# Monitoring Trace Metals in North and Central Victorian Waterways, Australia, Using Artificial Mussel (AM) Technology (2009-2010)

One of Goulburn Murray Water site - *Yarrabulla Creek (photo by Golam)*

One of Melbourne Water site - *Stony creek (photo by Golam)*

One of North Central CMA site- *Sailors Creek@ Sailors Falls (photo by Golam)*

**November 2010**

Golam Kibria, Graeme Allinson, Vince Pettigrove, Phillip Slessar, T.C Lau, and Rudolf Wu

**Cover layout and photos:** Golam Kibria

**General disclaimer**



*The technical report was the outcome of an international research collaboration between the Goulburn Murray Rural Water Corporation, Tatura, Victoria, Australia (G-MW), the Centre for Marine Environmental Research and Innovative Technology, City University of Hong Kong (CityU), the University of Hong Kong (HKU) and the Department of Primary Industries, Future Farming System Research Division, Queenscliff and Werribee Centre, Melbourne, Australia (DPI)*



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**By**

**Golam Kibria**
Goulburn Murray Rural Water Corporation
Tatura, Australia

**Graeme Allinson**
Department of Primary Industries, Future Farming Systems Research Division
Queenscliff Centre, Melbourne, Australia

**Vincent Pettigrove**
Melbourne Water, Victorian Centre for Aquatic Pollution Identification and Management (CAPIM),
University of Melbourne, Bio 21 Institute, University of Melbourne, Australia

**Phillip Slessar**
North Cental Catchment Management Authority (NCC MA), Bendigo, Australia

**T.C. Lau**
Department of Biology and Chemistry, City University of Hong Kong

**Rudolf Wu**
School of Biological Sciences,
The University of Hong Kong, Hong Kong

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## Correspondence about the technical report and R&D

Dr Golam Kibria
Goulburn Murray Rural Water Corporation
40 Casey Street, Tatura, VIC 3616
Australia
golamk@g-mwater.com.au
Web site: http://www.g-mwater.com.au/projects/researchanddevelopment

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# 1. Executive summary

During 2009-10, a monitoring study was conducted across North and Central Victoria covering Goulburn Murray Water catchments (GMW), several streams on the peri-urban fringe of Melbourne managed by Melbourne Water (MW) and several ephemeral streams in the upper Loddon River catchment managed by North Central CMA (NCCMA) to assess the risks posed by micro pollutants such as trace metals. The study used innovative artificial mussel (AM) passive sampling technology called AM technology (or AM), and, as such, is a part of Global AM Watch program being run in eight countries including Australia, Canada, China, Iceland, Portugal, Scotland, South Africa, the USA.

AMs deployed in waterways of three catchments (G-MW, MW and NCCMA) accumulated all or some of the targeted metals (cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), and zinc (Zn). The order of accumulation of metals in AM was as follows:

Zn>Cu>Pb>Cr>Cd>Hg

Copper and zinc were detected at most sites within GMW, MW and NCCMA, however, cadmium, lead and mercury concentrations were generally below the instrumental detection limits. Comparing the three catchments, both copper and zinc concentrations in AMs were highest levels at MW sites (mean Cu: 25.18 µg/g chelex resin; mean Zn: 33.92 µg/g chelex resin), lower at GMW sites (mean Cu: 17.52 µg/g chelex resin; mean Zn: 28.4 µg/g chelex resin), and lowest at NCCMA ((mean Cu: 9.23 µg/g chelex resin; mean Zn: 23.9µg/g chelex resin).

In order to convert AM chelex resin concentrations into time-weighted average water concentrations for the period of AM deployment, calibration (or uptake) factors for each metal are required. These are not currently available. A preliminary calibration and concentration factor experiment with AM was conducted at DPI Queenscliff Centre, but results were inconclusive, perhaps due to high levels of Cu found in the tap water used, and thus they cannot be used to produce quantitative average water metal concentration.

The analytical results of spot water samples collected at time of deployment and retrieval of the AMs showed that several sites within the three catchments investigated exceeded the *ANZECC & ARMCANZ (2000)* guidelines trigger value for protection of aquatic ecosystems at the 95% protection level as highlighted below:

- Four of the G-MW sites (Kerang and Kangaroo Lake, Shepparton and West Boort) exceeded the *ANZECC & ARMCANZ (2000)* guidelines trigger value for Cu of 1.4 µg/L. These sites were close to intensive orchards (pome and stone), vine yards, and areas growing olives and tomatoes. This may demonstrate that some localized copper inputs occurred in these areas, possibly from usage of agriculture chemicals such as copper fungicide to control bacterial and fungal diseases.

- Two of the MW sites (Stony Ck and Olinda Ck) exceeded the *ANZECC & ARMCANZ (2000)* guidelines trigger value for Cu (1.4 µg/L) and Zn (8.0 µg/L) for protection of aquatic ecosystems at the 95% protection level. The elevated Cu and Zn concentrations at these sites suggests that some localized copper inputs occurred in these areas, possibly from usage of agriculture chemicals such as copper fungicide to control bacterial and fungal diseases in orchards and vine yards (Stony Ck), and the influence of a small WWTP (Olinda Ck).

- Two of the NCCMA sites (Tipperary Springs and Bryces Flat) exceeded the *ANZECC & ARMCANZ (2000)* guidelines trigger value for Cu (1.4 µg/L) for protection of aquatic ecosystems at the 95% protection level. The source of these metals is as yet unclear.

Overall, the first year of the study demonstrate the usefulness of using innovative technology such as AM passive sampling techniques in monitoring metals in various waterways such as rivers and irrigation channels (G-MW), peri-urban streams (MW) and ephemeral streams (NCCMA). In case of G-MW, the first year study (Year 1 or 2009-10) was conducted during drought conditions when there was little water at G-MW storages. However, it is anticipated that the 2010-11 monitoring will provide a better picture of the metals in G-MW channels and waterways due to higher rainfall and runoff being experienced during the winter and spring of 2010. The study found that AM is a reliable tool for monitoring heavy metals in waterways and could be useful in risk assessment for various water utilities including recycled water, treated wastewaters, groundwater bores, rivers, and irrigation channels.

# 2. Contents

# 3. Acronyms and glossary

**Artificial mussel** :  or AM (see passive sampling).

**CityU :** City University of Hong Kong.

**Concentration :** The strength of a solution; number of molecules of a substance in a given volume.

**Calibration :**  To check, adjust, or determine by comparison with a standard.

**DPI :** Department of Primary Industries.

**G-MW :** Goulburn Murray Rural Water Corporation.

**Guideline  trigger values** : These are the concentrations (or loads) of the key performance indicators measured for the ecosystem, below which there exists a low risk that adverse biological (ecological) effects will occur.  They indicate a risk of impact if exceeded and should 'trigger' some action, either further ecosystems specific investigations or implementation of management /remedial actions.

**Water hardness:**  is a measure of the amount of calcium and magnesium salts in water. Calcium and magnesium enter water mainly through the weathering of rocks. The more calcium and magnesium in water, the harder the water. Water hardness is usually expressed in milligrams per liter (mg/l) of dissolved calcium and magnesium carbonate

**Heavy metals :** Are a group of metallic elements with an atomic weight greater than 20 and characterized by similar electron distribution in their external shell (e.g. mercury, chromium, cadmium, arsenic, and lead); can damage living things at low concentrations and tend to accumulate in the food chain.

**HKU :** the University of Hong Kong.

**Milli-Q** :  also called high purity water,  refers to water that has been purified and deionized to a high degree by water purification systems.

**Micropollutants:** are compounds which are detected in the concentration range of ng/L up to μg/L in the environment.

**Passive sampling** : A device that collects or accumulates pollutants (eg. Heavy metals) independently through a diffusion barrier onto a sorbent medium without use of a vacuum source or energy.

**Polyacrylamide:** Polyacrylamide (IUPAC poly(2-propenamide) or poly(1-carbamoylethylene)) is a polymer (-CH2CHCONH2-) formed from acrylamide subunits that can also be readily cross-linked.

**TWA :**  Time weighted average concentration; The average concentration of contaminants during a given period.

# 4. Background

Trace metals or heavy metals can pollute water supply systems through natural deposits, waste discharged from mining, industrial and agricultural activities. Water contaminated with metals may be unsuitable for irrigation, human drinking water, livestock drinking, aquatic ecosystems protection and recreation and aquaculture. Metal pollution may reduce biodiversity, eliminate sensitive species or reduce species abundance through reproductive impairment and increased incidence of diseases. Aquatic flora and fauna such as invertebrates (including molluscs) and fish can bioaccumulate metals at concentrations up to thousands times higher than the ambient environment, thereby posing health risks to humans and other predators through biomagnification via food consumption. Irrigation water may transport dissolved metals and contaminate agricultural soils, thereby affecting crops and human health. Exposure to some metals is known to cause kidney damage; bone fracture; reproductive failure, infertility; damage to nervous and immune system; DNA damage or cancer development and sperm damage, birth defects and miscarriages in human. As such, monitoring of metals in the environment is essential to safeguard ecosystem health and public health. The Australian and New Zealand Environment and Conservation Council have established guidelines for metals in raw water to be supplied for irrigation; stock and domestic supply (see *ANZECC &* ARMCANZ, *2000*).

One of the significant business risks for G-MW is the water that G-MW supplies to its customers. It is known that many of the catchments in which G-MW operates are heavily mineralized, as evidenced by the historical and current mining activities in these catchments. The EPA has reported elevated arsenic and mercury concentrations in the Loddon catchment (*USMP, 2001*), and the potential for bioaccumulation of mercury in Lake Eildon as a result of historical gold mining upstream (*Monash Review, 1983*) G-MW has a duty of care to ensure that the water it supplies to customers is fit for purpose. As a sustainable water authority, it is also obliged to adapt risk mitigation measures to reduce or minimize any impacts of pollutants (such as metals) on biodiversity, irrigation water, and drinking and recreation water quality and natural water course downstream of channels and drain outfalls.

Traditional monitoring of metals in the aquatic environment involves determining and comparing metals in water, sediment and biota, but each method has its own problems and limitations. For example, temporal variations in metal concentrations in water are typically large, which often require frequent sampling and analysis that are not cost effective. Bio-monitoring has been used extensively to monitoring metals in the last two decades, the notable example of which is the global mussel watch program. However, the metal concentration in bio-monitors is significantly affected by physical and biological factors. Importantly, the restricted natural distributions of biomonitoring species often prevent direct comparison between different geographical/ hydrographical regimes.

Until recently there were no reliable time integrated techniques to assess metal concentrations in water which could be used to assess the risk concentrations with respect to *ANZECC &* ARMCANZ *(2000)* water quality guidelines. However, recently *Wu et al (2007)* developed an 'Artificial Mussel' which can be used to monitor five different heavy metals in water. This new device is a cost effective monitoring tool which provides a time-integrated concentration of metals in the aquatic environment during the deployment period. G-MW recently used this artificial mussel technology to monitor metal concentrations in G-MW catchments as a pilot study (in cooperation with the City University of Hong Kong and DPI-Victoria). The pilot study found that artificial mussels (AM) technology was a very reliable tool for monitoring heavy metals in G-MW waterways as it detected all the targeted metals as well as some non-targeted metals (see *Kibria et al. 2010a; http://www.g-mwater.com.au/projects/researchanddevelopment/currentprojects/heavymetals*) . Moreover, there was good repeatability for the metal concentrations observed in the AMs deployed in fresh water. However, the pilot study only monitored five sites as a trial run (mainly to understand the technology, and how it works), therefore somewhat limiting the applicability of the data across the total extent of G-MWs catchments.

The present work is an expanded study beginning during FYR 2009-2010 to monitor metals in selected at risk sites within G-MW catchments using AMs. A number of sites outside G-MW catchments were also investigated for comparative purposes. The studies initial findings (i.e. year 1 of the two year study) are reported here in Interim Report-1.

# 5. Scope of the work

Goulburn-Murray Rural Water Corporation (G-MW) along with the City University of Hong Kong, (CityU), Hong Kong University (HKU), Department of Primary Industries, Victoria (Queenscliff & Werribee), Melbourne Water (MW) and North central Catchment Management Authority (NCCMA) agreed (see the milestone) to carryout a collaborative research to monitor metals in selected risk sites within north and central Victorian waterways by using novel 'artificial mussel's (AM) technology. According to their agreement, the parties agreed to provide the following support (5.1-5.3):

**Artificial mussels R&D project milestone (*G-MW 2009*)**

| Item | Due Date | Milestone deliverable |
|---|---|---|
| 1 | September 2009 | A draft report on calibration and concentrations experiments (all R&D partners) |
| 2 | August 2010 | A draft technical report on year -1 heavy metals monitoring (all R&D partners) |
| 3 | October 2011 | A draft technical report produced combining year 1 & 2 monitoring (all R&D partners) |
| 4 | November 2011 | Peer review of the technical report |
| 5 | December 2011 | Final report produced (all R&D partners) |

### *5.1 : Goulburn Murray Water (G-MW)*

- *Management of whole AM program (2009-2010 and 2010-2011) and liaison with all the research parties*
- *Plan and design of AM program for G-MW catchment*
- *Deployment and retrieval of AM within G-MW catchments*
- *Time to time assistance in field AM sampling at NCCMA, MW sites*
- *Shipment of AM retrieved from the field to Hong Kong*
- *Support in Queenscliff AM lab based experiments and supervising CityU students in running the experiments*
- *Preparation of draft and final technical reports.*

### *5.2: CityU and HKU*

- *Supply of artificial mussels (AM) for 2009-2010 and 2010-2011*
- *Analysis of AM for Cd, Cu, Cr, Hg, and Zn for 2009-2010 and 2010-2011*
- *Technical and scientific inputs as and when required (relevant to AM technology)*
- *Assist in technical report and journal paper preparation*
- *Assist to run Queenscliff AM Lab based experiments (provide two CityU honours students to run the experiments).*

### *5.3 : Department of Primary Industries, Victoria*

- *Selection of sites within Melbourne Water (MW) and NCCMA catchments*
- *Deployment and retrieval of AM in MW and NCCMA sites in 2009-10*
- *Analysis of spot water and sediment samples in 2009-10*
- *Assistance in technical report and journal paper preparation*
- *Support for running of flow through experiments with AM at DPI Queenscliff Centre in 2009-10.*

# 6. Objectives

- To use the novel 'artificial mussel' technology for monitoring and assessing the spatial and temporal loads of metals in waterways (north and central Victorian waterways, Australia)
- To compare the time integrated accumulation of metals in artificial mussels
- To evaluate the artificial mussel as a tool for monitoring metals in wider water
- To assess the ecological and public health risks of metal contamination within the targeted catchments.

# 7. Study description

## 7.1 : Trace metals monitoring strategy

Traditional monitoring of metals in the aquatic environment involves determining and comparing concentrations in water, sediment and biota but each method has its own problems and limitation. For example, there can be large temporal variations in metal concentrations in water, which often require frequent sampling and analysis that are not cost effective. Bio-monitoring has been used extensively to monitor metals in the last two decades, the notable example of which is the global "mussel watch" program (see *Monirith et al.* 2007). However, the metal concentration in bio-monitors is significantly affected by physical and biological factors and restricted natural distributions often prevent direct comparison between different biomonitoring species in different geographical/hydrographical regimes. Furthermore, in many environments, bivalves cannot survive because of adverse or unsuitable environmental conditions. The 'Artificial Mussel' (AM) (Figure 1 and 2) is a passive sampling device that can take up and release metals in a similar fashion to live mussels under laboratory conditions (see Table 1 for a comparison of sampling of heavy metals by spot sampling, bioindicators and artificial mussel technology and see Box 1 about AM technology and how it works). The current work is part of 'global artificial mussels watch program' being run in eight countries including Australia by Chair Professor Rudolf Wu of Hong University (see Figure 3).

**Figure 1 :** *'Artificial mussels' device used in heavy metals monitoring (photo by Golam Kibria)*

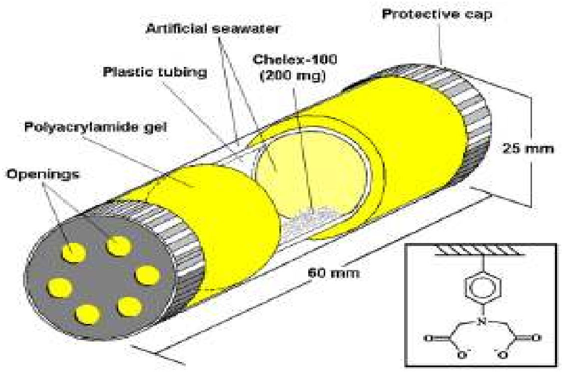



**Figure 2 :** *A schematic diagram showing the design of artificial mussel chemical structure of chelex-100 is shown in the inset (Wu et al. 2007)*

**Table 1 :** *A comparison of sampling of heavy metals by different techniques*

| Method of sampling | Remarks |
|---|---|
| A. Spot sampling | • Snap shot<br>• Requires frequent sampling<br>• Time consuming<br>• Costly<br>• Routine monitoring typically determines total metals but not-bioavailable or toxic fractions |
| B. Biomonitoring (live mussels) | • Requires killing of animals<br>• Metals accumulation affected by abiotic and biotic factors<br>• No standard mussels species are available for worldwide use<br>• Requires translocation of mussels from lab to field or local mussel species<br>• Requires complex analysis of biological samples<br>• Uptake both bio-available and toxic fractions |
| C. Artificial mussels (AM) technology | • Continuous monitoring<br>• No power or energy required<br>• Metal accumulation/uptake not affected by biotic and abiotic factors<br>• A standard tool for all waters worldwide (fresh, sea, recycled/waste water)<br>• AM can be placed where bio-indicator organisms are not available<br>• Simple to handle, deploy and retrieve<br>• Simple to analyse<br>• Uptake both bio-available and toxic fractions |

**BOX : 1 :** ***Artificial mussel technology and how it works?***

The 'Artificial Mussel (AM)' passive sampler is a device that collects or accumulates metals through a diffusion barrier onto a sorbent medium. The device (AM) consists of non permeable Perspex tubing (60 mm x 25 cm ) in which 200 mg Chelex-100 resin (50-100 mesh from Bio-Rad) is suspended in 8 mL seawater/freshwater inside the tubing (see Figure 2). Both ends of the tubing are further capped by a layer of polyacrylamide gel (thickness: 1 cm), to protect the gel from possible mechanical damages (Figure 1 and 2). Water diffuses through the polyacrylamide gel into the chelax-100 (metal binding agent) from which the complexed metals can later be extracted (see Figure 2). After several weeks, the chelating agent is sampled to determine its metal content.

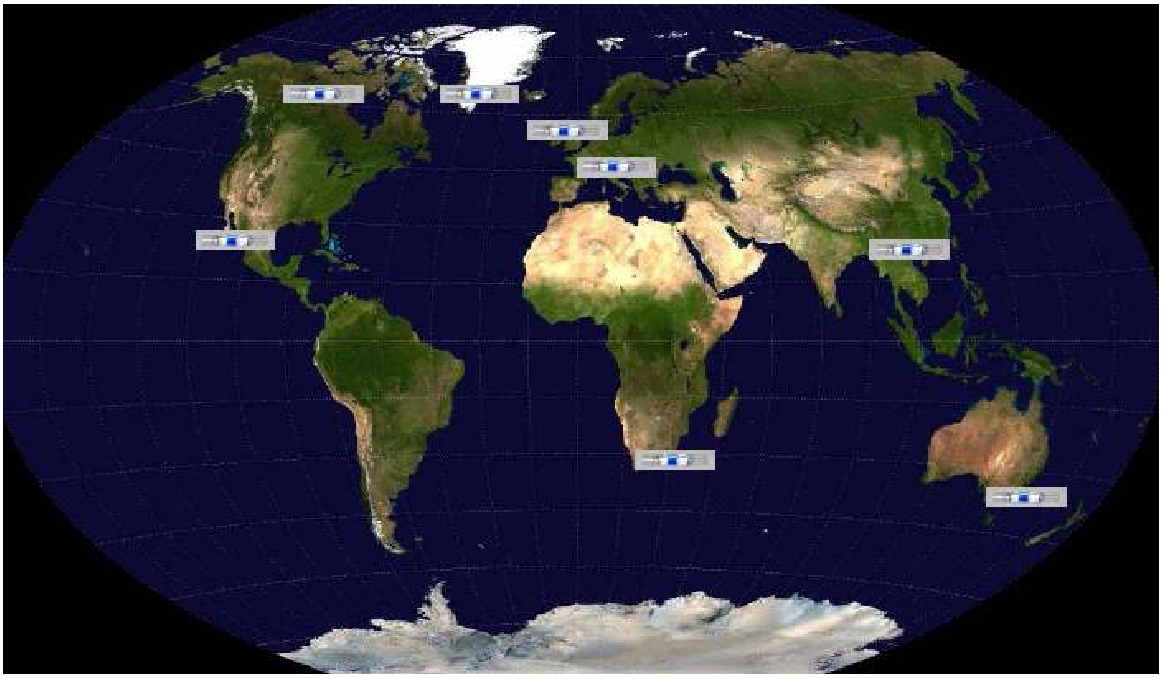


**Figure 3 :** ***Artificial mussel watch program being run in eight countries including Australia.***

## 7.2 : Monitoring sites

Artificial mussels were deployed in three Victorian regions (Figure 4) during 2009-2010 as listed below :

- Goulburn Murray Water catchment or G-MW (rivers and channels) : 10 sites (Table 3)
- Melbourne water, or MW (rivers and creeks) : 3 sites (Table 3)
- North Central Catchment Management Authority or NCCMA (rivers and creeks) : 4 sites (see Table 3).

## 7.3: Monitoring schedule

- Deployment and retrieval: G-MW, on seven occasions July 2009 – March 2010 (@ three replicates at each site; see Table 4 for retrieval dates); NC CMA on three occasions August-November 2009 (@ three replicates at each site); and MW on three occasions August 2009 – March 2010 (@ three replicates at each site).
- Duration of monitoring : July 2009- March 2010

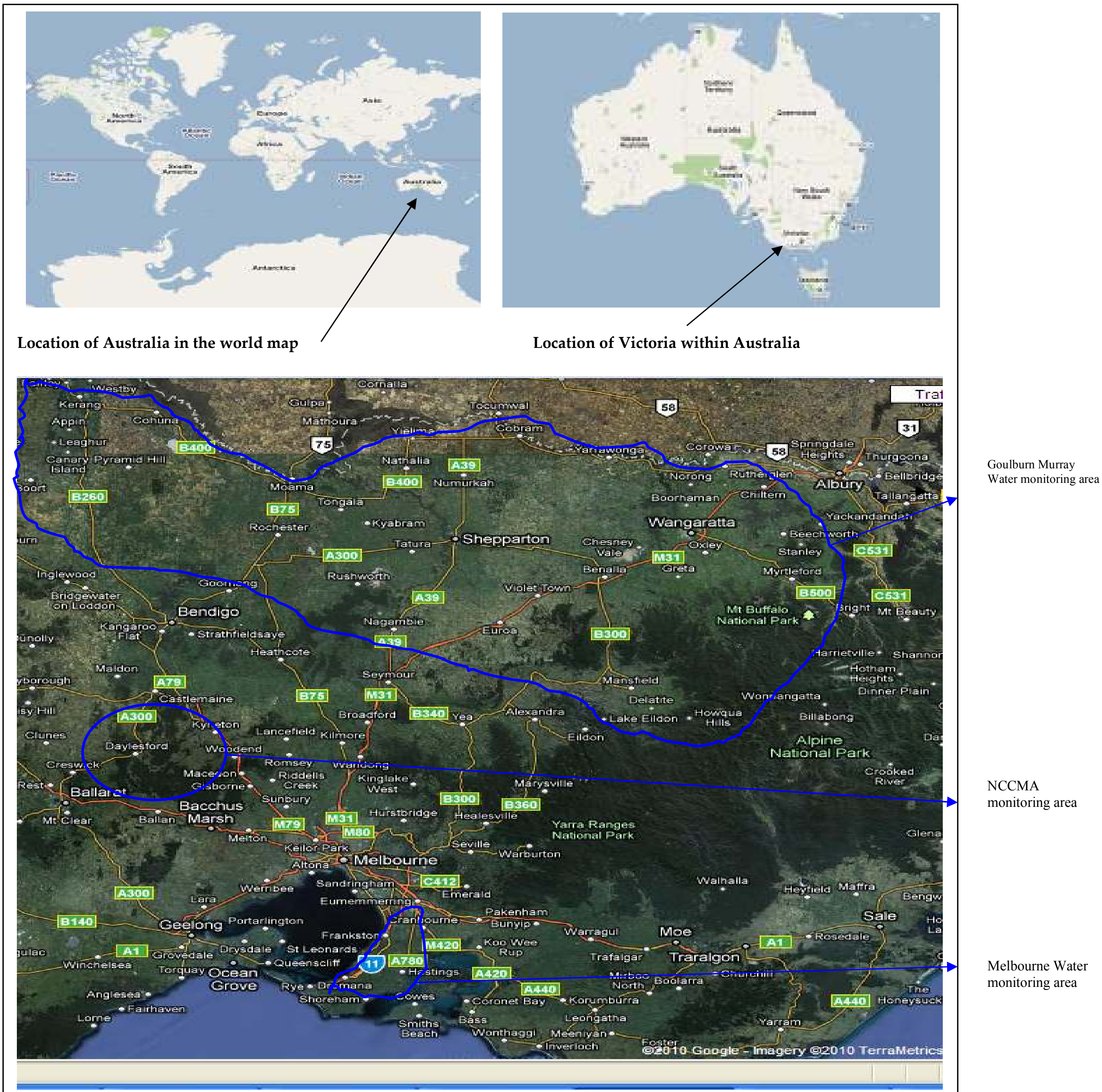
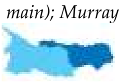



**Figure 4:** *Showing location of Australia (top left), Victoria (top right) and the location of three AM monitoring areas (bottom) - north and central Victoria.*

**Table 2:** ***Description of heavy metals monitoring sites in North and central Victorian waterways during 2009-2010*** [Note : G-MW-Goulburn Murray water; MW=Melbourne water region; NCCMA= North Central Catchment management region].

| Site number & description | Active region | Prime targets | Comments |
|---|---|---|---|
| **A. Goulburn Murray Water Catchment sites (GMW)** | | | |
| ***GMW01- Buffalo***<br>*@Yarrabulla creek, Lake Buffalo* | *Myrtleford* | *Reference- Murray River* | *u/s national forest;*<br>*d/s water supply to two districts- Murray Valley and Torrumbarr for irrigation, stock & domestic and town supply.* |
| ***GMW02- Howqua***<br>*@ Howqua River @Glen-esk-Woodspoint & Howqua River Road* | *Mansfield* | *Reference- Goulburn River* | *u/s national forest*<br>*d/s water supply to four Districts- Shepparton, Central Goulburn Rochester-Campaspe and Pyramid - Boort for irrigation, stock & domestic and town supply.* |
| ***GMW03- Cobram***<br>*@ irrigation channel(6/1 offtake of no 1 main); Murray Valley HWY*<br> | *Cobram East, Murray Valley* | *Intensive orchard; town supply??* | *u/s intensive orchards;* |
| ***GMW04 – Shepparton***<br>*@ Channel 12; Barmah-Shepparton Rd*<br> | *Shepparton North, Shepparton* | *Intensive Orchards* | *u/s : intensive orchards*<br>*d/s : pasture, horticulture, crops, stock & domestic supply* |
| ***GMW05- Mooroopna***<br>*@channel15/6/4, Ebbots regulator; Midland HWY-Cemetery Rd*<br> | *Mooroopna, Central Goulburn* | *Channel outfall* | *u/s intensive orchards and tomatoes;*<br>*d/s outfall to Goulburn River* |
| ***GMW06- Tatura***<br>*@ channel 3/5; Murchison-Tatura Rd*<br> | *Tatura, Central Goulburn* | *Intensive orchards and town supply* | *u/s pasture and crop;*<br>*d/s town supply offtake point.* |
| ***GMW07- Rochester***<br>*@ channel1 Waranga Western Channel; Winter Rd-Freeman Rd*<br> | *Rochester, Rochester-Campaspe* | *Town supply* | *us/ vine and tomatoes;*<br>*d/s town supply offtake point and stock & domestic supply.* |
| ***GMW08- West Boort***<br>*@ channel5 Waranga Western Channel;Boort-Charlon Rd-Hummel-Grandview Rd*<br> | *Boort, Pyramid- Boort* | *Intensive orchards (Olive) and town supply* | *u/s intensive olives;*<br>*d/s town supply offtake point and stock & domestic supply.* |
| ***GMW09-Kerang***<br>*@channel 14/2; Murray Valley HWY-Collins Rd*<br> | *Kerang, Torrumbarry* | *Town supply* | *u/s : pasture*<br>*d/s : raw town supply* |
| ***GMW-10-Kangaroo Lake***<br>*@channel 7; Murray Valley HWY-Mystic park Rd*<br> | | | *u/s intensive vines and Ramsar Lake;*<br>*d/s water supply to Swan Hill.* |
| **B. Melbourne Water, Yarra catchment sites (MW)** | | | |
| **Site number & description** | **Active region** | **Prime targets** | **Comments** |
| ***MW11-Stony creek***<br>*@Frankston-Flinders Rd at Shoreham* | *Mornington Peninsula* | *Elevated salinity* | *u/s mixed woodland and horticulture*<br>*d/s* |

| | | | |
|---|---|---|---|
| | | *reference* | *elevated salinity suggests that groundwater constitutes significan proportion of stream flow during drier months* |
| ***MW12- McCrae Creek*** *@ Healesville-KooWee Rup Rd* | *Yellingbo* | *??* | *d/s* |
| ***MW13-Olinda Ck*** *@Mc Intyre Lane* | *Yering* | *??* | *u/s* *d/s of sewage plant?* |
| **C. North Central CMA, Loddon Catchment sites (NCCMA)** | | | |
| *NCCMA 14- Sailors Ck @ Sailors Falls* | *Daylesford-Ballan Rd at Sailors Ck* | *Reference Loddon* | *u/s forest, pasture* |
| *NCCMA 15-Sailors Ck @ Tipperary Springs* | *end Tipperary Springs Rd at Daylesford* | *Mining* | *d/s of Daylesford and mine sites* |
| *NCCMA16- Loddon River at Kemps Bridge* | *Kemps bridge on Kemps Bridge Rd* | *Mining* | *u/s pasture and woodlands* *d/s pasture, woodlands, disused mine sites* |
| *NCCMA17 old picnic ground / ford off Drummond-Vaughan Rd* | *Loddon River at ford on Drummond-Vaughan Rd* | *Mining* | *u/s pasture, woodlands, disused mine sites* *d/s pasture and woodlands* |

New G-MW operational water districts (2010): Murray Valley = Murray North-East Operations; Shepparton = Goulburn-Broken Operations; Central Goulburn = Central Goulburn operations; Rochester-Campaspe = Campaspe operations; Pyramid-Boort =Loddon operations; Torrumbarry = Central Murray Operations

***Table 4: AM retrieval dates in G-MW, MW and NCCMA sites.***

| **Goulburn Murray Water catchments** | | **Melbourne Water/Yarra catchments** | | **NCCMA catchments** | |
|---|---|---|---|---|---|
| **Site** | **Date of retrieval** | **Site** | **Date of retrieval** | **Site** | **Date of retrie** |
| GMW-1 | 5 August 09 | MW-11_Stony Ck. | 19 August 2009 | | |
| GMW-2 | 4 August 09 | MW-12_McMrae Ck. | 19 August 2009 | | |
| | | MW-13_Olinda Ck. | 19 August 2009 | | |
| | | | | | |
| | | | | NCCMA-14_ Sailors Ck @Sailors falls | 29 September |
| | | | | NCCMA-15_Sailors Ck @ Tipperary Springs | 29 September |
| | | | | NCCMA-16_Sailors Creek @ Bryces Flat | 29 September |
| | | | | NCCMA-21_Wombat ck@two bridges | 29 September |
| | | | | | |
| GMW-3 | 7 October 09 | | | NCCMA-14_ Sailors Ck @Sailors falls | 28 October 20 |
| GMW-4 | 7 October 09 | | | NCCMA-15_Sailors Ck @ Tipperary Springs | 28 October 20 |
| GMW-5 | 7 October 09 | | | NCCMA-16_Sailors Creek @ Bryces Flat | 28 October 20 |
| GMW-6 | 7 October 09 | | | NCCMA-21_Wombat ck@two bridges | 28 October 20 |
| GMW-7 | 7 October 09 | | | | |
| GMW-8 | 8 October 09 | | | | |
| GMW-9 | 8 October 09 | | | | |
| GMW-10 | 8 October 09 | | | | |
| | | | | | |
| GMW-1 | 9 November 09 | MW-11_Sony Ck. | 25 November 2009 | NCCMA-14_ Sailors Ck @Sailors falls | 24 November |
| GMW-2 | 9 November 09 | MW-12_McMrae Ck. | 25 November 2009 | NCCMA-15_Sailors Ck @ Tipperary Springs | 24 November |
| GMW3 | 10 November 09 | MW-13_Olinda Ck. | 25 November 2009 | NCCMA-16_Sailors Creek @ Bryces Flat | 24 November |
| GMW-4 | 10 November 09 | | | NCCMA-21_Wombat ck@two bridges | 24 November |
| GMW-5 | 10 November 09 | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| GMW-6 | 10 November 09 | | | | | | |
| GMW-7 | 10 November 09 | | | | | | |
| GMW-8 | 12 November 09 | | | | | | |
| GMW-9 | 12 November 09 | | | | | | |
| GMW-10 | 12 November 09 | | | | | | |
| | | | | | | | |
| GMW-3 | 10 December 09 | | | | | | |
| GMW-4 | 10 December 09 | | | | | | |
| GMW-5 | 10 December 09 | | | | | | |
| GMW-6 | 10 December 09 | | | | | | |
| GMW-7 | 9 December 09 | | | | | | |
| GMW-8 | 9 December 09 | | | | | | |
| GMW-9 | 9 December 09 | | | | | | |
| GMW-10 | 9 December 09 | | | | | | |
| | | | | | | | |
| GMW-3 | 14 January 10 | | | | | | |
| GMW-4 | 14 January 10 | | | | | | |
| GMW-5 | 14 January 10 | | | | | | |
| GMW-6 | 14 January 10 | | | | | | |
| GMW-7 | 12 January 10 | | | | | | |
| GMW-8 | 12 January 10 | | | | | | |
| GMW-9 | 12 January 10 | | | | | | |
| GMW-10 | 12 January 10 | | | | | | |
| | | | | | | | |
| GMW-1 | 8 February 2010 | | | | | | |
| GMW-2 | 8 February 2010 | | | | | | |
| GMW-3 | 11 February 2010 | | | | | | |
| GMW-4 | 11 February 2010 | | | | | | |
| GMW-5 | 11 February 2010 | | | | | | |
| GMW-6 | 11 February 2010 | | | | | | |
| GMW-7 | 10 February 2010 | | | | | | |
| GMW-8 | 10 February 2010 | | | | | | |
| GMW-9 | 10 February 2010 | | | | | | |
| GMW-10 | 10 February 2010 | | | | | | |
| | | | | | | | |
| GMW-3 | 10 March 2010 | | MW-11_Stony Ck. | 26 March 2010 | | | |
| GMW-4 | 10 March 2010 | | MW-12_McMrae Ck. | 26 March 2010 | | | |
| GMW-5 | 10 March 2010 | | MW-13_Olinda Ck. | 26 March 2010 | | | |
| GMW-6 | 10 March 2010 | | | | | | |
| GMW-7 | 11 March 2010 | | | | | | |
| GMW-8 | 11 March 2010 | | | | | | |
| GMW-9 | 11 March 2010 | | | | | | |
| GMW-10 | 11 March 2010 | | | | | | |

# 8 : Methods

## 8.1 : Deployment and retrieval of artificial mussel in creeks, rivers and irrigation channels

The deployment and retrieval of artificial mussels consists of 6 steps as highlighted in Table 5. Field deployment and retrieval of AM followed procedures and protocols provided by the CityU. This involves placing AM in an autoclaved/plastic basket with one AM per basket (3 replicate at each site). The plastic basket was then submerged in channels and river sites. Nylon rope and pulleys were attached to star pickets to facilitate deployment and retrieval of autoclave baskets. Each batch of AM deployed at channels and rivers were retrieved at the end of four weeks (28 day) intervals and sent via express air courier to Hong Kong (TNT or Australia Post). Each AM was wrapped within a wet sponge with identification tags included inside each whirl pack bag before shipment (the following procedures being followed).

a. The surface of the AM was rinsed with the site water to remove attached fouling organisms (if any) .
b. Sponge/cotton pad (Johnson's pure cotton pads) soaked with water from the site and wrapped separately around each individual AM, held in place using rubber bands.
c. Each AM placed in an individual whirlpak bag/sterile bag (Solar-Cult cellulose Swab-SBDCS-100-1, Arrow Scientific Pty Ltd, NSW) and then in a re-sealable bag (Glad snap lock bag)
d. Each bag double labelled (with pencilled card inside + water proof label on each whirlpak bag).

**Table 5: Steps followed in deployment and retrieval of AM in GMW catchments**

| Steps | Description | Comments |
|---|---|---|
| Step-1 | Receive and storage of AM | • AMs Received were stored in MilliQ (deionised) water before deployment in the field It is essential to store AM fully hydrated condition to avoid cracking of the gel supporting the top and bottom layers of AM. |
| Step-2 | Set up of AM monitoring sites in waterways | **Requirements**<br>• Pole rammer, sledge hammer, side cutter, and pliers;<br>• Steel posts/star pickets; Cords-polypropylene braded (6 mm)<br>• Wire tie and awning pulleys (25 mm); Cable ties; Polyropes<br>• Autoclave basket used for safe placement of AM in waterways<br>• Personal protective equipment (PPE)/OHS gears if and when required (L-R): mosquito net, sun hat, high visibility vest, waders, PVC gloves, lab gloves/chemical proof gloves, safety glasses gum boots, life jacket, sturdy footwear, long sleeved shirt and trousers, sunscreen, insect repellent, warm clothes during cooler weather, mobile phone |
| Step-3 | Deployment of AM in waterways | • Autoclave baskets containing AM deployed in the river for four weeks |
| Step-4 | Preparation of bags for retrieval of AM from waterways- requirements | **Requirements**<br>• Whirl pack bag<br>• Cotton wool/sponge<br>• Resealable bags<br>• Name tags (showing the source, date, water type etc)<br>• Rubber band |
| Step-5 | Retrieval of AM from waterways | • Basket and AM can be covered with silt and aquatic plants, which require rinsing with the site water; AMs retrieved needs to be wrapped with wet cotton/sponges and to be placed in sterile sample bags/whirl pack bags and then into a resealable bag for shipment to Hong Kong |
| Step-6 | Shipment of AM to Hong Kong from Australia | • AM shipped to Hong Kong via express courier (Australia post or TNT); AM shipped with the custom declaration-ready for shipment; |

# 9. Water quality

## 9.1 : Water temperature

Surface water temperature of each G-MW site was recorded using a fractional degree thermometer (405 mm blue LO-tox TM filled) during retrieval of AM. Lowest temperatures was recorded in July (5.7 -9.7 $^{0}$C) and highest in February (range 23-32 $^{0}$C) (see Table 6)

**Table 6 : Average water temperature ($^{0}$C) of the ten monitoring sites within G-MW (2009-10).**

| | Jul-09 | Aug-09 | Sep-09 | Oct-09 | Nov-09 | Dec-09 | Jan-10 | Feb-10 | Mar-10 |
|---|---|---|---|---|---|---|---|---|---|
| Site 1-Buffalo | 5.7 | 9.7 | | 11.5 | 16.65 | | 20 | 23 | |
| Site 2-Howqua | 8.1 | 7.85 | | 10.5 | 22.55 | | 22 | 28.9 | |
| Site 3-Cobram | | | 13.05 | 15.85 | 28.75 | 23.4 | 28 | 32 | 21.25 |
| Site 4-Shepaprton | | | 12.54 | 12.5 | 24.6 | 21.1 | 23 | 28 | 18.5 |
| Site 5-Mooroopna | | | 11.65 | 13.35 | 23.7 | 21.9 | 20.25 | 26.6 | 16 |
| Site 6-Tatura | | | 10.1 | 13.35 | 23.45 | 21.45 | 22 | 26.8 | 18.1 |
| Site 7-Rochester | | | 13.75 | 14.9 | 28 | 22.45 | 29 | 30 | 21 |
| Site 8-West Boort | | | 14.9 | 13.15 | 29 | 21.9 | 28.75 | 30 | 18.6 |
| Site 9-Kerang | | | 11.7 | 10.6 | 27.5 | 18.25 | 25.3 | 28 | 15.7 |
| Site 10-Kangaroo lake | | | 13.35 | 12.05 | 27.8 | 21 | 25.35 | 27 | 16.85 |

*Note : Sampling in irrigation sites (site 3-10) were conducted between September and March (site 3 to site 10) (deployment @every four weeks) and in the reference sites (site 1 and 2) between July and May (deployment @ every three months deployment).*

## 9.2 : Water Hardness

Water hardness of each G-MW site was measured using Hatch water quality test strips (Cat 27452-50, Hatch Company Loveland, CO, USA). Water hardness varies from 50 mg/L to 250 mg/L (see Table 7). The procedures followed are as follows:

- dip the strip into water for 1 second
- shake off excess water
- compare the total hardness test pad with the colour chart

**Table 7: Average water hardness (mg/L) of the five monitoring sites (2009-10).**

| | Jul-09 | Aug-09 | Sep-09 | Oct-09 | Nov-09 | Dec-09 | Jan-10 | Feb-10 | Mar-10 | Mean of all months | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Site 1-Buffalo | 25 | 25 | | 0 | 25 | | 0 | 25 | | 16.67 | Soft |
| Site 2-Howqua | 50 | 25 | | 25 | 50 | | 20 | 25 | | 32.5 | Moderately |
| Site 3-Cobram | | | 25 | 20 | 120 | 50 | 50 | 50 | 25 | 48.57 | Slightly ha |
| Site 4-Shepaprton | | | 120 | 120 | 120 | 50 | 50 | 50 | 50 | 80 | Moderately |
| Site 5-Mooroopna | | | 50 | 120 | 250 | 120 | 50 | 50 | 50 | 98.57 | Hard |
| Site 6-Tatura | | | 50 | 120 | 120 | 50 | 50 | 50 | 50 | 70 | Moderately |
| Site 7-Rochester | | | 50 | 120 | 120 | 120 | 50 | 120 | 50 | 90 | Hard |
| Site 8-West Boort | | | 120 | 120 | 120 | 120 | 120 | 120 | 120 | 120 | Hard |
| Site 9-Kerang | | | 120 | 120 | 120 | 120 | 120 | 120 | 120 | 120 | Hard |
| Site 10-Kangaroo lake | | | 120 | 120 | 250 | 250 | 120 | 120 | 120 | 157.14 | Very hard |

*The following classification was used to classify the water hardness*
*Soft : 0 - 20 mg/L as calcium ; Moderately soft : 20 - 40 mg/L as calcium ; Slightly* hard : 40 - 60 mg/L as calcium ; Moderately hard : 60 - 80 mg/L as calcium; Hard : 80 - 120 mg/L as calcium; Very Hard : >120 mg/L as calcium

## 10 : Analytical techniques

The AMs were shipped to Hong Kong (CityU), where the contents of each AM were emptied onto a sintered glass filter, washed twice with nitric acid (6M, analytical grade; 2 × 12.5 mL), and the elutriant made up to volume with deionized water. The concentrations of metals were determined by either flame atomic absorption spectrophotometry (FAAS) and/or inductively coupled plasma atomic emission spectrometry (ICP-AES) by CityU. The water samples were also analysed for metals by CityU using inductively coupled plasma mass spectrometry (ICP-MS).

## 11 : Quality Assurance

Three replicate AM were deployed at each site to assess the variability in accumulation of heavy metals within a site. AM were analyzed by a professional chemist of the CityU of Hong Kong. To reduce any contamination either during deployment and retrieval, gloves and protective clothing was worn. AM retrieved were sent to Hong Kong via fast air courier.

## 12 : Occupational health and safety

A site specific risk assessment was conducted, and a safe work instruction (risk control measures) was developed for all the sampling sites

# 13. Results

## 13.1.Goulburn Murray Water Catchments (G-MW)

### *13.1.1: Metals in AM passive samplers*

The artificial mussels (AM) deployed in G-MW waterways (creeks, rivers and irrigation channels) accumulated all the targeted metals (cadmium, copper, lead, mercury and zinc). Although, elevated concentrations of copper and zinc were detected at most sites, cadmium, lead and mercury concentrations were generally below the instrumental detection limits (Tables 8-9 and Figures 5-8). Therefore, results and discussion hereafters refer only to Cu and Zn. The order of accumulation of metals in AM was as follows:

Zn>Cu>Pb>Cr>Cd>Hg

**Table 8 : Average metals accumulated (µg/g dry weight) in AMs (chelex resin) deployed at sites under the influence of Murray system (note : average of whole deployment periods).**

| | Reference Murray River-site 1 (Buffalo) | Irrigation channel site- 3 Cobram | Irrigation channel site- 9 Kerang | Irrigation channel site- 10 Kangaroo lake |
|---|---|---|---|---|
| Cadmium (Cd) | <0.8 | <0.8 | <0.8 | <0.8 |
| Copper (Cu) | 15.8 | 16.3 | 21 | 18.1 |
| Chromium (Cr) | <1.0 | <1.0 | <1.0 | <1.0 |
| Lead (Pb) | <2.0 | <2.0 | <2.0 | <2.0 |
| Mercury (Hg) | <0.4 | <0.4 | 0.5 | <0.4 |
| Zinc ( Zn) | 27 | 28.5 | 29.5 | 24 |

**Table 9 : Average metals accumulated (µg/g dry weight) in AMs (chelex resin) deployed at sites under the influence of Goulburn system (note: average of whole deployment periods).**

| | Reference Goulburn River-site 2 (Howqua) | Irrigation channel site- 4 Shepparton | Irrigation channel site- 5 Mooroopna | Irrigation channel site- 6 Tatura | Irrigation channel site- 7 Rochester | Irrigation channel site- 8 West Boort |
|---|---|---|---|---|---|---|
| Cadmium (Cd) | <0.8 | <0.8 | <0.8 | <0.8 | <0.8 | 1.0 |
| Copper (Cu) | 15.6 | 19.9 | 16.9 | 16.5 | 15.5 | 19.6 |
| Chromium (Cr) | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 | <1.0 |
| Lead (Pb) | <2.0 | 2.1 | 2.0 | <2.0 | <2.0 | <2.0 |
| Mercury (Hg) | <0.4 | <0.4 | <0.4 | <0.4 | 1.5 | <0.4 |
| Zinc ( Zn) | 24.3 | 33 | 32.4 | 33.7 | 25.7 | 37.3 |

**Copper:** The AM results showed both spatial and temporal variations between and within the monitoring sites (see Figures 5 to 6). Elevated concentrations of copper detected at most risk sites located within the irrigating areas (see Table 8 and 9). Channel sites such as Kerang, and Kangaroo lake (Murray system) and West Boort, Shepparton (Goulburn system) had highest copper concentrations. During December-February periods, the copper concentrations in AMs were found at their peak (range: 18.8-33 µg/g) and lowest during September-October (range: 1.1-7.6 µg/g) (Figures 5-6). The mean coefficient variation in Cu metal concentration observed between AMs deployed at any particular site was typically less than 16%.

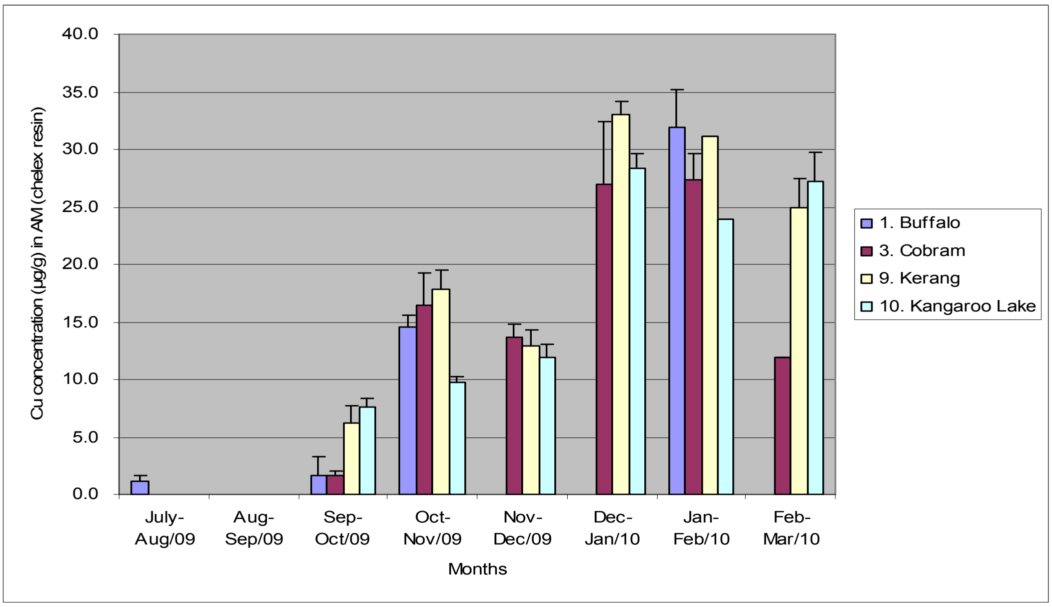



**Figure 5: Four week average copper (Cu) concentrations in artificial mussels (µg/g dry weight; mean (±S.E.M) for each deployment at sites under the influence of Murray River System.**

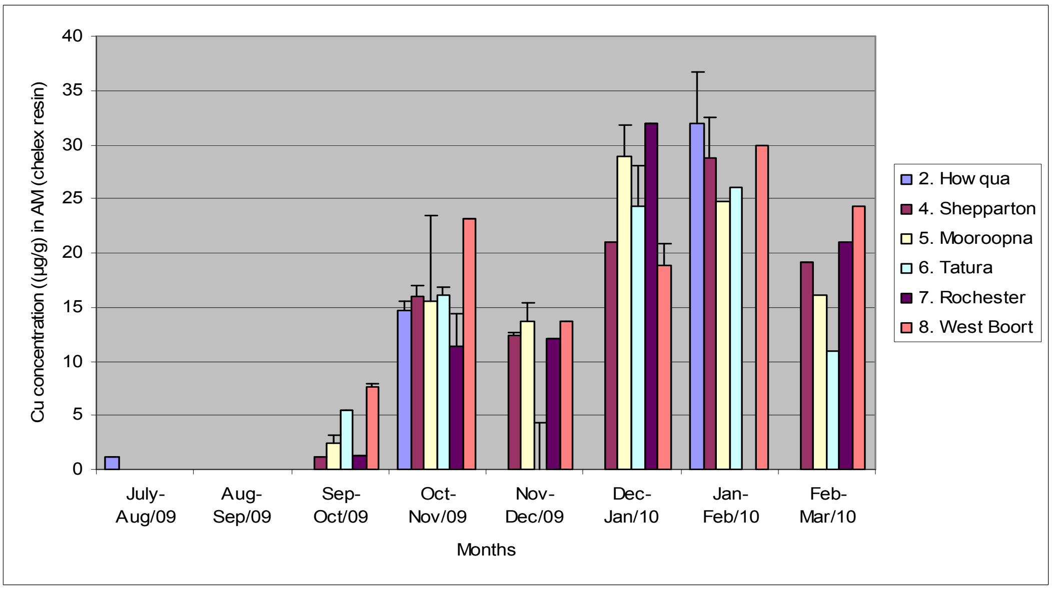



**Figure 6: Four week average copper (Cu) concentrations in artificial mussels (µg/g dry weight; mean (±S.E.M) for each deployment at sites under the influence of Goulburn River System.**

**Zinc:** The AM results showed both spatial and temporal variations between and within the monitoring sites (see Figures 7 to 8). Channel sites such as Kerang, and Cobram (Murray system) and West Boort, Tatura, Shepparton and Mooroopna (Goulburn system) had highest zinc concentrations (Table 8 and 9). During September-November periods the zinc concentrations in AMs were found at their peak (range: 22.9-80.4 µg/g) and lowest during February-March periods (range: 13.2-30.8 µg/g) (Figures 5-6). The mean coefficient variation in Zn metal concentration observed between AMs deployed at any particular site was typically less than 20%.

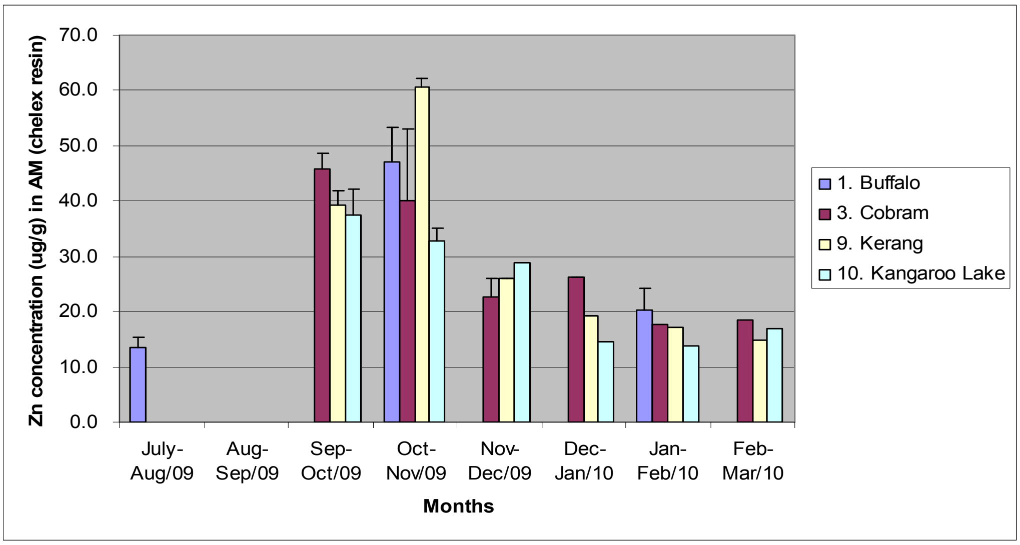



**Figure 7: Four week average zinc (Zn) concentrations in artificial mussels (µg/g dry weight; mean (±S.E.M) for each deployment at sites under the influence of Goulburn River System.**

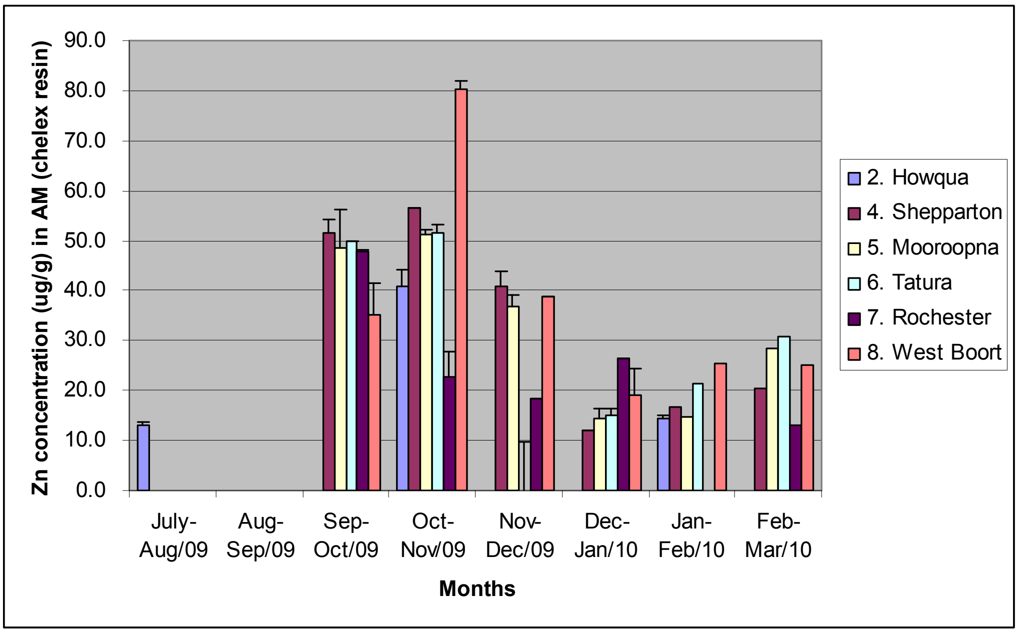



**Figure 8: Four week average zinc (Zn) concentrations in artificial mussels (µg/g dry weight; mean (±S.E.M) for each deployment at sites under the influence of Goulburn River System.**

**Other metals:** The Cd, Pb and Hg concentrations in the AMs were generally below the instrumental detection concentrations with the exception of the following occasions:

- one occasion when the average cadmium concentration at West Boort was 2 µg/g (Dec/ 09-Jan/10).
- one occasion when the average lead concentration was 2.2 and 2.3 µg/g at Mooroopna (Feb-Mar/10) and Shepparton (Feb-Mar/10) respectively.
- one occasion when the average mercury concentration was 3.1 and 0.7 µg/g at Rochester (Nov-Dec/09 ) and Kerang (Nov-Dec/09) respectively.

## 13.1.2: Metals in spot water samples-GMW

Cadmium, lead and mercury concentrations in spot water samples were generally below or close to the instrumental limits of reporting (Table 10). Elevated copper concentrations were detected at Kangaroo Lake, Kerang and Shepparton (Table 11). Sites such as Shepparton had highest average Zinc concentrations compared to other sites. (Table 12).

**Table 10: Average metals concentration (µg/L) in spot water samples (July 2009 to March 2010 averaged)-GMW (average of all months).**

| **Sites under the influence of Murray system** | | | | | |
|---|---|---|---|---|---|
| **Description** | **Cadmium** | **Copper** | **Lead** | **Zinc** | **Mercury** |
| GMW 01 – Buffalo (Ref-Murray) | <0.4 | <0.9 | <0.21 | 2.47 | <0.2 |
| GMW03 - Cobram | <0.4 | 1.18 | 0.26 | 1.7 | <0.2 |
| GMW 09 - Kerang | <0.4 | 2.01 | 0.37 | 1.6 | <0.2 |
| GMW 10 - Kangaroo Lake | <0.4 | 2.47 | <0.21 | 2.17 | <0.2 |
| **Sites under the influence of Goulburn system** | | | | | |
| GMW 02 – Howqua (Ref-Goulburn) | <0.4 | <0.9 | <0.21 | 3.35 | <0.2 |
| GMW 04 - Shepparton | <0.4 | 1.77 | 0.29 | 3.75 | <0.2 |
| GMW 05 - Mooroopna | <0.4 | 1.37 | 0.30 | 1.62 | <0.2 |
| GMW 05 - Tatura | <0.4 | 1.10 | 0.25 | 1.77 | <0.2 |
| GMW 07 - Rochester | <0.4 | 1.12 | 0.27 | 2 | <0.2 |
| GMW 08 - West Boort | <0.4 | 1.46 | <0.21 | 1.57 | <0.2 |

*FW aquatic ecosystems protection guideline values (95% protection): Cd- 0.2 µg/l; Cu- 1.4 µg/l; Pb- 3.4 µg/l; Hg- 0.06 µg/l and Zn- 8.0 µg/l (ANZECC & ARMCANZ , 2000).*

**Table 11: Monthly copper concentration in spot water samples**

| | Jul-Aug/09 | Aug-Sep/09 | Sep-Oct/09 | Oct-Nov/09 | Nov/Dec/09 | Dec/09-Jan/10 | Jan-Feb/ | | |
|---|---|---|---|---|---|---|---|---|---|
| Buffalo (Ref- Murray) | <0.9 | <0.9 | ns | <0.9 | <0.9 | ns | <0.9 | | |
| Cobram | | 1 | 0.9 | 1 | 1.1 | 0.9 | 2.3 | | |
| Kerang | | 2.3 | 1.8 | 1.9 | 2 | 2.1 | 2.1 | | |
| Kangaroo lake | | 2.1 | 2 | 2.7 | 2.5 | 2.8 | 2.5 | | |
| | | | | | | | | | |
| Howqua (Ref-Goulburn) | <0.9 | <0.9 | ns | <0.9 | <0.9 | ns | <0.9 | | |
| Shepparton | | 0.9 | 0.9 | 1.1 | 0.9 | 0.9 | 0.9 | | |
| Mooroopna | | 1.3 | 1 | 1.8 | 1.4 | 1.5 | 1.4 | | |
| Tatura | | 0.9 | 1.3 | 1 | 0.9 | 1.3 | 0.9 | | |
| Rochester | | 1.2 | 0.9 | 1.2 | 1 | 1.1 | 1.2 | | |
| West Boort | | 1 | 1 | 2 | 1.5 | 1.4 | 1.3 | | |

*Ns= not sampled; red fonts indicate ANZECC guideline for the protection (95%) of freshwater aquatic ecosystems*

**Table 12: Monthly zinc concentration in spot water samples**

| | Jul-Aug/09 | Aug-Sep/09 | Sep-Oct/09 | Oct-Nov/09 | Nov/Dec/09 | Dec/09-Jan/10 | Jan-Feb/ | | |
|---|---|---|---|---|---|---|---|---|---|
| Buffalo (Ref- Murray) | 2.2 | 2 | ns | <1.2 | 3.2 | ns | <1.2 | | |
| Cobram | | <1.2 | <1.2 | 2.6 | 1.2 | 1.3 | <1.2 | | |
| Kerang | | <1.2 | <1.2 | 2.1 | <1.2 | 1.3 | <1.2 | | |
| Kangaroo lake | | 3.5 | <1.2 | 1.7 | <1.2 | 1.3 | <1.2 | | |
| | | | | | | | | | |
| Howqua (Ref-Goulburn) | <1.2 | 1.3 | ns | <1.2 | 2.5 | ns | 3.1 | | |
| Shepparton | | <1.2 | <1.2 | 4.5 | <1.2 | <1.2 | <1.2 | | |
| Mooroopna | | 2 | <1.2 | 1.9 | 1.3 | 1.3 | <1.2 | | |
| Tatura | | 1.5 | 1.5 | 2.3 | <1.2 | <1.2 | <1.2 | | |
| Rochester | | 1.6 | <1.2 | 1.5 | 2.8 | 2.8 | 1.3 | | |
| West Boort | | <1.2 | <1.2 | 2.1 | 1.4 | 1.5 | <1.2 | | |

*Ns= not sampled*

## *1.3.1.3 Field concentration factors (FCF)*

Both field and laboratory experiments have demonstrated that concentrations of metals accumulated in AMs is representative of the mean concentrations of metals prevailing in the monitoring environment (*Wu et al. 2007*). Assuming the concentrations of metals in the spot water sample is representative of the mean metal level in the month, AM field concentration factors (FCF) can be calculated by dividing the mean metal concentration in AMs for the month by the mean of the spot sample concentration at the commencement of AM deployment and the spot sample concentration at AM retrieval after one month, for each site. The average FCFs for Cu and Zn were calculated as 13.42±3.8 and 22.26±3.6 (Table 14, 15) respectively which was close to other studies conducted in freshwater (see Table 16).

**Table 14: Calculated FCFs for Copper**

| Site | Site number. | Aug-Sep/09 | Sep-Oct/09 | Oct-Nov/09 | Nov/Dec/09 | Dec/09-Jan/10 | Jan-Feb/10 | Mean (FCF) |
|---|---|---|---|---|---|---|---|---|
| Cobram | 3 | 1.814815 | 18.1851852 | 13.01587 | 26.8667 | 17.03125 | 7 | 13.98563161 |
| Kerang | 9 | 3 | 9.6036036 | 6.598291 | 16.0976 | 14.857143 | 12.45 | 10.43443301 |
| Kangaroo lake | 10 | 3.707317 | 4.17021277 | 4.576923 | 10.717 | 9 | 10.46153846 | 7.105495418 |
| Shepparton | 4 | 1.3125 | 16.8421053 | 13.01754 | 49.2941 | 33.882353 | 5.38028169 | 19.9548169 |
| Mooroopna | 5 | 2.057971 | 11.1428571 | 8.5 | 19.954 | 17.103448 | 12.35897436 | 11.85287896 |
| Tatura | 6 | 5.142857 | 14.0289855 | n | 23.1429 | 24.714286 | 12.11111111 | 15.82801932 |
| Rochester | 7 | 1.3 | 11.2666667 | 11 | 30.381 | n | 19.09090909 | 14.60770563 |
| West Boort | 8 | 7.566667 | 15.4333333 | 7.771429 | 12.9655 | 22.222222 | 14.72727273 | 13.44774013 |
| | | | | | | | FCF of all sites | 13.4020901 |
| | | | | | | | SDEV | 3.807391738 |
| | | | | | | | CV% | 8.60474093 |

**Table 15: Calculated FCFs for Zinc**

| Site | Site number | Aug-Sep/09 | Sep-Oct/09 | Oct-Nov/09 | Nov/Dec/09 | Dec/09-Jan/10 | Jan-Feb/10 | M |
|---|---|---|---|---|---|---|---|---|
| Cobram | 3 | 45.73333333 | 22.33333333 | 11.94736842 | 21.06666667 | 15.39130435 | 18.5 | 2 |
| Kerang | 9 | 39.4 | 39.09677419 | 16.68817204 | 16.72463768 | 14.86956522 | 12.375 | 2 |
| Kangaroo lake | 10 | 16.64444444 | 24.24691358 | 21.2962963 | 12.57971014 | 12 | 16.85 | 1 |
| Shepparton | 4 | 51.55 | 20.58181818 | 14.81212121 | 11.9 | 16.63333333 | 10.15 | 2 |
| Mooroopna | 5 | 32.42222222 | 35.24137931 | 23.0625 | 11.12820513 | 12.84057971 | 28.5 | 2 |
| Tatura | 6 | 33.26666667 | 27.10526316 | n | 15 | 21.35 | 30.8333333 | 2 |
| Rochester | 7 | 39.25372146 | 18.29333333 | 8.534883721 | 9.392857143 | n | 11.4782609 | 1 |
| West Boort | 8 | 35.03333333 | 51.87096774 | 22.22857143 | 13.26436782 | 20.24 | 21.9130435 | 2 |
| | | | | | | | FCF of all sites | 2 |
| | | | | | | | SDEV | 3. |
| | | | | | | | CV% | 1 |

## 13.1.4: Discussion– GMW

Both AM (see Table 8 and 9) and spot water (see Table 10) quality monitoring data reveals elevated copper concentrations at Kerang, Kangaroo Lake, Shepparton and West Boort. This may demonstrate that some localized copper inputs occurred in these areas, possibly from usage of agriculture chemicals such as copper fungicide to control bacterial and fungal diseases. These sites were close to intensive orchards (pome and stone), vine yards, and areas growing olives and tomatoes.

Due to non-availability of calibration and concentration factor data it was not possible to convert qualitative time-weighted average (TWA) metal concentrations in the AM (chelex resin) into a more quantitative average water metal concentration for comparison with the *ANZECC & ARMCANZ (2000)* water quality guideline values for the protection of aquatic ecosystems. Because of the above, the analytical results of spot water samples (Table 7) were compared which showed that four sites (Kerang and Kangaroo Lake for Murray system; Shepparton and West Boort) exceeded the *ANZECC & ARMCANZ (2000)* guidelines trigger value for Cu for protection of aquatic ecosystems at the 95% protection level of 1.4 µg/l, but none of the sites exceeded 80% aquatic ecosystem protection values of copper of 2.5 µg/L. The sites where elevated copper detected were in 'artificial channels' not in natural waterways. The State Environment Protection Policy for the waters of Victoria (EPA, 2003) exempts artificial channels and drains from protection of beneficial use, including protection of aquatic ecosystems. Copper is highly toxic to fish, however the toxicity of copper to aquatic organisms is related to the hardness of water, i.e. toxicity decreases with increasing hardness. The water of four channel sites (Kerang, Kangaroo Lake, Shepparton and West Boort) where elevated copper concentrations detected were hard to very hard (> 80 mg/L) and the *ANZECC & ARMCANZ (2000)* guidelines for protection of aquatic species at the 95% protection level relates to hardness value of 30 mg/L. Zinc concentrations in spot water samples were within the *ANZECC & ARMCANZ (2000)* guideline threshold trigger values (95%) for aquatic ecosystems of 8.0 µg/L zinc.

Comment: On CV

Concentration factors in saline waters were reported by *Wu et al. 2007* as between 34 to 425 (Table 16) in the order Zn>Cd>Cu>Pb>Cr. The field concentration factors calculated in this study (conducted in freshwater) were in the range 0.45 to 22.26 and in the order of Zn>Cu>Cd>Hg>Pb>Cr. Though the FCFs in this study follows the same trend as reported by *Wu et al. 2007* , however, FCFs were several orders lower, the reason for this may demonstrate that the accumulation of metals with AM is lower in freshwater compared to saline water (see Table 16).

**Table 16: FCFs comparisons**

*Note: Shade boxes indicate that FCFs were estimated since AM and spot water results were below LOD*

| Authors | Zn | Cu | Cd | Hg | Pb | Cr | Comments |
|---|---|---|---|---|---|---|---|
| G-MW- Current study | 22.26 | 13.4 | 2 | 2 | 0.95 | 0.45 | Freshwater: G-MW catchmen and irrigation channels (10 si |
| GMW pilot study- *Rudolf et al. 2008* | 6.6 | 5.02 | 2.5 | 3 | 3 | 0.53 | Freshwater: G-MW catchmen Irrigation channels (5 sites) |
| NCCMA study- *Allinson 2010* | 12.1 | 8.6 | - | - | - | - | Freshwater: North central CM catchments : Loddon and Can Rivers |
| Hong Kong study- *Rudolf et. al. 2007* | 312-424 | 102-125 | 289-302 | - | 207-288 | 34-64 | Marine system- Lab based stu Hong Kong; at different temp (22 and 30 C) and different sal ppt and 30 ppt) |

# 13.2.Melbourne water/Yarra catchments (MW)

## *13.2.1: Metals in AM passive samplers*

The artificial mussels (AM) deployed in MW waterways (creeks) consistently accumulated only two of targeted metals (copper and zinc), although at all sites. Hg was detected on one occasion in each of McCrae Ck and Olinda Ck (0.5 and 0.8 µg/g chelex resin, respectively). Elevated copper concentrations were found at MW sites (creeks) during February-March periods (range: 58.8-62.53 µg/g) whereas lowest Cu concentrations found in July-August (0.97-1.07 µg/g) (Figure 9). Zinc concentrations in MW sites showed a peak during July-August periods (range: 54.93-77.5 µg/g) and significantly lower during February-March (range: 13.9-24.47 µg/g) (Figure 10).

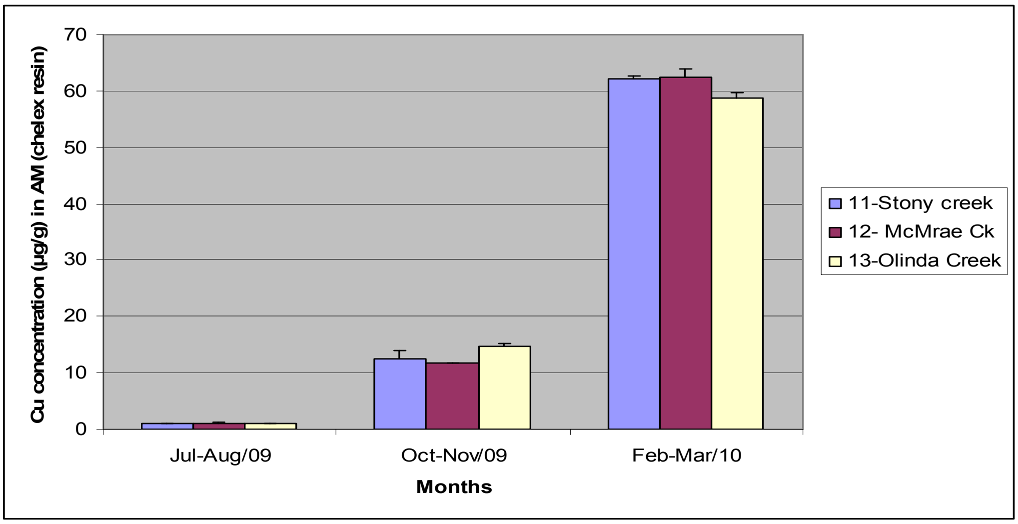



Figure 9:. **Figure 5: Four week average copper (Cu) concentrations in artificial mussels (µg/g dry weight; mean (±S.E.M) for each deployment at sites in the MW regions**.

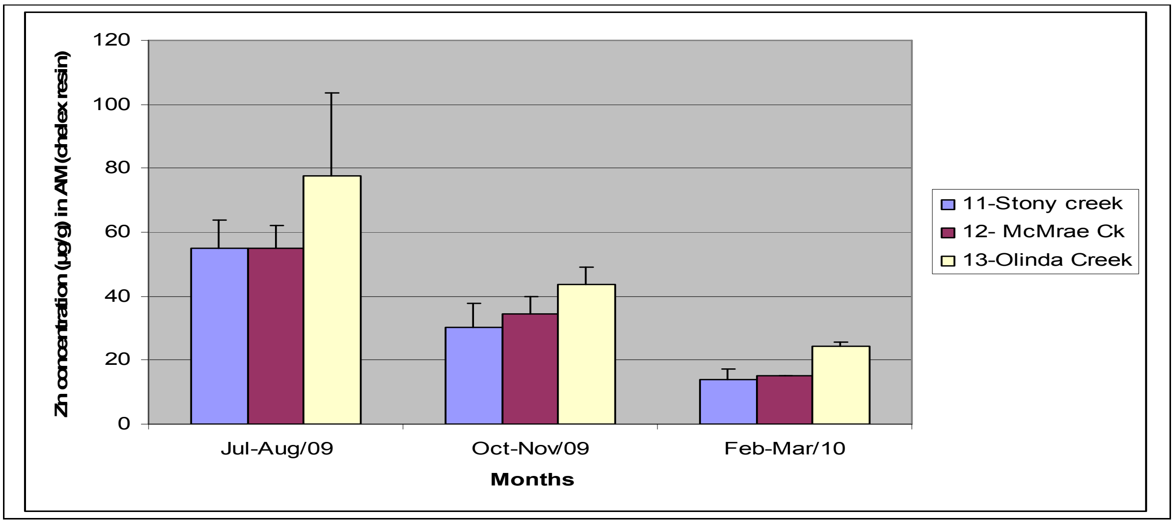



**Figure 10: Four week average zinc (Zn) concentrations in artificial mussels (µg/g dry weight; mean (±S.E.M) for each deployment at sites in the MW regions.**

## *13.2.2: Metals in spot water samples-MW*

The 2009 spot water quality monitoring data reveals elevated copper in Stony ck and Olinda ck and elevated zinc at Olinda Ck site (Table 17).

**Table 17 : Average metals concentration (µg/L) in spot water samples (July, August and November 2009)-MW.** *FW aquatic ecosystems protection guideline values: Cd- 0.2 µg/l; Cu- 1.4 µg/l; Pb- 3.4 µg/l; Hg- 0.06 µg/l and Zn- 8.0 µg/l (ANZECC & ARMCANZ , 2000).*

| Description | Cadmium | Copper | Lead | Zinc | Mercury |
|---|---|---|---|---|---|
| MW11 – Stony ck | <0.4 | 2.7 – 7.0 | < 0.2 | < 1.2 – 4.1 | < 0.2 |
| MW12- McCrae Ck | <0.4 | < 0.9 – 1.0 | < 0.2 | < 1.2 – 2.4 | < 0.2 |
| MW-13 – Olinda Ck | <0.4 | 2.3 – 4.5 | < 0.2 – 3.1 | 5 - 18 | < 0.2 |

## *13.2.3 Discussion-MW*

The AM results showed both spatial and temporal variations between and within the monitoring sites (see Figures 9 to 10). Due to non-availability of calibration and concentration factor data it was not possible to convert qualitative time-weighted average (TWA) metal concentrations in the AM (chelex resin) into a more quantitative average water metal concentration for comparison with the *ANZECC & ARMCANZ (2000)* water quality guideline values for the protection of aquatic ecosystems. Because of the above, the analytical results of spot water samples (Table 17) were compared which showed that site 11 (Stony ck) and 13 (Olinda ck) exceeded the *ANZECC & ARMCANZ (2000)* guidelines trigger value for Cu (1.4 µg/L) and Zn (8.0 µg/L) for protection of aquatic ecosystems at the 95% protection level. The elevated (i.e. above or occasionally above *ANZECC & ARMCANZ (2000)* trigger values) Cu and Zn concentrations at sites 11 and 13 suggests that some localized copper inputs occurred in these areas, possibly from usage of agriculture chemicals such as copper fungicide to control bacterial and fungal diseases in orchards and vine yards (Site 11), and the influence of a small WWTP (Site 13).

# 13.3.North Central CMA sites (NCCMA)

## *13.3.1: Metals in passive samplers - NC CMA*

The artificial mussels (AM) deployed in MW waterways (creeks) consistently accumulated only two of targeted metals (copper and zinc), although not at all times at all sites (Figure 11 and 12). Specifically, Zn was detected in the AMs at only one site (site 14) during the first deployment (August 2009). The AM deployed at three NCCMA sites during August to November 2009 showed that copper and zinc concentrations accumulated in the AMs at similar concentrations across all sites (Cu, 12 – 15.6 µg/g AM resin; Zn, 33.7 – 43.3 µg/g AM resin; *Allinson, 2010*). The variation in metal concentration observed between AMs deployed at any particular site was typically less than 20%, and consistent with previous reports of their use.

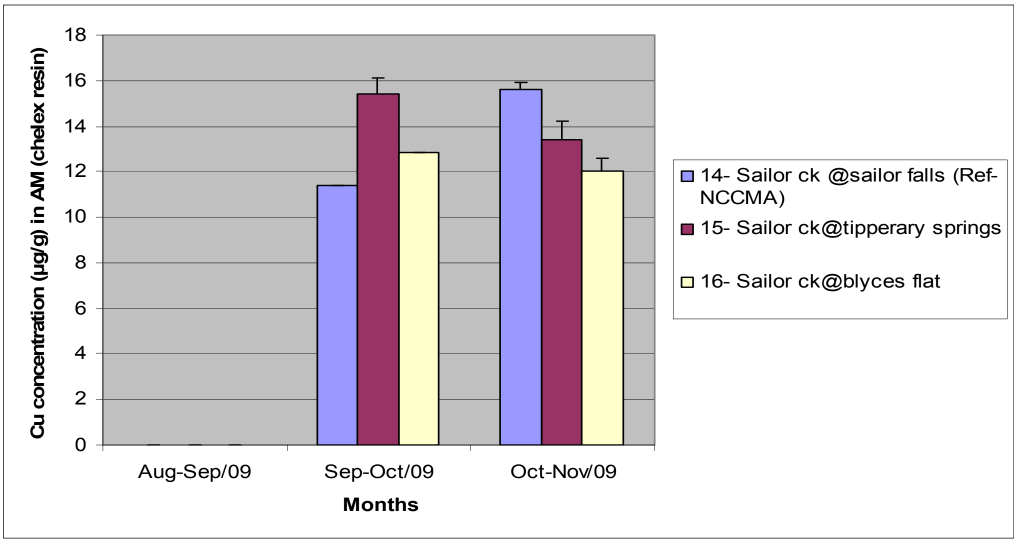



**Figure 11:. Four week average copper (Cu) concentrations in artificial mussels (µg/g dry weight; mean (±S.E.M) for each deployment at sites in the NCCMA regions. Months without a bar indicate concentrations levels were below the LOR (<0.9 µg/g).**

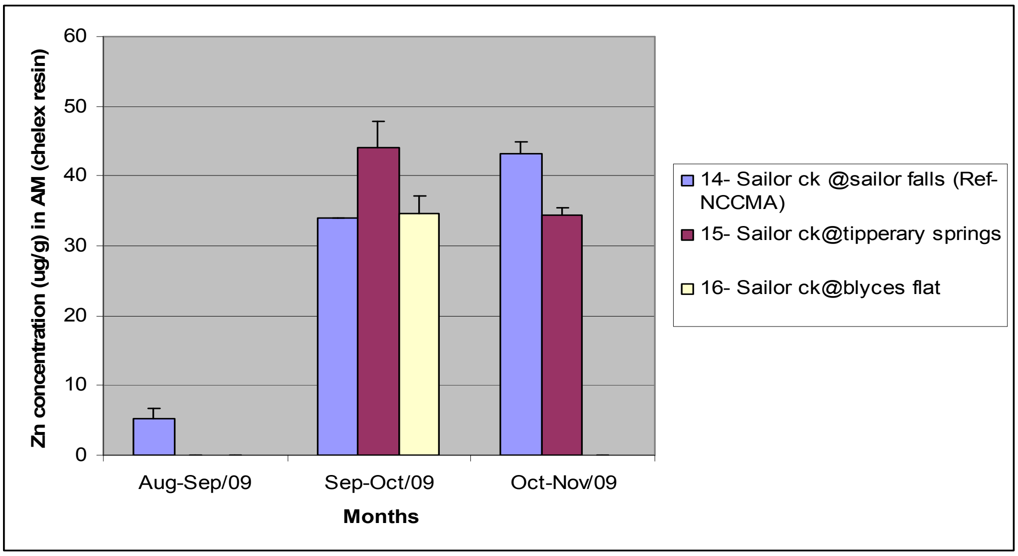



**Figure 12:. Four week average zinc (Zn) concentrations in artificial mussels (µg/g dry weight; mean (±S.E.M) for each deployment at sites in the NCCMA regions**.

## *13.3.2: Metals in spot water samples-NCCMA*

Cadmium, lead and mercury concentrations in spot water samples were below laboratory reporting concentrations (Table 18). Copper concentrations at site 15 and 16 exceeded the *ANZECC/ARMCANZ (2000)* guideline TV value for protection of aquatic ecosystems of copper of 1.4 µg/L  Zinc level at all the sites was below the aquatic ecosystems protection guideline value of 8.0 µg/L.

**Table 18: Average metals concentration (µg/L) in spot water samples (July 2009 to March 2010 average)-NCCMA.**

*ANZECC & ARMCANZ (2000): FW aquatic ecosystems protection guideline values: Cd- 0.2 µg/l; Cu- 1.4 µg/l; Pb- 3.4 µg/l; Hg- 0.06 µg/l and Zn- 8.0 µg/l*

| Description | Cadmium | Copper | Mercury | Lead | Zinc |
|---|---|---|---|---|---|
| GMW NCCMA 14 - Sailors Ck @ Sailors Falls - just below bridge | <0.4 | 1.1 | <0.2 | <0.21 | 1.9 |
| GMW NCCMA 15 - Sailors Ck @ Tipperary Springs | <0.4 | 1.8 | <0.2 | <0.21 | 5.8 |
| GMW NCCMA - 16 Sailors Creek @ Bryces Flat | <0.4 | 1.9 | <0.2 | <0.21 | 3.0 |

## *13.2.3: Discussion-NCCMA*

The AM results showed both spatial and temporal variations between and within the monitoring sites (see Figures 11 to 12). Due to non-availability of calibration and concentration factor data it was not possible to convert qualitative time-weighted average

(TWA) metal concentrations in the AM (chelex resin) into a more quantitative average water metal concentration for comparison with the *ANZECC & ARMCANZ (2000)* water quality guideline values for the protection of aquatic ecosystems. Because of the above, the analytical results of spot water samples (Table 18) were compared which showed that site 15 (Tipperary Springs) and 16 (Bryces Flat) exceeded the *ANZECC & ARMCANZ (2000)* guidelines trigger value for Cu (1.4 µg/L) for protection of aquatic ecosystems at the 95% protection level. However, the elevated (i.e. above or occasionally above ANZECC & ARMCANZ (2000) trigger values) Cu concentrations at some sites suggests that some localized copper inputs occurred in these areas. The source of these metals is as yet unclear.

# 14: Overall conclusion (G-MW, MW and NCCMA)

The AM results showed both spatial and temporal variations between and within the monitoring sites investigated. The artificial mussels (AM) deployed in three catchments consistently accumulated two of targeted metals (copper and zinc); on the other hand, cadmium, lead and mercury concentrations were generally below the instrumental detection limits. Comparing the three catchments, both copper and zinc concentrations were highest levels at MW sites, lower at GMW, and lowest at NCCMA sites in the following orders (see also Table 19).

MW>G-MW>NCCMA

**Table 19: Copper and zinc accumulation in AM at different catchments**

| Metals | Catchments | Range detected | Mean of all seasons | Low accumulation season | High accumulation season |
|---|---|---|---|---|---|
| Copper | GMW | 1.1- 33 | 17.52 | Sep/09-Oct/09<br>1.1-7.6 | Dec/09-Feb/10<br>18.8-33 |
| | MW | 0.87- 62.53 | 25.18 | Jul/09-Sep/09<br>0.97-1.07 | Feb/10-Mar/10<br>58.8-62.53 |
| | NCCMA | 0.7- 16.6 | 9.23 | Aug/09-Sep/09<br><0.9-<0.9 | Sep/09-Oct/09<br>11.4-16.6 |
| | | | | | |
| Zinc | GMW | 13.1-80.4 | 28.4 | Feb/10-Mar/10<br>13.2-30.8 | Sep/09-Nov/09<br>22.9-80.4 |
| | MW | 15.01-77.5 | 33.92 | Feb/10-Mar/10<br>13.9-24.47 | Jul/09-Aug/09<br>54.93-77.5 |
| | NCCMA | 1-44 | 23.9 | Aug/09-Sep/09<br>1-5.27 | Sep/09-Nov/09<br>33.9-44 |

In order to convert AM chelex resin concentrations into time-weighted average water concentrations for the period of AM deployment, calibration (or uptake) factors for each metal are required. These are not currently available. A preliminary calibration and concentration factor experiment with AM was conducted at DPI Queenscliff Centre *(Kibria et al. 2010b)*, but results were inconclusive, perhaps due to high levels of Cu (540 µg/l) found in the tap water used, and thus they cannot be used to produce quantitative average water metal concentration

The analytical results of spot water samples were compared which showed that several sites exceeded the *ANZECC & ARMCANZ (2000)* guidelines trigger value for either Cu or Zn for protection of aquatic ecosystems at the 95% protection level.

- Four of the G-MW sites (Kerang and Kangaroo Lake, Shepparton and West Boort) exceeded the *ANZECC & ARMCANZ (2000)* guidelines trigger value for Cu of 1.4 µg/L. These sites were close to intensive orchards (pome and stone), vine yards, and areas growing olives and tomatoes. This may demonstrate that some localized copper inputs occurred in these areas, possibly from usage of agriculture chemicals such as copper fungicide to control bacterial and fungal diseases.

- Two of the MW sites (Stony Ck and Olinda Ck) exceeded the *ANZECC & ARMCANZ (2000)* guidelines trigger value for Cu (1.4 µg/L) and Zn (8.0 µg/L) for protection of aquatic ecosystems at the 95% protection level. The elevated (i.e. above or occasionally above *ANZECC & ARMCANZ (2000)* trigger values) Cu and Zn concentrations at these sites suggests that some localized copper inputs occurred in these areas, possibly from usage of agriculture chemicals such as copper fungicide to control bacterial and fungal diseases in orchards and vine yards (Site 11), and the influence of a small WWTP (Site 13).

- Two of the NCCMA sites (Tipperary Springs and Bryces Flat) exceeded the *ANZECC & ARMCANZ (2000)* guidelines trigger value for Cu (1.4 µg/L) for protection of aquatic ecosystems at the 95% protection level. The source of these metals is as yet unclear.

Overall, the first year of the study demonstrate the usefulness of using innovative technology such as artificial mussels passive sampling techniques in monitoring metals in various waterways such as rivers and irrigation channels (G-MW), peri-urban streams (MW) and ephemeral streams (NCCMA). In case of G-MW, the first year study (Year 1 or 2009-10) was conducted during drought conditions when there was little water at G-MW storages. However, it is anticipated that the 2010-11 monitoring will provide a better picture of the metals in G-MW channels and waterways due to higher rainfall and runoff being experienced during the winter and spring of 2010.

# 15: References


Allinson G (2010). Passive sampling for metals in the waters of selected streams in the Upper Loddon and Campaspe River catchments. A report to North Central Catchment Management Authority. DPI Queenscliff

Australian and New Zealand Environment and Conservation Council (ANZECC) and Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ), (2000).Australian and New Zealand Guidelines for Fresh and Marine Water Quality, Volume 1, The Guidelines (Chapters 1-7).

EPA (2003). State Environment Protection Policy (Waters of Victoria) : Policy Impact Assessment. Southbank, EPA, Victoria. *EPA Publication no 905*, 91p

G-MW (2009. Monitoring of heavy metals in G-MW waterways using passive sampling with 'Artificial mussels' (stage II). G-MW docs 2571958, Goulburn Murray Water, Tatura, Victoria, Australia.

Kibria, G., Rose, G., Lau, T.C., Lung, Y.K., Chan, A.K.Y., Wu, R. (2010a). Monitoring heavy Metals in Goulburn-Murray waterways using passive sampling with artificial mussels (AM) – Pilot Study (trial of AM technology). Report prepared under a research collaboration agreement between Goulburn Murray Rural Water Corporation, Tatura, Australia, the City University of Hong Kong, the University of Hong Kong, and the Department of Primary Industries, Werribee, Victoria, Australia. 29p.
http://www.g-mwater.com.au/downloads/currentProjects/research/heavyMetalsG_MW.pdf

Kibria, G., Allinson, G., Allinson, M., Lau, T.C. and Wu, R. (2010b). *Calibration and Concentration Factors Experiments with Artificial Mussels at DPI Queenscliff Centre, Melbourne, Australia.*Report prepared under a research collaboration agreement between Goulburn Murray Rural Water Corporation, Tatura, the Department of Primary Industries, Werribee, Victoria Australia, the City University of Hong Kong, and the University of Hong Kong, and, Australia. 30p.

Monash Review (1983). Whats new in Education, Research and Community Service. Gold mines leave a legacy of mercury. 3 (83): p. 6-7.

USMP (2001). Urban Stormwater Management Plan (USMP). Victoria, Australia.

Wu, R., Rose, G., Lau, T.C., Lung, Y.K., Chan, A.K.Y., Wu, R. (2008). Monitoring heavy Metals in Goulburn-Murray waterways using passive sampling with artificial mussels (AM) – Pilot Study (trial of AM technology). Report prepared under a research collaboration agreement between Goulburn Murray Rural Water Corporation, Tatura, Australia, the City University of Hong Kong, the University of Hong Kong, and the Department of Primary Industries, Werribee, Victoria, Australia. 41p.

Wu, RSS, Lau, TC, Fung, WKM, Ko, PH and Leung, KMY (2007) An artificial mussel for monitoring heavy metals in a marine environments. *Environmental pollution*, 145, 104-110.