\text{m}$) which almost exclusively contributes to turbidity (Hart 1987a). It therefore seems likely that both the larger suspended particulates and the colloidal/soluble material, which contains the zinc, are derived from surface sediments. The non-linearity during the flood event could be

Table 3. Summary of previous determinations of total zinc concentrations in Magela Creek and billabongs

Location	Collection time	Zinc ($\mu\text{g/L}$)		
		Mean	SD	n
GS8210009 ^a	December to July 1978-1981	6.7	6.4	20
Mudginberri Billabong ^a	All year 1978-1981	7.5	9.5	36
GS8210028 ^a	December to September 1978-1981	4.9	6.5	22
Above Djalkmara Creek outflow ^b	January to March 1979	2.8	0.7	42
Mudginberri Billabong ^c	November 1978	0.9	0.2	8
GS8210009 and Sandy Crossing ^d	December 1982 to April 1983	0.8	0.9	147
GS8210009 ^e	February to April 1983	0.6	not stated	45
Sandy Crossing ^f	March 1983	0.6	-	1

^aN.T. Water Resources Division (n.d.); ^bHart et al. (1981, 1982); ^cDavies & Hart (1981); ^dHart et al. (1986); ^eHart et al. (1987); ^fB.N. Noller, unpublished data.

explained by a disproportionate mobilisation of soluble zinc and fine colloids compared with heavier sediments on the turbulent upward arm of the hydrograph with a transient depletion on the downward arm resulting from removal of zinc from surface sediments. Hart et al. (1987) have interpreted decreasing conductivity on the rising arm and increasing conductivity on the falling arm of the hydrograph in terms of a period dominated by surface runoff followed by a period when interflow and base flow are more important. This would suggest that zinc is closely associated with surface sediments and may argue strongly for a biogenic/rainwater rather than a groundwater source for the metal, and perhaps the sandstone catchment surface rather than the schist-clay surface further downstream.

Hart (1987a) did not observe an increase in the concentration of colloids on the rising arm of the hydrograph for this flood event. This result could indicate that the increase in zinc concentration was due to the soluble component. It is also possible that the unexpectedly low proportion of colloids was due to coagulation of the finest material during sample preparation.

The concentration of labile zinc at Bowerbird Billabong was less than half the value at the Georgetown site under normal flow conditions. This probably reflects the smaller cumulative net contribution of biogenic, rainwater and groundwater sources of the metal at the headwater location.

3.3 Implications for a statistically-based interim receiving water standard

Statistically-based interim receiving water standards are derived to allow a prudent estimate to be made of allowable concentrations of target constituents in receiving waters should a release of waste water be required before more appropriate standards are set. For the Alligator Rivers Region, the statistically-based criterion for the release of target constituents is that the mean concentration during release not be greater than the natural mean concentration by more than one standard deviation of the latter (Brown et al. 1985). This is a conservative criterion and ensures that the mean concentration during discharge is likely to remain within the natural concentration range of the constituent. If the data obtained from the present investigation were applied according to this criterion, the permitted mean concentration of zinc during release of stored water would be 460 ng/L, a value derived by adding the standard deviation for all determinations (149 ng/L) to the mean for all determinations (307 ng/L), rounded to two significant figures.

3.4 Implications for use of acute toxicity zinc data

It is of interest to compare available zinc toxicity data for Magela Creek species with the zinc concentrations measured in Magela Creek in this study. The present investigation measured labile zinc, that fraction considered to be available to biota in the short term.

There are only a few data on the toxicity of zinc to aquatic species from the Magela Creek system. Documented studies contain toxicity data for chequered rainbow-fish, black-banded rainbow-fish and fly-specked hardyhead (Baker & Walden 1984) and larval chequered rainbow-fish (McBride 1987b). The 96-hour median lethal concentrations for these were: 4.8, 6.8, 0.6 and ≈ 0.17 mg/L respectively for water hardness of 7.3, 7.3, 42 mg/L (as CaCO_3) and unspecified.

The most sensitive species in the more detailed investigation was the fly-specked hardyhead (Baker & Walden 1984). Increased mortality above control seemed to be evident for this species near 100 $\mu\text{g/L}$. There are at least three reasons why a concentration of 100 $\mu\text{g/L}$ may be unacceptably high for discharge to Magela Creek where the protection goal is ecosystem maintenance:

- i) The experiments were not performed using fish larvae, which are likely to be more sensitive to toxicants than more mature fish. A comparison of the 96-h LC_{50} values for larval (McBride 1987b) and adult (Baker & Walden 1984) chequered rainbow-fish suggests that the effect may be significant.
- ii) The hardness of the water in which the hardyheads were tested (42 mg/L as CaCO_3) was greater by a factor of 10 than that expected in Magela Creek (NT Water Resources Division, 1987). Increased water hardness (independently of the related parameter, alkalinity) has been shown to ameliorate the toxicity of heavy metals (Miller & Mackay 1980). This may be due to the homeostatic mechanisms for regulation of calcium also serving to exclude the toxicant (Brown 1976).
- iii) There are almost certainly species in the Magela Creek system more sensitive to zinc than those tested. Although no other publications dealing with the Alligator Rivers Region exist, Hart (1982) has reviewed a considerable body of zinc toxicity data. These data demonstrate that sensitivity to the metal can range over at least three orders of magnitude between taxonomic groups. Wide variations occur among fish and among invertebrates. Some cladocerans, a group of microinvertebrates which is represented in the Magela Creek system (McBride 1987a) have 48-h LC_{50} values of less than 100 $\mu\text{g/L}$ (Hart 1982). It is probable that adverse biological effects can be detected in them below this concentration.

It must be emphasised that when trying to protect ecosystems the LC_{50} concentration is of little use; the 'no-observed-effect-concentration' determined for a number of species and a number of end points is the only acceptable basis for assessing environmentally safe dilutions.

4 CONCLUSIONS

The present investigation demonstrates that the concentration of total labile zinc in Magela Creek near the Ranger uranium mine waste water discharge pipe is lower than many previous studies suggested. The present results are considered to be reliable because:

- i) a rigorous sampling and handling procedure, with internal checks, was developed to minimise contamination with extraneous zinc and to detect it if present, and

- ii) errors in zinc determinations are usually caused by contamination rather than losses, and the present results yield concentrations near the bottom of the range for all determinations in Magela Creek.

The zinc concentrations at Bowerbird Billabong, averaging about 100 ng/L, would be among the lowest concentrations ever measured in freshwater (Hart 1982). It is unlikely that the concentration of labile zinc in Magela Creek at the Georgetown site ever exceeds 1 $\mu\text{g/L}$, except perhaps as the creek rises to a major flood event. During normal flow conditions it is in the range 200-300 ng/L.

If the 'natural variations' statistical criterion for establishing interim receiving water standards (Brown et al. 1985) is applied to the present data, the mean concentration of zinc in receiving waters during discharge should not exceed 460 ng/L. Whether such a cautious limit should apply can only be determined by an analysis of the results for toxicity testing of organisms whose sensitivity to zinc is suspected to be of ecological significance. However, the data from the present study suggests a statistical estimate which is similar to estimates based on toxicity data from the Alligator Rivers Region and literature sources.

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APPENDIX TABLES

Table A1. Concentration of total and filtrable ($< 0.4 \mu\text{m}$) zinc in Magela Creek from 10 November 1978 - 29 September 1986

Concentrations are in $\mu\text{g/L}$. Data obtained from NT Water Resources Division (1987); for statistical purposes, values below the detection limit are assumed to be 0.

Mudginberri Billabong			GS8210009			GS8210028		
Date	Zinc total	Zinc $< 0.4 \mu\text{m}$	Date	Zinc total	Zinc $< 0.4 \mu\text{m}$	Date	Zinc total	Zinc $< 0.4 \mu\text{m}$
10.11.78	9.7	7.4	5.12.78	2.3	0.9	11.1.79	1.8	1.5
7.12.78	3.2	3.0	16.2.79	3.1	2.2	16.2.79	1.8	1.6
11.1.79	22.0	21.0	21.3.79	5.8	5.8	22.3.79	2.9	2.1
16.2.79	2.4	1.9	17.4.79	5.1	0.5	18.4.79	15.0	4.9
20.3.79	3.9	3.5	15.5.79	1.4	1.4	16.5.79	5.1	3.2
20.4.79	3.7	1.9	12.6.79	1.7	1.7	13.6.79	2.7	1.8
17.5.79	2.1	1.6	10.7.79	3.8	3.0	12.7.79	75.0	75.0*
14.6.79	3.8	1.3	8.1.80	5.0	1.5	9.1.80	13.0	9.0
12.7.79	8.7	6.2	22.1.80	1.0	1.0	25.1.80	2.5	0.5
10.8.79	3.0	3.0	6.2.80	3.5	0.5	7.2.80	3.5	1.5
6.9.79	5.7	5.6	21.2.80	1.0	1.0	20.2.80	4.5	3.0
2.10.79	5.4	2.8	5.3.80	6.0	2.5	5.3.80	13.0	13.0
18.10.79	5.3	5.3	1.4.80	22.0	20.0	1.4.80	85.0	81.0*
30.10.79	11.0	11.0	7.5.80	25.0	21.0	7.5.80	5.0	3.0
13.11.79	2.5	2.0	5.6.80	< 0.5	< 0.5	5.6.80	< 0.5	< 0.5
27.11.79	1.0	< 0.5	2.7.80	6.5	3.5	1.7.80	< 0.5	< 0.5
13.12.79	10.0	9.5	8.1.81	6.0	3.0	7.8.80	28.0	25.0
8.1.80	49.0	41.0	4.2.81	7.0	7.0	4.9.80	2.0	< 0.5
24.1.80	1.0	1.0	3.3.81	4.0	4.0	13.1.81	3.5	3.5
6.2.80	5.1	2.5	30.3.81	8.0	8.0	11.2.81	1.5	< 0.5
21.2.80	24.0	24.0	14.5.81	5.0	4.0	6.3.81	< 0.5	< 0.5
5.3.80	7.0	2.5	2.6.81	12.0	8.5	1.4.81	4.0	2.5
1.4.80	24.0	17.0	7.7.81	2.0	< 0.5	7.5.81	9.5	8.0
7.5.80	10.0	7.0	4.8.81	13.0	5.0	3.6.81	6.0	4.5
4.6.80	< 0.5	< 0.5	8.12.81	4.5	2.5	7.7.81	2.5	1.5
2.7.80	11.0	3.0	22.12.81	16.0	12.0	6.8.81	26.0	23.0
6.8.80	3.0	2.0	4.1.82	14.0	9.0	6.10.81	49.0	41.0
3.9.80	2.5	2.5	18.1.82	28.0	26.0	3.11.81	40.0	17.0
8.10.80	7.0	5.5	8.2.82	6.5	2.5	3.12.81	16.0	3.5
5.11.80	1.5	1.5	17.2.82	6.5	2.5	15.12.81	5.5	1.0
19.11.80	1.3	1.3	2.3.82	5.5	2.0	5.1.82	15.0	15.0
3.12.80	< 0.5	< 0.5	5.4.82	2.8	1.9	19.1.82	8.0	2.0
5.1.81	15.0	9.5	4.5.82	11.0	7.2	2.2.82	9.5	1.5
6.2.81	5.0	4.0	8.6.82	10.0	3.8	15.2.82	11.0	6.0
2.3.81	< 0.5	< 0.5	6.7.82	10.0	7.1	3.3.82	6.5	2.0
31.3.81	4.0	3.0	5.1.83	15.0	12.0	7.4.82	3.0	3.0
12.5.81	8.0	5.0	7.2.83	2.6	1.3	5.8.82	44.0	4.4
2.6.81	17.0	15.0	7.3.83	4.3	3.6	14.2.83	6.0	3.2
8.7.81	10.0	7.5	15.3.83	4.9	3.5	4.7.83	17.0	13.0
5.8.81	6.5	0.5	29.3.83	5.0	3.0	3.1.84	68.0	45.0*
6.10.81	39.0	11.0	6.4.83	6.0	4.5	3.7.84	4.7	3.6
5.11.81	7.0	7.0	27.4.83	61.0	60.0*	7.1.85	54.0	49.0*
1.12.81	21.0	2.5	4.5.83	5.0	3.9	9.5.85	3.7	1.1
22.12.81	33.0	11.0	6.6.83	20.0	18.0	9.12.85	15.0	9.9
11.1.82	21.0	13.0	4.7.83	6.1	1.8	13.1.86	6.0	2.8
18.1.82	4.5	3.0	6.12.83	5.2	3.0	19.2.86	11.0	8.8
8.2.82	8.0	4.0	3.1.84	14.0	12.0	7.5.86	11.0	8.4
19.12.82	6.5	2.0	6.2.84	3.9	2.4	3.6.86	57.0	33.0*
2.3.82	5.5	1.0	7.3.84	5.4	2.1	29.7.86	44.0	29.0
6.4.82	3.0	2.5	2.4.84	6.4	4.3	29.9.86	30.0	18.0
5.7.82	3.7	1.6	8.5.84	4.5	2.6			
5.1.83	4.9	3.8	5.6.84	3.4	2.1	Mean \pm SD	11 \pm 13	6.8 \pm 8.8

Table A1. cont.

Mudginberri Billabong			GS8210009			GS8210028		
Date	Zinc total	Zinc < 0.4 μm)	Date	Zinc total	Zinc < 0.4 μm	Date	Zinc total	Zinc < 0.4 μm
20.6.83	4.1	2.6	2.7.84	8.0	6.3			
5.7.83	10.0	7.3	30.7.84	13.0	8.0			
12.6.84	5.9	4.2	9.1.85	67.0	57.0*			
16.10.84	8.2	5.5	22.1.85	6.3	5.4			
2.12.85	18.0	7.2	30.1.85	14.0	8.1			
			6.2.85	410.0	410.0*			
Mean \pm SD	12 \pm 9.6	6.5 \pm 5.4	12.2.85	6.2	4.1			
			19.2.85	9.5	7.5			
			26.2.85	5.3	1.1			
			5.3.85	11.0	9.6			
			13.3.85	6.4	3.2			
			14.3.85	6.9	1.6			
			26.3.85	9.4	6.7			
			1.4.85	7.4	5.7			
			10.4.85	10.0	3.4			
			17.4.85	14.0	12.0			
			24.4.85	75.0	71.0*			
			1.5.85	3.8	2.7			
			8.5.85	3.5	2.4			
			19.6.85	7.8	5.9			
			9.12.85	19.0	11.0			
			13.1.86	14.0	11.0			
			31.1.86	12.0	6.4			
			12.2.86	27.0	21.0			
			17.2.86	9.9	8.7			
			10.3.86	8.5	4.3			
			1.5.86	12.0	6.6			
			3.6.86	19.0	13.0			
			Mean \pm SD	8.6 \pm 6.0	5.9 \pm 5.3			

*Not included in calculation of mean

Table A2. Spectrophotometer program for determination of zinc by graphite furnace atomic spectroscopy (Perkin Elmer model 5000AAS and model AS40)

Parameter	Value
Wave length	213.7 nm
Energy source	Hollow cathode lamp
Current	10 mA
Amplifier gain	318
Slit width	Low 0.7 nm
Integration mode	Peak height
Integration time	5 s
Calibration standard	0 and 1000 ng/L
Sample volume	35 μL
Absorbance (35 μL of 1000 ng/L)	0.29
Detection limit	15 ng/L

Table A3. Graphite furnace AAS program for determination of zinc in Magela Creek water (Perkin Elmer model HGA500)

Step	1	2	3	4
Function	Dry	Ash	Atomise	Clean-out
Temperature ($^{\circ}\text{C}$)	110	500	2300	2700
Ramp time(s)	5	5	0	1
Hold time(s)	25	10	2	2
Record trace(s)	No	No	-5	No
Initiate integration(s)	No	No	-1	No
Baseline correction	No	No	No	No
Gas flow (mL/min)	300	300	50	300

Table A4a. Average values for individual bottles for blank and sample determinations of zinc in Magela Creek water (Georgetown site)

Concentrations are in ng/L

Blanks (2 cups for each bottle)				Samples (3 cups for each bottle)			
Date	Bottle	Zinc \pm SD	Mean \pm SD	Date	Bottle	Zinc \pm SD	Mean \pm SD
18.3.86	1	39 \pm 9		18.3.86	1	194 \pm 7	
	2	35 \pm 6			2	204 \pm 20	
	3	27 \pm 6			3	221 \pm 26	
	4	27 \pm 6			4	182 \pm 9	
	5	21 \pm 2	30 \pm 7		5	178 \pm 7	196 \pm 17
19.3.86	1	23 \pm 6		19.3.86	1	876 \pm 25	
	2	27 \pm 6			2	681 \pm 26	
	3	23 \pm 4			3	723 \pm 66	
	4	26 \pm 8			4	670 \pm 38	
	5	24 \pm 5	25 \pm 2		5	742 \pm 102	738 \pm 82
20.3.86	1	37 \pm 5		20.3.86	1	553 \pm 34*	
	2	34 \pm 5			2	436 \pm 85*	
	3	28 \pm 3			3	308 \pm 29	
	4	30 \pm 6			4	288 \pm 49	
	5	25 \pm 8	31 \pm 5		5	320 \pm 44	305 \pm 16
21.3.86	1	34 \pm 7		21.3.86	1	256 \pm 15	
	2	44 \pm 8			2	253 \pm 25	
	3	40 \pm 6			3	240 \pm 6	
	4	44 \pm 12			4	235 \pm 11	
	5	50 \pm 7	42 \pm 6		5	235 \pm 9	244 \pm 17
24.3.86	1	121 \pm 24		24.3.86	1	200 \pm 7	
	2	113 \pm 6			2	219 \pm 5	
	3	102 \pm 9			3	188 \pm 7	
	4	112 \pm 2			4	216 \pm 35	
	5	107 \pm 4	111 \pm 7		5	210 \pm 22	207 \pm 13
25.3.86	1	21 \pm 3		25.3.86	1	369 \pm 22	
	2	24 \pm 6			2	360 \pm 23	
	3	20 \pm 2			3	341 \pm 13	
	4	26 \pm 3			4	315 \pm 23	
	5	17 \pm 2	21 \pm 5		5	327 \pm 6	342 \pm 22
26.3.86	1	542 \pm 72*		26.3.86	1	457 \pm 107	
	2	29 \pm 9			2	1050 \pm 80*	
	3	64 \pm 47			3	451 \pm 36	
	4	22 \pm 4			4	466 \pm 58	
	5	23 \pm 2	35 \pm 20		5	427 \pm 33	450 \pm 17
27.3.86	1	703 \pm 17*		27.3.86	1	240 \pm 8	
	2	639 \pm 10*			2	267 \pm 33	
	3	917 \pm 11*			3	284 \pm 29	
	4	21 \pm 4			4	293 \pm 28	
	5	641 \pm 7*	21		5	278 \pm 39	272 \pm 20
1.4.86	1	36 \pm 3		1.4.86	1	224 \pm 5	
	2	21 \pm 3			2	216 \pm 6	
	3	35 \pm 2			3	790 \pm 43*	
	4	29 \pm 4			4	580 \pm 53*	
	5	44 \pm 8	33 \pm 9		5	228 \pm 9	223 \pm 6
2.4.86	1	30 \pm 2		2.4.86	1	225 \pm 6	
	2	21 \pm 1			2	250 \pm 8	
	3	21 \pm 5			3	226 \pm 4	
	4	26 \pm 9			4	227 \pm 15	
	5	36 \pm 3	27 \pm 6		5	232 \pm 17	232 \pm 10

Table A4a cont.

Blanks (2 cups for each bottle)				Samples (3 cups for each bottle)			
Date	Bottle	Zinc \pm SD	Mean \pm SD	Date	Bottle	Zinc \pm SD	Mean \pm SD
3.4.86	1	24 \pm 4		3.4.86	1	243 \pm 6	
	2	21 \pm 3			2	225 \pm 8	
	3	21 \pm 3			3	219 \pm 9	
	4	18 \pm 2			4	242 \pm 13	
	5	22 \pm 2	21 \pm 2		5	242 \pm 7	232 \pm 11
4.4.86	1	25 \pm 7		4.4.86	1	206 \pm 9	
	2	24 \pm 4			2	203 \pm 10	
	3	18 \pm 2			3	237 \pm 11	
	4	24 \pm 6			4	187 \pm 6	
	5	28 \pm 4	24 \pm 4		5	180 \pm 10	203 \pm 22
10.4.86 (1150 h)	1	47 \pm 4		10.4.86 (1150h)	1	676 \pm 17	
	2	32 \pm 8			2	647 \pm 13	
	3	21 \pm 3			3	630 \pm 23	
	4	39 \pm 3			4	650 \pm 33	
	5	37 \pm 6	35 \pm 10		5	651 \pm 32	651 \pm 16
10.4.86 (1615 h)	1	20 \pm 2		10.4.86 (1615h)	1	286 \pm 15	
	2	21 \pm 3			2	322 \pm 32	
	3	18 \pm 3			3	266 \pm 7	
	4	21 \pm 4			4	290 \pm 8	
	5	23 \pm 4	21 \pm 2		5	298 \pm 13	292 \pm 20
11.4.86 (1145 h)	1	25 \pm 4		11.4.86 (1145h)	1	439 \pm 22*	
	2	24 \pm 2			2	229 \pm 7	
	3	29 \pm 7			3	225 \pm 6	
	4	25 \pm 3			4	227 \pm 6	
	5	18 \pm 2	24 \pm 4		5	273 \pm 7	239 \pm 23
11.4.86 (1730 h)	1	27 \pm 5		11.4.86 (1730h)	1	310 \pm 27	
	2	30 \pm 3			2	310 \pm 12	
	3	22 \pm 2			3	283 \pm 9	
	4	19 \pm 3			4	286 \pm 27	
	5	20 \pm 3	24 \pm 5		5	263 \pm 10	290 \pm 20
14.4.86	1	20 \pm 2		14.4.86	1	222 \pm 8	
	2	27 \pm 6			2	265 \pm 9	
	3	19 \pm 3			3	240 \pm 16	
	4	32 \pm 3			4	220 \pm 3	
	5	21 \pm 3	24 \pm 6		5	248 \pm 10	239 \pm 19
15.4.86	1	30 \pm 5		15.4.86	1	225 \pm 16	
	2	26 \pm 4			2	215 \pm 6	
	3	21 \pm 4			3	224 \pm 11	
	4	21 \pm 2			4	223 \pm 5	
	5	22 \pm 3	24 \pm 4		5	223 \pm 4	222 \pm 4
16.4.86	1	27 \pm 2		16.4.86	1	282 \pm 15	
	2	19 \pm 2			2	242 \pm 5	
	3	20 \pm 3			3	260 \pm 6	
	4	22 \pm 2			4	238 \pm 5	
	5	20 \pm 3	22 \pm 3		5	252 \pm 5	255 \pm 17

*These blanks and samples were not used in computing means

Table A4b. Average values for individual bottles for blank and sample determinations of zinc in Magela Creek water (Bowerbird Billabong, 15.4.86)

Concentrations are in ng/L

Location	Bottle	[Zinc] \pm SD	Mean \pm SD
Blanks (2 cups for each bottle)			
	1	26 \pm 2	
	2	21 \pm 3	
	3	22 \pm 3	
	4	27 \pm 3	
	5	17 \pm 2	23 \pm 4
Samples (3 cups for each bottle)			
Billabong	1	380 \pm 5*	
	2	153 \pm 6	
	3	141 \pm 7	
	4	162 \pm 5	
	5	93 \pm 3	
	6	106 \pm 9	
	7	124 \pm 2	
	8	91 \pm 4	
	9	88 \pm 3	
	10	128 \pm 6	121 \pm 28
Outflow	1	79 \pm 9	
	2	81 \pm 8	
	3	84 \pm 3	
	4	86 \pm 2	
	5	90 \pm 6	
	6	98 \pm 8	
	7	76 \pm 11	
	8	93 \pm 6	
	9	80 \pm 4	
	10	98 \pm 11	86 \pm 8

*This sample was not used in computing means

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RESEARCH PUBLICATIONS

Alligator Rivers Region Research Institute Research Report 1983-84
 Alligator Rivers Region Research Institute Annual Research Summary 1984-85
 Alligator Rivers Region Research Institute Annual Research Summary 1985-86
 Alligator Rivers Region Research Institute Annual Research Summary 1986-87

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RR 2	Water quality characteristics of eight billabongs in the Magela Creek catchment. December 1982 (pb, mf - 60 pp.)	B.T. Hart & R.J. McGregor
RR 3	A limnological survey of the Alligator Rivers Region. I. Diatoms (Bacillariophyceae) of the Region. August 1983 (pb, mf - 160 pp.)	D.P. Thomas
	*A limnological survey of the Alligator Rivers Region. II. Freshwater algae, exclusive of diatoms. 1986 (pb, mf - 176 pp.)	H.U. Ling & P.A. Tyler
RR 4	*Ecological studies on the freshwater fishes of the Alligator Rivers Region, Northern Territory. Volume I. Outline of the study, summary, conclusions and recommendations. 1986 (pb, mf - 63 pp.)	K.A. Bishop, S.A. Allen, D.A. Pollard & M.G. Cook
	Ecological studies on the freshwater fishes of the Alligator Rivers Region, Northern Territory. Volume II. (in press)	K.A. Bishop, S.A. Allen, D.A. Pollard & M.G. Cook
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RR 5	Macrophyte vegetation of the Magela Creek flood plain, Alligator Rivers Region, Northern Territory. March 1989 (pb - 41 pp.)	C.M. Finlayson, B.J. Bailey & I.D. Cowie
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TM 3	Transport of trace metals in the Magela Creek system, Northern Territory. III. Billabong sediments. December 1981 (pb, mf - 24 pp.)	P.A. Thomas, S.H.R. Davies & B.T. Hart
TM 4	The foraging behaviour of herons and egrets on the Magela Creek flood plain, Northern Territory. March 1982 (pb, mf - 20 pp.)	H.R. Recher & R.T. Holmes
TM 5	Flocculation of retention pond water. May 1982 (pb, mf - 8 pp.)	B.T. Hart & R.J. McGregor
TM 6	Dietary pathways through lizards of the Alligator Rivers Region Northern Territory. July 1984 (pb, mf - 15 pp.)	C.D. James, S.R. Morton, R.W. Braithwaite & J.C. Wombey
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TM 10	Oxidation of manganese(II) in Island Billabong water. October 1984	(pb, mf - 11 pp.)	B.T. Hart & M.J. Jones
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