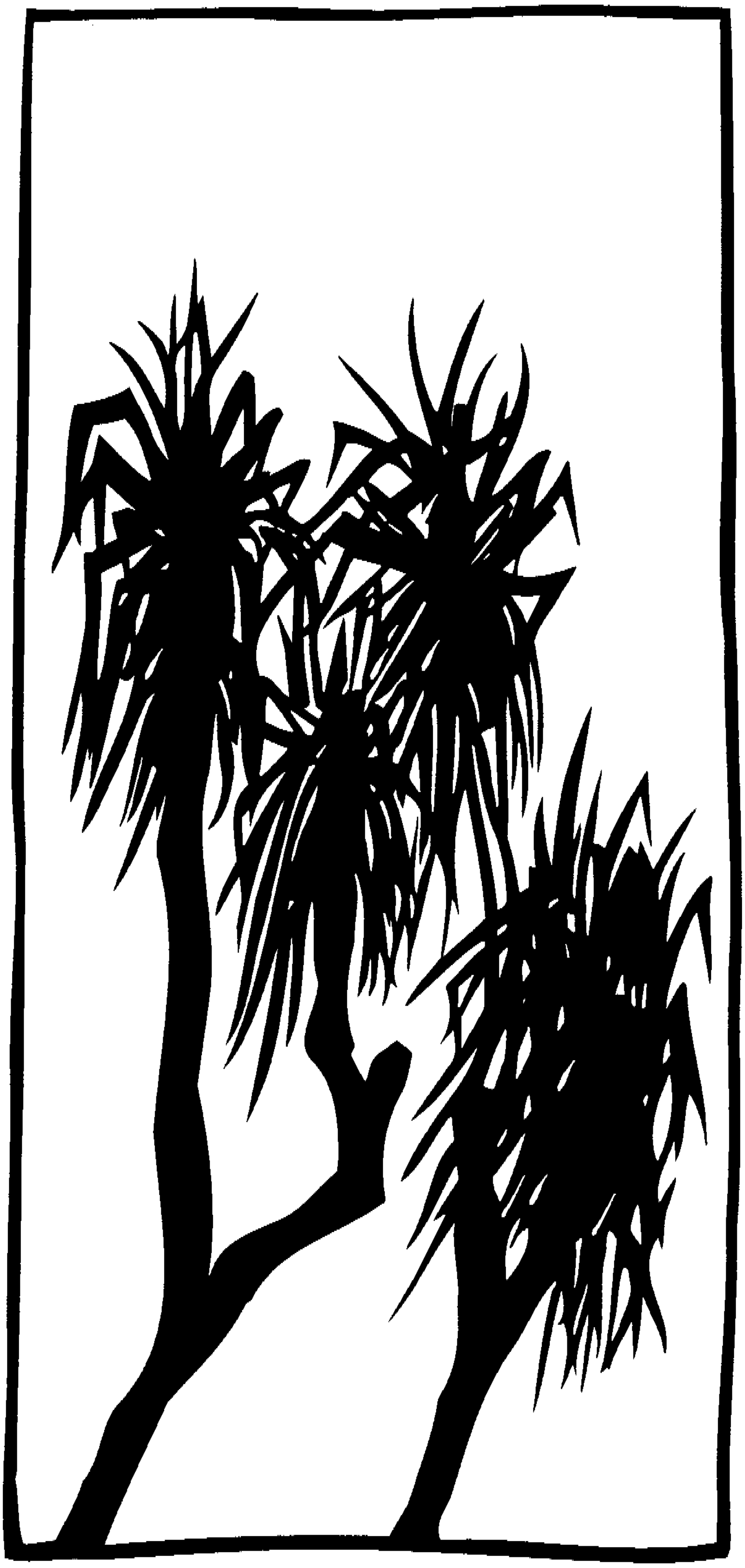
internal report **322**



The importance of hardness and alkalinity in assessing the potential impact of heavy metals on tropical freshwater organisms

N Reithmuller

S Markich

R van Dam

D Parry

August 1999

supervising scientist

The importance of hardness and alkalinity in assessing the potential impact of heavy metals on tropical freshwater organisms

Nadine Riethmuller[1,2], Scott Markich[3], Rick van Dam[1] & David Parry[2]

Presented by Nadine Riethmuller at the Scientific Meeting on Biomarkers in Environmental Toxicology
University of Canterbury, Christchurch, New Zealand
14-16th July 1999

Theme: "Pollution effects – Biomarkers in Environmental Toxicology"

[1]Wetland Risk Assessment, Environmental Research Institute of the Supervising Scientist (***eriss***), Locked Bag 2, Jabiru, NT, 0886, Australia.

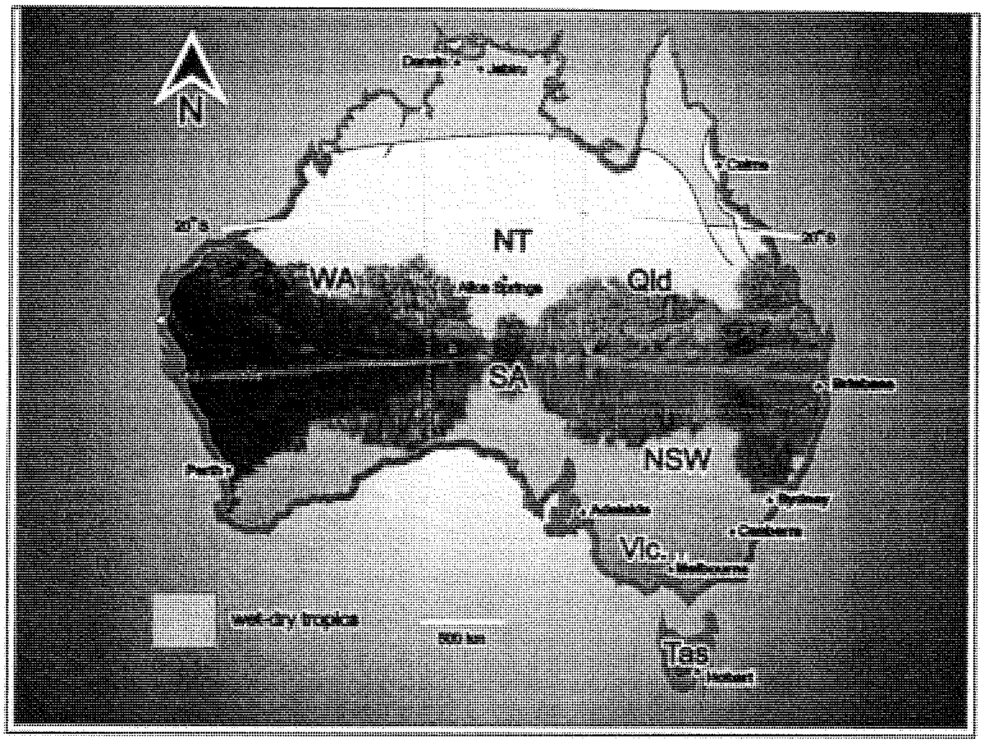
[2]School of Mathematics and Physical Sciences, Faculty of Science, Northern Territory University, Darwin, NT, 0909, Australia.

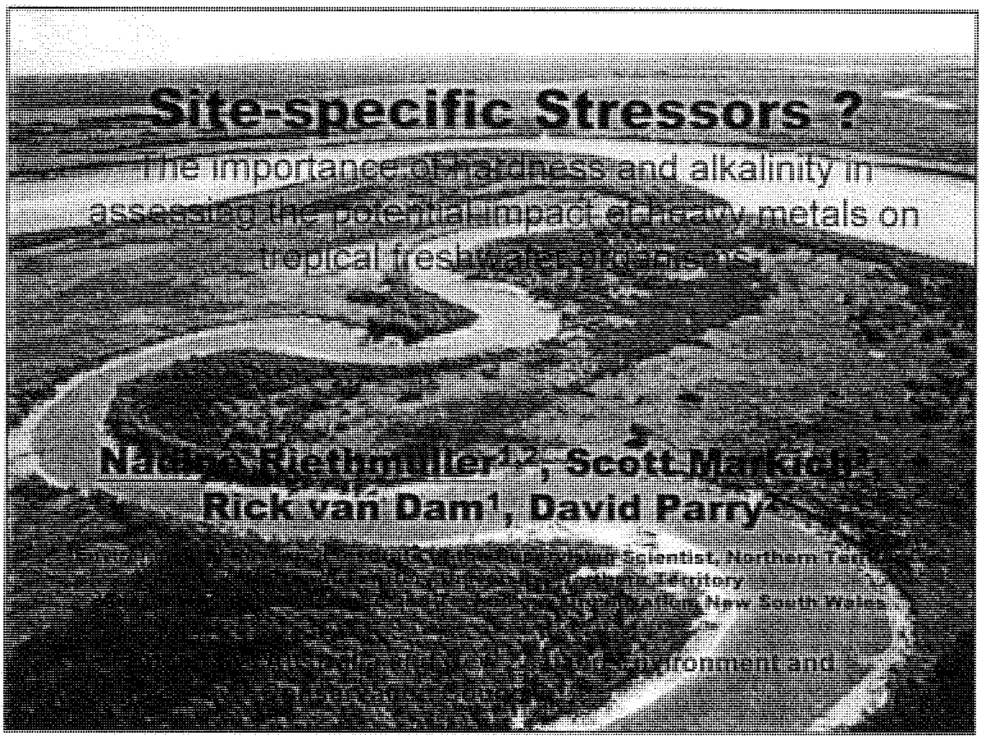
[3]Environment Division, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1, Menai, NSW, 2234, Australia.

The importance of hardness and alkalinity in assessing the potential impact of heavy metals on tropical freshwater organisms

The Australian and New Zealand water quality guidelines are aiming to supplement and modify existing criteria, which are mostly based on Northern Hemisphere toxicity data, with information relevant to Southern Hemisphere ecosystems as it becomes available. In the wet-dry tropics of Australia, uranium (U) and copper (Cu) are metals of particular concern, due to mining activities. Although, the toxicity of U and Cu to tropical freshwater species has previously been characterised, the influence of physico-chemical parameters on toxicity has not been defined. In contrast, temperate freshwater studies have investigated the effects of various physico-chemical parameters on Cu toxicity, and to a limited extent U toxicity. The reported results however, are contradictory. Thus, it is recognised that the development of a model based on key water quality variables would enhance the capacity to predict the potential site-specific impacts of U and Cu in tropical ecosystems.

This study aimed to separate the effects of true water hardness (6.6, 165 and 330 mg L^{-1} as $CaCO_3$) and alkalinity (4.0 and 102 mg L^{-1} as $CaCO_3$), at a constant pH, on the toxicity of U and Cu to *Hydra viridissima* (Green hydra, population growth) and *Mogurnda mogurnda* (Purple-spotted gudgeon, sac-fry survival). The effect of water hardness (Ca and Mg) varied depending on the metal and test organism. A 50-fold increase in hardness resulted in a 2-fold decrease in the toxicity of Cu to *M. mogurnda*, while it had no effect on U toxicity. The opposite was observed for *H. viridissima*, where increased hardness had no effect on Cu toxicity, but decreased U toxicity by approximately 2-fold. A 25-fold increase in alkalinity (carbonate) had no effect on Cu toxicity to *H. viridissima*, while it decreased U toxicity by approximately 10%. Gaining a fundamental understanding of the interactions between physico-chemical parameters and metals, and the subsequent potential impacts on freshwater ecosystems is an essential aspect of site-specific environmental risk assessment and water quality guideline derivation.


N
NT
WA
Qld
SA
NSW
Vic.
Tas
Alice Springs
wet-dry tropics


Site-specific Stressors ?
The importance of hardness and alkalinity in assessing the potential impact of heavy metals on tropical freshwater organisms
Nadine Riethmuller[1,2], Scott Markich[3], Rick van Dam[1], David Parry[2]

Outline

- Importance of physico-chemical parameters in determining metal toxicity
- What is known about the effects of hardness and alkalinity on Cu and U toxicity
- Where gaps lie and why
- How our findings fill some of these gaps
- Conclusions drawn from findings

Physico-chemical Parameters

- Influence the speciation and 'bioavailable' fraction of metals
- Difficult to separate
- Alkalinity and pH change free carbonate and hydroxide ion concentrations
- Hardness has no direct effect on speciation
- ANZECC guidelines recognise potential influence of hardness but lack a hardness-dependent metal toxicity formula

Known effects of hardness on Cu toxicity

- Increased water hardness
  - Reduces Cu toxicity (Sorenson 1991; Mayer et al 1994)
  - Little or no effect on Cu toxicity (Winner 1985; Lauren & McDonald 1986)
- Confounded effects of true water hardness with changes in alkalinity and pH
- When alkalinity and pH constant, hardness reduces toxicity and uptake of Cu (Horne & Dunson 1995; Erickson et al 1996)
- Ca greater effect than Mg (O'Shea & Mancy 1978; Erickson et al 1996)

Known effects of alkalinity on Cu toxicity

- Increased alkalinity
  - Reduces Cu toxicity (Howarth & Sprague 1978; Chakoumakos et al 1979)
  - No effect on Cu toxicity (Erickson et al 1996)
- Confounded effects of alkalinity with other cations (eg Na & K), and changes in water hardness and pH
- When hardness and pH constant, alkalinity reduces toxicity and uptake of Cu (Miller & Mackay 1980; Lauren & McDonald 1986; Daly et al 1990)

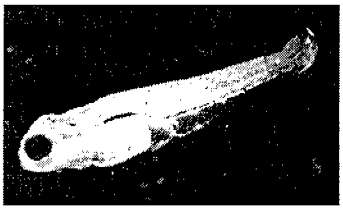
Known effects of hardness and alkalinity on U toxicity

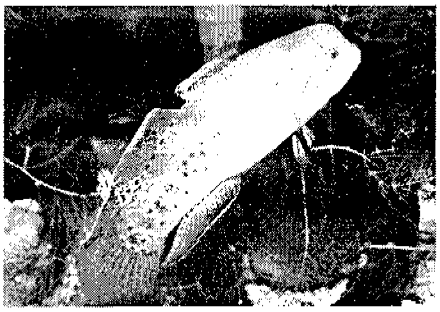
- Increased hardness and alkalinity
  - Reduce U toxicity (Tarzwell & Henderson 1960; Parkhurst et al 1984; Poston et al 1984)
- Confounded true water hardness and alkalinity effects with other parameters
- When hardness and pH constant, alkalinity reduces toxicity and uptake of U (Markich et al 1996)
- No studies describe effect of true water hardness on U toxicity to freshwater organisms

Purpose of Study

- Isolate hardness and alkalinity effects from other water parameters
- Identify the influence hardness and alkalinity each have on Cu and U toxicity
- Contribute to current water quality guidelines for Cu and U
- Consider need for site-specific risk assessment

Purple-spotted Gudgeon (*Mogurnda mogurnda*)

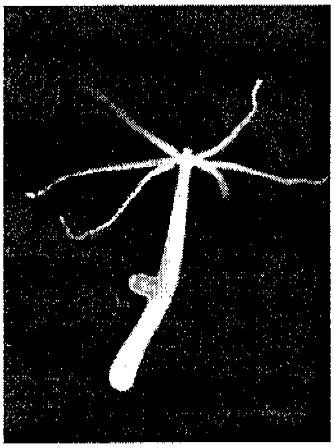




Lethal endpoint: Survival
Experimental exposure: 96 hours
(100% solution renewal every 24 hrs)
Statistical endpoint: LC_{50}
Feeding regime: Nil

Commence test with 10 individuals per replicate

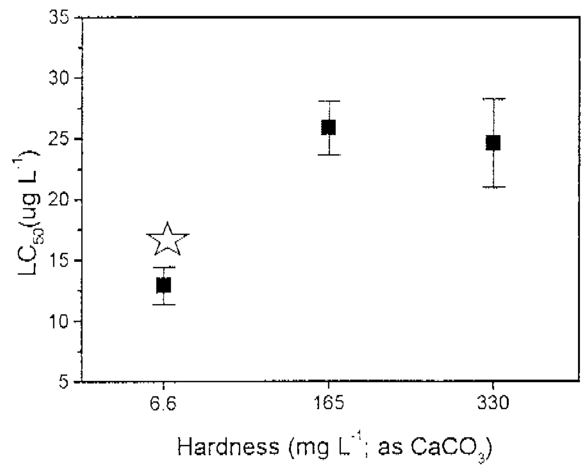
Green Hydra (*Hydra viridissima*)



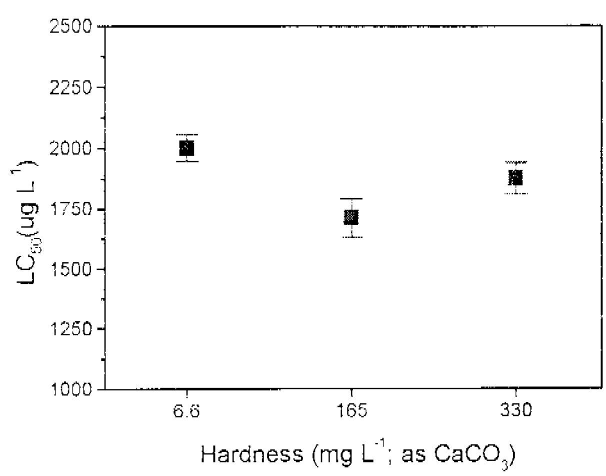
Sublethal endpoint: Population growth
Experimental exposure: 96 hours
(100% solution renewal every 24 hrs)
Statistical endpoint: EC_{50}
Feeding regime: Daily
(Brine shrimp, *Artemia franiscana*)

Commence test with 10 individuals per replicate

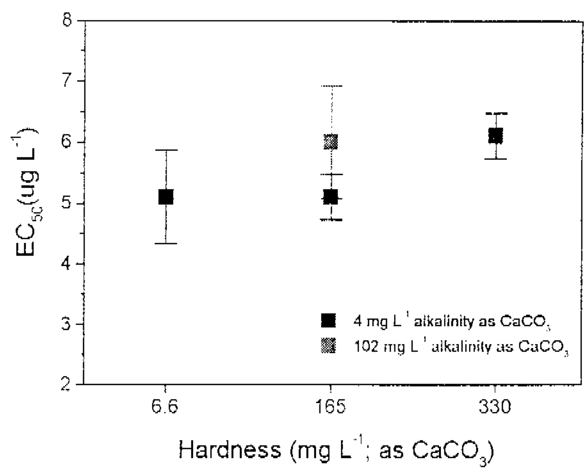
Effect of hardness on Cu toxicity to Purple-spotted Gudgeon



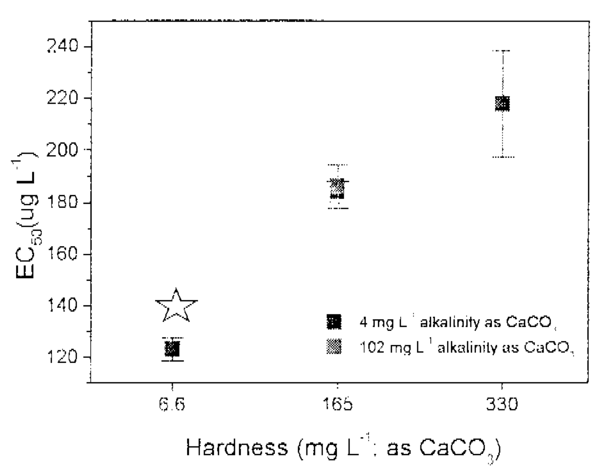
Effect of hardness on U toxicity to Purple-spotted Gudgeon



Effects of hardness and alkalinity on Cu toxicity to Green Hydra



Effects of hardness and alkalinity on U toxicity to Green Hydra



Summary

- Previous understanding was limited
- Increased hardness
  - Reduced Cu toxicity and had no effect on U toxicity to gudgeon
  - Reduced U toxicity and had no effect on Cu toxicity to hydra
- Increased alkalinity
  - Had no effect on Cu or U toxicity to hydra
- Help derive of more relevant guidelines
- Method separated the effects of hardness and alkalinity, facilitating an understanding of the influence parameters have on metal toxicity

Summary

- Carbonate ions had no effect on Cu and U toxicity compared to Ca and Mg ions
- Hardness is an important parameter to consider when assessing the impact of U and Cu toxicity
- Effect of hardness varied depending on test organism and metal
- Highlights the need for site-specific risk assessment