ASSESSMENT OF METALS AND METALLOIDS IN SURFACE WATER DISCHARGED FROM UPPER HUNTER COAL MINES AND POWER STATIONS

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Executive Summary

The Hunter Region supports a range of primary and resource based industries that include agriculture, energy generation, mining and tourism. Due to the unique geology and soil landscapes, the Hunter Valley has a natural abundance of salts that partially leach into ground water and rivers. As part of the regular coal mining process, saline waters collect in mine pits and shafts and must be pumped out. Power generation from the thermal coal plants at Bayswater and Liddell in the Upper Hunter rely on cooling via evaporative loss of water, a process that leads to the concentration of salts in the residual dam water in Lake Liddell. The management of excess salt water is challenging for these industries.

In the 1990's the Hunter River Salinity Trading Scheme (HRSTS) was developed through collaboration with the community, industry and government, as a water management strategy aimed at minimizing the cumulative impact of mining and energy generation on the Hunter River water quality to reduce salinity levels. The scheme essentially coordinates the discharge of excess water from mine sites and the AGL power stations, to coincide with high river flow conditions, to cap the maximum salt concentrations within an environmentally acceptable range, while still enabling the discharge of salt that has accumulated through industrial activities. The operation of HRSTS is widely regarded as a successful strategy, with data demonstrating water quality improvements in terms of salinity over the 23 years of operation. Despite rigorous assessment of salinity levels in relation to this scheme, other aspects of water quality, such as metal(loid)s, have not been a focus of monitoring and assessment and very little data exists on these aspects within the HRSTS.

The International Centre for Balanced Land use has been commissioned by the Upper Hunter Mining Dialogue to conduct a preliminary investigation on metal(loid)s across key storage dams within the HRSTS that intercept water from coal mines and power utilities operating in the Upper Hunter. Metal(loid) concentrations in the discharge water storage dams were compared against multiple reference sites representative of conditions in the Upper Hunter River affected by the HRSTS. Furthermore, the ANZECC (2000) national water quality guidelines were used as a filter to identify potential issues pollution issues associated with mine water discharge. The key findings and conclusions of this study are listed below:

- Metal(loid) concentrations in the discharge water storage dams were low across all sites. Levels for a few metal(loid)s exceeded guideline trigger values in a limited number of cases, in both discharge dams and Hunter River reference sites, indicating a natural background occurrence of these elements.
- There were slightly elevated concentrations of Arsenate (As(V)) in MTW dams and Zn in CHPP surge-dams. As discharge from these dams occurs only during periods of high-flow, a requirement under the operation of HRSTS, As(V) and Zn at the concentrations observed in this study will be well below ANZECC trigger values in the downstream environment. Further consideration of the source, spatial extent and seasonal variability of As(V) in storage dams and surrounding waterways will help inform management options.
- Nitrogen species were elevated in the discharge dams. Elevated nitrogen is common in the waterways of rural landscapes as it is widely used as fertilizer in agriculture. It is also used in mine land rehabilitation and blasting activities at mine sites. Further consideration of nitrogen in the dams and waterways adjacent to the Upper Hunter mines will help to assess the significance and management options for elevated nitrogen levels.
- The metal(loid) concentrations in sediments were below trigger values, with the exception of Nickel (Ni). Nickel was slightly elevated in the bottom sediments of some discharge dams and many of the Hunter River reference sites, indicating naturally occurring background levels.

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1. PROJECT SCOPE

To assess the potential for metal(loid) contamination of the Hunter River through the discharge of mine water under the Hunter River Salinity Trading Scheme.

1.1. SPECIFIC OBJECTIVES

Key objectives:

1) Quantify metal(loid)s in surface waters and benthic sediments in water storage dams that are used as part of the key infrastructure within the Hunter River Salinity Trading Scheme.
2) Evaluate the potential for metal(loid) contamination of the Hunter River through the Hunter River Salinity Trading Scheme.

1.2. PROJECT APPROACH

The project approach involves two broader tasks:

Task 1 - Assessment of metal(loid) concentrations against water quality guidelines in the surface water and benthic sediments in coal discharge water storages.

Task 2 - Information from Task 1 will be combined to provide a preliminary risk assessment for contamination of the Hunter River by metal(loid)s from coal operations and electricity generators in the Upper Hunter

2. BACKGROUND

Australia has been a major mining nation for more than 150 years. Wastewater from the extraction and refinement of coal may be discharged to the environment, through both planned and unplanned releases. Discharges are often saline and may contain dissolved solids, suspended solids, heavy metals, hydrocarbons and other compounds.

The Hunter River Salinity Trading Scheme (HRSTS) was developed in the 1990's as a regulatory strategy to minimize the cumulative impacts of coal mining on the water quality of the Hunter River to reduce maximum salinity levels. The scheme coordinates the discharge of excess water from mine sites to coincide with high-flow conditions in the Hunter River, in an effort to cap salt concentrations within an environmentally acceptable range. The capacity to store water and manage discharges against real-time flow conditions are the defining features of this scheme, which has proven effective in managing salinity in the Hunter River. Further information about HRSTS is publically available at: http://www.epa.nsw.gov.au/licensing-and-regulation/licensing/environment-protection-licences/emissions-trading/hunter-river-salinity-trading-scheme

Nutrients, suspended sediments, algae, organic and inorganic compounds, heavy metals and metalloids, and bacteria are other potential factors that can affect water quality. Metal(loid)s, hydrocarbons, salinity and acidity are common potential contaminants associated with mining activities. Technologies and approaches to protect water resources from contamination by either reducing, containing or treating contamination is core business for the industry and closely regulated by licensing authorities (e.g. Government Environmental Protection Agencies).

2.1.WATER MANAGEMENT IN COAL MINING OPERATIONS

Saline water discharged under the HRSTS is derived from the Hunter coal-fields (mainly groundwater) and from the evaporative-concentration of river water that has been used for power generation. The quality of mine water can vary due to its contact with coal, coal tailings, overburden and variability in geology of the mine catchment itself [3].

The coal mining industry consumes a relatively small quantity of water at national and global levels. Mining accounted for 4% of the water used in Canada, 2-3% of the total water consumed in Australia and 1% in the United States during 2005 [3, 4, 5].

Most coal mine waste is inert or benign, and therefore represents a low contamination risk to waterways when managed appropriately [1]. In some cases, mine waters can be high enough in quality that they require little treatment before being released to the environment. Shibdon Pond in England, for example, is an abandoned coal mine which has supported the development of a wetland and is now home to a sustainable ecosystem [7]. Treated mine water has many practical applications including augmentation to drinking water supplies and agricultural irrigation [8, 9].

Nevertheless, in some circumstances, mine water has the potential to affect the quality of surrounding surface waters and ground waters, which can impact on the environment. Water contaminated with high concentrations of metals, sulfide minerals, dissolved solids and/or salts can negatively affect the quality of surface waters, ground waters and aquatic ecosystems [11]. Therefore, the modern mining industry endeavors to recycles any waste and water resources. Advanced water management practices and mine designs have greatly reduced the potential for water contamination associated with mine sites over the past couple of decades. Waters are frequently monitored and comprehensive water management strategies have been developed to reduce the amount of mine water produced, with treatment to regulatory requirements (when necessary) before discharge to the environment a standard industry practice.

2.2. BACKGROUND SALINITY OF HUNTER RIVER

The Hunter River catchment drains an area of approximately 22,000 square kilometres on the central NSW coast. The valley comprises rugged mountain ranges in the north, undulating farmland in the central and western regions, and widespread fluvial/estuarine flatland coastal areas to the east. There are a variety of potential sources of salinity in the Hunter River catchment that include atmospheric deposition, run-off and infiltration, weathering of geological strata, groundwater and a range of anthropogenic sources. The Hunter Valley is generally saline due to the marine origin of some Permian sediments. However, recent land-use activities in the catchment may have contributed to rising salinity in streams such as the Goulburn River and Wollombi Brook. The Goulburn River tributary sub-catchment contributes higher salinity water to the Hunter River and this source of salts is outside (and upstream) of the HRSTS.

In a study of the salt inputs into the Hunter Valley catchments, Creelman (1994) suggested that rainfall released salts from weathered rocks and mine overburden. Kellet et al. (1989) found that input of groundwater from the Wittingham coal measures (in the mid-lower Hunter) was also of significance in terms of salinity contribution to the Hunter River catchment. The authors concluded that, of all the potential salt sources, regional geology was the dominant factor controlling the chemistry of Upper Hunter Valley groundwater and was the primary source of high background salinity in groundwater of the mid valley (e.g. Jerrys Plains and surrounds).

Overlaying the natural saline landscape in the Hunter River catchment are anthropogenic activities that can enhance salinity levels: mining, power generation and agriculture. These activities can either remove salts from the river system (e.g. via water extractions) or introduce them into the system (via licensed discharges and/or land run-off). The multiplicity of salt sources and the highly variable spatial and temporal interaction of natural and anthropogenic sources of salt create a complex challenge for managing salinity in the Hunter River catchment.

2.3. Hunter River Salinity Trading Scheme

The Hunter River Salinity Trading Scheme (HRSTS) operates to minimise the impact of saline waters discharged from industry to the Hunter River. The Scheme commenced as a pilot in 1995 and was formalised in 2002 under the Protection of the Environment Operations (Hunter River Salinity Trading Scheme) Regulation (2002). The Scheme's salinity targets apply only in the Hunter River between Glenbawn Dam at the upstream extent, and Singleton at the downstream extent, and only on the main channel of the Hunter River (i.e. not within any of the Hunter River tributaries).

River salinity targets have been established for three reference points in each of the River sectors (upper, middle and lower). Denman is the reference point for the upper sector; upstream of the Glennies Creek confluence for the middle sector; and Singleton for the lower sector (See Fig 1). The total allowable discharge of water and salt from participating mines and the power station is calculated so that salt concentration does not exceed 900 electrical conductivity units (EC) in the middle and lower sectors of the river, or 600 EC in the upper sector.

A recent review of the overall effectiveness of the HRSTS on surface water by the NSW Environmental Protection Agency reports:

- Little effect on flows and EC levels in the Hunter River upstream of Denman;
- Reduced EC levels at (and immediately upstream of) Singleton and Greta; and
- Potentially reduced EC levels at monitoring stations between Denman and Singleton

Based on these observations, the review concluded the HRSTS is achieving the overall goal of managing waters discharged to the Hunter River from mines and power generation.

2.4.CONTEXT OF THIS STUDY

Salinity, hydrocarbons, heavy metals and acidity are common potential contaminants associated with mining. Contamination can result from uncontrolled water discharges from mine sites, increased salinity in mine discharges and the formation of acid mine drainage (AMD) or alkaline waters on site due to the mineral specific composition, specific ore and overburden [2]. Technologies and approaches to protect water resources from contamination by either reducing, containing or treating contamination is core business for the mining industry and closely regulated by licensing authorities.

Among 29 coal mines that currently operate in the Hunter Valley, 10 are entitled to discharge under the HRSTS scheme. Although there is a large dataset on salinity contents in surface waters entering the Hunter River from mining [NSW EPA personal communication], there is limited information on the contents of metal(loids). Unlike other coal mine regions in Australia, at this stage heavy metals have not been identified as major water quality parameters of concern associated with coal mining in the Upper Hunter [8].

The Upper Hunter Mining Dialogue commissioned The University of Newcastle to conduct a preliminary screening for metal(loids) in discharge dams managed as part of the HRSTS. This preliminary investigation provides a snapshot of water quality data to screen for potential issues and inform the on-going management of the HRSTS.

3. METHODOLOGY

3.1.SITE SELECTION

The project team visited Rio-Tinto and Glencore on the 9th and 10th Aug 2017 to inspect and select representative sampling sites. Around 10 HRSTS discharge dams and 6 Hunter River reference sites were selected for this investigation in consultation with the UHMD Project Steering Committee. An additional site at Bengalla was included at the recommendation of the Steering Committee. The final list of 11 HRSTS discharge dams and six reference points in the Hunter River is given in Table 1 & Fig.1. The Hunter River reference sites spanned the HRSTS.

Table 1. Water and sediment sampling sites.

S. No	Sampling Site	Industry/Operator
Industry Sites		
1	Bengalla	Bengalla Mining operations
2	Lake Liddell	AGL Macquarie power generation
3	Reservoir North	Glencore
4	Ravensworth (RVS)	Glencore
5	Parnel’s Dam	HVO
6	Dam 11	HVO
7	Lake James	HVO
8	Dam 1N	MTW
9	Dam 9S	MTW
10	CHPP(Surge)	Glencore
11	ND 2	Glencore
Hunter River Reference Sites		
12	Hunter R@Dartbrook	Hunter River
13	Hunter R@Keys Bridge	
14	Hunter R@Denman	
15	Hunter R@Jerrys Plain	
16	Hunter R *u/s* Glennies Creek	
17	Hunter R@Singleton	

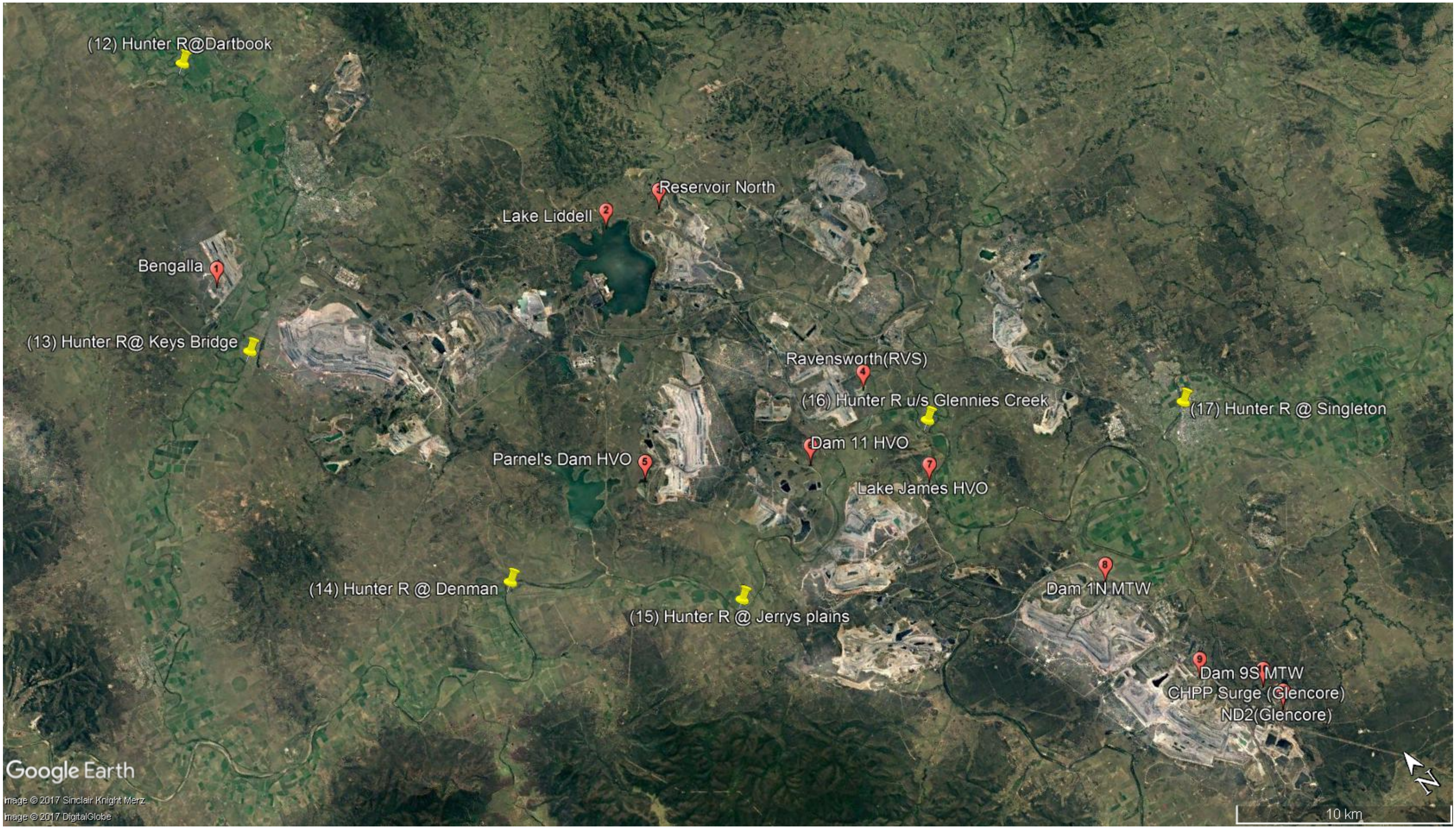

Figure 1. Sampling locations across the Hunter River Salinity Trading Scheme.

3.2. PRIMARY SAMPLE COLLECTION

To capture a snapshot of water and sediment quality to meet the objectives of this study, a one-off round of sampling was undertaken by qualified staff. Site access, staff induction and sampling logistics were undertaken in close consultation with mine operators, assuring compliance with Work Health & Safety requirements at each sampling location. Although outside the preliminary screening purpose of this study, it is important to note that water, sediment quality in the discharge dams may vary over time, and temporal variability was not accounted for by this study.

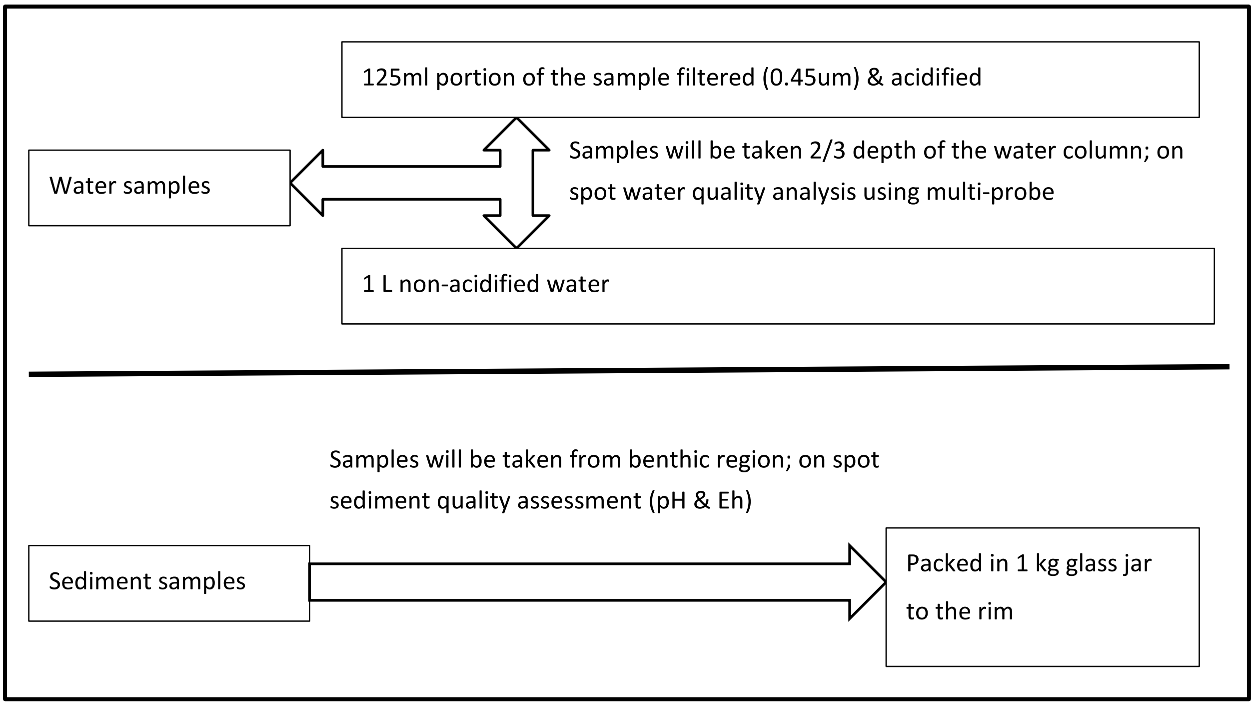

Figure.2. Schematic of the sampling approach

A total of 17 locations were sampled over a 10 day fieldwork campaign. Duplicate samples of water were collected at 2/3 the water-depth using sterile containers. This is a standard approach for normalizing the potential effects of stratified water chemistry. Samples were immediately filtered through a 0.45-micron filter paper to remove particulates, chilled and delivered to the laboratory to minimise sample degradation. Unstable sediment parameters (e.g.; pH, temperature, dissolved oxygen, redox and turbidity) were recorded in the field.

A composite sample from the upper 10cm layer of benthic sediment was collected using a van Veen grab sampler or push-corer. Chemical parameters were measured by Environmental Analysis Laboratory (EAL), a NATA (National Association of Testing Authorities) accredited laboratory (Lab. Acc. No. 14960).

3.2.WATER QUALITY ANALYSIS

For this investigation, water samples were tested for a comprehensive array of parameters. These parameters provide sufficient information to assess water geochemistry and quality.

Table.2. Water quality parameters included in this study

Parameters	**Target compounds**
General water quality parameters	pH Conductivity Total Suspended Solids (TSS) Biochemical Oxygen Demand (BOD) Total Nitrogen (TN) Total Phosphorus (TP) Alkalinity (Bicarbonate) Carbon-Dissolved Organic (DOC)
Heavy metals	Copper, Lead, Cadmium, Zinc, Arsenic, Selenium, Iron, Manganese, Silver, Chromium, Nickel, Aluminium, Mercury, Sodium, Potassium, Calcium, Magnesium, Chloride, Sulfur, Phosphorus, Boron, Barium, Cobalt, Molybdenum, Vanadium, Bromide and Silicon
Heavy metal speciation	Chromium VI – Hexavalent Total Arsenic, Arsenic(V) & (III)
Nutrients	Nitrate, Nitrite, Phosphate, Ammonium

3.3. BENTHIC SEDIMENT QUALITY ANALYSIS

Benthic sediment samples were analysed to understand the accumulation and potential for mobilisation of metals to the Hunter River (Table 3).

Table.3. Sediment quality parameters focused in this study

Parameters	**Target Compounds**
General sediment quality analysis	pH and EC(1:5) Basic colour and texture
Nutrients	Total Carbon (TC), Total Nitrogen (TN), Organic Matter, TC/TN Ratio
Available Nutrients	Calcium, Magnesium, Potassium, Ammonium, Nitrate, Phosphate, Sulfur
Exchangeable Nutrients	Sodium, Potassium, Calcium, Magnesium, Hydrogen, Aluminium, Cation Exchange Capacity
Available Micronutrients	Zinc, Manganese, Iron, Copper, Boron, Silicon
Heavy metals	Silver, Arsenic, Lead, Chromium, Nickel, Cadmium, Mercury
Total elemental analysis	Sodium, Potassium, Calcium, Magnesium, Sulfur, Phosphorus, Silicon, Cobalt, Molybdenum, Selenium, Zinc, Manganese, Iron, Copper, Boron and Aluminium

4. GUIDELINES AND TRIGGER VALUES FOR DATA INTERPRETATION

4.1. WATER QUALITY GUIDELINES

Water quality guidelines provide numerical concentration limits, or narrative statements, recommended to support and maintain a designated water use (i.e. drinking water, irrigation, stock and domestic water, environmental and ecological). The Australian and New Zealand Environment Conservation Council (ANZECC) published the revised *Australian and New Zealand guidelines for fresh and marine water quality* in 2000, which are available at www.deh.gov.au/water/quality/nwqms. The ANZECC guidelines provide the government and community – particularly regulators, industry, consultants, community groups and catchment and water managers – with a framework for assessing water with a purpose of conserving ambient water quality in rivers, lakes, estuaries and marine waters.

Water quality parameters can be divided into those with potential direct toxic effects on organisms and animals (e.g. insecticides, herbicides, heavy metals and temperature) and those which may indirectly affect ecosystems and impact specified environmental values (e.g. nutrients, turbidity and enrichment with organic matter). Whether the effects are direct or indirect, they can have important implications for management options, and for how a guideline 'trigger' value might be set.

Exceedance of the guidelines indicates that there is potential for an impact to occur (or to have occurred), but does not provide any certainty that an impact will occur (or has occurred). It is important to understand that guidelines and thresholds act only to identify potential issues, and generally identify the need for more detailed studies to quantify risk for impacts that incorporate site specific moderating factors, such as spatial scale, sensitivity of the environment and compounding effects of multiple environmental stressors.

The ANZECC guidelines offer three levels of protection, each tied to ecosystem condition. Level 2 "*slightly to moderately disturbed ecosystems'* and Level 3 "*highly disturbed ecosystems"* are appropriate for waterways within the HRSTS. For highly disturbed ecosystems that cannot feasibly be returned to a slight/moderately disturbed condition, the Guidelines provide advice to assist managers to derive alternative guidelines that give lower levels of protection. The level of protection applied to most waterways in NSW rural and regional areas is “*slightly to moderately disturbed ecosystems’* (Level 2).

4.2.TRIGGER VALUES

ANZECC guidelines use ‘trigger values’ to indicate a potential water and sediment quality contamination issue (Table 4 & 5). Trigger values are set as conservative assessment values, and according to the guidelines, should not be considered as a pass/fail compliance criterion. Local environmental conditions vary naturally between waterways and it may be necessary to fine-tune trigger values (to higher or lower threshold values) to better correlate with local conditions. The guidelines provide a process for refining the trigger values and the below protocols should be followed.

Where an indicator is **below the threshold value** or **within the desirable range** for in a waterway, the risk to the protection of the environment is low (Fig.3).

Figure.3. ANZEC trigger value with a threshold

Where an indicator is **higher than the threshold value** or **outside the desirable range** for its trigger value in a waterway, there may be a risk that environmental values will not be protected. This may ‘trigger’ either:

- Immediate action to address the likely causes of the value not being met, or

– Further investigations to determine whether the trigger value is inappropriately too conservative for local conditions, or that local conditions are impacting ambient levels and toxicity of the contaminant is concerning.

4.3. RISK BASED APPROACH-ALTERNATIVE TO TRIGGER VALUES

In some cases, trigger values will not be appropriate and it will be necessary to investigate further to refine trigger values that take into account specific localised conditions (Table 5 ANZECC Guidelines). In such cases, the ANZECC guidelines advocate a ‘risk-based’ approach. This means that any investigation into the cause of a water-quality problem reflects the level of risk associated with it.

A more comprehensive assessment is required where there is a higher likelihood, or greater consequence of an issue or activity having a negative impact on environmental values. The risk will vary depending on the nature and location of a land use, whether it is being carried out in a satisfactory manner, and the sensitivity of the local waterway. The judgement of the level of risk requires case-by-case interpretation in most situations, with many activities falling somewhere in between very low and very high risk.

4.4. INTERPRETATION OF ANZECC GUIDELINES IN THE HRSTS AND UPPER HUNTER MINES

The ANZEC guidelines and associated trigger values are not directly applicable to the discharge dams used in the HRSTS. The ANZECC framework is particularly relevant for conserving ambient water quality in rivers, lakes, estuaries and marine waters. Therefore, trigger values do not translate directly to discharge dams. This study used the ANZECC framework as a screening-filter only, to identify any potential water quality issues. In addition to ANZECC trigger values, the water and sediment quality is compared against Hunter River reference sites to provide a practical interpretation.

It is important also to note that a trigger value is not applied for total arsenic under current ANZECC guidelines. Therefore, in this study a total As value was considered against the irrigation water guidance value of 0.05 mg/L.

Table 4. ANZEC (2000) trigger values for metal(loid)s in fresh water. Values in grey shading are the trigger values which apply to typical *slightly–moderately disturbed systems*.

Chemical		**Trigger values for freshwater (µg L^{-1})**			
		Level of protection (% species)			
		99%	**95%**	**90%**	**80%**
Aluminium	pH 6.5	27	55	80	150
Aluminium	pH<6.5	ID	ID	ID	ID
Antimony		ID	ID	ID	ID
Arsenic (As III)		1	24	94 [C]	360 [C]
Arsenic (As V)		0.8	13	42	140 [C]
Beryllium		ID	ID	ID	ID
Bismuth		ID	ID	ID	ID
Boron		90	370 [C]	680 [C]	1300 [C]
Cadmium	H	0.06	0.2	0.4	0.8 [C]
Chromium (Cr III)	H	ID	ID	ID	ID
Chromium (Cr VI)		0.01	1.0 [C]	6 [A]	40 [A]
Cobalt		ID	ID	ID	ID
Copper	H	1.0	1.4	1.8 [C]	2.5 [C]
Gallium		ID	ID	ID	ID
Iron		ID	ID	ID	ID
Lanthanum		ID	ID	ID	ID
Lead	H	1.0	3.4	5.6	9.4 [C]
Manganese		1200	1900 [C]	2500 [C]	3600 [C]
Mercury (inorganic)	B	0.06	0.6	1.9 [C]	5.4 [A]
Mercury (methyl)		ID	ID	ID	ID
Molybdenum		ID	ID	ID	ID
Nickel	H	8	11	13	17 [C]
Selenium (Total)	B	5	11	18	34
Selenium (SeIV)	B	ID	ID	ID	ID
Silver		0.02	0.05	0.1	0.2 [C]
Thallium		ID	ID	ID	ID
Tin (inorganic, SnIV)		ID	ID	ID	ID
Tributyltin (as □g/L Sn)		ID	ID	ID	ID
Uranium		ID	ID	ID	ID
Vanadium		ID	ID	ID	ID
Zinc	H	2.4	8.0 [C]	15 [C]	31 [C]

Note: A=Acute toxicity; B = Chemicals for which possible bioaccumulation and secondary poisoning effects should be considered; C= Chronic toxicity; H = these metals should be adjusted to the site-specific hardness;

Table 5. ANZEC (2000) recommended sediment quality guidelines for metal(loid)s

Contaminant	ISQG-Low (Trigger value)	ISQG-High
METALS (mg/kg dry wt)		
Antimony	2	25
Cadmium	1.5	10
Chromium	80	370
Copper	65	270
Lead	50	220
Mercury	0.15	1
Nickel	21	52
Silver	1	3.7
Zinc	200	410
METALLOIDS (mg/kg dry wt)		
Arsenic	20	70

5. RESULTS AND DISCUSSION

5.1. BASIC WATER QUALITY PARAMETERS

Water quality data for the discharge dams is presented in Table.6. The pH is slightly alkaline, ranging from 8.5 - 9. Electrical conductivity (EC), the common measure for salinity, was elevated as expected, reaching a maximum of 9.45 ds/m in Dam 9S at the Mount Thorley Warkworth (MTW) mine site. Generally, the salinity, as measured by EC, is above the freshwater salinity range. The concentration of inorganic salts which include calcium, bicarbonate, nitrogen, phosphorus, iron and sulfur, follow the EC trend of the storage dams.

The pH of the Hunter River reference sites was also slightly alkaline (Table.7), with pH increasing progressively downstream, from (pH 8.03) at the upper extent of Dart Brook, to pH 8.63 at Singleton. EC of the reference samples were < 2 dS/m. Overall, the reference sites are within the prescribed range in the ANZECC lowland river guidelines (pH 6.5-9.0).

Nutrient concentrations varied widely among storage dams. The total nitrogen and nitrate-nitrogen were elevated in the mine site discharge dams. The trend for ammonia-nitrogen differed to TN and NO_3, suggesting that most of the ammonia-nitrogen has come from oxidized nitrates. Total phosphorus concentrations in the discharge dams was low and similar to the concentrations observed at the Hunter River reference sites.

Nitrogen chemistry in natural settings is complex, with numerous chemical and biological reaction paths and compounds involved with the cycling of this essential nutrient. In the Australian context, rivers and other waterways tend to be naturally nitrogen-poor. Interestingly, nutrient concentrations at Lake Liddell, which receives water from the Hunter River, also has low nitrogen contents. There are several possible sources of nitrogen at mine sites that include:

- Geological nitrogen released during the blasting and excavation process;
- Pit water and the use of ammonium-nitrate explosives;
- Various disposal facilities, such as pollution control dams, rock dumps, tailings dams, etc.; and
- Different industrial nitrogen-containing chemicals used in minerals processing,

including nitric acid (HNO_3), ammonium-chloride (NH_4Cl) and ammonium hydroxide (NH_4OH).

Elevated nitrogen concentration in mine water has been reported internationally and attributed to land rehabilitation, erosion and atmospheric deposition of nitrogen compounds from blasting exercise [1, 10]. Nitrogen can disturb water quality, although the concentrations of nitrogen that will transfer to the Hunter River under the managed release of saline waters with the HRSTS, will immediately dissipate to well-below ANZECC trigger values, when considering the small volume of water being discharged and the times of high flow within the Hunter River. Further studies would be helpful in identifying the sources of nitrogen in the HRSTS storage dams and how management may minimize this potential issue.

Table.6. General water quality parameters and nutrients in the discharge water storage dams

Parameters	**Bengalla**	**Lake Liddell**	**Reservoir North**	**RVS**	**Parnel's Dam HVO**	**Dam 11 HVO**	**Lake James HVO**	**Dam 1N MTW**	**Dam 9S MTW**	**CHPP (Surge)**	**ND 2**
pH	8.51	8.49	8.66	8.76	8.63	8.62	8.94	8.58	8.87	8.89	8.77
Conductivity (EC) (dS/m)	2.150	2.728	6.355	7.972	5.674	6.269	7.318	6.260	9.453	5.230	3.737
Total Dissolved Salts (mg/L)	1,462	1,855	4,321	5,421	3,858	4,263	4,976	4,257	6,428	3,556	2,541
Total Suspended Solids (mg/L)	40	3	11	6	4	9	9	44	14	34	13
Alkalinity (mg/L $CaCO_3$ equivalent)	380	130	780	680	340	500	800	1,040	1,340	560	560
Calcium (mg/L)	30.8	131.6	51.7	74.7	46.6	42.6	18.5	27.8	16.2	21.0	30.3
Magnesium (mg/L)	23.0	89.6	73.1	119.6	147.5	156.4	98.9	47.2	29.5	31.2	35.8
Potassium (mg/L)	4.6	15.9	10.4	17.8	21.1	31.1	33.2	15.5	29.0	14.1	12.9
Sodium (mg/L)	424	301	1,338	1,579	994	1,133	1,581	1,381	2,405	1,063	768
Chloride (mg/L)	199	300	744	911	734	792	929	873	1,178	675	438
Sulfur (mg/L)	73	206	276	501	326	342	283	79	385	178	129
Bromide (mg/L)	0.6	1.0	2.3	2.6	2.1	2.0	2.3	2.2	2.2	1.3	0.9
Dissolved Organic Carbon (mg/L)	6.7	7.4	6.7	5.2	7.2	4.6	6.3	3.4	4.3	9.8	14.8
Total Phosphorous (mg/L P)	0.14	0.02	0.03	0.02	0.01	0.02	0.03	0.06	0.02	0.07	0.03
Total Nitrogen (mg/L N)	4.34	0.56	4.55	13.10	1.57	4.36	1.55	1.78	3.65	4.40	1.10
Nitrate (mg/L N)	3.020	0.009	2.900	11.200	0.837	3.270	0.447	0.781	1.910	3.620	0.133
Ammonia (mg/L N)	0.183	0.042	0.444	0.044	0.186	0.031	0.348	0.557	0.454	0.028	0.041

Table.7. Selected basic water quality parameters and major ions in the Hunter River reference sites

Parameters	Hunter R@Dartbrook	Hunter R@Keys Bridge	Hunter R@Denman	Hunter R@Jerrys Plain	Hunter R *u/s* Glennies Creek	Hunter R@Singleton
pH	8.30	8.03	8.33	8.23	8.28	8.68
Conductivity (EC) (dS/m)	0.382	0.520	1.202	1.307	1.322	1.100
Total Dissolved Salts (mg/L)	260	354	817	889	899	748
Total Suspended Solids (mg/L)	2	9	10	19	14	4
Alkalinity (mg/L $CaCO_3$ equivalent)	130	150	210	240	230	160
Calcium (mg/L)	30.1	34.2	55.5	64.4	55.2	49.5
Magnesium (mg/L)	16.9	19.3	46.0	54.7	45.2	41.3
Potassium (mg/L)	1.5	1.4	3.2	3.6	2.7	3.0
Sodium (mg/L)	23	30	95	109	93	91
Chloride (mg/L)	9	21	141	170	127	141
Sulfur (mg/L)	6	7	13	16	13	13
Bromide (mg/L)	0.1	0.1	0.5	0.6	0.6	0.5
Dissolved Organic Carbon (mg/L)	3.6	4.2	4.4	3.6	3.6	4.3
Total Phosphorous (mg/L P)	0.01	0.03	0.07	0.07	0.07	0.03
Total Nitrogen (mg/L N)	0.19	0.48	0.39	0.35	0.30	0.34
Nitrate (mg/L N)	0.009	0.204	0.115	0.016	0.005	0.007
Ammonia (mg/L N)	0.030	0.033	0.056	0.057	0.039	0.042

5.1. METALS AND METALLOIDS IN THE WATER SAMPLES

The metals and metalloids in water samples are presented in Table 8. Most metals are well below ANZECC guideline trigger values. Water hardness is an important 'modifying factor' in the ANZECC guideline when setting the appropriate trigger values for metal contaminants. The applied trigger values for nickel and zinc adjusted for water hardness as per ANZEC guidelines applies a multiplier of 9.0. After adjustments, the total Zn concentrations exceeded trigger values in Dam 1N, Dam 9S and CHPP (surge) (Fig.6). Nickel in the Hunter River reference sites was also highly variable.

Total arsenic concentrations in the discharge dams was well below the irrigation water guideline trigger values. However, speciation analysis found that arsenate (As V) was approximately double the trigger level in the Mount Thorley Warkworth samples (Dam 1 N and Dam 9S) (Fig. 7 & 8). The presence of low concentrations of arsenic in ground water is not uncommon. Small amounts of arsenic have been reported in rocks, soils and sediments and arsenic can be detected at low concentrations in most natural waters – rainwater, rivers, lakes, groundwater and seawater [14]. Occasionally arsenic is present in much higher concentrations, which can be concerning when the water is used for drinking and the irrigation of crops.

The Mount Thorley Warkworth mines are located in the Permian coal seams (Permian Tomago) (Fig.4). The predominant As-hosting minerals in this geology are iron oxyhydroxides and As-bearing sulfides. In general, the lowering of groundwater, or excavation, is known to result in the oxidation of As-bearing minerals and the formation of iron oxides.

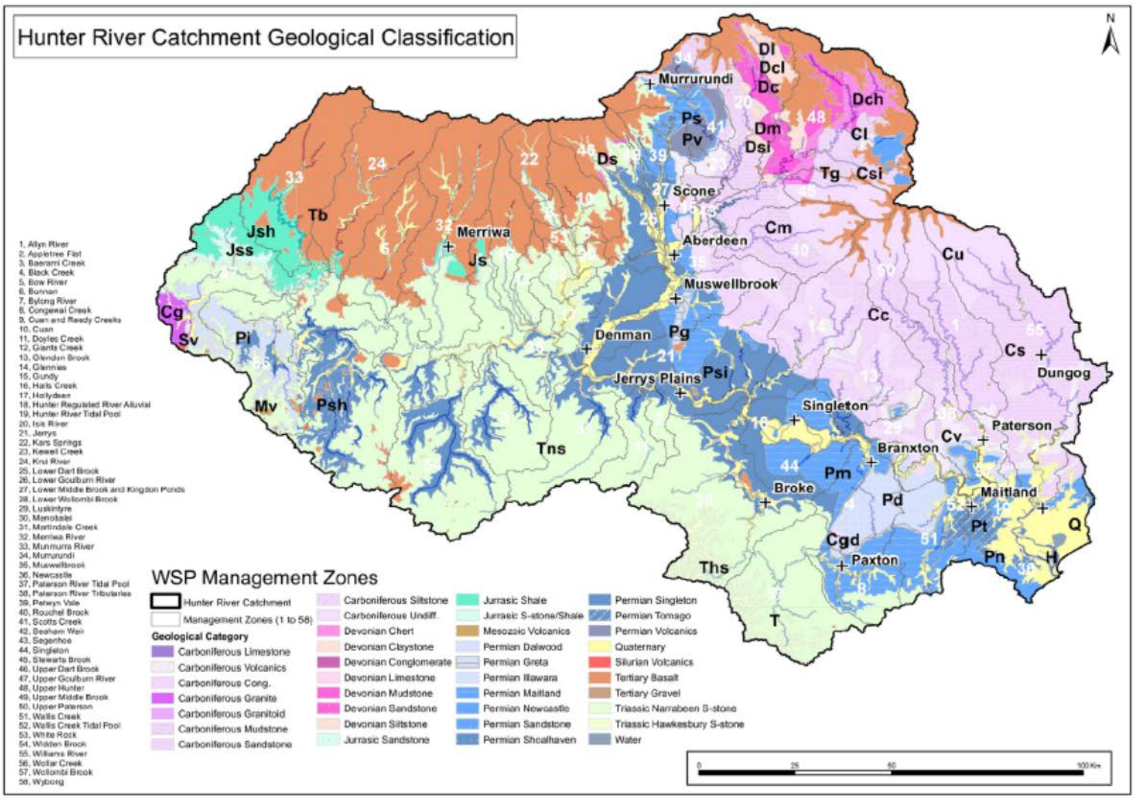

Figure.4. Hunter River Catchment geological classifications (Kellet et al. 1989)

Periodic fluctuations in groundwater, and /or progressive weathering of minerals and soil, can lead to the mobilization of arsenic to groundwater and surface water.

The environmental and health consequences of arsenic have been the focus of many studies [11]. A compounding factor is the effect of saline water, with its high ionic concentrations, such as Na^+, K^+, Mg^{2+}, HCO_3^- , Cl^-, and SO_4^2. The influence of saline conditions, such as those found in the Hunter Valley, on the fate and effects of arsenic have not been fully resolved.

Table.8. The dissolved metals and metalloids in the water samples (mg/L)

Sites/Parameters	Al	As[a]	As III	As V	Cu	Ni[b]	Pb[b]	Se	Zn[b]
Trigger Values	*0.055*	0.05	0.024	0.013	*0.0014*	*0.099*	*0.091*	*0.011*	*0.072*
Discharge water storage dams									
Bengalla	0.012	0.016	0.0002	0.0020	0.003	0.001	0.001	0.009	0.005
Lake Liddell	0.003	0.005	0.0004	0.0010	0.004	0.004	0.001	0.003	0.003
Liddell R	0.010	0.007	0.0002	0.0050	0.001	0.002	0.001	0.014	0.006
RVS	0.010	0.001	0.0002	0.0013	0.007	0.008	0.001	0.013	0.013
Parnel's Dam	0.013	0.002	0.0002	0.0010	0.001	0.006	0.001	0.005	0.005
Dam 11	0.013	0.005	0.0004	0.0010	0.001	0.009	0.001	0.008	0.018
Lake James	0.020	0.010	0.0002	0.0066	0.001	0.008	0.001	0.004	0.008
Dam 1N MTW	0.008	0.025	0.0002	0.0224	0.004	0.002	0.001	0.003	0.116
Dam 9S MTW	0.007	0.029	0.0002	0.0276	0.003	0.005	0.001	0.007	0.040
CHPP (Surge)	0.054	0.008	0.0002	0.0074	0.014	0.020	0.001	0.012	0.074
ND 2	0.019	0.001	0.0002	0.0004	0.002	0.003	0.001	0.002	0.004
Hunter River reference sites									
Hunter R@ Dartbrook	0.008	0.001	0.0002	0.0002	0.001	0.001	0.001	0.001	0.003
Hunter R@ Keys Bridge	0.003	0.001	<0.0002	0.0002	0.001	0.001	0.001	0.001	0.003
Hunter R@ Denman	0.003	0.001	0.0002	0.0002	0.001	0.001	0.001	0.001	0.019
Hunter R@ Jerrys Plain	0.004	0.001	0.0002	0.0002	0.001	0.001	0.001	0.001	0.018
Hunter R *u/s* Glennies Creek	0.023	0.001	0.0002	0.0002	0.001	0.001	0.001	0.001	0.320
Hunter R@ Singleton	0.005	0.001	0.0002	0.0002	0.002	0.001	0.001	0.001	0.003

Note: [a]There are no trigger values for total arsenic, therefore the irrigation water guidance value is considered for comparison (0.05mg/L); [b]Hardness adjusted trigger values as per ANZEC guidelines Table 3.4.3 (Ni and Zn conc x 9; Pb conc x 26.7).

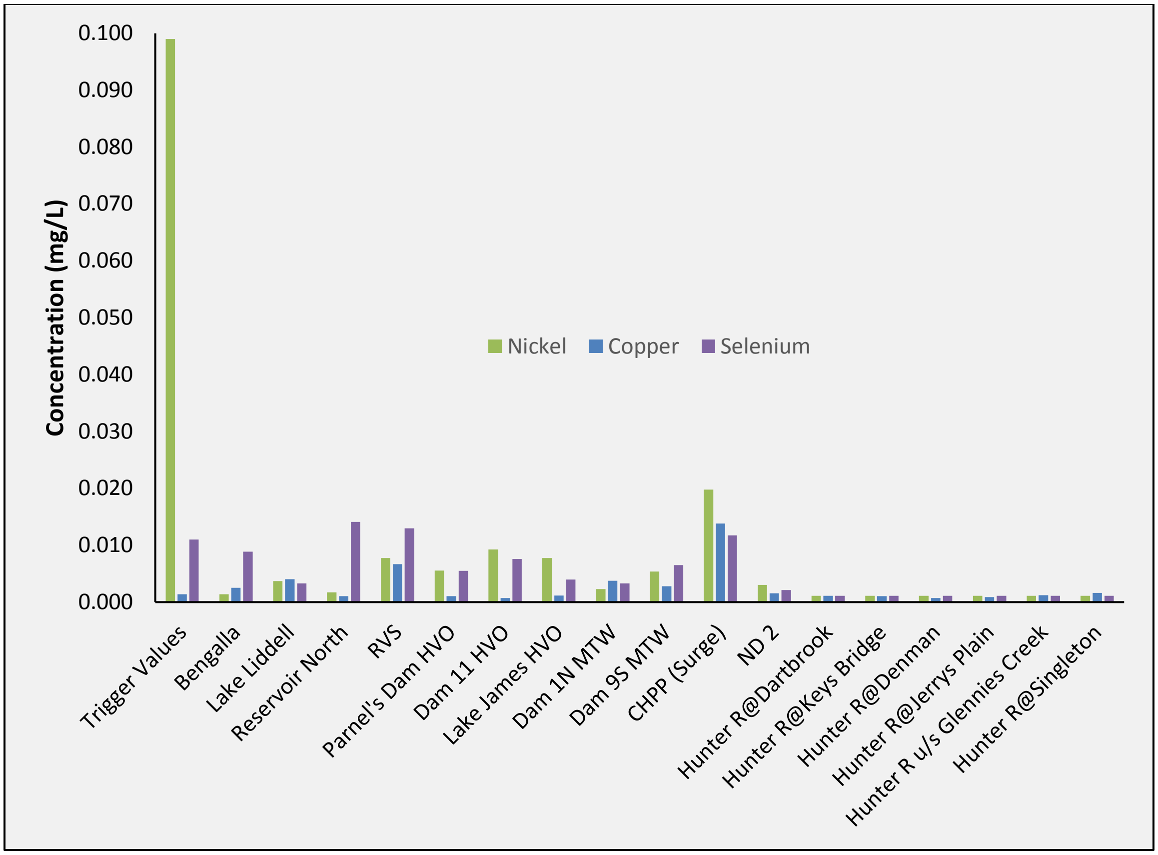

Figure.5. Total concentrations nickel, copper and selenium in water samples (mg/L)

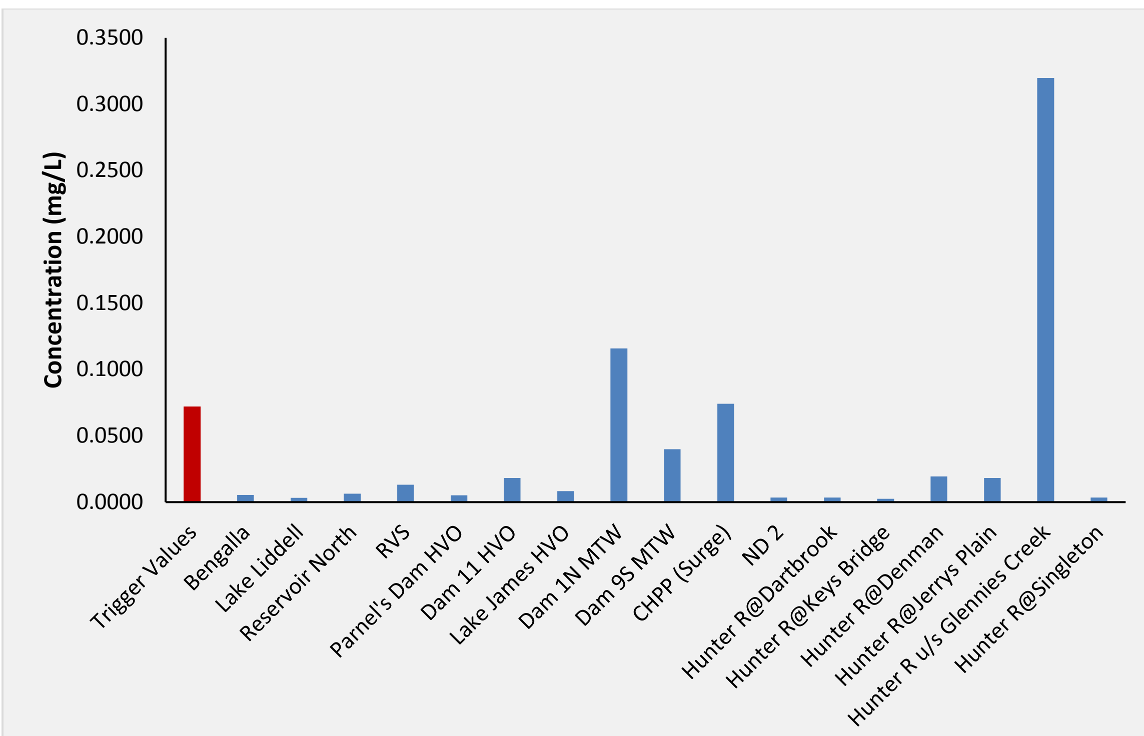

Figure.6. Total zinc in water samples (mg/L)

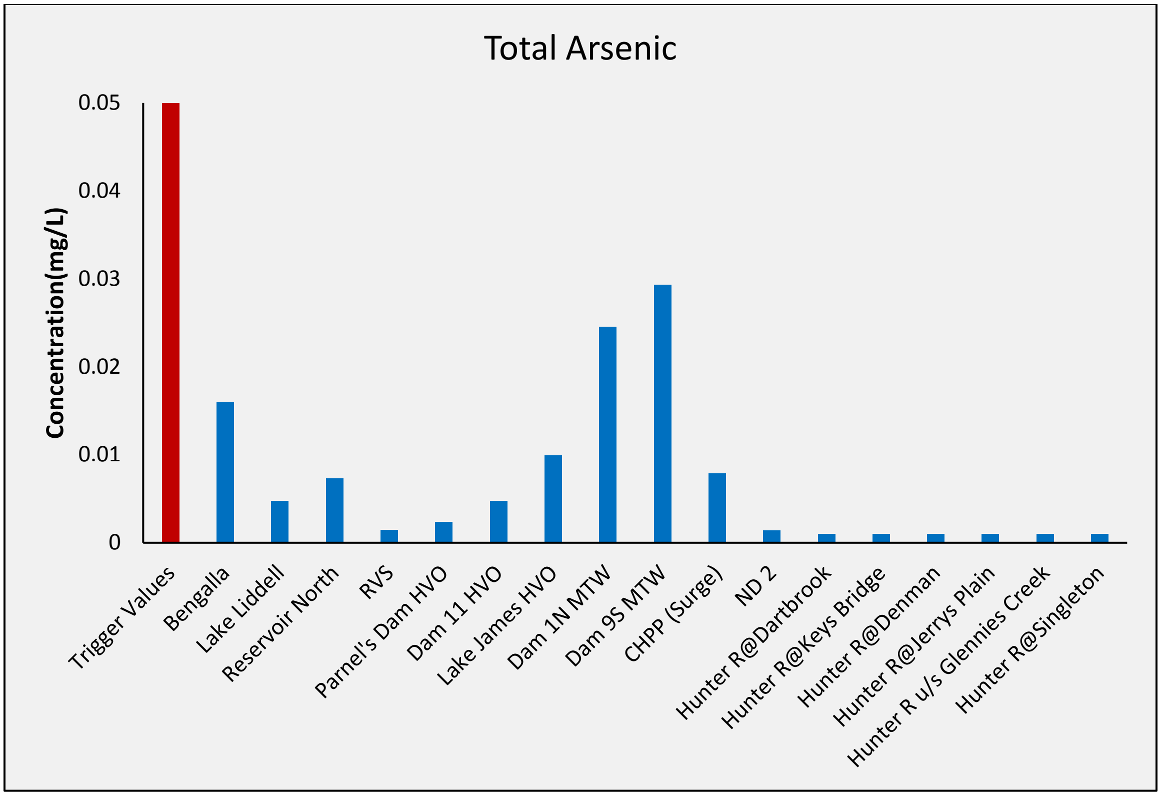

Figure.7. Total arsenic in the water samples (mg/L)

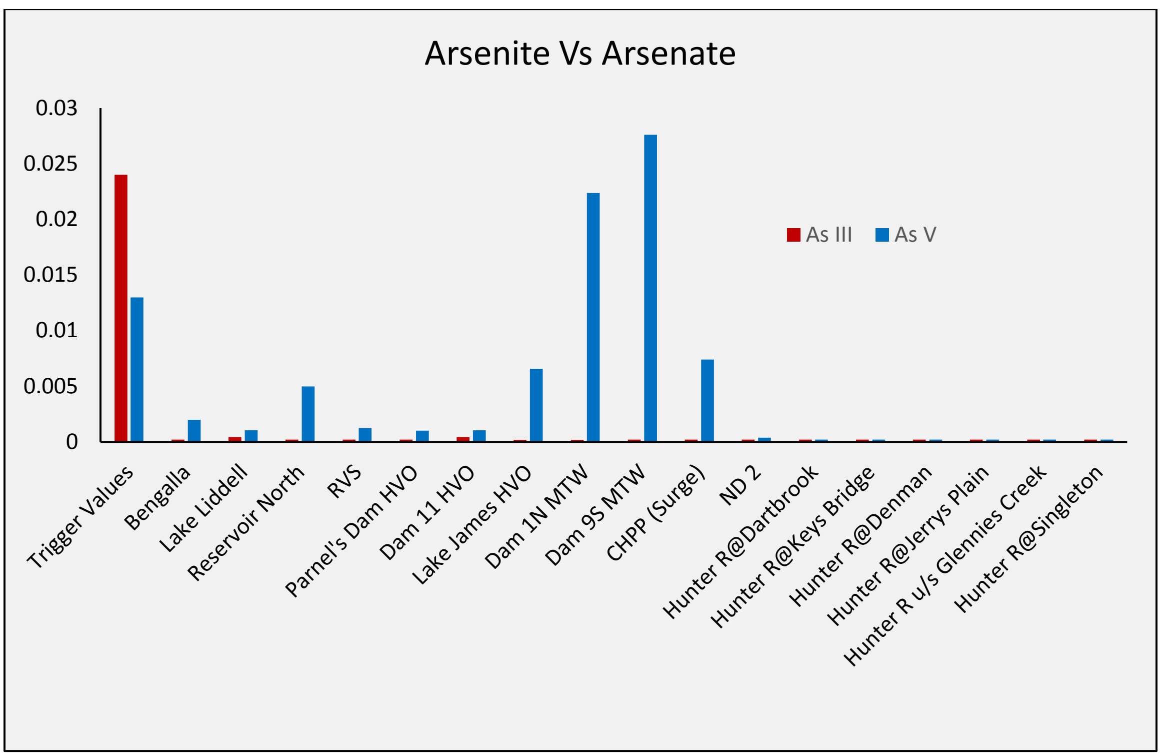

Figure.8. Speciation of arsenic in the water samples (mg/L)

5.2.SEDIMENT PARAMETERS

The physio-chemical parameters of sediments are presented in Table 9. The sediment pH within discharge dams was greater than pH 9, with the exception of Lake Liddell and ND2. This was consistently slightly higher than observed at the Hunter River reference sites, where sediment pH ranged from 8.09 to 8.93. The sediment EC in the discharge dams was comparatively low, ranging from 0.044 to 1.96 (dS/m), which logically demonstrates that high salinity in the overlying water held within the discharge dams is not originating from the dam sediments. For the Hunter River reference sites, salinity and pH increased in the downstream trajectory toward Singleton.

Table 9. General parameters of sampled sediments

Sites	pH	Electrical Conductivity (dS/m)	Calcium	Magnesium	Potassium	Sodium	Sulfur
Discharge water storage dams							
Bengalla	9.05	0.448	13,783	4,265	1,440	1,114	341
Lake Liddell	8.30	1.036	149886	5,370	1,063	980	7,989
Reservoir North	9.14	1.964	15,003	4,223	1,854	3,504	6,759
RVS	9.42	1.586	21,999	3,812	1,393	2,883	1,098
Parnel's Dam HVO	9.19	1.184	3,286	3,587	1,994	1,657	918
Dam 11 HVO	9.51	0.855	12,515	4,915	1,758	1,774	331
Lake James HVO	9.06	1.164	8,851	3,777	1,363	2,082	1,729
Dam 1N MTW	9.80	1.406	26,224	3,962	1,847	3,679	2,214
Dam 9S MTW	9.84	0.860	23,649	8,362	1,035	2,040	427
CHPP (Surge)	9.60	1.009	15,263	4,381	2,276	3,180	359
ND 2	8.36	0.976	21,555	2,180	1,395	1,758	2,631
Hunter River reference sites							
Hunter R@ Dartbrook	8.30	0.083	5,427	6,171	976	530	254
Hunter R@ Keys Bridge	8.09	0.198	6,163	6,073	1,143	648	470
Hunter R@ Denman	8.93	0.094	2,378	1,820	480	361	55
Hunter R@ Jerrys Plain	8.60	0.122	2,209	1,709	449	236	112
Hunter R *u/s* Glennies Creek	8.45	0.200	4,415	3,183	706	488	280
Hunter R@ Singleton	8.78	0.091	1,819	1,339	415	166	145

5.3.HEAVY METALS AND METALLOIDS IN SEDIMENT SAMPLES.

The heavy metal concentration of the sediment samples is given in Table 10. Except for total arsenic (As), zinc (Zn), nickel (Ni), lead (Pb), chromium (Cr) and copper (Cu), all other metals were below the analytical detection limit. The concentrations of As, Zn, Pb, Cr and Cu were below the '*Interim Sediment Quality Guidelines (ISQG) - low trigger values*'. Total Ni concentrations were within the trigger value range for most sites, with low value exceedances at the Bengalla discharge dam, Dam1N and CHPP (surge) samples, and the Hunter River reference samples collected from Dartbrook and Keys Bridge. Local conditions vary naturally between waterways and it is necessary to calibrate trigger values to local conditions and/or, develop 'local guideline levels', for these criteria to act as useful benchmarks for water quality (DEC,2006). In this study, the elevated Ni concentrations within the Hunter River reference sites highlight the relatively high regional baseline for this element.

Table 10. Total concentrations of heavy metals and metalloids in sediment samples (mg/kg)

Metals	**Arsenic**	**Zinc**	**Nickel**	**Lead**	**Chromium**	**Copper**
ISQG Low (Trigger Value)	20	200	21	50	80	65
ISQG-High	70	410	52	220	370	270
Discharge water storage dams						
Bengalla	12	54	31	13	27	17.9
Lake Liddell	12	53	17	7.7	12	52.2
Reservoir North	8.2	75	15	13	10	24.2
RVS	10	66	20	11	8.5	20.6
Parnel's Dam HVO	6.1	78	15	14	5.2	28.2
Dam 11 HVO	10	31	29	19	27	10.7
Lake James HVO	7.5	50	17	11	14	13.5
Dam 1N MTW	6.8	71	23	15	5.7	22.1
Dam 9S MTW	6.3	63	12	11	6.2	17.9
CHPP (Surge)	10	66	25	17	18	19.3
ND 2	6.3	55	20	12	7.5	9.8
Hunter River reference sites						
Hunter R@ Dartbrook	3.5	56	28	4.2	20	17.2
Hunter R@ Keys Bridge	3.5	68	31	6.9	24	20.5
Hunter R@ Denman	2	19	16	2.3	12	6.7
Hunter R@ Jerrys Plain	2	16	12	2.2	11	5.8
Hunter R *u/s* Glennies Creek	2.0	27	23	3.0	17	10.8
Hunter R@ Singleton	2	61	8.3	5.9	7.2	5.0

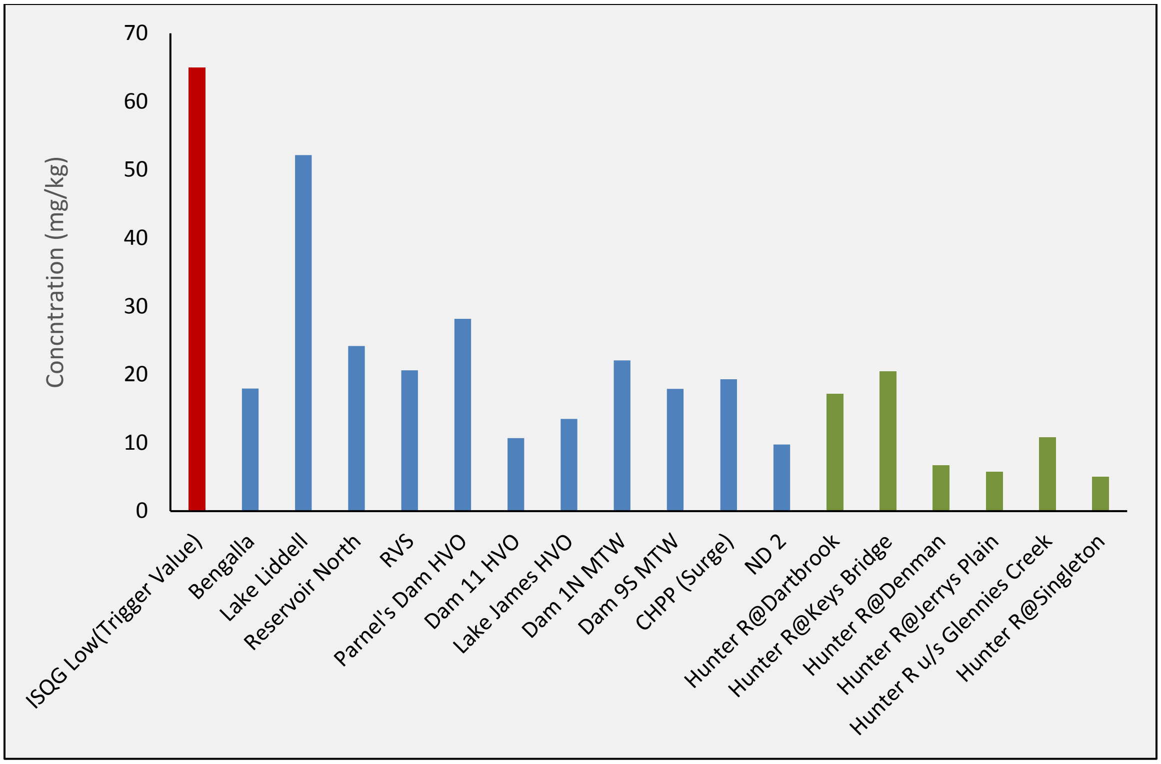

Figure.9. Total copper (Cu) in the sediments samples (mg/kg)

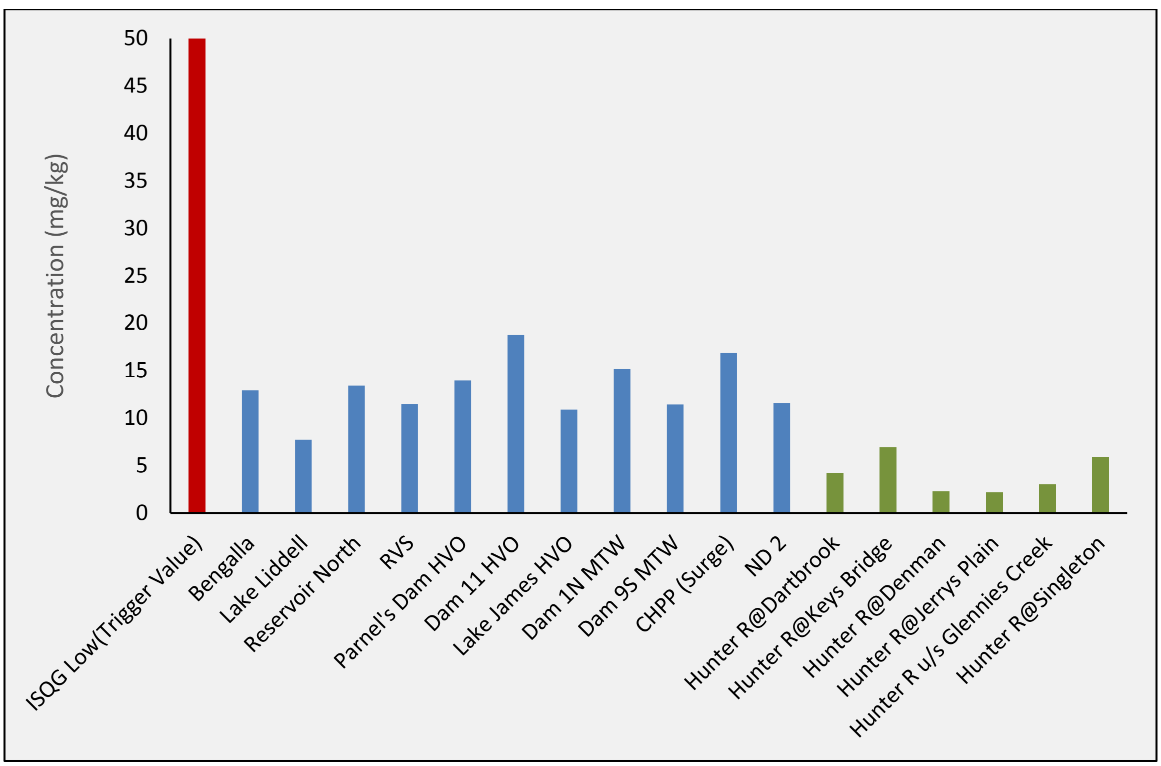

Figure.10. Total lead (Pb) in the sediment samples (mg/kg)

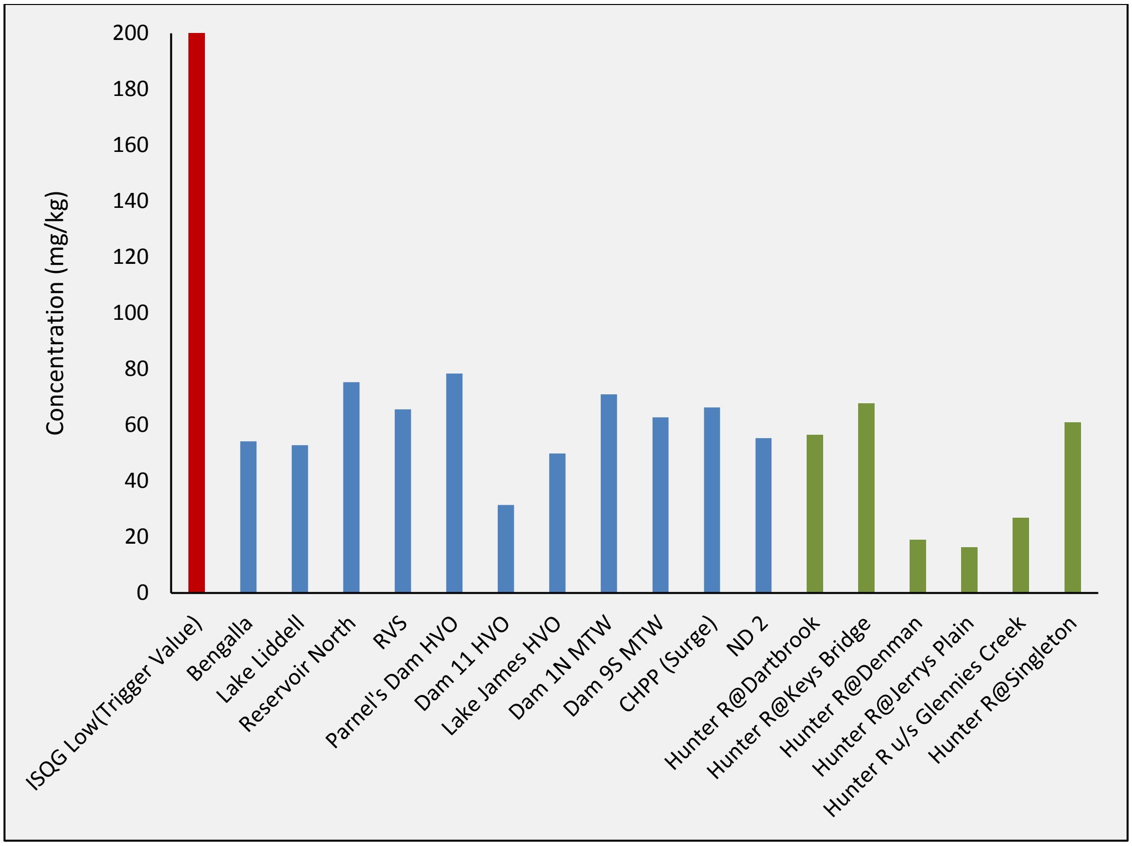

Figure.11. Total zinc (Zn) in the sediment samples (mg/kg)

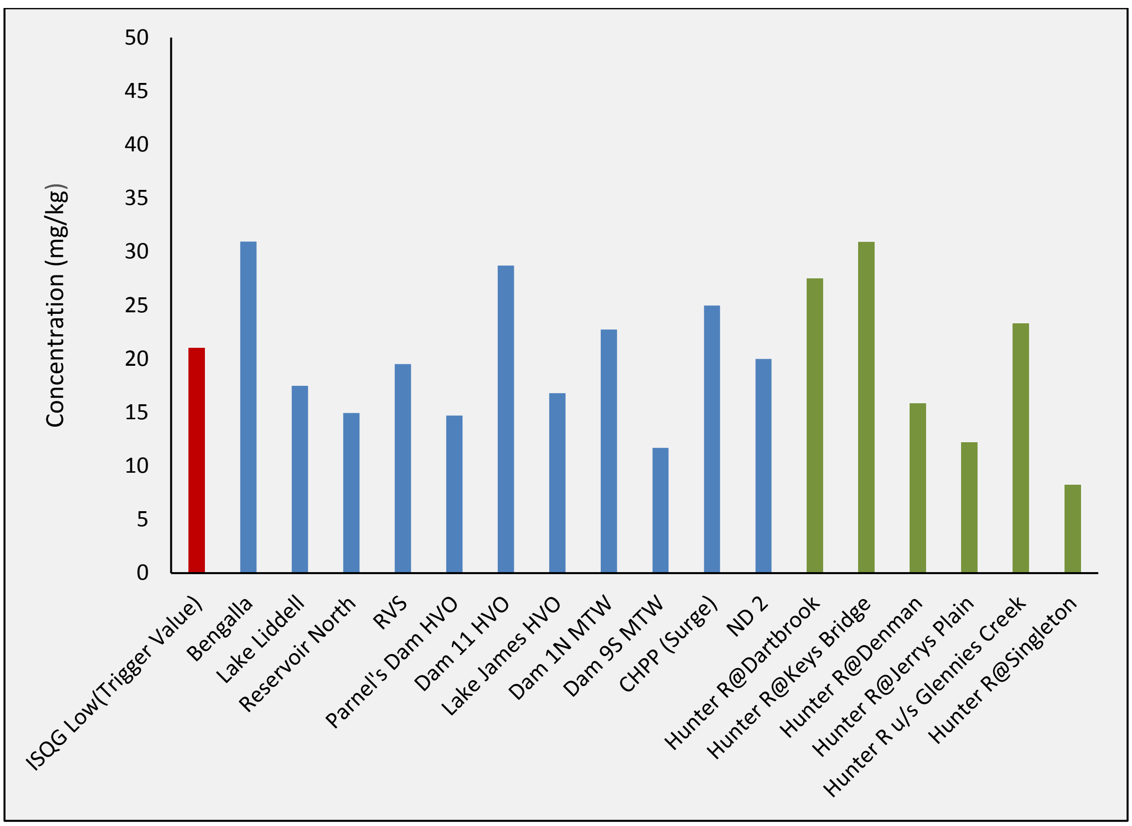

Figure. 12. Total nickel (Ni) in the sediment samples (mg/kg)

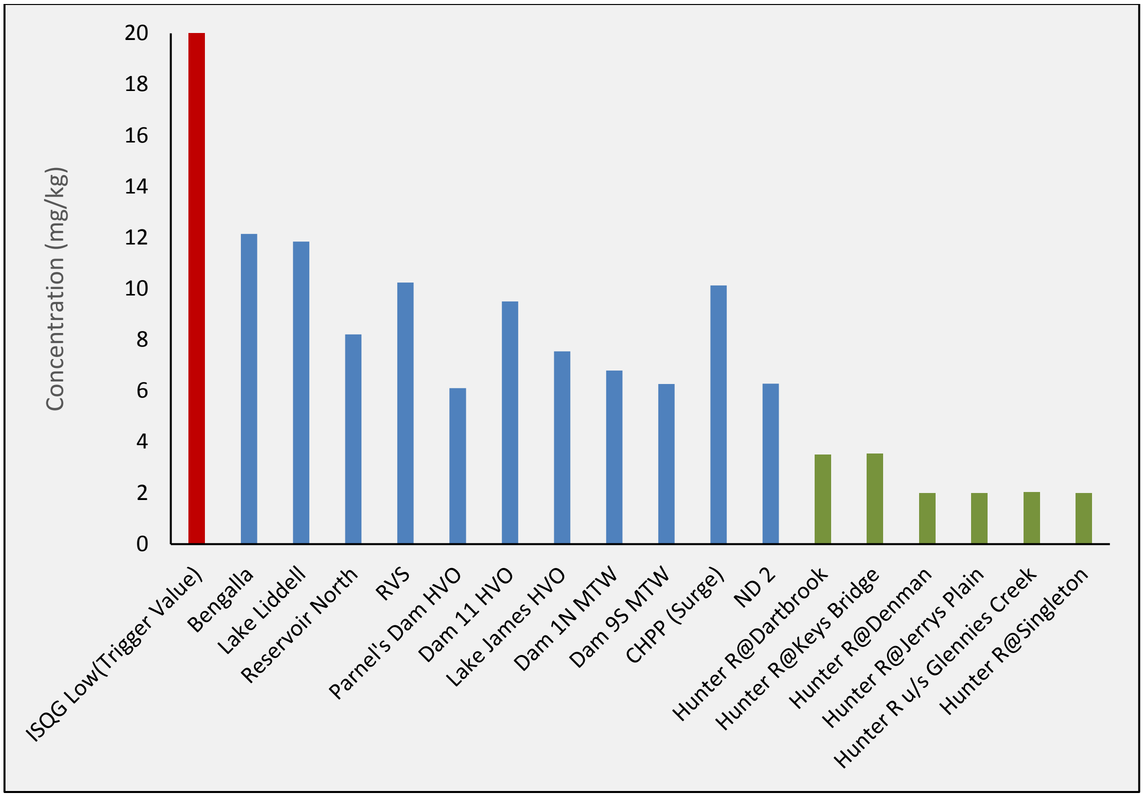

Figure 13. Total arsenic (As) in the sediment samples (mg/kg)

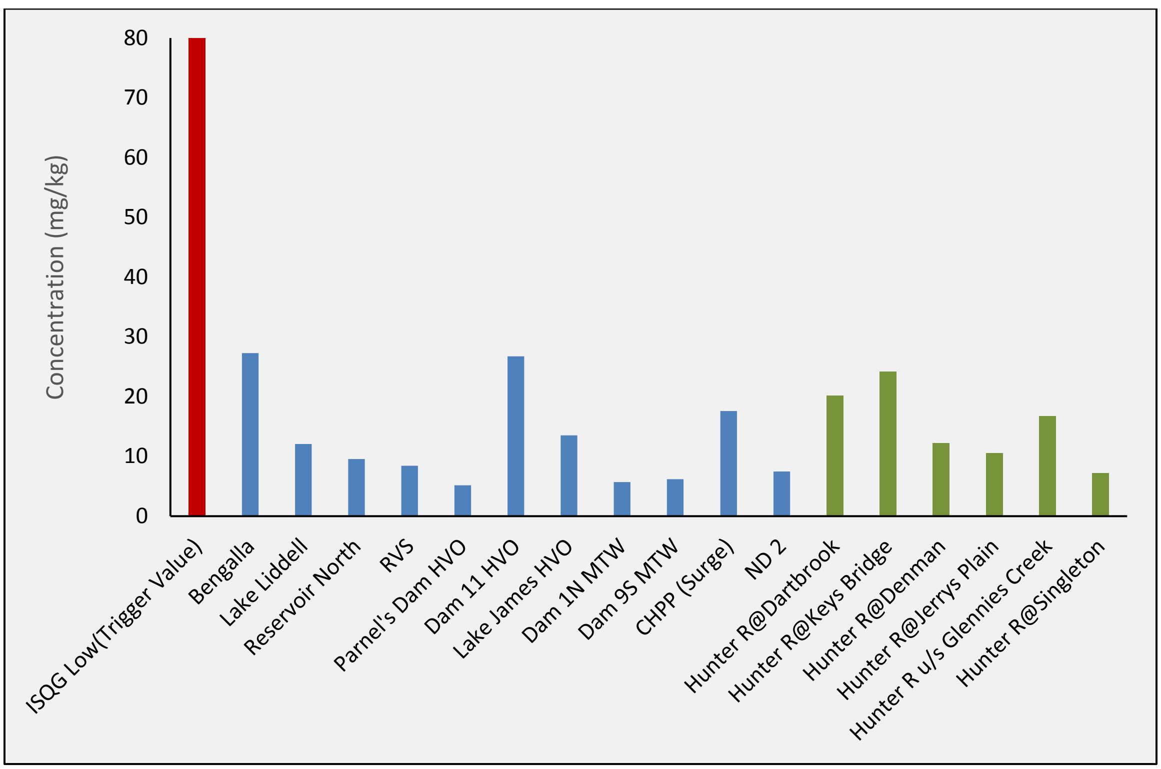

Figure14. Total chromium (Cr) in the sediment samples (mg/kg)

5.4. THE SALINITY DILUTION FACTOR AND ITS IMPLICATIONS FOR METAL(LOID)S

The HRSTS was implemented to manage the discharge of saline water from mine sites and power generators to the Hunter River (Dec 2006). The central aim of this scheme is to cap (i.e limit), the maximum salinity, measured by electrical conductivity (EC), to an acceptable level. The mechanism is though controlled discharge that balances high flow conditions in the Hunter River with saline water discharge from mining and power generation operators. Through careful control (seen in Fig. 15), the mixture of river and discharge water can be kept fresh to meet water quality standards for other water users and the environment.

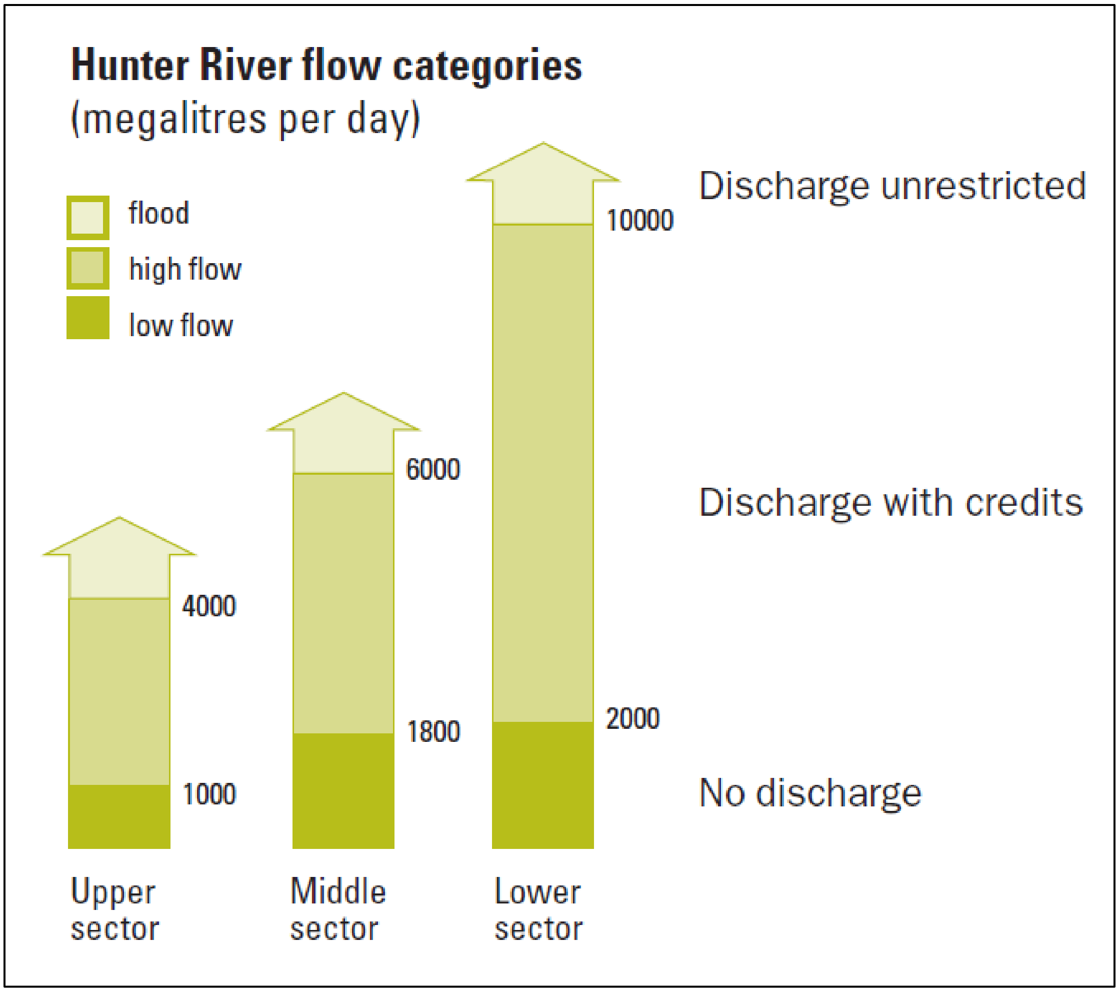

Figure 15. Hunter River flow categories (DEC, 2006)

For instance, the middle sector mine water discharge dam, Dam 9 at MTW operations last discharged ~10.45 ML. Considering the HRSTS rules, the Hunter River flow must be around 1800-6000 ML/day to be able to discharge. The 10.45 ML water discharged from Dam 9, may therefore be diluted up to 172 times, even at 1800ML - the lower end of river flow rate. Therefore the 0.027 mg/L of As (V) detected in Dam 9 would have been diluted to below detection limit and trigger value (0.15 µg/L). According to the UHMD water accounting framework (2016), during 2016, only 4 % of mine-water was discharged to Hunter River. The total flow of water in Hunter River was around 238 GL in 2016, in which 2.7 GL was discharged from the mines. There is a possibility of 100 times dilution effect of contaminants under normal discharge level. Furthermore, at times of release, pulse high flow events, the dilution effect could be even greater. Therefore, risk to downstream water users and the environment may be insignificant, as the concentration of As and other contaminants will be below threshold trigger values in the receiving environment when waters are permitted to be released under the HRSTS operations.

It is important to note that when the HRSTS scheme was initiated in 1995, salinity management was the only key water quality issue being considered. The principles of dilution as applied in the HRSTS to address the cumulative impact of salt discharge has not been fully considered with regards to applicability of this scheme for ecotoxicology and accumulative impact of other pollutants.

6. CONCLUSIONS AND RECOMMENDATION

- The pH of the discharge dam waters were alkaline and mostly above pH 9.

- The total nitrogen and nitrate-nitrogen were elevated in most of the discharge dams associated with the coal mines.

- The overall metal(loid) concentrations in discharge dams were low.

- Sampling was undertaken during a very dry period and therefore, is representative of a low-flow scenario where evaporation may enhance the concentration of soluble elements in the discharge dams.

- Few metal(loid)s exceed the ANZECC guideline trigger values for both discharge dams and Hunter River relevant reference sites. Therefore:
  - Total arsenic in water samples are below the trigger value, speciation data showed low level exceedance of Arsenate in MTW discharge dams.

  - Zn concentration was higher in MTW and CHPP (surge) samples. The highest Zn concentrations occurred in the Hunter River reference sites.

  - Metal(loid) concentrations in the sediment were below trigger values, except for Nickel. Nickel was higher in some discharge dams and the Hunter reference sites, indicative of naturally elevated concentrations in the Hunter Region.

- Under the operational protocols of the HRSTS, discharge waters will be diluted by at least a 10 - 100 x before entering the Hunter River. Therefore, any concentration of metals and nutrients will fall below trigger values based on the data in this study. The scope to consider implications to bioaccumulation, sub-threshold impacts, impacts of salts on contaminant uptake and nitrogen are not clear.

- The extremely dry seasonal conditions that have taken the Hunter Valley into drought at the time of sampling in mid-2017 and persistent evaporative loss of water from the discharge dams), are likely to have had a concentrating effect on soluble As(V), Zn, Ni and N. However, the potential effects (for increased and decreased) mobilisation and transport of salts and metals, through increased run-off and ground water (sub surface) contribution under normal to wetter rainfall conditions is difficult to predict and beyond the scope of this study to resolve.

- Based on the study findings and in accordance with the recommendations of the ANZECC guidelines and NSW Government directions, there is a basis to consider site-specific risk assessments for those locations where elevated concentrations of metal(loid)s and nutrients were identified. This may require further analyses to resolve the spatial and temporal variation, source apportionment and ecotoxicological implications of specific metals and nutrients. In addition, the comparative assessment of nitrogen in a broader range of water storages and isotopic analyses to fingerprint nitrogen sources may assist with the basic understanding and management of this aspect.

- When considering the overall water budget in the Upper Hunter, the elevated metal(loid)s and nitrogen reported in this study will exert a minimal effect on the downstream concentrations of these constituents under the HRSTS operations. Further data on the seasonal variability and identification of the source of metals and nitrogen within the mine sites and coal operations may prove useful for developing management options that seek to intervene and prevent their accumulation within the HRSTS discharge dams.

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