

Part 1: Ranger – current operations

Contaminant pathway conceptual models for Ranger uranium mine

S Parker, R van Dam & R Bartolo

Background

In its 2004–2006 Key Knowledge Needs (KKN), ARRTC under KKN 1.2.1 stated that:

In order to place the off-site contaminant issues at Ranger in a risk management context, a conceptual model of transport/exposure pathways should be developed. This process should include a review and assessment of the existing information on the risks of the bioaccumulation and trophic transfer (ie biomagnification) of uranium and other Ranger mining-related contaminants from all exposure pathways and including the identification of key information gaps.

To address this, a conceptual model defining the basic elements of contaminant pathways for Ranger uranium mine (Figure 1) and an associated sub-model for transport of inorganic toxicants via a direct surface water to surface water pathway (Figure 2) were progressed but not completed (van Dam & Bayliss 2006). This work built on previous conceptual modelling efforts by the Supervising Scientist (1982), Finlayson and Bayliss (2003), van Dam et al (2004) and others.

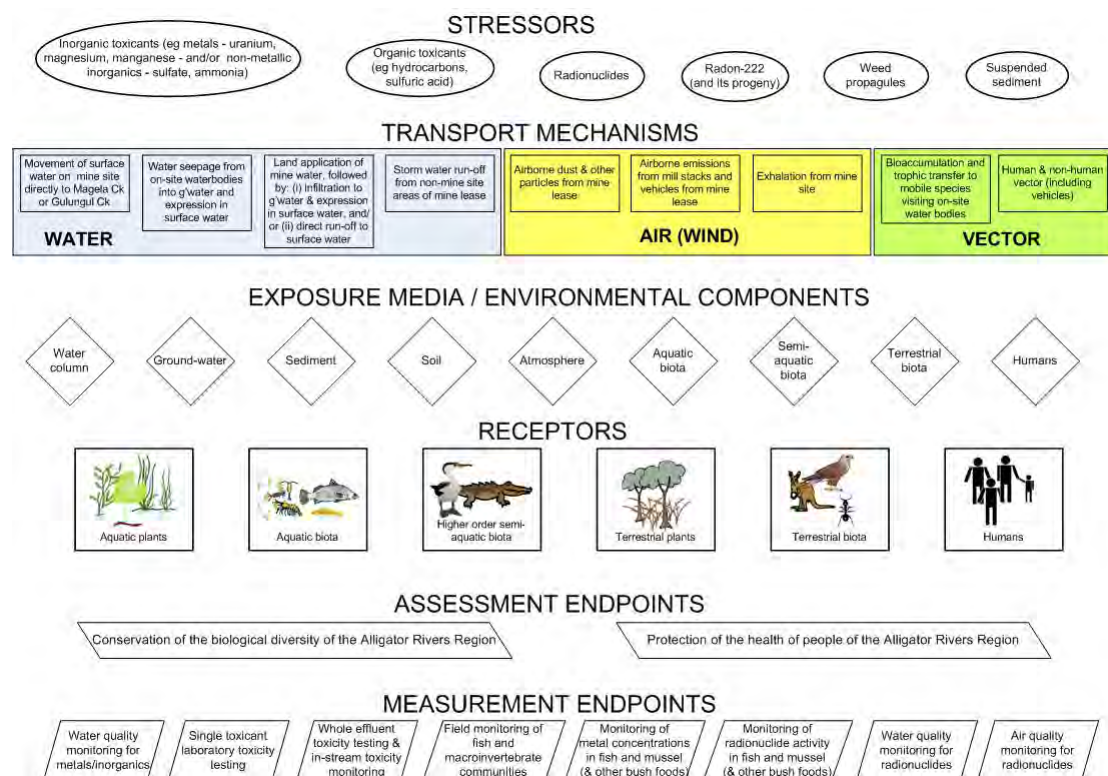


Figure 1 Basic elements of a contaminant pathways conceptual model for Ranger uranium mine (from van Dam & Bayliss 2006)

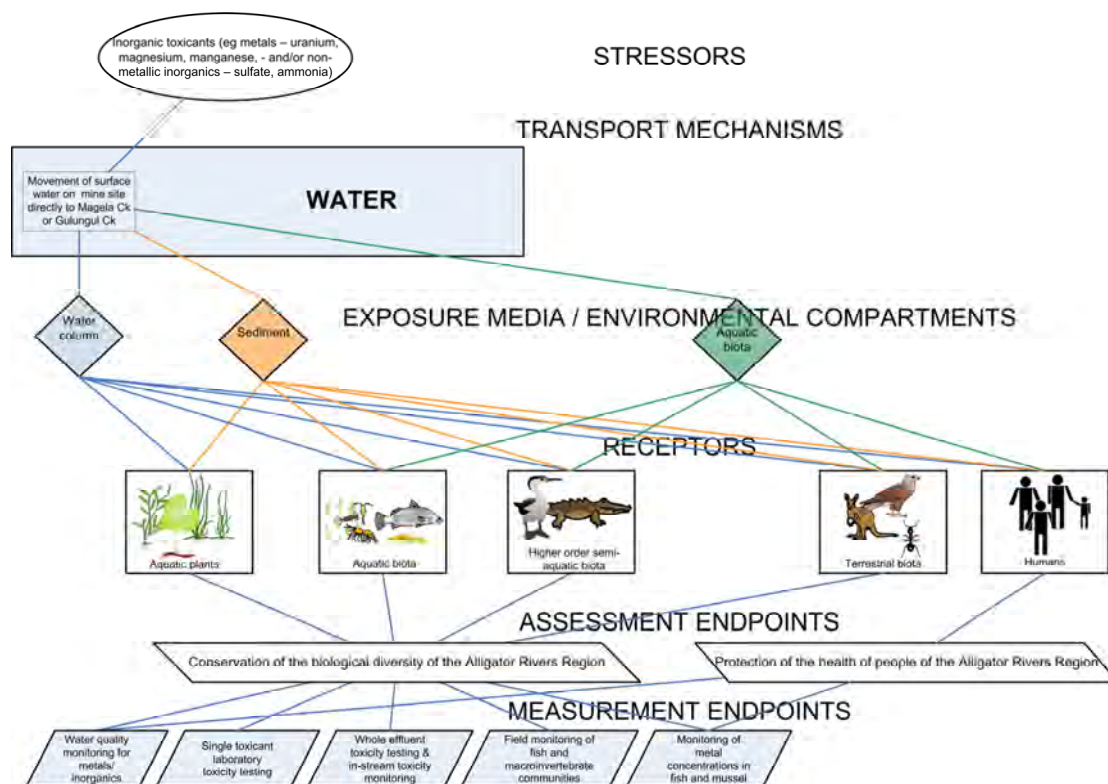


Figure 2 Conceptual model for transport of inorganic toxicants from Ranger uranium mine via a direct surface water to surface water pathway (from van Dam & Bayliss 2006)

The draft conceptual model identifies the key stressors (chemical, physico-chemical, radiological and biological contaminants) arising from Ranger and for each of these, their respective transport mechanisms off-site, affected environmental compartments, receptors, routes of exposure, types of effects and measures of effects.

In its revised 2008–2010 KKNs, ARRTC noted the work undertaken to date under KKN 1.2.1 and stated the process ‘...should be completed for all the contaminant/pathway sub-models, noting, however, that the level of effort for each needs to be proportionate to the level of concern of the issue’.

In recognition of the priority ARRTC and relevant stakeholders have attributed to the timely completion of the contaminant pathways conceptual models, a SSD staff member has been seconded to *eriss* for a period of six months to progress the project. The project is due to be completed by February 2010.

Scope

The project comprises the following two tasks:

1. developing exposure pathway sub-models for each of the identified contaminants and transport mechanisms; and
2. documenting the relevant scientific evidence for each sub-model and incorporating this into supporting narratives for each model, identifying knowledge gaps and uncertainties where possible.

A separate project will be undertaken to develop printed and computer-based communication products based on the contaminant pathways models which will assist in raising the awareness of, and providing reassurance to, relevant stakeholders regarding the actual levels of environmental and human health risks posed by each of the contaminants. The final design and functionality of the communication products and their delivery arrangements will be agreed with stakeholders once the conceptual sub-models have been completed and scientifically reviewed.

Progress and results

Senior *eriss* and EWL Sciences staff met on 11 September 2009 to discuss the scope of the project. EWL Sciences expressed support for the project and agreed to contribute relevant data and scientific information where possible. Draft sub-models for each of the key contaminant pathways have been prepared, based on key stressors and pathways identified by van Dam and Bayliss (2006). An internal SSD technical workshop was held on 25 September 2009 to review the draft sub-models. This was attended by *eriss* Program Leaders and other senior staff. The draft sub-models are being updated based on the outcomes of the workshop. Ongoing consultation with Program Leaders will be required to collate the scientific evidence and other supporting information required for the model narratives. Another workshop will be held in early 2010 to internally review the conceptual models and associated narratives. Consultation with stakeholders will also be required once the draft sub-models have been finalised.

References

- Finlayson M & Bayliss P 2003. Conceptual model of ecosystem processes and pathways for pollutant/propagule transport in the environment of the Alligator Rivers Region. Discussion Paper prepared for the 11th meeting of ARRTC, 17–19 February 2003.
- Supervising Scientist 1982. Submission to Australian Science and Technology Council (ASTEC). Supervising Scientist of the Alligator Rivers Region.
- van Dam R, Finlayson M & Bayliss P 2004. Progress on the development of a conceptual model of contaminant pathways from Ranger uranium mine. Internal Report 474, June, Supervising Scientist, Darwin. Unpublished paper.
- van Dam R & Bayliss P 2006. Development of a contaminant pathways conceptual model for Ranger mine. In *eriss research summary 2004–2005*. eds Evans KG, Rovis-Hermann J, Webb A & Jones DR, Supervising Scientist Report 189, Supervising Scientist, Darwin NT, 5–8.

Characterisation of contamination at land application areas at Ranger (collaborative project with EWLS)

A Bollhöfer, R Akber¹, P Lu², B Ryan & G Passmore²

Introduction

There has been ongoing stakeholder concern about the current radiological status of the Ranger land application areas (LAAs), in particular with regard to soils in the Magela LAA and their capacity to continue to adsorb radionuclides at the current rate of application. The concentration of radionuclides adsorbed in the soil may require the area to be rehabilitated at closure, based on the increase in external gamma dose rates alone. In addition there is the potential for radionuclides to be mobilised into Magela creek via erosion of the surface soil.

An EWLS report (Hollingsworth et al 2005) indicated that current application rates are likely to be sustainable in the context of the ongoing ability of the soil profile to bind radionuclides. However, this report did not address the issue of radiation doses to the public and the implications of this for the closure of the site. If levels are too high then specific rehabilitation strategies will need to be in place to minimise exposure of the public from radiation following rehabilitation of the Ranger Project Area.

A review of the Key Knowledge Needs during ARRTC 20 identified that:

investigations are required into the storage and transport of contaminants in the land irrigation areas adjacent to Magela Creek, particularly subsequent to decommissioning. Contaminants of interest/concern in addition to radionuclides are magnesium, sulfate and manganese. Results from these investigations should be sufficient to quantify the role of irrigation areas as part of satisfying KKN 1.2.1, and form the basis for risk management into the future.

This risk management needs to consider current radiological issues associated with the LAAs as a result of irrigation, and provide options for the rehabilitation of the LAAs if required. These options strongly depend on estimated radiation doses to people post rehabilitation.

This project is a collaboration between Earth Water Life Sciences (EWLS), Dr Riaz Akber (*SafeRadiation*) and *eriss*. *eriss* has been involved in planning and scoping the project from the early stages. A major part of the project will involve radioanalytical analyses by *eriss* of the different types of samples (soils, leaf litter, dust) from the Ranger LAAs and provision of assistance for the assessment of radon exhalation from the LAAs.

The aims of this project are to characterise the magnitude and extent of radiological contamination at the Ranger land application areas (LAAs) and to assist in the development of a dose model for the LAAs that can be used for rehabilitation planning.

¹ SafeRadiation, Brisbane

² Earth Water Life Sciences, Darwin

Methods

Soil samples have been collected by *SafeRadiation* and EWLS from all LAAs on the Ranger lease for measurement of radionuclide activity concentration. They have been collected at various distances from the sprinkler heads in order to determine depositional patterns and calculate the total load of radionuclides in LAA soils. Soil samples were dried and crushed, and pressed into a standard geometry for radionuclide analysis via gamma spectrometry at *eriss*.

Leaf litter samples were also taken at various distances from the sprinkler heads and samples having the same radial distance from the sprinkler heads were combined in large plastic bags. Samples were subsequently ashed and homogenised at *eriss* and cast in epoxy resin for radionuclide analysis via gamma spectrometry. A subsample was sent for metal analysis via ICPMS.

Soil and leaf litter samples from the LAAs are being analysed using the *eriss* HPGe gamma detectors. The methods are described in Murray et al (1987), Marten (1992) and Esparon and Pfitzner (in press).

Radon exhalation was measured at the LAAs at various distances from the sprinkler heads using conventional charcoal canisters. The methods are described elsewhere (Spehr & Johnston 1983, Bollhöfer et al 2005). Surveys were conducted in July/August 2008 (dry season) and in March 2009 (wet season) by R Akber and EWLS. There was no irrigation of mine waters during and immediately prior to charcoal cup exposure. Radon cups were then analysed using the *eriss* NaI gamma detector.

Five passive dust collection stations were also established by *SafeRadiation* and EWLS along transects that intersect the boundaries of the Magela A and Magela B land application areas (see Map 2). The stations inside the Magela B LAA were installed such that water from the sprinklers did not directly fall on the panels. The stations are triangular in shape and approximately 2 m high. Each face of the stations has four collector panels (0.3 m height) centred at 0.3 m, 0.7 m, 1.2 m and 1.5 m above ground (Figure 1). Each of these four collector panels represents the lying down, sitting, juvenile standing and adult standing breathing zones, respectively. The stations were deployed on 16 and 17 July 2008. They were recovered on 30 September and 1 October 2008 from the Magela B land application area and 14 and 15 October 2008 from Magela A. Unfortunately some of the panels from Magela A were lost due to a bushfire. Samples were measured for total alpha activity by *SafeRadiation* in Brisbane.

Results

Soil radionuclide activity concentration

More than 200 soil samples have been analysed for radionuclide activity concentration via gamma spectrometry. The maximum measured ^{226}Ra soil activity concentration is a little above 1000 Bq kg⁻¹, and a large number of values lie in the range 100–500 Bq kg⁻¹. It was found that applied radionuclides have been generally retained in the top 5–10 cm of the soils, in agreement with earlier studies conducted in the Magela land application area (Akber & Marten 1992, Hollingsworth et al 2005). Hence the exposure pathways that depend upon the magnitude of ^{226}Ra activity concentration throughout deeper sections of the soil profile, such as external gamma exposure (most of the terrestrial gamma dose rate originates from the top 0.5 m of the soil profile) and inhalation of radon progeny (1–2 m is the typical diffusion length for radon in soil), are likely to be less significant at the LAAs than at those areas that contain waste rock up to 2000 Bq kg⁻¹ to depths greater than 10 cm after rehabilitation.

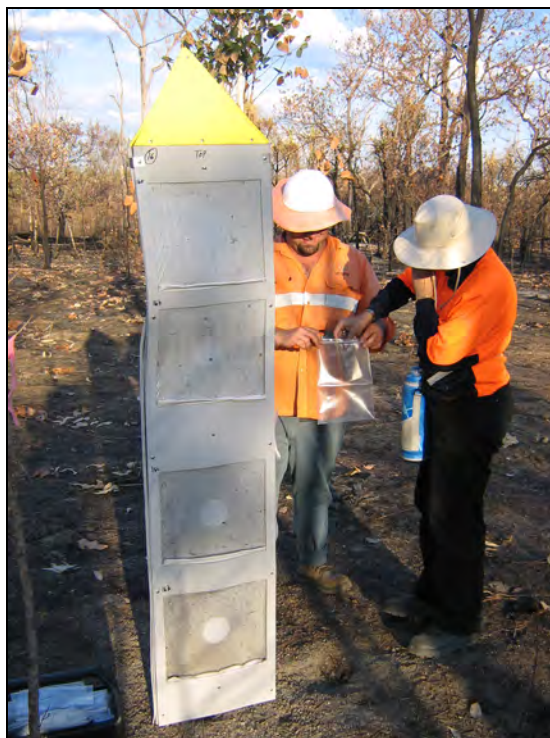


Figure 1 Passive dust sampling station

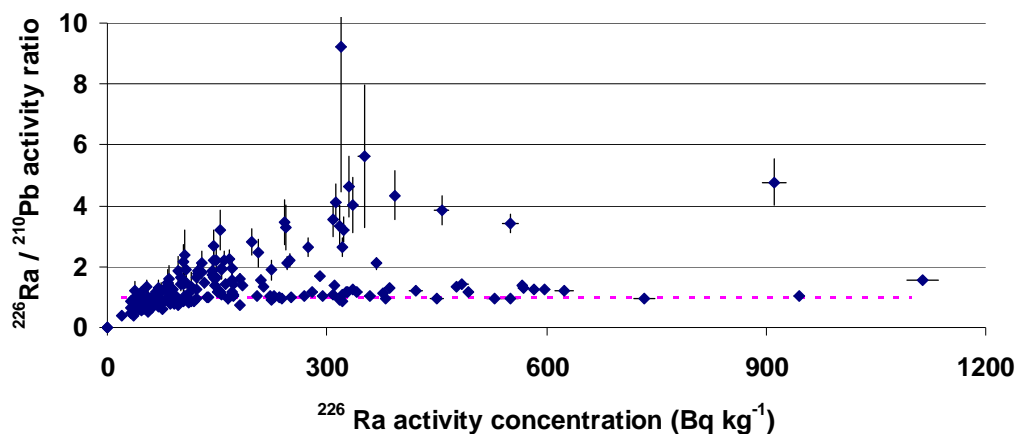


Figure 2 $^{226}\text{Ra}/^{210}\text{Pb}$ activity ratio plotted versus the ^{226}Ra activity concentration measured in soils from the Ranger land application areas. The dashed line indicates $^{226}\text{Ra}/^{210}\text{Pb} = 1$.

Figure 2 shows the $^{226}\text{Ra}/^{210}\text{Pb}$ activity ratio plotted versus the ^{226}Ra activity concentration measured in the soils. For natural background soils, ^{226}Ra and ^{210}Pb are in radioactive equilibrium within the soil grains but deposition of ^{210}Pb from the atmosphere shifts the measured $^{226}\text{Ra}/^{210}\text{Pb}$ activity ratio to values less than one. For natural, but above background activity soils, the $^{226}\text{Ra}/^{210}\text{Pb}$ activity ratio should be close to one and the effect of ^{210}Pb deposited from the atmosphere on the $^{226}\text{Ra}/^{210}\text{Pb}$ activity ratio will be negligible. For soils subject to land application of untreated site pond water, the ratio should be greater than one as this water contains significant amounts of ^{226}Ra . Most samples exhibit a $^{226}\text{Ra}/^{210}\text{Pb}$ activity ratio of ≥ 1 due to irrigation with these waters and most of the lower activity soils have a $^{226}\text{Ra}/^{210}\text{Pb}$ activity ratio < 1 . It should be noted that there are some areas of relatively high ^{226}Ra and ^{210}Pb activity concentrations with $^{226}\text{Ra}/^{210}\text{Pb}$ activity ratios close to radioactive equilibrium, indicating that there are some areas within the LAAs that have naturally elevated

^{226}Ra activity concentrations. Ratios close to radioactive equilibrium would also be expected for areas consisting predominantly of waste rock, given the relatively high activity concentration of uranium series radionuclides (up to 2 kBq kg^{-1} ^{238}U) in waste rock as compared to natural sites.

Figure 3a (left) shows the location of the soil samples collected, their $^{226}\text{Ra}/^{210}\text{Pb}$ activity ratio (yellow: $^{226}\text{Ra}/^{210}\text{Pb} < 0.9$; red: $0.9 < ^{226}\text{Ra}/^{210}\text{Pb} < 1.1$; blue: $^{226}\text{Ra}/^{210}\text{Pb} > 1.1$) and a classification with regards to their ^{226}Ra activity concentration indicated by the size of the circle. Figure 3b (right) shows the same data overlaid on results from an airborne gamma survey conducted in 1976. It is apparent that soils with high ^{226}Ra activity concentration that exhibit a $^{226}\text{Ra}/^{210}\text{Pb}$ activity ratio of approximately 1 are located within areas that exhibited higher natural backgrounds before mining started. This is in particular obvious in samples from the Djalkmara LAA (near pit 3). The yellow circles ($^{226}\text{Ra}/^{210}\text{Pb} < 0.9$) are generally small in size and some of these samples are outside the zone of influence from the sprinklers.

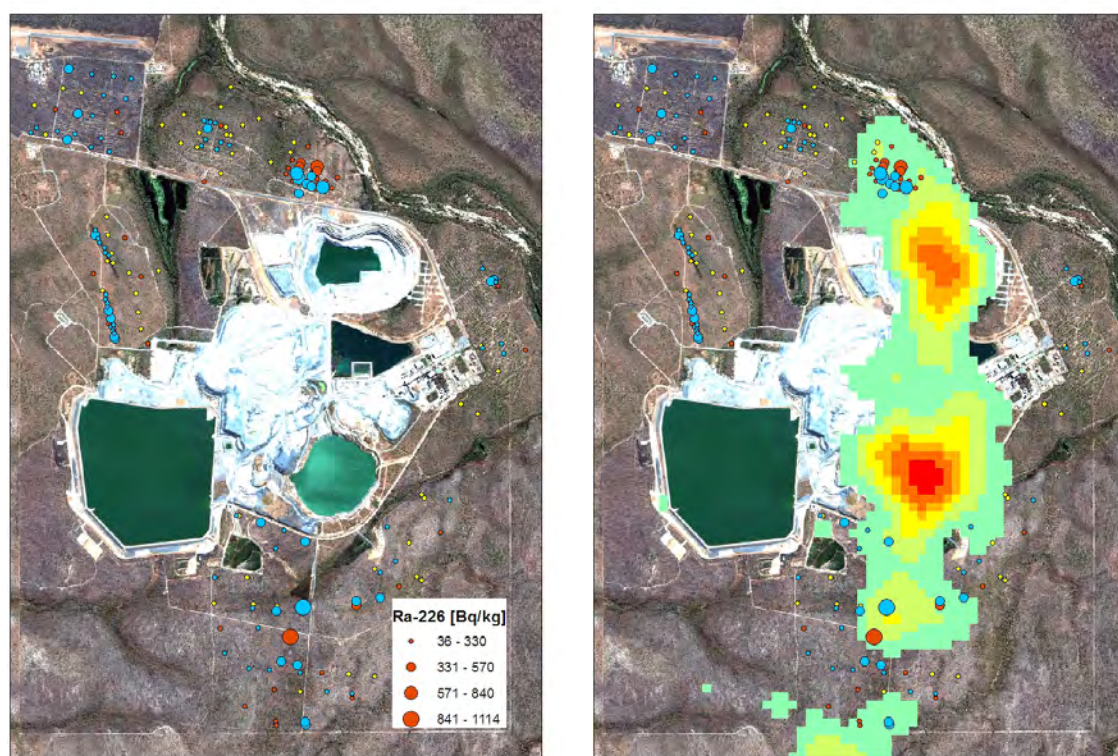


Figure 3 (a) $^{226}\text{Ra}/^{210}\text{Pb}$ activity ratio (yellow: $^{226}\text{Ra}/^{210}\text{Pb} < 0.9$; red: $0.9 < ^{226}\text{Ra}/^{210}\text{Pb} < 1.1$; blue: $^{226}\text{Ra}/^{210}\text{Pb} > 1.1$) and ^{226}Ra activity concentration of the soil samples collected. (b) Data overlaid on results from an 1976 airborne gamma survey. Areas which exhibited counts per seconds in the airborne gamma survey significantly above background are indicated. Green is lowest red is highest.

The uranium activity concentration decreases approximately exponentially with distance from the sprinkler heads. This exponential decrease has been used to calculate average radionuclide activity concentrations deposited within the sprinkler halo. The overall results derived from the direct measurement of soil activities compare well with application loads calculated from historical RP2 radionuclide inventories and irrigation rates provided by ERA. The measurement of radionuclide loads in the leaf litter samples is underway and will complement the soils data set.

Preliminary analysis of the radioanalytical results produced by this study was presented by Dr Riaz Akber, consultant to Earth Water Life Sciences (EWLS), at ARRTC23 meeting, March 2009.

Radon exhalation

Dry and wet season measurements of radon exhalation rates were conducted in 2008/09. More than 200 measurements have been finalised and a summary of the results is shown in Figure 4. In this figure radon flux densities measured in the dry season (Aug 08) and wet season (Mar 09) are shown plotted versus distance from the sprinklers at various Ranger land application areas.

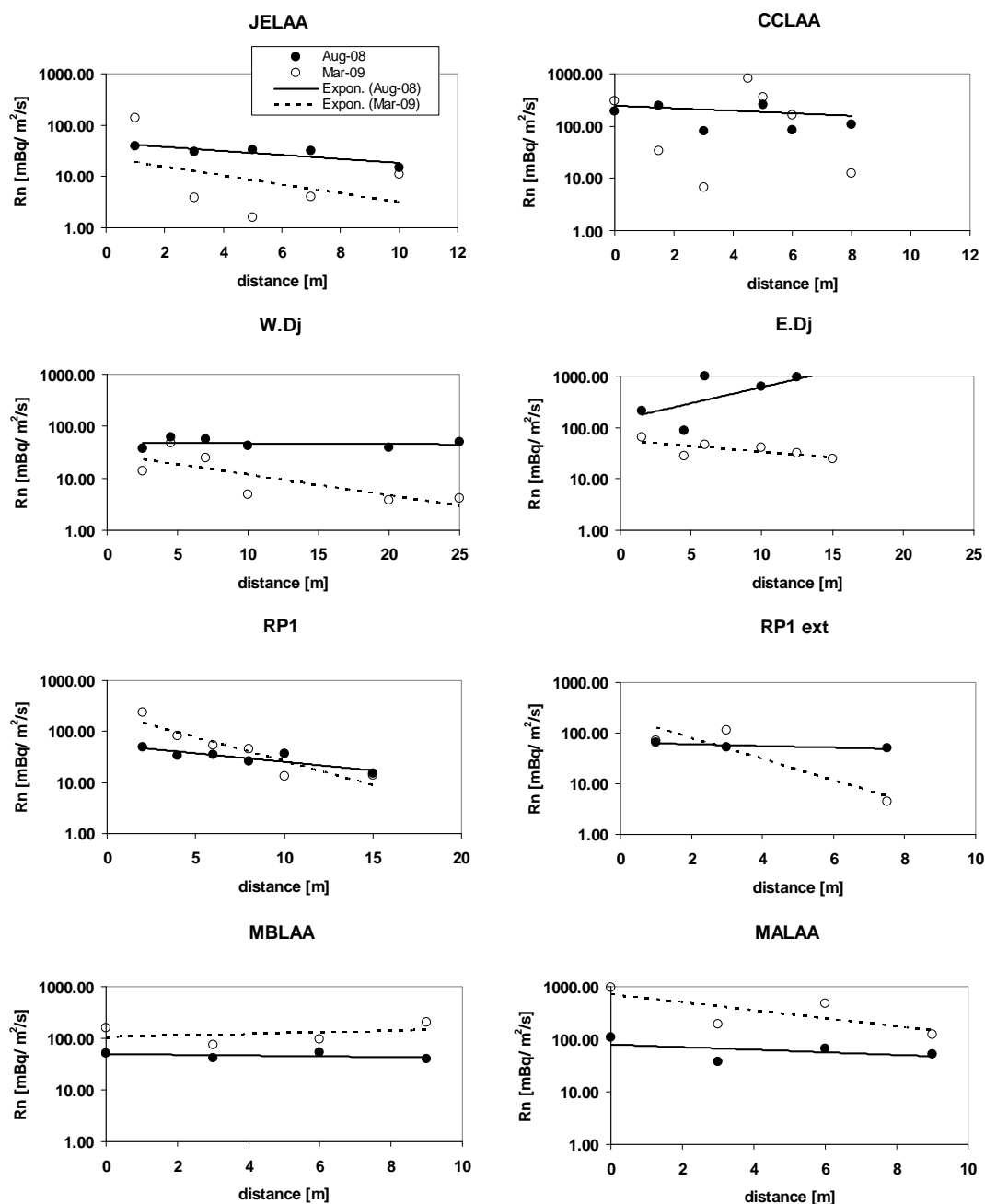


Figure 4 Radon flux densities measured in the dry season (Aug 08) and wet season (Mar 09), respectively, at various distances from the sprinklers at land application areas on the Ranger lease. The lines are exponential fits to the data.

Generally, the decrease of radon flux densities with increasing distance from the sprinklers is more pronounced during the wet season as compared with the dry. The Jabiru East (JE), Corridor Creek (CC) and Djalkmara land (W.Dj & E.Dj) application areas show higher radon flux densities during the dry season compared with the wet – due mostly to the lower soil moisture during the dry (Lawrence et al 2009). In contrast, the Magela and RP1 land application areas show higher radon flux densities in March 2009, at the end of the wet season. The reasons for these different behaviours are being investigated.

Dust

Dust samples collected by passive dust samplers have been analysed for total alpha activity by *SafeRadiation*. The analyses showed that alpha activity is generally higher in the samples closer to the ground indicating that a person sleeping may receive a higher dose from inhalation of dust than a person standing up.

Figure 5 shows the total alpha activity results from the transects in the Magela B land application area. It is apparent that there is a sharp drop of more than one order of magnitude in total alpha activity collected on the filters within the first 70 m distance outside from the LAA boundary. Total alpha activity in the breathing zone of an adult (and child) drops to about 0.01 CPM per day – a value similar to values measured at the Jabiru Field Station 4 km northwest of the transect.

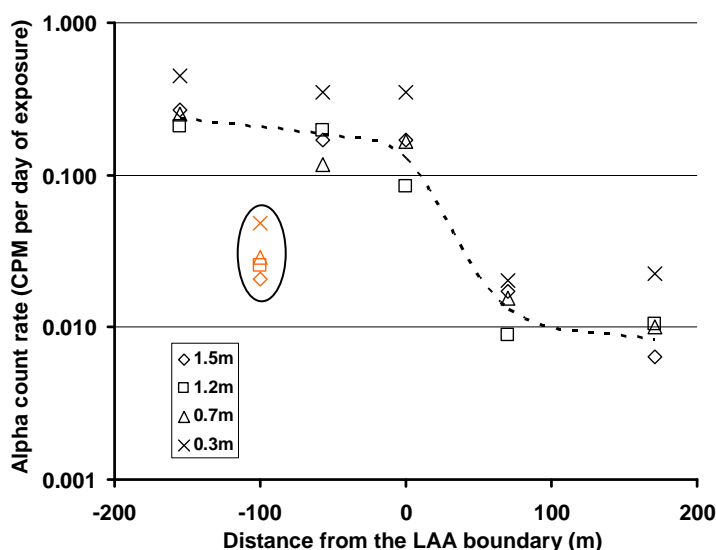


Figure 5 Total alpha activity measured in passive dust collectors along a transect in the Magela B land application area. Positive distances are outside the boundary of the LAA negative distances within. The circled values are for collectors recovered from the *eriss* Field Station.

Preliminary analysis of the results of this study was presented by Dr Riaz Akber at ARRTC23 meeting, March 2009.

Steps for completion

eriss will continue to provide input to the project via discussion and planning, data evaluation, interpretation and review. *eriss* will also continue to assist with the investigation of radionuclide transport pathways in the LAAs via the measurement of radionuclides in leaf litter samples (gamma spectrometry) and passive dust collectors (alpha spectrometry). These

samples are being analysed at present and will add to the value of the present data set. Activity ratios of radionuclides collected on the passive dust collectors will provide a measure of the relative contribution of radionuclides in airborne dust due to land irrigation. *eriss* will also assist with the modelling of ingestion doses and provide key references and data necessary for the evaluation of this exposure pathway.

The results from this work will enable the magnitude of radiation doses from the various key exposure pathways to be determined, including the inhalation of radon progeny and dust, and via the ingestion of soil and food.

Acknowledgments

The Northern Territory Geological Survey is acknowledged for the provision of the 1976 AGS data.

References

- Akber RA & Marten R 1992. Fate of radionuclides applied to soil in Ranger Uranium Mine land application area. In *Proceedings of the Workshop on Land Application of Effluent Water from Uranium Mines in the Alligator Rivers Region*. ed Akber RA, Jabiru 11–13 September 1991, Supervising Scientist for the Alligator Rivers Region, AGPS, Canberra, 139–165.
- Bollhöfer A, Storm J, Martin P & Tims S 2005. Geographic variability in radon exhalation at a rehabilitated uranium mine in the Northern Territory, Australia. *Environmental Monitoring and Assessment* 114, 313–330.
- Esparon A & Pfitzner J (in press). Visual Gamma – Gamma Analysis Manual. Internal Report 539, Supervising Scientist, Darwin.
- Hollingsworth I, Overall R & Puhlovich A 2005. Status of the Ranger Irrigation Areas – Final Report. EWL Sciences Pty Ltd, Darwin, Australia.
- Lawrence CE, Akber RA, Bollhöfer A & Martin P 2009. Radon-222 exhalation from open ground on and around a uranium mine in the wet-dry tropics. *Journal of Environmental Radioactivity* 100, 1–8.
- Marten R 1992. Procedures for routine analysis of naturally occurring radionuclides in environmental samples by gamma-ray spectrometry with HPGe detectors. Internal report 76, Supervising Scientist for the Alligator Rivers Region, Canberra. Unpublished paper.
- Murray AS, Marten R, Johnston A & Martin P 1987. Analysis for naturally occurring radionuclides at environmental concentrations by gamma spectrometry. *Journal of Radioanalytical and Nuclear Chemistry*, Articles 115, 263–288.
- Spehr W & Johnston A 1983. The measurement of radon exhalation rates using activated charcoal. *Radiation Protection in Australia* 1(3), 113–116.

Chronic toxicity of uranium to larval purple-spotted gudgeon (*Mogurnda mogurnda*)

K Cheng, D Parry¹, S Markich², A Hogan, A Harford & R van Dam

Background

During 2006–07 and 2007–08, a project was undertaken to assess the chronic toxicity of uranium (U) to the northern trout gudgeon, *Mogurnda mogurnda*.³ The project involved the development of a 28-day larval growth (and survival) test and the subsequent use of the test to assess the toxicity of U. The key purpose of the study was to compare the U toxicity results with those of Holdway (1992) who assessed the same species but for shorter exposure durations. The previous work on this project was summarised by Cheng (2008) and Cheng et al (2008, 2009).

Two 28-d U toxicity tests were undertaken. A key finding was that U toxicity was substantially different between the two tests, with a two-fold difference between the LC50s (Table 1). Cheng et al (2009) noted that larval whole body U concentrations did not appear to explain the difference in toxicity between the tests (ie the higher toxicity in test 2 was not explainable by higher whole body U concentrations in larvae from this test). However, the whole body U concentrations may have included adsorbed as well as absorbed U and, therefore, this measurement may not have been a good indicator of U uptake. To try to further resolve the reason for the difference in U toxicity between the two tests, geochemical speciation modelling was undertaken to predict the speciation of U under the specific physico-chemical conditions of the tests.

Table 1 Summary of uranium toxicity to *M mogurnda* following 28-d exposure

Test	Endpoint	NOEC ($\mu\text{g L}^{-1}$ U)	IC ₁₀ ($\mu\text{g L}^{-1}$ U)	IC/LC ₅₀ ($\mu\text{g L}^{-1}$ U)
1 (June 2007)	Survival	1400	-	2090 (1990–2200)
	Dry Weight	770	860 (0–1050)	>1400
	Length	770	1160 (1120–1300)	>1400
2 (February 2008)	Survival	800	-	1070 (930–1240)
	Dry Weight	410	660 (600–750)	1130 (1040–1240)
	Length	410	850 (790–890)	>1200

Methods

The speciation of U in the test solutions was calculated using the HARPHRQ geochemical speciation code. Input parameters were based on physico-chemical data measured in the toxicity test solutions (Table 2). The binding of U with dissolved organic carbon (DOC) was calculated as a function of its binding with fulvic acid (FA), the major component (~90%) of

¹ Australian Institute of Marine Science (AIMS NT), Arafura Timor Research Facility, PO Box 41775 Casuarina NT 0811

² Aquatic Solutions International, Cammeray, NSW

³ Project undertaken under Charles Darwin University Animal Ethics Approval Ref No. A06008

humic substances in natural fresh surface waters, using a finite mixture of simple organic ligands (Markich et al 2000). This approach has been shown to provide a very good measure of U binding with natural FA (and hence DOC) in natural Magela Creek water (NMCW) from pH 5.0–6.5 (Markich & Brown 1999, Markich et al 2000).

Table 2 Water chemistry of natural Magela Creek water used for uranium chronic toxicity tests^a

Physico-chemical variable	Natural Magela Creek water (NMCW)	
	Test 1	Test 2
pH	6.58 (C), 6.68, 6.70, 6.70, 6.72, 6.72, 6.75 ^b	6.26 (C), 6.22, 6.12, 5.98, 5.75, 5.73, 5.67 ^b
EC ($\mu\text{S cm}^{-1}$)	19–23 ^c	24 ^c
Alkalinity (mg L^{-1} as CaCO_3)	7	5
DOC (mg L^{-1})	2.1	4.2
NH_3 (mg L^{-1})	<0.5 ^d	<0.5 ^d
Na (mg L^{-1})	1.38	0.94
K (mg L^{-1}) ^e	0.37	0.37
Ca (mg L^{-1})	0.47	0.23
Mg (mg L^{-1})	0.74	0.27
Cl (mg L^{-1})	1.3	1.3
SO_4 (mg L^{-1})	0.20	0.20
NO_3 ($\mu\text{g L}^{-1}$) ^e	15	15
PO_4 ($\mu\text{g L}^{-1}$) ^e	7.0	7.0
Fe ($\mu\text{g L}^{-1}$)	189	128
Al ($\mu\text{g L}^{-1}$)	18	56
Cd ($\mu\text{g L}^{-1}$)	<0.02	<0.02
Co ($\mu\text{g L}^{-1}$)	0.03	0.11
Cr ($\mu\text{g L}^{-1}$)	<0.1	0.17
Cu ($\mu\text{g L}^{-1}$)	0.48	0.48
Mn ($\mu\text{g L}^{-1}$)	0.81	5.5
Ni ($\mu\text{g L}^{-1}$)	0.29	0.53
Pb ($\mu\text{g L}^{-1}$)	0.05	0.13
Se ($\mu\text{g L}^{-1}$)	0.20	0.20
U ($\mu\text{g L}^{-1}$)	0.02	0.02
Zn ($\mu\text{g L}^{-1}$)	1.58	4.5

^a Unless otherwise stated, all values represent a single measurement from the batch of NMCW that was used for each of the toxicity tests.

^b Values represent the mean measurements for the control (C) and increasing U treatments thereafter (n = 3).

^c Values represent the range of measurement across the control and all U treatments.

^d Values are based on daily measurements throughout the toxicity tests.

^e Long-term (~25 years) mean values for NMCW; these were used for the speciation calculations as they were not measured as part of the present study.

Progress

Uranium speciation calculations for both toxicity tests are summarised in Table 3. In both tests, the majority of U was bound to FA/DOC. Given the higher DOC concentration in Test 2 (4.2 mg/L) compared with Test 1 (2.1 mg/L), the proportion of UO_2FA was higher in Test 2.

Whereas the proportion of UO_2FA decreased with increasing U concentration, the proportions of other key U species increased with increasing U concentration. The free uranyl ion, UO_2^{2+} , represented only a small proportion of the total U. However, in Test 2, the proportions of U as UO_2^{2+} at U concentrations of greater than $800 \mu\text{g L}^{-1}$ were at least 2.5 to 10 times greater than at similar concentrations in Test 1. The percentages of U as UO_2^{2+} at the LC_{50} concentrations for Test 1 ($2090 \mu\text{g L}^{-1}$) and Test 2 ($1070 \mu\text{g L}^{-1}$) were 0.63% and 1.26%, respectively, corresponding to UO_2^{2+} concentrations of 13.2 and $13.5 \mu\text{g L}^{-1}$, respectively. When percentage survival of *M. mogurnda* larvae was plotted against UO_2^{2+} concentration, the responses of the larvae were very similar (ie standardised for the bioavailable UO_2^{2+} fraction) between the two toxicity tests (Figure 1).

Table 3 Calculated speciation of uranium in the two uranium chronic toxicity tests

U species	Speciation (% of total U)						
Test 1	U ($\mu\text{g L}^{-1}$)						
	0.02	90	184	381	768	1397	3182
UO_2^{2+}	0.38	0.34	0.40	0.58	0.69	0.68	0.55
UO_2OH^+	6.1	5.9	6.4	10	21	20	17
$\text{UO}_2(\text{OH})_2$	0.80	1.0	1.4	1.7	2.1	2.1	2.0
UO_2CO_3	5.7	5.8	6.3	9.9	12	12	8.9
$(\text{UO}_2)_3(\text{OH})_5^+$	<0.1	<0.1	0.22	0.38	3.0	10	24
UO_2Fa^a	87	87	85	77	61	53	47
Test 2	U ($\mu\text{g L}^{-1}$)						
	0.03	406	803	1226	1576	2070	2242
UO_2^{2+}	0.10	0.24	0.56	1.7	4.4	4.9	6.2
UO_2OH^+	0.70	1.0	1.7	3.3	7.2	9.5	14
$\text{UO}_2(\text{OH})_2$	0.07	0.10	0.24	0.80	2.0	2.3	2.7
UO_2CO_3	0.10	0.24	0.54	1.6	4.3	4.8	5.6
UO_2FA	99	98	97	93	82	78	71

a FA: fulvic acid

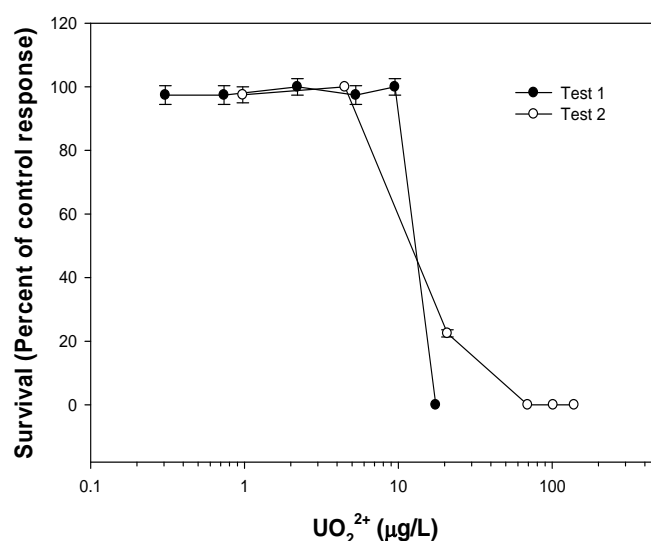


Figure 1 Mean (\pm SEM) survival (as a function of control survival) of *M. mogurnda* following 28 d exposure to uranyl ion, UO_2^{2+} , as calculated by HARPHRQ, for the two uranium chronic toxicity tests

The key driver of the difference in U speciation between the two tests was most likely the pH of the test solutions, which was (on average) 0.7 units lower in Test 2 (mean pH 6.0) compared to Test 1 (mean pH 6.7). The lower pH in Test 2 resulted in more bioavailable U and, therefore, higher toxicity, than at the lower pH in Test 1. The free uranyl ion is the predominant species at pH ≤ 5.0 and becomes less significant above pH 6.0 as complexation with hydroxides and carbonates increases (Markich 2002, Fortin et al 2007; as shown in Table 3). Dissolved organic carbon complexes with U and reduces its toxicity to freshwater biota (Markich et al 2000, Hogan et al 2005, Houston et al 2009). Although the two-fold higher DOC concentration in Test 2, compared with Test 1, is predicted to result in a higher proportion of U present as UO_2FA , this effect was not sufficient, at higher U concentrations, to counter the increase in the proportion of U as UO_2^{2+} as a result of the lower pH. Hence, the pH difference between the two tests had a much greater influence on U toxicity than did the difference in DOC concentration.

Steps for completion

This project is completed. A manuscript is currently in review with *Aquatic Toxicology*.

References

- Cheng KL 2008. The development and application of a 28 day larval fish toxicity test. Research thesis, BSc (Hons), Charles Darwin University, Darwin NT, Internal Report 535, June, Supervising Scientist, Darwin. Unpublished paper.
- Cheng K, van Dam R, Hogan A & Parry D 2008. Chronic toxicity of uranium to larval purple-spotted gudgeon (*Mogurnda mogurnda*). In *eriss research summary 2006–2007*, eds Jones DR, Humphrey C, van Dam R & Webb A, Supervising Scientist Report 196, Supervising Scientist, Darwin NT, 8–10.
- Cheng K, Parry D, Hogan A & van Dam R 2009. Chronic toxicity of uranium to larval purple-spotted gudgeon (*Mogurnda mogurnda*). In *eriss research summary 2007–2008*, eds Jones DR & Webb A, Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 2–5.
- Fortin C, Denison FH, Garnier-Laplace J 2007. Metal-phytoplankton interactions: Modeling the effect of competing ions (H^+ , Ca^{2+} , and Mg^{2+}) on uranium uptake. *Environmental Toxicology & Chemistry* 26, 242–248.
- Hogan A, van Dam R, Markich S & Camilleri C 2005. Chronic toxicity of uranium to a tropical green alga (*Chlorella* sp) in natural waters and the influence of dissolved organic carbon. *Aquatic Toxicology* 75, 343–353.
- Holdway DA 1992. Uranium toxicity to two species of Australian tropical fish. *The Science of the Total Environment* 125, 137–158.
- Houston M, Ng J, Noller B, Markich S & van Dam R 2009. Influence of dissolved organic carbon on the toxicity of uranium. In *eriss research summary 2007–2008*, eds Jones DR & Webb A, Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 6–11.
- Markich SJ 2002. Uranium speciation and bioavailability in aquatic systems: an overview. *The Scientific World Journal* 2, 707–729.
- Markich SJ & Brown PL 1999. Thermochemical data for environmentally-relevant elements. ANSTO/E735. Australian Nuclear Science and Technology Organisation, Sydney.
- Markich SJ, Brown PL, Jeffree RA & Lim RP 2000. Valve movement responses of *Velesunio angasi* (Bivalvia: Hyriidae) to Mn and U: An exception to the free ion activity model. *Aquatic Toxicology* 51, 155–175.

Amelioration of uranium toxicity by dissolved organic carbon

M Houston, J Ng¹, B Noller², S Markich³ & R van Dam

Background

This work is part of a PhD project studying the influence of dissolved organic carbon (DOC) on the toxicity of uranium (U), aluminium (Al) and arsenic (As) to freshwater biota.

With an increase in U mining, milling, use and disposal comes increased concern of the risks to human and ecological health due to U toxicity (Leshner et al 2008). Both historical and current U mining operations in tropical Australia may result in increased amounts of U in aquatic ecosystems, which, with its high capacity for solubilisation and migration in natural water (Morse & Choppin 1991), may pose a risk to aquatic biota. Uranium is of specific relevance for the Magela Creek system adjacent to the Ranger mine.

In 2007–08, the influence of a standard DOC on U toxicity to three Australian tropical freshwater species, the northern trout gudgeon (*Mogurnda mogurnda*), green hydra (*Hydra viridissima*) and unicellular green alga (*Chlorella* sp), was measured in synthetic Magela Creek water (SMCW), the composition of which is characteristic of sandy braided streams in tropical Australia. The DOC used for this work was the Suwannee River Fulvic Acid Standard I (SRFA) produced by the International Humic Substances Society (IHSS). The SRFA was selected for initial evaluation of the effects of DOC because it is an international reference material whose composition and properties has been extensively characterised (Cabaniss & Shuman 1988). A fulvic acid (FA) was selected because FAs account for a large proportion of DOC in natural fresh waters (Maurice & Namjesnik-Dejanovic 1999). The results obtained for the SRFA were summarised in Houston et al (2009).

The objective of the second phase of the U toxicity component of the PhD research program is to compare the influence on U toxicity to three tropical freshwater species of a standard riverine DOC source (Suwannee River fulvic acid) with that of a local DOC source from the Alligator Rivers Region (Sandy Billabong water).

Methods

In 2008–09, the toxicity of U to the three species listed above was assessed using DOC-rich natural water from Sandy Billabong (SBW) located in Kakadu National Park. This site was selected based on its location within the Alligator Rivers Region and for the high DOC content (10 mg/L) of the water (*eriss*, unpublished data). The DOC in this water is produced primarily by leaching of leaf litter, and release from coarse particulate matter, soil, bark and twigs (O'Connell et al 2000). Different concentrations of DOC (0, 1, 5 & 10 mg/L) in SBW were obtained by diluting SBW with SMCW, which is of very similar ionic composition to SBW but lacks DOC. Two tests, each comprising the four DOC concentrations in

¹ National Research Centre for Environmental Toxicology, The University of Queensland, Coopers Plains QLD 4108

² Centre for Mined Land Rehabilitation, The University of Queensland, St Lucia, QLD 4067

³ Aquatic Solutions International, Cammeray, NSW 2062

combination with a range of U concentrations, were conducted for each species (under fixed conditions of pH, water hardness and alkalinity).

Test durations and endpoints were as follows: *M. mogurnda* – 96-h sac-fry survival; *H. viridissima* – 96-h population growth rate; *Chlorella* sp – 72-h population growth rate. For all tests, pH, dissolved oxygen and electrical conductivity were monitored daily. Water samples were taken for analyses of DOC, alkalinity, hardness and a standard suite of metals and major ions. For each species, response data from the two tests were pooled, and concentration-response relationships were determined. Physico-chemical variables were input into the HARPHRQ geochemical speciation computer model to determine the effect of DOC on U speciation to ascertain if the proportion of U bound by the DOC could account for the observed changes in U toxicity. For the initial modelling calculations presented here, the binding constant (logK) value published for SRFA (Glaus et al 2000) was also used for SBW. The speciation calculations for the SBW will be run again once the specific U binding constant for SBW FA has been determined.

To enable characterisation of the FA in SBW, 120L of SBW was transported to the Curtin Water Quality Research Centre at Curtin University, Perth. The FA fraction was isolated from the water according to the procedures outlined by the International Humic Substances Society (Thurman & Malcolm 1981). Amberlite® XAD-8 resin was used to initially adsorb the humic acids (HAs) and FAs, which through a series of adsorptions and elutions from XAD-8 resin, were concentrated and had salts removed (using a cation exchange resin). The purified concentrated solutions of HAs and FAs were then finally freeze dried to yield the solid products (approximately 5 mg and 80 mg respectively). The physico-chemical characteristics of the SBW FA were compared with those of SRFA using the following techniques:

- Elemental analysis by Chemical & Microanalytical Services (to determine % C, H, N, S & O);
- Size exclusion chromatography by Curtin Water Quality Research Centre (to determine molecular weight);
- ¹³C NMR spectroscopy by Monash University (to compare proportions of functional groups);
- Acid/base titrations by University of Szeged, Hungary (to obtain estimates of the content of proton-binding sites)
- Fourier Transform Infra-Red spectroscopy by Environmental Chemistry University of New Mexico (to obtain a quantitative measurement of carboxylic acid content to be used to calculate the U binding constant for SBW FA).

Progress

Table 1 summarises the reduction in U toxicity that occurred with increasing concentrations of SBW and compares it with the amelioration that occurred for SRFA, all tests using SMCW as the diluting medium. Figure 1 compares linear regressions of U toxicity (expressed as IC/LC50) against DOC (expressed as the molar concentration of the FA) for each of the three test species, for SRFA and SBW. FA (M) was calculated by adjusting DOC concentration (mg/L) for the % C of each FA, converting this to g/L and dividing by the molecular weight of the FA.

Table 1 Effect of local (sandy billabong water; sbw) and standard (Suwannee River Fulvic Acid Standard i; srfa) dissolved organic carbon (doc – at 0 and 10 mg/l), on the toxicity of uranium to three local freshwater species

Species	DOC ^a (mg/L)	IC ₅₀ ^b (95%CL) ^c		Rate of amelioration of U toxicity (µg/L U µM FA ⁻¹) ^f		Difference (SRFA:SBW)
		SBW ^d	SMCW+SRFA ^e	SBW	SMCW+SRFA	
<i>Mogurnda mogurnda</i> ^g (northern trout gudgeon)	0	1690 (1499–1964)	1550 (1057–1961)	77	129	1.7x
	10	3093 (2829–3459)	4330 (4152–4575)			
<i>Hydra viridissima</i> (green hydra)	0	50 (18–81)	65 (8–85)	4	11	2.8x
	10	115 (44–191)	310 (247–491)			
<i>Chlorella</i> sp (unicellular alga)	0	15 (8–24)	38 (22–69)	7.5	15	2x
	10	144 (114–168)	394(248–766)			

a DOC: dissolved organic carbon, b IC₅₀: this is the concentration that results in a 50% inhibition of the test response relative to the control response; c 95% confidence limits; d SBW: Sandy Billabong water; e SMCW + SRFA: Synthetic Magela Creek water with Suwannee River fulvic acid; f Rates calculated from Figure 1 regression slopes; g For *M. mogurnda*, toxicity estimates relate to concentrations that affect percentage survival (as a % of control survival), compared with sub-lethal endpoints, such as growth and reproduction, for the other species

U toxicity was reduced approximately 10-fold for *Chlorella*, and 2-fold for *M. mogurnda* and *H. viridissima*, in SBW containing 10 mg/L DOC compared with SMCW lacking DOC. SRFA was twice as effective as SBW at reducing U toxicity for all three species (see Table 1). Preliminary geochemical speciation modelling showed that both forms of DOC resulted in the formation of similar proportions of UO₂ FA complex (Figure 2).

Characterisation of the SBW FA showed that it has properties similar to that of SRFA and many other aquatic FAs. The two FAs were found to be similar in molecular weight, elemental composition (Table 2) and their proportion of acidic (primarily carboxylate) functional groups responsible for metal complexation (Figure 3 – note that this comparison shows relative, not absolute, values). Acid/base titration also showed that the FAs have a similar proportion of proton-binding sites (not shown). Work is currently underway to quantitatively measure the carboxylic acid content of SBW FA, as this may explain why this FA reduces U toxicity to a lesser extent than SRFA.

Table 2 Comparison of molecular weight (mn) and elemental composition of Sandy Billabong fulvic acid (SBW FA) and Suwannee River fulvic acid (SRFA)

FA	Mn (d)	% C ^a	% H ^a	% N ^a	% S	% O
SRFA	856	49.9	4.6	0.6	0.33	43.6
SBW FA	1075	51.5	4.8	1.4	0.39	39.5

^a Uncertainty associated with C, H, N measurements is ± 0.1–0.3%

Both the SRFA standard and SBW FA resulted in a reduction in U toxicity to the three freshwater species studied. At this stage the SRFA's ability to ameliorate U toxicity more than that of the SBW FA could not be explained by differences in UO₂²⁺·FA complexation (as calculated by the speciation modelling). Using a binding constant specific for the SBW FA may however significantly alter the speciation results for the SBW tests.

Based on characterisation studies conducted so far, the characteristics of the two FAs appear to be quite similar. If final speciation modelling does not suggest a difference in the FAs capacity to complex U, the lesser degree of amelioration of U toxicity occurring in the billabong water may be due to the influence of other components present in Sandy Billabong water.

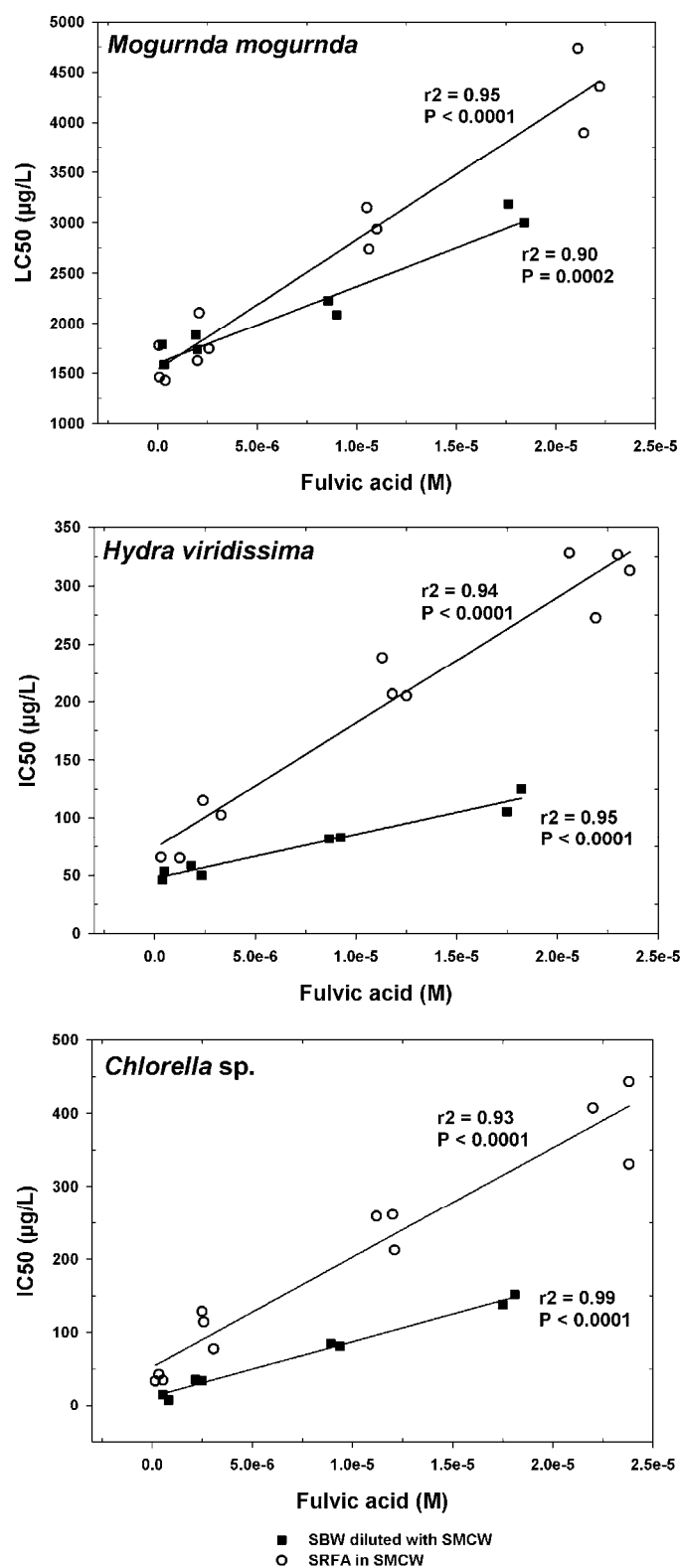


Figure 1 Effect of increasing DOC (expressed as fulvic acid concentration) on U toxicity to *Mogurnda mogurnda*, *Hydra viridissima* and *Chlorella* sp. Fitted linear regressions have been overlaid. Sandy Billabong water (SBW) diluted with synthetic Magela Creek water (SMCW); Suwannee River fulvic acid (SRFA) in SMCW.

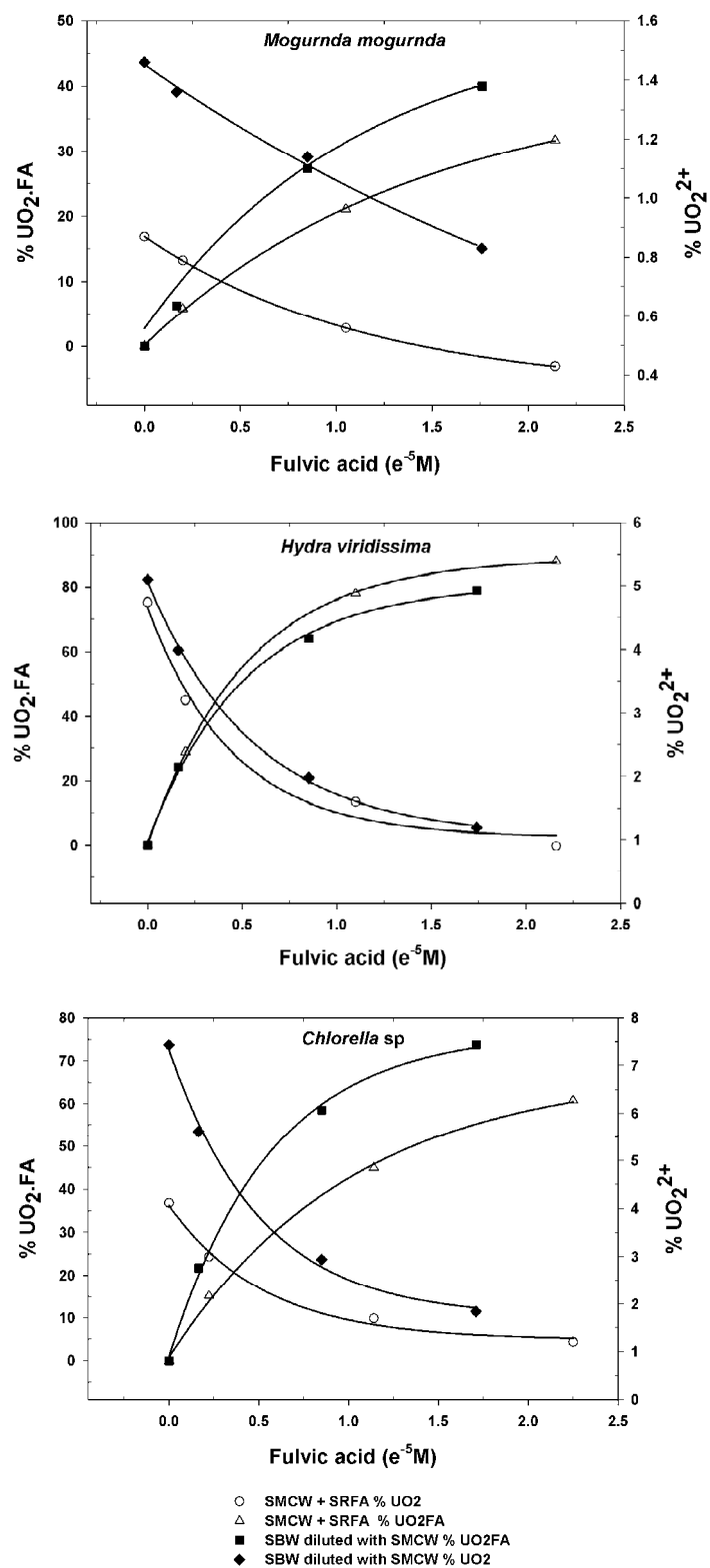


Figure 2 The proportion of UO_2^{2+} and $UO_2.FA$ complex formed both in Synthetic Magela Creek Water with Suwannee River Fulvic Acid (SMCW + SRFA) and in Sandy Billabong Water (SBW) diluted with SMCW for *Mogurnda mogurnda*, *Hydra viridissima* and *Chlorella* sp. U speciation was calculated using HARPHRQ Version 1.02.

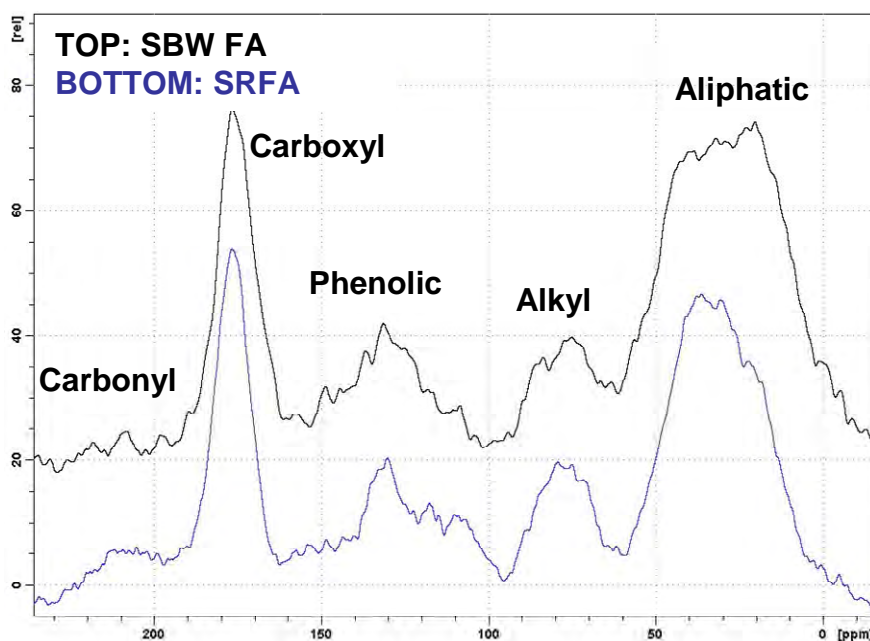


Figure 3 ^{13}C NMR results showing proportions of the major functional groups for Suwannee River Fulvic Acid (SRFA) and Sandy Billabong Water (SBW FA). Analysis conducted by Jenny Pringle, Monash University.

The evidence of attenuation of U toxicity by a local DOC source has important implications for impacted billabongs on the Ranger lease, where DOC concentrations can reach 20 mg/L, which is considerably higher than in Magela Creek (typically 1–5 mg/L). Consideration of the effects of DOC in ameliorating toxicity will be required as part of the process for deriving water quality closure criteria for U in these waterbodies.

Work will continue to derive a U binding constant for the Sandy Billabong FA for use in the speciation modelling. It may also be possible to validate the results of the speciation modelling using field flow fractionation in combination with ICPMS to measure the concentrations of uranyl ion and $\text{UO}_2^{2+}\cdot\text{FA}$ complex present in each of the water types at various DOC concentrations (Ranville et al 2007). U toxicity testing work will be completed using the freshwater unicellular species, *Euglena gracilis* to investigate cellular mechanisms of U toxicity. Measurements of Al toxicity are almost complete for the three species and will be completed using all four species of test organisms. The results from this work will be published in the peer-reviewed literature and documented in subsequent annual reports.

References

- Cabaniss SE & Shuman MS 1988. Copper binding by dissolved organic matter: I. Suwannee River fulvic acid equilibria. *Geochimica et Cosmochimica Acta* 52, 185–193.
- Glaus M, Hummel W & Van Loon L 2000. Trace metal-humate interactions. I. Experimental determination of conditional stability constants. *Applied Geochemistry* 15, 953–973.
- Houston M, Ng J, Noller B, Markich S & van Dam R 2009. Influence of dissolved organic carbon on the toxicity of uranium. In *eriss research summary 2007–2008*. eds Jones DR & Webb A, Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 6–11.
- Leshner E, Ranville J & Honeyman B 2008. Hyphenation of field flow fractionation with ICP-MS to determine Pore-Scale Uranium (VI) Speciation. Oral Presentation (presented by

- Ranville) at the 5th Congress Society for Environmental Toxicology and Chemistry World Congress, Sydney, Australia, August 2008.
- Maurice P & Namjesnik-Dejanovic K 1999. Aggregate structures of sorbed humic substances observed in aqueous solution. *Environmental Science & Technology* 33, 1538–1541.
- Morse JW & Choppin GR 1991. The chemistry of transuranic elements in natural waters. *Review of Aquatic Sciences* 4, 1–22.
- O’Connell M, Baldwin D, Robertson A. & Rees G. 2000. Release and bioavailability of dissolved organic matter from floodplain litter: influence of origin and oxygen levels. *Freshwater Biology* 45, 333–342.
- Ranville JF, Hendry MJ, Reszat TN, Xie Q & Honeyman BD. 2007 Quantifying uranium complexation by groundwater dissolved organic carbon using asymmetrical flow field-flow fractionation. *Journal of Contaminant Hydrology* 91, 233–246.
- Thurman E & Malcolm R 1981. Preparative isolation of aquatic humic substances. *Environmental Science & Technology* 15, 463–466.

Development of a reference toxicity testing program for routine toxicity test species

K Cheng, R van Dam, A Hogan, A Harford, C Costello,
D White & M Houston

Background

Over the past five years, and in response to recommendations by van Dam (2004) and Dr Jenny Stauber at ARRTC's 14th meeting (September 2004), the *eriss* Ecotoxicology Laboratory has been progressively implementing a program of reference toxicant testing, using uranium, for its routine suite of test species. Since 2004–05, reference toxicant control charts have been developed for four of the five routine testing species. The aims for 2008–09 were to:

1. continue with the established reference toxicity testing programs for *Moinodaphnia macleayi*, *Chlorella* sp., *Hydra viridissima* and *Mogurnda mogurnda*;
2. continue to investigate identified difficulties with the *Lemna aequinoctialis* reference toxicity test with the objective of establishing an acceptably stable reference test

Methods

Descriptions of the testing procedures are provided in 'Ecotoxicological testing protocols for Australian tropical freshwater ecosystems' Supervising Scientist Report 173 (Riethmuller et al 2003).

Progress

In total, 15 reference toxicants tests (*Chlorella* – 3; *Hydra* – 5; *Moinodaphnia* – 4; and *Mogurnda* – 3) were completed during 2008–09. Ten of these tests provided valid results, as summarised in Table 1. The associated control charts are presented in Figure 1.

A summary of the issues identified during 2008–09 for each component of the reference toxicity test program is provided below.

Chlorella sp

Only one of three *Chlorella* sp tests was valid for the period. Two of the tests were not valid with both having growth rates lower than the acceptability criterion of 1.4 ± 0.3 doublings/day (Riethmuller et al 2003). There were no problems with general test conditions (ie temperature, lighting, EC, pH and DO) and it was suspected that low nutrient concentrations were the cause of lower than normal growth. Investigations into nutrient stock solutions are on-going with more details to follow in the 2009–10 summary. The latest advice from Northern Territory Environmental Laboratories (NTEL) was to make up new stocks as needed rather than have bulk stocks that will be kept for prolonged periods. A repeated test is anticipated in the near future with newly prepared nutrient stocks to determine if this improves growth rates.

Table 1 Summary of uranium reference toxicity test results for 2008–09

Species & endpoint	Test Code	IC ₅₀ (µg/L)	Valid test?	Comments
<i>Chlorella</i> sp (72-h cell division rate)	966G	43 (33, 50)	No	Control growth rate below criterion ^b
	993G		Yes	
	1021G		No	Control growth rate below criterion ^a
<i>Moinodaphnia macleayi</i> (48-h immobilisation)	948I	238 (224, 253)	No	No effect at highest conc ^a
	949I		No	No effect at highest conc ^a
	991I		No	Not included in control chart ^a
	1001I	36 (31, 41)	Yes	
<i>Hydra viridissima</i> (96-h population growth)	962B	86 (71, 99)	Yes	
	963B	54 (18, 78)	Yes	
	969B	46 (31, 81)	Yes	
	989B	69 (47, 105)	Yes	
	1015B	53 (36, 82) ^a	Yes	
<i>Mogurnda mogurnda</i> (96-h sac fry survival)	950E	1191 (974, 1456)	Yes	
	984E	1685 (1258, 2256)	Yes	
	1006E	1231 (11156, 1310)	Yes	

^a Values in parentheses represent 95% confidence limits

^b See text for discussion

H. viridissima

All five reference toxicity tests for *H. viridissima* were valid. There are no issues associated with this protocol. The running mean IC₅₀ is 87 µg/L U with the results from all but one of the tests lying within the upper and lower warning limits (± 2 standard deviations) of 145 and 56 µg/L U, respectively. The IC₅₀ for test 1015B was slightly under the lower warning limit. This may have been due to sub-optimal culture stock health at the time, possibly due to stress related to acclimation to new diluent waters, which has, on occasion, affected *Hydra* health.

M. macleayi

Of the four reference toxicity tests for *M. macleayi*, only one was valid. The first two tests (948I and 949I) were invalid due to 100% survival of *M. macleayi* exposed to the highest concentration tested of ~80 µg/L U. The third test (991I) investigated U concentrations over a broader range (control, 5, 20, 80, 160, 320 µg/L) to determine an effect concentration. At 160 and 320 µg/L U, there was 100% and 0% survival of *M. macleayi*, respectively, resulting in an EC₅₀ of 238 µg/L U. These three tests indicated a lower sensitivity of *M. macleayi* to U than previously found. In fact, in previous years there was an indication of a possible trend towards an increase in sensitivity of the laboratory culture (as reported in Cheng et al 2009).

A new UO₂SO₄·7H₂O stock was prepared to determine if problems with this were responsible for the apparently lower sensitivity of *M. macleayi* to U (noting, however, that similar changes in responses were not observed for the other species). The fourth test (1001I), using the new U stock solution, resulted in a more typical response; 90% mortality was observed at 70 µg/L U and 100% mortality at 139 and 287 µg/L U, and the EC₅₀ was 36 µg/L U. This species will again be closely monitored during 2009–10 to determine if there has been a change in species sensitivity.

M. mogurnda

All three reference toxicity tests for *M. mogurnda* were valid with all IC₅₀ values within the warning limits. There are no problems associated with this protocol.

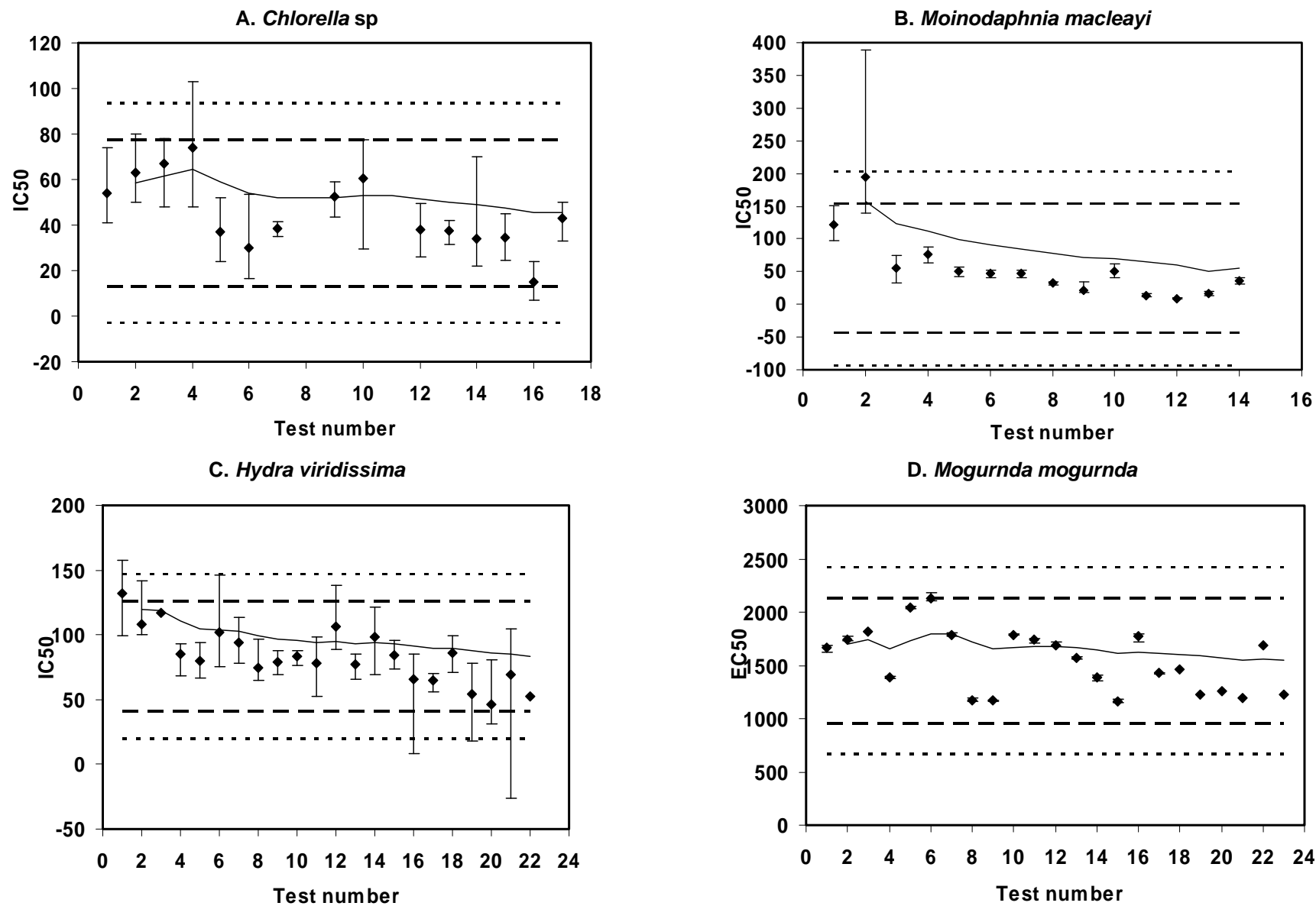


Figure 1 Reference toxicant control charts for A. *Chlorella* sp, B. *M. macleayi*, C. *H. viridissima* and D. *M. mogurnda*, as of September 2008. Data points represent IC₅₀ or EC₅₀ toxicity estimates and their 95% confidence limits (CLs). Reference lines represent the following: dotted lines – upper and lower 99% confidence limits of the whole data set; broken lines – upper and lower warning limits (± 2 standard deviations); unbroken line – running mean.

Reference toxicity test development for *L. aequinoctialis*

Test development for *L. aequinoctialis* is on-going. Previous growth trials using 2.5% CAAC plant growth medium (the medium used to culture this species; Riethmuller et al 2003) have shown that it supported good growth and generally met the growth criteria. However, due to the very high concentrations of nutrients and essential elements in the CAAC medium, very high reference toxicant (U) concentrations are required to elicit a toxic response. At the time of completion of this summary, additional testing was underway to assess the suitability of using this concentration of CAAC in the reference toxicity test method.

Planned testing in 2009–10

The reference toxicity testing programs for *Chlorella* sp, *M. macleayi*, *H. viridissima* and *M. mogurnda* will continue in 2009–10, with the aim of completing at least four tests per species. In addition, further reference toxicity testing of *L. aequinoctialis* will take place to develop the control chart and to trouble-shoot the last remaining issues for this protocol. In addition to the reference toxicity test protocol, work will continue on the development of an additional endpoint, based on plant surface area or dry weight. The development of this endpoint will be done in conjunction with the reference toxicity test work.

References

- Cheng K, Costello, C, van Dam R, Hogan A, Harford A & Houston M 2009. Development of a toxicity testing program for routine toxicity test species. In *eriss research summary 2007–2008*. eds Jones DR & Webb A, Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 25–28.
- Riethmuller N, Camilleri C, Franklin N, Hogan AC, King A, Koch A, Markich SJ, Turley C & van Dam R 2003. *Ecotoxicological testing protocols for Australian tropical freshwater ecosystems*. Supervising Scientist Report 173, Supervising Scientist, Darwin NT.
- van Dam R 2004. *A review of the eriss Ecotoxicology Program*. Supervising Scientist Report 182, Supervising Scientist, Darwin NT.

Effects of magnesium pulse exposures on aquatic organisms

A Hogan, R van Dam, A Harford, K Cheng & K Turner

Background

Acquisition of continuous water quality monitoring data in Magela Creek downstream of Ranger since the 2005–06 wet season has enabled quantification of the magnitude, duration and frequency of transient magnesium (Mg) concentrations resulting from mine water discharges (Section 3.1, Supervising Scientist annual report 2007–2008 & 2008–2009). The mine discharge signal is tracked using Electrical Conductivity (EC) as a surrogate for Mg concentration. This is possible since a strong relationship between EC and Mg concentration has been established in grab samples collected over many years for water quality analysis (see ‘Surface water transport of mine-related solutes in the Magela Creek catchment using continuous monitoring techniques’ pp 58–65 in this volume for full details).

The monitoring data show that peak Mg concentrations associated with pulse events at times exceed the provisional site-specific Limit for Mg (3 mg/L) in Magela Creek, and have, on one occasion, reached a maximum value of approximately 16 mg/L. However, the majority of these pulses occur over timescales of only minutes to hours. In contrast, the ecotoxicity data upon which the Mg provisional limit was derived are based on continuous exposures over three to six days (depending on the test species). Consequently, it was unknown if these shorter duration exceedences were having adverse effects on aquatic biota, and an assessment of the toxicity of Mg under a pulse exposure regime was initiated.

At the commencement of this study, the provisional site-specific Trigger Value (TV) for Mg in Magela Creek was 4.6 mg/L Mg (van Dam et al 2008). Over the four wet seasons that Mg has been continuously monitored, the maximum duration over which this value was exceeded (ie the ‘worst case’ duration) was only 4 h, which, therefore, represented the duration of greatest interest. Following a subsequent revision of the provisional TV to 2.5 mg/L Mg (van Dam et al 2010)⁹, the maximum exceedence duration above this lower value was 137 h (almost six days), although the vast majority of exceedences (51 out of 53), occurred for 24 h or less. Consequently, pulse exposure durations of up to 24 h are now also considered of relevance. As such, this summary paper describes the results of toxicity tests that assessed the effects of both 4 and 24 h Mg pulses on local aquatic species.

Methods

To date, an assessment of the effects of a single Mg pulse of 4 hours duration to five local species (duckweed, hydra, cladoceran, gastropod and fish) and a single 24 h pulse to three local species (duckweed, hydra and fish) has been undertaken. Test species were exposed to the Mg pulse over a range of Mg concentrations except for the fish, which, due to its relative

⁹ The trigger value was revised after it was agreed to use 10% inhibition concentrations (IC_{10s}) instead of 15% inhibition concentrations (IC_{15s}) from the individual toxicity tests for the trigger value derivation. The use of IC_{10s} was more aligned with current practices elsewhere.

insensitivity, was only exposed to a very high concentration (4 g/L Mg). The pulse was administered at the beginning of the test, after which time the organisms were returned to natural Magela Creek water for the remainder of the standard test period (four to six days).

In addition, because the cladoceran test protocol involves tracking individuals from newly hatched neonate to reproducing adult, it was possible to investigate the influence of the effect of pulse timing with respect to test organism developmental stage. Consequently, an additional test was conducted for this species where the four hour pulse was administered around the time of the onset of reproductive maturity, when the juvenile cladocerans were 27 h old and developing their first brood offspring (approximately 24 h into the experiment).

The results from all tests were compared with those from tests where the organisms were continuously exposed to Mg throughout the standard test period.

Results

4 h Mg pulses

Toxicity test data for each species undergoing a 4 h Mg pulse are presented in Table 1 and Figure 1. For all five species, the toxicity of a single 4 h Mg pulse at test commencement was consistently lower than when the organisms were continuously exposed to Mg. The relative toxicity across tests was determined by comparing the concentrations that caused a 50% inhibition of the test endpoint (IC50s; based on hydra or lemna growth rate and cladoceran or gastropod reproduction). Where point estimates could not be calculated (eg for the fish and the gastropod 4 h pulse test) a comparison of the different concentration responses is described.

Magnesium was approximately half as toxic to the green hydra, *Hydra viridissima*, under the 4 h pulse regime compared with the continuous exposure. No effects were observed when either the duckweed, *Lemna aequinoctialis*, or the fish, *Mogurnda mogurnda*, were exposed to a pulse of up to 4 g/L Mg. Whilst the concentration response observed for the gastropod, *Amerianna cumingi*, is questionable (with the test needing to be repeated), the snails were producing high egg numbers, similar to those of the controls, at very high concentrations (2 g/L Mg) compared to the continuous exposure IC50 for this species of 100 mg/L Mg. A 4 h Mg pulse at test commencement was approximately an order of magnitude less toxic to the cladoceran, *M. macleayi*, than the continuous exposure. However, when *M. macleayi* was exposed to the 4 h pulse at the onset of reproductive maturity, Mg was only approximately two times less toxic than the continuous exposure, indicating that the timing of the pulse is a key factor for this species.

24 h Mg pulses

The severity of response by both *L. aequinoctialis* and *H. viridissima* to a 24 h pulse was more extreme than that observed after a 4 h pulse, but still less than that following continuous exposure (Table 1 & Figure 1). Some variability was observed between the two tests undertaken for each species and, thus, repeat tests will be required to provide more confident confirmation of the initial findings. The IC50 values for the two 24 h pulse exposures of *L. aequinoctialis* were 2567 and 3144 mg/L Mg, compared to a continuous exposure IC50 of 1393 mg/L. For *H. viridissima*, the response in one 24 h pulse experiment was more aligned with a continuous exposure (continuous IC50 = 663 and 24 h pulse IC50 = 789 mg/L Mg), while the other test gave a less sensitive result, similar to a 4 h pulse (4 h pulse IC50 ~1300

and 24 h pulse $IC_{50} = 1084$ mg/L Mg). *M. mogurnda* was unaffected by a 24 h pulse concentration up to 4.1 g/L Mg. This was not unexpected given the low sensitivity of this species to Mg even under a continuous exposure regime.

Table 1 Toxicity of pulse exposed Magnesium compared with continuous exposure

Species	Continuous exposure	4 h pulse at test commencement ^c	4 h pulse at onset of maturity (24 h into test)	24 h pulse at test commencement ^c
IC_{50} (95%CL)^a mg/L Mg				
<i>Hydra viridissima</i> (green hydra)	663 (518–746)	1231 (1160–1252) 1393 (1363–1419)	Not applicable	789 (735–903) 1084 (1056–1100)
<i>Lemna aequinoctialis</i> (duckweed)	1393 (664–3207)	>4220	Not applicable	3144 (2626–3621) 2567 (2114–3379)
<i>Moinodaphnia macleayi</i> (cladoceran)	130 (116–144)	1180 (1070–1321) 1498 (1271–2051) 1430 (1163–1990)	305 (289–338)	To be conducted
<i>Amerianna cumingi</i> (gastropod)	100 (31–243)	Not calculable ^d	Not applicable	To be conducted
LC_{50} (95%CL)^b mg/L Mg				
<i>Mogurnda mogurnda</i> (fish)	4054 (4046–4063)	Not calculable ^e	Not applicable	Not calculable ^e

a IC_{50} = Concentration causing a 50% inhibition of the test endpoint (associated 95% confidence limits).

b LC_{50} = Concentration resulting in 50% lethality of the test organisms (associated 95% confidence limits).

c The results of multiple tests are reported for some species.

d Not calculable due to interrupted concentration response (Figure 1) and low overall egg numbers.

e Not calculable as only one Mg treatment was tested.

For the species tested thus far using two pulse durations the concentrations of Mg that exhibited toxic effects were much greater than the maximum concentration (16 mg/L) that has been reported in Magela Creek downstream of the mine. Even in the most sensitive test, where *M. macleayi* was exposed at the onset of reproductive maturity, the concentration of 208 mg/L Mg that caused a 10% inhibition of the test endpoint (IC_{10} ; generally considered an ‘acceptable’ level of effect), was still approximately 13 times higher than the reported maximum Mg concentration.

Conclusions

The experiments completed to date show that pulse exposures of Mg of ≤ 24 h are generally substantially less toxic than continuous exposures over 3 to 6 days. However, the degree to which this is the case depends on the species and, for at least one species (ie *M. macleayi*), the life stage that is exposed. The Mg concentrations at which (sub-lethal) toxic effects have been observed are well in excess of those measured during pulse events in Magela Creek. However, ultimately, Mg concentrations in Magela Creek will need to be compared to pulse exposure trigger values derived from data for all the tested species, rather than toxicity values for individual species.

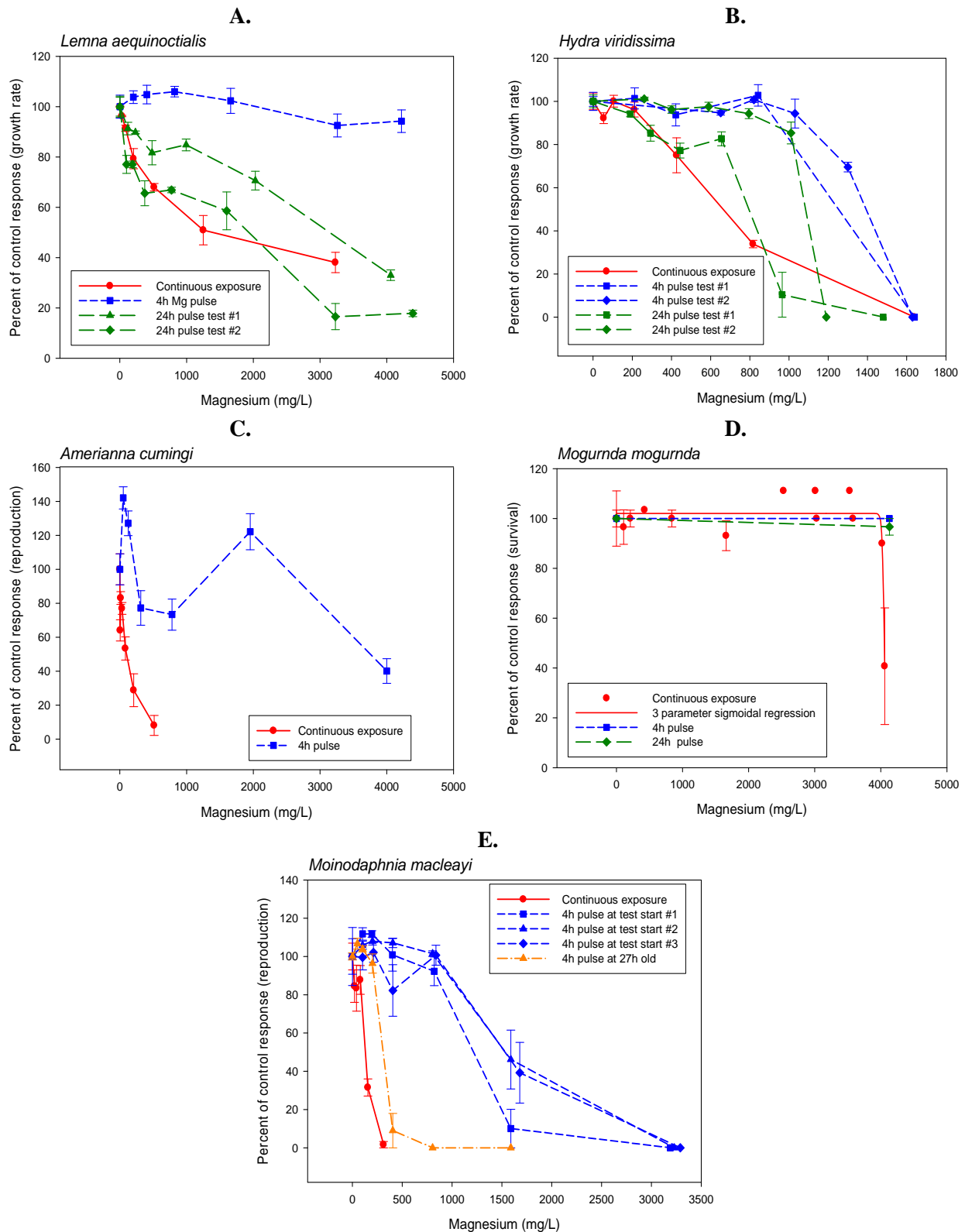


Figure 1 Toxicity of magnesium to the A. duckweed, *Lemna aequinoctialis*, B. green hydra, *Hydra viridissima*, C. gastropod, *Amerianna cumingi*, D. fish, *Mogurnda mogurnda*, and E. cladoceran, *Moinodaphnia macleayi*. Data from continuous exposure experiments are represented by a solid line while 4 h pulse data are represented by short dashed lines and 24 h pulse data by long dashed lines.

Steps for completion

At least two single 4 and 24 h pulse experiments need to be completed for all six species routinely tested at *eriss*. Some technical challenges are envisaged with respect to pulsing the unicellular alga *Chlorella* sp, and some method development testing may be required for this species. Work will also commence soon on testing an intermediate pulse duration (eg 10 h). Once data are available for all six test species for each pulse duration, TVs will be derived for each exposure duration using the species sensitivity distribution approach.

The following phase of the research will involve testing multiple pulses given that exceedences of the 2.5 mg/L TV are so numerous that pulse frequency and recovery period between pulses are also important.

Further research into toxicokinetic modelling may also be warranted considering the expansion of the current testing program with the revision of the TV from 4.6 to 2.5 mg/L. Pulsing scenarios in the creek are likely to be much more complex and variable when compared to a benchmark of 2.5 mg/L Mg, and these scenarios may not always be matched to those tested in the laboratory. Therefore there may be a future need for the predictive ability that could be achieved through such modelling approaches (see Ashauer et al 2006, Diamond et al 2006).

References

- Ashauer R, Boxhall ABA & Brown CD 2006. Predicting effects on aquatic organisms from fluctuating or pulsed exposure to pesticides. *Environmental Toxicology and Chemistry* 25(7), 1899–1912.
- Diamond JM, Klaine SJ & Butcher JB 2006. Implications of pulsed chemical exposures for aquatic life criteria and wastewater permit limits. *Environmental Science and Technology* 40, 5132–5138.
- van Dam R, Hogan A, McCullough C & Humphrey C 2008. Toxicity of magnesium sulfate in Magela Creek water to tropical freshwater species. In *eriss research summary 2006–2007*, eds Jones DR, Humphrey C, van Dam R & Webb A, Supervising Scientist Report 196, Supervising Scientist, Darwin NT, 11–14.
- van Dam RA, Hogan AC, McCullough C, Houston M, Humphrey CJ & Harford AJ 2010. Aquatic toxicity of magnesium sulphate, and the influence of calcium, in very low ionic concentration water. *Environmental Toxicology and Chemistry* 29(2), 410–421.

The effects of suspended sediment on tropical freshwater biota

A Harford, M Saynor, R van Dam, A Hogan & D White

Background

The issue of suspended particulate matter (SPM) as an aquatic ecosystem stressor in Magela Creek will likely assume greater significance during the decommissioning and initial rehabilitation phases of the Ranger minesite. However, there may also be an increased risk of suspended sediment in runoff from the site as a result of works associated with the proposed heap leach operation and construction of a second tailings containment facility. These new works will be located in the catchment of Gulungul Creek.

Apart from an investigation conducted by *eriss* on the effects of suspended sediment in a creek downstream of the Jim Jim Falls road crossing (Stowar 1997), there has been no systematic program of research to characterise the potential biological impacts of increased SPM on aquatic ecosystems in the ARR. A robust assessment of the effects of SPM is needed to provide the basis for developing operational water management triggers and closure criteria. Nationally, the issue of SPM as an ecosystem stressor has been ranked as the third highest priority for waterway management following salinity and eutrophication (Land and Water Australia 2007). In contrast to the large volume of research that has been conducted during the last four decades on dissolved contaminants, there has been little advance in water quality guidelines for SPM. This situation probably reflects the relative complexity of experimental design and degree of difficulty required to unambiguously establish the effects of suspended sediment (a heterogeneous system) compared with the protocols required to establish the effects versus concentration response for dissolved toxicants (a homogeneous aqueous system).

In reviewing the literature on the biological effects of SPM, Berry et al (2003) noted the need for more comprehensive experimental concentration-response data to better understand the responses of aquatic species within and between habitat types. A key principle of such an approach, and one that applies also to the assessment of dissolved toxicant impacts, is that both the concentration and duration of suspended sediment exposure are important determinants of the level of impact, with the frequency of exposure also being an important variable. Unfortunately, the majority of past SPM toxicity studies have reported nominal concentrations (ie not measured concentration but inferred from the mass of sediment added to test solutions) of sediment, which does not allow for an assessment of the accuracy of SPM concentrations in the tests. Additionally, there is little discussion in the literature concerning the methods of exposure of suspended sediment to the organisms (eg mixing to keep in suspension or allowing particles to settle) and the way the method of presentation affects dose to the organism.

Bilotta and Brazier (2008) noted that particle size distribution and particle chemistry are both important determinants of effects of suspended sediment. Likewise, recent developments in toxicology of particulates (specifically nanoparticles) have led to the conclusion that the physicochemical characterisation of particles is fundamental to determining appropriate 'dose'-response models. The numerous particle characteristics that may drive the behaviour of

particles in the environment and the response of an organism include particle size, particle shape, mineralogy and composition, surface area and charge, porosity and surface chemistry.

The objective of this project is to assess the effects of a SPM 'reference material' comprising the <63 µm fraction of the lateritic material that is intended to be used as a component of the surface cover layer on the rehabilitated Ranger landform. 'Lateritic material' refers to sediment (generally iron-rich) that comes from the weathered horizon of the regolith. It usually contains a high percentage of smaller particles including of clay minerals. This weathered horizon can extend to 40 m in depth below the ground surface.

It is intended to mix approximately 30% by volume of the laterite material with waste rock in the top 2 to 5 m of the rehabilitated landform. The reason that the laterite is being incorporated in the cover layer is that it contains a substantial proportion of fine-grained material that will improve the moisture-retaining characteristics of the surface layer of the landform and by inference provide a superior growth substrate. The consequences of the use of laterite will be the presence of a much more erodible component in the surface of the rehabilitated landform. Hence, there is a higher probability of fine-grained material being delivered to Magela Creek during the decommissioning and rehabilitation phases of the Ranger minesite.

In order to better understand cause-effect relationships observed for test organisms, the project will include detailed physico-chemical characterisation of the SPM 'reference material'. Concentrations (eg particles/mL) and particle size distribution of the SPM will also be measured in the toxicity test media containing the particles for the duration of the exposures. This will provide a more accurate assessment of SPM 'concentrations' and greater confidence in the concentration-response models. This project is a collaboration between the *eriss* Ecotoxicology and Hydrological & Geomorphic Processes (HGP) groups.

Methods

Development of <63 µm sediment separation method

A bulk sample of lateritic (weathered horizon) material was collected on 8 September 2008 from Pit 3 at the Ranger mine. Possible methods for extracting and preparing the <63 µm fraction were assessed during late 2008 to early 2009. The methods investigated were dry and wet sieving for extraction, and oven and freeze drying for preparation. Particle size distributions and particle morphology were investigated using electrozone sensing (ie Coulter counting) and microscopy techniques.

Range-finding toxicity tests

An initial <63 µm fraction that was isolated from a sub-sample of the Ranger Pit 3 laterite was used in three 'range-finding' toxicity tests. This enabled estimation of the mass of material required to conduct definitive toxicity tests and also an evaluation of the appropriateness of the standard algal (*Chlorella* sp) toxicity test Riethmuller et al (2003). *Lemna aequinotialis* (duckweed) and *Mogurnda mogurnda* (purple-spotted gudgeon) were also used for the range-finding tests as they were suspected to be the least sensitive (based on responses to Mg and U) of the suite of species used at *eriss*. Using a less sensitive species would yield a conservative estimate of the total mass of SPM likely to be required for future test work.

Production of the SPM Standard Reference Material (SRM)

The SPM-SRM is currently being produced from a 100 kg bulk sample of material, collected from the trial rehabilitation landform, using a process of wet-sieving, followed by a dehydration step of centrifugation and freeze drying. Although lateritic material was originally identified by Energy Resources of Australia Ltd as the preferred material for the trial landform cover, a transitional material was also used. Transitional material refers to the material that is located between the surficial lateritic material and the deeper rocks containing the uranium ore.

There was difficulty sourcing sufficient lateritic material for the construction of the trial landform and it was supplemented with the use of transitional material. Discussions on site during construction suggested that there would be a similar problem with the supply of lateritic material for the final rehabilitation and that large amounts of the transitional material could be used. Consequently, it was decided to use the transitional material for the initial toxicity tests.

Results and discussion

Development of <63 µm sediment separation method

The average mass of fines obtained from the wet sieving process was approximately 10% of the total initial weight of the bulk sample, which was an order of magnitude greater than that produced by the dry sieving process. Additionally, microscopy demonstrated that a larger proportion of fine particles were present in the wet-sieved samples (Figure 1). Thus, wet-sieving was deemed a superior method to dry sieving, especially considering that the fine particles are of most interest because they will remain in suspension for longer periods and are likely to be more biologically active than larger particles.

However, the main disadvantage with the wet-sieving method was the large volume of water required in the process. This water needed to be removed without significantly modifying the particles' physico-chemical properties. Consequently, centrifugation followed by freeze drying was identified as the most appropriate method. Electrozone analysis (using a Coulter Counter) of the wet-sieved samples showed that the majority of particles were <2 µm (spherical volume) (Figure 2a) in size, which is typically below the resolution of what this method of particle size analysis (PSA) can measure. Microscopy of the samples showed that some of the particles were flat and transparent mica particles (Figure 2b), which would present additional challenges for particle size analysis using methods that report particle size results on the basis of equivalent spherical volume. Subsequently, other methods (eg laser diffraction, sedimentography and others) and commercial suppliers offering particle size analysis services are currently being investigated to further characterise the SRM.

Range-finding toxicity tests

The range-finding studies showed that nominal concentrations of 0.5 and 1 g/L of SPM resulted in significant reductions in survival of *M. mogurnda* and growth of *L. aequinotialis*, respectively (Figure 3). From these results, it was estimated that 270 g of SPM-SRM would be required as a minimum amount to accommodate the initially planned suite of toxicity tests, ie 4 tests for each of the 5 species, including experiments to investigate the effects of different methods of keeping particles in suspension. However, larger amounts would be required for characterisation of the material and any further toxicity tests (eg comparison with field samples and spiking the sediment with uranium). Thus, 1 kg was considered a suitable target.

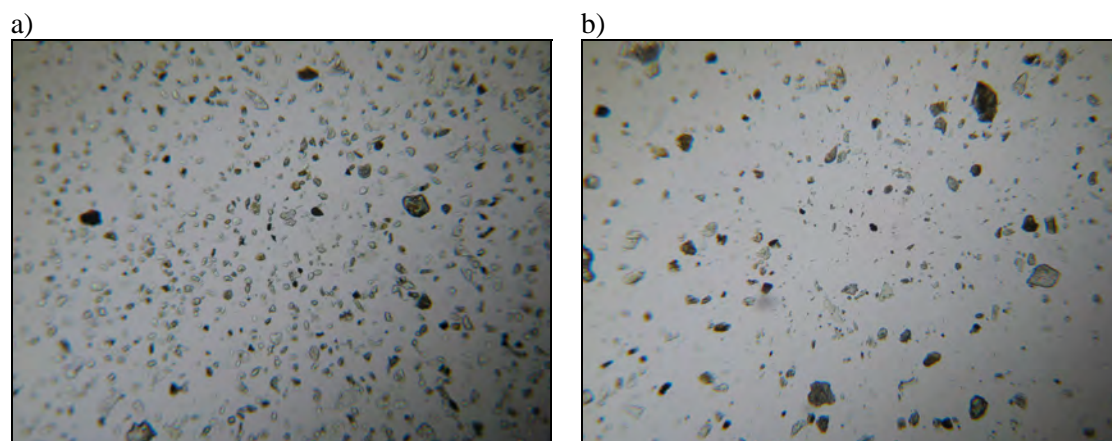


Figure 1 Images from a compound microscope (x100) showing a) a wet-sieved sample and b) a dry sieved sample. Both samples were the same mass per volume concentration.

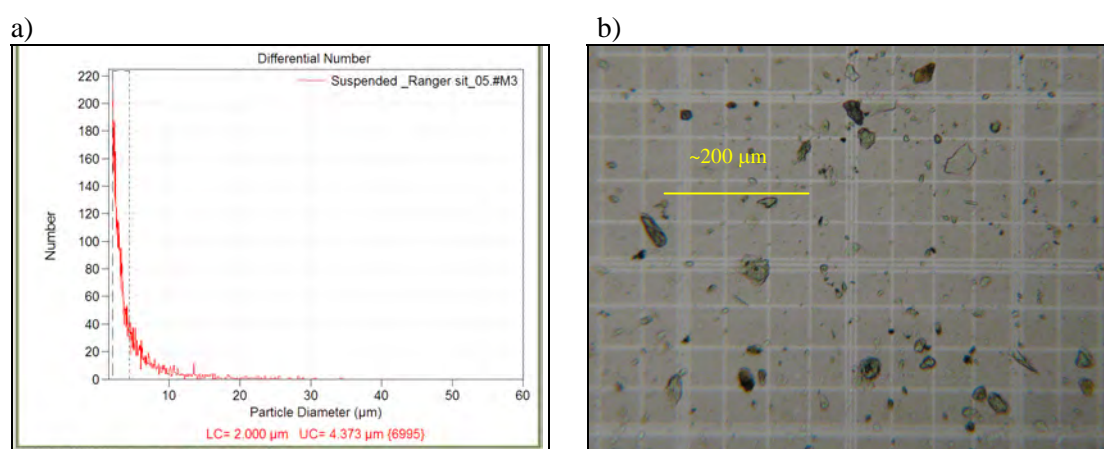


Figure 2 Laterite sample from Ranger Pit 3. Wet-sieved and diluted 1:1200 (unknown concentration).
a) Particle size analysis from the Coulter counter showing the majority of particles are $<2 \mu\text{m}$
b) an image of the same sample from a compound microscope.

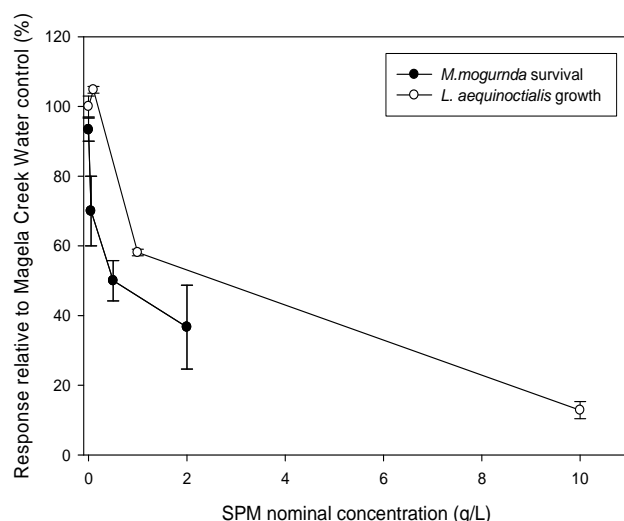


Figure 3 Effect of SPM isolated from Pit 3 on the survival of *M. mogurnda* and the growth of *L. aequinoctialis*. Data points represent the mean \pm standard error of three replicates.

The initial toxicity test with *Chlorella* sp identified that electronic particle counting and light microscopy were unable to distinguish algal cells in the presence of sediment particles. Subsequently, a mercury vapour lamp (Leitz) was procured to upgrade the laboratory's microscope capability to distinguish living (auto-fluorescent) and non-living (inorganic) particles.

Production of the SPM Standard Reference Material (SRM)

The transitional waste rock material collected from the trial landform had a 10% yield of fine particles (ie <63 µm fraction). This composition of fine material was comparable with the 'laterite' material collected from Pit 3, although improvements in the isolation process may have increased the yields. Currently, 600 g of this material has been produced with an aim of producing a total of 1 kg prior to the start of the comprehensive program of toxicity testing.

Steps for completion

The current focus of this project is the production of SPM-SRM, which is proceeding steadily. Following collection of a suitable amount of this material, the physico-chemistry of the SPM-SRM will be characterised in detail. However, this material presents a number of significant challenges due to its heterogeneity and unique optical properties. Thus different methods need to be compared and measurement results validated. Consequently, a significant collaboration with the National Measurement Institute (NMI) is in the process of being developed. Potential studies will include physico-chemical characterisation of the SPM-SRM as a powder, and in Magela Creek Water and Synthetic Soft Water over the test durations, measurement of test solution concentrations, investigations into the effect of dissolved organic carbon on particle agglomeration and comparisons with field samples of interest (eg trial landform runoff).

Laboratory-based concentration-response testing for the *eriss* suite of six species will commence in late 2009. This may involve developing and employing novel test designs, eg fluorescence microscopy will be used for the algal assay. Further concentration-response experiments will investigate the effects of different methods (eg the use of orbital shakers) for maintaining particles in suspension and will also incorporate different exposure durations (and possibly frequencies). In addition, samples of runoff obtained from the trial landform project will be used to compare the toxicity and physico-chemistry of sediments being washed from the mine site to that of the SPM-SRM produced in the laboratory.

References

- Berry W, Rubinstein N & Melzian B 2003. *The biological effects of suspended and bedded sediment (SABS) in aquatic systems: A review*. Internal Report National Health and Environmental Effects Laboratory, Office of Research and Development, United States Environmental Protection Agency, Narragansett, RI, USA.
- Bilotta GS & Brazier RE 2008. Understanding the influence of suspended solids on water quality and aquatic biota. *Water Research* 42, 2849–2861.
- Land and Water Australia 2007. Salt, nutrient, sediment and interactions: Findings from the national river contaminants program, <http://lwa.gov.au/files/products/river-landscapes/pk071328/pk071328.pdf>. Accessed: 9 September 2009
- Riethmuller N, Camilleri C, Franklin N, Hogan AC, King A, Koch A, Markich SJ, Turley C & van Dam R 2003. *Ecotoxicological testing protocols for Australian tropical freshwater ecosystems*. Supervising Scientist Report 173, Supervising Scientist, Darwin NT.
- Stowar M 1997. Effects of suspended solids on benthic macroinvertebrate fauna downstream of a road crossing, Jim Jim Creek, Kakadu National Park. Internal report 256, Supervising Scientist, Canberra. Unpublished paper.

The toxicity of uranium to sediment biota of Magela Creek backflow billabong environments

R van Dam, C Humphrey, A Harford, S Simpson¹, K Gibb² & J Stauber¹

Background

Research and monitoring of the aquatic impacts of the Ranger Uranium Mine has historically focused on water quality analysis, ecotoxicity testing and in situ monitoring of biota during mine water release, and longer-term biological monitoring of in stream macroinvertebrate and fish communities. This focus on the water column has understandably been a consequence of the fact that water is the primary transport vector for solutes released from the minesite. However, since solutes such as uranium (U) have a high affinity for sediments, sediment quality assessment and derivation of protection trigger values for sediments are aspects of aquatic ecosystem protection that also need to be considered. Such trigger values will have application both for operational water management as well as the development of sediment quality closure criteria for the site.

Internationally there has been little work done on the toxicity of U in sediments to aquatic biota, and the toxicity estimates produced by the few studies that have been published have varied by at least three orders of magnitude. This lack of sediment quality toxicity data is of some concern, not only for the local situation, but also given the projected expansion of the uranium mining industry in Australia. In the only Ranger-related site-specific sediment toxicity study that has been conducted to date, Peck et al (2002) reported that the local chironomid, *Chironomus crassiforceps*, was not affected by sediment U concentrations up to 5000 mg/kg dry weight. The RP1 constructed treatment wetland was the context for this work. However, two recent overseas studies reported significant (~10%) effects of U in sediment at 3 mg/kg dry weight, for the chironomid, *Chironomus riparius* (Dias et al 2008), and 600 mg/kg dry weight, for the worm, *Tubifex tubifex* (Lagauzère et al 2009), with LC50 values of 5.3 mg/kg dry weight and 2900 mg/kg dry weight, respectively.

On the Ranger lease, recent (2007) sediment U concentrations in mine-influenced waterbodies, such as Georgetown Billabong (< 45 mg/kg), are much higher than reference waterbodies (1.2–4.3 mg/kg; eg. Sandy and Buba Billabongs). While U concentrations in the sediments of Georgetown have been systematically higher than those of other natural billabongs of the region since before the start of mining (Noller & Hart 1993), the recent sediment concentrations appear to represent an increase since about 2002 (Humphrey et al 2009). It is unknown whether the concentrations in Georgetown Billabong represent a risk to sediment dwelling biota, but the work by Dias et al (2008) and Lagauzère et al (2009) demonstrates that an investigation is warranted.

In relation to the operational phase of mining, benthic macroinvertebrate communities in the mine-influenced, off-site waterbodies, Georgetown and Coonjimba Billabongs, currently exhibit lower diversity than reference billabongs. Good quality sediment U toxicity data are required to help determine whether the observed impairment is due to U in sediments or to

¹ CSIRO Centre for Environmental Contaminants Research, Lucas Heights, NSW

² School of Science & Primary Industries, Charles Darwin University, NT 0909

other mining or non-mining related factors. For mine closure, sediment quality criteria will also be required for on-site sentinel wetlands, which will serve to capture and ‘polish’ seepage and runoff waters from the rehabilitated mine site, as well as for downstream receptor wetlands.

To address these knowledge needs, a field sediment U toxicity experiment will be undertaken, in collaboration with the CSIRO Centre for Environmental Contaminants Research and Charles Darwin University. A field experiment has several benefits over a laboratory assessment, the key ones being that a field experiment will be more time and cost effective than a laboratory approach (not requiring selection and culturing of suitable local test species, nor development of test protocols) and will be able to assess responses of whole communities of organisms.

Methods

The proposed approach will involve the deployment of U-spiked sediments (in retrievable containers) in (unimpacted) Gulungul Billabong, over the duration of a wet season. At the end of the exposure period, the extent of colonisation of macroinvertebrate, microinvertebrate and microbial communities will be measured in the control and test replicates.

The project plan comprises initial characterisation of sediment biota in the target water body (composition and densities) at the end of the 2008–09 wet season, a pilot range-finding exposure study to be conducted during the 2009–10 wet season and the main experiment to be conducted during the 2010–11 wet season. The initial characterisation study will inform the design of the pilot study which in turn will be used to evaluate/trouble-shoot the proposed approach and exposure design to be used for the main experiment.

Site characterisation

Site biological characterisation was undertaken following a sampling trip to Gulungul Billabong in April 2009. After the study site was identified, 18 sediment samples ($20 \times 20 \times 5$ – 10 cm) were collected along a transect of approximately 15 m at a water depth of 55–60 cm. An additional smaller sample (100 mL), for microbial community analysis (see below), was collected immediately adjacent to the larger sample. The larger samples were wet-sieved through a series of mesh screens (8 mm, 500 μ m, 125 μ m and 63 μ m). The >8 mm fraction was discarded (after ensuring no macro-fauna was present), and the remaining three sediment fractions were collected and preserved in 90% ethanol for microinvertebrate (by Dr Russ Shiel, University of Adelaide, 125 μ m and 63 μ m fractions) and macroinvertebrate (by *eriss*, 500 μ m fraction) sorting, identification and data analysis. Four additional sediment samples (~ 50 mL) were collected along the transect for physico-chemical analysis.

Microbial analysis of the sediments involved total DNA extraction from each sediment sample. The DNA was further analysed by terminal restriction fragment length polymorphism (TRFLP) analysis in which DNA fingerprints are generated that theoretically represent each bacterial species present in the sediment. TRFLP is a low cost snapshot of diversity, and one of the reasons for incorporating it into this study was to determine if the method actually worked on billabong sediment (ie the method is often used to assess the microbiology of arable soils, so this is a relatively new application). To obtain a thorough inventory of bacterial diversity for further comparative studies and to assess the validity of the TRFLP approach, the sediment DNA was also subjected to exhaustive direct sequencing using a new technique called 454 pyrosequencing. CDU has completed the experimental work and is

currently awaiting data analysis from the Australian Genome Research Facility (AGRF). Only the TRFLP results are reported here.

Pilot field study

Moist sediment (~150 kg) was collected to a depth of 5–10 cm from the exposed littoral zone at the study site in August 2009. The sediment was transported to *eriss* where it was prepared for the pilot study. Preparation involved freezing for one week (to sterilise the samples, acknowledging, however, that a number of microinvertebrate forms may survive freezing, Dr Russ Shiel, pers comm), followed by wet sieving through a 2 mm mesh size with deionised water in order to create a slurry (1:1.4 sediment:water) for spiking and mixing. The slurry was split into four 30 L batches for the following treatments: control; 5400 mg/kg sulfate control (as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$); 400 mg/kg U; and 4000 mg/kg U (latter two treatments as $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$). Each sediment batch was placed into three 20 L plastic buckets each with 10 L of slurry. The buckets were sealed and were mixed in a cement mixer for 1 h once every two days until each bucket had been mixed 7 times (14 days).

Following mixing, the sediments for each treatment were recombined in a 50 L Nally® bin, mixed thoroughly, and placed in a cool room in the dark at 4 °C for an initial equilibration period to allow the adsorption of spiked metal (or ion) to the sediment. After 21 days, the sediments were removed from the cool room and placed outdoors (still in the Nally® bins) at ambient temperature (24–35°C) for 10 days to dry to a point where they could be transferred to the experimental containers. Sub-samples for sediment and pore water chemistry were collected on days 0, 7, 14, 21 and 28 post-mixing.

Sub-samples of the bulk sediments were then transferred to the experimental containers (~20 × 20 × 15 cm plastic containers with ~5 mm mesh size sides and base). For each treatment, approximately 2 L (or 2000 cm³ – 20 × 20 × 5 cm) of sediment was placed into each of nine replicate containers. The test containers were then placed in holding containers, covered, and left in a cool room in the dark at 4°C prior to their deployment in the field.

Progress/Results

Site characterisation

Sediment physico-chemistry

The total organic carbon content of the sediment was 5%. Concentrations of key metals/metalloids in whole sediment were as follows (mean ± standard deviation; n = 4): uranium – 6.2 ± 0.5 mg/kg; aluminium – 48 000 ± 4500 mg/kg; arsenic – 2.4 ± 0.3 mg/kg; copper – 32 ± 3.9 mg/kg; iron – 12 000 ± 940 mg/kg; lead – 12 ± 0.9 mg/kg; manganese – 62 ± 5.2 mg/kg; nickel – 18 ± 1.7 mg/kg; and zinc – 13 ± 1.5 mg/kg. Further physico-chemical data were unavailable at the time of completion of this summary.

Microbes

There were significant differences in microbial community level diversity (based on the DNA profiles) amongst the 18 sampling sites (ANOSIM, $p = 0.001$). When ANOSIM was run using transect distance instead of sample site as the factor, communities from the same general location tended to be more closely related ($p = 0.004$). This suggests that species composition was not homogeneous along the transect but exhibited some spatial variation. This is not particularly surprising as communities of microbiota would be expected to exhibit some spatial variation along a transect of reasonable length. This issue can be addressed by taking

additional replicates at each site and/or for each sample. Moreover, experimental units in the pilot and main study will be placed along the transect in a randomly-stratified manner, to account for any systematic natural variability.

The DNA community profiling method can also be used to identify species or ‘operational taxonomic units’ by comparing DNA profiles against an international database of bacterial DNA profiles. The success of this depends on achieving matches to the database, which contains over 30 000 entries, many of which are from temperate regions. Species matches for the sample sites are shown in Table 1. They reveal plausible matches and provide insights into key biogeochemical processes in this system. Unfortunately, the database contains lists of uncultured bacteria with no additional information so these have been grouped together to give an indication of their proportional representation in the community.

The dominant genus was *Burkholderia*, which occupies remarkably diverse ecological niches, ranging from contaminated soils and water to the respiratory tract of humans (Coenye & Vandamme 2003). The most frequently occurring species was the nitrogen fixing *B. tropica*, which is associated with plant roots, and has a climatic range from temperate sub-humid to hot humid (Reis et al 2004). This genus includes the causative agent of Melioidosis *B. pseudomallei* (not found in the current study), which is commonly found in soil and water in this region (Kaestli et al 2007). *Clostridium sulfidogenes* is a recently described mesophilic bacterium isolated from pond sediment, which can degrade peptides and reduce thiosulfate and sulfur (Sallam & Steinbüchel 2009). *C. sulfidogenes* may be involved in sulfur cycling in this system. The lactic acid bacterium, *Lactobacillus ingluviei*, is a member of a genus that is commonly found associated with bird faeces and, although the literature only mentions it in association with pigeons (Nazef et al 2008), it is likely to be associated with a wide range of native bird species. The genus *Pelosinus* was only described in 2007 (Shelobolina et al 2007) and one species that occurs regularly in studies is a fermentative organism that can reduce Fe(III) in the presence of fermentative substrates such as those anions typically found in organic matter (eg formate, acetate, lactate, etc.). Members of this genus may be important to iron geochemistry in this system. The Phylum *Acidobacteria* occurred at most sites, but was not as diverse as *Burkholderia*. This Phylum could be important as the project progresses because its members are ubiquitous, diverse, and abundant in soils and sediments, and can withstand metal-contaminated, acidic, and other extreme environments, including sediments contaminated with U and other potentially toxic materials (Barns et al 2007). Little is known about members of the novel Phyla *Verrucomicrobia* or *Planctomycetes* other than they are proving to be widespread and active in the environment (Joseph et al 2003). Members have been reported from Australia and include thermoacidophilic (acid and heat tolerant) members, which use methane as their sole carbon source (methanotrophs). So far all members appear to play an important role in biogeochemical carbon cycles (Islam et al 2009).

In summary, the TRFLP worked well in that interesting and plausible species were identified, many of which are fastidious anaerobes that would probably have been overlooked in conventional cultivation techniques. The real test for this method will be whether the diversity list has any similarity to the list derived from the exhaustive sequencing exercise. The interest in using TRFLP in the longer term is that it is a very simple and inexpensive laboratory technique requiring little molecular expertise, and lending itself to high throughput, environmental-scale sample analysis.

Table 1 Community summary TRFLP information for microbes occurring in natural Gulungul Billabong sediment samples, April 2009

	Species match	# OTUs ¹	Sample																													
			1a	2a	3a	3b	4a	4b	5a	5b	6a	6b	7a	7b	8b	9a	9b	11a	11b	12a	12b	13a	14a	14b	15a	15b	16a	16b	17a	17b	18a	18b
41	<i>Burkholderia</i> sp	51	X	X	X		X	X	X	X	X	X	X			X	X	X				X	X	X		X	X	X				
	<i>Clostridium sulfidogenes</i>	1																											X		X	
	<i>Lactobacillus ingluviei</i>	1																														X
	<i>Pelosinus</i> sp	1																X														
	<i>Spiroplasma</i> sp	1										X																				
	<i>Thermus yunnanensis</i>	1										X																				
	uncultured Acidobacteria bacterium	1	X	X	X		X	X	X		X	X	X			X	X		X		X	X	X	X			X					
	uncultured <i>Planctomyces</i> sp	1																													X	
	uncultured <i>Pseudomonas</i> sp	1	X	X	X		X	X	X	X	X	X	X	X				X	X			X	X	X		X	X	X				
	uncultured soil bacterium	2						X	X						X		X					X	X	X		X		X				
	uncultured Verrucomicrobia bacterium	1										X	X											X								
	uncultured Xiphinematobacteriaceae	1					X															X										
	uncultured bacterium misc	70	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X
	Total no. OTUs present per site		49	48	44	1	70	52	57	42	51	67	61	40	3	3	6	44	46	1	8	62	52	80	1	51	65	66	1	15	21	20

¹ OTU: Operational taxonomic unit – representative of a genetic variant, and could represent different species and different strains of the same species.

Micro- and macroinvertebrates

Processing of the 63 and 125 μm fractions for microinvertebrates by Dr Russell Shiel was limited mainly to development of a suitable protocol for sub-sampling and extracting organisms, based upon just two or three of the 18 samples. The fine-grained (mud) sediments characteristic of backflow billabongs (such as Gulungul) present particular difficulties for sample processing, requiring meticulous separation of (often) cryptic taxa from sediment particles using fine tungsten needles. Hence sample processing is a slow task. Based upon these results and time estimates for sample processing, more substantive funding has been reserved for processing of samples arising from the pilot study to ensure timely completion of microinvertebrate sorting and identifications.

For the samples that were sub-sampled and processed, taxa lists and relative abundances were provided. Table 2 contains community summary information for these samples. (Summary estimates are minima because only a limited number of samples was processed.) Amongst all samples processed, the microinvertebrate fauna was dominated by protists (in particular, Rhizopoda, Diffugiidae – amoeboids inhabiting a test or shell) and rotifers (in particular, the Lecanidae). According to Dr Shiel, most of the fauna is characteristic of low dissolved oxygen environments. The sediment size fraction with greatest species diversity was the $>63\ \mu\text{m}$ fraction, with the $>125\ \mu\text{m}$ fraction containing a subset of taxa found in the finer fraction (data not provided here).

Table 2 Community summary information for micro- and macroinvertebrates occurring in natural Gulungul Billabong sediment samples, April 2009. (Samples were between 2000-4000 cm^3 volume of sediment.)

Aquatic organism group	Community summary	Sample fraction		
		63–125 μm	125–500 μm	>500 μm
Macroinvertebrates	Total no. taxa recorded (minimum)	–	–	32
	Ave. taxa number per sample (min)	–	–	8.4
	Ave. total abundance per sample	–	–	335
Microinvertebrates	Total no. taxa recorded (min)	34	21	–
	Ave. taxa number per sample (min)	18	12	–
	Ave. total abundance per sample	182 500	17 660	–

For macroinvertebrates contained in the $>500\ \mu\text{m}$ fraction, preserved samples were sub-sampled and sorted under a stereo microscope in the laboratory. All 18 samples were processed, with community summary information for these samples shown in Table 2. In the case of macroinvertebrates, summary estimates are minima because the data are summarised at family-level only for the purposes of this report. Taxa numbers and abundances in the sediments were low, reflecting possibly the fine-grained sediment particles (restricting habitat availability) and low dissolved oxygen environment characteristic of billabong waters at the end of the 2008–09 wet season. Total abundance of macroinvertebrates varied between 82 and 685 organisms per sample (mean = 335, SD=183). The faunal assemblage was dominated by worms, mites, midge larvae and microcrustaceans (Table 3). Relative to typical macroinvertebrate datasets, the data from the full 18 samples demonstrated relatively low variation across the transect.

Table 3 Macroinvertebrate taxa occurring in natural Gulungul Billabong sediment samples, April 2009, ranked by decreasing abundance in samples. Only taxa for which mean number of organisms per sample exceeded one are provided. (Samples were between 2000–4000 cm³ volume of sediment.)

Taxon	Common name	Ave no. per sample
Nematoda	Nematodes (unsegmented worms)	189.2
Oligochaeta	Segmented worms	44.7
Oribatida	Water mites	23.8
Chironomidae	Non-biting midge larvae	15.7
Copepoda	Copepods (microcrustaceans)	9.4
Ostracoda	Ostracods (microcrustaceans)	9.2
Cladocera	Water fleas (microcrustaceans)	8.6
Coleoptera larvae (unident)	Beetle larvae	7.9
Acarina	Water mites	6.1
Ceratopogonidae	Biting midge larvae	3.3
Araneae	Aquatic spiders	3.0
Planorbidae	Freshwater snails	1.9
Chaoboridae	Phantom midge larvae	1.9
Leptoceridae	Caddisfly larvae	1.8
Collembola	Springtails	1.6
Chironomidae	Non-biting midge pupae	1.5
Caenidae	Mayfly larvae	1.1

Pilot study

Sediment physico-chemistry results for the pilot study were unavailable at the time of completion of this summary.

Conclusions

As noted above, the results of the initial site characterisation are being used to inform aspects of the design of the pilot and definitive experiments. They have identified a need to carefully consider the timing of sediment retrieval so as to maximise macroinvertebrate diversity (ie earlier late wet season retrieval when DO levels are higher). The data also serve as a baseline for natural sediments, and have indicated that such fine-grained sediments, DO issues aside, are not optimal for macrobenthic colonisation. This has emphasised the importance of also measuring other components of the sediment biota (microinvertebrates and microbes). Initial microbial analysis based on TRFLP was found to be informative, and identified numerous bacteria of interest. Finally, the data on the variability of the biological communities will be used to optimise the experimental design for the definitive study (eg through power analysis), although the data from the pilot study will be most useful for this purpose.

Steps for completion

- *Pilot study (mid 09 – ~May 10):* Dec 09 – deployment of sediment (in containers) in Gulungul Billabong; April 2010 – retrieval of containers from study site; May–July 2010 – biological and physico-chemical data collection and analysis.

- *Main experiment (mid 10 – ~May 11)* – full scale study to assess the toxicity of sediment-bound U to benthic biota. This will include: June-July 2010 – design of experiment; Aug 2010 – collection of test sediment; Aug-Dec 2010 – spiking and equilibration of test sediment; Dec 2010-May 2011 – deployment of sediment (in containers) in Gulungul Billabong through wet season (possibly with periodic sampling to assess U loss from sediments); May-Aug 2011 – biological and physico-chemical data collection and analysis; and July-Dec 2011 – write up.

References

- Barns SM, Cain EC, Sommerville L & Kuske CR 2007. *Acidobacteria* Phylum sequences in uranium-contaminated subsurface sediments greatly expand the known diversity within the Phylum. *Applied and Environmental Microbiology* 73, 3113–3116.
- Coenye T & Vandamme P 2003. Diversity and significance of *Burkholderia* species occupying diverse ecological niches. *Environmental Microbiology* 5, 719–729.
- Dias V, Vasseur C & Bonzom J-M 2008. Exposure of *Chironomus riparius* larvae to uranium: Effects on survival, development time, growth, and mouthpart deformities. *Chemosphere* 71, 574–581.
- Humphrey C, Turner K & Jones D 2009. Developing water quality closure criteria for Ranger billabongs using macroinvertebrate community data. In *eriss research summary 2007–2008*, eds Jones DR & Webb A, Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 130–135.
- Islam T, Jensen S, Johanne Reigstad L, Larsen Ø & Birkeland N-K 2009. Methane oxidation at 55°C and pH 2 by a thermoacidophilic bacterium belonging to the *Verrucomicrobia* phylum. *Proceedings of the National Academy of Sciences* 105, 300–304.
- Joseph SJ, Hugenholtz P, Sangwan P, Osborne CA & Janssen PH 2003. Laboratory cultivation of widespread and previously uncultured soil bacteria. *Applied and Environmental Microbiology* 69, 7210–7215.
- Kaestli M, Mayo M, Harrington G, Watt F, Hill J, Gal d & Currie BJ 2007. Sensitive and specific molecular detection of *Burkholderia pseudomallei*, the causative agent of Melioidosis, in the soil of tropical northern Australia. *Applied and Environmental Microbiology* 73, 6891–6897.
- Lagauzère S, Terrail R & Bonzom J-M 2009. Ecotoxicity of uranium to *Tubifex tubifex* worms (Annelida, Clitellata, Tubificidae) exposed to contaminated sediment. *Ecotoxicology & Environmental Safety* 72, 527–537.
- Nazef L, Belguesmia Y, Tani A, Prévost H & Drider D 2008. Identification of lactic acid bacteria from poultry feces: Evidence on anti-*Campylobacter* and anti-*Listeria* activities. *Poultry Science* 87, 329–334.
- Noller BN & Hart BT 1993. Uranium in sediments from the Magela Creek catchment, Northern Territory, Australia. *Environmental Technology* 14, 649–656.
- Peck MR, Klessa DA & Baird DJ 2002. A tropical sediment toxicity test using the dipteran *Chironomus crassiforceps* to test metal bioavailability with sediment pH change in tropical acid-sulfate sediments. *Environmental Toxicology & Chemistry* 21, 720–728.
- Reis VM, Estrada-de los Santos P, Tenorio-Salgado S, Vogel J, Stoffels M, Guyon S, Mavingui P, Baldani VLD, Schmid M, Baldani JI, Balandreau J, Hartmann A &

- Caballero-Mellado J 2004. *Burkholderia tropica* sp. nov., a novel nitrogen-fixing, plant-associated bacterium. *International Journal of Systematic and Evolutionary Microbiology* 54, 2155–2162.
- Sallam A & Steinbüchel A 2009. *Clostridium sulfidogenes* sp. nov., a new mesophilic, proteolytic bacterium isolated from a pond sediment, able to reduce thiosulfate and sulfur. *International Journal of Systematic and Evolutionary Microbiology* 59, 1661.
- Shelobolina ES, Nevin KP, Blakeney-Hayward JD, Johnsen CV, Plaia TW, Krader P, Woodard T, Holmes DE, VanPraagh CG & Derek RL 2007. *Geobacter pickeringii* sp. nov., *Geobacter argillaceus* sp. nov. and *Pelosinus fermentans* gen. nov., sp. nov., isolated from subsurface kaolin lenses. *International Journal of Systematic and Evolutionary Microbiology* 57, 126–135.

Atmospheric radiological monitoring in the vicinity of Ranger and Jabiluka

A Bollhöfer, R Cahill, R Thorn, J Pfitzner & A Esparon

Introduction

The inhalation pathway has previously been identified as the main contributor to public dose from the Ranger mine site for an adult living in Jabiru and working in Jabiru East during the operational phase (Martin 2000). Both Energy Resources of Australia Ltd and SSD monitor the two airborne exposure pathways in the region. The two potential pathways are radioactivity trapped in or on dust (or long lived alpha activity, LLAA) and radon decay products (RDP). Of these two airborne pathways, RDP accounts for most of the dose received by the public (Supervising Scientist 2007, ERA 2009).

The dose limit to the public for exposure from a planned exposure situation (such as an operating uranium mine) recommended by the International Commission on Radiation Protection (ICRP) is 1 milli Sievert (mSv) per year and applies to the sum of all pathways and relevant practices to which people could potentially be exposed. Furthermore, the ICRP (2007) recommends that in order to optimise radiation protection for planned exposure situations a public dose constraint should be selected, that is 'less than 1 mSv and a value of no more than about 0.3 mSv would be appropriate'. Consequently, a dose constraint of 0.3 mSv has been applied when assessing radiological monitoring data for the Ranger mine.

Since the main areas of habitation in the vicinity of Ranger and Jabiluka are Jabiru, Mudginberri and Jabiru East, the SSD monitoring program focuses on those three population centres (see Map 3). RDP and LLAA concentrations in the air are measured monthly and the results are compared with those from ERA's atmospheric radiological monitoring program.

Results

Radon pathway

Figure 1 shows the quarterly RDP data from Jabiru Water Tower, Jabiru East and the Mudginberri Four Gates Road Radon Station measured by *eriss* from early 2003 to September 2009. Two Environmental Radon Decay Product Monitors (ERDM) are now used for RDP monitoring. The instrument located at Mudginberri Radon Station logs data continuously, whereas the second instrument is moved between sites at Jabiru and Jabiru East.

A two sample t-test shows there is no statistically significant difference ($p = 0.974$) between the RDP concentrations measured at Jabiru Water Tower and Mudginberri Four Gates Road Radon Station, the latter of which is considered a background site. Average RDP concentration measured from July 2003 to June 2009 at the Mudginberri and Jabiru Water Tower site is $0.046 \mu\text{J}/\text{m}^3$. The Jabiru East values are significantly higher ($p = 0.003$) and the average is $0.072 \mu\text{J}/\text{m}^3$. RDP concentrations at Jabiru East show more variation due to the closer proximity of Jabiru East to the mine pit and ore stockpiles, the largest localised sources of radon in the area.

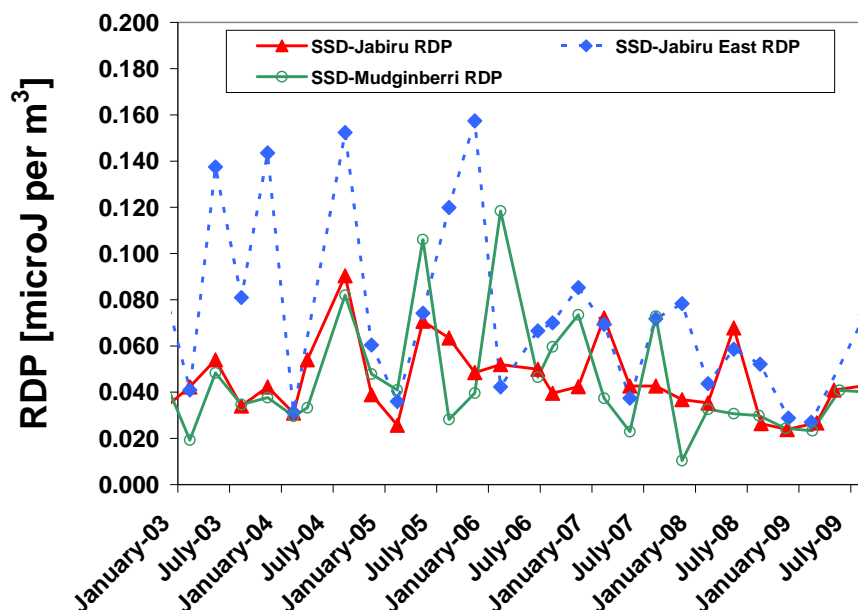


Figure 1 Radon decay product concentration measured by SSD at Jabiru, Jabiru East and Mudginberri

In Jabiru, most of the mine origin radon has dispersed, and variations in concentrations are mainly caused by diurnal meteorological effects, and the annual cycle of wet and dry seasons. Airborne radon concentrations are generally lower during the wet season, as radon exhalation from the soil decreases with increasing soil moisture content. The influence of other factors such as soil ^{226}Ra activity concentration, soil morphology, and vegetation cover have been investigated and the results from this study have been published (Lawrence et al 2009).

ERA estimates the mine origin RDP using a wind correlation model and calculates the exposure via the radon pathway. Table 1 shows the annual averages for the radon decay product concentrations measured by *eriss*, and reported by ERA, at Jabiru and Jabiru East, and the calculated total annual doses from RDP inhalation. This dose calculation assumes an occupancy of 8760 hrs (1 year) and a dose conversion factor for the public of 0.0011 mSv per $\mu\text{J}/\text{hr}/\text{m}^3$. The RDP concentration for the mine related dose calculated for 2008 is very small and is only about 3% of the public dose constraint.

Table 1 Average radon decay product concentrations (ERA 2008, in brackets) at Jabiru, Jabiru East and Mudginberri, and associated total and mine derived annual doses received at Jabiru, between 2006 and 2008

		2006	2007	2008
RDP concentration [$\mu\text{J}/\text{m}^3$]	Jabiru East	0.066 (0.071)	0.064 (0.059)	0.046 (0.033)
	Jabiru	0.046 (0.039)	0.049 (0.038)	0.038 (0.037)
	Mudginberri	0.075	0.036	0.029
Total annual dose [mSv] Jabiru		0.44 (0.38)	0.47 (0.37)	0.37 (0.36)
Mine derived dose [mSv] at Jabiru ^a		0.003	0	0.010

^a predicted from wind field model

Dust pathway

Atmospheric dust activity concentrations are routinely monitored by both *eriss* (Jabiru, Jabiru East and Mudginberri radon station) and ERA (Jabiru and Jabiru East). Figure 2 shows

the LLAA at Jabiru, Jabiru East and Mudginberri measured by *eriss* from early 2003 to July 2009. In 2007, permanent dust samplers were installed at Jabiru and the Mudginberri Four Gates Rd radon stations, to allow for regular sampling of LLAA at these locations.

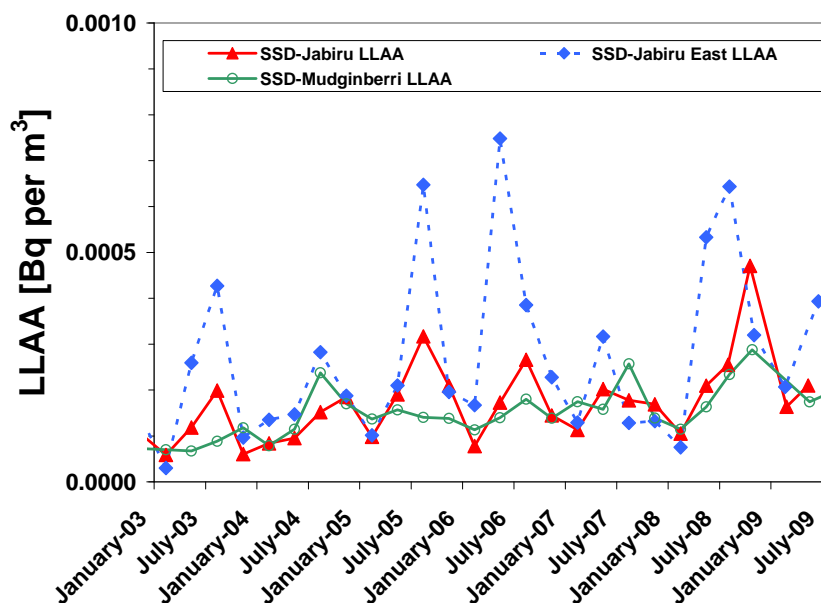


Figure 2 Long lived alpha activity concentration measured at Jabiru, Jabiru East and Mudginberri

Similar to the atmospheric radon concentration, the dust concentration is lower during the wet season due to the higher soil moisture content that suppresses dust generation. Generally, the LLAA concentration is higher at Jabiru East due to its closer proximity to the mine. The averages measured from early 2003 to June 2009 at Jabiru, Jabiru East and Mudginberri are 0.00018, 0.00028 and 0.00016 Bq·m⁻³, respectively. There is no statistically significant difference between the Mudginberri and Jabiru sites ($p = 0.316$).

The total annual dose from inhalation of dust is calculated using a dose conversion factor for of 0.0057 mSv per alpha decay per second (Zapantis 2001) and a breathing rate of 7300 m³ per year for adults (UNSCEAR 2000). The total dose was 11 µSv per annum in Jabiru for 2008, and only a small fraction (ie ~2 µSv for a person working in Jabiru East and living in Jabiru) of that dose would be mine-related (Bollhöfer et al 2006).

Steps for completion

The routine monitoring of dust and radon progeny will continue at Jabiru, Mudginberri Four Gates Road Radon Station and Jabiru East. Permanent dust samplers have now been installed at the three monitoring sites. Continuous RDP monitors have been acquired and tested at Mudginberri Four Gates Road Radon Station, and two additional units will be permanently deployed at the Jabiru Water Tower and the Jabiru Field Station in 2009.

Summary

Monitoring of radon and dust exposure pathways over the past 7 years has shown that the only significant contribution to radiological exposure of the public at Jabiru via inhalation is the inhalation of radon decay products. Although the contribution from the mine site has been

shown consistently to be much less than the public dose constraint of 0.3 mSv per year and is of no concern according to current best practice standards, atmospheric monitoring will continue to provide re-assurance to the public that the risk from inhalation of mine derived radionuclides remains very low.

References

- Bollhöfer A, Honeybun R, Rosman KJR and Martin P 2006. The lead isotopic composition of dust in the vicinity of a uranium mine in northern Australia and its use for radiation dose assessment. *Science of the Total Environment* 366, 579–589.
- ERA 2009. Radiation Protection and Atmospheric Monitoring Program, Report for the Year Ending 31 December 2008. Energy Resources of Australia Ltd Ranger Mine, Jabiru NT.
- Lawrence CE, Akber RA, Bollhöfer A and Martin P 2009. Radon-222 exhalation from open ground on and around a uranium mine in the wet-dry tropics. *Journal of Environmental Radioactivity* 100, 1–8.
- Martin P 2000. Radiological impact assessment of uranium mining and milling. PhD thesis. Queensland University of Technology, Brisbane.
- Supervising Scientist 2007. *Annual Report 2006–2007*. Supervising Scientist, Darwin.
- UNSCEAR 2000. *Source and effects of ionising radiation, vol 1–2*. United Nations Scientific Committee on the Effects of Atomic Radiation. United Nations, NY.
- Zapantis A 2001. Derivation of the dose conversion factor for the inhalation of uranium ore dust considering the effects of radon loss. *Radiation Protection in Australasia* 18, 35–41.

Monitoring of radionuclides in groundwater at Ranger

B Ryan

Introduction

Groundwater samples are collected from Ranger uranium mine on an annual basis by the Northern Territory Department of Resources (DOR; formerly known as Department of Regional Development, Primary Industry, Fisheries and Resources). These samples are analysed for a suite of dissolved metals and radionuclides by the Supervising Scientist Division (SSD) and for metals and major ions by DOR. The results produced contribute to the understanding of the temporal and spatial variability in particular of uranium and radium in groundwater at the mine.

The data collected over the years assist in providing insights into contaminant sources and groundwater transport processes. More importantly, the contemporary and historical data from SSD, DOR and Earth Water Life Sciences (EWLS) will contribute to the production of an agreed pre-mining baseline dataset, which will in turn help develop closure criteria for groundwater quality and provide the basis for validating hydrogeological modelling of the backfilled pits and other rehabilitated structures.

The groundwater monitoring program will need to be continued during and following the mine's rehabilitation to assess the rehabilitation success and the integrity of the pits as tailings repositories.

Methods

Radionuclide activity and metal concentrations are measured in groundwater samples collected annually by DOR at the end of the dry season from selected bores around the site. Heavy metal concentrations are determined via a combination of ICP-MS and ICP-OES methods. Radionuclides of interest are radiochemically separated from the bulk water samples, and measured via alpha spectrometry. Radiochemical methods are published in Martin and Hancock (2004) and Medley et al (2005).

As thorium and lead are particle reactive and readily adsorbed and removed from solution, it is not expected that either of these metals will migrate significant distances through the groundwater aquifers. Consequently, the priority list for the more mobile U-series radionuclides that may contaminate the groundwater comprises: ^{238}U , ^{234}U and ^{226}Ra . These radioisotopes are the focus of the groundwater monitoring program. The $^{234}\text{U}/^{238}\text{U}$ activity ratio in particular may be a useful tracer to discriminate natural ($^{234}\text{U}/^{238}\text{U}$ generally > 1) from mine related ($^{234}\text{U}/^{238}\text{U} \approx 1$) uranium in groundwater (Ryan & Bollhöfer 2007).

Results

All the groundwater data that have been collected at Ranger by the Supervising Scientist Division over the last 25 years have been validated and checked for quality. A summary of the bores that have been monitored is presented in Table 1. The number of years for which

data are available are listed in the table, although it should be noted that not all analytes were measured every year, and sometimes only a limited suite of dissolved metals were analysed. A full version of the table will be contained in an Internal Report to be produced on Ranger groundwater data collected by SSD.

Ranger bore histories and bore logs have been acquired from EWLS in 2009 and this information will be used to enhance the knowledge and understanding of the Ranger groundwater sampling sites. Lithological and stratigraphical information from these logs will allow the standardising of geological descriptions. The screen depths and hence the aquifers the bores draw from will be able to be assigned to each hole. All of this information will be placed on the SSD Ranger groundwater GIS database which is being developed to facilitate the review and examination of the data.

Table 1 A summary of all historical groundwater data collected by SSD 1984–2008

Bore	Collection years	^{234,238} U	²¹⁰ Po	^{226,228} Ra	^{230,232} Th	²²⁷ Ac	²¹⁰ Pb	⁴⁰ K	¹³⁷ Cs	ICPMS
79/1	85–96	x		x	x		x			
79/2	85–89	x		x	x		x			
79/6A	89–92	x		x	x	x	x	x	X	
79/9	89–96	x		x	x		x	x		
83_1	03–06	x		x						x
83_1 Deep	06–07	x		x						x
B11	Sep-06–07	x		x						x
C1SHALLOW	03	x		x						
MBH	03	x		x						
MBL	03	x		x						
MC24	03	x		x						
MC27	03–04	x		x						
MC27 Deep	Sep-06	x		x						
OB1A	89–08	x		x	x	x	x	x	X	x
OB2A	88–02	x		x						
OB4A	88–01	x		x	x	x	x	x	X	x
OB6A	88–02	x	X	x	x	x	x	x	X	x
OB7A	89–02	x		x	x	x	x		X	
OB9A	88–99	x	X	x	x	x	x	x	X	x
OB10A	89–02	x	X	x	x	x	x	x		
OB11A	85–97	x	X	x	x	x	x	x	X	
OB12A	89–96	x		x	x	x	x			
OB13A	85–98	x	X	x	x	x	x		X	
OB15	88–96	x	X	x	x	x	x	x	X	
OB15A	96–97	x								
OB16	85–97	x	X	x	x	x	x	x	X	
OB17A	88–02	x		x	x		x	x	X	x
OB18A	88	x	X	x	x	x	x	x	X	
OB19A	89–2	x	X	x	x	x	x		X	x
OB20	89–08	x		x	x		x	x		x
OB21A	89–08	x		x	x		x	x	X	x
OB22	84–89	x	X	x	x	x	x	x		x
OB23	89–08	x		x	x		x	x		x
OB24	89–02	x		x	x		x			X
OB26	88–89	x	X	x	x	x	x	x		
OB27	03–08	x		x						x
OB28	89–00	x		x	x		x	x		
OB29	85–02	x		x	x		x	X		x
OB30	89–08	x		x	x		x	x		x
OB41	89			x	x		x	x	X	

Bore	Collection years	^{234,238} U	²¹⁰ Po	^{226,228} Ra	^{230,232} Th	²²⁷ Ac	²¹⁰ Pb	⁴⁰ K	¹³⁷ Cs	ICPMS
OB43	89			x	x		x		X	
OB44	89–02	x	x	x	x	x	x	x		x
OB46	89	x	X	x	x	x	x			
OB47	89–90	x	X	x	x	x				
OB48	89–90	x	X	x	x	x				
OB49	89	x	X	x	x	x				
OB50	89	x	X	x	x	x				
OB51	89	x	X	x	x	x				
OB79/6A	92	x								
OB79B	96	x								
RN23551	89–07	x		x	x	x				x
RN9329	03–08	x		x						x
RP1N1	03	x		x						
RP1N2	03	x		x						
TDSCN	89	x		x		x				
TDSC-S	89					x				
TD(East Wall)	89	x		x						
TD(Westall)	89					x				
C12	08									x
MC24	03									x
MC27	03–04									x
MC27DEEP	06									x
RN22211	08									x
RN23562	08									x

Steps for completion

SSD has reviewed and organised its historical groundwater data and placed the data into spreadsheets and databases. All spatial information for the bores sampled by SSD has been entered into the SSD Ranger groundwater ArcGIS database. The aim for 2009–10 is for DOR and EWLS to complete the processing of their respective available data sets so data can be combined and entered into an overall groundwater GIS database, with each organisation validating and entering their data into this database.

It is then intended to review the data from a hydrogeological perspective and determine their appropriateness for representation of the groundwater characteristics in the Ranger area. In particular, the aim is to produce an agreed set of groundwater quality baseline data that will be used to develop closure criteria for Ranger groundwater. This is a high priority objective given the hydrogeo/chemical modelling outputs that will be required to support the closure strategy for Pit 1 in the short term, and Pit 3 in the longer term.

The review will also provide the basis for each organisation to reassess the scopes of their respective groundwater sampling programs and allow any significant inadequacies to be addressed. The information gained will form the basis of recommendations for possible changes to the scope and extent of far-field groundwater quality monitoring at Ranger and the involvement of the Supervising Scientist Division.

Acknowledgments

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References

- Martin P & Hancock GJ 2004. *Routine analysis of naturally occurring radionuclides in environmental samples by alpha-particle spectrometry*. Supervising Scientist Report 180, Supervising Scientist, Darwin NT.
- Medley P, Bollhöfer A, Iles M, Ryan B & Martin P 2005. Barium sulphate method for radium-226 analysis by alpha spectrometry. Internal Report 501, June, Supervising Scientist, Darwin. Unpublished paper.
- Ryan B & Bollhöfer A 2007. A summary of radionuclide activity and dissolved metal concentrations in Nabarlek borewaters from 1996 to 2005. Internal Report 530, September, Supervising Scientist, Darwin. Unpublished paper.

Surface water radiological monitoring in the vicinity of Ranger and Jabiluka

P Medley, A Bollhöfer & K Turner

Introduction

Surface water samples in the vicinity of the Ranger and Jabiluka project areas are routinely measured for their radium-226 (^{226}Ra) activity concentrations to check for any significant increase in ^{226}Ra activity concentrations downstream of the impacted areas. This is due to the potential risk of increased exposure to radiation via the biophysical pathway due to mining activities. Mussels, in particular, bioaccumulate radium, which may then be incorporated into the human body upon consumption. Water samples are collected weekly in Magela Creek (Ranger) from both upstream and downstream sites, and monthly from Ngarradj Creek (Jabiluka) downstream site. Samples are not collected from these locations during the dry season when there is no contiguous surface water flow.

All Ngarradj samples are analysed for total ^{226}Ra by *eriss*'s environmental radioactivity laboratory using a method described in Medley et al (2005). From the 2006–07 wet season onwards, weekly samples obtained from Magela Creek have been combined to give monthly averages. Analyses of the complete data set and combined wet season samples from previous years had shown that combining weekly samples would provide valid monthly radium results.

Results

Magela Creek

The ^{226}Ra activity concentration data for the 08–09 wet season in Magela Creek are compared with previous wet seasons in Figure 1.

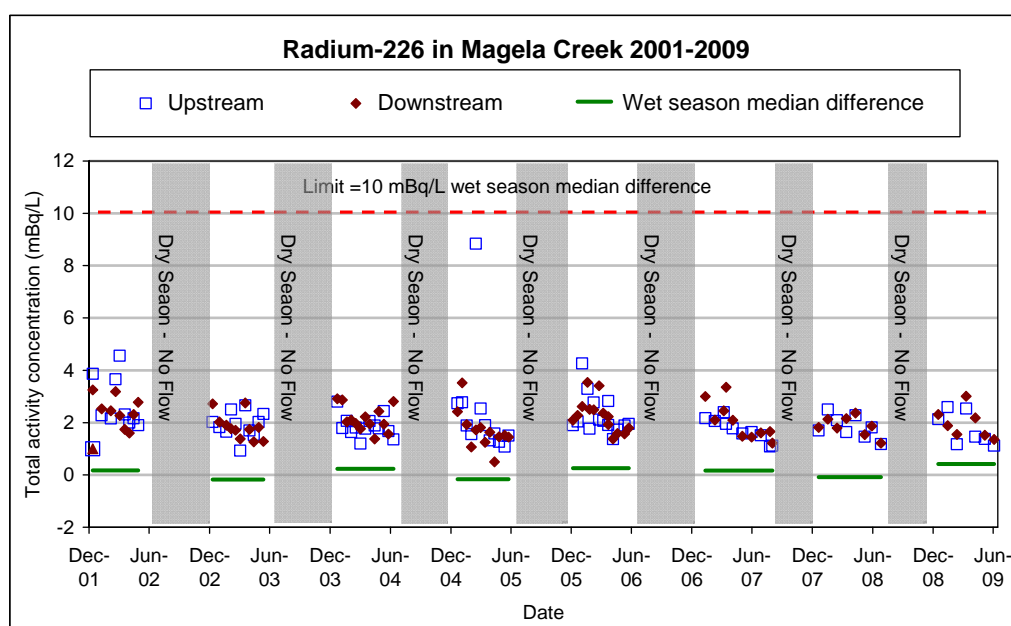


Figure 1 Radium-226 in Magela Creek for the 2001–09 wet seasons

The data show that not only are the levels of ^{226}Ra very low both upstream and downstream of Ranger mine, but also there is no difference between these locations. Wet season median values for each location and the wet season median difference between locations are reported in Tables 1 and 2.

Table 1 Median and standard deviations of the ^{226}Ra activity concentration for individual wet seasons (2002–06)

		2002–03	2003–04	2004–05	2005–06
Magela Creek					
Median and standard deviation	upstream	2.0 (\pm 0.5)	1.8 (\pm 0.4)	1.7 (\pm 2.1)	2.0 (\pm 0.8)
	downstream	1.8 (\pm 0.5)	2.0 (\pm 0.5)	1.6 (\pm 0.7)	2.3 (\pm 0.7)
Wet season median difference		-0.2	0.2	-0.2	0.3
Ngarradj					
Median and standard deviation	upstream	1.4 (0.6)	1.1 (\pm 0.4)	1.3 (\pm 0.3)	1.0 (\pm 0.4)
	downstream	1.1 (1.5)	0.9 (\pm 0.9)	1.0 (\pm 0.6)	0.5 (\pm 0.5)
Wet season median difference		-0.3	-0.2	-0.3	-0.5

Table 2 Median and standard deviations of the ^{226}Ra activity concentration for individual wet seasons (2006–09) and for the entire study period (2001–09)

		2006–07	2007–08	2008–09	All years 2001–09
Magela Creek					
Median and standard deviation	upstream	1.7 (\pm 0.4)	2.0 (\pm 0.5)	1.5 (\pm 0.6)	1.9 (\pm 1.0)
	downstream	1.9 (\pm 0.7)	1.9 (\pm 0.4)	1.9 (\pm 0.6)	1.9 (\pm 0.6)
Wet season median difference		0.2	-0.1	0.4	0.0
Ngarradj					
Median and standard deviation	upstream	1.1 (\pm 0.5)	N/A	N/A	1.1 (\pm 0.5)
	downstream	1.0 (\pm 0.3)	1.0 (\pm 0.3)	1.0 (\pm 0.3)	1.0 (\pm 1.7)
Wet season median difference		-0.1	N/A	N/A	-0.1 [#]

[#] median for 2001–2007

A limit of 10 mBq/L increase above natural (upstream) background in total ^{226}Ra concentration in surface waters downstream of Ranger has been defined for human radiological protection purposes (Klessa 2001). This value was based on the potential dose received from the ingestion of ^{226}Ra in the freshwater mussel *Velesunio angasi* (Martin et al 1998).

Each wet season the difference value is calculated by subtracting the upstream median from the downstream median (Sauerland et al 2005). This difference is called the wet season median difference (shown by the solid green lines in Figures 1 and 2) and should not be more than the limit of 10 mBq/L. The wet season median difference for the entire 2001–09 wet season data set is approximately zero. The data for the eight sampling seasons indicate that

^{226}Ra levels in Magela Creek are due to the natural occurrence of radium in the environment (upstream data) and that ^{226}Ra activity concentrations in Magela Creek water are not elevated (wet season median difference of zero) downstream of Ranger mine.

Ngarradj Creek

^{226}Ra activity concentrations in Ngarradj are very low. Although there were significant upstream-downstream differences observed in individual samples during the first two wet seasons, Figure 2 shows that ^{226}Ra activity concentrations at the Ngarradj downstream site have been similar to those at the upstream site since December 2003. This coincides with the establishment of the long-term care and maintenance phase at Jabiluka in the 2003 dry season. The wet season median difference is approximately zero for all years, except for the 2001–02 wet season. However, even in that season the wet season median difference was very low ($< 2 \text{ mBq}\cdot\text{L}^{-1}$), indicating human health was not at risk from the presence of ^{226}Ra in Ngarradj.

Since monitoring data from 2003 onwards have shown that there has been no significant difference between upstream and downstream values, and moreover since the absolute values are in any case very low and barely above detection limit, monitoring at the upstream site has been discontinued while Jabiluka remains in long-term care and maintenance. From the 2007–08 wet season onwards, the downstream data for each season are compared with the previous season's data for this location to check that there are no significant upward deviations from this control record. ^{226}Ra results (monthly samples) for the 2008–2009 wet season at the Ngarradj downstream site are comparable with the very low values of previous years, indicating that the downstream environment remains unimpacted. A t-test indicated that there is no significant difference between the 2008–09 data and the previous 5 wet seasons ($P = 0.476$).

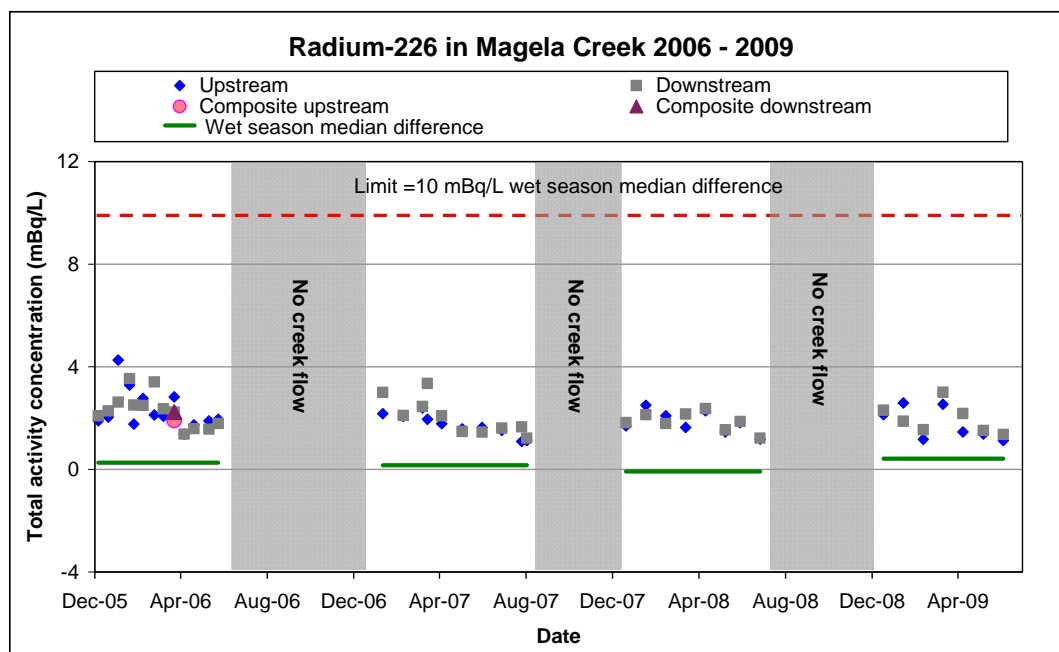


Figure 2 ^{226}Ra Radium in Ngarradj Creek for the 2001–09 wet seasons

References

- Klessa D 2001. Water Quality in Magela creek upstream and downstream of Ranger. Internal Report 380, Supervising Scientist, Darwin, Unpublished paper.
- Martin P, Hancock GJ, Johnston A & Murray AS 1998. Natural-series radionuclides in traditional north Australian Aboriginal foods. *Journal of Environmental Radioactivity* 40, 37–58.
- Medley P, Bollhöfer A, Iles M, Ryan B & Martin P 2005. Barium sulphate method for radium-226 analysis by alpha spectrometry, Internal Report 501, Supervising Scientist, Darwin, Unpublished paper.
- Sauerland C, Martin P & Humphrey C 2005. Radium 226 in Magela Creek, northern Australia: Application of protection limits from radiation for humans and biota, *Radioprotection*, Suppl 1, 40(2005), 451–456.

Surface water transport of mine-related solutes in the Magela Creek catchment using continuous monitoring techniques

K Turner & D Jones

Background

Continuous monitoring of surface waters around Ranger mine is conducted by both SSD (at Magela Creek upstream and downstream sites, MCUGT and MCDW respectively) and ERA (at RP1 and GC2). These data are used for the assessment of potential impacts arising from activities carried out on the mine site (Supervising Scientist 2007, 2008, Turner et al 2008a,b, Turner 2009, Turner & Jones 2009). Relevant background information has been reported previously at ARRTC 22 (see Turner & Jones 2009).

A critical attribute of SSD's continuous monitoring network is the ability to remotely monitor (via 3G telemetry) events in the creek system. Telemetry provides a means for early warning of increases in sediment or solute inputs from the minesite. The continuous monitoring data are also used to quantify annual loads of solutes and sediment, with the aim of tracking overall performance of the mine's water management system from year to year (Turner & Jones 2009). Since 2005–06, Mg loads in Magela Creek have been derived each wet season using continuous EC data recorded at 10 minute intervals. By comparing the total mass of solutes measured downstream of the mine in Magela Creek with the mass of solutes from point and diffuse sources from upstream of the mine, a dynamic assessment of the intra- and inter-seasonal fluxes of salts in the system can be made.

Methods

Detailed continuous monitoring methods have been reported previously at ARRTC 22 (Turner & Jones 2009). Continuous monitoring over 2008–09 wet season included some changes to the reported methods summarised as follows:

- 1 Up until the 2008–09 wet season, two downstream monitoring stations were maintained, each located in different channels in an anastomosed section of Magela Creek slightly downstream of G8210009. During 2008–09 wet season, only the station located within the western-most channel of Magela Creek was monitored (MCDW);
- 2 Grab samples collected as part of the routine weekly grab sampling program were collected alongside the pontoons, allowing direct comparison between grab and continuous data (see 'Results of the stream monitoring program in Magela Creek catchment', *eriss* research summary 2007–08, Brazier 2009);
- 3 The automatic samplers were programmed to collect:
 - a weekly samples at the upstream and downstream stations on the same day as the routine weekly grab sampling program;
 - b event-based samples at the downstream station according to pre-set criteria that statistically define significant changes in stream turbidity and EC.

Results

The flow conditions in each of the minesite tributaries and in Magela Creek depend on rainfall occurring both in the upper Magela catchment and in the vicinity of the minesite. Annual total rainfall measured at Jabiru airport (by the Bureau of Meteorology) and cumulative annual flow volumes for Magela Creek (as measured at GS210009, adjacent to the 009C compliance site) since inception of the continuous monitoring program are shown in Table 1. These data show the variability in annual rainfall and resultant discharge.

Table 1 Jabiru rainfall and Magela creek wet season flow conditions since 2005

Year	Annual cumulative rainfall (mm)	Annual cumulative discharge (GL)
2005–06	2107	485.4
2006–07	2540	845.2
2007–08	1673	416.6
2008–09	1186	235.2

Electrical conductivity – magnesium relationships

Relationships between EC and Mg at each of the four continuous monitoring locations (MCUGT, MCDW, RP1 and GC2) have been derived by correlating Mg concentrations in grab water samples with concurrent measurements of in situ EC. These relationships were reported at ARRTC 22 (see Turner & Jones 2009).

The data collected over the 2008–09 wet season have been used to refine the EC-Mg relationships at each of the sites. This was particularly important for:

- 1 MCDW as it lacked higher EC ($>35 \mu\text{S}/\text{cm}$) data points to provide a sufficiently high level of confidence in the fit of the data in this region of the relationship (Turner et al 2009);
- 2 RP1 as Mg concentrations have been on an upward trend over the past few years (ERA 2008).

Inclusion of the higher concentrations of Mg in the MCDW (captured using event-based sampling) and RP1 datasets has resulted in the relationships of best fit changing from linear to a slightly curved quadratic (Figure 1). A linear relationship is still the best fit for the Mg-EC relationships for MCUGT and GC2 (Figure 1).

Different EC-Mg relationships exist for each of the sites as a result of different Mg sources, concentration ranges and relative contributions of the constituent major ions present at each of the sites (Figure 1.). The slope of the regressions for RP1 and GC2 are similar where EC $<500 \mu\text{S}/\text{cm}$, consistent with the similarity of major ion compositions at both sites (Figure 1b and 1c respectively). The non-linear relationship for RP1 where EC $>500 \mu\text{S}/\text{cm}$ is due to the formation of the zero-charged ion pair (MgSO_4^0) which occurs in waters with higher solute concentrations. A neutral ion pair does not contribute to the measured EC. Solution speciation modelling using the thermodynamic computer model MINTQA2 indicates that at the highest concentrations of Mg measured in RP1, the neutral ion pair accounts for approximately 25% of the Mg present. As a result of the formation of the neutral ion pair in RP1, the relationship between EC and Mg is quadratic (Figure 1b).

The slopes for the Magela Creek upstream and downstream sites are similar for periods of flow characterised by EC values of 0 to $20 \mu\text{S}/\text{cm}$, during which periods the solute load is

dominated by water from upstream of the mine site (Figure 1a). This condition can occur when there is little or no input from the minesite, or during flood flows where total load is dominated by solutes coming from upstream. For $EC > 20 \mu S/cm$, the slope for the downstream site is higher, indicating a greater influence of Mg on EC compared with other solutes present, as is expected with input of Mg-dominated mine waters. The existence of these two regimes at the downstream site is a result of variable mixing of upstream waters with mine waters. The resultant composite fit for the EC-Mg relationship is best described by a quadratic function (Figure 1a).

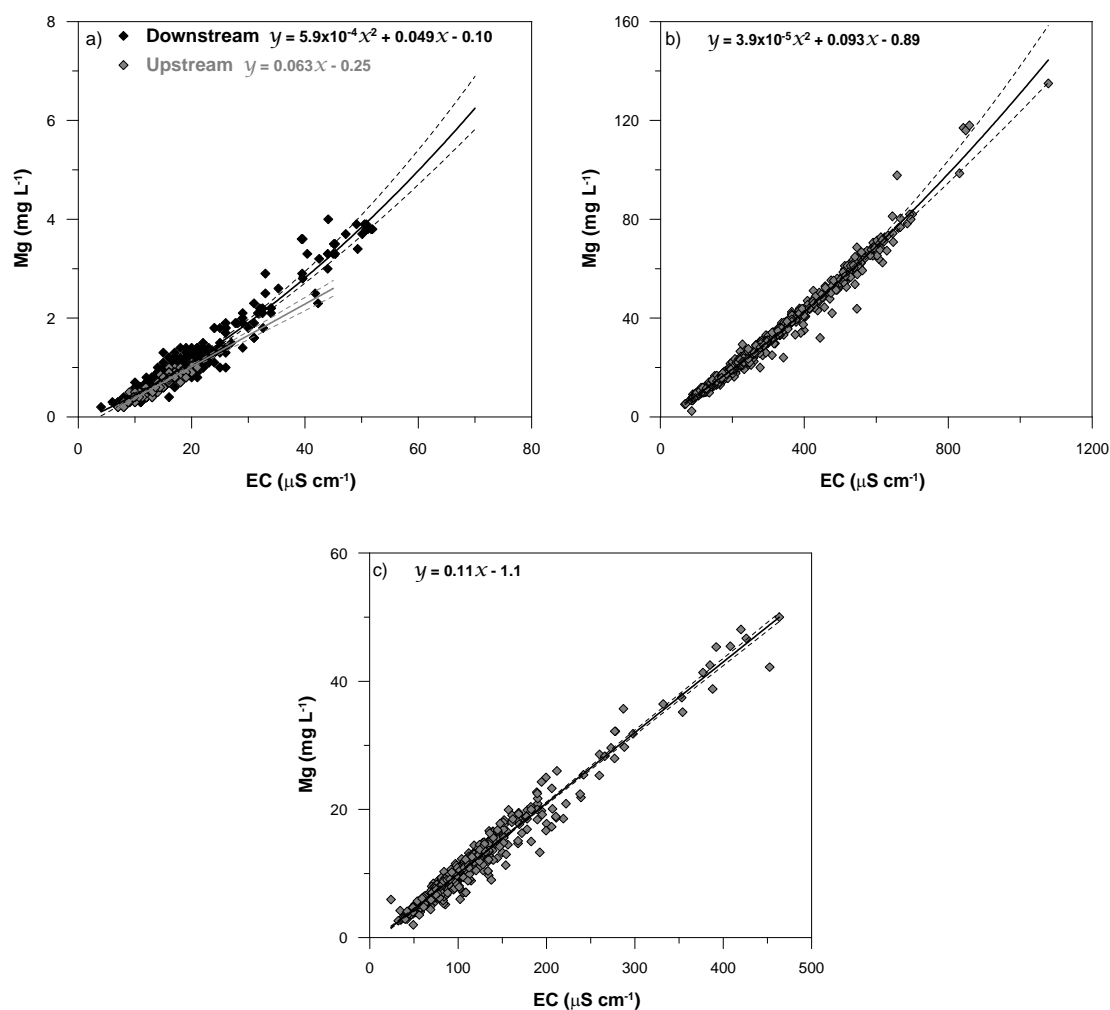


Figure 1 Relationships between EC and Mg concentration and upper and lower 95% confidence limits for the a) upstream ($R^2 = 0.86$, $P < 0.0001$) and downstream ($R^2 = 0.94$, $P < 0.0001$) sites on Magela Creek, b) RP1 ($R^2 = 0.99$, $P < 0.0001$) in the Coonjimba Creek catchment and c) GC2 ($R^2 = 0.96$, $P < 0.0001$) in the Corridor Creek catchment

Magnesium loads

The method used for predicting Mg concentrations using the continuous EC data was described in ARRTC 22 (see Turner & Jones 2009).

Minesite point sources

The Mg concentrations predicted using the continuous EC measurements in the minesite tributaries have been used in conjunction with the measured flows at these locations to calculate

Mg loads moving down these catchment lines through each wet season since 2005–06 (Table 2).

Table 2 Estimated Mg loads (t) exported from Coonjimba (RP1) and Corridor Creeks (GC2) for the 2005–06 to 2008–09 wet seasons

Year	RP1		GC2	
	Volume discharge (GL)	Mg load	Volume discharge (GL)	Mg load
2005–06	1.4	55	2.6	14
2006–07	3.4	110	4.9	17
2007–08	3.1	160	3.4	20
2008–09	0.35	61 ¹	1.3	29

¹ Total is made up of the sum of the load passively discharged (46 t) over the RP1 weir and the load discharged from pumping and siphoning (15 t)

The Mg loads in Table 2 are within the range of previously reported values for RP1 (derived using interpolated weekly grab sample data), with the low value for the 2008–09 wet season reflecting the well below average wet season rainfall (ERA 2008a).

The increased annual Mg load exported from GC2 during 2008–09 is due to additional Mg inputs to the Corridor Creek system, including dry season surface flows from the Pit 1 catchment works and a period of pumped discharge of water (7.05 ML) from RP1 into the upper Corridor Creek catchment during February 2009 (ERA 2008a).

Mine site diffuse sources

To provide an estimate of the Mg load potentially available for export to Magela Creek from the Land Application Areas (LAAs) via shallow groundwater flow during a given wet season, the Mg load added to each of the LAAs during the antecedent dry season has been estimated using water systems management data supplied by ERA in its Annual Wet Season (2008a) and Annual Environment Reports (2008b). The total annual load of Mg applied to each LAA has been estimated using monthly irrigation volumes taken from Ranger Annual Environment Reports (October 2005 to July 2009) and mean monthly Mg concentrations in irrigation waters (RP2 for MLAA and JELAA and cell 9 of RP1WLF for Djalkmara LAA) (Table 3) (ERA 2008a).

Table 3 Mg loads (tonnes) applied to the Magela, Jabiru East and Djalkmara LAAs

Antecedent dry season	Magela LAA	Jabiru East ¹	Djalkmara	Total Mg load
2005	69.5	–	37.4	106.9
2006	75.1	57.2	55.1	187.4
2007	86.3	56.2	64.5	207.0
2008	0.2	2.8	5.4	8.4

¹ Jabiru East was commissioned in 2006

Magela Creek

Magnesium loads in Magela Creek have been calculated over the past four wet seasons using the continuous EC data measured at MCUGT and MCDW and total Magela discharge measured at GS8210009 (Table 4).

The Mg loads measured upstream in Magela Creek during the 2008–09 wet season were lower than for previous years which is consistent with the lower rainfall and consequent runoff experienced in the region during this period. The loads measured at RP1 and GC2 are consistent with values from previous years. The lower loads applied to the LAAs during the 2008 dry season reflect the lower rainfall (and hence runoff) of the preceding wet season.

Table 4 Mg loads (t) measured in Magela Creek (upstream and downstream of the mine) and mine waters (RP1 and GC2) and applied to LAAs

Time period	Magela Creek		Minesite		
	US	DS	RP1	GC2	LAAs
2005–06	174	405	55	14	106.9
2006–07	140	592	114	17	187.4
2007–08	145	371	163	20	207.0
2008–09	82	203	61	29	8.4

US = Upstream; DS = downstream

Load balance at Magela Creek downstream

The total annual Mg load measured in Magela Creek downstream of the mine (*DS*) in any given wet season should be described by Equation 1. Note that LAAs on mine site tributaries (RP1 LAA and Corridor Creek LAA) are assumed to report to Coonjimba Creek or Corridor Creek upstream of the monitoring points RP1 and GC2, respectively, and hence are accounted for in the loads estimated at these point sources.

$$DS = US + RP1 + GC2 + ROC \quad (1)$$

DS = the total annual Mg load measured in Magela Creek downstream of the mine

US = the natural background Mg load for the Magela Creek catchment upstream of the mine site

RP1 = the Mg load input from the Coonjimba Creek catchment including RP1

GC2 = is the Mg load input from the Corridor Creek catchment

ROC = is the Mg load from the rest of the catchment which should be dominated by wet season washout of shallow groundwater from the LAAs on the mine site that are adjacent to Magela Creek (Magela LAA, Djalkmara LAAs and Jabiru East LAA)

Currently, there are two unknowns or unconstrained terms in the above equation. Firstly, the Mg load estimated at the downstream site is a potential overestimate since it is derived using EC data from the west channel only, and Magela flow across all three channels (described in Turner & Jones 2009, Development of Magela Catchment area solute budget using continuous monitoring systems). Secondly, the extent of inter-seasonal washout of Mg from the soil profile in the LAAs has to be inferred as there is no direct measure of this. If there was complete washout, the difference between the loads at the upstream site and the downstream site should equate to the input of mine-derived solutes. Table 5 compares the difference between the upstream and downstream Mg loads in Magela Creek with the sum of potential inputs from mine sources.

The RPD between the measured and predicted downstream Mg loads is typically >100% (with the exception of the anomalous 2007–08 season where the RP1 discharge is questionable), with the measured downstream load being greater than the sum of mine-derived inputs. This is likely to be because the loads estimated at the downstream site are overestimates by virtue of the cross-channel gradient in EC that occurs at low to medium flows at this location (Supervising Scientist 2008).

Table 5 Comparison of the difference between measured and predicted downstream MG loads (tonnes)

Time period	Measured DS load	Predicted DS load (US + RP1 + GC2 + ROC)	RPD%
2005–06	405	350	131
2006–07	592	458	142
2007–08	371	535	58
2008–09	203	180	123

DS = Magela Creek downstream

US = Magela Creek upstream

RPD% = relative % difference between measured and predicted DS Mg load

This flow-dependent lateral distribution of mine-derived Mg has implications for deriving the total Mg load for the creek (across all channels), DS, as the apportioning of the total stream discharge (and EC) between the three channels has not previously been well-defined as a function of flow. Since the Mg loads estimated at MCDW have been calculated by multiplying the total flow across Magela Creek by the characteristically higher Mg measured in the western channel, the loads derived using this procedure are likely overestimates.

This particular issue was addressed during the 2008–09 wet season by measurement of cross channel EC profiles and concurrent discharge in the western channel at MCDW. An Acoustic Doppler Current Profiler (ADCP) was acquired by SSD to facilitate routine measurement of cross channel stream discharges in Magela Creek. To determine the proportion of flow traveling down the western channel at MCDW, the discharge measured in this channel alone was compared to the total discharge measured concurrently at GS8210009 (Magela Creek discharge across all three channels). The data obtained for the 2008–09 wet season (8 gaugings carried out at MCDW over 5 days) show that a log relationship ($R^2 = 0.98$) exists between the flow at the two sites (Figure 2). Up to 60% of the total Magela flow travels down the western channel at MCDW under low flow conditions ($\leq 20 \text{ m}^3/\text{s}$) (Figure 3). The proportion of total Magela flow travelling in the western channel at MCDW decreases with increasing total flow. Under high flow conditions, greater proportions of the total Magela flow travel along the central and eastern channels.

During the 2008–09 wet season, ERA carried out some cross-sectional EC profiling in Magela Creek at the compliance site G8210009, located a few hundred metres upstream of MCDW. The data provided by ERA showed that when Magela flow was between 20 and 120 m^3/s , there was a definite EC gradient across the stream, with higher EC measured close to the west bank compared with the EC measured along the cross section profile towards the central channel. More intensive cross sectional EC and flow profiling will be carried out by SSD during the 2009–10 wet season at both G8210009 and MCDW.

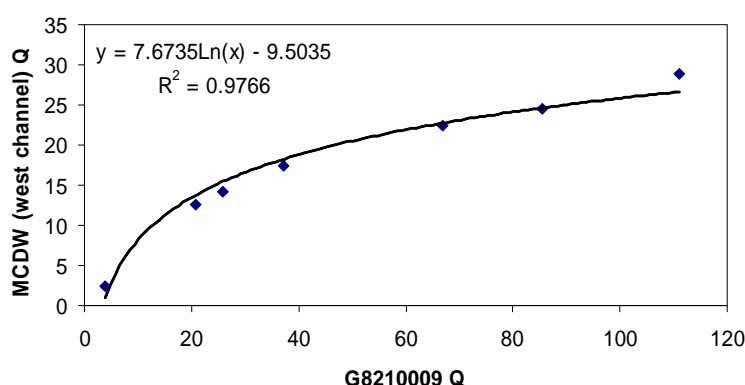


Figure 2 Discharge measured in the western channel at MCDW against total Magela Creek discharge measured at G8210009

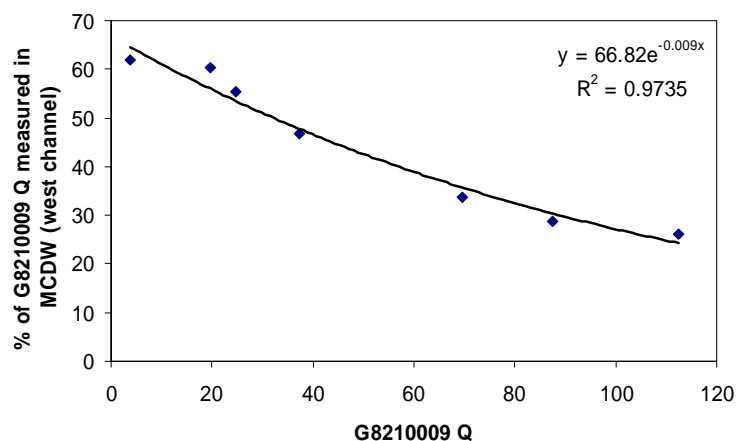


Figure 3 Percentage of discharge travelling along the western channel as a function of total Magela Creek discharge measured at G8210009

Steps for completion

Construction of a reliable load balance is dependent on resolving one or both of the unknowns in equation 1. Recent analysis of flow gaugings carried out at MCDW has shown that it may be possible to use the continuous discharge measured at G8210009 to predict flow in the western channel at MCDW, thereby increasing the reliability of the Mg loads calculated at this site. While there is a significant non-linear relationship between total Magela Creek flow and the flow in the western channel at MCDW for measurements made between January and March 2009, more data from high flow events are needed before flow measured at G8210009 can be used as a reliable predictor under the full range of flow conditions for west channel flow at MCDW. Gaugings will be conducted over a greater range of flows to determine if the current relationship applies to higher flows. This work will be done during the 2009–10 wet season.

The total Mg load transported in Magela Creek downstream of the mine, *DS*, will then be able to be calculated by adding the loads measured at MCDW and the loads estimated in the central and eastern channels (using the distribution of flow between the three channels and the concentration of Mg from upstream). Once the *DS* loads have been adjusted accordingly, then equation 1 can be rearranged to solve for *ROC* which will allow quantification of Mg inputs derived from the LAA and any other potential diffuse sources.

References

- Brazier J 2009. Chemical and physical monitoring. In *eriss research summary 2007–2008*. eds Jones DR & Webb A, Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 46–50.
- ERA 2008a. *ERA Ranger Mine Wet Season Report*. Energy Resources of Australia Ltd, Darwin, NT.
- ERA 2008b. *ERA Annual Environment Report*. Energy Resources of Australia Ltd, Darwin, NT.
- Supervising Scientist 2007. *Annual Report 2006–2007*. Supervising Scientist, Darwin.
- Supervising Scientist 2008. *Annual Report 2007–2008*. Supervising Scientist, Darwin.

- Turner K 2009. Continuous monitoring of water quality in Magela Creek. In *eriss research summary 2007–2008*. eds Jones DR & Webb A. Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 71–74.
- Turner K & Jones D 2009. Development of Magela Catchment area solute budget using continuous monitoring systems. In *eriss research summary 2007–2008*. eds Jones DR & Webb A. Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 75–85.
- Turner K, Moliere D, Humphrey C & Jones D 2008a. Continuous monitoring of water quality in Magela Creek. In *eriss research summary 2006–2007*. eds Jones DR, Humphrey C, van Dam R & Webb A. Supervising Scientist Report 196, Supervising Scientist, Darwin NT, 37–42.
- Turner K, Moliere D, Humphrey C & Jones D 2008b. Characterisation of solute transport in a seasonal stream using continuous in-situ water quality monitoring, In *Water Down Under 2008*, Proceedings of the 31st Hydrology and Water Resources Symposium and 4th International Conference on Water Resources, 15–17 April 2008, Adelaide, South Australia, Engineers Australia (CD).

Review of solute selection for water quality and bioaccumulation monitoring

K Turner & D Jones

Background

The suite of major ions and trace metals measured by SSD as part of its surface water chemistry and bioaccumulation monitoring programs was initially selected based on a number of assessments carried out prior to commencement of mining, and during the mine's initial operational period (Office of the Supervising Scientist 2002, Klessa 2000, 2001a,b). Baseline data were collected as early as 1975 to characterise natural inputs to Magela Creek. Potential metals of concern for the future mining operation were identified by comparing metal concentrations in samples of ore and waste with 'background' concentrations from unmineralised areas, coupled with the results from a leaching study conducted on a pad of material from the Ranger 1 orebody (Milnes & Fazey 1988). The suite of metals identified by these early studies has largely been maintained to the present day in the routine analysis of water samples collected by SSD. However, the reason why some of these metals continue to be analysed is for reasons of sample quality control rather than environmental impact assessment. The latter aspect is discussed in more detail below.

There are many metals/metalloids that have historically been identified worldwide as having a potential to bioaccumulate. They are (listed in order of decreasing potential to bioaccumulate) cadmium, mercury, selenium, arsenic, beryllium, chromium, cobalt, copper, iron, lead, manganese, silver, uranium, vanadium and zinc. All of these metals were analysed as part of the trace element suite for the original SSD bioaccumulation program. However, it was found that all were present at extremely low levels in mussels and a number of fish species.

Rather than simply continuing to analyse, a priori, for all of these metals in biota collected in Magela Creek and in billabongs downstream of Ranger, it was determined that a risk assessment should be carried out using the results from chemical analysis of catchment drainage lines contributing metals to the system. This approach took the assessment of relevant metals beyond that based on simple comparison of mineralised and unmineralised rock since it will identify those metals that are actually being dissolved by contact with water and hence potentially capable of being transported downstream along minesite catchments.

Comparison of the composition of minesite waters with composition of the water from Magela Creek upstream and downstream of the mine enabled a risk assessment to be made of those metals that are of most potential concern. It is those metals that are present at higher-than-background levels downstream of the mine that should be considered more closely for inclusion in the routine water quality monitoring program to assess downstream impact of operations at the Ranger mine.

A detailed chemical assessment of the full trace metal profile of minesite waterbodies and major catchment runoff lines had not been carried out since the cessation of mining of Pit1 and the start of mining of Pit 3 in 1996. Since that time, the waste stockpiles have come to be dominated by material from Pit 3, and it is possible that the trace element composition of runoff and seepage water could have changed as a result of the different provenance of this second orebody. Consequently, contemporary trace element data were required since the

previous data would not provide a sufficiently robust basis upon which to carry out a contemporary risk assessment.

To this end, comprehensive chemical analysis of on-site waterbodies, catchment drainage waters and Magela Creek upstream and downstream of the minesite was undertaken during the 2005–06 wet season. A range of analytes was identified to be of potential environmental importance, based upon: i) concentrations present in mine waterbodies relative to background concentrations; ii) attenuation by natural processes in catchment drainage lines; and iii) likely or inferred potential for biological impact.

Ranger mine and Magela Creek

The minesite is located within the Magela Creek catchment area which runs through the north-east corner of the Ranger Project Area. During the wet season months Magela Creek receives mine-derived waters that are passively released along Coonjimba and Corridor Creek catchment lines, as well as mine-related constituents that are leached from the land application areas (LAAs) in the vicinity of these creeks (see Map 1 for locations of these sites).

Both the Coonjimba and Corridor Creek catchment lines have been substantially modified, with the construction of wetland filters and various bunds and weirs to assist with flow control and passive water treatment. The Ranger Water Management Plan (ERA, 2005) outlines the company's water management practices and provides details of the components of the site water management system. In summary, the management system is divided into three components based on the source of the water and degree of interaction between the water and mining or milling processes.

- **Process water:** Confined to the tailings dam and Pit 1, process water has to be retained on site and can only be disposed of by evaporation or following treatment to a prescribed level.
- **Pond water:** Runoff and seepage from the mill and mine areas, including the low grade ore stockpiles, are directed to Ranger retention pond 2 (RP2). If RP2 capacity is reached, the excess water flows via a spillway structure into Pit 3. Pond water is currently disposed of or treated by a combination of methods, including wetland filtration, land application and treatment in a Microfiltration/Reverse Osmosis (MF/RO) plant.
- **Sediment control water:** Runoff from waste rock dumps and natural woodland areas that reports to RP1 (northern part of the minesite) and the Corridor Creek wetlands (southern part of mine site), which ultimately discharge into Magela Creek via the Corridor Creek and Coonjimba Creek flow lines, respectively.

Only the pond and sediment control waters can impact directly, or indirectly, on water quality in Magela Creek.

Methods

Surface water samples were collected from a number of tributaries and constructed waterbodies on the Ranger lease as well as upstream (control) and downstream (exposed) locations in Magela Creek (Table 1).

Minesite waterbodies that discharge to Magela Creek during the wet season were the focus of this study.

Table 1 Sampling sites

Site	Description	Major inputs
MCUS	Magela Creek upstream	Undisturbed areas of Magela catchment upstream of Ranger mine
009C & 009W	Magela Creek downstream, central channel and west channel, respectively	MCUS, Corridor Creek via Georgetown Billabong, RP1 via Coonjimba Billabong and land application area runoff
VLGCRC2	Very Low Grade Cross Road Culvert	Runoff from waste rock and low grade ore stockpile
CCWLF (Cell 1)	Corridor Constructed Wetland Filter	VLGCRC2, land application area runoff
GC2	Corridor Creek downstream	CCWLF, land application area runoff
RP2	Retention Pond 2	Water from Pit 3, runoff and seepage from stock piles, processing and milling area and haul roads
RP1	Retention Pond 1	RP1 Constructed Wetland Filter, land application area runoff and seepage from bunded structures in the upper catchment

During the 2005–06 wet season, samples were collected on four occasions (Table 2) over the period of initial, mid and recessional creek flow to determine the extent to which the composition of the waters changed over the course of the wet season and the effect, if any, this would have on the risk assessment.

Table 2 Sampling dates

Date	Sites		
	Status of discharge to Magela Creek	Mine lease area	Magela Creek
21 Dec 2005	Prior to release of RP2 and GC2 water to Magela Creek	RP2, RP1, GC2, CCWLF	MCUS, 009C, 009W
19 Jan 2006	Initial period of release from RP1 and GC2	RP2, RP1, GC2, VLGCRC2	MCUS, 009C, 009W
22 & 23 Mar 2006	Release flow established at RP2 and GC2	RP2, RP1, GC2, VLGCRC2	MCUS, 009C, 009W
20 & 21 Jun 2006	After cessation of RP1 and GC2 water to Magela Creek	RP2, RP1, GC2	MCUS, 009C, 009W

On each sampling occasion pH, electrical conductivity (EC), temperature, dissolved oxygen (DO) and turbidity were measured in situ and in the laboratory. Water samples were filtered in the field at time of collection and acidified at SSD's Jabiru Field Station prior to analysis for an extensive suite of dissolved trace metals by Inductively Coupled Plasma Mass Spectrometry (ICPMS).

Results

The mean values of pH and EC measured in the Ranger retention ponds, GC2 and at the upstream and downstream sites in Magela Creek during the 2005–06 wet season are shown in Table 3. Each of the waterbodies studied showed some variation in pH over the wet season, most notably in RP1 and RP2, where pH decreased during the rainfall months. The locations

sampled on the minesite had higher mean EC values compared with Magela Creek, reflecting the much higher concentrations of major ions in these site waters.

Table 3 Mean and standard deviation of pH, EC and turbidity from each site

Site	pH		EC	
	Mean	SD	Mean	SD
RP2	5.7	1.2	1252	25
RP1	7.2	0.9	423	178
GC2	6.4	0.3	101	46
009C	5.8	0.5	15	4
MCUS	5.8	0.5	13.5	3.5

Any metals measured in the mine-derived waters at concentrations less than the corresponding analytical detection limits were considered to present negligible risk to the environment. Hence they will not be discussed further. The mean concentrations of metals/metalloids present at levels higher than detection limits in mine waters and in Magela Creek over the 2005–06 wet season are presented in Table 4. For each element the sites are arranged in descending order of mean concentrations values, with the standard deviations associated with each mean shown in parentheses.

The concentrations of metals in RP2 and VLGCR2 are higher than in RP1 and GC2. VLGCR2 and RP2 both receive surface runoff and seepage from waste rock and low grade ore stockpiles and contain metals dissolved by water in direct contact with high surface areas of exposed rock. Although many metals are present in RP2 at elevated concentrations, they are not of direct risk to the surrounding environment as untreated RP2 water is not discharged into Magela Creek.

RP1 and GC2 receive waters that are ‘polished’ by passage through wetland filters as well as being further diluted by water from cleaner sub-catchments. RP1 and GC2 also receive runoff and seepage from land application areas, where metals initially present in the RP2 water are attenuated by absorption in the soil profile (Hollingsworth et al 2005).

The elements that may pose the greatest potential risk to the natural receiving aquatic system are those that are present in substantially higher concentrations in RP1 and GC2 relative to upstream Magela Creek, as water from both of these minesite locations ultimately discharges into Magela Creek. However, it must also be recognised that there are natural billabongs located between RP1 and GC2 and Magela Creek that provide additional polishing of discharge waters. In the case of GC2 it is Georgetown Billabong, and in the case of RP1 it is Coonjimba Billabong (see Map 2 for locations).

The log-transformed concentration data produced from the four wet season sampling occasions were analysed using ANOVA, followed by a Tukey’s test to distinguish significant differences ($P < 0.05$) between sites (Table 5). It is important to note that the low sample sizes and high standard deviations associated with data arising from seasonal sampling over the 2005–06 wet season will somewhat reduce the power of the statistical analyses.

Table 4 Summary of mean element concentrations (standard deviation) measured in mine waterbodies and in Magela Creek ordered from the highest to lowest concentration for each element

Element	Site			
	Concentration (standard deviation)			
Aluminium	GC2	MCUS	009C	RP1
	109 (61.0)	55.4 (39.7)	55.3 (40.2)	20.0 (15.7)
Arsenic	RP1	GC2	009C	MCUS
	0.23 (0.098)	0.183 (0.058)	0.095 (0.057)	0.079 (0.046)
Boron	RP1	GC2	009C	MCUS
	18.8 (7.16)	12.7 (3.75)	8.20 (0.570)	8.00 (0.837)
Barium	RP1	GC2	009C	MCUS
	36.6 (17.7)	15.3 (11.8)	3.11 (0.498)	2.86 (0.493)
Cadmium	RP1	GC2	009C	MCUS
	5.86 (2.21)	2.10 (1.10)	0.480 (0.192)	0.467 (0.225)
Copper	GC2	RP1	MCUS	009C
	1.32 (0.767)	0.406 (0.375)	0.238 (0.231)	0.190 (0.123)
Iron	GC2	009C	MCUS	RP1
	213 (75.7)	124 (32.9)	113 (24.2)	64.0 (45.6)
Magnesium	RP1	GC2	009C	MCUS
	58.8 (24.5)	9.27 (3.67)	0.860 (0.313)	0.650 (0.274)
Lead	GC2	RP1	MCUS	009C
	0.237 (0.035)	0.072 (0.078)	0.03 (0.024)	0.023 (0.022)
Rubidium	RP1	GC2	009C	MCUS
	9.84 (3.51)	3.76 (1.49)	0.492 (0.095)	0.432 (0.088)
Sulfate	RP1	GC2	009C	MCUS
	223 (89.2)	30.2 (20.0)	1.2 (1.03)	0.300 (0.089)
Uranium	GC2	RP1	009C	MCUS
	11.4 (3.85)	7.55 (3.69)	0.059 (0.021)	0.0207 (0.008)

Aluminium, As, B, Ba, Ca, Cu, Fe, Mg, Pb, Rb, SO₄ and U were present in RP1 and/or GC2 at concentrations significantly higher ($P < 0.05$) than those measured upstream in Magela Creek. However, uranium and SO₄ were the only analytes that were significantly elevated ($P < 0.05$) at the downstream site in Magela Creek compared with the upstream site.

To further refine the above analysis, Student t-tests were used to compare the Magela upstream and downstream weekly water quality monitoring data measured between 2001 and 2009 (a large dataset, $n > 200$). Concentrations of Ca, Fe, Mg, Mn, SO₄ and U observed downstream of the mine were significantly ($P < 0.05$) higher than values observed at the upstream site. The remaining analytes (Al, Cu, Pb and Zn) were not significantly different between the upstream and downstream sites. This indicates that while there are many elements present at concentrations greater than background in the mine waters at source, the majority of these elements are essentially completely attenuated during passage of the water through the tributary creek lines, in Georgetown and Coonjimba Billabongs and by dilution or adsorption on particulates present in Magela Creek.

Table 5 Summary of results from one-way ANOVA and Tukey's *post hoc* tests on differences in element concentrations measured in mine waterbodies and in Magela Creek

Element	df	F	P	Tukey's HSD multiple comparison test			
				SITE			
				Concentration (standard deviation)			
Aluminium	3	3.903	0.030	GC2	MCUS	009C	RP1
Arsenic	3	4.316	0.022	RP1	GC2	009C	MCUS
Boron	3	12.67	<0.000	RP1	GC2	009C	MCUS
Barium	3	34.87	<0.000	RP1	GC2	009C	MCUS
Cadmium	3	38.32	<0.000	RP1	GC2	009C	MCUS
Copper	3	5.889	0.007	GC2	RP1	MCUS	009C
Iron	3	5.9	0.007	GC2	009C	MCUS	RP1
Magnesium	3	135.2	<0.000	RP1	GC2	009C	MCUS
Lead	3	8.01	0.002	GC2	RP1	MCUS	009C
Rubidium	3	111.8	<0.000	RP1	GC2	009C	MCUS
Sulfate	3	152.1	<0.000	RP1	GC2	009C	MCUS
Uranium	3	242.0	<0.000	GC2	RP1	009C	MCUS

Sites joined by a common line are not significantly different from each other.

Concentrations are in µg/L except for magnesium and sulfate which are in mg/L.

Variables that were similar amongst all sites (not significantly different) have not been included in the table. Sample sizes: RP1, n = 5; GC2, n = 3; 009C, n = 5; and MCUS, n = 6.

df = degrees of freedom, F = F-ratio, P = significance

Conclusions

The current routine suite of water quality analytes for Magela Creek comprises Mg, Ca and SO₄ as the major ions, with Al, Cu, Fe, Pb, Mn, U and Zn as the measured trace elements (Supervising Scientist 2002). The current suite clearly includes all of the potential 'risk' metals/solutes identified above, as well as some additional ones, namely Al, Pb and Zn. It should be noted that these latter three metals continue to be analysed primarily for quality control purposes, rather than for environmental impact assessment because they provide sensitive markers of sample contamination during collection or in the chemical analysis laboratory. A high value for either one or all of these three metals provides a warning that the rigorous (clean) procedures involved in collection or handling a sample for trace metal analysis have been compromised.

Steps for completion

Results from this study provide a high degree of confidence that the routine water quality and bioaccumulation sampling programs conducted by SSD are not omitting any potential metals that could be of concern from either toxicological or bioaccumulation perspectives. A full trace metal profile (as described above) of relevant mine waters and upstream and downstream sites in Magela Creek will be conducted at least once per wet season in future. This will provide a quality control check to ensure that all mine-related metals that might (now or in the future) pose a risk to the receiving waterways are included in the routine monitoring suite.

References

- ERA 2005. Water Management Plan 2005–2006. Company Report.
- Hollingsworth I, Overall R & Puhlovich A 2005. Status of the Ranger irrigation areas – Final Report. Report to ERA.
- Klessa DA 2000. *The chemistry of Magela Creek: A baseline for assessing change downstream of Ranger*. Supervising Scientist Report 151, Supervising Scientist, Darwin.
- Klessa DA 2001a. A review of groundwater chemistry monitoring data at Ranger. Internal Report 363, Supervising Scientist, Darwin. Unpublished paper.
- Klessa DA 2001b. Water quality in Magela Creek upstream and downstream of Ranger: A summary of performance for 2000–2001 and derived triggers and limits for 2001–2002. Internal Report 380, Supervising Scientist, Darwin. Unpublished paper.
- Milnes AR & Fazey PG 1988. *Acid leaching of uranium from ore stockpiles and waste dumps in the Ranger Project area, East Jabiru*. Technical paper no 2 to Ranger Uranium Mines Pty Ltd.
- Office of the Supervising Scientist 2002. Review of water standards (historic document). Internal Report 397, December, Supervising Scientist, Darwin. Unpublished paper.
- Supervising Scientist 2002. Supervising Scientist Monitoring Program: Instigating an environmental monitoring program to protect aquatic ecosystems and humans from possible mining impacts in the Alligator Rivers Region.
www.environment.gov.au/ssd/monitoring/pubs/env-mon-prog-background.pdf
(accessed 24 April 2009)

Results from the routine stream monitoring program in Magela Creek catchment, 2008–09

Introduction

C Humphrey, A Bollhöfer & D Jones

Progress under this KKN for the stream monitoring program in the Magela Creek catchment is reported by way of (i) results of the routine monitoring program conducted for the 2008–09 period, and (ii) monitoring support tasks for the same period, including research and development, reviews and reporting. The latter tasks are reported separately in ‘Ranger stream monitoring: Research and development’, pp 94–104, this volume.

Since 2001, routine water quality monitoring and ecotoxicity programs have been deployed by SSD for environmental assessment of aquatic ecosystems in the ARR. The objective of this work has been to provide independent assurance that the aquatic environment remains protected from current and past mining-associated activities in the region. The monitoring program incorporates chemical, physical and biological components.

The techniques and ‘indicators’ used in the monitoring program satisfy two important needs for environmental protection: (i) the early detection of potential significant effects to avoid ecologically important impacts; and (ii) information on the ecological importance of any likely impact (biodiversity assessment). Monitoring techniques adopted by SSD that meet these requirements are:

(i) Early detection of short or longer-term changes

- *Water physico-chemistry*:
 - Grab samples for water quality measurement: includes pH, electrical conductivity (EC), suspended solids, uranium, magnesium, calcium, manganese and sulfate (weekly sampling during the wet season) and radium (samples collected weekly but combined to make monthly composites),
 - Continuous monitoring: use of multi-probe loggers for continuous measurement of pH, EC, turbidity and temperature in Magela Creek, and EC and turbidity in Gulungul Creek;
- *Toxicity monitoring* of reproduction in freshwater snails (four-day tests conducted in situ, at fortnightly intervals);
- *Bioaccumulation* – concentrations of chemicals (including radionuclides) in the tissues of freshwater mussels in Mudginberri Billabong to detect far-field effects including those arising from any potential accumulation of mine-derived contaminants in sediments (mussels sampled every late-dry season).

(ii) Assessment of changes in biodiversity

- *Benthic macroinvertebrate communities* at stream sites (sampled at end of each wet season);
- *Fish communities in billabongs* (sampled at the end of each wet season).

In accordance with the concepts of best practice and optimisation, the routine monitoring program has evolved through time as technologies (eg continuous physicochemical monitoring using datasondes and telemetry) have evolved, and improved methodologies for biological assessment (eg in situ monitoring using snails) have been developed under the SSD research program.

The results from the stream chemical and biological monitoring program for 2008–09 are summarised below. ²²⁶Radium activity concentrations in Magela Creek for 2008–09 are reported separately (see ‘Surface water radiological monitoring in the vicinity of Ranger and Jabiluka’, pp 54–57, in this volume).

Chemical and physical monitoring

J Brazier

Routine weekly sampling program in Magela Creek

An overview of the water quality objectives for Magela Creek and the measures of success applied to meeting those objectives is provided in Iles (2004).

The 2008–09 wet season is the first time that water quality grab sampling and continuous monitoring have been co-located. This action was approved by ARRTC and the MTC following detailed statistical analysis (Brazier et al 2009) of the time series data collected at both the upstream (reference) and downstream locations. This analysis concluded that there would be no loss in power to detect potential impact by co-location

The first water chemistry samples for the 2008–09 wet season surface water monitoring program were collected from Magela Creek on 26 November 2008, immediately after commencement of surface flow. Weekly sampling continued throughout the season with the last samples collected on 10 June 2009. On 16 June 2009, MTC stakeholders agreed that continuous surface flow had ceased in Magela Creek and monitoring of the creek was no longer required.

On 11 February 2009, a value for electrical conductivity (EC) of 45 $\mu\text{S}/\text{cm}$ was measured in the grab sample collected from the downstream site (Figure 1). This exceeded the statistically derived guideline value of 43 $\mu\text{S}/\text{cm}$, and corresponded with elevated magnesium (3.3 mg/L) and sulfate (12.2 mg/L). The continuous monitoring data (Figure 2) showed that the value of 45 $\mu\text{S}/\text{cm}$ corresponded with the peak of an EC event that lasted 30 hours and for which EC remained above 43 $\mu\text{S}/\text{cm}$ for 5 hours.

SSD considers that the pulse of magnesium and sulfate originated from RP1 (via Coonjimba Billabong). It is likely that an increase in flow (and water level) in Magela Creek that occurred on 8–9 February had initially restricted flow from Coonjimba Billabong. As the Magela Creek water level dropped between 9 and 11 February, water held back in Coonjimba Billabong drained out causing the increase in EC at the downstream site (Figure 2).

Ecotoxicological research conducted by SSD suggests that there was no detrimental environmental impact from this short-lived event (see ‘Effects of magnesium pulse exposure on aquatic organisms, pp 27–31, in this volume).

On 18 February, uranium was approximately 6% of the limit (0.37 $\mu\text{g}/\text{L}$) at SSD’s downstream site compared with 0.028 $\mu\text{g}/\text{L}$ at the upstream site (Figure 3). This concentration is similar to uranium concentrations measured by the creekside field toxicity monitoring program on two occasions in 2002–2003, and once in the 2006–2007 wet season. On each of these occasions, field toxicity monitoring (including the in situ test conducted 16–20 February 2009) showed no detectable biological effects (as expected, noting that the ecotoxicologically-derived guideline value for U is 6 $\mu\text{g}/\text{L}$).

The routine grab sample collected on 18 March 2009 coincided with another higher EC event at the downstream site (Figure 1). The values of EC, magnesium and sulfate measured in this sample were 44 $\mu\text{S}/\text{cm}$, 3 mg/L and 10 mg/L, respectively. Continuous monitoring data (Figure 2) showed that this event peaked at 47 $\mu\text{S}/\text{cm}$ and lasted about 20 hours, with EC exceeding 43 $\mu\text{S}/\text{cm}$ for 8 hours. There had been increased discharge in Magela Creek during

the previous day (from increased rainfall in the catchment) and the resultant water level decrease on 18 March would have led to increased drainage from Coonjimba Billabong back into Magela Creek, hence explaining the increase in EC.

From mid-April, typical end-of-wet-season trends were apparent as the water level decreased. Manganese concentrations at the downstream site increased as groundwater influences started to dominate, and electrical conductivity between the upstream and downstream sites became similar as minesite influences decreased.

Overall, the data from the continuous and water quality grab sample monitoring programs indicate that water quality in Magela Creek was comparable with previous seasons (for the west channel). Figure 4 shows that uranium concentrations for the 2008–09 wet season were comparable with previous seasons for the downstream west channel environment.

The results from the in situ toxicity monitoring program using freshwater snails (see later in this paper) provided reassurance that the aquatic environment of Magela Creek remained protected from activities at the Ranger mine.

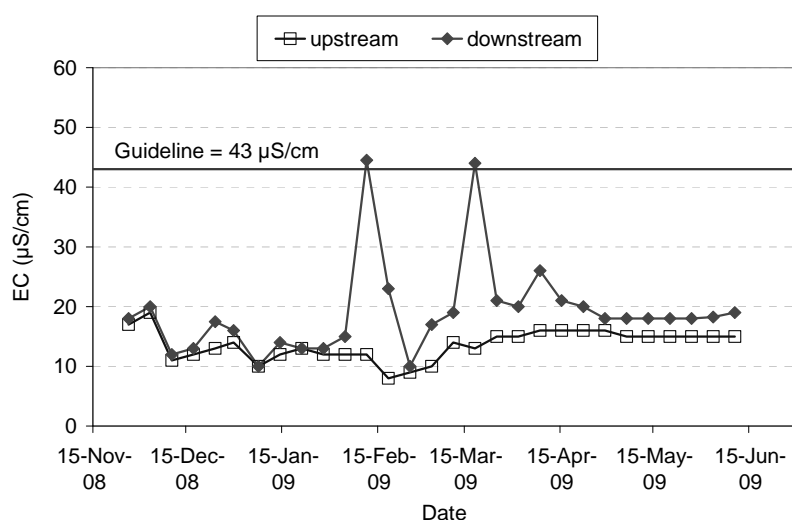


Figure 1 Electrical conductivity measurements in Magela Creek (SSD data) between November 2008 and June 2009

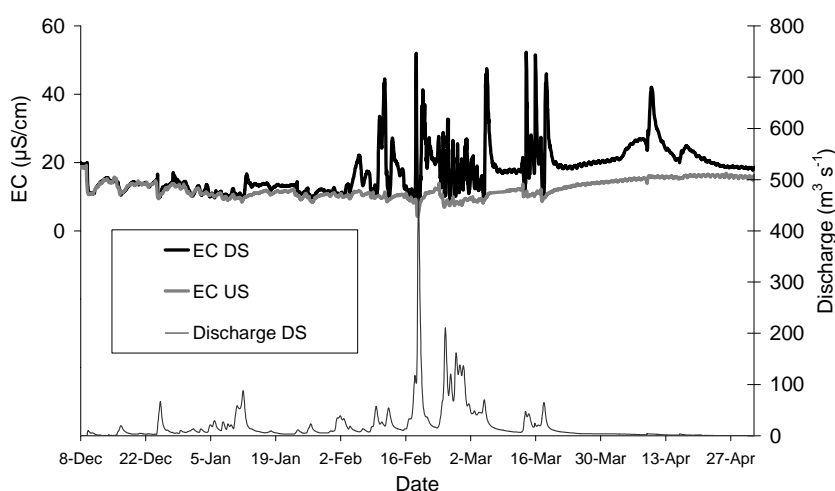


Figure 2 Electrical conductivity and discharge measurements in Magela Creek between December 2008 and April 2009 – continuous monitoring data

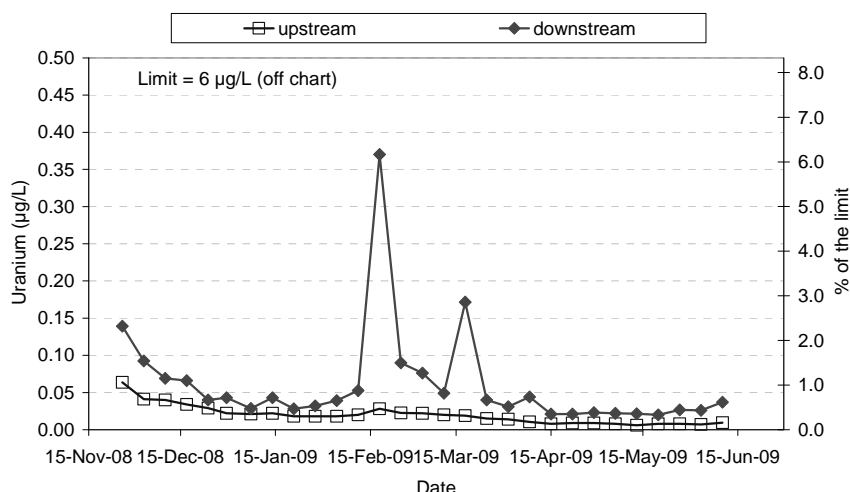


Figure 3 Uranium concentrations measured in Magela Creek by SSD between November 2008 and June 2009

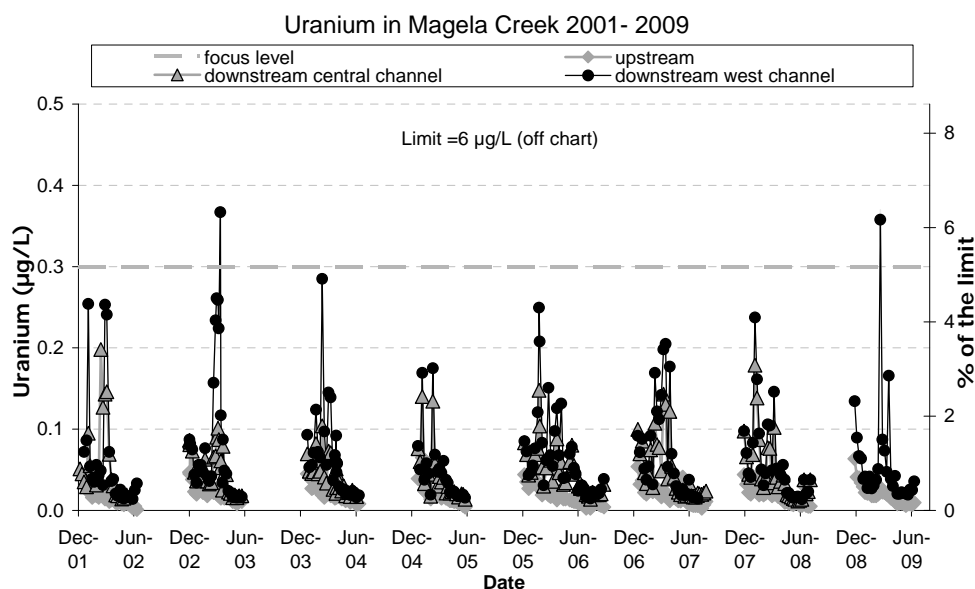


Figure 4 Uranium concentrations in Magela Creek between 2001 and 2009 (SSD data)

Chemical and physical monitoring of Gulungul Creek

Weekly grab sampling for routine analysis of water chemistry variables at the upstream site was discontinued for the 2008–09 wet season because this site does not represent a useful reference location for the Gulungul catchment. Water chemistry data measured at this site indicate that upstream (natural) catchment influences compromise its effectiveness for assessing downstream impacts from the mine. Weekly grab sample monitoring continued at the downstream site. Continuous monitoring of flow, electrical conductivity (EC) and turbidity was maintained at both the downstream and upstream sites.

The first water chemistry samples for SSD's 2008–09 wet season surface water monitoring program were collected from Gulungul Creek on 30 December 2008, immediately after commencement of surface flow. Weekly sampling continued throughout the season with the last samples collected on 20 May 2009. On 22 May 2009, MTC stakeholders agreed that

continuous surface flow had ceased in Gulungul Creek and monitoring of the creek was no longer required.

There was considerable work carried out during the 2008 dry season on raising the embankment height of the tailings storage facility (TSF), using substantial quantities of waste rock sourced from the southern waste rock dump. Water run-off from this waste rock may have contributed to the observed elevations in EC (Figures 5 & 6), uranium (Figure 7) and sulfate concentrations at the Gulungul Creek downstream site compared with concentrations observed in the recent past few years. Discharge in Gulungul Creek (Figure 6) was also lower than previous years due to less rainfall in the catchment, and hence dilution of solutes would also have been less compared with previous years.

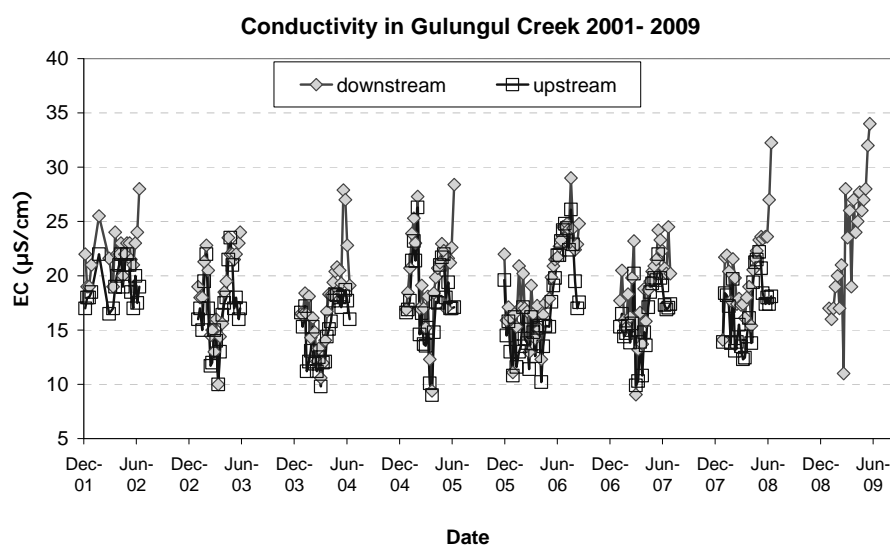


Figure 5 Electrical conductivity measurements in Gulungul Creek for the 2008–09 wet season

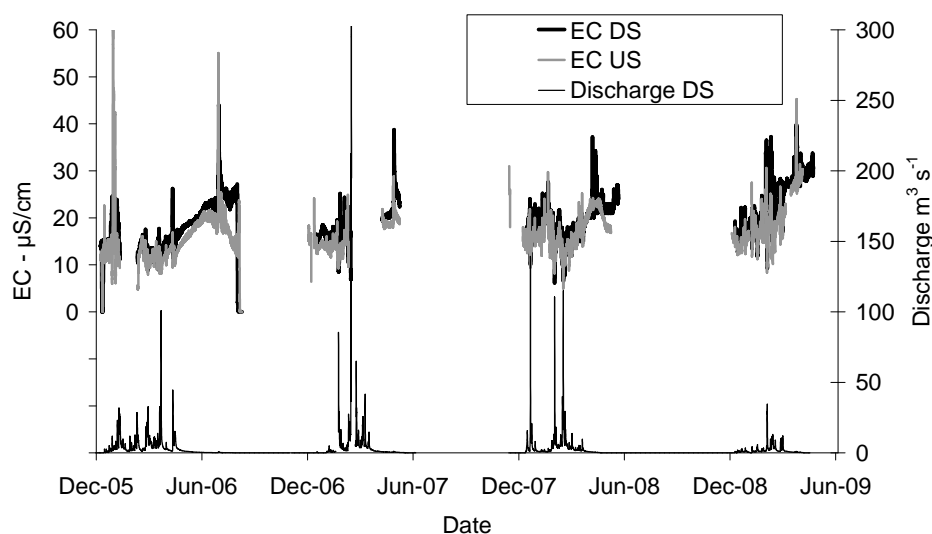


Figure 6 Electrical conductivity and discharge in Gulungul Creek 2005–2009 – continuous monitoring

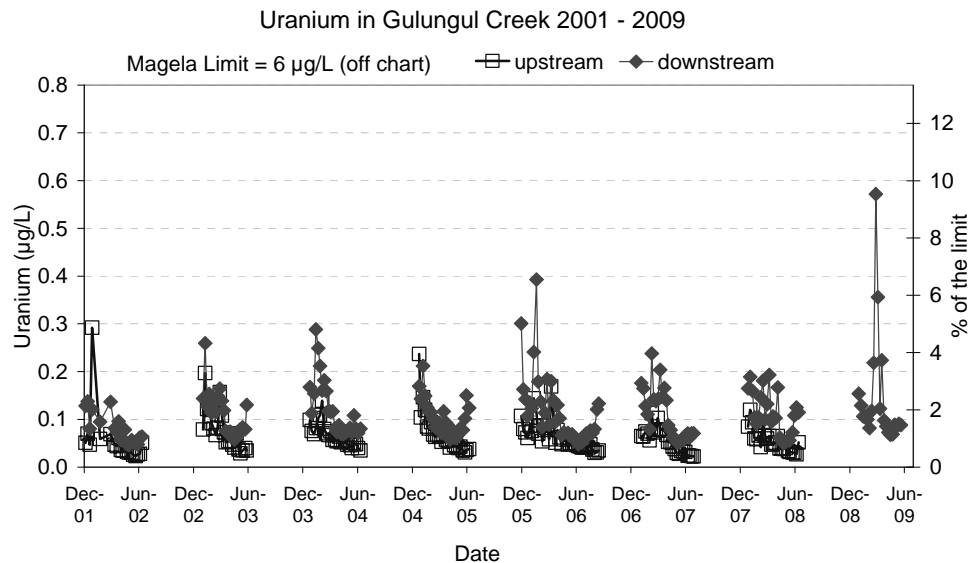


Figure 7 Uranium concentrations in Gulungul Creek between 2000 and 2009 (SSD data)

On 25 February 2009, a uranium value of 0.57 µg/L (Figure 8) measured at the downstream site (<10% of the Magela Creek limit) coincided with slightly elevated electrical conductivity (28 µS/cm) and sulfate concentration (2.7 mg/L). On 4 March 2009, uranium measured 0.36 µg/L at the downstream site (Figure 8), again coinciding with slightly elevated EC (24 µS/cm) and sulfate concentration (2.7 mg/L). Since the results of biological monitoring of macroinvertebrates in Gulungul Creek during recession flows (see later in this paper) show no evidence of impact, and the values of the chemical variables are less than the guidelines and limits set for Magela Creek, it is considered that none of these excursions are environmentally significant.

After mid March 2009, uranium decreased to concentrations less than 0.2 µg/L (< 2% of the limit) which is similar to previous season's measurements (Figure 7).

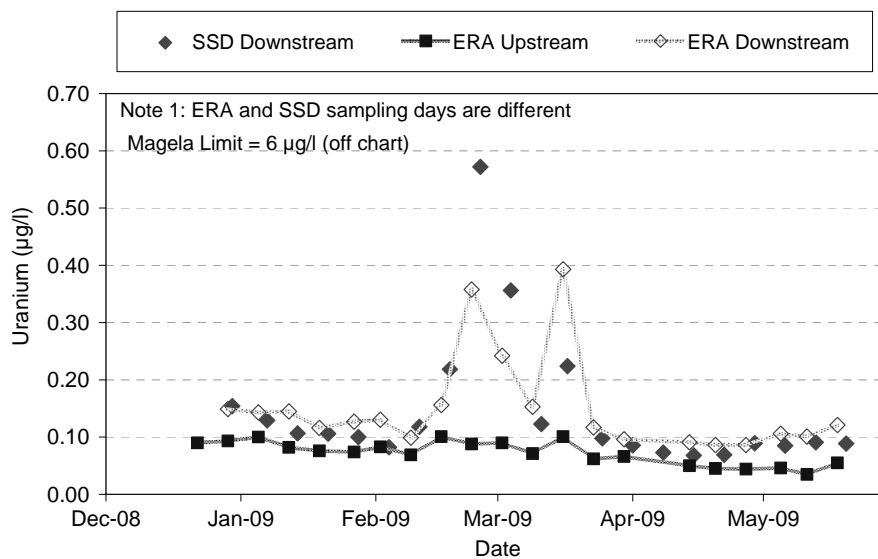


Figure 8 Uranium concentrations measured in Gulungul Creek by SSD and ERA during the 2008–09 wet season

From early April, recession flow characteristics became apparent with electrical conductivity at the upstream and downstream sites becoming more similar and manganese concentrations increasing as groundwater inputs started to dominate.

Overall, the water quality of Gulungul Creek suggests that the aquatic environment in the creek remained protected from activities at the Ranger mine for the 2008–2009 season.

References

- Brazier J, Humphrey C & Buckle D 2009. Future of the weekly water grab sampling program in Magela Creek catchment. In *eriss research summary 2007–2008*. eds Jones DR & Webb A, Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 66–70.
- Iles M 2004. Water quality objectives for Magela creek – revised November 2004. Internal Report 489, December, Supervising Scientist, Darwin. Unpublished paper.

Toxicity monitoring in Magela Creek

C Humphrey, C Davies & D Buckle

In this form of monitoring, effects of water from the Ranger minesite on receiving waters are evaluated using responses of aquatic animals exposed to creek water. The response indicator has been reproduction (egg production) in freshwater snails, *Amerianna cumingi*, with each test running over a four-day exposure period.

For wet seasons between 1990–91 and 2007–08, toxicity monitoring was carried out using the ‘creekside’ methodology, in which a continuous flow of water from the adjacent Magela Creek was pumped through tanks containing test animals located under a shelter on the creek bank. There were a number of practical constraints with this method, including high staff demands, reliance on complex powered pumping systems (in an area of high electrical storm activity) and vulnerability to extreme flood events. These constraints led to a rigorous evaluation of the viability of an in situ testing technique whereby floating containers are deployed directly in the creek. This method offered the potential of substantially lower staffing, infrastructure and maintenance requirements. Humphrey et al (2009a) describe in detail the results of the two-year creekside versus in situ comparative assessment that demonstrated that the in situ technique is technically robust and constitutes an appropriate replacement for the creekside methodology. During the 2008–09 wet season, in situ toxicity monitoring was undertaken for the first time as the sole toxicity monitoring procedure.

Nine in situ toxicity tests were conducted on a fortnightly basis (ie every other week) over the 2008–09 wet season. The first test commenced on 4 December 2008 and the final test for the season commenced on 30 March 2009. Snail egg production at upstream and downstream sites was generally similar across all nine tests (Figure 1A) and the pattern of egg production across all tests was similar to that observed in previous wet seasons. Importantly, the mean upstream-downstream difference value across the nine wet season tests plots around the running mean (since 1991–92 wet season, Figure 1B) while individual difference values (Figure 1A) are within the maximum and minimum values recorded over this time series (full dataset not shown here).

Improvements to the statistical analysis of toxicity monitoring data using Analysis Of Variance (ANOVA) testing were described in Humphrey et al (2009b). The most important of the ANOVA factors tests for differences in the upstream-downstream difference values between two time periods – in this case and, in particular, test results for the current (2008–09) wet season versus all pre-2008–09 test data. No significant difference was found between the 2008–09 data and data from previous wet seasons ($p = 0.886$), confirming the visual assessment made from the graphical results. From these results it is concluded that no adverse effects on freshwater snails from inputs of Ranger minesite waters to Magela Creek occurred during the 2008–09 wet season.

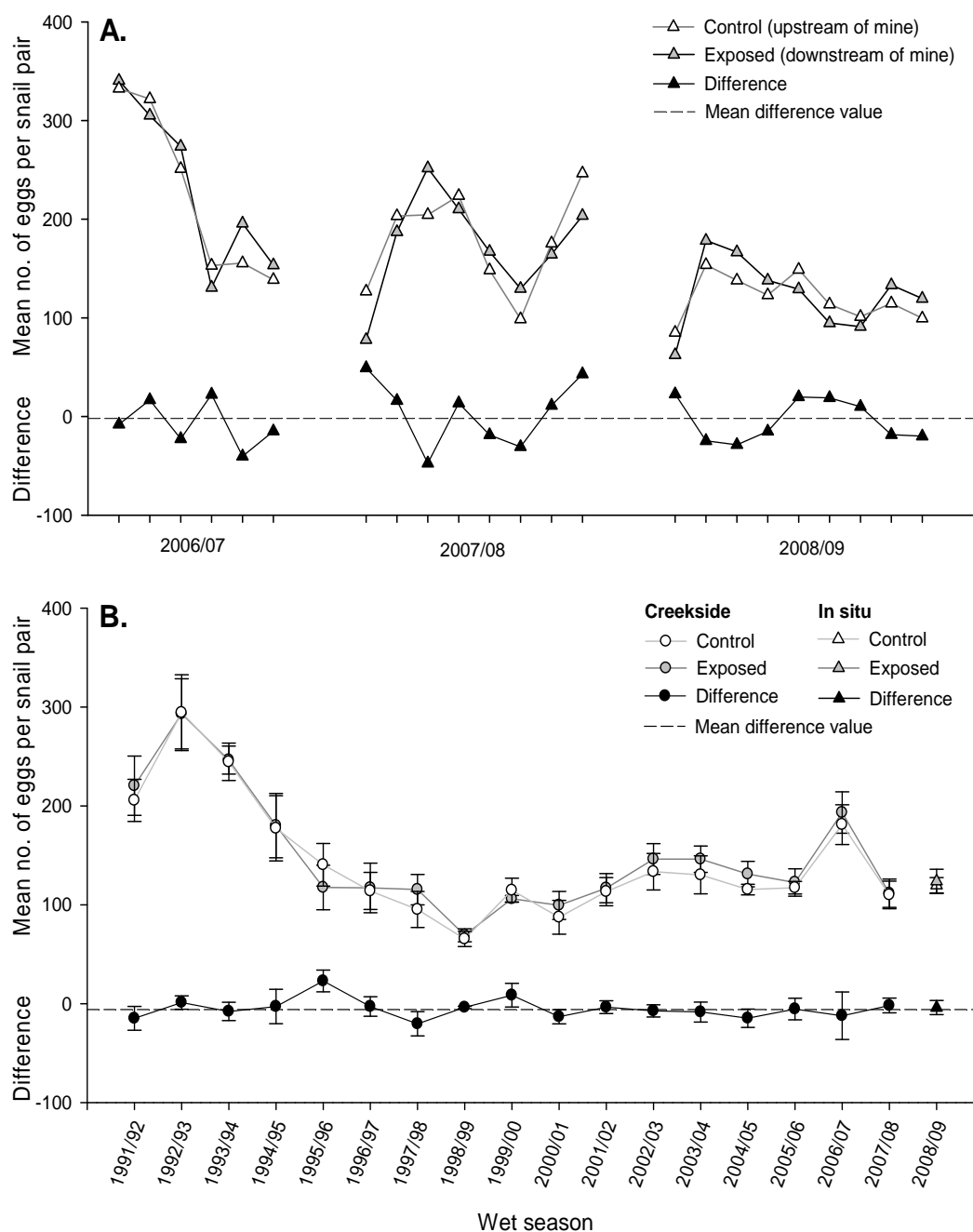


Figure 1 A In situ toxicity monitoring results for freshwater snail egg production for past three wet seasons. B. Toxicity monitoring results for the entire period between 1992 and 2009. Error bars represent standard errors about the mean.

References

- Humphrey C, Buckle D & Davies C 2009a. Development of in situ toxicity monitoring methods for Magela Creek. In *eriss research summary 2007–2008*. eds Jones DR & Webb A, Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 86–90.
- Humphrey C, Davies C & Buckle D 2009b. Toxicity monitoring in Magela Creek. In *eriss research summary 2007–2008*. eds Jones DR & Webb A, Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 51–52.

Bioaccumulation of uranium and radium in freshwater mussels from Mudginberri Billabong

A Bollhöfer, C Humphrey, B Ryan & D Buckle

Mudginberri Billabong is the first major permanent waterbody downstream (12 km) of Ranger mine. Local Aboriginal people harvest aquatic food items, in particular mussels, from the billabong and hence it is essential that they are fit for human consumption. Consequently, concentrations of metals and/or radionuclides in the tissues and organs of aquatic biota attributable to mine-derived inputs to Magela Creek must remain within acceptable levels. Enhanced body burdens of mine-derived solutes in biota could also potentially reach limits that may harm the organisms themselves as well as provide early warning of bioavailability of metals and radionuclides. Hence the bioaccumulation monitoring program serves an ecosystem protection role in addition to the human health aspect.

Mussel bioaccumulation data were obtained intermittently by SSD from Mudginberri Billabong from 1980 to 2001. From 2002 onwards, there has been regular (annual) sampling from Mudginberri Billabong and a control site in the nearby Nourlangie catchment (Sandy Billabong). Only data from 2000 onwards (where methods were standardised and control sites included) will be discussed in this paper. The data gathered prior to 2000 have been presented and discussed in the relevant and respective SSD annual reports.

Uranium concentrations in freshwater mussels, water and sediment samples collected from Mudginberri and Sandy Billabongs are shown in Figure 1. The mean concentrations of uranium in mussels from both Mudginberri and Sandy Billabongs are very similar from 2000 onwards, with no evidence of an increasing trend in concentration in Mudginberri mussels over time.

The lack of any increase in concentration of U in mussel tissues through time, with essentially constant levels observed between 1989 and 1995 (as reported in previous reports), and consistently low levels from 2000 to the last sample taken in October 2008, indicates absence of any significant mining influence.

Concentrations of Ra in mussels are age-dependent (Figure 2) and also appear to be related to growth rates, seasonal soft body weights, water chemistry and sediment characteristics (Brazier et al 2009, also see 'A study of radionuclide and metal uptake in mussels from Mudginberri Billabong', pp 99–104, in this volume. A longitudinal study along the Magela Creek catchment conducted in 2007 measuring uptake of radium and uranium in mussels showed that radium uptake was largely due to natural catchment influences rather than a mining-related feature (Brazier et al 2009).

The average annual committed effective doses calculated for a 10-year old child who eats 2 kg of mussel flesh, based upon average concentrations of ^{226}Ra and ^{210}Pb from Mudginberri Billabong mussels collected between 2000 and 2008 is approximately 0.2 mSv. The average for Sandy Billabong mussels collected between 2002 and 2008 is approximately 0.1 mSv.

The generally consistent relationship between mussel age and Ra concentration for each billabong (Figure 2) currently provides a robust baseline against which any future mine-related change in Ra concentrations can be detected.

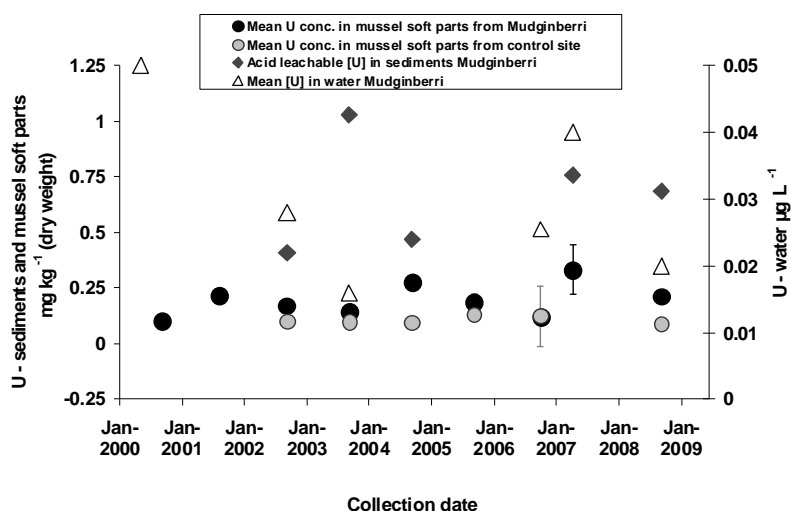


Figure 1 Mean concentrations of uranium measured in mussel soft-parts, sediment and water samples collected from Mudginberri Billabong and Sandy Billabong since 2000

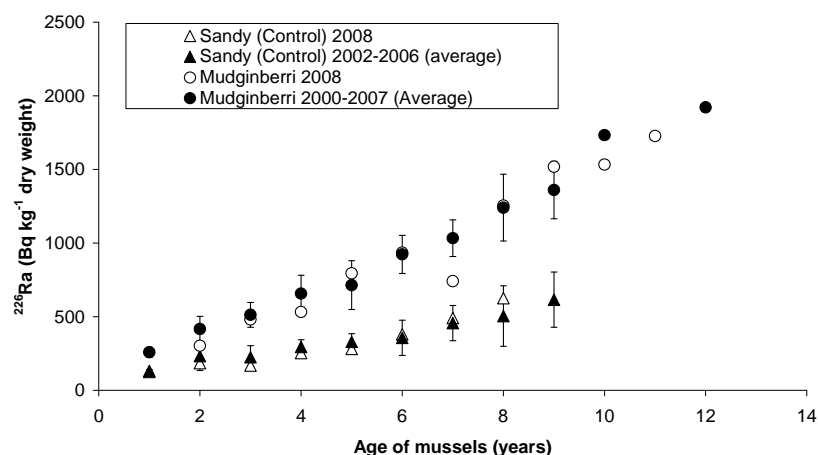


Figure 2 ^{226}Ra activity concentrations in the dried flesh of freshwater mussels collected from Mudginberri Billabong 2000–2008 and Sandy Billabong 2002–2008. Mussels were not collected from Sandy Billabong in 2007. The error bars are ± 1 standard deviation.

In October 2008, a longitudinal study of radium and uranium uptake in mussels in Mudginberri Billabong was undertaken to determine if the location of sampling in the billabong had a significant effect on the levels of Ra and U measured in mussels. The findings from this work are presented in ‘A study of radionuclide and metal uptake in mussels from Mudginberri Billabong’, pp 99–104, in this volume.

References

Brazier J, Bollhöfer A, Humphrey C & Ryan B 2009. A longitudinal study of radionuclide and metal uptake in mussels from Magela Creek and Mudginberri Billabong. In *eriss research summary 2007–2008*. eds Jones DR & Webb A, Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 91–97.

Monitoring using macroinvertebrate community structure

C Humphrey, L Chandler & C Camilleri

Macroinvertebrate communities have been sampled from a number of sites in Magela Creek at the end of significant wet season flows, each year from 1988 to the present. The design and methodology have been gradually refined over this period (changes are described in Supervising Scientist 2004). The design is now a balanced one comprising upstream and downstream sites at two ‘exposed’ streams (Gulungul and Magela Creeks) and two control streams (Burdulba and Nourlangie Creeks).

Samples were collected from each site at the end of each wet season (between April and May). For each sampling occasion and for each pair of sites for a particular stream, dissimilarity indices are calculated. These indices are a measure of the extent to which macroinvertebrate communities of the two sites differ from one another. A value of ‘zero’ indicates macroinvertebrate communities identical in structure while a value of ‘one’ indicates totally dissimilar communities, sharing no common taxa.

Disturbed sites, including those impacted by activities other than mining, may be associated with significantly higher dissimilarity values compared with undisturbed sites. Compilation of the full macroinvertebrate dataset from 1988 to 2009 has been completed with results shown in Figure 1. This figure plots the paired-site dissimilarity values using family-level (log-transformed) data, for the two ‘exposed’ streams and the two ‘control’ streams.

Improvements to the presentation and statistical analysis of macroinvertebrate data were described in Humphrey et al (2009). Multi-factor ANOVA can be used to test whether or not macroinvertebrate community structure has altered significantly at the exposed sites for the recent wet season of interest, using dissimilarity values derived for each of the five possible randomly-paired upstream and downstream replicates. Only data gathered since 1998 have been used for this analysis. Data gathered prior to this time were based upon different and less rigorous sampling and sample processing methods, and/or the absence of any sampling in three of the four streams. (Sampling in Gulungul Creek and the control streams only commenced in 1994.)

Inferences that may be drawn from the data shown in Figure 1 are weakened because there are no baseline (pre-1980) data upon which to assess whether or not significant changes have occurred as a consequence of mining. Notwithstanding, a four-factor ANOVA based upon replicate, paired-site dissimilarity values and using the factors Before/After (BA; fixed), Control/Impact (CI; fixed), Year (nested within BA; fixed) and Site (nested within CI; random) showed no significant difference (in dissimilarity) between the control and exposed streams from earlier years (back to 1998) compared with those from 2009 (ie the BA x CI interaction is not significant). While the Year x Site (BA CI) interaction is significant in the same analysis ($p = 0.011$), this simply indicates that dissimilarity values for the different streams – regardless of their status (Before, After, Control, Impact) – show differences through time. The dissimilarity plots shown in Figure 1 corroborate these results, showing reasonable constancy in the mean dissimilarity values for each stream across all years.

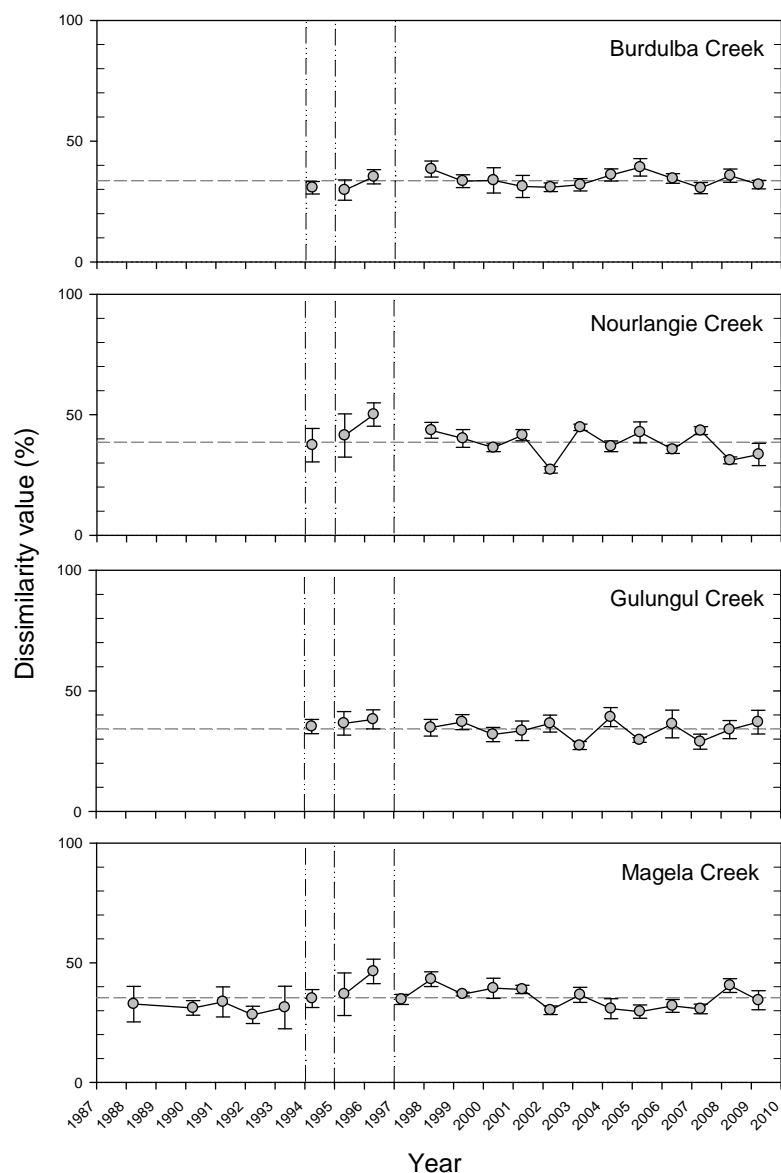


Figure 1 Paired upstream-downstream dissimilarity values (using the Bray-Curtis measure) calculated for community structure of macroinvertebrate families in several streams in the vicinity of Ranger mine for the period 1988 to 2009. The dashed vertical lines delineate periods for which a different sampling and/or sample processing method was used. Dashed horizontal lines indicate mean dissimilarity across years. Dissimilarity values represent means (\pm standard error) of the 5 possible (randomly-selected) pairwise comparisons of upstream-downstream replicate samples within each stream.

Dissimilarity indices such as those used in Figure 1 may also be ‘mapped’ using multivariate ordination techniques to depict the relationship of the community sampled at any one site and sampling occasion with all other possible samples. Samples close to one another in the ordination space indicate a similar community structure. Figure 2 depicts the ordination derived using the *pooled* (average) within-site macroinvertebrate data (unlike the replicate data used to construct the dissimilarity plots in Figure 1). Data points are displayed in terms of the sites sampled in Magela and Gulungul Creeks downstream of Ranger for each year of study (to 2009), relative to Magela and Gulungul Creek upstream (control) sites for 2009, and all other control sites sampled up to 2009 (Magela and Gulungul upstream sites, all sites in Burdulba and Nourlangie). Because the data-points associated with these two sites are generally interspersed among the points representing the control sites, this indicates that these ‘exposed’ sites have

macroinvertebrate communities that are similar to those occurring at control sites. This was verified using ANOSIM (ANalysis Of SIMilarity, effectively an analogue of the univariate ANOVA) testing, to determine if exposed sites (Magela and Gulungul downstream) are significantly different from control sites in multivariate space. ANOSIM conducted on pooled (within-site) data from all years to 2009 showed no significant separation of exposed and control sites for the respective comparisons ($P > 0.05$).

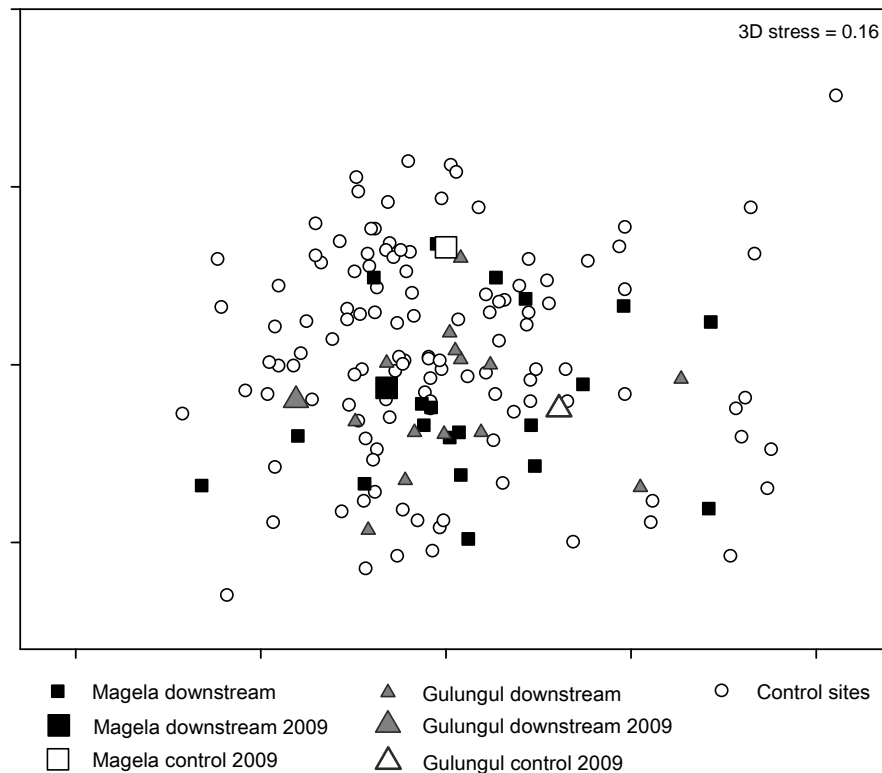


Figure 2 Ordination plot of macroinvertebrate community structure data from sites sampled in several streams in the vicinity of Ranger mine for the period 1988 to 2009. Data from Magela and Gulungul Creeks for 2009 are indicated by the enlarged symbols.

Collectively, these graphical and statistical results provide good evidence that changes to water quality downstream of Ranger as a consequence of mining in the period 1994 to 2009 have not adversely affected macroinvertebrate communities.

References

- Humphrey C, Chandler L & Hanley J 2009. Monitoring using macroinvertebrate community structure. In *eriss research summary 2007–2008*. eds Jones DR & Webb A, Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 57–59.
- Supervising Scientist 2004. *Annual Report 2003–2004*. Supervising Scientist, Darwin.

Monitoring using fish community structure

D Buckle, C Humphrey & C Davies

Assessment of fish communities in billabongs is conducted between late April and July each sampling year. Data are gathered using non-destructive sampling methods from ‘exposed’ and ‘control’ sites in deep channel billabongs annually, and shallow lowland billabongs dominated by aquatic plants, biennially (every other year). Details of the sampling methods and sites were provided in the 2003–04 Supervising Scientist annual report (Supervising Scientist 2004, chapter 2, section 2.2.3). These programs were reviewed in October 2006 and the refinements to their design detailed in Buckle and Humphrey (2008, 2009; shallow and channel billabong fish communities respectively).

For both deep channel and shallow lowland billabongs, comparisons are made between a directly-exposed billabong (Mudginberri) in the Magela Creek catchment downstream of Ranger mine versus control billabongs from an independent catchment (Nourlangie Creek and Wirnmuyurr Creek). The similarity of fish communities in exposed sites to those in control sites is determined using multivariate dissimilarity indices, calculated for each sampling occasion. The use of dissimilarity indices has been described and defined above (see ‘Monitoring using macroinvertebrate community structure’, pp 85–87, in this volume). A significant change or trend in the dissimilarity values over time could imply mining impact.

Channel billabongs

The similarity of fish communities in Mudginberri Billabong (directly exposed site downstream of Ranger in Magela Creek catchment) and Sandy Billabong (control site in the Nourlangie Creek catchment) was determined using multivariate dissimilarity indices calculated for each annual sampling occasion. A plot of the dissimilarity values from 1994 to 2009 is shown in Figure 1.

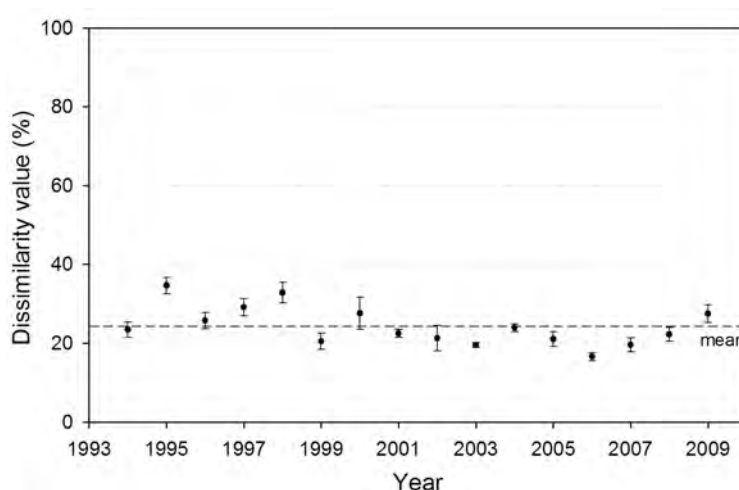


Figure 1 Paired control-exposed dissimilarity values (using the Bray-Curtis measure) calculated for community structure of fish in Mudginberri (‘exposed’) and Sandy (‘control’) Billabongs in the vicinity of Ranger mine over time. Values are means (\pm standard error) of the 5 possible (randomly-selected) pairwise comparisons of transect data between the two billabongs.

In the 2003–04 Supervising Scientist annual report, a decline in paired-site dissimilarity measures over time was noted. This decline in dissimilarity remains significant over the full dataset (1994 to 2009, $P < 0.001$), despite the increase in dissimilarity that has occurred since 2006 (Figure 1). In Buckle and Humphrey (2009), a change in method procedure between the visual canoe (1989–2000) to the visual boat (2001–present) was identified as an issue that required closer scrutiny in the context of the changes seen in the dissimilarity index. This change potentially confounds the observed decline over time due to a significant increase in the time taken to complete each replicate visual count since 2001. The increase in transect times (since 2001) corresponds with a significant step down in the community dissimilarity value, which could potentially explain the overall decline over time. Increased transect times have typically resulted in increased observations of the more cryptic species. Theoretically, this could alter the paired-site community dissimilarity values between the two billabongs, particularly where observations of these less common species are more pronounced in one of the billabongs relative to the other billabong. To date, however, it has not been possible to characterise and quantify the effect, if any, that altered transect times have had on the community dissimilarity values. This is largely due to the complexities of changes in species abundances and their cumulative influence over the dissimilarity value over time.

Notwithstanding, the dissimilarity observed in 2009 (the highest recorded since the introduction of the visual boat in 2001) has occurred without change in sampling method, suggesting that transect times accompanying the change in observation method may not be so influential in determining dissimilarity values. The paired-site fish community dissimilarity value has increased since 2006 and may suggest that natural shifts in community structure over time are occurring. If this is the case, the nature of the community shift should become more evident over the next few years, leading to a possible explanation for the previously-identified decline or step down over time in community dissimilarity values.

In Humphrey et al (2006), the chequered rainbowfish (*Melanotaenia splendida inornata*) was identified as the species that has had most influence on the change in the paired-billabong dissimilarity value. This species, due to its habit, appears unaffected by differences in transect times coinciding with the change to the observation method (Buckle & Humphrey 2009) and as such, the abundances of this species may be regarded as reliable for the entire period that sampling has been conducted in Mudginberri Billabong, from 1989 to 2009. Chequered rainbowfish declined significantly in abundance after about 1996 with relatively low abundances sustained until 2008 (Figure 2) (Buckle & Humphrey 2009). The elevated abundance in rainbowfish in 2009 (Figure 2) provides insights as to the possible cause of population fluctuations, and by association, therefore, the possible cause of interannual changes to the paired-billabong dissimilarity values.

For example, one of the environmental correlates identified in the decline in rainbowfish between 1989 and 2008 is the increase in grasses, and in particular the exotic para grass (*Urochloa mutica*), on Magela floodplain (Humphrey et al (2006). These grasses are still expanding on the floodplain yet rainbowfish abundances in 2009 have returned to values akin to those observed pre-1996 (Figure 2), suggesting the habitat conditions on Magela floodplain (the recruitment source for these fishes) may not be overly important.

In both Humphrey et al (2006) and Buckle and Humphrey (2009) measures of wet season discharge in Magela Creek were identified as correlates of rainbowfish abundance. Rainbowfish abundance from 1989 to 2009 remains negatively correlated with wet season discharge (total monthly discharge in January ($p = 0.016$), February ($p = 0.016$) and the wet season total ($p = 0.029$)), supporting the suggestion that wet season intensity is a factor

controlling the population numbers. Thus rainbowfish abundance is higher following wet seasons of relatively low rainfall (Figure 2).

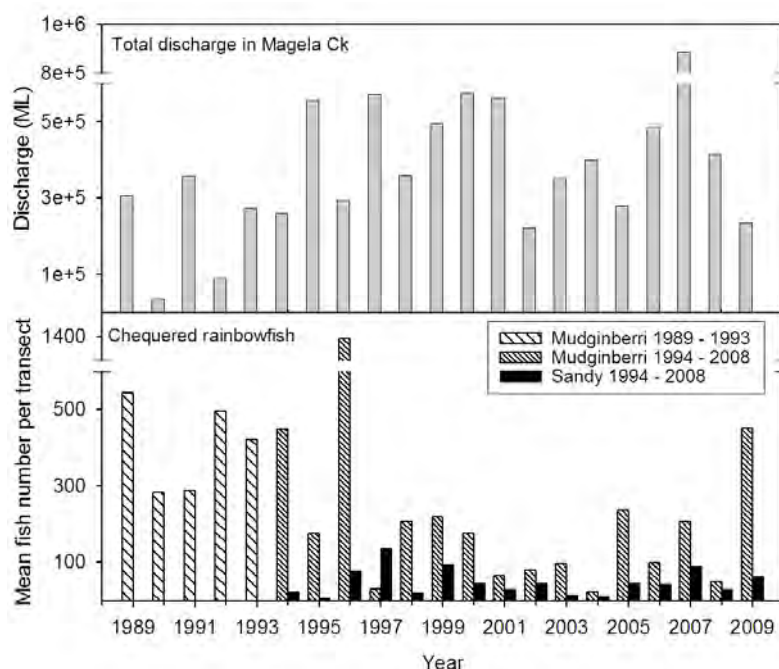


Figure 2 Relative abundance of chequered rainbowfish in Mudginberri and Sandy billabongs from 1989 to 2009 with associated total discharge in Magela Creek (gauging station G8210009)

A possible explanation for this relationship was proposed in Humphrey et al (2006). In field toxicity monitoring tests, larval rainbowfish have been observed to be relatively intolerant of naturally low solute (including nutrient) concentrations that characterise surface waters in wet seasons of high stream discharge. Another causal link may relate to the greater dispersion of fish in wet seasons of higher discharge. In wet seasons of low discharge, stimuli for migration (flood pulses) are reduced, which may lead to fish concentrating more in lowland channel billabongs (Buckle & Humphrey 2009).

Importantly, the abundance of rainbowfish does not appear to be related to any change in water quality over time as a consequence of water management practices at Ranger mine. The net input of magnesium (Mg) from Ranger has been used as a reasonably reliable surrogate measure of mine water inputs to Magela Creek (see Humphrey et al 2006 for further information). For the wet seasons over the period of record from 1988–89 to 2008–09, no significant relationship has been observed between the mine contribution of Mg and corresponding rainbowfish abundance in Mudginberri Billabong. This is not surprising as concentrations of U and Mg in Magela Creek arising from mine waste water discharges are at least two orders of magnitude lower than those known to adversely affect larval fishes including, in the case of uranium, chequered rainbowfish (Supervising Scientist 2004, chapter 3, section 3.4.1 & Humphrey et al 2006).

Shallow lowland billabongs

The last assessment of fish communities in shallow lowland billabongs (a biennial program) was conducted in May 2007 with results reported in Buckle and Humphrey (2008). This paper discusses results from sampling conducted in April and May 2009.

The monitoring program for fish communities in shallow billabongs is conducted biennially in six billabongs, comprising three 'control' versus 'exposed' billabong pairs. In a similar manner to fish communities in channel billabongs (discussed above), the similarity of fish communities in the directly exposed sites downstream of Ranger on Magela Creek (Georgetown, Coonjimba and Gulungul Billabongs) to those of the control sites (Sandy Swamp and Buba Billabongs on Nourlangie Creek and Wirnmuyurr Billabong – a Magela floodplain tributary) was determined using multivariate dissimilarity indices calculated for each sampling occasion. A plot of the dissimilarity values of the control-exposed site pairings – Coonjimba-Buba, Georgetown-Sandy Swamp and Gulungul-Wirnmuyurr Billabongs – from 1994 to the present, is shown in Figure 3.

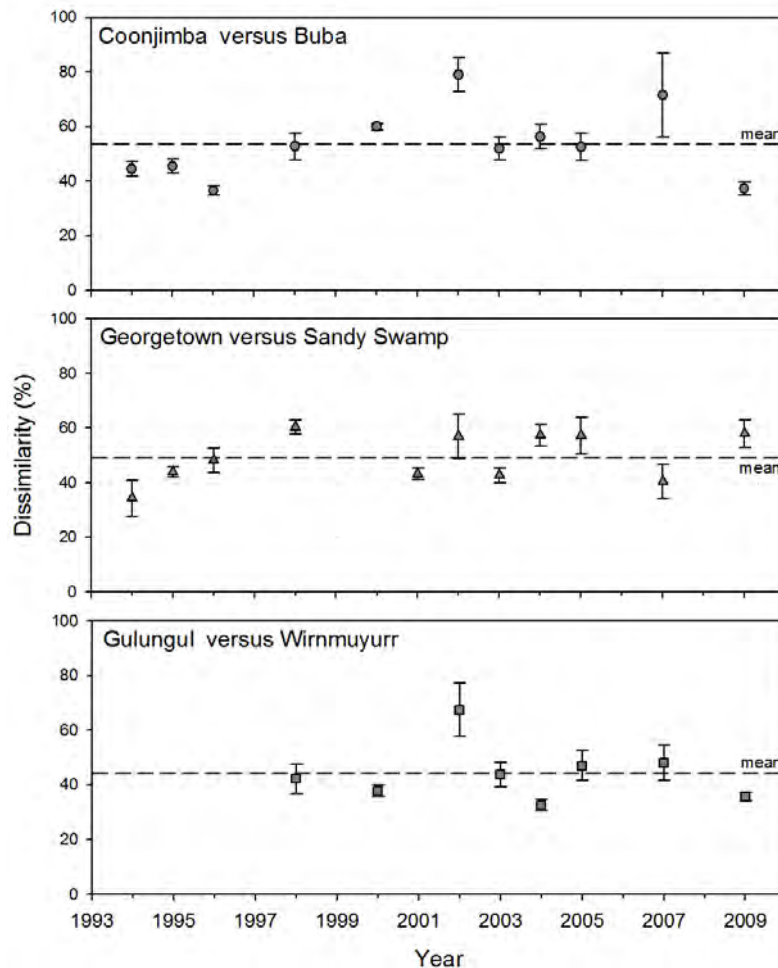


Figure 3 Paired control-exposed site dissimilarity values (using the Bray-Curtis measure) calculated for community structure of fish in 'directly-exposed' Magela and 'control' Nourlangie and Magela Billabongs in the vicinity of Ranger mine over time. Values are means (\pm standard error) of the 5 possible (randomly-selected) pairwise comparisons of average trap enclosure data between the pairwise billabong comparisons, Coonjimba-Buba, Gulungul-Wirnmuyurr and Georgetown-Sandy Billabongs.

The paired-site dissimilarities shown in Figure 3 average between 40 and 60% indicating fish communities in each of the billabongs comprising a site pairing are quite different from one another. In Buckle and Humphrey (2008) it was identified that the particularly high dissimilarity values observed in the Coonjimba-Buba pairing for 2002 and 2007, and the Gulungul-Wirnmuyurr site pairing for 2002 (Figure 3) were attributable to high densities of particular aquatic plant types in one or both of the billabongs. Excessive plant densities are unfavourable for fish communities as fish movement, and hence residency, is physically

prevented. The influence of aquatic plants on fish community structure is further supported by the slightly increased dissimilarity observed in the Georgetown-Sandy Swamp pairing in 2009. The increased dissimilarity appears to be related to an increase in the density of the emergent aquatic plant *Eleocharis* sp in Georgetown Billabong, combined with reduced plant density (dominated by emergent lilies), in Sandy Billabong. The divergence in aquatic plant habitats between the two billabongs appears to have resulted in reduced similarity (increased dissimilarity) in fish community structures between these locations (Figure 3).

In Buckle and Humphrey (2008), an increase over time was observed in the paired Coonjimba-Buba billabong dissimilarity values, irrespective of the removal of years 2002 and 2007 for which high values are associated with unusually high aquatic vegetation density in one or other of the billabongs (discussed above). The reduced dissimilarity found for 2009 has allayed concerns of increasing dissimilarity over time, as a weak relationship only is now present when the years 2002 and 2007 are included in data analysis ($p = 0.03$).

References

- Buckle D & Humphrey C 2008. Monitoring of Ranger mine using fish community structure. In *eriss research summary 2006–2007*. eds Jones DR, Humphrey C, van Dam R & Webb A, Supervising Scientist Report 196, Supervising Scientist, Darwin NT, 56–59.
- Buckle D & Humphrey C 2009. Monitoring of Ranger mine using fish community structure. In *eriss research summary 2007–2008*. eds Jones DR & Webb A, Supervising Scientist Report 200, Supervising Scientist, Darwin NT, 60–63.
- Humphrey C, Buckle D & Pidgeon R 2006. Fish communities in channel billabongs. In *eriss research summary 2004–2005*. eds Evans KG, Rovis-Hermann J, Webb A & Jones DR, Supervising Scientist Report 189, Supervising Scientist, Darwin NT, 48–53.
- Supervising Scientist 2004. *Annual Report 2003–2004*. Supervising Scientist, Darwin.

Stream monitoring program for the Magela Creek catchment: research and development

Introduction

C Humphrey, A Bollhöfer & D Jones

Progress under this component of the stream monitoring program for the Magela Creek catchment is reported by way of (i) results from the monitoring program conducted in the 2008–09 period, and (ii) monitoring support tasks for the same period, including research and development, reviews and reporting. Results under Part (i) are reported in ‘Results from the routine stream monitoring program in Magela Creek catchment, 2008–09’, pp 74–92, this volume.

Tasks under Part (ii) are reported below where the following two summaries are provided:

- 1 enhancements to SSD’s stream monitoring program for Ranger,
- 2 a study of radionuclide and metal uptake in mussels from Mudginberri Billabong.

Prior to reading these summaries, it is advisable to read the introductory section of the accompanying Part (i) paper describing the rationale of the monitoring program and hence the context for the research and development outlined below.

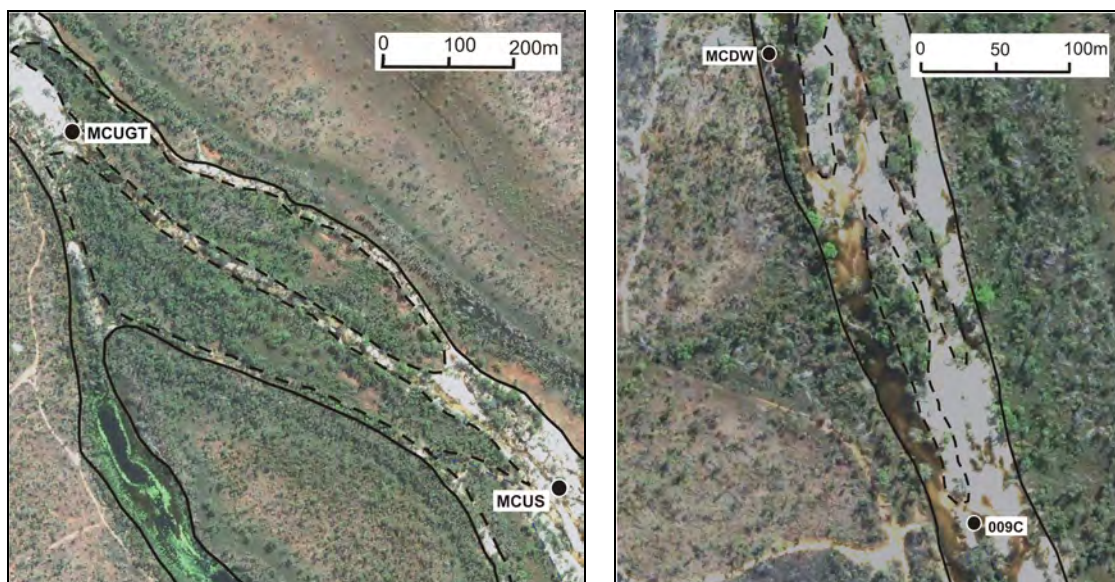
Enhancements to SSD's stream monitoring program for Ranger

J Brazier, C Humphrey, K Turner, D Jones & D Buckle

Ongoing optimisation of existing monitoring methods is one of the processes followed by SSD to ensure that best practice continues to be employed for detection of possible impacts arising from the Ranger mining operation. To this end, some significant changes were made to the Ranger stream monitoring program commencing in the 2008–09 wet season, as outlined below.

Relocation of sampling sites in Magela Creek

The key change made to the water quality monitoring program has been to relocate the Magela Creek sites at which weekly surface water chemistry grab samples have been historically collected. The upstream reference and downstream impacts detection sites, formerly MCUS and 009C (respectively), have been moved to be co-located with the continuous monitoring and in situ toxicity (biological) monitoring pontoon sites – MCUGT and MCDW, respectively (Figure 1). The reason for this change is to provide complete integration among the elements of SSD's water quality monitoring program and thereby reduce replication of effort and possible inconsistency of results between the different locations and monitoring methods. The MCDW downstream site provides a more sensitive location for detecting impacts from the minesite and thus complements rather than replicates the grab sample data produced by the compliance monitoring program carried out by Energy Resources Australia Ltd (ERA), and the check monitoring performed by the Department of Regional Development, Primary Industries, Fisheries and Resources (DRDPIFR).



A Upstream monitoring sites on Magela Creek

B Downstream monitoring sites on Magela Creek

Figure 1 Upstream and downstream monitoring sites used in the SSD's water chemistry (grab sampling and continuous) and toxicity monitoring programs. Channel boundaries are indicated by the continuous or broken (water-level-dependent) lines.

To examine the potential effect of changing the locations of the grab sampling sites on the ability of SSD's program to detect impacts from the minesite, chemical data gathered weekly from MCUGT and MCDW between the 2001 and 2008 wet seasons as part of the creekside toxicity monitoring program were compared with corresponding data collected from MCUS and 009C (the historical reference and compliance sites, respectively) as part of the routine grab sample monitoring program. Concentrations of the key analytes, magnesium, sulfate and uranium, were compared statistically between the sites using Analysis Of Variance testing (Brazier & Humphrey 2009).

The concentrations of the three analytes were shown to be statistically similar between the new upstream reference site (MCUGT) and the historical upstream reference site (MCUS) ($p > 0.05$).

In contrast, the concentrations measured at the proposed new downstream site (MCDW) were found to be significantly higher ($p < 0.05$), albeit by only a very small margin, than those from the compliance site (009C). This is because the compliance site is located in the central channel of Magela Creek while the new site is located in the west channel of Magela Creek. Contaminant levels downstream of Ranger have historically been higher in the west channel compared with the central channel, particularly in relation to discharge events emanating from Ranger Retention Pond 1 (RP1). Water released from RP1 enters Coonjimba Billabong, which eventually drains into the west side of Magela Creek. Results obtained for electrical conductivity (EC) from continuous and grab sample EC monitoring programs in previous years show that water from RP1 mixes incompletely across the west channel and preferentially follows the western bank, particularly during low flow periods.

While the concentrations measured at the MCDW location are statistically higher than values at the compliance site 009C further upstream, the actual magnitude of the difference is only minor, and is not regarded as being sufficient to compromise any assessment of the significance of inputs from the minesite, compared with the use of the 009C location for this purpose. Indeed, sampling in the west channel at the location of the current continuous monitoring and toxicity monitoring will, if anything, result in a more conservative assessment of the contribution of the Ranger mine to solutes in Magela Creek.

Other changes to SSD's weekly grab sampling program in Magela Creek

Commencing with the 2008–09 wet season, physicochemical parameters such as EC, turbidity and pH are being measured in the field only. This change in procedure has been made following several years of good agreement between concurrent field and laboratory measurements, demonstrating that it is possible to obtain reliable measurements in the field with well-calibrated instruments equipped with probes optimised for use in very low EC media.

To provide a further integrity check on the field measurement, the field technician is now comparing the readings taken from the field meter with those being recorded at the same time by the continuous monitoring sonde (data are remotely accessible in the laboratory). If there is good agreement (allowing for known systematic offsets in the continuous readouts), then the field measurement is recorded as valid and reported to stakeholders. If there is disagreement (ie the difference between the two measurements is outside of pre-determined tolerances), then a backup sample of water that was also collected in the field is checked in the laboratory. During the 2008–09 wet season, out-of-tolerance differences between the in situ and field probe measurements occurred on only three occasions. If the discrepancy is attributable to the field measurement, then the continuous monitoring value is reported. If the continuous

monitoring measurement is deemed to be inaccurate, then the field technician will report the concern to the continuous monitoring team to allow them to correct any issues. In all three cases that occurred in the 2008–09 wet season, the lack of agreement between the continuous monitoring and field meter occurred with pH for the lower ionic strength waters from the upstream control site in Magela Creek.

The research emphasis for the water quality monitoring program during the 2008–09 wet season was placed on event-based sampling to capture episodes of elevated EC (ie higher inputs of solutes from the minesite). The data produced by this targeted program of sampling are currently being analysed to determine if there is a functional correlation between EC and U at higher EC values. If such a relationship is found then it may be possible to use this to infer U concentrations from the continuous EC trace during events of elevated EC.

Due to the remote location of the continuous monitoring autosamplers, there is often a time lag (up to 1 week) between sample collection and the physical retrieval of the sample from the field (and subsequent filtration and processing in the laboratory). Alterations to the chemical characteristics of water samples may occur when they are sitting for extended periods, which can lead to loss of dissolved metals (ie in the $<0.45\ \mu\text{m}$ fraction) by binding to particulate matter or sample bottle walls. To assess how the composition of Magela Creek water changes over time, a desk top study will be conducted using historical water quality monitoring data and more recent data acquired from samples collected using the autosamplers. The key objective of this study is to investigate how the dissolved ($<0.45\ \mu\text{m}$) U in a sample changes over time and as a function of turbidity (suspended sediment concentration).

The results from the data analysis project described above will provide the basis for determining if event-based sampling (using the continuous monitoring system and autosamplers) may be able to provide a reliable measure of dissolved concentrations of U during periods of inputs of elevated levels of solutes from the minesite.

Changes to the weekly grab sampling program in Gulungul Creek

Weekly grab sampling for routine analysis of water chemistry variables was discontinued at the upstream location commencing with the 2008–09 wet season. This is because this site may be influenced by upstream (natural) uraniferous catchment effects that compromise its effectiveness for assessing downstream impacts from the mine. Weekly monitoring has continued at the downstream site (GCH). Continuous monitoring of EC and turbidity is being maintained at both the downstream and upstream sites.

Use of in situ testing for ongoing toxicity monitoring

As reported in the Supervising Scientist Annual Report for 2007–08 (section 3.2), a comparative assessment was made between the results from two methods for toxicity monitoring: firstly, creekside monitoring conducted for 17 wet seasons since 1992, and secondly, in situ testing that has been trialled for the past three wet seasons. Both methods of toxicity monitoring use the number of eggs produced by the freshwater snail (*Amerianna cumingi*) as the test endpoint.

Creekside monitoring, which involves pumping a continuous flow of water from the creek through tanks containing test animals located under shelters on the creek's bank, has much higher staff and infrastructure resourcing needs than in situ testing. Comparative testing of the

two methods was conducted over two wet seasons. The results showed greater snail egg production in the in situ method compared with the creekside method but no differences in the upstream-downstream difference values (the critical comparative measure and response end-point) between the two methods. This finding led to the decision to replace creekside with in situ toxicity monitoring, commencing in the 2008–09 wet season.

The in situ toxicity method is providing a more environmentally-relevant testing regime compared with the creekside procedure, whilst requiring substantially reduced staff time and eliminating the need for maintenance-intensive, complex infrastructure.

Continuous monitoring intranet reporting

An automated intranet reporting system was developed prior to the start of the 2008–09 wet season to enable daily upload of continuous data collected from all the SSD continuous monitoring sites (Magela Creek, Gulungul Creek, Ngarradj Creek, Georgetown Billabong, Ranger mine trial landform) to the Department's intranet for immediate assessment by SSD staff. Quality-assessed, validated data are uploaded to the intranet on a monthly basis. The data, which include EC, pH, turbidity, stage height, discharge and rainfall, are presented in the form of time-series plots enabling visual assessment of each parameter (Figure 2).

SSD's continuous monitoring intranet reporting system has been upgraded during the 2009 dry season to ensure timely production, viewing and reporting of data for SSD staff for the 2009–10 wet season.

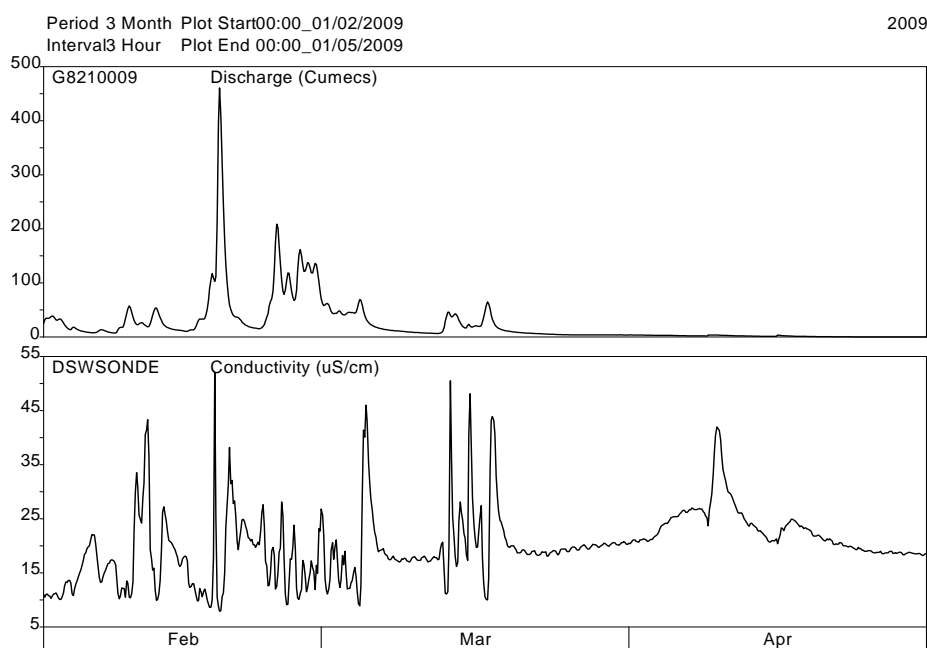


Figure 2 Time-series plot showing validated discharge and electrical conductivity data measured at the upstream site on Magela Creek between February and April 2009

Reference

Brazier J & Humphrey C 2009. Ranger stream monitoring program: relocation of surface water chemistry grab monitoring sites in Magela Creek. Internal Report 563, June, Supervising Scientist, Darwin. Unpublished Paper.

A study of radionuclide and metal uptake in mussels from Mudginberri Billabong

A Bollhöfer, C Humphrey, B Ryan & D Buckle

Background

An important component of the stream monitoring program for Ranger mine measures uptake of selected metals and radionuclides by freshwater mussels, *Velesunio angasi*, from Mudginberri Billabong. Among the suite of radionuclides measured, radium-226 (^{226}Ra) is of particular relevance as ^{226}Ra in mussels has been identified as the major contributor to the total radiological dose from ingestion of bush foods by local indigenous people (Martin et al 1998). There are several factors contributing to this: (a) freshwater mussels are an integral component of the diet of the Mudginberri Aboriginal community located downstream of the mine; (b) the high concentration factor of 19 000 for radium in freshwater mussels (Johnston 1987); and (c) the large ingestion dose coefficient for ^{226}Ra of $0.28 \mu\text{Sv/Bq}$ (ICRP 1996).

During the 22nd ARRTC meeting (October 2008), results were reported from a longitudinal study of radionuclide and metal uptake in mussels from upstream of the mine down to Mudginberri Billabong in the Magela Creek catchment, a total distance of about 30 km. The study was designed to test the hypothesis that Ranger mine was not contributing to the higher radium activity concentrations found in mussels from Mudginberri Billabong compared with concentrations found in mussels from Sandy Billabong, a control site in another (adjacent) catchment. The study showed that radium and metal body burdens in freshwater mussels along the Magela catchment are driven by a number of factors such as mussel growth rate and (soft) body weight, as well as natural water chemistry gradients, particularly Ca and Mg, along the catchment that are unrelated to current mining activity at Ranger. Three observations led to this conclusion: (i) uranium concentrations in the mussels from sites in the longitudinal study were comparable with pre-mining values from 1980; (ii) $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios in mussel flesh decrease gradually along the catchment; and (iii) stable lead isotope ratios in mussel flesh and sediments change gradually as well, rather than a step change which would be expected for a contemporary (point source) mining-related impact (Bollhöfer et al 2010).

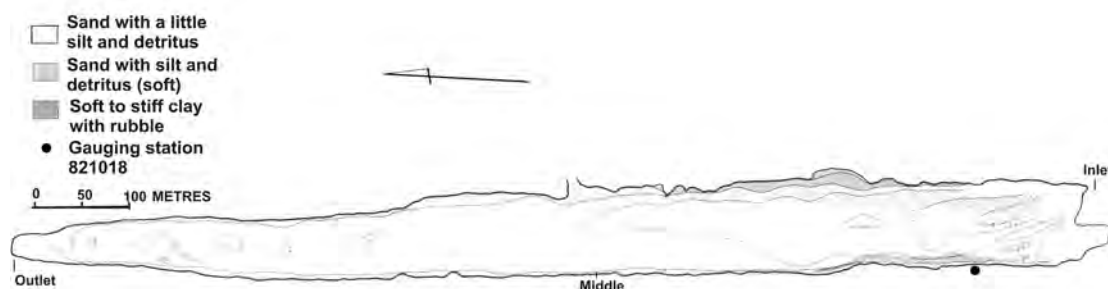


Figure 1 Mudginberri Billabong and location of 2008 sampling sites

To test whether the sampling location and associated variability in the amount of fine sediments have an influence on radium activity and metal concentrations in freshwater mussels from Mudginberri Billabong, mussels were collected for metal, stable lead isotope and radionuclide analyses from the inlet, middle and outlet of the billabong (Figure 3). Sampling occurred at the end of the 2008 dry season. The billabong edges were sampled at the three locations, as the edges are where mussels are typically concentrated and able to be harvested by local Aboriginal people.

Methods

Mussels were collected using a dredge and placed into acid-washed containers holding water collected from the billabong. Surface water samples were collected at the time of mussel collection in acid-washed plastic containers. In addition, between 300 and 400 g of the top 3–5 cm layer of sediment that the mussels were associated with was collected from each site using an Ekman grab. The sediment was placed into zip lock plastic bags and taken to the laboratory for processing.

After collection, mussels were transported to the SSD Darwin laboratories and purged for 6–7 days in billabong water before being measured for weight, length and width, and dissected to remove the flesh. Samples were freeze-dried to determine the dry weight. The age of each mussel was determined by counting the number of annual growth bands (annuli). The dried and ground flesh of each mussel was combined by age class and site, and the average dry weight per age class determined. A composite sample of each age class was cast in epoxy resin for determination of radioisotopes of radium (^{226}Ra & ^{228}Ra), lead (^{210}Pb), and thorium (^{228}Th) by gamma spectrometry. Those mussels less than 1 year of age, or in an age class with insufficient total mass (< 2 g) for analysis by gamma spectrometry, were analysed by alpha spectrometry. Aliquots of the samples were also sent for acid digestion and ICP-MS analysis of lead isotopes and heavy metals.

Results

Radionuclides in mussels

Each mussel age class was measured for the radioisotopes of lead (^{210}Pb), thorium (^{228}Th) and radium (^{226}Ra & ^{228}Ra) by gamma spectrometry and alpha spectrometry, respectively. Figure 2 shows the average ^{226}Ra activity concentration and the $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio per mussel age class for the recent 2008 collection (inlet, middle and outlet values shown separately) compared with data from previous end of dry season collections. ^{226}Ra activity concentrations in mussels collected in 2008 are comparable with activity concentrations determined previously.

^{226}Ra and ^{210}Pb activity concentrations are positively correlated with age, indicating bioaccumulation of these radionuclides, with the ^{226}Ra -age relationship shown in Figure 4. Differences in radionuclide activity concentrations in mussels amongst the three sites were tested, using analysis of covariance (ANCOVA) which, after taking age into account, tests for differences in regression intercepts and slopes. There was no statistically significant difference in the mussel ^{226}Ra activity concentrations ($P=0.45$) and there was a small but statistically insignificant difference in the Ra-age regression slopes ($P=0.061$) among locations, with the middle location exhibiting a slightly larger rate of increase in ^{226}Ra activity concentration with mussel age. There was no difference in the ^{210}Pb activity concentrations ($P=0.67$) nor the ^{210}Pb -age regression slope ($P=0.16$) amongst locations, respectively.

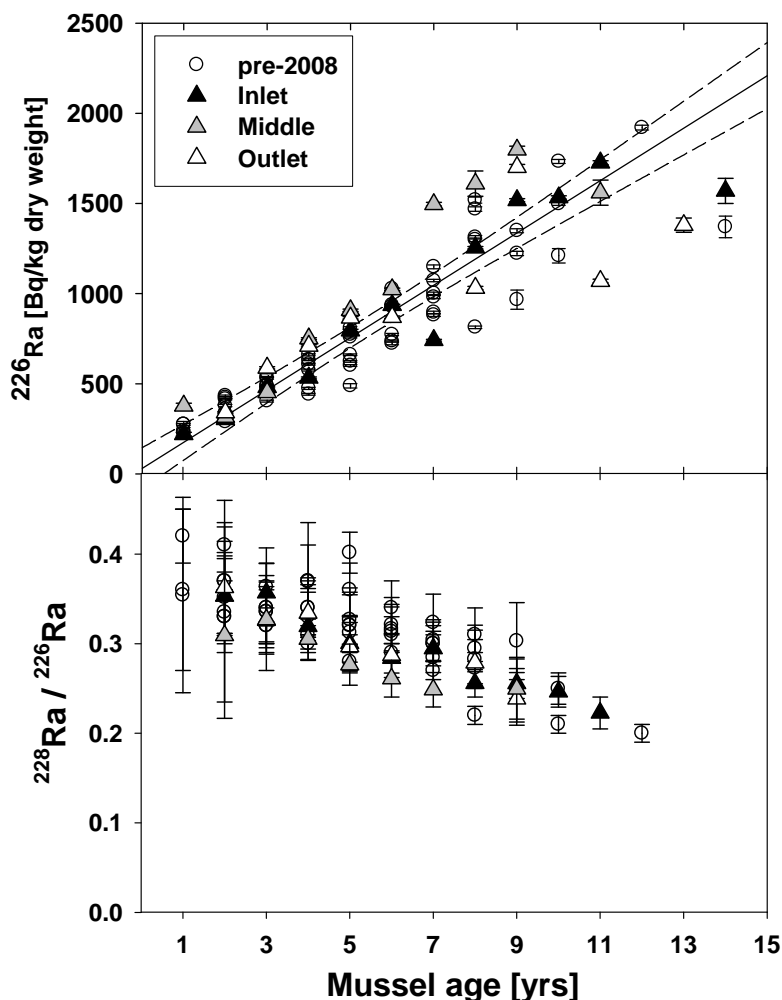


Figure 2 ^{226}Ra activity concentrations (top) and $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios (bottom) measured in mussels collected in 2008, and a comparison with results from previous end of the dry season collections (open circles). The solid line in the activity plot is a linear fit to all of the pre-2008 data, and the dashed lines show the associated 95% confidence limits for this dataset.

^{226}Ra is a member of the uranium decay series and ^{228}Ra of the thorium decay series. Hence the activity ratio of the two radioisotopes provides a measure of the relative contribution of uranium and thorium-rich sources, respectively, to the radium activity concentration in a sample. The lower the $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio is in sediments or mussels, the lower the relative contribution of radium derived from a thorium-rich source and the higher the contribution of radium derived from a uranium rich source, respectively. ANCOVA testing of the $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio measured in age-determined mussels (Figure 4) shows that after taking age into account, there is a significant difference in the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio ($P=0.035$) amongst sites, with mussels collected in the middle exhibiting lower ratios than mussels from the inlet and outlet of the billabong, respectively.

Even though there are differences in the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio measured in the mussels at the three locations, location in the billabong has no measurable effect on the ^{226}Ra and ^{210}Pb activity concentrations in freshwater mussels. Consequently, differences that have been observed over the years for ^{226}Ra and ^{210}Pb data for mussels obtained from a number of sampling locations in Mudginberri Billabong must be the result of other factors, such as the timing of mussel collection (wet versus dry season) or the duration and intensity of the preceding wet season.

Uranium and stable lead in mussels

Uranium and lead concentrations in water, whole sediment, in the $< 63 \mu\text{m}$ sediment fraction (mud and clays) and in dried mussel flesh combined from each age class, were measured by inductively coupled plasma mass spectrometry.

Both uranium and lead concentrations measured in mussel flesh are positively correlated with age. ANCOVA combined with a Tukey's multiple comparison testing showed that this increase with age is highest in mussels from the middle section of the billabong ($P < 0.05$), whereas mussels from the inlet and outlet show similar values. This site difference in concentrations cannot be explained by mussel condition (relative body weights), which, in agreement with earlier studies from the early 1980s, are highest at the inlet and gradually decrease towards the outlet (Figure 3) (Humphrey & Simpson 1985).

Measurements of the concentration of uranium and lead in water collected at the three sites showed no difference amongst the sites. However, the concentrations of metals in whole sediment were generally higher in the middle, as a consequence of the higher proportion of mud and clays (65%) found there compared with the inlet (29%) and outlet (13%) sampling locations in the billabong. It appears that the higher proportion of fines may be the cause of the higher metal concentrations observed in mussel tissue from the middle of the billabong.

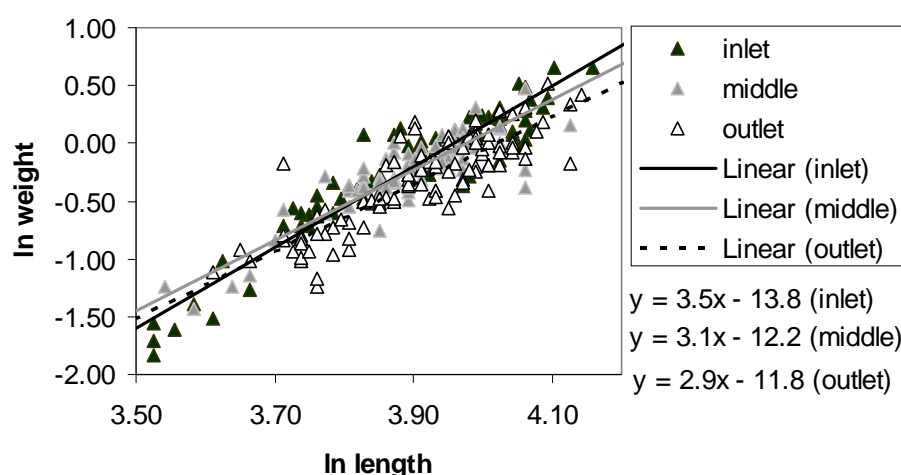


Figure 3 Mussel dry weight (\log_e transformed) plotted against (\log_e transformed) shell length. The slope is lowest at the outlet, indicating poorest mussel condition, and highest at the inlet.

^{206}Pb and ^{207}Pb are the stable end-members of the uranium decay series (^{238}U and ^{235}U , respectively), while ^{208}Pb is the stable end-member of thorium decay (^{232}Th). In Figure 4 the $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios measured in mussel tissue are plotted against the $^{208}\text{Pb}/^{207}\text{Pb}$ ratio and a comparison is made with data from the 2007 longitudinal study and from a previous collection in 2005. This method enables the determination of the relative contribution of different sources to the total lead concentration in a sample.

Common lead isotope signatures are, for example, the PDAC (Present Day Average Crustal) ($^{206}\text{Pb}/^{207}\text{Pb} \approx 1.20$ and $^{208}\text{Pb}/^{207}\text{Pb} \approx 2.48$) or the Broken Hill and Mt Isa lead isotope signatures ($^{206}\text{Pb}/^{207}\text{Pb} < 1.04$ and $^{208}\text{Pb}/^{207}\text{Pb} < 2.32$), respectively (Doe 1970). Broken Hill and Mt Isa lead has been used in Australia and worldwide for many decades for the manufacturing of industrial lead products, and contamination with this type of lead can be traced via its low $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ isotopic fingerprint (Bollhöfer & Rosman 2000, 2001). In contrast, high $^{206}\text{Pb}/^{207}\text{Pb}$ and low $^{208}\text{Pb}/^{207}\text{Pb}$ ratios indicate a contribution from a

uranium rich source, whereas high $^{208}\text{Pb}/^{207}\text{Pb}$ indicates a thorium rich source. As lead isotopes are physically and chemically alike and not discriminated by environmental processes, varying proportions of lead from different sources in a biological sample can be directly related to the total lead isotopic composition seen in the sample.

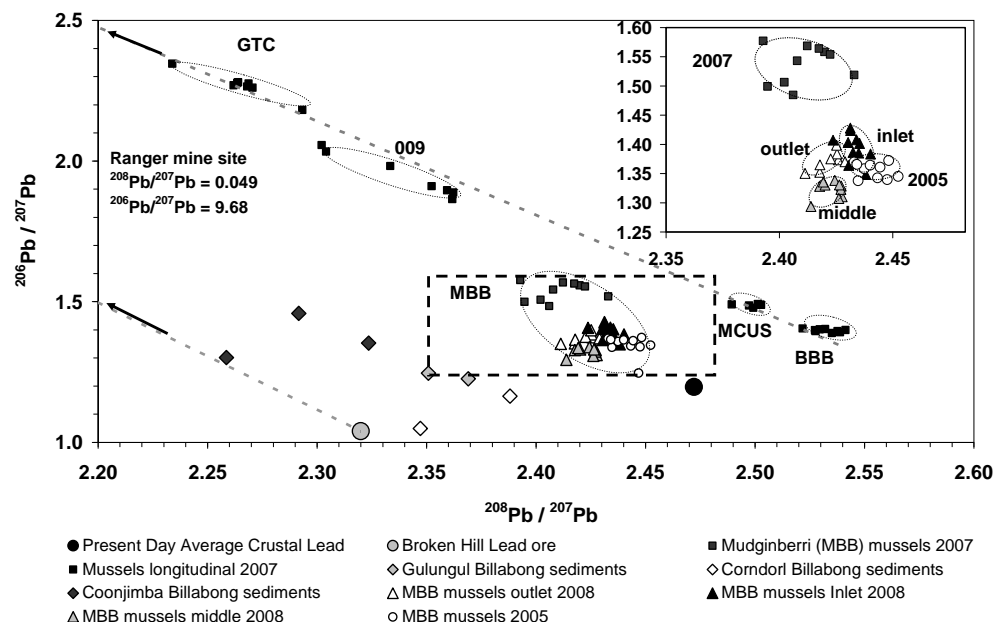


Figure 4 $^{206}\text{Pb}/^{207}\text{Pb}$ plotted against $^{208}\text{Pb}/^{207}\text{Pb}$ isotope ratios measured in mussel tissue from Mudginberri Billabong, and previous data from Magela Creek. Trendlines (dashed) assume mixing of radiogenic lead with the Ranger ore signature and lead with an Upper Magela catchment signature and Broken Hill lead, respectively. Each site's mussel lead isotope signature is circled with the site label. BBB: Bowerbird Billabong, MCUS: Magela Creek upstream; GTC: Georgetown confluence; G8210009: Magela Creek downstream; MBB: Mudginberri Billabong (Supervising Scientist 2007). The inset shows a magnification of the dashed rectangle depicting the Mudginberri Billabong data only.

Figure 4 illustrates that there are within-billabong variations in the lead isotope ratios measured in mussel flesh, although these differences are much less pronounced than those observed along Magela Creek for the 2007 longitudinal study. While there are only small differences in Pb isotope ratios in mussels between the two end of dry season collections from the inlet (October 2005 and October 2008, respectively), mussels collected in May 2007 exhibit a more uraniferous signature. This is most likely caused by a difference in sampling location. Due to accessibility issues at the end of the wet season, mussels were sampled further upstream, closer to the Magela Creek channel in May 2007, and hence the lead isotope ratios are more similar to those measured at G8210009. In contrast, the sampling site in 2008 was influenced to a much greater extent by billabong mud and clays, which typically show Pb isotope ratios closer to PDAC.

Lead isotope signatures measured in mussels collected in 2008 from the outlet lie in between those of the inlet and middle isotope ratios (Figure 4). Mussels collected from the middle appear to be influenced by an additional (industrial) source that exhibits lead isotope ratios similar to those found in Corndorl Billabong sediments, a location unaffected by runoff from the Ranger minesite. This is indicative of contamination with lead from sources such as lead shot, fishing sinkers, or other manufactured products containing Pb from commercial Australian orebodies. The middle sampling site is closest to (and directly downstream of) the boat ramp and would also be the site most exposed to runoff from the Mudginberri community as well as from the

adjacent paddocks of the historic Mudginberri pastoral station. Together, these factors would place this site at highest risk of contamination from industrial lead.

Conclusion

This study found subtle variations in the relative contribution of sources of lead and uranium in the tissue of freshwater mussels collected from within Mudginberri Billabong. The concentrations of these metals in mussels appear to be mainly influenced by the proportion of fine sediment ($< 63 \mu\text{m}$) at the sampling site. The lead isotope ratios indicate an additional industrial source of lead, in the middle or western edge of the billabong.

Importantly, ^{226}Ra and ^{210}Pb activity concentrations in mussels (which determine most of the dose received via the ingestion of mussels) are not statistically different amongst sites. Thus the site of collection of mussels in Mudginberri Billabong is unlikely to affect the levels of ^{226}Ra and ^{210}Pb measured for the purposes of conducting a dose assessment. The results provide increased confidence that the data from previous mussel collections conducted from several locations in the billabong over the years can be directly compared, if factors that affect mussel condition, such as timing of mussel collection and the duration and intensity of the preceding wet season, are taken into account.

References

- Bollhöfer A & Rosman KJR 2000. Isotopic source signatures for atmospheric lead: The Southern Hemisphere. *Geochim. Cosmochim. Acta* 64, 3251–3262.
- Bollhöfer A & Rosman KJR 2001. Isotopic source signatures for atmospheric lead: The Northern Hemisphere. *Geochim. Cosmochim. Acta* 65, 1727–1740.
- Bollhöfer A, Brazier J, Ryan B, Humphrey C & Esparon A 2010. A study of radium bioaccumulation in freshwater mussels, *Velesunio angasi*, in the Magela Creek catchment, Northern Territory, Australia. submitted to the *Journal of Environmental Radioactivity*
- Brazier J & Humphrey C 2009. Ranger stream monitoring program: relocation of surface water chemistry grab monitoring sites in Magela Creek. Internal Report 563, June, Supervising Scientist, Darwin. Unpublished Paper.
- Doe BR 1970. *Lead isotopes*. Springer-Verlag, Berlin, Germany.
- Humphrey CL & Simpson RD 1985. The biology and ecology of *Velesunio Angasi* (Bivalvia: Hyriidae) in the Magel Creek, Northern Territory. Open File Record 38. Supervising Scientist for the Alligator Rivers Region.
- ICRP 1996. Age-dependent doses to members of the public from the intake of radionuclides: part 5. Compilation of Ingestion and Inhalation dose coefficients. ICRP Publication 72, Elsevier.
- Johnston A 1987. *Radiation exposure of members of the public resulting from operations of the Ranger Uranium Mine*. Technical memorandum 20, Supervising Scientist for the Alligator Rivers Region, AGPS, Canberra.
- Martin P, Hancock GJ, Johnston A & Murray AS 1998. Natural-series radionuclides in traditional north Australian Aboriginal foods. *Journal of Environmental Radioactivity* 40, 37–58.
- Supervising Scientist 2007. *Annual Report 2006–2007*. Supervising Scientist, Darwin.