The Finniss River
A Natural Laboratory of Mining Impacts - Past, Present and Future

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Finniss

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A Natural Laboratory of Mining Impacts – Past, Present and Future

Edited by

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Preface

The Rum Jungle uranium-copper mine in tropical northern Australia has been a source of acid rock drainage contaminants since the 1950s, which have had adverse impacts on the receiving waters of the Finniss River. During the late 1960s and early 1970s the annual contaminant loads of Cu, Zn, Mn and sulfate from Rum Jungle, that were received by the Finniss River, were quantified. The geographical scale and intensity of detriment to the aquatic biota of the Finniss River were also investigated, particularly with respect to effects on the diversity and abundance of fish and macroinvertebrates. These historical investigations clearly defined the impacted and unimpacted regions of the river: they also provided the pre-remedial benchmark of ecological detriment.

Mine site remediation began in 1982 followed by long-term monitoring of water quality and flow, based on daily measurements within the Finniss River system. Based on these data, both annual-cycle contaminant loads and frequency distributions of contaminant water concentrations have been determined; and hence their changes following remediation could be assessed. These data provided an objective measure of the efficacy of the remediation at the mine site, with regard to pollution of the Finniss River. A decade or more after the initiation of these remedial activities, a set of investigations have been completed that have measured the post-remedial ecological status of the Finniss River system, relative to this environmental benchmark. These studies have also been complemented by studies on various other ecological endpoints.

Moreover, the Finniss River system has provided unique opportunities for broader scientific goals to be pursued. Because it has been so well-monitored, it can be viewed as a natural laboratory to investigate the impacts of acid rock drainage on tropical freshwater biodiversity.

Its unique qualities include:

- The well-defined measured annual contaminant loads.
- Substantial measured reductions in these annual loads that followed remediation.
- Well-defined water chemistry based on daily measurements.
- Long time scales of quantified pollution exposure of the aquatic biota.
- Two scales of exposure and detriment in the Finniss River and its East Branch, that could be used to cross-reference interpretations of the patterns of ecological detriment.

The scientific papers presented at this symposium address a broad spectrum of issues that are directly related to environmental sustainability and mining. The topics range across future contaminant scenarios and their predicted ecological impacts, the various metrics used to assess ecological detriment to biodiversity, the abilities of laminated biological structures to act as archives of pollution history, and also spin-off applications in environmental and wildlife management. Furthermore, the participation of many stakeholders in open discussion during the symposium provided an important set of views and opinions on the needs for future studies in the Finniss River system. These are also included within the rapporteurs' report.

Ross A. Jeffree

Symposium convenor

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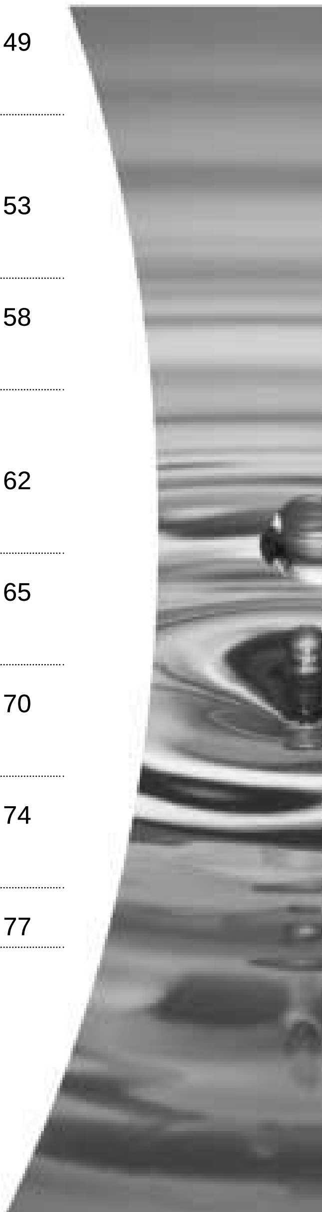

The Effectiveness of the Covers on the Rum Jungle Overburden Heaps after Fifteen Years

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Covers are widely used as a means of controlling pollutant generation from sulfidic waste piles. To date, there has been little data available to test the effectiveness of such covers. Monitoring of two waste rock dumps at Rum Jungle over more than fifteen years has provided the opportunity to assess cover effectiveness in the medium term. For the first nine years the infiltration rate through the cover on Whites dump was less than the design figure of 5% of rainfall. In subsequent years, however, the rate has increased to 5-10%, as shown in **Figure 1**.

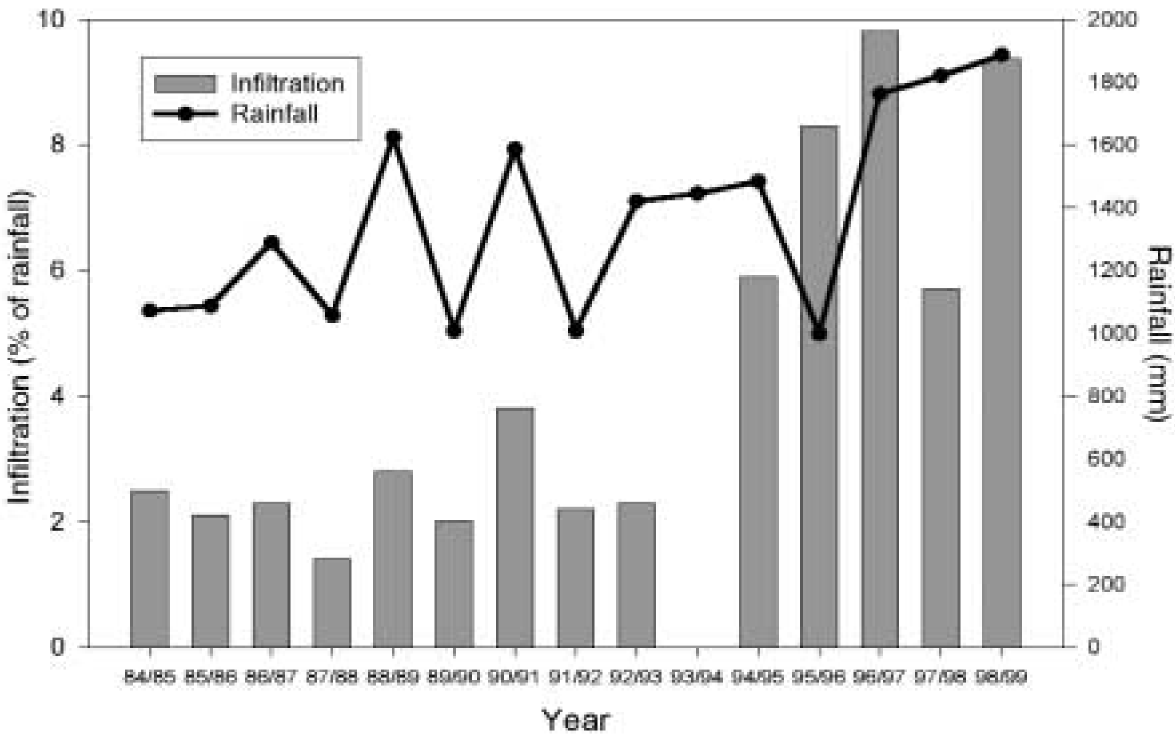

Figure 1. Infiltration into White's Dump at Rum Jungle after it was covered in 1984, and annual rainfall over the same period.

Oxygen and temperature profiles measured below the covers have been used to estimate the overall oxidation rate in the two dumps, Whites and Intermediate. This is between 30 and 50% of the oxidation rate prior to installation of the cover. The effect these results have on pollutant loads in drainage in the long-term depends on the nature of the control mechanisms in the system, as represented schematically in **Figure 2**. If pollutant concentrations in drainage are determined by secondary mineralisation within the dumps, then pollutant loads in the long-term will be essentially proportional to any further increase in the infiltration rate. If the pollutant loads in drainage are largely determined by the overall oxidation rates, then we can expect the pollutant loads from the two dumps to increase in the long term to a level about one third to one half of that prior to rehabilitation. In this context, ‘long-term’ means about 40 years after installation of the cover system.

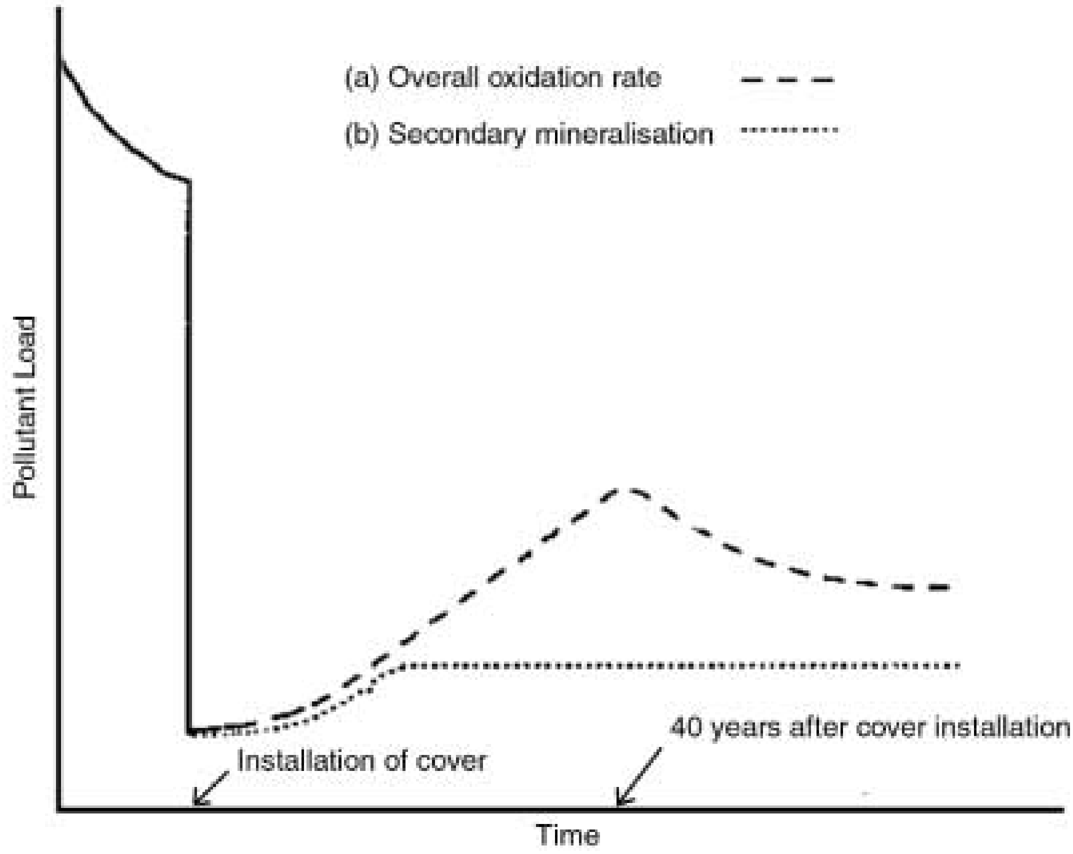

Figure 2. Schematic diagram of the pollutant loads in drainage in the long term where the system is controlled by either (a) overall oxidation rate or (b) secondary mineralisation.

Given the significant implications this work may have for the mining industry concerning the use of soil covers in controlling pollutant generation and release from piles of sulfidic wastes, the following additional studies should be undertaken:

- A measurement program to quantify pollution loads from Intermediate and Whites waste rock dumps.
- A program of computation, backed by acquisition of mineralogical data on the wastes, to address the question of controls on concentration and load in effluent from the two dumps.
- A measurement program to determine the reason for the deteriorating performance of the covers at Rum Jungle.

Bearing the Loads: Quantifying Contaminant Transport from the Rum Jungle Mine Site to the East Finniss River

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A program of work that has included the estimation of key contaminant loads exiting the Rum Jungle mine site to the receiving waters of the East Finniss River has operated over a considerable period (**Table 1**). Load reduction (70% for copper and zinc, 56% for manganese) was seen as a key objective of the rehabilitation program undertaken in 1983-86 and monitoring of loads since rehabilitation and ongoing compliance with these load reductions was seen as a key performance indicator of the integrity of the rehabilitation (Allen and Verhoeven, 1986). Sample collection and chemical analysis methods varied significantly over the period of data collection as resources and technologies changed, making comparisons on a year by year basis subject to significant uncertainties. In addition, there was a flow/load relationship prior to rehabilitation (clearly higher run-off led to increased mobilisation of unsecured tailings). A post-rehabilitation relationship is also apparent, but different in character (**Figure 1**). The same gauging station (GS 8150097), 5.6 km downstream of the Rum Jungle mine, was used for all measurements.

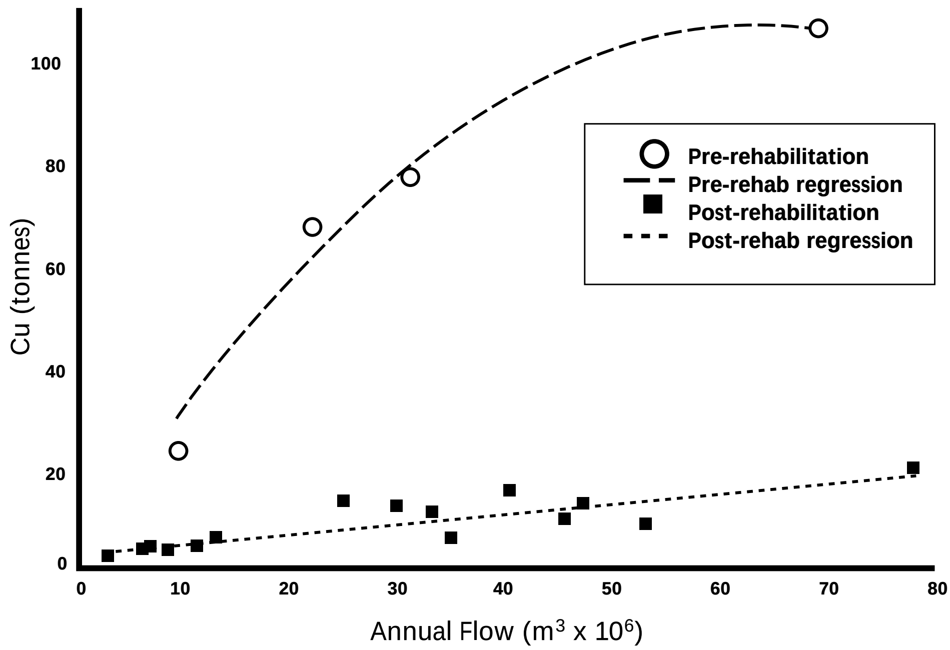


Figure 1. Selected copper loads (tonnes) measured at GS 8150097 from 1970 to 2000 (Table 1) versus total annual flow ($m^3 \times 10^6$).

Table 1. Historical load data (tonnes) of selected pollutants sourced from the Rum Jungle mine site measured at GS 8150097[a]. Flow (at the gauging station) and rainfall (at the mine site) data are also included

Year	Flow ($m^3 \times 10^6$)	Rainfall (mm)	Cu (total)	Cu (dissolved)	Zn (total)	Zn (dissolved)	Mn (total)	Mn (dissolved)	Sulfate
1969/70	7	896	44				46		3300
1970/71	33	1611	77		24		110		12000
1971/72	31	1542	77		24		84		6600
1972/73	22	1545	67		22		77		5500
1973/74	69	2000	106		30		87		13000
1982/83	9.5	1121	23		5		6		1520
1983/84	48	1704	28		9		21		3600
1984/85	11.7	1136	9.1		4.1		7.2		1600
1985/86	11.4	1185	3.7		2.7		8.2		4400
1986/87	13.2	1222	5.6		2.7		8.6		2870
1987/88	6.3	1064		3.2		2		5.4	1230
1988/89	35	1600		5.4		4.4		19.2	3940
1989/90	3.1	900		1.8		1.6		3.9	760
1990/91	40.5	1590	14.9	3	7.4	6	30.5	24.1	4000
1991/92	7.1	1002	3.8	2.8	2.7	2.6	9.1	8.9	1260
1992/93	29.9	1421	11.9	5	3.9	3.9	24.7	21.8	2696
1993/94	26.1	1367	12.7	4.6	5.3	4.4	17.9	16.9	2281
1994/95	33.3	1580	10.6	4.5	5.8	5.0	18.9	17.6	2994
1995/96	9.0	996	2.9	1.7	3.0	2.5	8.7	8.1	1352
1996/97	77.9	1716	19.3	5.5	7.4	6.1	25.4	20.1	4357
1997/98	47.3	1688	12.4	4.3	6.8	5.8	28.4	24.9	4812
1998/99	53.2	1888	8.2	1.4	5.5	3.8	13.9	9.3	3682
1999/00	45.6	1712	9.0	1.0	4.5	0.8	15.1	6.2	3023

a Data sourced (in part) from Davy et al. (1975) and annual NT PAWA surface water monitoring reports (1983-1991). Shaded cells indicate that metal analysis was performed on unacidified samples only.

An alternate assessment approach that might be used for the rehabilitation process, and perhaps one more related to biological measures of detriment, is to examine the frequency-distribution analyses of certain water quality attributes and, in particular for the Rum Jungle situation, pH and copper concentrations. This approach is demonstrated below with some examples.

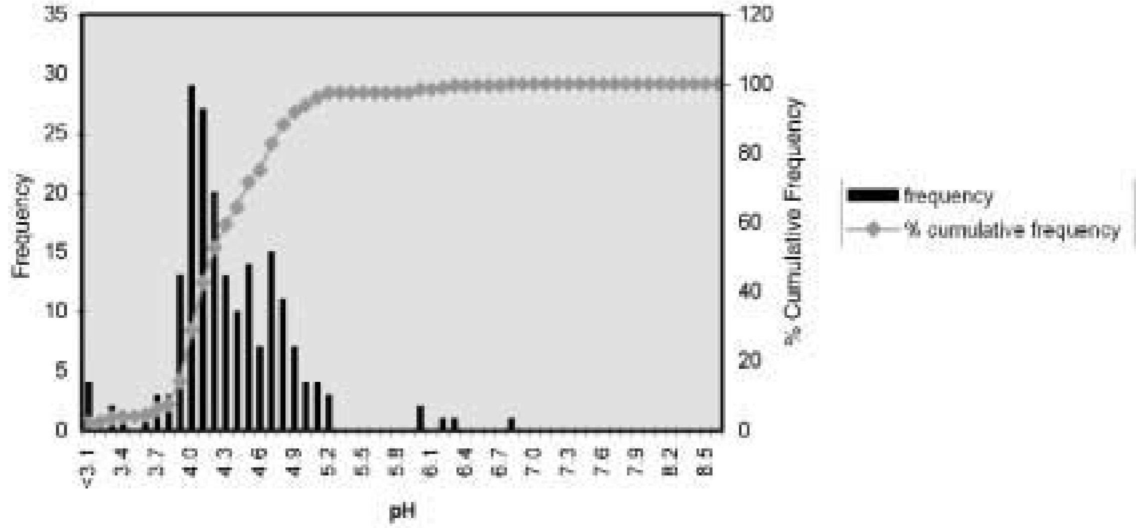


Figure 2. Frequency distribution of pH measures at GS 8150097 from 1967-71.

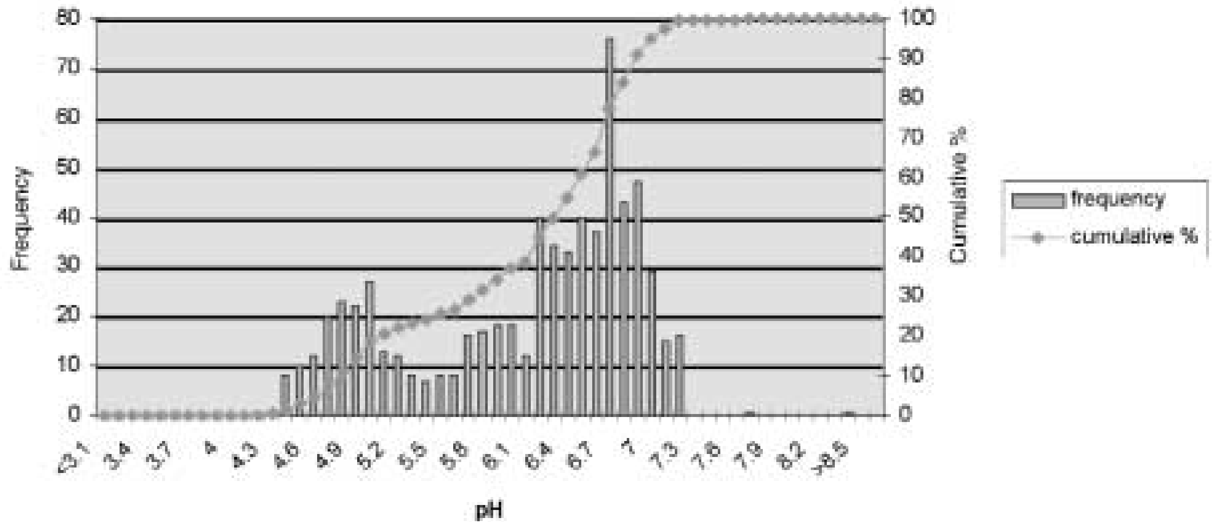


Figure 3. Frequency distribution of pH measures at GS 8150097 from 1990-95.

Figures 2 and **3** plot analysis data from individual water samples collected at GS 8150097. The 50th percentile value for the data sets occurs at pH 4.2 for the pre-rehabilitation period and at pH 6.3 for the five year period from 1990 to 1995. This represents a significant improvement in water quality in terms of acidity and bioavailability of certain acid-labile metals.

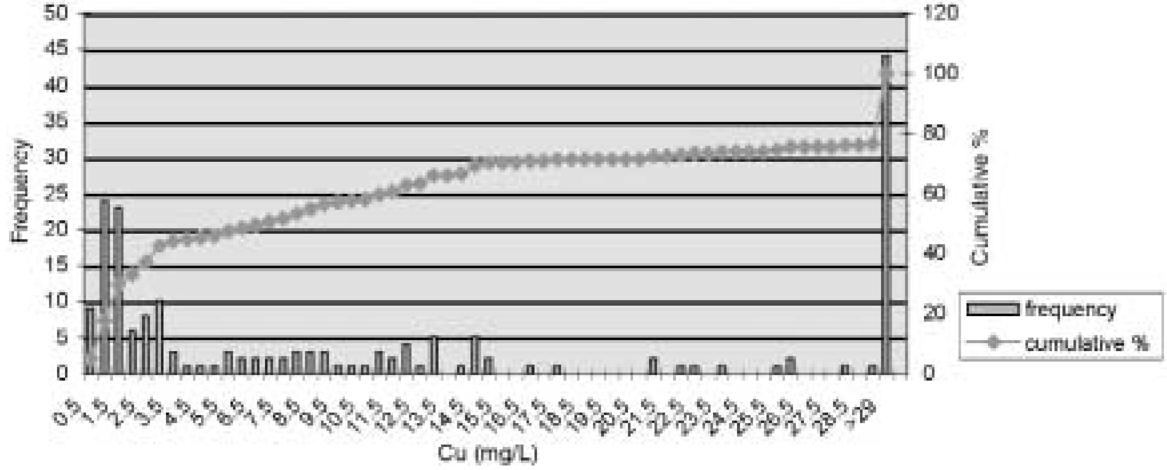


Figure 4. Frequency and cumulative percent frequency histogram of copper concentration values (mg L^{-1}) at GS 8150097 during the pre-rehabilitation period (1968-81). The number of samples analysed during this period was 188.

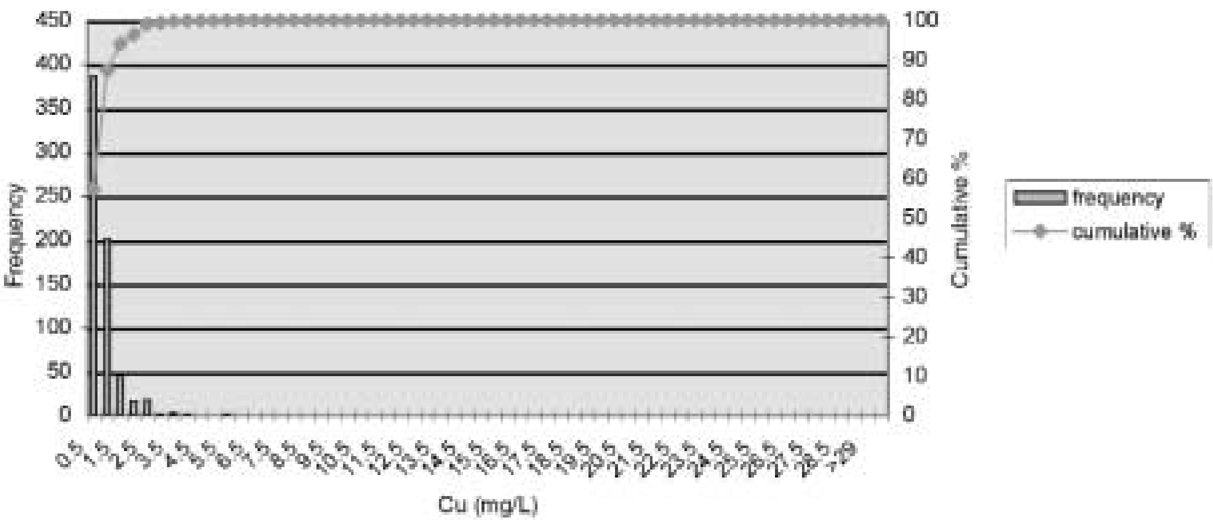
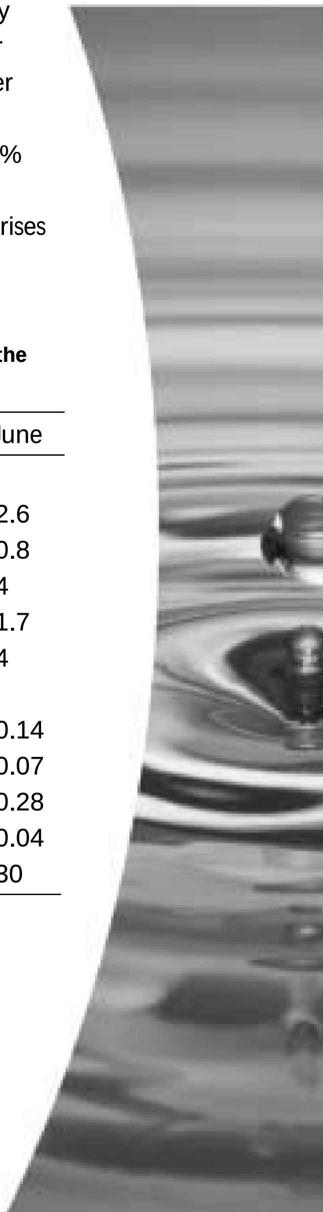


Figure 5. Frequency and cumulative percent frequency histogram of copper concentration values (mg L^{-1}) at GS 8150097 during 1990-95. Samples were collected daily over five consecutive wet seasons. The total number of daily samples collected during this period was 673.

Cumulative frequency histograms of copper concentrations in water sampled at GS 8150097 during pre-rehabilitation (1968–81) and post-rehabilitation (1990–95) are shown in **Figures 4** and **5**, respectively. The pre-rehabilitation 50th percentile copper concentration at GS 8150097 was approximately 7 mg L^{-1}, whereas post-rehabilitation was <0.5 mg L^{-1}. The difference between these two concentration values represents a significant improvement in water quality with respect to copper concentration, and perhaps a more meaningful performance indicator of the effectiveness of the rehabilitation than overall load measurements. Almost 90% of water samples collected during 1990–95 had a copper concentration <1 mg L^{-1} (**Figure 5**). This contrasts with data presented in **Figure 4**, where a substantial number of samples (almost 10% of all samples analysed) registered a copper concentration of >28.5 mg L^{-1} and only 30% of samples collected contained ≤ 1 mg L^{-1} of copper. A further data treatment approach summarises contaminant concentration variation over the duration of any given wet season and how this temporal profile has changed following rehabilitation (**Table 2** and **Figure 6**).

Table 2. Statistical analyses of copper concentrations of water samples from GS8150097 as a function of the month of collection comparing pre-rehabilitation (1968–85) and post-rehabilitation (1990–95) data

Measure	Dec	Jan	Feb	Mar	April	May	June
Pre-rehabilitation (1968-85)							
mean	34.1	29.4	5.6	1.6	1.5	2.5	2.6
std. dev.	32.9	44.1	9.3	2.0	5.2	2.9	0.8
max	122	182	48	12	42	21	4
min	0.1	0.2	0.1	0.1	0.1	0.3	1.7
n	67	116	70	101	64	53	4
Post-rehabilitation (1990-95)							
mean	1.08	0.61	0.76	0.60	0.37	0.33	0.14
std. dev.	0.56	0.46	0.52	0.74	0.39	0.19	0.07
max	2.48	2.48	3.07	5.18	2.51	1.19	0.28
min	0.12	0.08	0.16	0.01	0.05	0.06	0.04
n	53	109	121	136	119	105	30



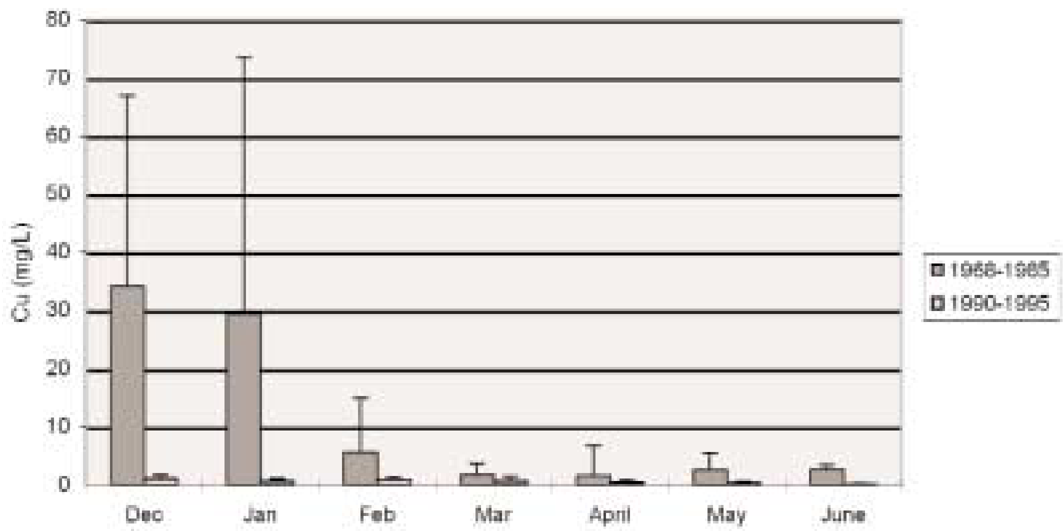


Figure 6. Mean monthly copper concentrations of water samples collected at GS 8150097 during two separate periods: 1968–85 and 1990–95. Error bars represent standard deviations.

Figure 6 illustrates the scheduling of contaminant delivery from the mine site to the receiving environment over the course of a wet season. Copper (and other contaminants not discussed here but included in **Table 1**) has highly variable and elevated concentrations early in the wet season and is most probably associated with high ecological impact relative to late wet season flows which are characterised by attenuated concentration profiles.

General conclusions

The Rum Jungle rehabilitation project, undertaken from 1983 to 1986, used specified percentile reductions in contaminant loads exiting the mine site as its key performance criteria. This approach has merit in allowing broad assessment of the efficacy of engineered structures to contain contaminants on-site, but has little relationship with ecological outcomes in the receiving waters. Presentation of monitoring data in terms of occurrence frequencies for key parameter concentrations provides an opportunity to better relate receiving water quality to known ecotoxicological relationships (ANZECC and ARMCANZ, 2000), and hence the effectiveness of the rehabilitation in terms of environmental impact.

In order to establish appropriate guidelines and/or criteria for off-site discharges or rehabilitation works, proper attention should be given to how toxicants are ‘presented’ to the receiving waters in light of their potential ecological impacts. Where contaminated discharges are inevitable (or deemed acceptable subject to conditions) as a result of mining activity, a strategic management assessment of how and when release might occur is vital to minimise detriment to acceptable levels. This strategic approach should be promoted in place of fixed contaminant load specifications or allowances. The linkage between toxicants and local or regional ecological detriment needs to be well understood to move forward with this approach.

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Mining in the Northern Territory: Evolution of Regulation

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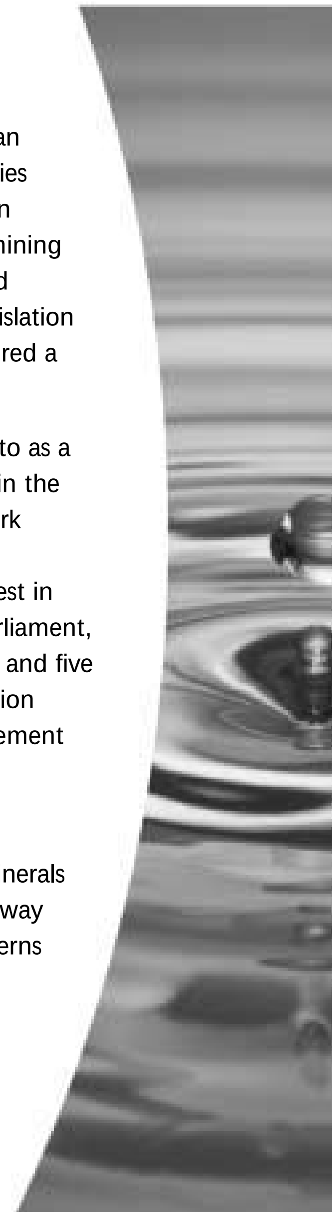
History of Northern Territory mining legislation with reference to uranium

The Northern Territory (NT) was administered by the Commonwealth Government until 1978, when it was granted self-government. At self government, the Commonwealth reserved certain 'state' powers for itself, including powers in relation to uranium mining, National Parks and the power to disallow NT legislation. The new NT administration considered the issue of approval for new uranium mining projects to be fundamental to the NTs economic wellbeing. Furthermore, the environmental condition of abandoned uranium mines, which had operated under Commonwealth jurisdiction, was a concern to the new government and they demanded rehabilitation funding.

The history of uranium mining started with the Rum Jungle deposits in 1949, although the presence of uranium secondaries had been noted there over fifty years earlier. This commenced the first phase of uranium exploration, which lasted some ten years and included the Rum Jungle/Adelaide River area, the South Alligator valley, the McArthur Basin and Pandanus Creek. In 1953 the Minerals Acquisition Act was passed and all minerals became the property of the Crown. The Rum Jungle uranium field was declared a restricted area under the provisions of the Defence (Special Undertakings) Act. All mining operations in the area were managed by Territory Enterprises Pty Ltd, a wholly owned subsidiary of CRA Ltd, on behalf of the Australian Atomic Energy Commission (now known as ANSTO). The second phase of uranium discoveries commenced in the late 1960s and led to the discovery of the world class uranium deposits in the Alligator Rivers Region. This exploration phase was short-lived and by November 1973 mining companies were told that those parts of their exploration licences that may become parkland (Kakadu) would not be renewed, but fresh licences would be granted once the NT Parks legislation became law. In October 1974, the Australian Atomic Energy Commission compulsorily acquired a 50% interest in the Ranger project.

After 4 June 1976, all mining titles or other interests in Aboriginal land became subject to veto as a result of the Aboriginal Land Rights (NT) Act. Apart from minor exploration which occurred in the following years at Ranger 68 and Coronation Hill, there has been virtually no exploration work conducted on what Deputy Prime Minister Doug Anthony then called 'the world's largest uncommitted uranium province'. Major uranium companies have retained an ongoing interest in Western Arnhem Land. By 1980, the Supervising Scientist, in his second annual report to parliament, listed 26 Commonwealth Acts and Regulations, 138 Northern Territory Acts and Regulations and five Agreements as being "prescribed instruments" for the purposes of the Environmental Protection (Alligator Rivers Region) Act. This has meant that it has been virtually impossible to get agreement on further uranium developments since that time.



The present Northern Territory mining industry

Mining is still the NTs largest industry sector and increased exploration and investment in minerals is vital to underpin its future economic growth. Mining is and always has been a part of the way of life and major contributor to the economic prosperity of the NT, but there are some concerns that this should not be taken for granted in the future. Using the most recent

Australian Bureau of Statistics figures, minerals and petroleum accounted for about 17.7% of NT Gross State Product in 1999-2000. This does not include alumina production of about $431 million. In 1999-2000, the value of production for minerals and petroleum totalled $2.86 billion, which is significantly more than 1998-99 figure of $1.31 billion. The petroleum industry contributed around half of the 1999-2000 total. Extractive minerals contributed around $A54 million to 1999-2000s total value of minerals production and this is a good indicator of the health of the building and infrastructure industry.

In 1999-2000, 3,671 people were employed in mining, quarrying, extractive and exploration activities in the NT. Salary and wages for could exceed $A220 million. A large portion of this will be injected back into the NT economy by way of consumer spending. However, there is still a large component of fly in/fly out workers (particularly in the oil and gas industry) who spend their earnings elsewhere.

Northern Territory minerals potential

The NTs foundations were laid on the discovery and development of minerals. Production values for past years emphasise the significant role minerals have played in the NTs economic, social and political growth. Indeed, the towns of Bachelor, Nhulunbuy, Jabiru, Pine Creek, Tennant Creek and Alyangula owe their existence to the development of minerals. Declining world commodity prices have been met with some notable closure of NT mines, particularly Mount Todd, Rustler's Roost, Woodcutters and mines in the Tennant Creek field. Most of the remaining mines have responded to the challenge by increasing throughput and raising the head grade. Both of these responses shorten mine life and several other projects have announced their imminent closure. The backbone of the NT minerals industry consists of four world-class ore bodies—namely bauxite at Gove, manganese at Groote Eylandt, uranium at Jabiru and lead-zinc concentrate at McArthur River. These four mines accounted for two thirds ($A623.7 million) of the value of minerals production in 1999-2000.

Exploration

The uncertainty of Government process and decreasing world commodity prices has impacted negatively on exploration expenditure. Australian mining companies are now concentrating around 40% of their exploration expenditure overseas with predictions that this proportion will increase. Despite this trend, exploration expenditure in Australia is still increasing overall, however the NT is noticeably being bypassed. It is no secret that the rate at which major new mines are being discovered in Australia has declined over the past decade. The NT minerals industry is still living off the results of past exploration and interestingly enough, the mines that resulted from this may be the only ones which will survive the next decade (**Table 1**). Impediments to exploration have become so serious that they now threaten the long-term continuity of the mining industry. With the possible exception of the Browns prospect at Rum Jungle, no world class ore bodies have been discovered in the NT since Jabiluka in 1973. There is typically a long lead-time between the discovery of large deposits and their development and there is very real possibility that the existing large mines will be exhausted before any major new deposits are found, proven up and brought into production.

Table 1. Life expectancy of major Northern Territory mines

Mine	Date discovered	Projected life
McArthur River	1955	2005-2015
Nabalco	1957	2030
GEMCO	1962	2032
Ranger	1970	2008
Jabiluka	1973	2028

It is a harsh reality that the minerals industry is at the mercy of world market forces. In 1999-2000 gold production accounted for 26.7% ($A326.5 million) of NT minerals production, and is currently dominated by several relatively short life mines. The outlook for the Tennant Creek area is of particular concern as the main mines have closed and the workers have now moved elsewhere. Despite some interesting exploration results, there are no significant gold projects being planned for the near future in the NT to replace the existing mines. Northern Territory minerals exploration expenditure totalled some $A57.5million in 1999-2000. Much of the expenditure occurs on secure titles adjacent to existing mills known as brownfields exploration. Major new mines are most likely to result from greenfields exploration. It is of concern that three quarters of greenfields expenditure was accounted for by just 10 exploration companies. Furthermore, it should be borne in mind that most of the brownfields expenditure occurred at only five mine sites.

The NT accounted for only 8.5% of the $6.8 billion spent on exploration in Australia in 1999-00. This is despite expert geological opinion that the NT lies in world class geological terrain and is far more prospective than exploration to date suggests. Discovery is intrinsically linked to the level of exploration and the NT has become unattractive to explorers. It is critical that these reasons are explored and corrected, if possible.

Obstacles to be overcome

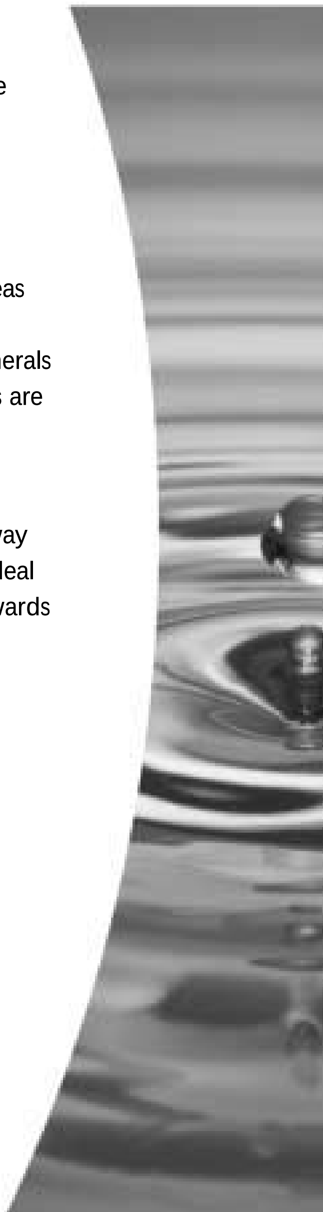
The hurdles being erected by all Governments to exploration, mining and downstream processing are becoming harder to jump. The complexities of government process have created uncertainty and a sometimes hostile regulatory environment. Solutions will only come from goodwill and cooperation between industry, Government (Federal, State and Local) and key stakeholders. The NT minerals industry has been particularly hard hit by Commonwealth Government policies. These have resulted, amongst other things, in the cancellation of the Coronation Hill mine, the deferral (for 30 years so far) of the Jabiluka and Koongarra mines, and the virtual sterilisation of some 50% of the NT from exploration. Land access has become difficult in the NT compared to the rest of Australia, and clearly we must try to resolve this impasse as Aboriginal participation is essential to the future of a viable minerals industry.

The industry's response to the restrictive exploration environment and complicated approval process in the NT has been to shift emphasis from greenfields exploration to brownfields developments, where approvals have already been given or to move exploration effort overseas where Government processes may be more certain and less costly. Remoteness and lack of infrastructure typically associated with the NT are not necessarily seen as impediments to minerals development, as they can be factored into the overall project costs. Most of the impediments are not within the capacity of the NT Department of Mines and Energy to resolve alone.

Modern regulatory process

It is widely recognised that heavy-handed regulatory systems are not a particularly effective way to achieve best practice outcomes – a more holistic approach to regulation is required. The ideal situation is to have Government and industry jointly setting goals and reviewing progress towards those goals. The NT Government is shifting away from the traditional command and control prescriptive style regulation, to self-regulation with its increased emphasis on company responsibility. Benchmarking in the areas of environment, health and safety are key steps in this shift.

In April 1997 the NT Government approved a review of the NT Mining Act and Mine Management Act to address changes necessary for the move toward self-regulation. The new legislation, the Mining Management Act 2001, was passed in July 2001 and it focusses on the issue of a licence or authorisation to operate with the provision of environmental management plans by operators



being central to individual developments. Financial securities to ensure rehabilitation upon mine closure are also an integral part of the legislative process as is an increase of powers to deal with environmental offenders. There are four levels of environmental offences ranging from the most serious (level 1) to the least serious (level 4). A level 1 offence carries individual penalties of up to $A250,000 and/or imprisonment and corporate penalties of up to $A1.25 million.

Planning for better environmental performance

It is now a requirement of Government to require planning as an integral part of an operation through the whole life cycle of a mine. On the environmental side, the requirement of a pre-mining environmental impact assessment has long been normal practice in the NT and elsewhere in Australia. This approach dates from the mid seventies and contains some elements of best practice. In 1997 the concept of mining and environmental management plans (MEMPs) was initiated to incorporate planning principles into the operational phase of mining. A MEMP details the work which will be carried out in the next period, usually one year, both in terms of environmental practice and health and safety. A MEMP does not by itself mean that an operation will achieve a high level of performance, but its implementation provides a structured and systematic tool that can contribute to optimal outcomes for all parties. Ideally a MEMP should evolve from the pre-mining assessment process picking up environmental objectives from this process with which to compare later performance. A MEMP lends itself to the philosophy of continuing improvement through goal setting and audit and transparency of process is guaranteed if the MEMP is subsequently made public.

With the assistance of industry the Government is also developing audit based management practices. Auditing of environmental management systems on mineral operations in the NT was another move towards adopting best practice principles and a part of the general move towards self-regulation. System audits provide a systematic documented alternative to the traditional command and control style of mines inspectors and provide the missing link of independent oversight of management. By contrast, policing of standards is both expensive and reactive and does not necessarily lead to improved outcomes. Management system auditing, being outcome oriented, has a much broader focus than an inspectorial approach. Audits check for both the existence and the linkage between policy, planning, implementation and operation, checking and corrective action and management review. This is the cycle of continuing improvement. The audit process has been positively received by the minerals industry and 25 NT mines produce regular environmental management plans. Over 170 comprehensive audits have been conducted by the NT Department of Mines and Energy in the last two years. These audits are providing feedback to the industry on how they perform against best practice standards and presenting clear direction on Government requirements.

Occupational health and safety systems

On the occupational health and safety (OH&S) side the NT has a consistently good safety record in comparison to the other states with a lost time injury frequency rate of 8.5 in 1999-2000. This compares to 25.2 in 1990-91. However, there is no room for complacency. The lost time duration rate is increasing (8.4 in 1992-93 compared to 14.7 in 1999-2000), indicating that while less serious incidents are being managed successfully, there is an underlying rate of serious accidents to be addressed. By developing a safety culture in the workplace and improving management, many of these injuries can be reduced.

The Government is gradually extending its formal audit process to encompass health and safety systems management. In the last year, eighteen comprehensive OH&S audits have been carried out at major mines and 132 audits of smaller operations. Nine OH&S audits have been conducted on larger mines. It is expected that this direction will positively impact on the minerals industry's safety performance. In both the environment and health and safety, there is a more proactive focus on analysing critical incidents, namely those that may not have caused a serious injury or environmental damage, but have the potential to do so. In this way the cause can be tackled before it becomes a fatality or an environmental issue. This information can then be passed to other mine sites locally and nationally to help formulate a picture of key areas to address.

Adopting new practices and processes takes considerable time and commitment. The NTs large minerals operations have the personnel and the systems which they are using to endeavour to reach best practice in mining operations and environmental, health and safety practice. However, smaller operations do not have the luxury of full time staff to comprehensively cover these areas. To address this the NT Department of Mines and Energy is placing more emphasis on ensuring that small operators are aware of their obligations and that they target improvement in these areas. This is being primarily done through audits and inspections.

Summary

In essence, the partnership between the NT Department of Mines and Energy and the NT minerals industry is adopting a proactive approach as it travels the road to self-regulation. The key to self-regulation's success is communication. It is imperative that the industry has non-bureaucratic forums for openly discussing future directions. A number of Government initiatives including industry workshops, recognition awards, mine rescue competitions and newsletters have been implemented to improve communication.

Whilst strong partnerships are being forged within the minerals industry there is undisputedly a need for better relationships outside the industry. By taking a reactive stance, the industry has allowed minority lobby groups to empower themselves and influence public opinion largely through misinformation. The industry needs to be more unified and proactive in rectifying its perceived poor reputation on the environment and safety and in educating the community to the vital role minerals play in their lifestyles. Unequivocal community support for mining will only come from responsible mining and advertising its positive achievements.

Browns Project: An Opportunity for the Finniss River

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Compass Resources NL is evaluating The Browns Project near Batchelor in the Northern Territory. The Browns Project development objectives include:

- Responsible development as a world scale "portable energy mine".
- A major exporter of value added products.
- To plan mine closure from day one.
- To listen, share and understand the impacts of the Browns development and ensure its positives far outweigh any negatives.
- To create a "win-win" project.

The Browns area contains large undeveloped mineral resources with 82 million tonnes of identified resources containing 1.9 million tonnes of lead, 98,000 tonnes of cobalt, 614,000 tonnes of copper, along with nickel, silver and zinc. Resources quoted in the Compass Resources NL 2000 Annual Report are summarised in **Table 1**. Since purchasing the Browns area in December 1994, Compass has expanded the resource to 82 million tonnes (and still open at depth and along strike) and gained an R & D Start Grant to integrate latest proven technologies into an innovative flowsheet. The project is immediately along strike from the former Rum Jungle operations.

Table 1. Quantity of undeveloped metal ores in the Browns Project area

	Million tonnes	Copper (%)	Lead (%)	Cobalt (%)	Nickel (%)
Browns	39	0.44	3.61	0.11	0.09
Browns East	31	1.29	1.28	0.13	0.13
Area 55	12	0.49	0.56	0.14	0.14
	82 (total)	0.77 (mean)	2.28 (mean)	0.12 (mean)	0.11 (mean)

Waste management strategies for acid rock drainage are to apply from day one. Alternatives being considered include encapsulate and seal, treatment and control, blend acid generating rock with acid consuming rock, and a combination of these. Indicative water balance considerations include a surplus during the wet season and a requirement for water during the dry season. Water management opportunities include increased flushing (possibly year round), controlled discharge of high quality water, possible use of acid water from the existing Intermediate and Whites open cuts, and waste and tailings run-off water used in plant. A full environmental and management plan will consider these and other water uses.

Browns offers a number of opportunities in the overall management of the East Branch of the Finniss River. Compass' aim is to develop the project to the benefit of stakeholders as a whole and to the local area in particular. The goal is to achieve a "win-win" outcome.

Characterisation of the Impacts of Pre- and Post- Remedial Contaminant Loads from Rum Jungle on Riparian Vegetation and Fishes of the Finniss River System

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Introduction

The status of the riparian vegetation and fish biodiversity in the Finniss River (FR) system is compared before and after remediation at the Rum Jungle (RJ) mine site with the following datasets:

- Riparian vegetation in the East Branch (EB): (a) still colour transparencies and recorded observations of obvious detriment in 1974 (Jeffree and Williams, 1975, 1980); and (b) aerial photography and quantitative analysis using the E-RMS Geographical Information System (GIS) for the years 1941 (pre-mining), 1963 (during mining), 1978 (post-mining and pre-remediation) and 1990 (8 years after remediation began) (Stratford, 1994).

- Observations in the FR on fish diversity and abundances in pre-remedial (1974) and post-remedial (1992-1995) periods for (a) quantitative abundances of seven species and species groups, based on effort-corrected numbers caught in a suite of enmeshing nets (Jeffree et al., 2001), and (b) presence/absence data for 17 species or species groups caught in the same nets (Jeffree, in prep.).

Riparian vegetation

Whereas observations recorded during pre-remedial field studies in 1974 indicate no obvious effects of mine effluents on the riparian vegetation in the FR, the impacts in the EB were severe, as summarised in the following recorded observations (Jeffree and Williams, 1975, 1980):

- No rooted or submerged plants.
- Live bankside Pandanus were rare, although dead stumps were common.
- Shallow gullying, gently sloping banks and sand deposits were associated with the absence of bank-side roots.

The quantitative analysis of the EBs riparian vegetation by aerial photography and GIS analysis gave the following results (Stratford, 1994):

- Whereas the canopy of riparian vegetation in 1941 virtually covered the EB, areas of bare soil increased by factors of 35 in 1963 and by 47 in 1978.
- Since remediation at RJ there has been some improvement in riparian vegetation as well as reduction in the areas of bare soil, but its factor of increase compared with 1941 was still ca. 30, based on 1990 data.
- Regeneration of riparian species was also observed in the 1994 dry season.

Fish biodiversity

Pre-remedial studies in the FR showed an appreciable decline in fish diversity and abundance for at least 15 km downstream of the confluence with the EB, during dry season sampling (**Figure 1**) and also following the fish-kills observed at the beginning of two wet seasons. Sites in the FR immediately downstream of the confluence with the EB showed lower numbers of species and individuals than those upstream, or further downstream. There was a gradual recovery in both the number of species and individuals in the FR with increasing distance downstream of the confluence with the EB (Jeffree and Williams, 1975).

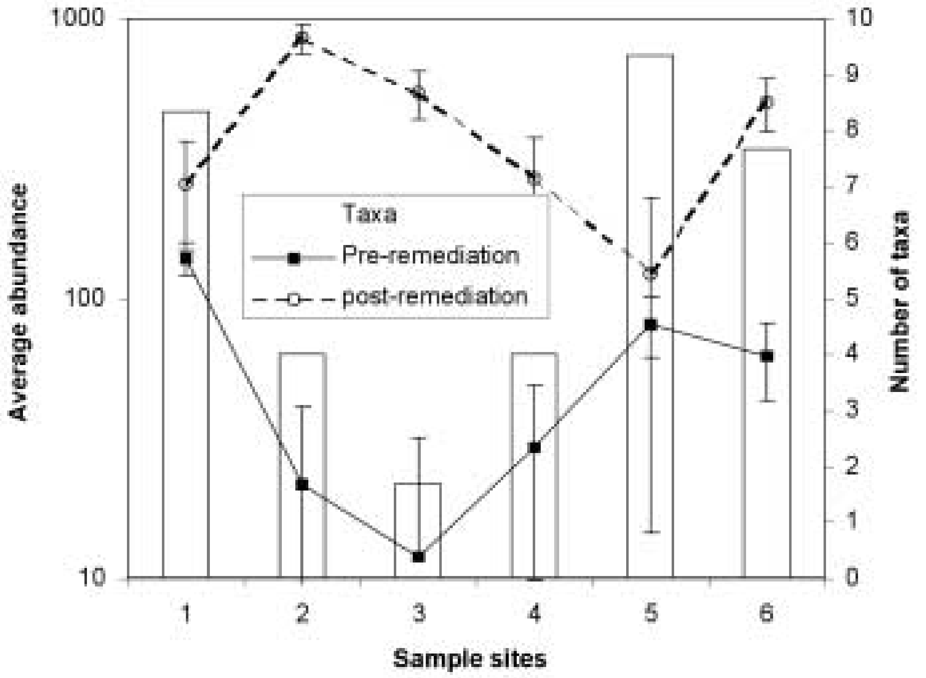


Figure 1. Accumulated number of total species caught at each site during sampling periods prior to remediation, and average abundances of seven species during pre- and post-remedial sampling (from Jeffree et al., 2001).

The effects of early wet season 'first flushes' from the EB on the fishes of the FR were also observed during 1973-74 and 1974-75. Fishes were recovered dead or moribund in the FR downstream of the EB junction (a) over a river length of 500 m during 1973-74 and (b) over a total distance of 4 km from observations made at points of access along the river. Following remediation at RJ, that began in 1981-82, the following changes to contaminant delivery to the FR were measured; (a) reductions of in situ contaminant water concentrations of various contaminants at the time of fish samplings in the dry season, and (b) reductions in annual-cycle contaminant loads of sulfate, Cu, Zn and Mn by factors of 3-7. Also, under intense observation, there was no fish-kill in the FR during the 1997-98 'first flush' (Jeffree et al., 2001).

The effects of varying pre- and post-remedial contaminant loads on the relative abundances of seven fish species were determined by non-metric multidimensional scaling, in combination with cluster-analysis and other non-parametric statistical techniques. These analyses showed that:

- Prior to remediation, the impacted region of the FR in 1974 showed significantly ($P <0.001$) dissimilar and more heterogeneous fish communities, generally characterised by reduced diversity and abundance (cf. **Figure 1**), compared to sites unexposed to elevated contaminant water concentrations.
- Post-remediation, fish communities from the impacted region in both 1992 and 1995 were not dissimilar from those sampled at either contemporary ($P = 0.16$) or pre-remedial unimpacted sites, indicating their recovery. The species most important in discerning between samples from pre-remedial impacted sites and all others is shown in **Table 1**.

Table 1. Average abundances of fish species and their percentage contribution to average dissimilarity measures between samples from pre-remedial impacted sites and all other samples (from Jeffree et al., 2001)

Fish species	Average abundances		% contribution to average dissimilarity
	Impacted, pre-remedial sites	All other sites	
Nematalosa	3.1	216	28.2
Neosilurus	1.4	30.3	20.7
Amniataba	0	4.3	11.3
Megalops	12.9	30.3	10.8
Toxotes	0	5.8	10.0
Black bream	0.3	3.8	9.6
Melanotaenia	5.7	2.4	9.5

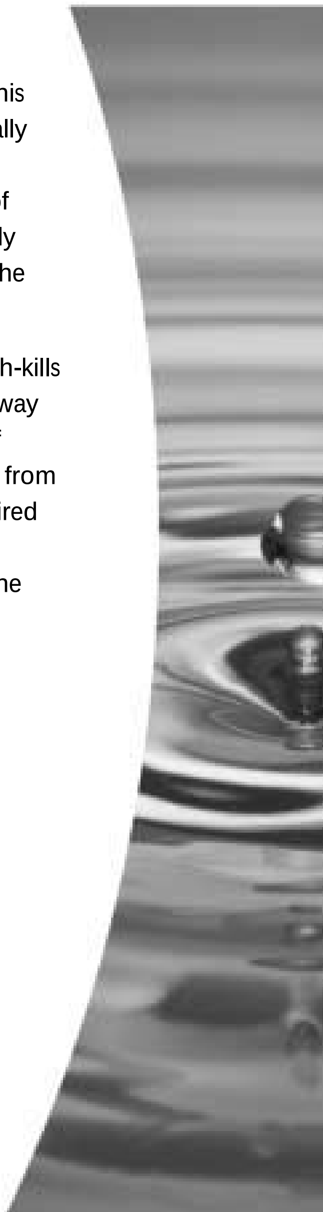
Comparable results were obtained from a similar set of analyses conducted on the presence/absence of 17 species or species groups (Jeffree, in prep.), that included the newly discovered species, and possibly new genus, of freshwater Teraponid (H. Larson, pers. comm.).

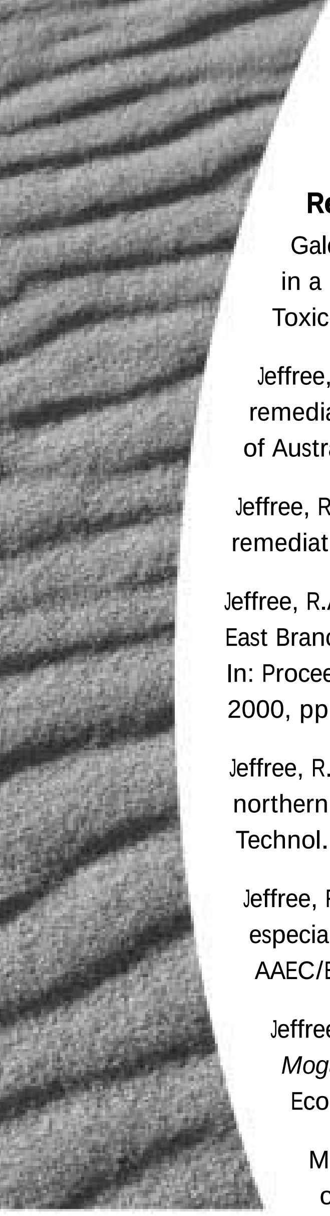
Even though considerable contaminant loads are still being delivered to the impacted region of the FR over the annual cycle, the recovery in fish abundance and biodiversity is consistent with:

- Reductions of in situ contaminant water concentrations at the time of fish sampling.
- Reductions in annual-cycle contaminant loads of sulfate, Cu, Zn and Mn by factors of 3-7.
- Greatly reduced frequencies of occurrence and magnitude of elevated contaminant water concentrations over the annual cycle, that was most pronounced for Cu.
- The absence of extensive fish-kills during the first-flushes of contaminants into the FR at the beginning of the wet season, that were observed prior to remediation.

The post-remedial recovery of fish biodiversity in the FR, as determined by two measures of community structure, indicates that mine site remediation has been of ecological benefit to this tropical freshwater system. The recovery in the FR, where no post-remedial impact is statistically discernible, is consistent with the post-remedial annual contaminant loads being ecologically sustainable by this aquatic system, as measured by fish biodiversity. Moreover, the presence of freshwater bivalves (*Velesunio angasi*) in the impacted region of the FR, that extend in age only back to the end of the remedial period (1986) (Markich et al., 2002), is also consistent with the post-remedial loads being ecologically sustainable.

If our interpretation of the major mechanism of detriment to fish biodiversity is correct, viz fish-kills during the ‘first flush’, then the temporal pattern of contaminant delivery to the FR, and the way remediation has greatly modified this pattern, are also important factors in the observation of sustainability in the face of still considerable annual contaminant loads. The broader message from these findings is that an understanding of the mechanism of detriment to biodiversity is required to more cost-effectively design remedial programs at mine sites, so as to reap the greatest ecological benefits (Jeffree, 2001). Similarly, the tolerance to Cu that has been measured in one fish species (Gale et al., submitted) suggests the possibility that the exposure of the fish community to contaminant loadings over more than four decades may have led to the development of tolerance that may also contribute to the ecological recovery that has been observed.





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An Evaluation of Seasonal Change in Benthic Macroinvertebrate Community Composition in the East Branch of the Finniss River

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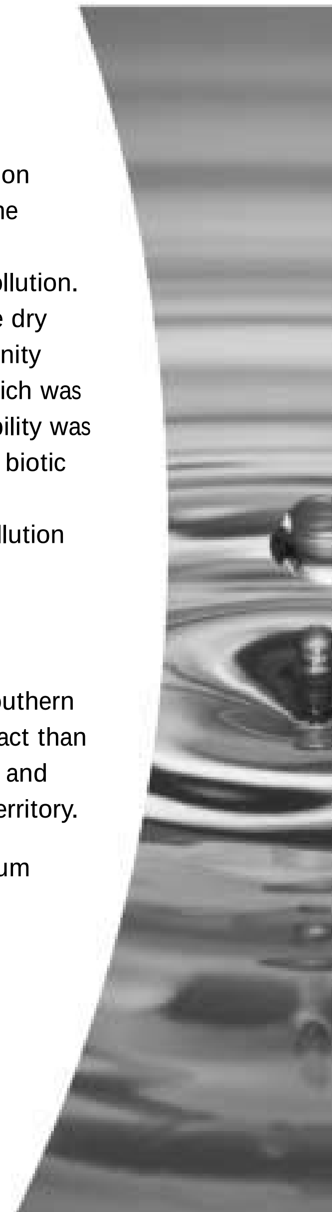
Acid rock drainage (ARD) is recognised as a significant global problem resulting from mining of metalliferous ores of high sulfur content or particular types of coal deposits. Although many studies overseas examined the effect of ARD on aquatic macroinvertebrates, only a limited number of similar studies exist in Australia. All but three of the Australian studies occur in southern temperate regions and only two are located within the wet/dry (monsoonal) tropical environment of northern Australia. Rum Jungle is an abandoned uranium-copper mine responsible for ARD into the surface waters of the intermittent East Branch and the channel of the Finniss Rivers. Prior to large-scale remediation in the mid 1980s, the East Branch was biologically dead for 8.5 km downstream to the confluence with the Finniss River, and suffered substantial ecological impairment for a further 15 km downstream. Recent studies suggest some recovery in fish diversity and abundance in the Finniss River, but only minor recovery in the macroinvertebrate fauna of the East Branch. This study was designed to quantitatively evaluate spatial and temporal patterns in macroinvertebrate community composition in relation to seasonal changes in heavy metal contamination and acidity in the East Branch. Benthic macroinvertebrates, as well as physical and chemical variables, were collected over a one-year period (including the 1994-5 wet season).



A marked seasonal trend in environmental variables identified three discreet levels of impact on the surface waters of the East Branch. The most significant pollution levels occurred late in the dry-season at sites closest to the mine. All other sites and sampling times formed a mid-level pollution group and all reference site samples formed a third group representing minimal pollution. Sites in the East Branch furthest from the mine displayed some degree of recovery late in the dry season and were closely associated with the reference site group. Macroinvertebrate community composition displayed significant modification in structure both spatially and temporally, which was highly correlated with observed patterns in physical and chemical water quality. Some variability was evident between sampling years, which may be due to time of cessation of flow, pH, and/or biotic interactions such as predator/prey relationships. Studies of the East Branch and Finniss River confluence and the evaluation of spatial variability in the Finniss River, suggest continued pollution from the East Branch is evident in both water chemistry and macroinvertebrate patterns in composition. However, results were inconclusive and require further investigation.

This study adds greatly to the knowledge of ARD effects on macroinvertebrate community composition in the wet/dry tropics of northern Australia. Striking similarities to research in southern Australia and overseas suggest the modifying influence of ARD is far more significant an impact than biogeographical differences. Findings of this study can contribute significantly to monitoring and assessment of ARD in northern Australia, especially in intermittent streams in the Northern Territory.

Extracted from: Edwards, C. A. 2001. Effects of Acid Rock Drainage from the Remediated Rum Jungle Mine on the Macroinvertebrate Community Composition in the East Finniss River, Northern Territory. MSc Thesis, University of Technology Sydney, Australia.

Initial Evaluations of the Use of Microbial Measures to Quantify Impact of Acid Rock Drainage on the Finniss River (East Branch)

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Biological measures assessing the impact of pollution on aquatic ecosystems have been increasingly used over the last ten years to examine ecosystem health. The focus, however, has been on diversity and abundance of higher organisms, such as fish, frogs and macroinvertebrates, and it is desirable that such measures be made across all trophic levels of the ecosystem. In this study, phospholipid-fatty acid analysis and microbial carbon substrate utilisation assays (BIOLOG) of sediment and water samples were conducted to evaluate their usefulness as a measure of the effect of acid rock drainage (ARD) on the East Branch of the Finniss River.

Phospholipid fatty acids (PLFAs) are components of cell membranes and walls that occur in all microbes, and their abundance and diversity in samples reflect differences in microbial community structure and abundance. In addition, PLFAs rapidly breakdown after death of microorganisms and thus total PLFA is a good measure of the viable microbial biomass present in a sample. BIOLOG assays were originally designed for bacterial identification and utilise commercially available 96 well microtitre plates where each well contains a freeze-dried carbon substrate, nutrients and a redox dye. Utilisation of the substrates is indicated by colour development which can be quantified by measurement of absorbance at 590 nm. Garland and Mills (1991) demonstrated the potential application of the plates for rapid characterisation of heterotrophic microbial communities from different habitats. BIOLOG plates have since been utilised in substrate utilisation profiling to characterise microbial communities in a range of environmental samples, including plant soil communities, soils, freshwater (Lehman et al., 1997) and groundwater. The range of substrates utilised is a measure of functional diversity, whereas the strength of colour development is a function of microbial numbers. We have modified the BIOLOG assay and data processing by not normalising inoculum size or absorbance data to generate an integrated measure of abundance and diversity. Both PLFA, and BIOLOG assays, generate data well suited to multivariate analysis and previous studies of the impact of ARD from the Brukunga mine (South Australia) have demonstrated the ability to distinguish between the effect of ARD, nutrients and dry-land salinity on microbial populations (Harch et al., 1999; Foster et al., 2000; Holden et al., 2000; Wilde et al., 2000).

Sediment and water samples were collected 15-21 June 1999, at 20 sites on the Finniss River (East Branch) in the Northern Territory, and at selected reference sites unaffected by ARD from the Rum Jungle mine site (**Figure 1**). These sites included Little Finniss River (LFRA and LFRB), Fitch Creek (FCA and FCB), Hanna Spring (HS) and a tributary creek known designated 4S. East Branch sites included immediately above the mine (EB8A and EB8B), Whites Overflow (WO)æthe ARD input from Whites overburden heap, immediately downstream of the mine (EB7), EB6, EB6B and EB5D downstream, EB4U upstream of the confluence with the reference creek (4S), EB4D downstream of that confluence, EB3A upstream of the confluence with Hanna Spring, EB2 downstream of the

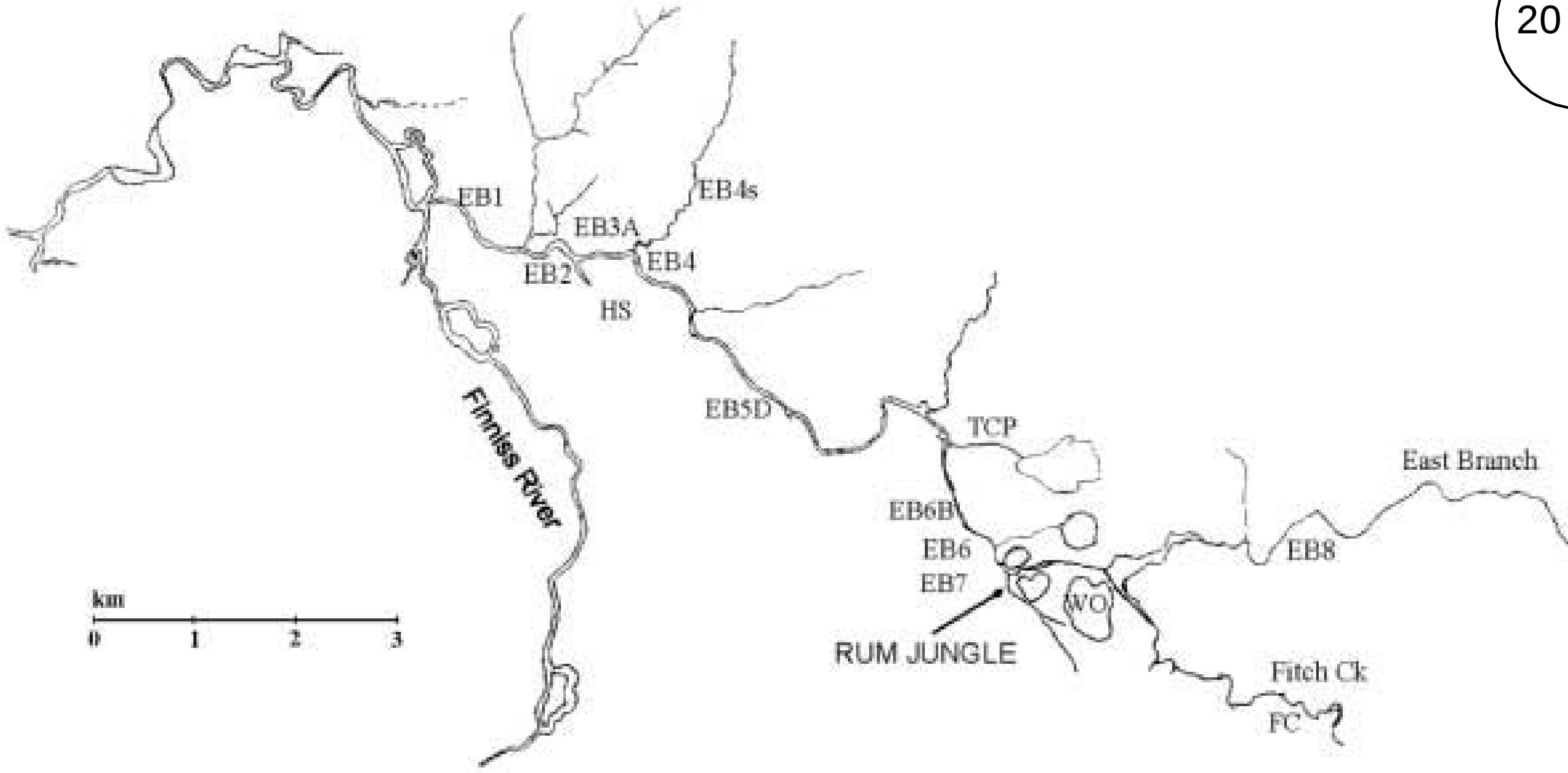

Figure 1. Map of the East Branch of the Finniss River showing sampling sites.

confluence with Hanna Spring, and EB1U before the confluence with the Finniss River. All samples were kept on ice in the field and at 4ºC until return to the laboratory. Water samples were analysed for Al, Ca, Cd, Co, Cu, Fe, Mg, Mn, Na and Ni (inductively coupled plasma atomic emission spectroscopy), anions (liquid chromatography), conductivity and pH. Phospholipids from the sediments were solvent extracted quantitatively by the modified one-phase Bligh-Dyer method (White et al., 1979) and purified by silicic acid column chromatography (Franzmann et al., 1996). Fatty acids derived from the phospholipid fraction were converted to fatty acid methyl esters (FAMES). These were identified and quantified using gas chromatography mass spectrometry. The PLFA profiles, as absolute abundance, were treated as multivariate data and analysed using hierarchical cluster analysis and principal component analysis (PCA) using the PC-based software package, Canoco for Windows version 4.0 (Centre for Biometry, Wageningen, The Netherlands). The absolute abundance of FAME (nmol g^{-1}) and relative abundance within a sample (mole %) were transformed to a logarithmic scale and the data were ordinated by PCA and redundancy analysis (RDA). Both PCA and RDA assume a linear model between each FAME species and the ordination axes.

Contrary to expectation, total PLFA was higher at sites most affected by ARD in comparison with most reference and downstream sites. The sediment from the outflow of White's overburden dump contained >6 nmol PLFA g^{-1} and the sites immediately downstream were also elevated in comparison with sites 8A and 8B immediately above the mine (<2 nmol g^{-1}). Tailings Creek pond (TCP) was also affected by ARD and had elevated Total PLFA (4 nmol g^{-1}). The downstream sites, EB4D and Hanna Spring, also had elevated total PLFA. Fitch Creek was the only reference site displaying high PLFA (12 nmol g^{-1}). The increased total PLFA at heavily affected ARD affected sites was thought to be due to proliferation of the acidophilic bacteria *Acidithiobacillus* spp, as they are known to be well adapted to such habitats. These findings contrast with those obtained in examining the impact of ARD in the Dawesley Creek system where ARD impacted sites had significantly lower total PLFA than reference sites (Foster et al., 2000; Holden et al., 2000).

Ordination using PCA of the variation of individual PLFAs versus sampling sites did not produce discrete clustering of ARD affected sites (not shown). Whites Overburden (1 and 2), Hanna Spring and EB4D reported in a similar position on the X-axis (61.9% of variation) but were divergent on the Y-axis (11.2% of variation). The remaining sites formed a cluster on the X-axis with EB6, EB7 and on the edge closest to the first cluster. However reference sites reported closely with these sites. However, Redundancy analysis of PLFAs and sites with respect to water quality parameters did produce a clearer separation. **Figure 2** shows an RDA of PLFA, sites and SO_4, Al, Fe and pH. The reference sites clustered separately from ARD affected sites and within the ARD cluster, downstream sites formed a sub cluster separated on the Y-axis.

In the case of substrate utilisation assays, sediment samples were incubated with sodium pyrophosphate solution to detach microbes, centrifuged at low speed to remove large particulates and the cell suspension inoculated into BIOLOG ECO plates after 1:100 dilution. The ECO plates contain 32 different substrates in triplicate. Water samples were diluted 1/10 prior to inoculation. The plates were incubated at 30^{o}C and absorbance at 590 nm measured. These results were used to calculate an average well colour development (AWCD) value for each sample. Multivariate analysis of the full data sets was also conducted. AWCD values for assays of both water and sediment samples were clearly lower at ARD affected sites closest to the mine with the effect being more dramatic in the water sample assays (not shown).

Above the mine, sites 8A and 8B had AWCDs of 0.58 and 0.54 for assays of water samples, whereas from Whites Overburden downstream the AWCDs ranged from 0 to 0.23 until site EB4S (0.77). The number of carbon compounds utilised by the microbiota in the samples also followed a similar pattern.

Principal component analysis of activity against individual carbon compounds versus sample site gave two clusters with East Branch downstream sites overlapping with the reference site cluster (**Figure 3**).

The following conclusions were reached:

- Initial analyses suggested that total PLFA doesn't correlate well with water and sediment quality.
- Multivariate redundancy analysis separated ARD affected and reference sites based on PLFA species and the water quality parameters SO4, Al and Fe.
- BIOLOG AWCDs, and number of carbon compounds utilised, reflected sediment quality with the notable exception of Hanna Spring.
- BIOLOG AWCDs were depressed at sites whose water quality reflected ARD.
- Principal component analysis separated reference from ARD sites with an overlap at downstream sites.
- RDA separated sites based on sediment quality vs BIOLOG with Fe, Ni and Zn accounting for most of the variation in the data (not shown).

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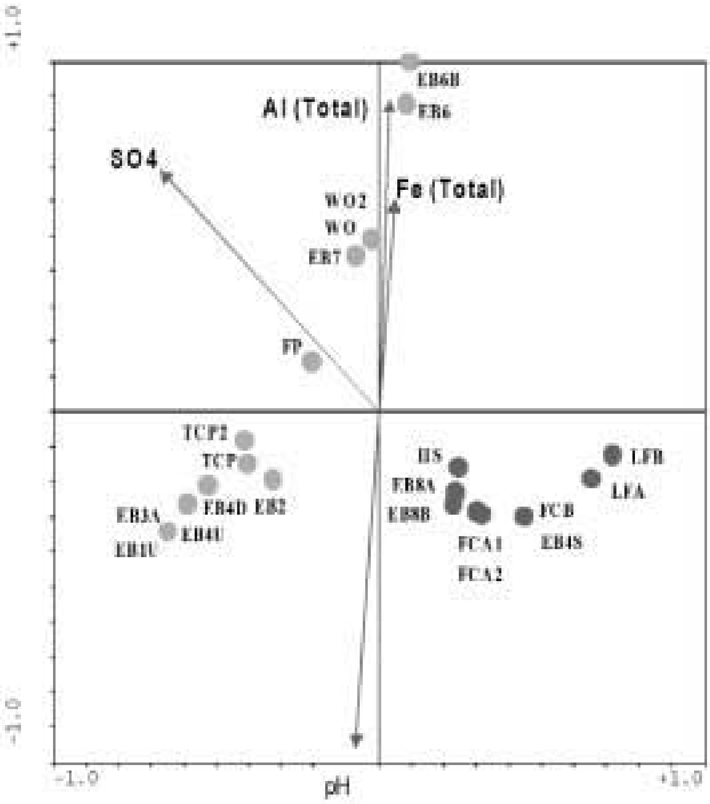

Figure 2. Redundancy analysis of PLFA data and samples sites with respect to environmental variables.

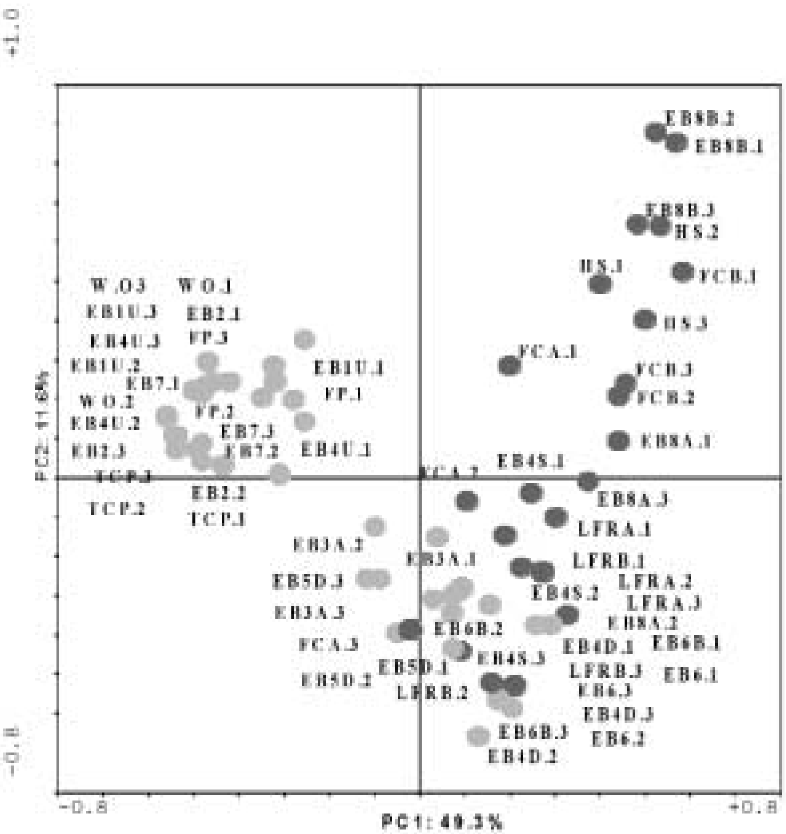

Figure 3. Principal Component Analysis of Sample Sites and data from BIOLOG assays of sediment microbiota. X-axis accounts for 49.3% of variation and Y-axis 11.6%.

Microbial Exoenzymes as Bioindicators of Acid Rock Drainage Impacts in the Finniss River

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Organic matter decomposition and inorganic nutrient regeneration are important in sustaining the food web in aquatic ecosystems. Heterotrophic microorganisms play a key role in the recycling of carbon, nitrogen and phosphorus in these systems—the so-called microbial loop (**Figure 1**). Utilisation of the macronutrients by microbial communities is dependent on the production of extracellular enzymes (hereafter, referred to as exoenzymes) for hydrolysing macromolecular organic materials into oligomeric and monomeric compounds that can be transported across cell membranes.

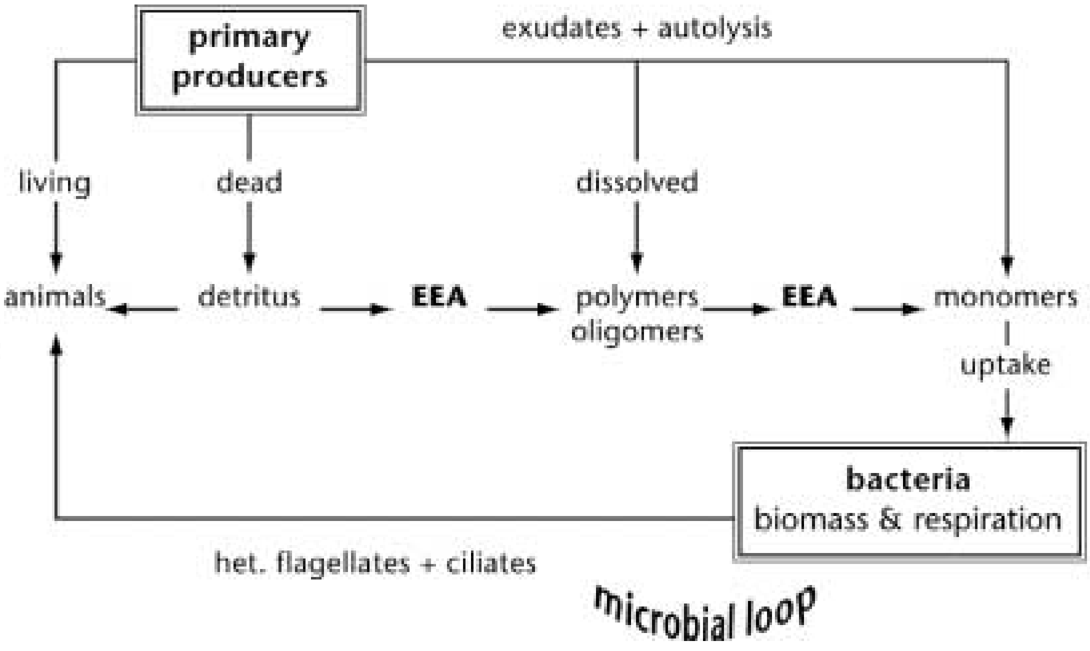


Figure 1. Microbial loop model supplemented with pathways of organic matter trans-formation from primary producers to bacteria via extracellular enzymatic activity (EEA).

Microorganisms, particularly bacteria, have a number of potential advantages over other organisms as biological indicators of river health. They are present in very large numbers, grow very rapidly, are responsible for many ecosystem functions, and probably respond to ecosystem changes more rapidly than other biological components, certainly more rapidly than macroinvertebrates or fish. The investigation on the effects of acid rock drainage (ARD) on the microbial community diversity and function involved the measuring of extracellular enzymatic activity (EEA) in reference and impacted sites along the East Branch of the Finniss River. The possibility existed that these measures could be used as rapid, sensitive bioindicators of ARD.

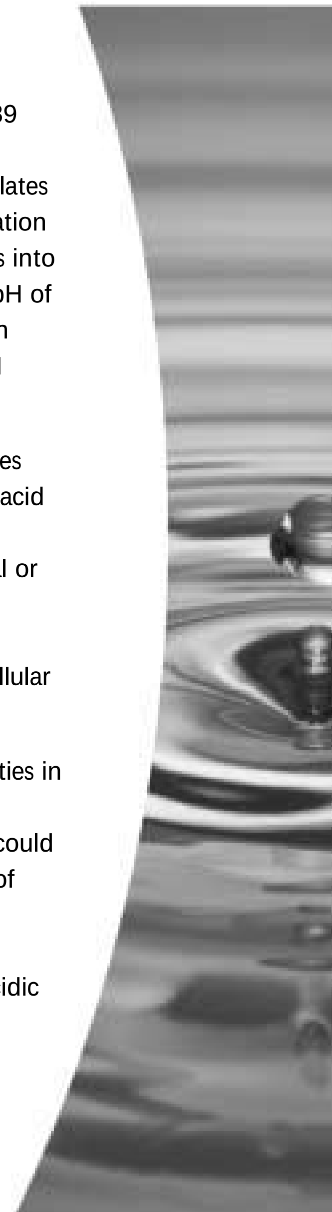
Sediment samples were collected from several sites along the East Branch of the Finniss River during the dry season (June, 1999), when the East Branch is drying into a series of ponds. The sites (refer to **Figure 1** in Holden et al., this volume) included those upstream from the Rum Jungle mine site (EB8A, EB8B, FCA, FCB), a site receiving acid leachate from the waste rock (WO), sites downstream from the mine that are impacted by acid and metal contamination (EB6, TCP, EB5D, EB4U, EB2) and reference sites not subject to ARD (HS, EB4S, LFRB). Exoenzyme activities were measured with a spectrofluorometric technique that involved measuring the increase in fluorescence when an artificial fluorogenic substrate (that mimics the natural substrate) is hydrolysed to a highly fluorescent product. This assay system is very sensitive and measures activity at the nanomolar level five minutes to two hours after addition of the substrate to the sediment slurry. The activities of the exoenzymes that are responsible for the hydrolysis of the major organic constituents in sediments were measured. The natural substrate and the relevant enzyme were as follows: β-linked polysaccharides, β-D-glucosidase; proteins, leucine-aminopeptidase, and organo-phosphoric esters, phosphatases. Maximal activities were measured by ensuring that the initial linear rate of the enzyme reaction was measured and that a saturating substrate concentration was used.

The activities of phosphatases, leucine-aminopeptidase and β-glucosidase measured in sediment slurries from impacted and reference sites along the East Branch of the Finniss River are shown in **Figure 2**. The highest activities were found for the phosphatases because inorganic phosphate was limiting for the growth of microorganisms in these environs. Surprisingly, the activities of the three groups of enzymes were highest at the WO site that receives acid leachate contaminated with high concentrations of metals. The leucine-aminopeptidase activity was markedly reduced at the ARD impacted sites, except site WO. Leucine-aminopeptidase is a zinc-containing metalloenzyme and would be inhibited by the high concentrations of copper, nickel and lead found in the sediments from the ARD impacted sites.

The activity of β-glucosidase was reduced at the impacted sites, except for site WO and site TCP that received effluent from the tailings pond. It was noted that the organic matter (OM) content in the sediment from site WO was very high (about 0.1 g OM g^{-1} of dry matter) compared with the other impacted sites (< 0.02 g OM g^{-1} of dry matter). Linear regression analysis revealed that the activities of phosphatases and β-glucosidase were significantly ($P \leq 0.05$) related to the OM content of the sediment from impacted and reference sites ($r^2 = 0.89$ and 0.70, respectively). Previous studies have shown that in aquatic ecosystems exoenzyme activity is the rate limiting step in bacterial macronutrient procurement and in general, correlates with organic carbon levels and bacterial productivity (Chrost, 1991). Therefore, any perturbation that reduces the input of OM from autotrophic primary production or allochthonous sources into riverine systems will also decrease exoenzyme activity. Enzyme activity is dependent on the pH of the assay system. The high exoenzyme activities at site WO could have been due to either an increase in the quantity of exoenzymes produced by the microorganisms or a shift of the pH optimum into the low pH region.

These possibilities were investigated by carrying out the exoenzyme assays of sediment slurries over a range of pH from 2.0 to 10. It was found that phosphatases and β-glucosidases from acid impacted sites had lower pH optima; there was no change in the pH optimum for leucine aminopeptidase. Previous studies have shown that microorganisms can produce acid, neutral or alkaline phosphatases. Prior to the present study, β-glucosidase was reported to have a pH optimum between 5 and 6. The present findings indicate that the ARD impacted sediments contain acidophilic, heterotrophic microorganisms, bacteria and/or fungi, producing extracellular enzymes adapted to the acid conditions.

In conclusion, this study has demonstrated that measurements of extracellular enzyme activities in river sediments provide a rapid, sensitive technique for determining microbial activity and productivity. In aquatic ecosystems some exoenzymes, particularly leucine-aminopeptidase, could be used as bioindicators of pollution from ARD. Further characterisation of the acid stability of exoenzymes produced by acidophilic heterotrophic microorganisms adapted to these ARD impacted systems is warranted (see Johnson, 1998). The utilisation of these heterotrophic acidophils has potential for industrial applications such as the degradation of pollutants in acidic waste waters.



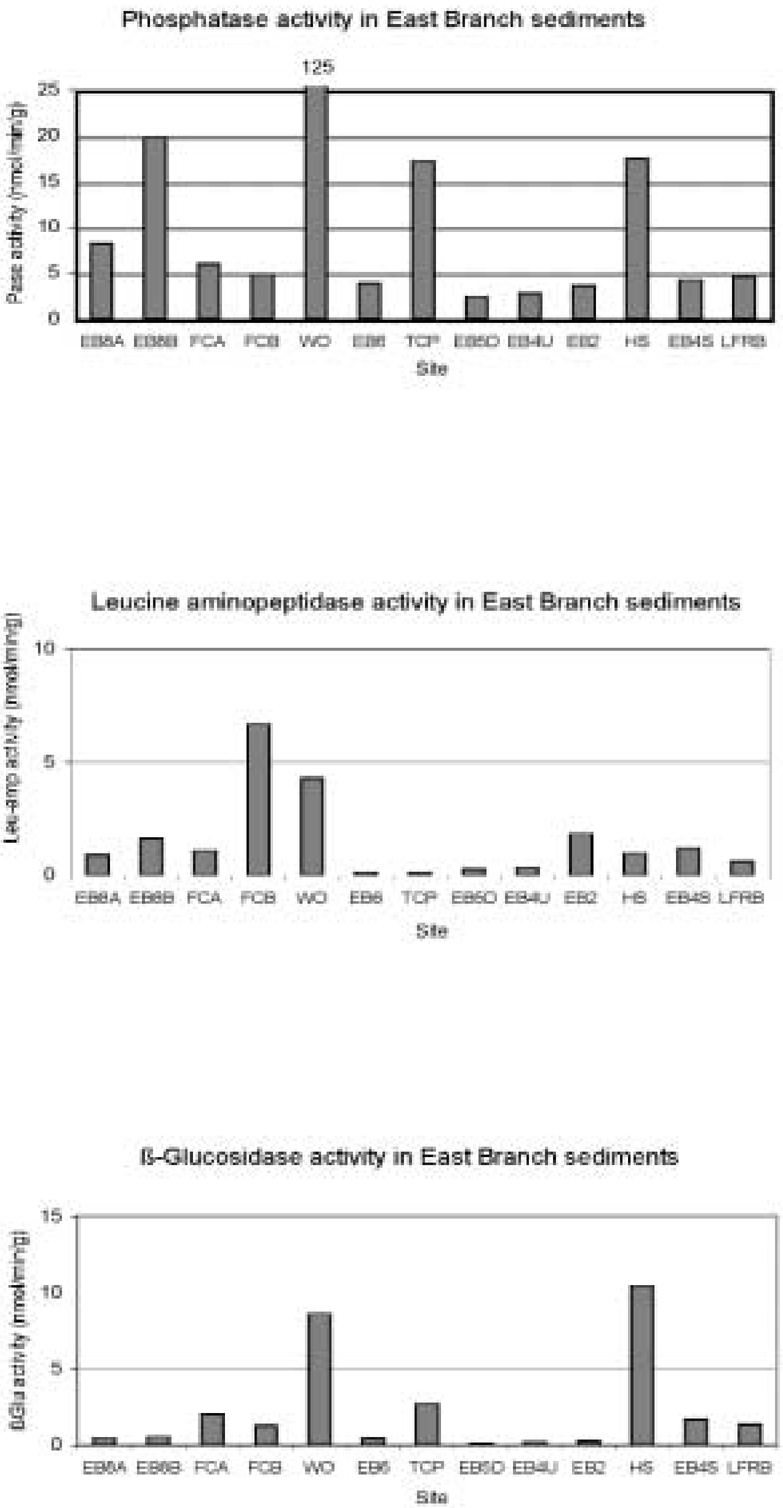


Figure 2. Exoenzyme activities in the East Branch of the Finniss River (the location of the sites is given in the text).

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Diatoms as Biomonitors in Two Temporary Streams Affected by Acid Drainage from Disused Mines

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Introduction

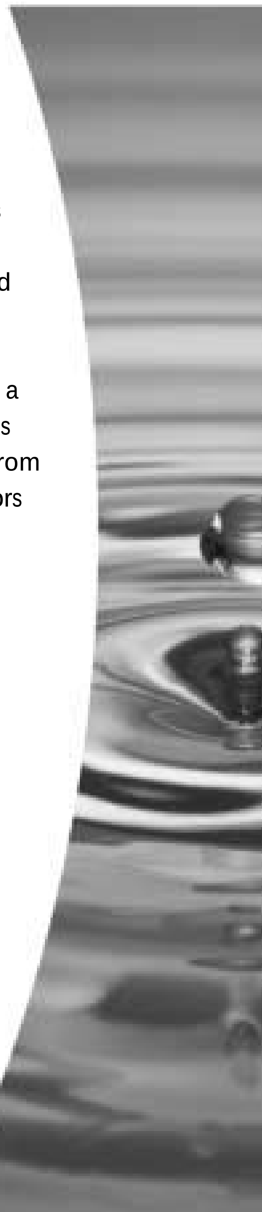
Diatoms are increasingly used as biomonitors of water quality in Australia, partly as an extension of the AUSRIVAS concept and partly through the increasing emphasis on biological/ecological monitoring of stream health that is acknowledged in the Australian and New Zealand water quality guidelines (ANZECC and ARMCANZ, 2000). This work brings together the findings of three studies relating diatom populations to the water chemistry of two temporary streams affected by acid drainage.

1. Sand-associated Diatoms in the Finniss River East Branch

In the first study, the changing diatom flora of the Finniss River East Branch was found to relate to a gradient of acid drainage pollution that developed in the recessional flow period of the early Dry season of 1995. Copper was assumed to be the most toxic of the range of metals present in the acidic water draining from waste rock heaps of the Rum Jungle mine site. Copper concentrations declined exponentially from ca. 30,000 to 40 µg L^{-1} across 16 sites sampled between the mine and just upstream from Hanna's Spring Creek (see Figure 1 in Holden et al., this volume) where the acid drainage-affected stream section extends from EB7 to a little upstream of EB2). The pH varied from 2.8 to 8.2 in the same 6.5 km stream section. Six reference sites, sampled in the upper East Branch, Fitch Creek and the Little Finniss River, had Cu concentrations ranging from <5 to 5.1 µg L^{-1} and a pH range from 5.8 to 7.4. The 'richness' of the diatom flora (sand-associated benthic diatoms) was from 30 to 45 species at the reference sites and ranged from only a few species to 23 species along the gradient of acid-drainage affected sites. A principal components analysis of the relative species abundances (**Figure 1**) showed a clear separation of reference sites from even the least polluted 'gradient' site, on axis-1. This primary axis was best correlated with indicators of the pollution gradient, such as Ca and Cu concentrations and pH.

This study of a polluted system in an otherwise clean environment found that:

- Changes in benthic diatoms did reflect the pollution gradient that develops in the Finniss East Branch during the early dry season.
- The East Branch, upstream from Hanna's Spring Creek, had not recovered to closely resemble reference sites by 1995.



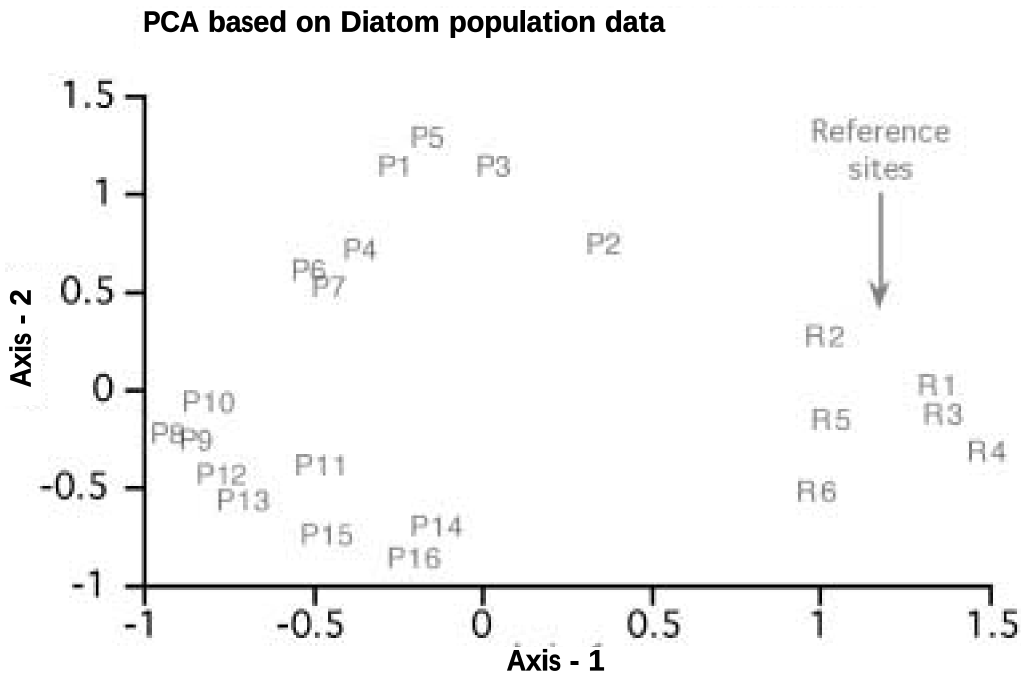


Figure 1. Principal components analysis of diatom data (percentage relative abundance of species). There is a clear separation of reference sites (R1-6) from 'polluted' sites (P1-16) along axis-1.

2. Rock- and Mud-associated Diatoms in Dawesley Creek, South Australia

The second study was of Dawesley Creek, which drains the disused Brukunga pyrite mine in South Australia (**Figure 2**). Here, aluminium represents one of the most toxic metals, ranging in concentration from approximately 240,000 to 500 µg L^{-1} in a 30 km stream section including the mine site. The pH ranged from 2.7 to 7.5 along the acid drainage gradient downstream from the mine site. Reference sites upstream and in side-streams ranged in Al concentration from 220 to 1000 µg L^{-1}, with a pH ranging between 6.7 and 7.7. In contrast to the Finniss River study, some of the reference sites in this drainage system were characterised by pronounced nutrient and saline pollution. In Dawesley Creek upstream of the Brukunga site, maximum concentrations of total phosphorus and total nitrogen were 23 and 53 mg L^{-1}, respectively. Downstream, at the point were the stream joins the Bremer River, water quality was affected by dry-land saline drainage. A conductivity of 8100 µS cm^{-1} was recorded at the reference site in the Bremer River above its confluence with Mt Barker Creek.

The 'richness' of the diatom flora (rock- and mud-associated benthic diatoms) was in the range 18 to 35 species at the reference sites and ranged from 5 to 36 species along the gradient of potentially acid-drainage affected sites. A canonical correspondence analysis of the relative species abundances (**Figure 3**) showed a clear separation of the five most acid-drainage affected sites from all other sites, on axis-1. This first axis was best correlated with indicators of acid drainage pollution, such as Al concentration and pH. The second axis separated the most nutrient-polluted sites (especially 1, 2, 3, 9 and 10; **Figure 2**) from other sites, and this axis was best correlated with concentrations of phosphorus and nitrogen.

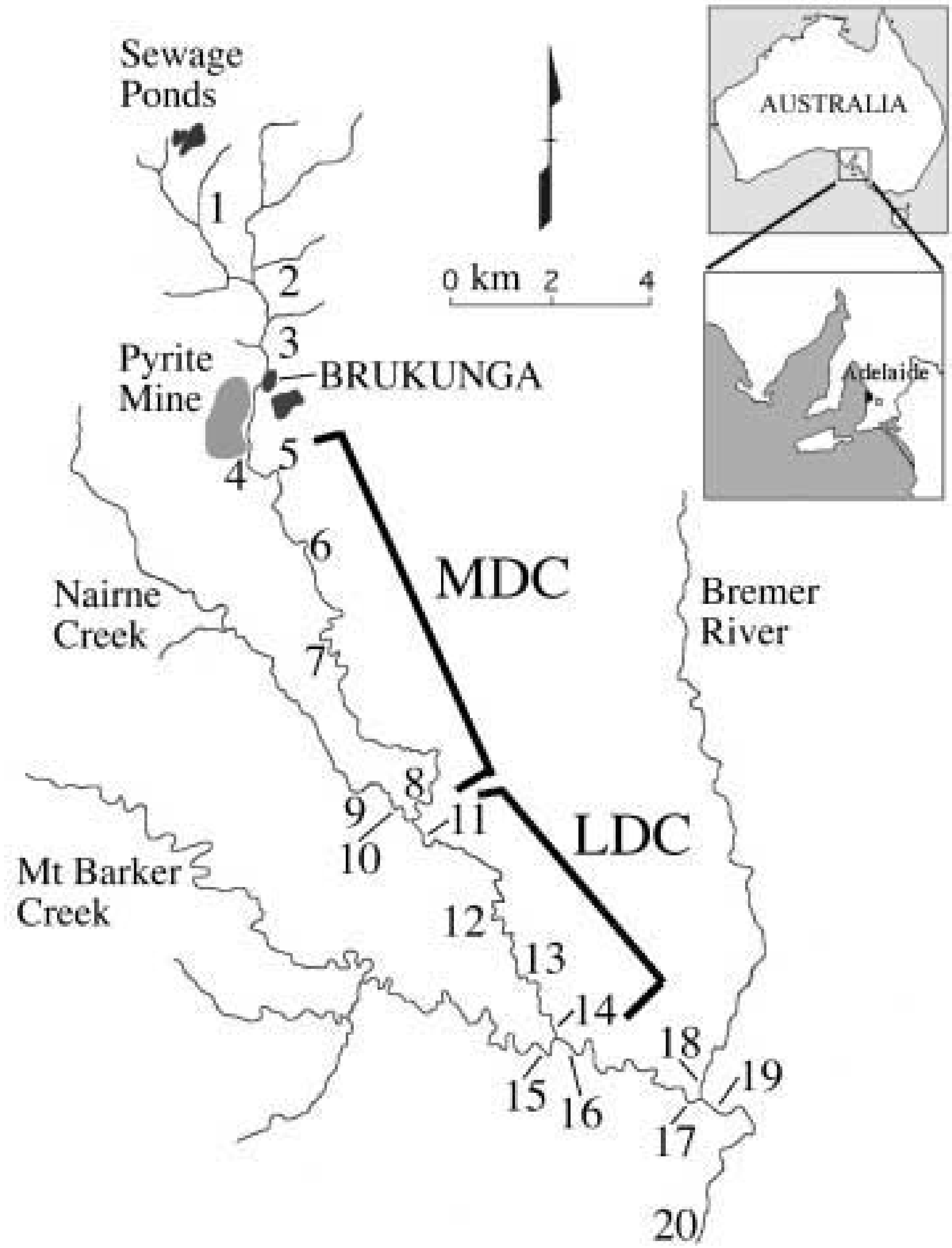


Figure 2. Map showing sampling sites in the Dawesley Creek–Bremer River drainage system, the position of the disused Brukunga mine, the source of nutrient pollution upstream from the mine site (sewage ponds) and the stream sections used in geochemical modelling and ecological risk assessment (see section 3).

This study of a polluted system within an already polluted environment found that:

- Benthic diatoms (rock- and mud-associated) clearly showed the effects of acid drainage in both reduced species richness and through finding species of *Navicula* and *Nitzschia*, not identifiable from standard taxonomic texts, that were largely confined to the most acid drainage-affected sites.

- The diatom flora distinguished between two of the three pollutants: excess nutrients and acid drainage. The coincidence between the downstream decline in nutrient concentration and increasing salinity (as conductivity) obscured any obvious effect of salinity.

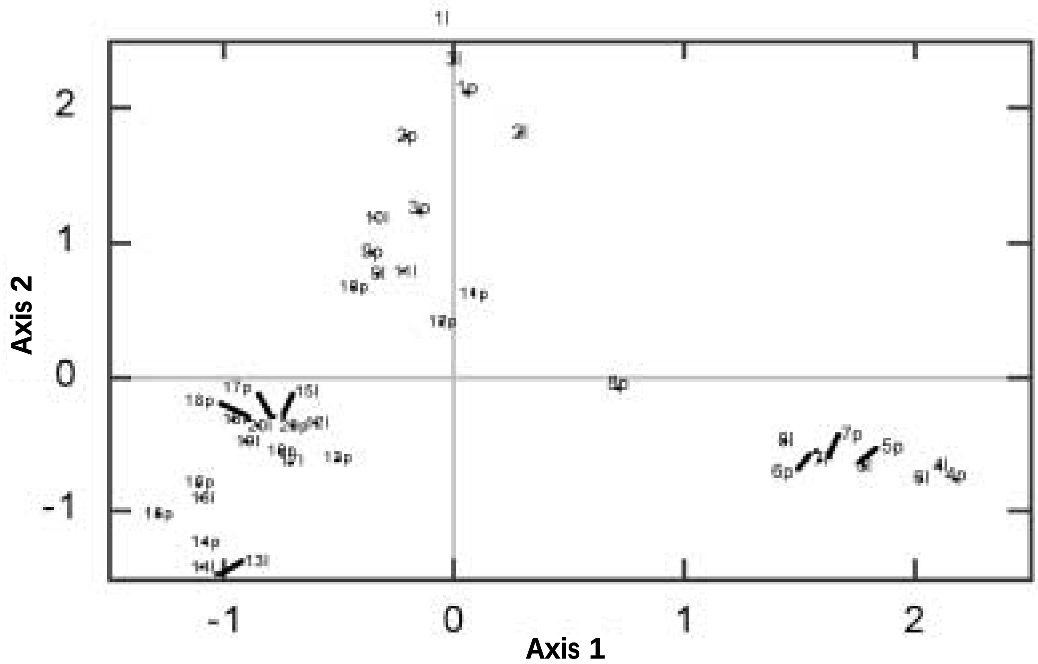


Figure 3. A canonical correspondence analysis, based on diatom data and environmental variables, such as the concentration of metals and nutrients. Each sample site (1–20) is represented by two sub-samples, where l denotes rock-associated diatoms and p mud-associated diatoms. Axis-1 is best correlated with Al concentration (r = 0.92) and pH (r = -0.88), while axis-2 is best correlated with nutrient concentrations (r = 0.94 for total P and r = 0.77 for total Kjeldahl nitrogen). Taken from Ferris et al. (2000a).

3. Combining Ecological Risk Assessment with Geochemical Modelling and Diatom Sampling

The third study was also conducted on data from Brukunga and was designed to relate field measures of diatom populations to ecological risk assessment and geochemical modelling. An extended abstract of this work is published elsewhere (Ferris et al. 2000b). Reports of a white floc forming where Nairne Creek entered Dawesley Creek (**Figure 2**) raised the question as to the predictability and ecological significance of this chemical event, presumed to involve precipitation of dissolved aluminium. The median water chemistry of upstream sites (MDC, sites 4-8; acid drainage-affected) and Nairne Creek (reference sites 9 and 10) was input to the geochemical code MODPHRQ in volume proportions of approximately $1/8^{th}$ MDC water to $7/8^{th}$s Nairne Creek water. These proportions were found to reproduce the median field measurements of pH for the downstream stream section (LDC, sites 11-14; downstream of Dawesley-Nairne Creek confluence). The geochemical code successfully predicted flocculation of Al-phosphate and Al-hydroxide with Fe-hydroxide.

The same water chemistry was also input to the ecological risk assessment code, AQUARISK, which predicted the percentage of species that would be affected by the total and bioavailable (geochemically modelled) fractions of aluminium. This 'desktop' study was then compared to the median field measurements of diatom species richness in the MDC and LDC stream sections, to provide an independent test of the ecological risk predictions (**Figure 4**). This comparison showed that the flocculation event was associated with a considerable reduction in aquatic ecotoxicity. The comparison also showed a reasonable agreement between AQUARISK and the independent diatom data. In the case of the downstream site, however, this was only the case when the concentration of bioavailable aluminium was used to predict the percentage of species likely to be affected.

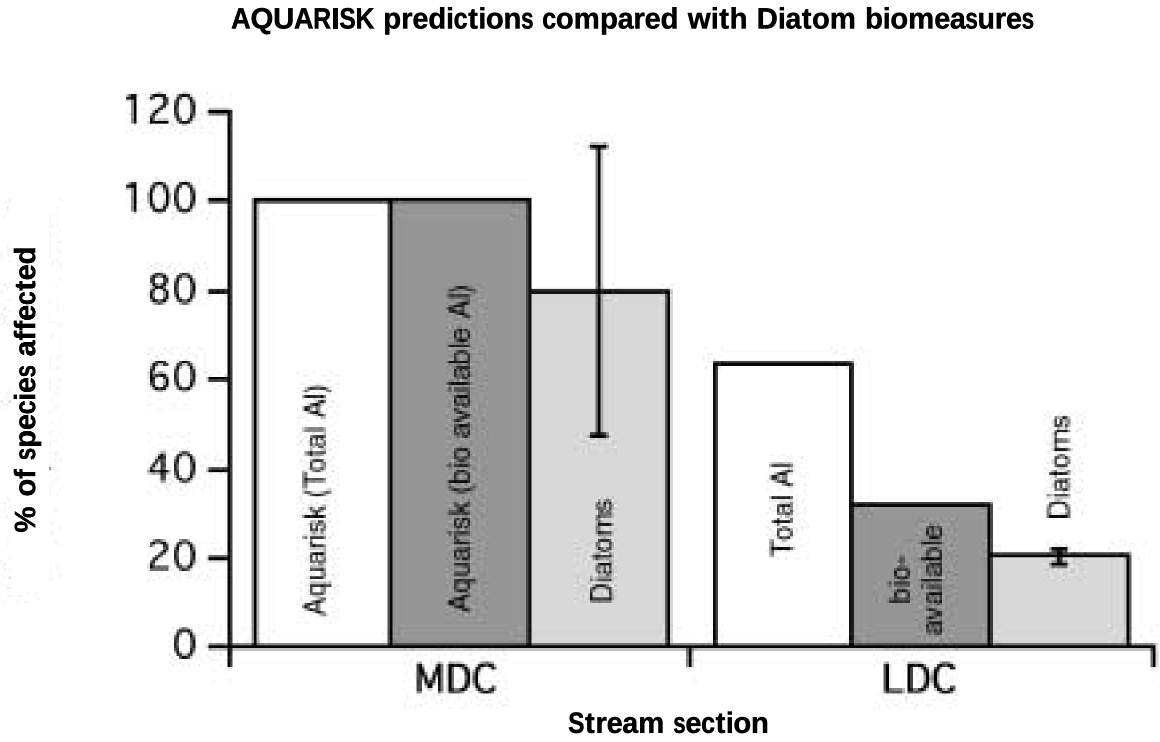


Figure 4. Predicted ecological risk (as percentage of species likely to be affected by median total and bioavailable Al) compared with field-measured numbers of diatom species (expressed as a percentage of the maximum number of species found in the local area). The diatom data are shown as median ± interquartile range for the site groups shown in Figure 2.

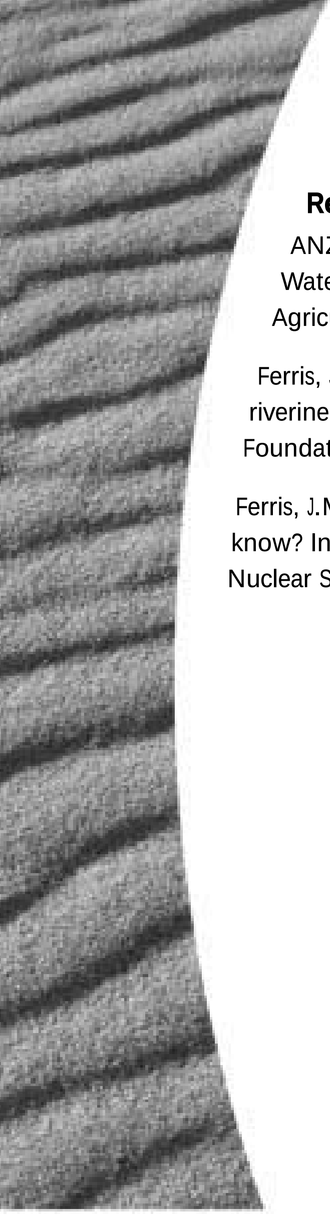
This study of the changing ecological risk associated with an aluminium-based flocculation event found that:

- The geochemical code, MODPHRQ, could successfully model an aluminium-based flocculation at the confluence of acid drainage affected Dawesley Creek with Nairne Creek.
- The reduced concentration of bioavailable aluminium, downstream from this flocculation event, was associated with increased species richness of benthic diatoms.
- There was reasonable agreement between the ecological risk predicted for measured aluminium concentrations using AQUARISK and the ecological risk estimated using field-sampling of diatom flora, as long as bio-availability was taken into account.

Conclusion

In the three studies reported, changes in the benthic diatom flora have been successfully used to:

- Show the toxic effects of acid drainage from two mine sites.
- Differentiate between nutrient and acid drainage pollution in a stream system affected by more than one pollutant.
- Provide independent corroboration of the AQUARISK ecological risk assessment code.



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Mechanism of Copper Tolerance in Black-Banded Rainbowfish *(Melanotaenia nigrans)* from the East Branch, Finniss River

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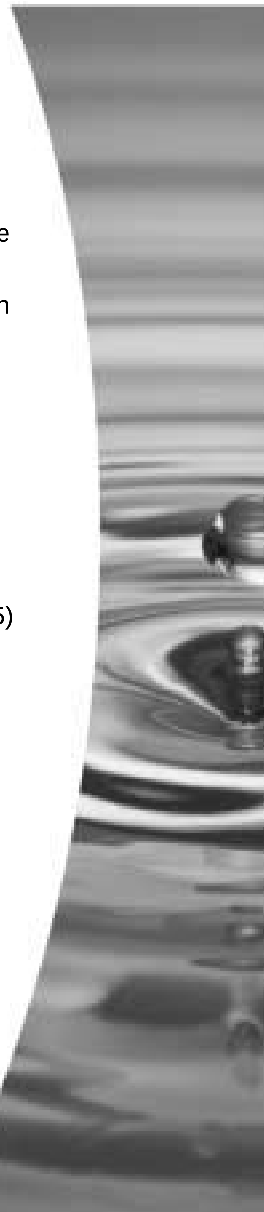
Mining is a common cause of copper pollution in the aquatic environment. Several studies have demonstrated the ability of fish to develop copper tolerance in the laboratory following sublethal exposure (Dixon and Sprague, 1981; Buckley et al., 1982; Taylor et al., 2000). Metal tolerance can be either the result of phenotypic plastic responses following exposure to sublethal concentrations (physiological acclimation), or it can be inherited (genetically-based tolerance) (Mulvey and Diamond, 1991). The mechanism of copper tolerance in fish is unresolved and has not been investigated in wild populations or in populations exposed to elevated copper concentrations for consecutive generations. Mulvey and Diamond (1991) identified three possible mechanisms of metal tolerance: changes to metal uptake or elimination rates, the ability to bind or sequester metals, and decreased enzyme sensitivity to inhibition by metals.

The population of black-banded rainbowfish (*Melanotaenia nigrans*) (Richardson) inhabiting the East Branch, Finniss River, Northern Territory, Australia, has been exposed to elevated copper concentrations for over 40 years, due to metal contaminated leachate from the Rum Jungle uranium-copper mine. It was hypothesised that due to the selective pressure of lethal exposure, the exposed fish may have developed copper tolerance. This study aimed to demonstrate copper tolerance in the exposed fish and determine the mechanism(s) involved. In May 2000, exposed fish were collected from the East Branch, 6 km downstream of Rum Jungle mine. Reference fish were collected from Coomalie Creek, an uncontaminated catchment nearby.

Fish imbalance was used as a sublethal measure of copper exposure. The 96 h EC_{50} (i.e. the concentration of copper that affects 50% of fish over 96 h) of the reference and exposed fish was used as an initial indicator of copper tolerance. At the time of collection, the 96 h EC_{50} of exposed fish was 8-fold higher than that of reference fish. Following two months exposure to low copper concentrations (24 mg Cu L^{-1}) during housing, the 96h EC_{50} of reference fish increased 5-fold, representing physiological acclimation. The 96h EC_{50} of exposed fish did not significantly ($P > 0.05$) change during this period, and remained 1.6-fold higher than that of the reference fish.

The bioconcentration of $^{64/67}Cu$ was used to investigate the mechanism of copper tolerance in exposed fish. Both exposed and reference fish were exposed to low (30 mg L^{-1}) and elevated (300 mg L^{-1}) copper concentrations for 24 and 48 h, respectively. Radioactivity was measured in four tissue sections: head region (gills, heart and brain), internal organs (including the gastrointestinal tract, liver, kidneys and gonads), muscle section, and whole body. Radioactivity correlated to the total copper concentration in the tissue section. One-compartment bioconcentration models were fitted to data for reference and exposed fish (**Figure 1**) and the regressions compared using an F-test.



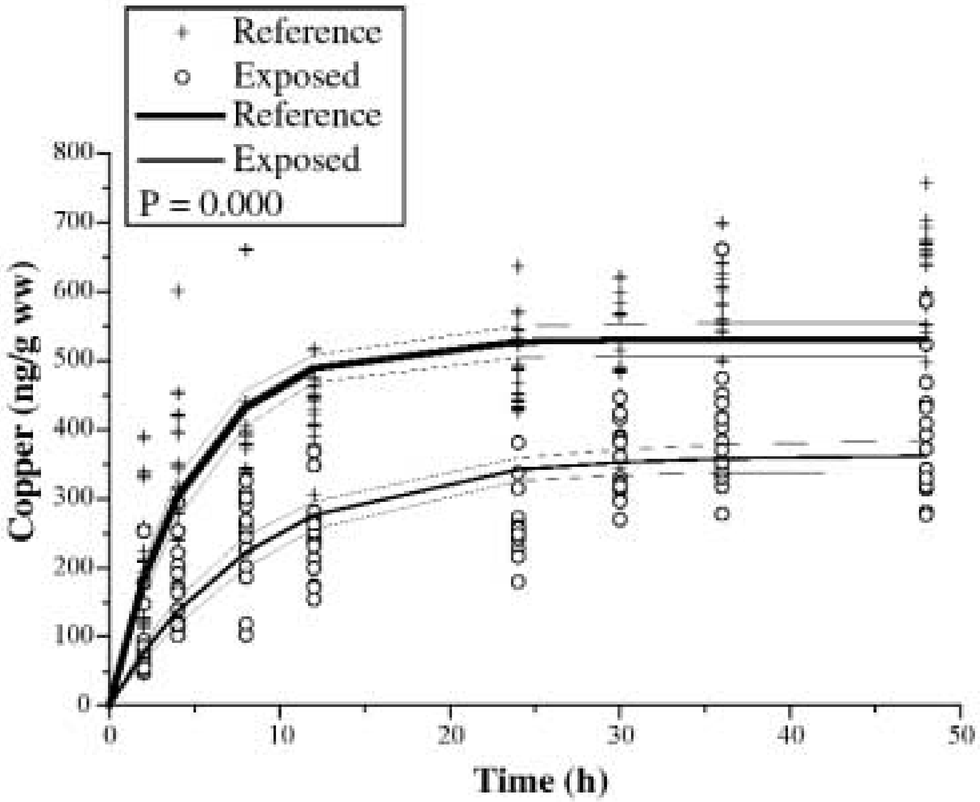


Figure 1. Accumulation of copper in the head region (gills, heart and brain) of reference and exposed fish during exposure to (a) low copper (30 mg Cu L^{-1}) and (b) elevated copper (300 mg L^{-1}) concentrations. Observed values, fitted models and 95% confidence intervals of the models are presented. Head Section included. ww; wet weight.

Copper accumulation in all tissue sections was significantly ($P \leq 0.05$) less (up to 50%) in exposed fish compared to the respective parts of the reference fish. However, copper accumulation in the internal organs was not significantly different ($P > 0.05$) between exposed and reference fish during exposure to elevated copper concentrations. Reduced copper accumulation by exposed fish indicated that binding or sequestration of copper was an unlikely mechanism of copper tolerance. The elimination rate constant was not consistently different ($P > 0.05$) between exposed and reference fish, indicating that increased elimination was also an unlikely mechanism of copper tolerance. Therefore, the reduced copper accumulation by exposed fish was due to reduced copper uptake, and as the gills are the primary site of copper uptake, the mechanism of reduced uptake is likely to occur there. Reduced gill uptake in exposed fish may have been due to changes in gill binding sites, gill surface area or gill mucus secretion rates, compared to reference fish.

Allozyme electrophoresis of seven enzymes was used to determine if genetic selection had occurred in the exposed fish population. Allozyme frequencies at the aspartate amino transferase-1 (AAT-1) and glucose-6-phosphate isomerase-1 (GPI-1) loci were significantly ($P \leq 0.05$) different between exposed and non-exposed fish (reference and captive-bred) (**Table 1**). Heterozygosity was reduced in exposed fish compared to that of unexposed fish. Collectively these results suggest that genetic selection may have occurred in the exposed fish population. Consequently, the selection of allozymes less sensitive to copper may be another mechanism of copper tolerance of exposed fish.

Table 1. Allozyme frequencies at two loci, AAT-1 and GPI-1, for fish exposed and not exposed (reference and captive-bred) to elevated copper concentrations

	Exposed	Reference	Captive-bred
AAT-1			
a	0.70	0.20	0.00
b	0.30	0.20	0.40
c	0.00	0.60	0.60
GPI-1			
a	0.00	0.40	0.05
b	0.10	0.35	0.45
c	0.80	0.10	0.30
d	0.10	0.15	0.20

This is the first study of the mechanism of copper tolerance in a wild fish population that has been exposed to elevated copper concentrations for consecutive generations. This study emphasises the importance of sample selection, and its implication for toxicity testing and risk assessment. Furthermore, as copper tolerance was due to exclusion rather than sequestration, the potential for toxic effects on higher levels of the food chain is less likely.

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Post remedial Ecological Recovery in the East Branch of the Finniss River: Fish and Decapods

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This paper reports on the recovery of fish and decapod fauna in the East Branch (EB) of the Finniss River following the remediation of the Rum Jungle mine site in the mid 1980s. The degree of ecological detriment was measured by Jeffree and Williams (1975) and subsequent field surveys and observations in the 1990s (funded by the Commonwealth Department of Industry, Science and Resources and the Australian Nuclear Science and Technology Organisation, through the Rum Jungle Monitoring Committee) have provided information of re-colonisation.

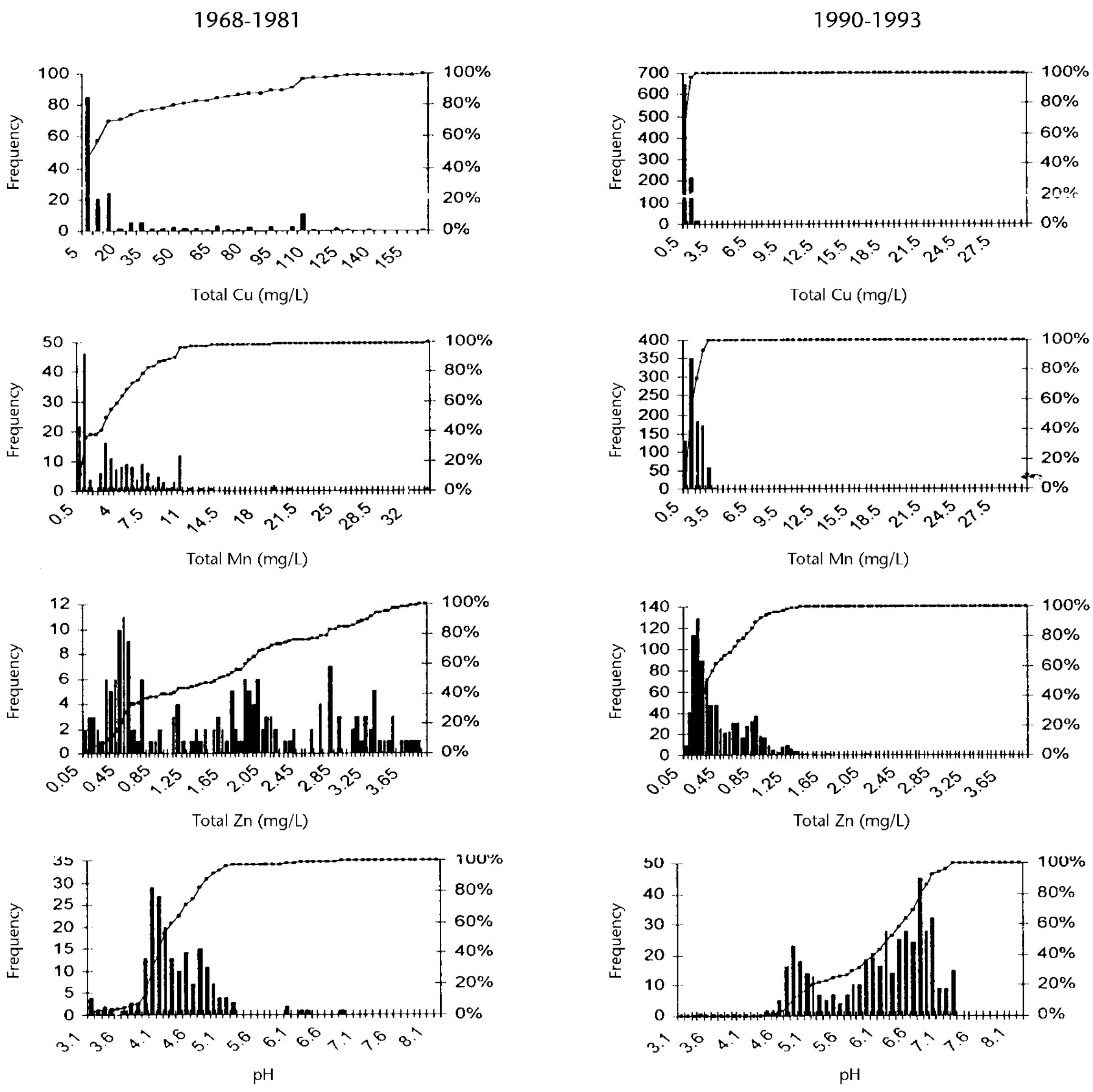

Figure 1. Frequency distributions of toxicant values pre and post-remediation of the Rum Jungle mine site (from Jeffree et al., 2001).

During the pre-remedial period, total copper concentrations as high as 160 mg L^{-1} and pH values as low as 3 were measured at GS815097 on the EB (Monitoring data 1968-81; NT Dept. of Lands, Planning and Environment). Higher concentrations and lower pH values were inevitable at locations closer to the mine. Copper at 250 mg L^{-1} was recorded closer to the mine in 1973 by Jeffree and Williams (1975). **Figure 1** compares some toxicants pre- and post-remediation. One of the major constraints on such a study is the lack of knowledge on what fauna were present prior to the establishment of mine operations. Hence, the standard for comparison with undisturbed conditions can only be made with reference sites in unaffected areas of drainage.
These sites include the EB above the mine, sides-streams to the EB and adjacent catchments of similar size and habitat structure, namely Florence Creek, South and upper Finniss River.

Table 1. Fish and decapod crustacea that are, or should be, present in the EB downstream of the Rum Jungle mine. FR, Finniss River; N, not found; GS, grid station

Common name	Scientific name	Present in 1973-4	Present in the 1990s (observed distribution)
FISH			
Black striped rainbow fish	*Melanotaenia nigrans*	Alive and dead	To above Tailings Creek 93, 94, 95, 96, 97
Purple spotted gudgeon	*Mogurnda mogurnda*	Alive and dead	To the railway crossing 94, 95, 97
Perchlets	*Ambassis maclaeyi* *A. agrammus*	Dead N	Near FR confluence 94 N
Eel-tail catfish	*Neosilurus ater*	Dead	Dead, near FR confluence
Fly-speckled hardyhead	*Cratercephalus stercusmuscarum*	Dead	N
Spangled grunter	*Leiopotherapon unicolor*	N	To the railway crossing 97
Red tailed rainbow fish	*Melanotaenia. sp. splendida*	N	To GS 097 93, 94, 96
Tarpon	*Megalops cyprinooides*	N	Once, below GS 097 during early flows 96
Mouth almighty	*Glossamia aprion*	N	Near FR confluence 94
Single-gilled eel	*Ophisternon gutterale*	N	N
Spotted blue eye	*Pseudomugil sp.*	N	N
Flathead goby	*Glossogobius giuris*	N	N
Archer fish	*Toxotes chatareus*	N	N
Strawman	*Quirichthyes sp*	N	N
[Bony bream]	[*Nematolosa erebi*]	N	N
[Long tom]	[*Strogylura kreffti*]	N	N
[Sleepy cod]	[*Oxyeleotris lineolata*]	N	N
DECAPODS			
[Red claw yabby]	[*Cherax quadricarinatus*]	N	N
Freshwater crab	*Parathelphusa transversa*	Dead	Once, below Hanna's Spring
Long-claw prawn	*Macrobrachium bullatum*	N	Near and below Hanna's Spring
Glass shrimp	*Caradina gracilirostris* *Caradina nilotica*	Dead N	N N
Caradinidies wilkinsi	N	N	

Table 1 shows the species list of animals that have been collected and/or observed in all relevant catchments, or that are noted as being in the Finniss River and suited to the habitat by Larson and Martin (1989). Sampling and observation comprised the following methodologies: poisoning (1973-4 only); baited traps; dip nets; seine nets and visual observation from the bank. Details are available in Jeffree and Williams (1975) and Twining (1995).

Decapods are particularly sensitive to heavy metal toxicity and low pH (e.g. Williams et al., 1991). None were found living in the EB prior to remediation. No fish were found between GS 097 and the mine site prior to remediation. On one occasion in 1973, healthy specimens of *M. nigrans* and *M. mogurnda* were observed in the EB, after flow had stopped, adjacent to inflow from a permanent spring below GS 097. However, other live animals observed or collected in the EB prior to remediation were typically either moribund or were with dead members of the same species. In 1974, fish kills were observed to be associated with fish entering the EB from side streams. Fish kills were still occurring in the EB post-remediation. During 1996, dead, moribund and living M. nigrans were opportunistically observed below the rail crossing during early flow on October 20. Six days later, similarly conditioned *M. nigrans* and dead *M. mogurnda* and *M. bullatum* were collected below GS 097. On October 29, live, moribund and dead M. splendida sp and a moribund *Neosilurus* sp were collected above the confluence with the Finniss River. During first flows in December 1997, dead shrimp and fish (unspecified) were also observed downstream of GS 097.

These results show a substantial recovery in fish and decapod occurrence within the EB below the Rum Jungle mine site subsequent to remediation. Whereas only two species of fish, and no decapods, were observed alive prior to remediation, up to seven species of fish and two decapod species have now been seen living in the stream. The penetration towards the mine has also increased with *M. nigrans* now occurring to within 1 km downstream of the site. The mobility of many taxa in the wet/dry tropics has evolved to allow for rapid recruitment, particularly into ephemeral streams such as the EB. Hence, the recovery probably reflects both the reduced toxicity of the stream, as well as the ecological robustness of the fish and decapod fauna to the dramatic seasonal variation.

However, the improvement to date is from a heavily impacted baseline where few individuals were able to tolerate conditions for extended periods of time. Whilst the number of species present represents a recovery, it still falls well short of the potential diversity of up to 15-18 fish species and 5-6 species of decapods that can be found in similar habitats elsewhere within the Finniss River system. There are still areas of the EB where neither fish nor decapods are found. Hence, the ecological risk presented by the currently reduced contaminant levels is still higher than would be accepted for an undisturbed system. Further reductions in contaminant loads are required to improve this situation. An example of a quantitative ecological risk assessment that provides remedial toxicant concentration targets for the EB is given in a subsequent paper in this volume.

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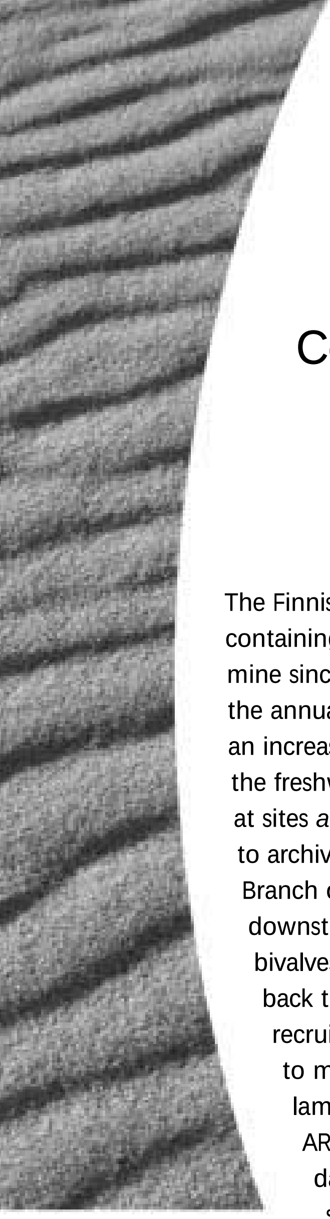

Freshwater Bivalve Shells as Archival Indicators of Metal Pollution from a Copper-Uranium Mine in Tropical Northern Australia

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The Finniss River system in tropical northern Australia has received acid rock drainage (ARD), containing elevated concentrations of metals and sulfate, from the Rum Jungle copper-uranium mine since 1954 (**Figure 1**). Rehabilitation of the mine (1983–1985) led to measured reductions in the annual loads of Cu, Mn, Zn and sulfate (40–70%) leaving the site, which has been followed by an increased diversity and abundance of freshwater biota in the Finniss River. Natural populations of the freshwater unionoid bivalve, *Velesunio angasi*, were sampled in 1996 from the Finniss River system at sites *a priori* exposed and non-exposed to ARD (**Figure 1**), to investigate the ability of their shells to archive annual metal inputs, particularly Cu, Mn and Zn. *V. angasi* were not found in the East Branch of the Finniss River downstream of the mine, or in the first 10 km of the Finniss River channel downstream of the East Branch confluence—the most contaminated region. The longest-lived bivalves (10 years) at contaminated sites in closest proximity to the East Branch confluence dated back to 1986 (i.e. end of rehabilitation), indicating an unfavourable environment for bivalve recruitment and/or survival before this time Secondary ion mass spectrometry (SIMS) was used to measure the Cu, Mn, Zn, U, Ni, Co, Pb and Fe signal, as a ratio of Ca, across the annual shell laminations of the longest-lived bivalves found at each site (**Figure 2**). At sites not exposed to ARD, a relatively constant and similar signal was found for all metals in the shells of *V. angasi*, dating back to 1965. For sites exposed to ARD, a relatively constant, but variably elevated, signal was evident for Mn, Zn, Ni and Co in the shell. In the case of Cu, the elevated signal declined exponentially (by 20%) from 1986 to 1988 and remained relatively constant thereafter. Since rehabilitation, the temporal patterns of Cu, Zn and Mn observed in the shells at the most contaminated sites reflected those of the measured annual dissolved loads of these metals in the surface waters of the East Branch (**Figure 3**). Using matching shell valves, the SIMS metal signals (i.e. counts) in the shells were converted into concentrations using inductively coupled plasma mass spectrometry. The average concentrations for Cu, Mn, Zn, Ni and Co in the shells of *V. angasi* decreased (3–13 fold) with increasing distance downstream of the mine site, until concentrations characteristic of the non-exposed sites were reached (i.e. 30 km downstream). This geographic pattern of decline in pollution signal in the shell with increasing distance downstream of the pollution input is consistent with the pattern established for water and sediment chemistry. This trend was not evident for Pb and Fe, with concentrations in the shell remaining similar to those of the reference sites. Highly significant ($P < 0.001$) positive linear relationships ($r^2 = 0.78–0.97$) were found between the total concentrations of Cu U, Mn, Zn, Co and Ni in the shells of *V. angasi* and in the surface waters of the Finniss River system. In contrast, no significant ($P > 0.05$) linear relationships were found between the total concentrations of metals in the shells and those in the sediments. However, when sediment metal concentrations were normalised to Fe, significant ($P \leq 0.05$) linear relationships were found for Cu, Zn and Ni. Overall, the results support the proposition that the shells of *V. angasi* can be used as archival indicators of metal pollution in surface waters of the Finniss River system over their lifetime.

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Markich, S.J., Jeffree, R.A. and Burke, P.T. 2002. Freshwater bivalve shells as archival Indicators of metal pollution from a copper-uranium mine in tropical northern Australia. Environ. Sci. Technol. 36, 821-832.

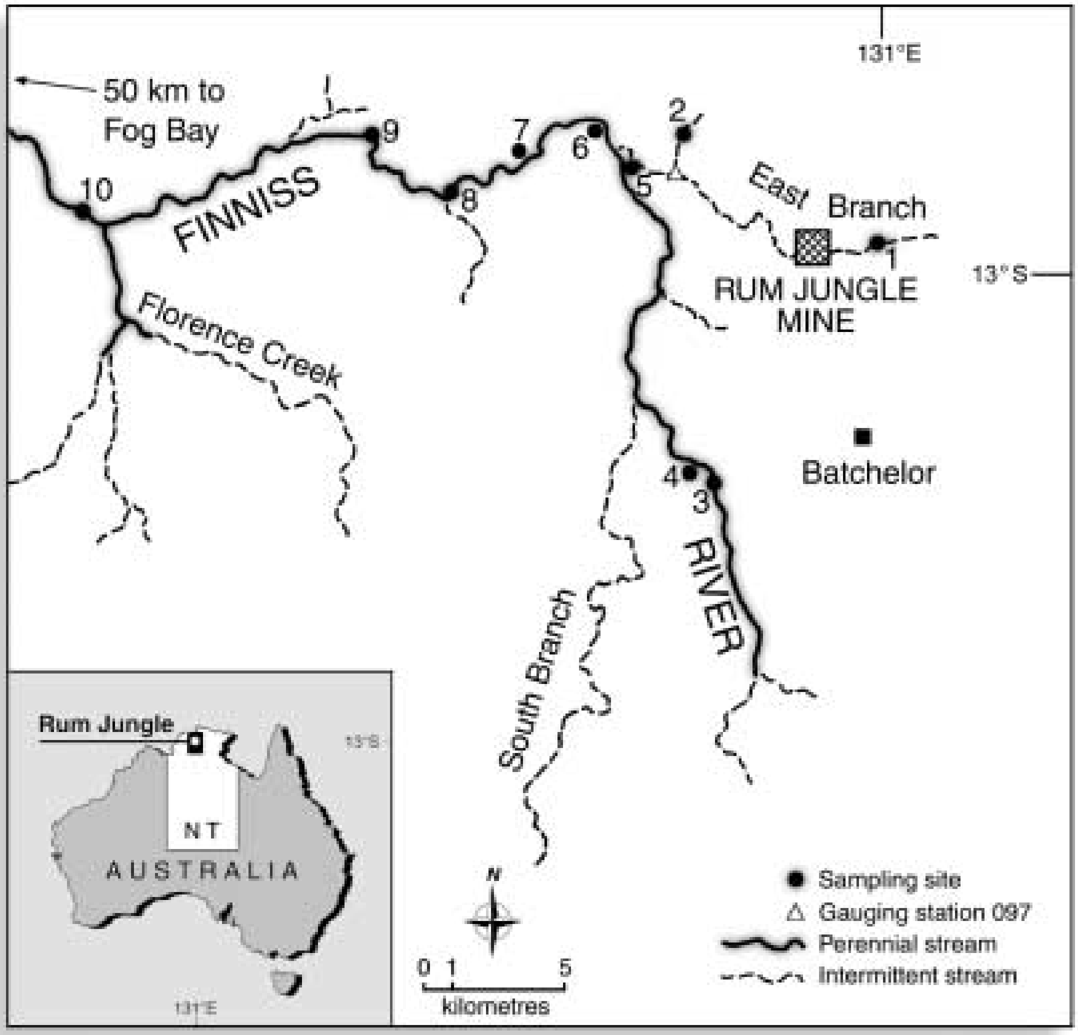

Figure 1. Location map showing the ten sampling sites for bivalves and sediment in the Finniss River system.

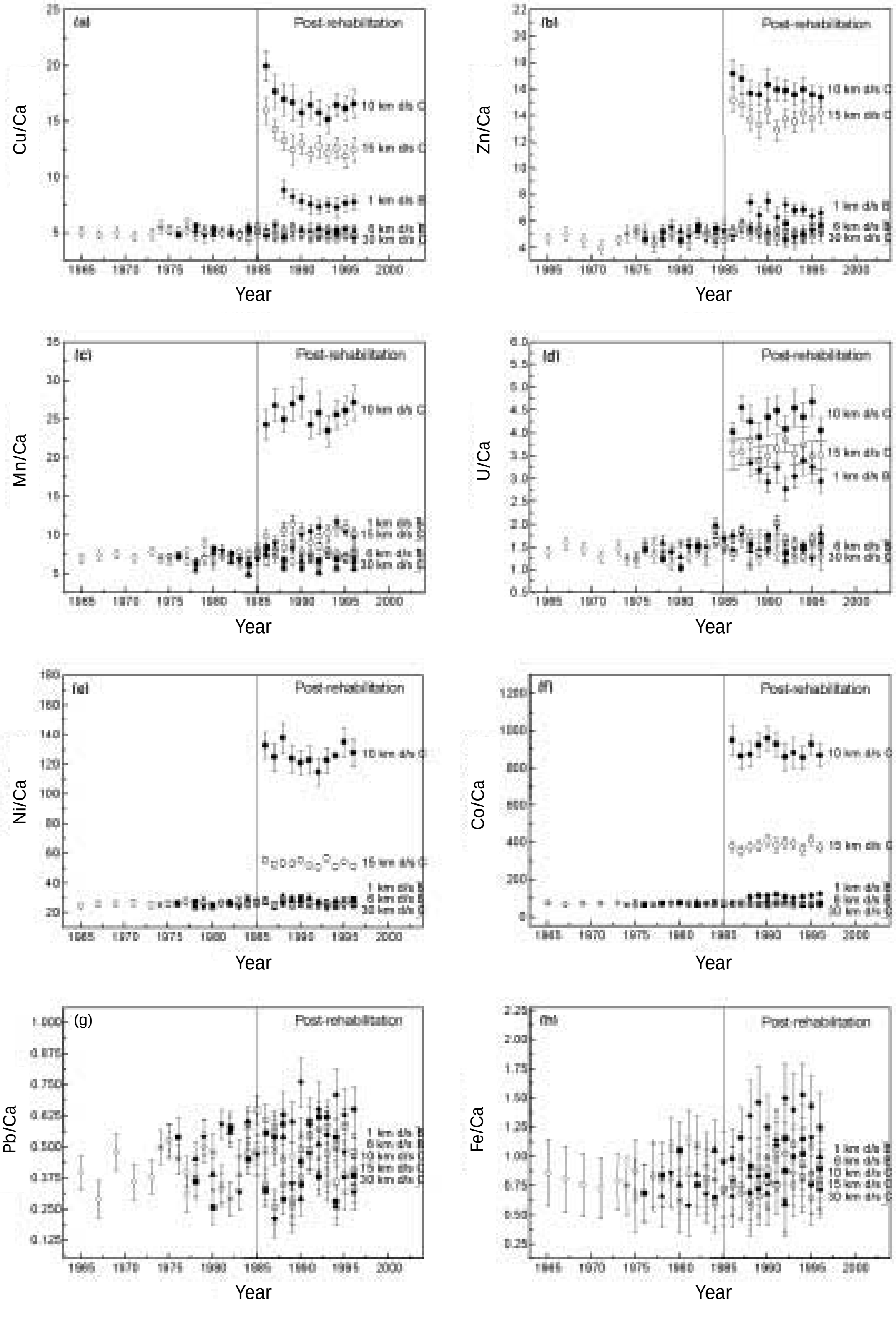

Figure 2. Mean (and standard deviation) Cu, Zn, Mn, U, Ni, Co, Pb and Fe counts (x 10^3), normalised to Ca, across the shells of the two oldest bivalves at each sampling site over their lifetime. For brevity, only sites a priori exposed to acid rock drainage (sites 6–10) are labelled. B, billabong, C, channel.

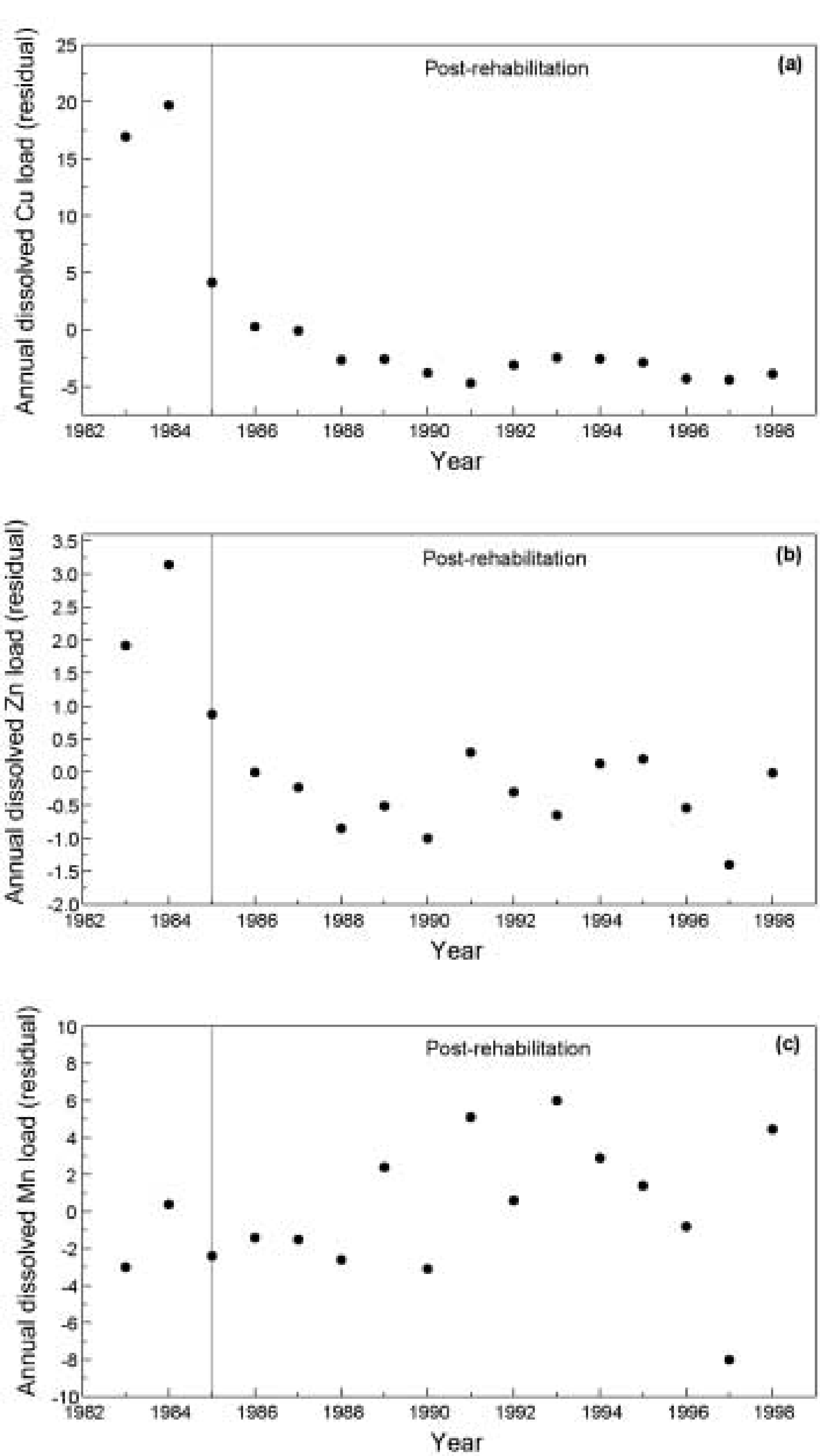

Figure 3. Annual dissolved Cu, Zn and Mn loads (expressed as residuals after correction for water discharge) in the East Branch of the Finniss River (GS 097; Figure 1) from 1982-83 to 1997-98.

Use of the freshwater Mussel, *Velesunio angasi*, in the Monitoring and Assessment of Mining Impact in Top End Streams

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Since the early 1980s, a large number of studies have been conducted on the freshwater mussel, Velesunio angasi, in coastal streams of the Northern Territory, particularly populations from Magela Creek (East Alligator River catchment) and the Finniss River. Ecological, toxicological, chemical and radiological studies have been carried out by the Environmental Research Institute of the Supervising Scientist and its consultants, as well as ANSTO, to assess the indicator potential of *V. angasi* for detecting and assessing mining impact, and for ongoing monitoring of mining activities.

A number of features of freshwater mussels make them well suited as indicators of past environments and present-day environmental health, including their sedentary habit, low position in food chains, large size (for procuring flesh and for ease of sampling), long life-spans, ecological importance (large biomass and significant filtering capacity), shell size and shape very responsive to the surrounding environment, good preservation of shells, and in some cases importance as a resource for humans (Humphrey and Simpson, 1985).

The specific categories of studies that have been investigated under the broad areas of environmental and human health are summarised in **Table 1**. Under environmental health, particularly water quality, responses of mussels may be used for the early detection of changes and for the wider assessment of ecological importance of change through field population studies (sensu ANZECC and ARMCANZ, 2000). For these assessments, a number of attributes listed above make freshwater mussels particularly valuable as archival monitors. In general, *V. angasi* has limited value as a laboratory organism for ecotoxicological assessment, due to the inability to culture stocks, high filtering rates and food demands, and/or ability to close the valves at threshold contaminant concentrations (e.g. ARRRI, 1987b, 1988).

Proven or potential value of measured responses from the field for past (archival) and present-day monitoring has been demonstrated for presence/absence data, reproduction, shell form, size and growth rates, chemistry of shell laminations, and chemical and radionuclide content of soft tissues (Humphrey and Simpson, 1985; ARRRI, 1984, 1985, 1987a, 1987b, 1988, 1991, 1992a, 1992b; Jeffree, 1985, 1988; Allison and Simpson, 1989; Humphrey, 1995; Markich et al., 2002). Survey and age data from field populations may be particularly useful for assessing the success of rehabilitation efforts in streams over the long-term. However, correct interpretation of these data and responses requires a good understanding of the ecology of *V. angasi* across a broad geographical range (**Table 1**).

Table 1. The indicator potential of *Velesunio angasi* for detecting and assessing mining impact. (Superscripts refer to numbered specific studies listed in column 2)

General attribute	Specific study	Indicator potential: ADVANTAGES	Indicator potential: DISADVANTAGES (or caveats)
ECOSYSTEM CONDITION OR HEALTH Early detection			
Laboratory -sublethal	1. Glochidial snap rate (mortality, behavioural) 2. Valve response (behavioural) 3. Growth and survival of metamorphosed juveniles	• Sensitive [1,2] (up to threshold concentrations [3]) • Multiple life stage test possible (larvae ⇒ encysted larvae ⇒ juvenile) [3] • Husbandry requirements elucidated for young juveniles [3]	• Dependence on field-collected material [1,2,3] • Behavioural responses not recognised as ecologically relevant [1,2] • Husbandry requirements not well understood and may be demanding for post-juveniles [1,2,3] • Valve closure (⇒ lack of exposure) at threshold concentrations [2]
Field -sublethal	1. Growth and survival of metamorphosed juveniles 2. Reproduction: larval production in females 3. Bioaccumulation (bioavailability)	• Sensitive [1,2] • Enhanced natural survival and growth under lotic conditions [1] • When breeding synchronised, possible to track timing of impact and recovery [2] • Possible to determine sex and larval brooding stages without injury to mussels [2] • May be enhanced contaminant signal (cf water) [3] • Flux of some elements well understood [3]	• Dependence on field-collected larvae[1] • Response not correlated with population or community-level response [1,2,3] • Studies limited where natural densities are low (destructive sampling) [3] • Flux of elements in mussels should be determined [3]
Population study and archival monitoring	1. Presence/absence: sedentary and long-lived ⇒ assessing long-term rehabilitation 2. Reproduction: larval production in females (field) 3. Shell form, size and growth rates 4. Chemistry of shell laminations 5. Chemical and radionuclide content of soft tissues	• Integrative: short to long-term historical record available of past environments, exposures and/or insults [1,2,3,4,5] • Biology and ecology of *V. angasi* well understood [1-5] • Ecologically relevant [1, others?] • See superscript 2 comments in cell above, relevant to reproduction • Superscript 3 comments in cell above also relevant to chemical and radionuclide content of soft tissues	• Requires good understanding of ecology across geographical range, including habitat preferences, causes of growth checks, and environmental correlates of shell form and life history parameters generally • Flux of elements in mussels should be determined [4,5]
HUMAN HEALTH Body burdens	Chemical and radionuclide content of soft tissues	• Significant food source for some aboriginal groups • May concentrate contaminants to high levels • Non-destructive, live-counting approaches available for isotopes of radium and their progeny	• Bioaccumulation studies involving non-radionuclides may be limited where natural densities are low (destructive sampling)

The burdens and flux of some metals and radionuclides in tissues of *V. angasi* have been well studied and this information has been used in ongoing bioaccumulation studies in Magela Creek. These studies are used for the early detection of changes in water quality and to ensure elemental concentrations are within limits safe for human consumption. Known half-lives of different elements in mussels, including uranium (Allison and Simpson, 1989) and various radionuclides (ARRRI, 1984, 1985, 1987a, 1987b), infers a short- to long-term monitoring potential of tissue burdens, depending upon the element. Radium and thorium isotope loads, and activity ratios such as Ra-228/Ra-226 and Th-228/Ra-228, are strongly age-dependent (ARRRI, 1985, 1987a). Determination of this dependency for a site can give information on pollution events even several years later. For this type of investigation, radioisotope activity ratios are more sensitive and reliable indicators than concentrations or loads of individual radionuclides.

An example of the archival potential of the Ra-228/Ra-226 ratio in mussels for demonstrating downstream effects in Magela Creek of hypothetical releases of process water from the Ranger uranium mine is shown in **Figure 1**. The Ra-228/Ra-226 activity ratio decreases with age due to the disproportionate decay of the two isotopes: 6 year half-life for Ra-228 vs 1600 year half-life for Ra-226. Hence, the ratio is lower in older mussels as the Ra-228 activity incorporated early in life has partially decayed (**Figure 1**). If there had been an "event" several years ago, this would be observed in the age-dependence of the ratio. For example, if radium was released from Ranger eight years ago resulting in a permanent increase in Ra-226 in the creek system then (dashed line in **Figure 1**):

- The increase in Ra-226 would result in a lowered Ra-228/Ra-226 ratio. In **Figure 1** it has been assumed that the Ra-226 concentration in the creek water has doubled, resulting in a decrease in the y-intercept (i.e. ratio at age = 0) from 0.75 down to the observed value of 0.37.
- Assuming that the 'new', hypothetical equilibrium ratio is 0.37, then the ratio in mussels younger than eight years, exposed only to the new, post-event ratio, would decline because of the disproportionate decay of the two isotopes (as prior to the 'event').
- Mussels older than eight years would have a higher ratio than expected from the curve fit because they had experienced the higher ratio (0.75) in the water prior to the event. This is indicated by the dashed line in the figure.

In the Australian context, most metal bioaccumulation work has been performed on the species, *V. angasi, V. ambiguus* and *Hyridella depressa* (e.g., Allison and Simpson, 1989; Jeffree and Brown, 1992; Jeffree et al., 1993; Markich and Jeffree, 1994; Brown et al., 1996; Markich et al., 2001). Many of these papers have attempted to construct models leading to mechanistic insights into bioaccumulation. Uranium provides an unusual example of metal absorption and bioaccumulation. In one field study (Allison and Simpson, 1989) mussels were placed in water containing an elevated concentration of U for a number of weeks, then removed to a billabong with a background U concentration. These experiments showed that U is rapidly lost from mussel tissue, with a half-life of a few days. This observation superficially disagrees with the findings of Markich et al. (2001), who showed that about 90% of the soft-tissue U burden of *H. depressa* and *V. ambiguus* resided in the extracellular granules. The solubility of UO_2PO_4 is very low, which is inconsistent with rapid mobilisation and loss of U from tissues. However, the tissue-water concentration ratio for U, as measured by Markich et al. (2001), is also very low compared with the presumed slow rate of exchange from the $CaHPO_4$ matrix.

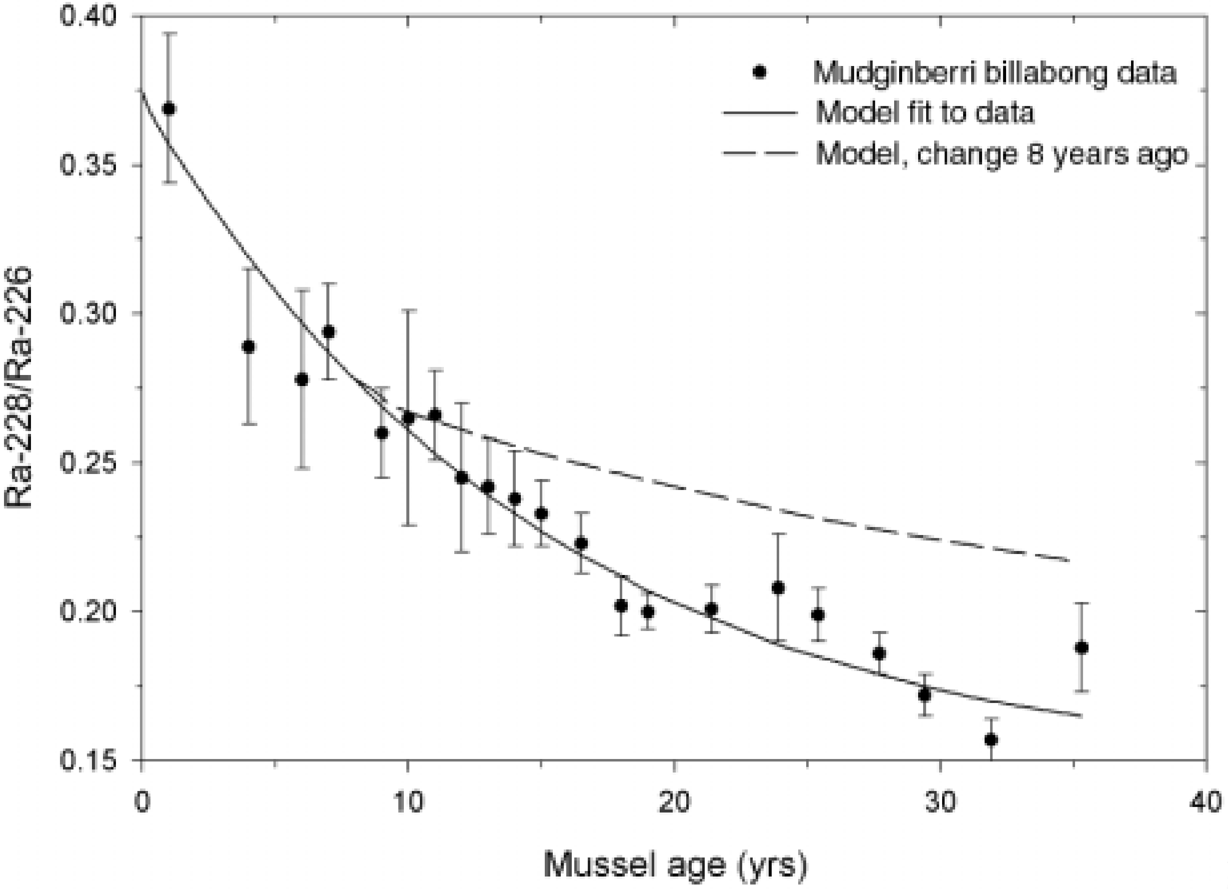

Figure 1. Dependence of the radium activity ratio on age for mussels from Magela Creek billabongs.

The overall evidence suggests that, although U has a short half-life in mussel protoplasm, the transport mechanism to extracellular granules is impeded in a way that does not occur with many other divalent ions. This may be because UO_2^{2+} is mainly only nominally divalent at physiological and most naturally-occurring pH values. The transport of metals from an intracellular environment to an extracellular phosphate granule probably involves a decomplexation step. For most divalent metals, extracellular pH is unlikely to be sufficiently high to cause significant hydrolysis.
For U, however, extensive hydrolysis occurs at pH > 4 (Moulin et al., 1995), lowering the effective charge on the U species, and restricting its incorporation (as an unhydrolysed UO_2^{2+} ion) into the phosphate crystal structure. At the physiological pH of mussel body fluid (~7.8; Brown et al., 1996), the fraction of U present as UO_2^{2+} is ~0.3% (calculated from Moulin et al., 1995).
The low percentage of the metal readily fixed in the granules, coupled with (in most cases) a low ambient concentration of total soluble U, may provide a high kinetic barrier to retention in the granules.

This may explain the observation of Markich et al. (2001) that the concentration ratio (tissue: water) for U was comparatively low, despite the very low solubility of UO_2PO_4. For Cd (pK_a ~10.3), Co (pK_a ~10.5), Cu (pK_a ~7.5), Mn (pK_a ~10.6), Ni (pK_a ~9.9), Pb (pK_a ~7.8) and Zn (pK_a ~9.0), the fraction of metals present in divalent form at pH 7.8 is about 100%, 100%, 33%, 100%, 99%, 50% and 94%, respectively (Aylward and Findlay, 1974; Hogfeldt, 1982). For these elements, there should be little kinetic barrier to incorporation of the ion into phosphate granules, as sufficient divalent form is available. After incorporation of metals into the granules, the equilibrium shifts to produce more divalent ion in the aqueous phase, by mass action. It may be worthwhile to study the incorporation of U, and other easily hydrolysed divalent metal ions, into phosphate granules as a function of ambient pH.

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Crocodile Bones as archives of Pollution Exposure: Lead Contamination in Kakadu National Park, and what's in Sweetheart's Osteoderms?

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Investigations of biological archives using secondary ion mass spectrometry (SIMS) has been extended from freshwater bivalves to other long-lived fauna with laminated calcified structures, such as estuarine crocodiles, that have been exposed to metal contaminants in their aquatic environments.

Estuarine crocodiles (*Crocodylus porosus*) in some sections of Kakadu National Park (KNP) are known to consume fauna shot with lead ammunition, leading to concerns that they may be contaminated with lead. A program of sampling both crocodile osteoderms and edible flesh, over a wide size range of animals from the three main catchments of KNP, provided samples for analysis of lead (Twining et al., 1999). Analysis of the lead in the osteoderms and flesh of 40 crocodiles sampled throughout KNP showed elevated levels ($P < 0.001$) in both tissues from individuals in the two exposed habitats, relative to all other individuals. Analysis by SIMS of the Pb-208/Ca-42 signal ratios across the osteodermal laminations of lead-exposed crocodiles confirmed they were elevated and relatively constant (Twining et al., 1999). These results suggested that: (a) the crocodilian digestive system can retain lead ammunition following ingestion and solubilise and absorb it into the body, and (b) crocodiles were exposed to elevated lead levels during most of their life, that they could apparently tolerate.

An experimental study undertaken at Crocodylus Park, northern Australia, demonstrated the following. After ingestion of lead shot the lead concentration in the blood immediately increased, appearing to have reached an equilibrium concentration in 30-40 days of ca. 350 mg dL-1, which was an increase above background of more than an order of magnitude (**Figure 1**). This result confirmed the ability of the digestive system of C. porosus to solubilise lead from the ingested shot and absorb it into the blood at a rapid rate. The subsequent lavage and radiography of the stomachs of exposed crocodiles retrieved or identified more than 70% of the individual ingested lead shot pellets, confirming their ability to retain lead shot (Jeffree et al., 2001).

These experimental findings made it then possible to evaluate the hypothesis that the osteodermal laminations would record enhanced blood lead concentrations resulting from the ingestion of lead shot. At about 140 days following lead shot ingestion, two osteoderms were removed from each exposed and control animal. SIMS analysis of Pb-208 and Ca-42 signal intensities was then performed on sections that were prepared and analysed using similar methods previously used on field-collected specimens (Twining et al., 1999).

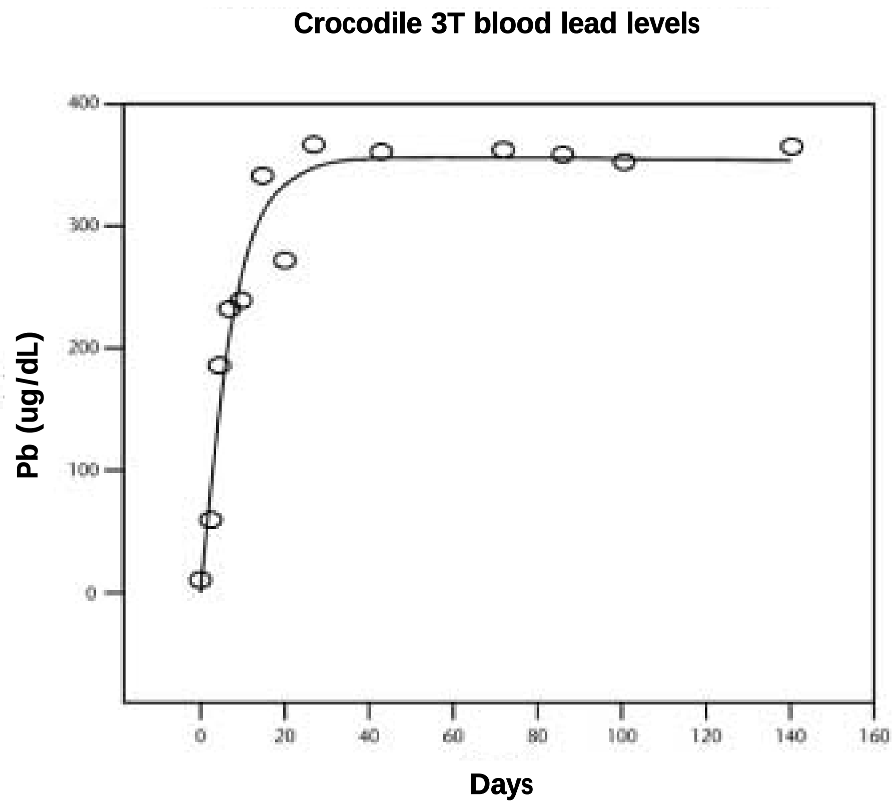
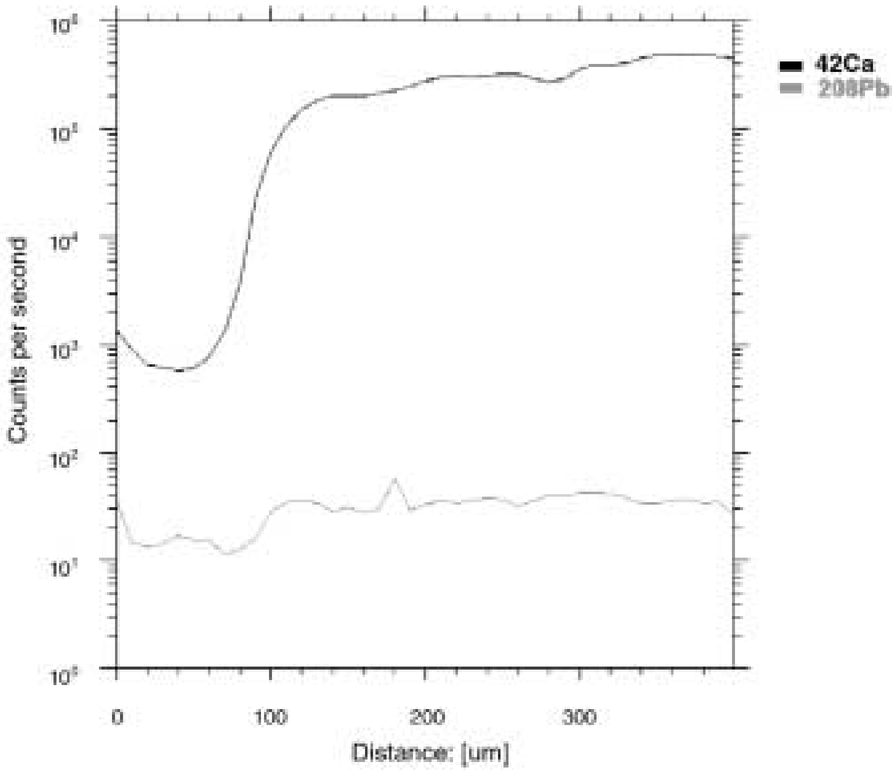


Figure 1. Pattern of lead concentration (μg dL^{-1}) in the blood of *C. porosus* plotted against time (days) following ingestion of lead shot pellets (five).

Figure 2 shows SIMS line scans for these two isotopes, that begin in the skin (0), in which the osteoderms are constructed, and move through the skin/bone interface (~100 μm), through the most recently deposited laminations to those progressively constructed at greater periods prior to experimental treatment (>100 to 200 μm), for both a control specimen (i) and one that had ingested five lead shot (ii). For both specimens, the Ca signal increases through the skin/bone interface to remain elevated through the rest of the osteodermal laminations. However for lead, the signal is relatively constant throughout the control section but the lead-exposed animal shows an increase in signal intensity by more than an order of magnitude through the skin/bone interface and most recently constructed laminar material, before declining by an order of magnitude in the previously constructed laminations of the osteoderm. These initial findings are consistent with the hypothesis that incremental laminations of the osteoderm will archive a lead signal that responds to enhanced levels of lead in the animal's blood during its life.

These results indicated that the osteoderms from the skin of 'Sweetheart', that was captured at Sweet's Lookout in the Finniss River in 1978, and was at least 50 years of age, may record metal concentrations in its aquatic environment during both the pre-mining and mining phase, particularly that period before contaminant loads were measured. Accordingly, two osteodermal cores were obtained from the mounted skin of Sweetheart in the Museum and Art Gallery of the Northern Territory, Darwin. These were prepared for scanning electron microscopy with microprobe EDS and SIMS analysis, using techniques similar to those described in Twining et al. (1999).

Linescan across control osteoderm - no Pb exposure



Linescan across osteoderm exposed to 5 lead shots

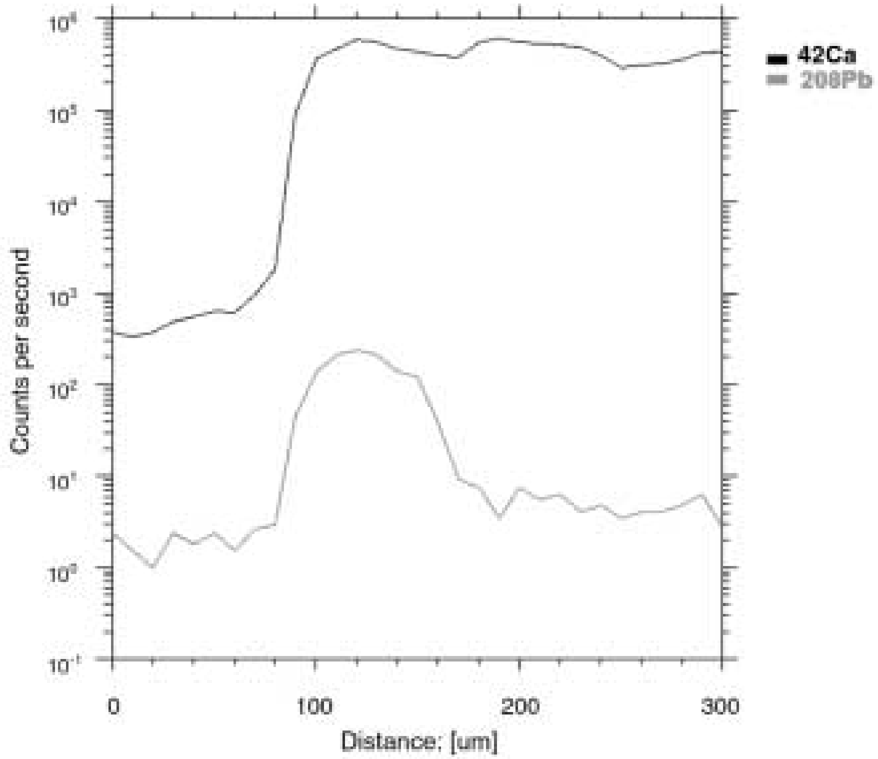


Figure 2. SIMS line scans of Ca-42 and Pb-208 signals across the skin and laminated osteoderm from *C. porosus* (i) unexposed and (ii) exposed to lead shot ammunition previously ingested with food.

SEM analysis identified the laminated structure of the osteoderm, however microprobe analysis did not detect appreciable amounts of even Ca and P, although the organic matrix was obviously present. It is proposed that this anomalous result is due to the preparatory tanning of the skin, in acid solution, that could be expected to leach elements from the organic matrix. An analogy is drawn with the decalcified skeletons in the bodies of the Druid sacrifices due their deposition in acid swamp waters in the UK.

The challenge is now to sample osteoderms from large crocodiles in the Finniss River, preferably in close proximity to the Rum Jungle mine site, where any archived pollution signal would be more intense, and then repeat this analytical investigation of the osteodermal history of contaminant loadings.

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Catchment-specific Element Signatures in Estuarine Crocodiles (*Crocodylus porosus*) From the Alligator Rivers Region, Northern Australia

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The concentrations of Na, K, Ca, Mg, Ba, Sr, Fe, Al, Mn, Zn, Pb, Cu, Ni, Cr, Co, Se, U and Ti were determined in the osteoderms and/or flesh of estuarine crocodiles (*Crocodylus porosus*) captured in three adjacent catchments within the Alligator Rivers Region (ARR) of northern Australia (**Table 1** and **2, Figure 1**). Results from multivariate analysis of variance showed that when all metals were considered simultaneously, catchment effects were significant ($P \leq 0.05$). Despite considerable within-catchment variability, linear discriminant analysis showed that differences in elemental signatures in the osteoderms and/or flesh of *C. porosus* amongst the catchments were sufficient to classify individuals accurately to their catchment of occurrence (**Figure 2**). Using cross-validation, the accuracy of classifying a crocodile to its catchment of occurrence was 76% for osteoderms and 60% for flesh. These data suggest that osteoderms provide better predictive accuracy than flesh for discriminating crocodiles amongst catchments. There was no advantage in combining the osteoderm and flesh results to increase the accuracy of classification (i.e. 67%). Based on the discriminant function coefficients for the osteoderm data, Ca, Co, Mg and U were the most important elements for discriminating amongst the three catchments. For flesh data, Ca, K, Mg, Na, Ni and Pb were the most important metals for discriminating amongst the catchments. Reasons for differences in the elemental signatures of crocodiles between catchments are generally not interpretable, due to limited data on surface water and sediment chemistry of the catchments or chemical composition of dietary items of *C. porosus*. From a wildlife management perspective, the provenance or source catchment(s) of 'problem' crocodiles captured at settlements or recreational areas along the ARR coastline may be established using catchment-specific elemental signatures. If the incidence of problem crocodiles can be reduced in settled or recreational areas by effective management at their source, then public safety concerns about these predators may be moderated, as well as the cost of their capture and removal.

Reference

Markich, S.J., Jeffree, R.A. and Harch, B.D. 2002. Catchment-specific element signatures in estuarine erocodiles (*Crocodylus porosus*) from the Alligator Rivers Region, Northern Australia. Sci. Total Environ. 287, 83-95.

Table 1. Summary statistics for metal concentrations in the osteoderms of C. porosus from three adjacent catchments within the Alligator Rivers Region of northern Australia

South Alligator Catchment (n=11)

	Ca	Mg	Ba	Sr	Fe	Mn	Pb	Cu	Zn	Cr	Co	Ni	U
Minimum	191	2.25	1.90	121	1.91	0.29	1.20	2.20	2.88	0.08	0.22	1.16	0.03
1st Quartile	213	2.73	10.7	227	5.91	1.44	2.35	3.10	3.75	0.18	0.25	2.65	0.03
Median	219	3.01	31.3	321	10.6	2.69	3.34	5.16	4.91	0.21	0.30	3.71	0.04
Mean	220	2.93	21.5	297	10.6	1.90	3.10	3.80	5.09	0.22	0.33	3.65	0.03
3rd Quartile	231	3.39	34.1	443	13.9	3.31	3.80	6.80	5.51	0.26	0.33	4.68	0.04
Maximum	239	3.50	143	507	21.1	11.8	6.90	13.1	8.15	0.30	0.40	6.54	0.06
Standard deviation	14.2	0.41	35.9	128	6.22	2.77	1.60	3.01	1.46	0.06	0.06	1.63	0.01

East Alligator Catchment (n=15)

	Ca	Mg	Ba	Sr	Fe	Mn	Pb	Cu	Zn	Cr	Co	Ni	U
Minimum	200	2.00	4.10	123	4.58	1.53	1.50	2.40	2.28	0.07	0.31	1.60	0.03
1st Quartile	212	2.48	9.15	306	5.62	2.26	1.70	2.75	3.33	0.14	0.35	3.55	0.04
Median	222	2.76	21.8	331	11.8	5.34	2.89	4.42	4.33	0.22	0.38	4.25	0.05
Mean	224	2.74	14.2	336	11.4	4.12	2.40	3.40	4.25	0.22	0.36	4.22	0.05
3rd Quartile	230	3.08	24.1	374	17.7	7.79	3.50	6.25	5.24	0.28	0.41	4.57	0.05
Maximum	241	3.56	72.5	474	21.2	12.2	5.90	7.90	6.55	0.39	0.45	6.54	0.07
Standard deviation	12.8	0.46	20.9	95.1	6.63	3.62	1.51	2.13	1.29	0.10	0.05	1.33	0.01

West Alligator/Wildman Catchment (n=8)

	Ca	Mg	Ba	Sr	Fe	Mn	Pb	Cu	Zn	Cr	Co	Ni	U
Minimum	210	2.91	27.7	169	1.33	3.81	1.80	3.50	1.73	0.11	0.23	3.38	0.02
1st Quartile	218	3.22	30.7	308	2.42	6.25	2.55	3.73	4.82	0.15	0.36	3.84	0.03
Median	223	3.61	54.8	482	3.87	8.09	4.18	4.75	5.53	0.21	0.38	4.82	0.03
Mean	222	3.69	36.5	378	3.35	8.32	2.80	4.30	6.30	0.20	0.38	4.37	0.03
3rd Quartile	226	3.90	61.8	696	5.20	9.47	4.35	4.88	6.51	0.28	0.42	5.62	0.03
Maximum	242	4.44	117	923	7.94	13.4	9.40	8.70	8.72	0.34	0.50	7.22	0.03
Standard deviation	9.33	0.52	38.4	262	2.24	3.21	3.03	1.70	2.32	0.08	0.08	1.39	0.00

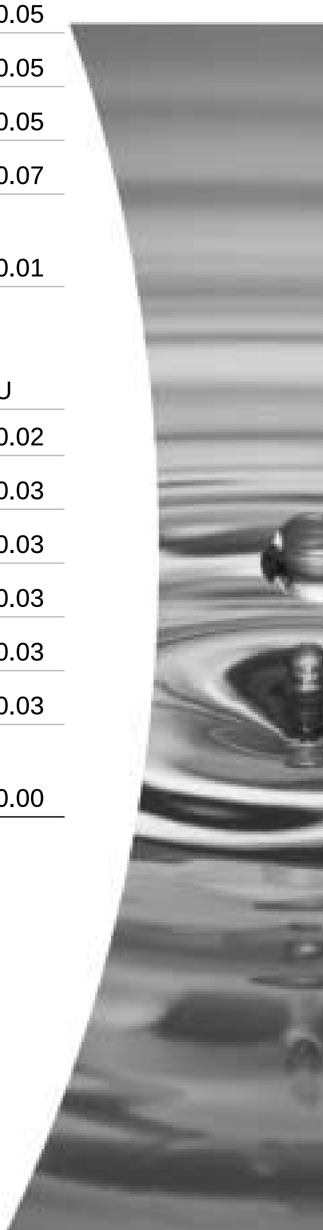

Table 2. Summary statistics for metal concentrations in the flesh of C. porosus from three adjacent catchments within the Alligator Rivers Region of Northern Australia

South Alligator Catchment (n=7)

	Ba	Pb	Ca	Fe	Al	Mn	Na	Cu	Cr	Ni	K	Se	Ti	Mg	Zn
Minimum	0.27	0.21	10	41.0	26.0	0.51	1280	0.43	0.21	0.25	8.4	0.44	1.8	589	53.0
1st Quartile	0.40	0.26	171	80.5	62.0	0.62	2030	1.24	0.43	0.32	9.5	0.94	4.8	781	66.0
Median	0.52	0.30	197	129	83.3	0.80	2210	1.37	0.50	0.43	10.9	1.11	6.6	836	102
Mean	0.54	0.28	196	97.0	91.0	0.77	2080	1.42	0.51	0.40	9.8	1.04	7.1	877	101
3rd Quartile	0.64	0.33	215	159	104	0.87	2450	1.54	0.62	0.48	11.6	1.20	8.2	896	116
Maximum	0.85	0.39	288	303	125	1.30	3220	2.02	0.74	0.76	15.7	2.00	9.8	1020	192
Standard deviation	0.16	0.06	44.1	77.8	29.4	0.24	524	0.39	0.15	0.15	2.2	0.36	2.4	121	41.6

East Alligator Catchment (n=5)

	Ba	Pb	Ca	Fe	Al	Mn	Na	Cu	Cr	Ni	K	Se	Ti	Mg	Zn
Minimum	0.39	0.12	170	13.0	40.0	0.40	1300	0.34	0.17	0.14	8.0	0.67	3.2	708	55.0
1st Quartile	0.48	0.20	172	43.0	50.5	0.47	1650	0.78	0.20	0.28	10.5	0.82	5.1	788	73.5
Median	0.53	0.26	244	63.3	64.3	0.58	2710	0.88	0.26	0.36	10.7	0.95	6.7	839	81.2
Mean	0.53	0.22	172	61.0	51.0	0.61	1850	0.98	0.25	0.36	10.9	0.87	7.1	817	76.9
3rd Quartile	0.58	0.34	183	85.0	76.0	0.63	2980	1.02	0.31	0.46	11.5	1.00	8.0	884	90.0
Maximum	0.68	0.38	660	113	106	0.84	6560	1.28	0.37	0.56	12.3	1.47	10.2	1000	110
Standard deviation	0.17	0.07	30.2	79.1	15.5	0.18	454	0.38	0.24	0.10	1.4	0.26	2.0	168	35.9

West Alligator/Wildman Catchment (n=8)

	Ba	Pb	Ca	Fe	Al	Mn	Na	Cu	Cr	Ni	K	Se	Ti	Mg	Zn
Minimum	0.54	0.26	178	47.0	91.0	0.52	1550	0.55	0.12	0.52	8.1	0.52	3.1	684	45.0
1st Quartile	0.55	0.34	190	77.5	105	0.65	2020	0.68	0.27	0.55	8.9	0.66	5.9	713	56.0
Median	0.73	0.37	216	116	115	0.76	2260	0.98	0.41	0.64	10.0	0.86	6.5	835	84.6
Mean	0.76	0.39	219	88.5	117	0.71	2190	0.86	0.34	0.63	10.0	0.83	7.2	774	80.0
3rd Quartile	0.88	0.42	237	118	130	0.87	2510	1.34	0.47	0.70	11.1	1.10	7.8	897	106
Maximum	0.92	0.45	253	290	132	1.06	2890	1.55	0.81	0.78	12.1	1.20	8.2	1100	141
Standard deviation	0.17	0.07	30.2	79.1	15.5	0.18	454	0.38	0.24	0.10	1.4	0.26	2.0	168	35.9

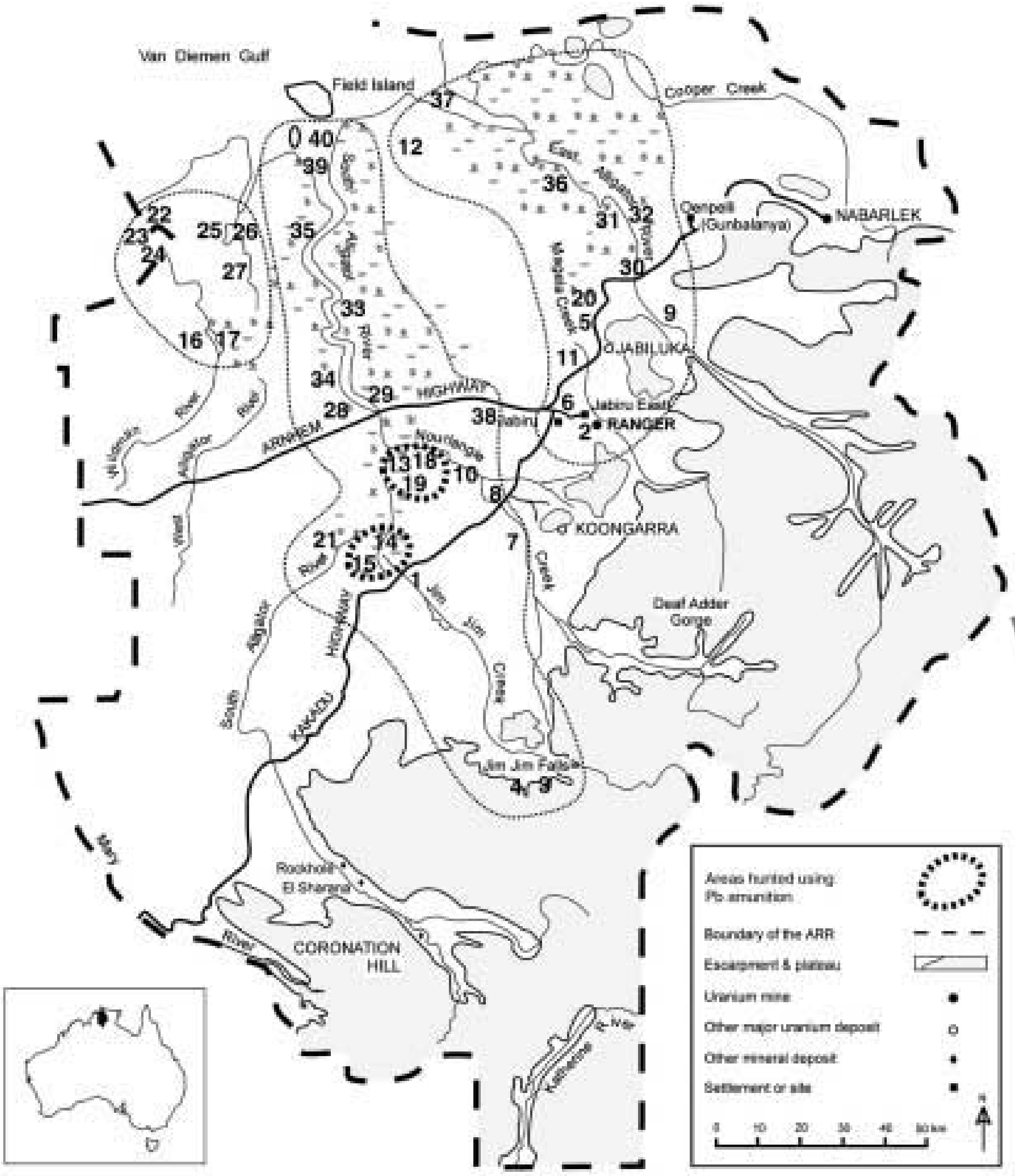

Figure 1. Map of the Alligator Rivers Region in the Northern Territory of Australia, showing each river catchment and the locations of the sampled crocodiles (numbered 1 to 40).

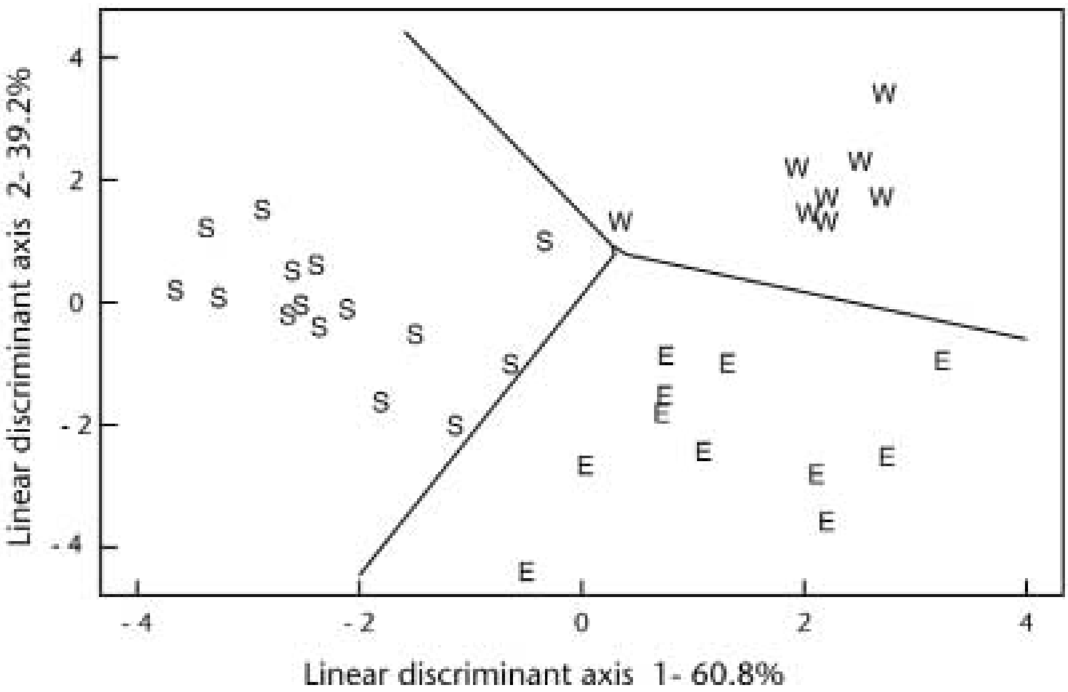

Figure 2a. Decision rule for elemental concentrations ($\log_e$) in the osteoderms of *C. porosus* plotted on the two discriminant function axes. E, East Alligator river catchment; S, South Alligator river catchment; W, West Alligator/Wildman river catchment.

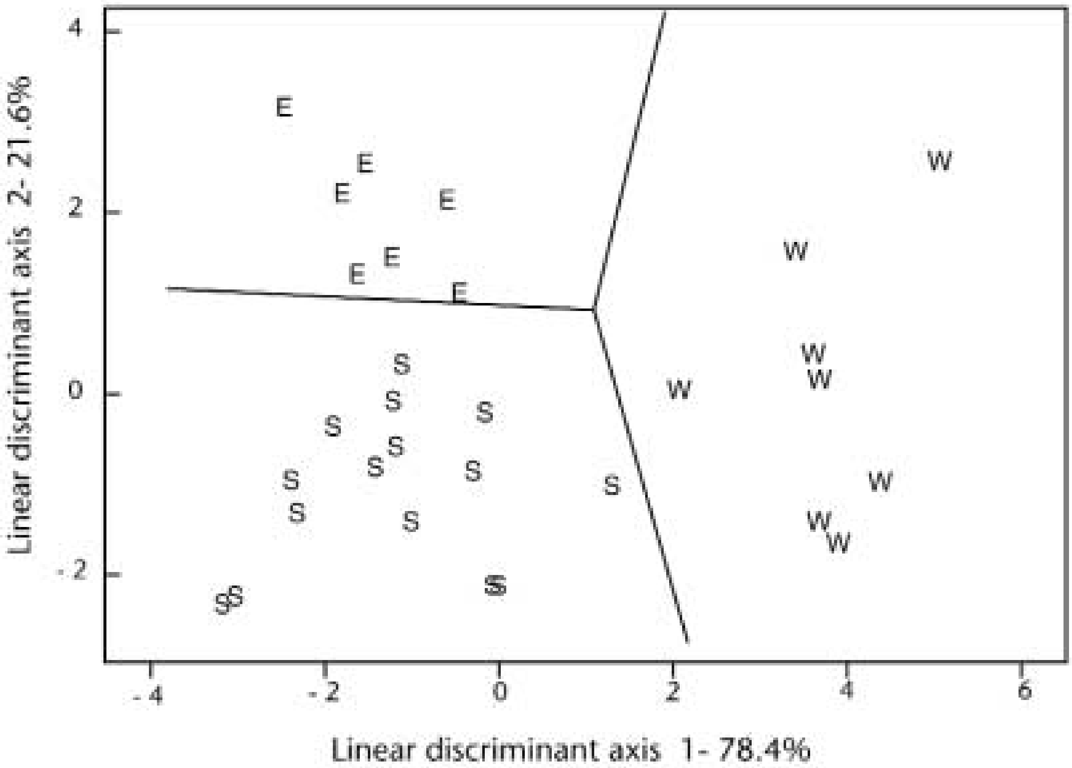

Figure 2b. Decision rule for elemental concentrations ($\log_e$) in the flesh of *C. porosus* plotted on the two discriminant function axes. E, East Alligator river catchment; S, South Alligator river catchment; W, West Alligator/Wildman river catchment.

Trace Element Concentrations of Wild Saltwater Crocodile Eggs

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Saltwater crocodiles (*Crocodylus porosus*) accumulate trace elements from the environment into their flesh and bones (Jeffree et al., 2001a). Elevated levels of metals (e.g. Hg, Zn, Pb), organochlorines (e.g. DDT) and radionuclides (e.g. radiocesium) have been recorded in blood, tissues and eggs of several crocodilian species (Manolis et al., this volume). Given their longevity (> 50 years; Webb et al., 1978), and their position in the food chain, crocodilians may be useful bioindicators for monitoring long-term changes in the environment (Brisbin et al., 1998; Burger et al., 2000). *C. porosus* eggs have been collected throughout the Northern Territory of Australia since 1980-81 (Webb et al., 1983, 2000), including areas downstream of the Rum Jungle mine. This mine was active from 1953 to 1971, resulting in parts of the Finniss River system receiving acid drainage from the site. Although mining ceased in 1971, high levels of contaminants continued to enter the river, reducing the abundance of aquatic biota (e.g. crustaceans, fish; Jeffree et al., 2001b). Monitoring of remedial actions undertaken after closure of the mine has primarily involved testing water for sulfate, copper, zinc and manganese (Jeffree et al., 2001b).

In this study the concentrations of various elements (including metals) were measured in the yolk of *C. porosus* eggs collected from the Finniss River and two other distant nesting sites (Melacca Swamp, a spring-fed freshwater swamp; Adelaide River, a tidal river) during the 2000-01 nesting season. Infertile eggs from 30 clutches (Adelaide 12, Melacca 8, Finniss 10) were opened and the yolk contents removed (after Webb et al., 1987) and frozen. Samples of yolk were then oven-dried, digested in nitric acid and hydrogen peroxide. The digest solutions were then analysed for 20 elements (see **Table 1**) using inductively coupled plasma mass spectroscopy. Some data (Department of Primary Industry and Fisheries, NT) were available from *C. porosus* eggs collected from the Finniss, Reynolds and Adelaide Rivers and Melacca Swamp during the 1987-88 season. All element concentrations in eggs sampled from 1987-88, from all areas, were typically higher than those in the 2000-01 season (**Table 1**), possibly due to differences in methodology or calculation errors associated at the time of analysis in 1987-88. Unfortunately the raw data and personnel are no longer available for verification (J. Alcock, pers. comm.), thus limiting the 1987-88 data to comparisons within that season only. Despite some differences in element concentrations between areas (e.g. K, Mg and Na), the Finniss River was generally similar to the other areas examined in 1987-88.

The 2000-01 data, considered definitive regarding trace element concentrations in *C. porosus* eggs from different areas, also indicated that the Finniss River was generally similar to the Adelaide River and Melacca Swamp (**Table 1**). There were exceptions; concentrations of Sr, Sn and Al were significantly ($P \leq 0.05$) different from the Adelaide, but not Melacca, and Hg was significantly ($P \leq 0.05$) different from Melacca, but not the Adelaide. These differences may reflect the habitat types in each area (Finniss is freshwater, Adelaide is tidal), and are the focus of a more detailed study.

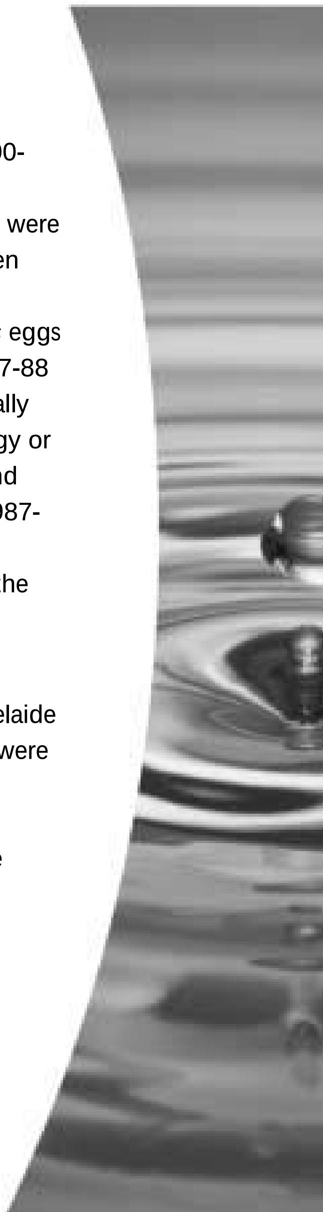

Table 1. Mean concentrations (µg g^{-1} dry weight) of elements in the yolk of wild, infertile *Crocodylus porosus* eggs collected during 1987-88 (see text) and 2000-01 nesting seasons. Numbers in parentheses indicate one standard error of the mean and the sample size (n)

	Adelaide River		Melacca Swamp		Finniss River		Reynolds River
	1987-88	2000-01	1987-88	2000-01	1987-88	2000-01	1987-88
Al	–	0.58	–	0.56	–	0.04	–
	–	(0.12; 12)		(0.52; 8)	–	(0.02; 10)	–
Ba	–	4.06	–	3.81	–	2.67	–
		(1.28; 12)	–	(0.88; 8)	–	(0.25; 10)	–
Ca	7520	6210	6630	6050	7430	6320	7.37
	(270; 10)	(160; 12)	(260; 2)	(150; 8)	(210; 5)	(144; 10)	(0.27; 5)
Cd	–	0.003	–	0.038	–	0.011	–
		(0.003; 12)		(0.027; 8)		(0.007; 10)	–
Cu	6.48	2.39	7.16	2.14	7.63	2.07	7.13
	(0.38; 10)	(0.13; 12)	(1.19; 2)	(0.18; 8)	(0.51; 5)	(0.20; 10)	(0.43; 5)
Cr	–	0.054	–	0.028	–	0.031	–
		(0.015; 12)		(0.009; 8)		(0.019; 10)	
Fe	83	42	66	40	86	40	84
	(35; 10)	(15; 12)	(10; 2)	(5; 8)	(4; 5)	(3; 10)	(20; 5)
Hg	–	0.030	–	0.098	–	0.040	–
		(0.008; 12)		(0.023; 8)		(0.006; 10)	
K	4.91	4.84	4.07	4.71	4.62	4.65	5.05
	(0.21; 10)	(0.16; 12)	(0.11; 2)	(0.11; 8)	(0.13; 5)	(0.076; 10)	(0.26; 5)
Mg	500	411	410	390	470	384	460
	(30; 10)	(14; 12)	(10; 2)	(12; 8)	(20; 5)	(10; 10)	(20; 5)
Mn	2.22	0.54	1.99	0.58	2.33	0.55	2.26
	(0.02; 10)	(0.04; 12)	(-; 2)	(0.08; 8)	(0.04; 5)	(0.07; 10)	(0.08; 5)
Na	1810	1110	1530	1085	2110	1150	1650
	(130; 10)	(46; 12)	(70; 2)	(89; 8)	(160; 5)	(48; 10)	(70; 5)
Ni	–	0.063	–	0.67	–	0.19	–
		(0.043; 12)		(0.55; 8)		(0.10; 10)	
P	12470	11110	11020	12340	12380	12140	12790
	(270; 10)	(335; 12)	(470; 2)	(373; 8)	(320; 5)	(254; 10)	(730; 5)
Pb	–	0.34	–	0.18	–	0.24	–
		(0.11; 12)		(0.06; 8)		(0.16; 10)	
S	3510	3920	3270	3920	3380	4190	3740
	(120; 10)	(126; 12)	(280; 2)	(124; 8)	(140; 5)	(89; 10)	(70; 5)
Se	–	0.97	–	1.12	–	1.38	–
		(0.10; 12)		(0.20; 8)		(0.33; 10)	
Sn	–	0.054	–	0.043	–	0.004	–
		(0.015; 12)		(0.021; 8)		(0.004; 10)	
Sr	–	17	–	14	–	11	–
		(1.0; 12)		(2.0; 8)		(0.5; 10)	
Zn	54	33	49	31	53	29	53
	(1.0; 10)	(1.0; 12)	(30; 2)	(2.0; 8)	(3.0; 5)	(1.0; 10)	(4.0; 5)

Freshwater sections of the Finniss River are more than 100 km (straight line) from the Adelaide River and Melacca Swamp, and are fed by completely separate streams (Webb et al., 1983). The Reynolds River is about 20 km from the Finniss River, and both systems are similar in that they have short tidal sections and are comprised mainly of freshwater floodplain billabongs isolated during the dry season (May-November) and linked during the wet season (Webb and Manolis, 1989).

Similarities between the elemental composition of eggs from the three areas suggests that downstream contamination from Rum Jungle Mine is not apparent in *C. porosus* nesting in the Finniss River. These nesting areas are some 60 km downstream of the mine site, and contaminants are probably greatly diluted during the wet season. *C. porosus* were also intensively hunted in the Finniss River area during the 1950s and 1960s, until their protection in 1971 (Webb et al. 1984). Some females would have been recruited into the population after the period of mining. Long-term effects of the mine may be apparent in areas with Australian freshwater crocodiles (*C. johnstoni*), mainly upstream of *C. porosus* nesting areas and up to the mine. Examination of tissues and eggs of *C. johnstoni* may provide more information on the historical effects of the mine.

With the exception of one egg clutch, elemental analyses were carried out on single eggs from each clutch. In *C. porosus* egg yolk deposition occurs evenly and simultaneously in a cohort of enlarging ova (Astheimer et al., 1989), so variation between eggs in a clutch should be minimal. Using limited data from American alligators (*Alligator mississippiensis*), time from initiation of follicular growth to complete yolk deposition in *C. porosus* is estimated to take 75-80 days (Astheimer et al., 1989). During this period, contaminants may be transferred from the female to her eggs, although the nature and extent of such transfers is unknown. High contaminant levels in freshwater turtle eggs increase embryo mortality and decrease hatchling fitness, although not all contaminants are transferred from the female to her eggs (Nagle et al., 2001). Given the crocodilian embryo's similar reliance on the egg contents for growth and development (Manolis et al., 1987), a similar situation could be expected in crocodilians.

Concentrations of copper, zinc, cadmium and lead in a single wild, infertile Chinese alligator (*A. sinensis*) egg were quantified by Ding et al. (2001). Notwithstanding the limited data on alligator eggs, cadmium and lead concentrations were higher, zinc was lower and copper was similar to *C. porosus* (**Table 2**). Pollution is one of the threats to the remaining wild Chinese alligator populations (Thorbjarnarson et al., 1999), and the high lead and cadmium levels in the eggs are indicative of pollution in alligator habitats.

Table 2. Mean concentrations (µg g-1 dry weight) of metals in wild, infertile eggs from *C. porosus* and the Chinese alligator (*Alligator sinensis*). Numbers in parentheses indicate the sample size (n)

	Cd	Cu	Pb	Zn	Reference
C. porosus	0.015 (30)	2.2 (30)	0.26 (30)	31 (30)	This study
A. sinensis	0.056 (1)	2.2 (1)	0.73 (1)	6 (1)	Ding et al. (2001)

Lead levels in *C. porosus* eggs (2000-01 season; **Table 1**) varied between clutches. Most eggs (63%) had concentrations of <0.2 µg g^{-1}; 30% had 0.2-0.8 µg g^{-1} and two eggs had levels of 1.23 µg g^{-1} (Adelaide River) and 1.64 µg g^{-1} (Finniss River), respectively. The higher lead levels may reflect ingestion of lead pellets in hunted waterfowl (Twining et al. 1999)

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Experimental study on the Effect of Ingested Lead Shot on Estuarine Crocodiles: Significance for Finniss River Field Studies

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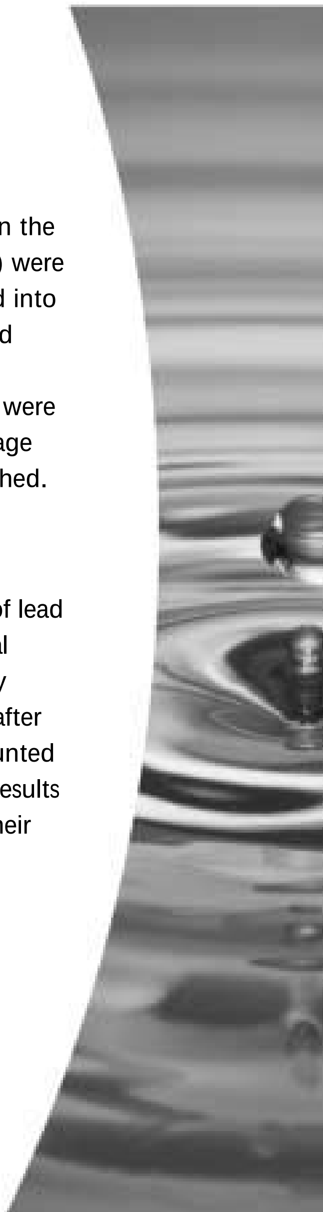
Lead has long been recognised as a cumulative metabolic poison in humans, domestic animals and wildlife. Because of the many industrial activities that have brought about its widespread distribution, lead is ubiquitous in the environment. For example, uranium mining at the Rum Jungle site on the Finniss River, Northern Territory, resulted in contamination of river sediments with lead. Today, lead levels remain at about 250 mg kg^{-1} of wet river sediment within the immediate vicinity of the mine.

Another potential source of lead poisoning in wildlife is the use of lead gunshot for hunting. Mortality in wild waterfowl caused by the ingestion of spent lead shot has been recognised in North America and Europe for over a century. Secondary poisoning has been reported for several species of raptors that consumed prey containing lead shot. Previous studies at ANSTO showed that free-ranging estuarine crocodiles (*Crocodylus porosus*) sampled within areas in the Kakadu National Park, used for hunting by Aboriginals, contained elevated lead concentrations in their bones and flesh (Twining et al., 1999). As well, post-mortem examinations of crocodiles found dead in these areas found lead shot in their stomachs. It was proposed that crocodiles retain and dissolve lead shot in their stomachs followed by absorption into the blood and tissues that may result in lead poisoning. This proposal is summarised in **Figure 1**.

An experimental study was undertaken to assess the above hypothesis on the effects of lead in the environs of crocodiles. Six crocodiles (2 to 3 year old; length about 2 m; weight about 20 kg) were bred and housed at Crocodylus Park, Darwin. Lead shot (about 200 mg each) were packaged into kangaroo meat boluses and fed to the crocodiles. Three crocodiles were administered five lead shot (crocodiles 3T, 4T and 5T), one crocodile ten lead shot (crocodile 6T) and two control crocodiles (crocodiles 1C and 2C) were given pebbles to mimic the lead shot. Blood samples were taken at varying intervals over 20 weeks after lead shot ingestion. At 20 weeks a stomach lavage was carried out in order to recover retained lead shot after which the animals were radiographed. Further blood samples were taken over the next 22 weeks when a stomach lavage and radiography were repeated.

When the stomach lavage and radiography were performed at 20 weeks after the ingestion of lead shot, 18 of the 25 lead shot administered were accounted for. From 13 to 30% of the original weight of the lead shot had been dissolved in the stomach during the 20 weeks. Radiography revealed that two crocodiles (4T and 5T) had retained three and one lead shot, respectively, after the lavage. At 42 weeks after ingestion of lead shot, a stomach lavage and radiography accounted for two of these four lead shot. The weight loss for the lead shot recovered was 77%. These results confirmed the hypothesis that crocodiles have the ability to retain and dissolve lead shot in their stomachs. Throughout the experimental period the crocodiles remained in good physical condition and increased in their body weight and body length.



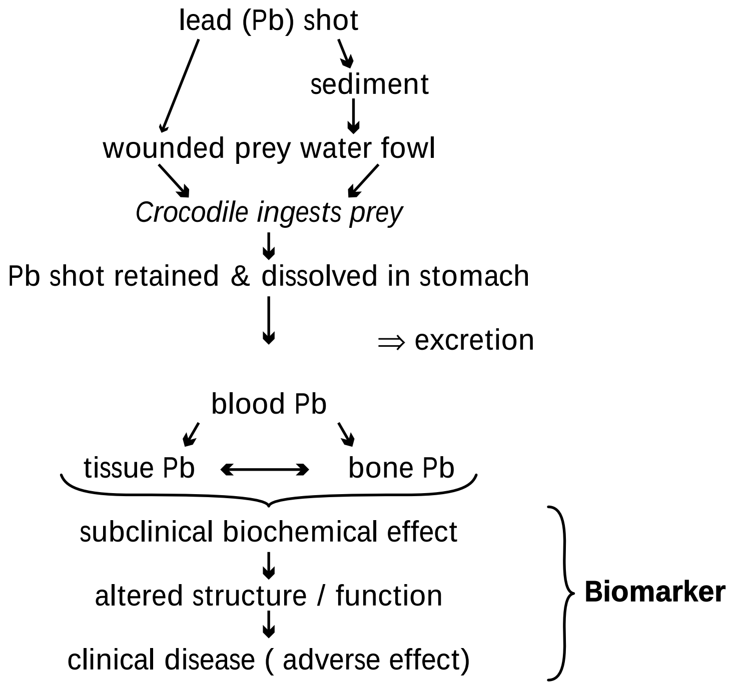


Figure 1. Flow chart of lead shot entering the crocodile from its environment.

Blood samples were diluted in 1% nitric acid and analysed for lead with inductively coupled plasma mass spectrometry. The background lead concentrations in the blood ranged from 10 to 30 µg dL^{-1} and remained within this range in the control crocodiles (1C and 2C). In the crocodiles dosed with lead shot, there was an order of magnitude increase in blood lead (BPb) during the first week after shot ingestion. The BPb in crocodiles dosed with five lead shot increased from pre-exposure levels to concentrations of 230, 300 and 320 µg dL^{-1} in crocodiles 3T, 4T and 5T, respectively, after which the BPb remained stable up to 20 weeks. In crocodile 6T, dosed with 10 lead shot, BPb increased to 550 µg dL^{-1} and remained stable. After the removal of the lead shot with the stomach lavage, BPb declined to pre-exposure levels over the subsequent 20 weeks. These results demonstrated that the dissolved lead from the lead shot was continually absorbed into the blood and a steady-state equilibrium between absorption, excretion and distribution to the tissues was maintained. Even though the steady-state levels of BPb were similar to those observed in birds after ingestion of lead shot, the rate of dissolution in the crocodilian stomach and the metabolism of lead were much slower than that obtained in birds.

Lead poisoning is a complex disorder and affects many organs in the body, including developing red blood cells, the kidneys and the nervous system. One of the most prominent effects is on the biosynthesis of haem, the prosthetic group in haemoglobin, cytochromes, catalases and peroxidases. The specific effects of lead intoxication arise mainly from the interaction of lead with the enzymatic processes in the haem biosynthetic pathway. One of these enzymes, δ-aminolevulinic acid dehydratase (ALAD), catalyses the condensation of two molecules of aminolevulinic acid to produce the pyrrole, porphobilinogen, the building block of the haem molecule. ALAD is a metalloenzyme requiring zinc for activity and is inhibited by lead displacing the essential zinc. This inhibition of ALAD by lead has been used as a specific biomarker for lead poisoning in fish, birds and mammals.

An assay system was developed for the measurement of ALAD activity in crocodilian blood. It was found that ALAD was inhibited by up to 90% during the first week after exposure of the crocodiles to lead shot. There was an inverse correlation between BPb and ALAD activity throughout the 42 week experimental period. BPb concentrations greater than 100 µg dL^{-1} produced significant inhibition of ALAD. The results indicated that ALAD inhibition could be used as a specific biomarker of lead toxicity in crocodiles.

The development of specific biomarkers of heavy metal contamination in river water and sediments will be very useful in determining the health of impacted ecosystems. Recently it has been demonstrated that the enzyme ALAD can be used as a bioindicator of lead pollution in riverine systems for vertebrates (fish; Nakagawa et al., 1998) and invertebrates (amphipods; Kutlu and Sumer, 1998). The biological specimens can be easily decontaminated of the lead in the sample and ALAD activity used as a specific biomarker of lead toxicity. The present studies on the effects of lead exposure in crocodiles and the development of suitable assay systems for biomarkers such as ALAD could be extended to evaluating the health of biota in pollution impacted riverine ecosystems.

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Crocodilians and other Reptiles: Bioindicators of Pollution

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The detrimental effects of environmental contamination and pollution (e.g. heavy metals, organochlorines, radionuclides) on wildlife are generally not well known or understood. Research is providing baseline information for various groups of animals, usually because of their sensitivity to changes in their environment (e.g. fish, amphibians), but also where there is a potential conservation threat (e.g. marine mammals). Little research has been directed at reptiles, which may be good bioindicators of their environment. Crocodilians in particular, because of their position in the food chain, aquatic habits and longevity (generally >50 years; Webb and Manolis 1989) may reflect changes in an area over longer periods (Burger et al., 2000). This paper provides a brief overview on environmental contamination and reptiles, with particular reference to crocodilians.

Lizards and Snakes

Lizards and snakes have been shown to act as indicators of environmental pollution, particularly organochlorines. For example, in the Canary Islands, where agrochemical use has increased dramatically over the last 20 years, the lizard *Gallotia galloti* was considered a better indicator of organophosphorus contamination than birds (Fossi et al., 1995). Bauerle et al. (1975) quantified lead and pesticide levels in the liver and fat respectively of Gopher Snakes (*Pituophis catenifer*) and Prairie Rattlesnakes (*Crotalus viridis*), and suggested that relatively low levels detected in these tissues were correlated with limited use in the study area. Radiocesium levels in nineteen snakes species from contaminated areas were found to be much higher than in those from uncontaminated areas (Brisbin et al., 1974). Detectable levels of plutonium (^{239}Pu) were reported in the liver and bone tissues of three snake species (*Coluber constrictor, Pituophis melanoleucus, C. viridis*) in habitats contaminated by plutonium-laden oil (Geiger and Winsor, 1977).

Turtles

The effect of contamination (particularly pesticide-related compounds) on freshwater turtles (e.g. *Chrysemys picta, Chelydra serpentina, Graptemys geographica, Terrapene carolina, Trachemys scripta, Trionyx spinifer*) has been investigated in detail, and their potential as bioindicators of environmental pollution has been discussed. For example, Snapping Turtle (*C. serpentina*) eggs from the St Lawrence River, Canada, reveal very high concentrations of organochlorine residues, indicative of significant contamination in the area (De Solla et al., 2001). Differences in contamination between eggs of Snapping Turtles and Herring Gulls were thought to be due to local sources of contaminants and diet (Bishop et al., 1996).

Slider Turtle (*T. scripta*) eggs laid in contaminated soils exhibited reduced embryo survivorship (Nagle et al., 2001). Although adult turtles from contaminated areas had high levels of As, Cd, Cr and Se in their tissues, only Se was transferred maternally to hatchlings at relatively high levels, and may have contributed to differences in physiology (fitness) between hatchlings from polluted and non-polluted areas (Nagle et al., 2001). The physiology of radium and calcium accumulation from the environment by Australian freshwater turtles has been investigated by Jeffree (1991) and Jeffree and Jones (1992).

Compared to freshwater turtles, research on contaminant accumulation in marine turtles has been limited to assessments of organochlorines and heavy metals in the eggs and/or tissues of free-living animals (*Caretta caretta, Chelonia mydas, Dermochelys coriacea, Lepidochelys kempii*) (e.g. Hillestad et al., 1974; Thompson et al., 1974; Stoneburner et al., 1980; Witowski and Frazier, 1982; McKim and Johnson, 1983; Clark and Krynitsky, 1985; Davenport and Wrench, 1990; Sis et al., 1993; Rybitski et al., 1995; Cobb and Wood, 1996).

Crocodilians

Brisbin et al. (1998) summarised the literature on organic, heavy metal and radioactive contaminants in crocodilians, most of which related to the American alligator (*Alligator mississippiensis*). The recent finding that the flesh and bones (osteoderms) of the saltwater crocodile (*Crocodylus porosus*) reflected the chemical characteristics of their environment (Jeffree et al., 2001) emphasises the potential importance of crocodilians as bioindicators of contamination. Twining et al. (1999) reported the first case of anthropogenically enhanced lead exposure in wild *C. porosus*, with increased levels being reflected in annual laminations of the osteoderms in the dorsal skin. Due to the lack of data on the toxicological effect of lead on crocodilians, the biological significance of this finding could not be assessed. Later research indicated high lead levels can be present without crocodiles exhibiting recognisable visible effects (Hammerton, this volume).

Elevated levels of lead were detected in the blood of farmed American alligators fed meat contaminated by lead shot, but levels in the muscle were very low, and did not pose a threat for human consumption (Camus et al., 1998). Cook et al. (1989) reported elevated lead levels in the blood of two adult False Gharials (*Tomistoma schlegelii*) and an adult Cuban crocodile (*C. rhombifer*), which were attributed to diet (pigeons). High plasma zinc levels were recorded in a Cuban crocodile which had ingested coins and other metal objects (Cook et al., 1989). Odierna (unpublished; cited in Brazaitis et al., 1996) investigated lead levels in two species of caiman (*Caiman crocodilus, C. yacare*) in Brazil, with only 18% of animals sampled having levels below the level of detection.

The possible health risks associated with local people eating contaminated crocodilian meat was highlighted by Brazaitis et al. (1996). The production of American alligator meat for human consumption in the USA has also prompted various studies to quantify mercury levels in meat (e.g. Delaney et al., 1988; Hord et al., 1990; Ruckel, 1993; Jagoe et al., 1998), with unacceptable levels for human consumption being recorded in some cases (e.g. Hord et al., 1990).

Radioactive contaminants are not generally encountered in crocodilian populations. Radiocesium levels in American alligators living near a reservoir receiving radionuclide-contaminated water from a nuclear reactor were quantified by Brisbin (1989); levels were lower than in various prey items (e.g. fish, waterbirds).

Xenobiotic compounds entering the environment are known to have a detrimental effect on wildlife. Guillette et al. (1999, 2000) summarised the effects of a range of endocrine disrupting contaminants on reproduction in the American alligator. The underlying physiological mechanisms associated with contaminant-induced modifications to the reproductive system of alligators was investigated by Guillette et al. (1995). Burger et al. (2000) suggested that levels of various metals (Pb, Cd, Se, Cr, Mn, As, Sn, Hg), lower than recorded elsewhere in Florida, were not implicated in reproductive impairment. Phelps et al. (1989) provided data on DDT residues in the fat of Nile crocodiles (*C. niloticus*).

The accumulation of contaminants in crocodilian eggs has received little attention. Woodward et al. (1993) attempted to correlate low clutch viability and high alligator mortalities with levels of contamination in the water and other factors. Heinz et al. (1991), however, was unable to correlate levels of organochlorines in the eggs to low clutch viability. Hall et al. (1979) detected a variety of organochlorines in the eggs of the American crocodile (*C. acutus*), levels of which were higher than in most birds, fish and invertebrates from the same area. Stoneburner and Kushlan (1984) investigated metal levels in American crocodile eggs. Organochlorine and metal levels in Nile crocodile and Morelet's crocodile (*C. moreletii*) eggs have been quantified (Phelps et al., 1986; Skaare et al., 1991; Rainwater et al., 1997). Concentrations of Cu, Zn, Cd and Pb in wild and captive-laid Chinese alligator (*A. sinensis*) eggs were quantified by Ding et al. (2001); high Cd and Pb levels are considered to be indicative of pollution in the few remaining alligator habitats.

Expanding our knowledge on the effects of contaminants on crocodilians has implications for crocodilian conservation [e.g. reintroduction programs with the Siamese crocodile

(*C. siamensis*), Chinese alligator (*A. sinensis*) and Philippine crocodile (*C. mindorensis*)], human health (consumption of crocodilian meat and eggs) and the crocodilian farming industry. Crocodilians may also enable long-term monitoring of the status of environments through their accumulation of elements.

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Ecological Risk Assessment of the East Branch, Finniss River

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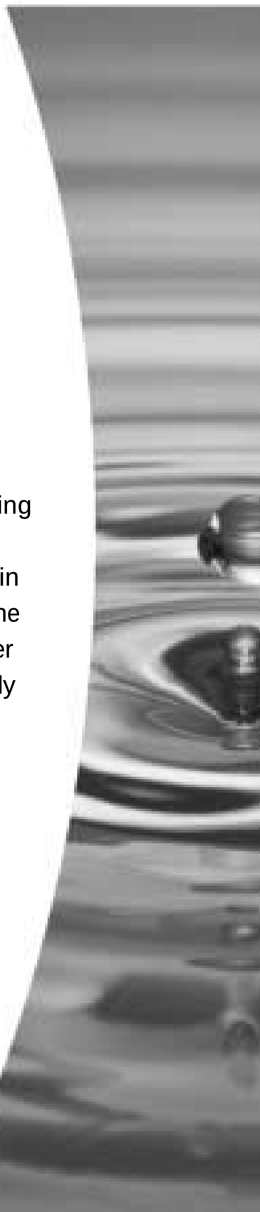
Quantitative ecological risk assessment (ERA) is a means whereby the risk posed by a toxicant in any system can be evaluated by comparing the distribution of its measured or modelled concentrations (water quality data (WQD)) with available information on the range of concentrations that are known to adversely affect biota within that, or similar, habitats (dose-response data (DRD)). Initially, the WQD are compared with regulatory criteria (e.g. ANZECC and ARMCANZ, 2000). If they fail this test, then, on the assumption that both data sets comprise subsets of the entire range of concentrations, probability density functions are derived assuming a standard distribution formætypically log-normal. The WQD and DRD distributions are then convoluted to estimate (a) the likelihood that WQD will exceed set criteria derived from the DRD (see below), and (b) the proportion of taxa (e.g. species, genera etc.) likely to be affected. The criteria derived from the DRD usually comprise an estimate of the concentration that is hazardous (HC) to a set proportion of taxa (e.g. HC_5 for 5% of taxa) and an estimate of the uncertainty (e.g. $HC_{5;95}$ would be the 95% lower uncertainty value of the HC_5).

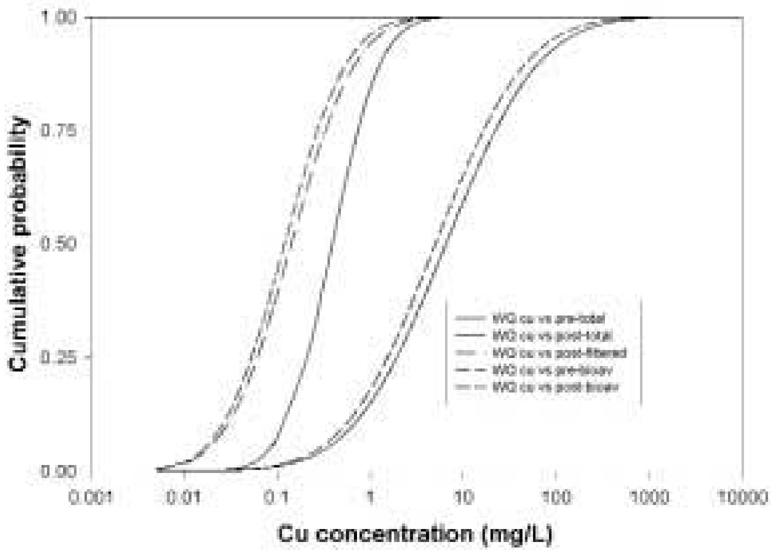
The AQUARISK code (Twining et al., 1999) has been developed to derive these criteria and estimate the risk of their exceedence. In addition, the geochemical speciation code MODPHRQ (a modular version of HARPHRQ, Brown et al., 1991) has been included in AQUARISK to evaluate the bioavailable fraction (i.e. the concentrations of those metal species present that are able to cross biological membranes) for copper and other metals in water. The speciation modelling is designed to overestimate the actual bioavailable concentration when any of the influential parameters are unknown. This approach is an appropriate application of the Precautionary Principle (O'Riordan and Cameron, 1994). AQUARISK also estimates the average concentration that should be achieved to satisfy the regulatory or DRD derived criteria, with an agreed exceedence, or that is likely to be tolerated by a set proportion of taxa.



In this paper, AQUARISK has been used to estimate the risk posed by copper in effluent from the Rum Jungle mine site, pre- and post-remediation, and the proportion of taxa likely to be affected in the East Branch (EB) of the Finniss River downstream of the mine. In addition, the average concentrations required to achieve no more that 5% exceedence of the various criteria, or 67% tolerance by affected taxa, have also been evaluated. The WQD used to evaluate risk were monitoring data from gauging station 097 (M. Lawton, unpublished) located about 5km downstream of the mine. Sampling was less regular prior to remediation, but included intensities as often as daily within the period from February 1968 to May 1981. The post-remedial data were collected daily during the period of flow at the site between December 1990 and June 1995. The data comprised total copper concentrations and, usually, pH and sulfate concentrations. Filtered copper concentrations were only reported after remediation. In addition, some information was given on the major cations, calcium and magnesium, and to a lesser extent sodium. If these parameters were highly correlated ($P < 0.001$) with sulfate within the period of assessed risk, then missing values were estimated from the sulfate concentrations, by linear regression, for the purposes of estimating bioavailable copper concentrations. As these parameters represent only a proportion of those that are likely to reduce bioavailability of copper, the final estimates are higher than in reality, and hence, allow for a reasonable, conservative risk assessment.

The DRD used derive from the default set for copper provided with the AQUARISK code. Four subsets were compiled: all taxa or only primary consumers across either all or only lethal effects. Five probability distribution functions (PDFs) were derived from the available WQD: Pre-remediation total and bioavailable copper and post-remediation total, filtered and bioavailable copper. **Figure 1** plots these distributions relative to each other. The distributions show the significant shift towards lower Cu concentrations in the post-remedial period with a reduction of approximately two orders of magnitude at the higher concentrations for all fractions. The overall reduction due to remediation becomes less at lower concentrations, particularly when considering total copper concentrations, but the general pattern is consistent.

Figure 1. Cumulative probability distribution functions of measured (total or filtered) and modelled (bioavailable) copper concentrations in samples from GS 097 collected pre-remediation (n = 189) and post-remediation (n = 583).



It should be noted that the pre-remedial bioavailable estimates are likely to be significant overestimates. They are based on total copper concentrations rather than filtered values and do not have the advantage of excluding particulate-bound copper. Given the limited data available on other water quality parameters, the estimates of bioavailability are conservative as Cu-complexation by bicarbonate or organic carbon present in the water cannot be assessed. Of the four sets of DRD selected, the most sensitive are lethal and sub-lethal data for primary consumers (predominantly larval macroinvertebrates). The least sensitive is for lethal data on all taxa. The PDFs for these sets are shown in **Figure 2**. Estimates of the hazardous concentrations to 5% of species and their lower uncertainties (HC_5 and $HC_{5;95}$) are given in **Table 1**. Due to the number of data the 95% lower uncertainty estimate is equivalent to the median estimate in some cases. The 2000 national guideline for protection of (moderately disturbed) freshwater ecosystems is included in **Table 2** for comparison.

Figure 2. Cumulative probability distribution functions of the most-sensitive (Lethal and sub-lethal macroinvertebrates) and least-sensitive (lethal data for all taxa) dose-response data sets.

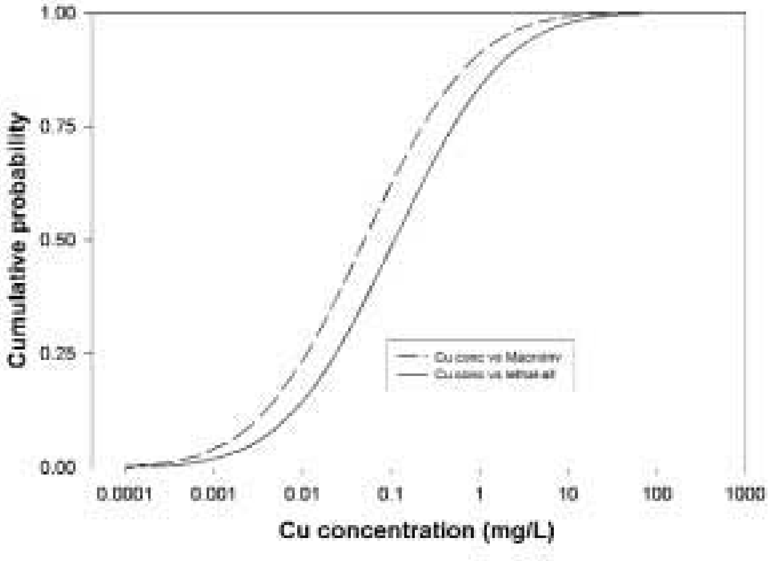


Table 1. Hazardous concentrations (µg L^{-1}) to 5% of selected taxa and their 95% lower uncertainty estimates as derived from various dose-response data subsets. The 2001 guideline value is included for comparison. n, number of data used

Data set	HC_5	$HC_{5;95}$	n
All taxa: all endpoints	1.72	1.72	869
All taxa: lethal endpoints	2.66	2.66	503
Macroinvertebrates: all endpoints	1.26	0.97	297
Macroinvertebrates: lethal endpoints	1.68	1.10	160
2000 trigger value (95% moderately disturbed)		1.4	

Due to high copper concentrations, both pre-remedial distributions (**Figure 1**) have 100% probability of exceeding the regulatory guideline values and the HC_5 values. Even allowing for obvious reductions post-remediation, these criteria are likely to be exceeded with greater than 99% probability by any fraction of copper (the best was an 0.08% chance of non-exceedence of the $HC_{5;95}$ by bioavailable copper using lethal data for all taxa). Hence, it is apparent that the biology in the EB of the Finniss River downstream of the mine has been, and remains, under high levels of toxic stress. It is interesting to note, however, that AQUARISK predicts some species should be able to tolerate these conditions. **Table 2** gives the estimated proportions of taxa that are likely to be affected by the measured or modelled copper concentrations. Despite the risk of any impact remaining unacceptably high, the proportion of species able to tolerate conditions at the monitoring site has increased from $\leq$ 9% prior to remediation to as much as 48% post-remediation, based on probabilistic assessments performed by AQUARISK. This implies a dramatic improvement in community structure.

In 1993 the average number of macroinvertebrate families present at unpolluted sites within the EB ranged from 12 to 17 compared with 3 to 4 within the general vicinity of GS 097 (Jackson and Ferris, 1998). Similarly, sampling by Edwards in 1995 (Twining et al., 2002) found 10-13 families at reference sites compared to 3-5 at GS 097. Assuming a consistent community structure along the stream, these values imply that between 18-25% and 23-50%, respectively for those two studies, of all macroinvertebrate families were able to tolerate post-remedial copper concentrations at, or near, the monitoring site. Given that the modelled bioavailable copper concentrations are likely to be overestimates, and that other contaminants are likely to contribute to the observed reduction in biological diversity, these values compare favourably with the AQUARISK estimate of 36% as a tolerant proportion of macroinvertebrates assuming both lethal and sub-lethal impacts of copper alone.

Table 2. AQUARISK estimates of the proportion of taxa likely to affected by the measured or modelled copper concentrations at GS 097, pre- and post-remediation (Tolerance = 1 – affected fraction)

Taxa	Pre-remediation		Post-remediation		
	Total	Bioavailable	Total	Filtered	Bioavailable
All taxa	.931	.920	.732	.583	.558
Macroinvertebrates	.956	.948	.804	.661	.637
Lethal, all	.922	.910	.700	.542	.515
Lethal, macroinvertebrates	.945	.935	.767	.616	.591

Pre-remedial biological monitoring was sparse, due to the obviously depauperate fauna in the heavily impacted EB (Jeffree and Williams, 1975). Jackson and Ferris (1998) compared these earlier data with their own samples collected in 1993. The total number of families sampled at GS 097 in 1993 was 11 compared to 5 sampled in 1973-4, a ratio of 2.2. Using this ratio, the implied pre-remedial species tolerance values reduce to between 8 and 11% which are again in reasonable agreement with the AQUARISK estimate of 5%. In this case, AQUARISK is also likely to underestimate biological tolerance, as some species are able to effectively isolate themselves from the hazard. The most obvious fauna found at the polluted sites of the EB are adults of the Dytiscidae. These are air-breathing beetles that also insulate themselves from the aquatic environment with a blanket of air when submerged. Thus, they are not directly exposed to the toxicant and are therefore extremely resilient.

AQUARISK has also been used to estimate the average concentration that should be achieved to allow 5% exceedence of the ANZECC and AMRCANZ (2000) regulatory guideline concentration (1.4 $\mu g\ L^{-1}$) or $HC_{5;95}$ criteria derived from each of the DRD. The average target concentration for acceptable regulatory guideline exceedence in all cases ranges between 0.4-0.5 $\mu g\ L^{-1}$. Similarly, acceptable exceedence of the $HC_{5;95}$ could be achieved with average concentrations ranging from 0.3 $\mu g\ L^{-1}$ based on lethal and sub-lethal macroinvertebrate data to 0.9 $\mu g\ L^{-1}$ based on lethal data for all taxa. The estimates of the required bioavailable concentration for 67% of species to tolerate conditions at the monitoring site range from 34-73 $\mu g\ L^{-1}$ across all DRD sets. The pre- and post-remediation average bioavailable copper concentrations are 22,900 and 230 $\mu g\ L^{-1}$ respectively. Hence, to achieve compliance, a further reduction in post-remedial bioavailable copper concentrations by a factor of 660 is required. To achieve the more reasonable target of recovery to 67% species diversity at this heavily impacted site, the reduction is more modest, ranging between factors of 3.2 to 6.8.

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The Finniss River Symposium: Rapporteurs report

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Introduction

In this abstract we attempt to provide a very brief overview of the papers and to bring out at least some important elements of the discussion that ensued. Our perspective is that from the symposium itself, without reference to the subsequent written contributions that form the bulk of this volume. Our perspective is also that of 'interested' research parties and active participants in discussion, rather than as passive recorders of events. We hope that our view is not overly biased, nor too limited as a result.

The session began with a brief presentation that very broadly summarised the work presented to the symposium, identified some future environmental challenges as well as strengths and weaknesses of the completed research, and listed some potential discussion 'issues'. Participants were then invited to identify other issues of importance to them and to involve themselves in the general discussion.

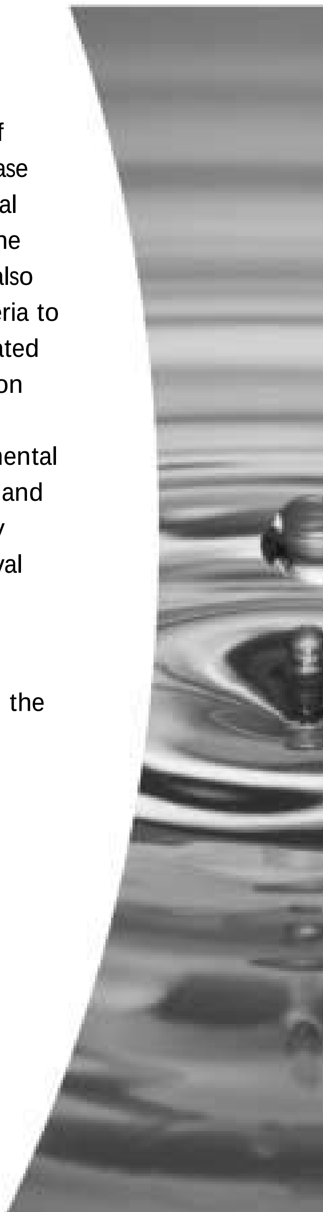
Presentation

Brief and broad summary

The symposium began with papers that provided the larger, legislative and historical context within which to understand the development, subsequent rehabilitation and changing environmental effect of the Rum Jungle uranium-copper mine. The chemical consequences of rehabilitation, specifically the changes in the 'pollution source term' and its potential to increase with progressive failure of 'covers', were presented. Other talks covered pre- and post-remedial ecological studies and investigations that extended the range of biota looked atæeffectively the search for useful biomeasures of the ecological detriment associated with acid drainage, but also with other sources of metal pollutants. The organisms studied or reviewed ranged from bacteria to reptiles, with several talks on the charismatic 'top predator': crocodiles. Studies that incorporated biochemical markers of pollutant effects as well as the possibility of localised genetic adaptation were also presented. Ecological risk assessment was explained and applied to future treatment/development scenarios. Several papers could be described as presenting 'environmental forensics' to look at metal signatures in archival monitors such as the calcified material (shells and bone) from freshwater mussels and estuarine crocodiles. Most presentations were followed by questions, with a 'toolkit of biomeasures', ecological risk assessment and the U-ratios in archival monitors generating some active participation.

Future environmental challenges

Probably the major environmental challenges that could be identified for the East Branch and the Finniss River were:
- The potential failure of rock-heap covers over the next decade or so.
- Development of Brown's Prospect.
- Settlement along the Finniss River.



Another challenge is to keep an eye on the larger game of understanding acid drainage, in all its aspects, at a level that supports generalisation to other systems.

Strengths

The Finniss River system clearly does provide a natural laboratory for studying the transport of metals and radionuclides through tropical aquatic ecosystems (including the temporary East Branch). Pollution from the Rum Jungle mine site is uniquely well characterized for such an ecosystem. Also, the area represents a study site with a clear pollution signal (metals, acid and some radionuclides) and a low background of other pollutants.

Weaknesses

Some of the more obvious gaps in our collective efforts to understand the Finniss River system relate to:

- Groundwater movement and its effect.
- The role of riparian vegetation.
- The importance of sediment and erosion.
- The potential for better integrating completed and future studies.

Some questions

A variety of dot-point questions were presented to stimulate discussion. These included:

- Are the covers failing and what will be the future dissolved/bioavailable metal loads in the system?
- What are the direct and indirect contributions of sediment to ecological detriment?
- Is the riparian vegetation recovering (particularly in the East Branch) and is active rehabilitation required?
- What are the likely effects of Brown's Prospect and what would be the best water management strategy for the Finniss ecosystem?
- Where does the diversity of accepted and experimental bioindicator tools fit and what represents the best biomonitoring strategy, in future?
- What is the role of acclimation in ameliorating ecological impact and mediating biological recovery?

Discussion

The discussion began with the seed question 'what else don't we know?' and ramified from there. We have attempted to group points relevant to similar topics.

The question of 'final voids' (lakes formed in the disused open-cut pits) was raised and the opinion expressed that the deepwater chemistry of these was not well known for the Rum Jungle site. It was also said that there needed to be more focus on both movement and potential heath effects of radioactive materials (e.g. radium in the pits). The potential influence of such voids on groundwater flows was also mentioned. It was suggested that ratios of U isotopes (^{234}U and ^{238}U) could indicate groundwater movement near the pits. The general lack of information on groundwater movement and contamination was noted, although it was pointed out that work being done in relation to Brown's Prospect was relevant to this knowledge-gap.

The apparently deteriorating performance of the waste rock covers was discussed, and the role of vegetation (specifically their roots), bioturbation by termites and the effects of fire were mentioned as potential contributors to a loss of integrity in such covers. There was a call for better modelling of various aspects of existing pollutant sources (waste rock heaps, pit lakes and tailings), as well as for examination of future development scenarios. This discussion raised the potential benefit of better characterising the mineralogy of the waste rock heaps. The need to better determine input variables for risk assessment was also asserted.

The health implications of consuming traditional foods that may contain increased levels of metals and radionuclides was raised as an area in need of more study. The recovery of riparian vegetation along the East Branch was also mentioned as being of concern to the traditional owners, as was the effect of this apparently slow recovery on in-stream ecology.

Towards the end of the allotted time, the questions of future monitoring and funding were raised. It was asserted that there are, presently, no funds for continued monitoring or other studies of the system. It was said that, in reality, this remained a Commonwealth responsibility. Discussion touched on the development of Brown's Prospect, adjacent to the East Branch, and the cost of monitoring its environmental effects.

An opinion was expressed of the need to place priority on gaining basic environmental information (e.g. flow data) about the Finniss River, given that land development is accelerating there. The potential for using remote sensing to map and characterise the whole Finniss River system was mentioned.

The discussion was of necessity brief, but it served to raise issues that were not considered in the presentations made to the Symposium, as well as providing a forum for the opinions of a variety of people with diverse interests in the ecosystems of the Finniss River system.

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