

---

## Review of solute selection for water quality and bioaccumulation monitoring at a northern Australian uranium mine

Alison Frostick, David Jones, Kate Turner

*Supervising Scientist Division, DSEWPAC, GPO Box 461, Darwin NT 0801, Australia;  
alison.frostick@environment.gov.au*

### Abstract

The suite of analytes measured in the surface water chemistry and bioaccumulation monitoring programs carried out by the Supervising Scientist Division is based on periodical risk assessment that identifies those analytes of most concern for the environment.

Analytes are identified to be of potential environmental importance based upon:

- their presence at higher-than-background concentrations in the on-site mine water management ponds and in the receiving environment downstream of the mine;
- their potential for attenuation by natural physical and chemical processes; and
- their potential for biological impact based on concentrations present.

**Keywords:** uranium mining, surface water chemistry, bioaccumulation, water quality guidelines, solute selection

### Introduction

The role of the Supervising Scientist Division (SSD) is to undertake environmental research and reviews of the environmental performance of uranium mines in the Alligator Rivers Region in the Northern Territory to ensure the region's environment, including Kakadu National Park (KNP), remains protected from the potential impacts of uranium mining. KNP is recognised internationally for its outstanding natural and cultural values by inscription on the World Heritage List. The Ranger mine lease (Figure 1) lies within the Magela Creek catchment within KNP, upstream of the Ramsar-listed Magela Creek wetlands. The full scope of the integrated water quality and biological monitoring program conducted by SSD is described in Jones et al (2009) and provides the background context for the work that is described here.

Prior to commencement of mining, potential metals of concern for the mining operation were originally identified by comparing metal concentrations in samples of ore with 'background' concentrations from unmineralised areas (Klessa 2000, 2001a, b, Office of the Supervising Scientist 2002). This is a useful first approach. However, since the initial assessments were carried out, there have been major improvements in analytical equipment, methods and detection limits for trace metals, the Australian and New Zealand Environment and Conservation Council [ANZECC] and Agriculture and Resource Management Council of Australia and New Zealand [ARMCANZ] published updated recommendations/guidelines for water quality assessment (ANZECC & ARMCANZ

2000), and there was a shift from mining of Pit 1 to Pit 3 in 1997 causing potential changes to the trace element composition of mine runoff and seepage waters.

To ensure that the monitoring programs continue to provide the most relevant data for detecting changes in mine-related inputs, the analysis suite needs to be reviewed periodically in response to changes in mine operations, site water management strategies, and changes to the monitoring performed by other parties. This paper specifically addresses the non-radionuclide component of the water quality monitoring program. Details about the radionuclide component, which is focussed on measurements of  $^{226}\text{Ra}$  activity, can be found in Sauerland et al (2005) and references therein.

A detailed review of the analysis suite was carried out by assessing the full trace metal and selected major anion/cation profile of minesite waterbodies and major catchment runoff lines that transport mine-derived runoff to the receiving environment during the 2005-06 wet season (Turner & Jones 2009) with a follow up done in the 2010-11 wet season (this paper).

These assessments identified solutes that are capable of being delivered to the receiving waterway (Magela Creek) by surface water transport along the minesite catchment tributaries. The results facilitated a risk assessment and the subsequent re-assessment of the analysis suite used in both the surface water chemistry monitoring and bioaccumulation monitoring programs carried out in the Magela Creek catchment.

#### *Description of Study Area*

The Alligator Rivers Region, including the Ranger Project Area, has a wet-dry monsoonal climate, with an average rainfall of 1500 mm that falls during a well defined six-month period (November-April). During the peak wet season months of creek flow (January-April) Magela Creek receives mine-derived waters that are actively released along the Coonjimba and Corridor Creek catchment lines, as well as mine-related constituents that are remobilised from the land application areas (LAAs) in the vicinity of these creeks (Figure 2). Land application areas are a means of disposal of polished waters via evapo-transpiration. There are also minor surface run-off discharges from sumps and culverts located around the northern rim of Pit #3 (Figure 2).

Both the Coonjimba and Corridor Creek catchment lines have been substantially modified over time, with the construction of wetland filters to 'polish' release waters and various bunds and weirs to assist with sediment retention, flow control and measurement. The Ranger water management system applies to a range of water classes including: process water (zero-release processing and TSF circuit), pond water (seepage and runoff from waste rock and stockpiles), managed release water, potable water and pond water microfiltration/reverse osmosis (MF/RO) treatment plant permeate. Each class of water differs according to its composition, which dictates the way it is managed (ERA 2010a, 2011a). Refer to Figure 2 for site locations.

It is important to note that pond water and managed release water are the most relevant classes for this paper, since they are the only classes that can interact with

the external environment. The catchment area for pond water covers the active mine-site area, mineralised waste rock stockpiles, stormwater runoff from the plant footprint and pond water outflow from the processing plant. The major pond water storage facility is retention pond 2 (RP2). Pond water is currently disposed of or treated by a combination of methods of wetland filtration and active MF/RO treatment. The catchment area for managed release water covers RP1, Corridor Creek and the crest of Pit #3. Runoff from natural woodland areas, borrow pits and adjacent land application areas reports to RP1 and the Corridor Creek wetlands, which ultimately discharge into Magela Creek via the Coonjimba Billabong and Corridor Creek (via GC2) flow lines, respectively. Gulungul Creek receives relatively small volumes of passively released surface water run-off from the south and west walls of the tailings storage facility (Figure 2). Results for Gulungul Creek have been excluded from this paper, which focuses on the pond water and managed release water reporting to Magela Creek.

## Methods

Surface water samples were collected during the 2005-06 and 2010-11 wet seasons from a number of tributaries and constructed waterbodies on the Ranger lease as well as upstream (control, Magela u/s) and downstream (exposed, Magela d/s) locations in Magela Creek (Table 1 and Figure 2).

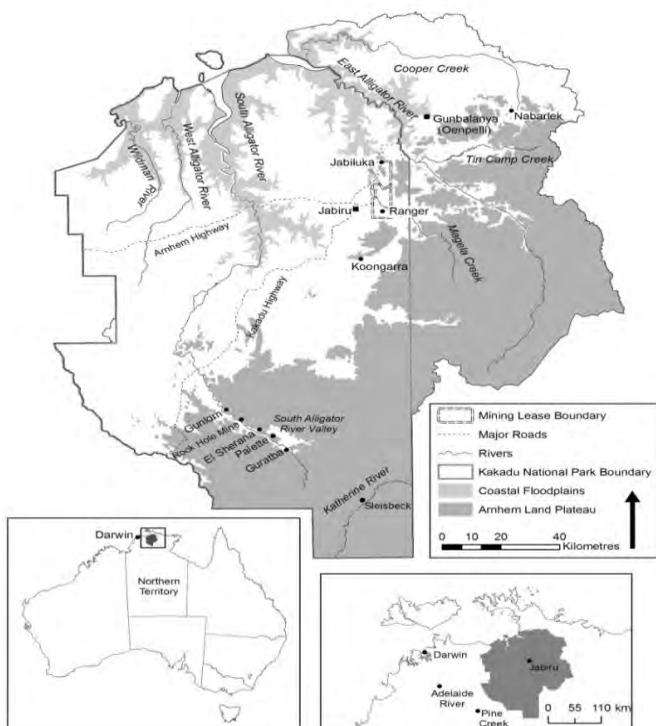
**Table 1** Sampling sites

Site	Description		Major inputs
Magela u/s	Magela upstream	Creek	Undisturbed areas of Magela catchment upstream of Ranger mine
Magela d/s	Magela downstream	Creek west channel	Magela u/s, Corridor Creek via Georgetown Billabong, RP1 via Coonjimba Billabong, land application area runoff
CCWLF (Cell 1)	Corridor Wetland Filter	Creek	Runoff from stock piles, pond water treatment plant permeate
GC2	Corridor downstream	Creek	CCWLF, land application area runoff
RP1	Retention Pond 1		RP1 Constructed Wetland Filter, land application area runoff and seepage from bunded structures in the upper catchment
RP2	Retention Pond 2		Water from Pit 3, runoff and seepage from stock piles, processing and milling area and haul roads, water treatment plant brines

Water samples were analysed for dissolved metals (filtered in-situ to <45 µm). All samples were sent to a National Association of Testing Authorities (NATA) accredited laboratory for the analysis of major anions and cations and the full suite of trace metals (60+ analytes that can be provided by a quantitative Inductively Coupled Plasma Mass Spectrometry (ICPMS) element scan.

## Results and discussion

There are many metals/metalloids that have historically been identified worldwide as having a potential to bioaccumulate and/or to biomagnify. 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. Silver, beryllium, cadmium, chromium and mercury were present in the mine-derived waters at concentrations less than or equal to the corresponding analytical detection limits (DL). Since these values were so low as to present negligible risk to the environment, the data for these elements will not be discussed further. Concentrations of metals/metalloids present at higher than DL in mine-derived waters and Magela Creek collected during the 2005-06 and 2010-2011 wet seasons are presented in Table 2.



**Figure 1** Location of Ranger mine

**Table 2** Median dissolved analyte concentrations measured in mine waterbodies and in Magela Creek. (Values are µg/L except elements marked\* which are mg/L)

Element	Magela u/s		Magela d/s		CCWLF		GC2		RP1		RP2	
	6 2005/6	1 2011	6 2005/6	1 2011	1 2005/6	4 2011	3 2005/6	1 2011	5 2005/6	2 2011	7 2005/6	2 2011
Aluminium (Al)	55.4	82.3	77.2	71.5	7.5	1.6	109	19.7	20.0	1.7	346	45.1
Arsenic (As)	0.08	0.05	0.09	<DL	0.25	0.2	0.18	0.05	0.23	0.15	0.83	<DL
Cobalt (Co)	0.13	0.11	0.13	0.08	4.1	0.11	0.33	0.03	0.09	0.02	12.2	2.54
Copper (Cu)	0.15	0.18	0.18	0.22	4.1	1.01	1.3	0.36	0.41	0.45	23.7	6.49
Iron (Fe)	113	80	127	60	10	<DL	21.3	100	64.0	80	77	<DL
Magnesium (Mg)*	0.65	0.9	1.3	1.0	30.5	2.8	9.27	4	58.8	30.2	176	339
Manganese (Mn)	5.69	4.09	6.4	4.77	140	34.6	37.2	5.88	13.2	2.49	489	79.3
Lead (Pb)	0.03	0.01	0.018	0.04	0.14	0.02	0.24	0.05	0.072	0.05	44.3	8.7
Sulfate (SO <sub>4</sub> )*	0.3	0.2	0.3	0.8	3.0	5.3	30.2	8.1	223	106	797	1520
Selenium (Se)	0.1	<DL	0.1	<DL	2.0	<DL	0.3	<DL	0.26	<DL	11.9	43
Uranium (U)	0.021	0.008	0.117	0.035	1150	12.4	11.4	2.13	7.55	3.12	4034	3260
Vanadium (V)	0.35	0.55	0.38	0.35	0.1	<DL	0.3	0.1	0.2	0.05	0.29	0.55
Zinc (Zn)	0.54	0.4	0.95	0.5	4.9	2.2	0.57	0.3	2.58	0.5	40.9	34.2

<DL: less than the practical quantitation limit for analysis

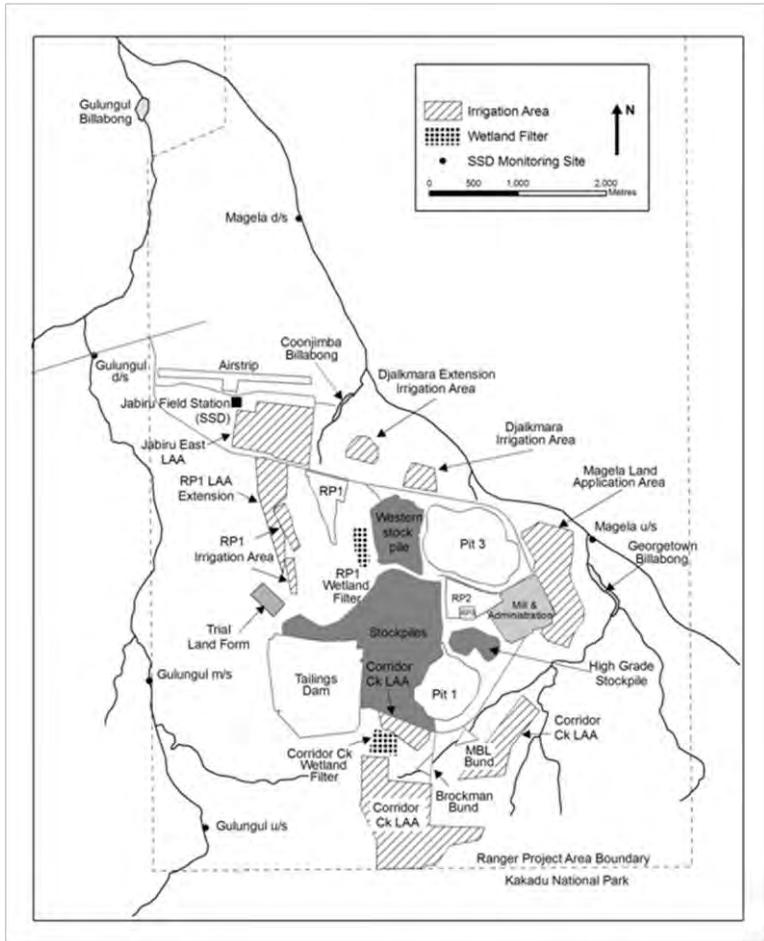
*Risk based on release potential*

The data in Table 2 show that the median concentrations of metals in RP2 are much higher than in RP1 and Corridor Creek at GC2 (located downstream of GCMBL in Figure 2). 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 (ERA 2010a, 2011a). Site-specific ecotoxicological assessment using a suite of six local aquatic species has determined a statutory limit trigger value of 6 µg/L for U in Magela Creek (Hogan et al 2003). Site-specific guidelines have been determined for manganese (26 µg/L) via statistical analysis of upstream water quality, and guideline values for magnesium and sulfate determined by statistical distribution of 'proxy' electrical conductivity data recognising that these two ions dominate the major ion chemistry (Klessa 2001b). For other analytes the recommended ANZECC & ARMCANZ 99% species protection level (ANZECC & ARMCANZ 2000), where available, have been used to evaluate the potential for ecological impact.

Over the five year period between the 2006 and 2011 solute assessments, there have been many changes in the mining operation, water management practices and monitoring programs run by the mine operator, Energy Resources of Australia Ltd (ERA). The waste rock piles, especially the Western stockpile, have increased substantially in terms of their volume and footprint area as mining has progressed in Pit #3. The increased surface run-off and seepage from the stockpiles delivered increasing solute loads to RP1 between 2005 and 2010, with water quality in this pond progressively deteriorating over this period. Peak uranium (U) and magnesium (Mg) concentrations in RP1 increased from 9.8 µg/L and 80.3 mg/L to historical maxima of 59.2 µg/L and 152 mg/L respectively, between 2006 and 2009 (ERA 2010b, 2011b).

To reduce the inputs of solutes into RP1 via lateral shallow groundwater seepage from the Western stockpile, ERA installed an interception trench, called the Western Stockpile Interception System (WSIS), during the 2010 dry season. The WSIS collects runoff and seepage from the northern and western side of the western stockpile and its extension, the RP1 Wetland Filter (RP1WLF) and from mineralised stockpiles located to the south of RP1. The collected seepage is transferred to the pond water circuit (RP2). 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 and pond water treatment plant permeate. The transfer of pond water permeate to RP1 and Corridor Creek (via CCWLF and GCMBL) during 2010-11, together with the WSIS, has proven effective at reducing the concentration of solutes (Table 2).

Zinc concentrations at all monitoring sites and copper concentrations in the majority of on-site waterbodies, except CCWLF, exhibited a decrease in concentration between 2005-06 and 2011. The concentrations of Zn, Pb and Cu are generally below their 99% guidelines of 2.4 µg/L, 1 µg/L and 1 µg/L respectively with the exception of RP2, and CCWLF for Cu.



**Figure 2** Map of Ranger minesite showing adjacent billabongs, creek systems and key water quality monitoring sites

The attenuation and dilution of these elements within the tributaries and sentinel waterbodies on site means that these metals are not of environmental concern for Magela Creek. These elements, however, provide an excellent indicator of sample contamination that may inadvertently and occasionally occur as a result of lapse in sample collection practice or contamination in the receiving laboratory.

#### *Risk based on background concentrations*

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 the mine discharge points (RP1 and GC2) and Magela Creek that provide additional polishing of discharge waters. In the case of GC2 it is Georgetown Billabong (GTB), and in the case of RP1 it is Coonjimba Billabong (Figure 2). Additionally, in the case of GC2, substantial downstream dilution is provided by tributary creeks entering between that location and Georgetown Billabong. Whilst attenuation (via physicochemical and biological uptake processes) of very low concentrations of solutes can occur through these intermediary waterbodies it is not to be implied that these systems are a de facto part of the minewater treatment system, or that the values of these waterbodies are being compromised. In this context periodic assessment of the macroinvertebrate assemblages in GTB in 1994, 1996 and 2005 have shown no significant differences to a number of non-mine impacted reference billabongs in the region (Jones et al 2009).

The data in Table 2 show that arsenic, copper, magnesium, manganese, lead, sulfate, uranium and zinc are present in RP1 and/or GC2 at concentrations higher than those measured upstream in Magela Creek (Magela u/s). Of these analytes, copper, magnesium, manganese, sulfate, uranium and zinc are higher at the downstream site in Magela Creek compared with the upstream site.

#### *Risk based on comparison with current guidelines*

For the known bioaccumulators, arsenic and vanadium, concentrations were less than the ANZECC & ARMCANZ 99% guidelines of 1 µg/L As (III), 0.8 µg/L As (V) and the low reliability guideline of 6 µg/L for V for all samples and time periods. The only exception was the median concentration of As (V) at 0.83 µg/L measured in RP2 during 2005-06. Concentrations of cobalt, selenium and zinc were below the 99% guidelines of 2.8 µg/L, 5.0 µg/L and 2.4 µg/L respectively at all sites except RP2. Whilst the 2005-06 review showed an increase in anlyte concentrations in both on-site waterbodies and creeks at the end of the wet season (Turner and Jones 2010), the observed ~4 fold increase in selenium concentration in RP2 water between 2005-06 and 2011, together with a similar proportional increase in Mg and SO<sub>4</sub>, is possibly due to the transfer of water treatment plant brines and WSIS waters into RP2 that occurred during the 2010-11 wet season.

Iron concentrations were below the ANZECC 99% guideline of 300 µg/L for both 2005-06 and 2011. Aluminium concentrations (compared to the 99% guideline of 27 µg/L) appear naturally elevated within the lotic environment of Magela Creek and its tributaries (see Magela u/s, Table 2). Within lentic on-site waterbodies, concentrations of Al in CCWLF and RP1 were reduced in comparison with lotic monitoring sites, most likely due to geochemical processes (adsorption and deposition of particulates).

As a result of the water quality assessments carried out in 2006 and 2011, the current routine suite of water quality analytes for the Magela Creek monitoring programs includes all solutes that pose a potential risk to the receiving environment. These solutes include Mg, Ca and SO<sub>4</sub> as the major ions, with Al, Cu, Fe, Pb, Mn, U and Zn as the measured trace elements. SSD monitoring data at the downstream monitoring site in Magela Creek from 2001-2011 exhibit median

concentrations of filterable Cu (0.23 µg/L), Fe (100 µg/L), Pb (0.02 µg/L) and Zn (0.7 µg/L) significantly below the applicable ANZECC water quality guidelines for aquatic species protection (ANZECC & ARM CANZ 2000). The median concentrations of Al from 2001-2011 at Magela u/s and Magela d/s are 24.8 µg/L and 29.9 µg/L, respectively. Whilst the Al concentration at the downstream site is marginally above the 99% ANZECC & ARM CANZ guideline, the very small difference between the upstream and downstream indicates that the concentrations of Al are naturally elevated within the catchment with only a minor contribution from the mine site.

## Conclusions

Results from this solute review indicate that while there are many analytes, including potential bioaccumulating metals, present at concentrations much greater than the Magela Creek upstream background in the mine site pond waters, the concentrations of these analytes are substantially reduced by attenuation during passage of the water through the tributary creek lines incorporating mine water polishing wetlands, in Georgetown and Coonjimba Billabongs and by dilution or adsorption on particulates present in Magela Creek.

The current routine suite of analytes includes all of the potential at risk metals/solutes identified above, namely, U, Mg, Mn and SO<sub>4</sub>. Some additional metals are included but these are primarily for quality control purposes, rather than for environmental impact assessment because they provide sensitive markers of sample contamination that may occur during collection or in the chemical analysis laboratory. Measured concentrations that are higher than a predetermined tolerance limit(s) for either one or all of this secondary suite of metals provides a warning that the rigorous (clean) procedures involved in collection or handling a sample for trace metal analysis have been compromised.

Results from this study provide confidence that the non-radiological component of the water quality monitoring program conducted by SSD, is not overlooking any potential analytes that could be of concern from either toxicological or bioaccumulation perspectives.

## Acknowledgements

The authors would like to thank Keith Tayler for reviewing this paper.

## References

- ANZECC & ARM CANZ (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council, and Agriculture and Resource Management Council of Australia and New Zealand, Canberra.
- Department of Resources (2011) Ranger Authorisation 0108-13. Northern Territory Government, Darwin NT.
- ERA Ltd (2010a) ERA Ranger Water Management Plan 2010-2011.
- ERA Ltd (2010b) ERA Ranger Wet Season Report 2010-2011.
- ERA Ltd (2011a) ERA Ranger Water Management Plan 2011-2012.
- ERA Ltd (2011b) ERA Ranger Wet Season Report 2011-2012.

- Hogan AC, van Dam RA, Markich SJ, Camilleri C (2003) Chronic toxicity of uranium to the tropical green alga *Chlorella* sp. for the derivation of a site specific Trigger Value for Magela Creek. Internal Report 412, Supervising Scientist, Darwin. Unpublished paper.
- Jones DR, Humphrey C, van Dam R, Harford A, Turner K & Bollhöfer A (2009) Integrated chemical, radiological and biological monitoring for an Australian uranium mine: a best practice case study. In *Proceedings International Mine Water Conference*, 19–23 October, Pretoria, South Africa, Water Institute of South Africa, ISBN 978-0-9802623-5-3, 95–104.
- 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.
- Office of the Supervising Scientist (2002) Review of water standards (historic document). Internal Report 397, December, 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, vol 40, S451–S456.
- Turner K, Jones D (2010) Review of solute selection for water quality and bioaccumulation monitoring. In: Jones DR, Webb A (Eds) eriss research summary 2008–2009, Supervising Scientist Report 201, Supervising Scientist, Darwin NT, 66–72.