

WEST CLIFF MINE

ASSESSMENT OF

POTENTIAL ECOTOXICANTS

BRENNANS CREEK DAM DISCHARGE

SEPTEMBER 2012



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1. GLOSSARY

AWQC	Ambient Water Quality Criteria published by USEPA, refer: http://water.epa.gov/scitech/swguidance/standards/criteria/index.cfm
Acute ecotoxicity	toxicity to organisms exposed to a contaminant for a short period of time in relation to the overall lifecycle of the organism
Al	Aluminium
NH₄⁺	Ammonium, a constituent chemical species of total ammonia
As	Arsenic
As(III)	Arsenic in the three oxidation state
As(V)	Arsenic in the five oxidation state
Biotic	Associated with biota
BCD	Brennans Creek Dam the largest (and primary) water storage within the precincts of West Cliff Mine
BHPIC	BHP Billiton Illawarra Coal
BLM	Biotic Ligand Model; refer: http://en.wikipedia.org/wiki/Biotic_Ligand_Model Note currently USEPA uses the BLM as a tool to outline AWQCs for fresh surface waters
Ca	Calcium
Carboxylate	Principal metals- binding ligand group within DOM, NOM, Humate and fulvate etc.
Chronic ecotoxicity	toxicity to organisms exposed to a contaminant for a substantial proportion of the overall lifecycle of the organism
Cl	Chloride
Co	Cobalt
Colloidal	small particles in water <1 µm in size. Many easily pass through a 0.45 µm filter
CO₃	Carbonate (properly CO ₃ ⁻²). One of two ligands (with HCO ₃ ⁻) whose (inorganic) complexing effect on Ni speciation is still controversial.
CPP	West Cliff Coal Preparation Plant
DOC	Dissolved Organic Carbon (defined as passing 0.45 µm filter)
DOM	Dissolved Organic Matter (defined as passing 0.45 µm filter)
DTA	Direct Toxicity Assessment; ecotoxicity measurements made <i>in situ</i> or in the laboratory on discharges waters
EC	Electrical Conductivity, a measure of salinity
Fe	Iron
Ferruginous	Containing iron and manganese

Filt.	A prefix used to refer to chemicals species which pass through a 0.45 µm filter. An operational classification not necessarily equivalent to a truly dissolved (soluble) state.
FIAM	Free Ion Activity Model. Model that states that metal toxicity is proportional to the activity (similar to concentration) of the free metal ion, and possibly to other cationic metal species. Predecessor of BLM and incorporated into it.
Fulvate	Class of natural organic ligands which can complex-with metals. Molecular weight approximately 650. Sub-class of DOM, NOM etc.
HCO₃	Abbreviation for bicarbonate (properly HCO ₃ ⁻).
HFO	Hydrous ferric oxide. Common form of insoluble iron in surface waters.
Ligand	Dissolved chemical species (inorganic and/or organic) which can combine with metals (to alter or reduce ecotoxicity of species)
Humate	Class of natural organic ligands which can complex-with metals. Molecular weight approximately 2000. Sub-class of DOM, NOM etc. DOM leached from coals and shales known to exhibit similar but generally stronger metal-complexing ability (than Humate) due to the higher density of phenolic and carboxylate groups.
K	Potassium
KTH	Dept. Of Land and Water Resources Engineering, Sweden
Magnasol 572	BASF commercial cationic coagulant formulation used to enhance settling and water clarification in the concrete sedimentation tanks downstream of the CPP. Active material comprised of 98% PAC and 2% a quaternary ammonium cationic organic polymer of 8% nitrogen content and approximately 150,000 molecular weight.
Mg	Magnesium
MINTEQA2	Common aqueous chemistry model and database disseminated by USEPA; refer: http://www.epa.gov/ceampubl/mmedia/minteq/
Mn	Manganese
Na	Sodium
NERC	Natural Resource Research Council (United Kingdom)
NH₃	Total ammonia, used to refer to all chemical species of ammonia
NH₃-N	Ammonia Nitrogen
NOM	Natural Organic Matter (generally defined as passing 0.45 µm filter)
NPOC	Non-particulate organic carbon (similar to DOC but different measurement method)
OEH	(NSW) Office of Environment and Heritage
PAC	Polyaluminium chloride (cationic coagulant principal component of Magnasol 572)
PHREEQC	Most popular free (open source code) aqueous chemistry model disseminated by USGS, uses multiple databases variously optimized. Refer: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html

Point 9	Scour Line (bottom drain) for BCD with intake in a concrete pit located 1.5 m below the actual bottom of BCD
Point 10	Licensed Discharge Point 10 West Cliff Mine discharge to Brennans Creek currently piped from Point 9
Point 15	A floating off-take taking in water from approximately 1.8 m below the surface of BCD. Currently used to provide the underground mine non-potable water supply
Ni	Nickel
NH₃-N	Total Ammonia Nitrogen (also known as TAN)
Pb	Lead
SD	Standard deviation within which approx. 68% of all values expected to lie (on either side of the mean). Approximately 95% of all values expected to lie with ± 2 standard deviations
SiO₂	Silica
SI	Saturation Index. A logarithmic scale of mineral solubility with all values of 0.00 indicating equilibrium thermodynamic insolubility
SO₄	Sulfate
TAN	Total Ammonia Nitrogen (also NH ₃ -N)
T.Alk.	Total Alkalinity usually expressed in units of mg/L as CaCO ₃ (calcium carbonate)
TKN	Total Kjeldahl Nitrogen (=Total Organic Nitrogen + NH ₃ -N). Note also Dissolved TKN = Diss. TKN = DON + NH ₃ -N
Turbidity	A field measure of Total Suspended Solids, expressed in Nephelometric Turbidity Units (NTU)
TSS	Total Suspended Solids (determined by laboratory gravimetric analysis)
Trophic	Level broadly referring to ecosystem type and status
Un-ionized NH₃	Chemical species of ammonia generally regarded to comprise the ecotoxic species (a fraction of total ammonia)
USEPA	United States Environment Protection Agency
USGS	United States Geological Survey
VISUAL MINTEQ version 3.0	Popular free (closed source code) aqueous chemistry model produced by Prof. J. P. Gustaffson at KTH (Sweden) since 2000. Code originally built on USEPA's MINTEQA2. Three databases optimized for metal complexing effects of DOM. Refer: http://www2.lwr.kth.se/English/OurSoftware/vminteq/
WHAM version 7.0	Popular (closed source code) aqueous chemistry model and database especially optimized for metal complexing effects of DOM. Disseminated by NERC (UK). Version VI database included with PHREEQC. Refer: http://www.ceh.ac.uk/products/software/wham/
Zn	Zinc

2. INTRODUCTION

The West Cliff Colliery (hereafter referred to as “the Mine”) owned by BHP Billiton Illawarra Coal (I.C.) includes the West Cliff Mine and the West Cliff Coal Preparation Plant (CPP). The Mine operates under Environment Protection Licence 2504 (EPL 2504), constituted under Section 55 of the *Protection of the Environment Act* (NSW) 1997.

The EPL regulates, among other things, the discharge of water from the Mine into Brennans Creek via the licensed discharge Point 10. Quantified limits currently stated in EPL 2504 for Point 10 include an acceptable pH range of 6.5 to 9.0, a Total Suspended Solids (TSS) upper limit of 50 mg/L, and an Oil and Grease (O&G) limit of 10 mg/L.

In addition to meeting the Licence requirements, the Mine needs to manage Brennans Creek Dam (BCD) to satisfy the water requirements of its own operations. To date the Mine has complied with the EPL limits by dilution of saline water from the Mine operations with rainfall run-off collected in the Brennans Creek catchment.

OEH has asked IC to propose a set of quantified contaminant discharge limits similar to the current limits on pH, TSS and O&G. Such limits would apply to a range of parameters of potential environmental significance such as salinity, ammonia and a suite of metals associated with coal production. These limits must be both scientifically justifiable and practical should be protective of the existing environmental values of the upper Georges River.

3. RECORDS OF PAST EPL2504 POINT 10 DISCHARGES

Water quality data have been collected by Ecoengineers Pty Ltd (Ecoengineers) for (licensed discharge) Point 10 since 4 August 2004, including once weekly (or even more frequent) on-site monitoring of pH, EC and turbidity.

Samples were collected monthly, over some or all of that period, for laboratory analysis of numerous parameters including major cations and anions, alkalinity, total suspended solids (TSS), a suite of metalloids and metals (including in particular As, Al, Ni, Cu, Zn, Pb), and nutrients (N and P species).

Thus a substantial historical record of chemical parameters is available covering a period of more than 8 years.

These data have two very useful applications. They are a useful record of site-specific chemistry parameters that can be used to model the system. They also give an historical record of the range of potential contaminant concentrations to allow estimation of future contaminant concentrations and hence gauge the ability of the Mine to comply with any proposed limits.

Table 3.1 summarises the historical water quality record for the discharge through Point 10 and also Point 15. Note that the number in brackets is the total number of measurements (for that parameter). From Table 3.1, it is noted that NH₃-N, As and Pb are generally below the NWQG default trigger values for protection of 90% and 95% of all species.

The other parameters are generally higher than the default trigger values, some substantially so, and yet no acute ecotoxicity was observed during the tests conducted-for PRP11. This is

not a contradiction but serves as a reminder that the trigger values are the start of a decision tree process.

For example, the toxicity of metals in this case is clearly ameliorated by factors that decrease the bioavailable fraction of the metals by reducing either their solubility (from truly soluble to colloidal) or by altering their solute speciation.

Table 3.1 Record of water quality parameters for Point 10 and Point 15

Parameter	Point 10	Point 15	NWQG 95% trigger value ¹	NWQG 90% trigger value ²
EC (µS/cm)	2496 ± 434 (1323)	2125 ± 619 (562)	2200 ³	
pH	8.44 ± 0.30 (1304)	8.76 ± 0.25 (563)	(9.0) ⁴	
TSS (mg/L)	11±10 (96)	13±22 (70)	(50) ⁵	
O & G (mg/L)	2.9 ± 1.2 (92)	Not available	(10) ⁶	
Na (mg/L)	584±137 (70)	542±167 (70)	NA	NA
K (mg/L)	3.8±0.8 (70)	3.7±0.9 (70)	NA	NA
Ca (mg/L)	5.2±1.1 (70)	4.6±1.2 (70)	NA	NA
Mg (mg/L)	2.4±0.6 (70)	2.0±0.5 (70)	NA	NA
Cl (mg/L)	198±52 (77)	183±61 (70)	NA	NA
SO ₄ (mg/L)	30.6±9.6 (70)	31.3±10.3 (70)	NA	NA
T.Alk. (mg/L as CaCO ₃)	953±222 (76)	859±294 (70)	NA	NA
Total Fe (mg/L)	1.113±0.877 (94)	Not available	NA	NA
Filt. Mn (mg/L)	0.025±0.025 (52)	0.007±0.006 (70)	1.9	2.5
DOC (mg/L)	7±3 (73)	6±2 (70)	NA	NA
NH ₃ -N (mg/L)	0.16±0.12 (46)	0.052±0.053 (68)	0.18 ⁷	NA
NO _x -N ⁵ (mg/L)	0.89±0.45 (46)	0.91±0.35 (68)	0.158 ⁸	3.4
TKN (mg/L)	0.96±0.52 (46)	0.78±0.39 (68)	NA	NA
Filt. As (mg/L)	0.010±0.003 (52)	0.009±0.004 (70)	0.013 ⁹	0.042
Filt. Al (mg/L)	0.668±0.312 (52)	0.790±0.355 (70)	0.055 ¹⁰	0.080
Filt. Cu (mg/L)	0.005±0.002 (52)	0.008±0.013 (70)	0.0014	0.0018
Filt. Ni (mg/L)	0.150±0.046 (52)	0.134±0.057 (70)	0.011	0.013
Filt. Pb (mg/L)	0.002±0.001 (52)	0.002±0.002 (70)	0.0034	0.0056
Filt. Zn (mg/L)	0.039±0.024 (52)	0.046±0.029 (70)	0.008	0.015

¹ Trigger value for protection of 95% of species

² Trigger value for protection of 90% of species

³ Trigger value for lowland rivers

⁴ Current EPL 2054 upper limit

⁵ Current EPL 2054 upper limit

⁶ Current EPL 2054 upper limit

⁷ Trigger value for NH₃-N at pH = 9. At lower pH values, the trigger value is higher.

⁸ NO_x-N includes nitrite and nitrate. In well-oxygenated waters, most NO_x will exist as nitrate.

⁹ Trigger value for As(V). Trigger value for As(III) is 0.024 mg/L

¹⁰ Trigger value for Al at pH > 6.5

4. SALINITY

The NWQG suggest upper salinity limits for protection of slightly-to-moderately impacted systems in south eastern Australia of 350 $\mu\text{S}/\text{cm}$ in upland rivers and 2200 $\mu\text{S}/\text{cm}$ in lowland rivers. The distinction between upland and lowland rivers is arbitrarily set at an altitude of approximately 150 m in the NWQG. Note that Point 10 sits at an altitude of approximately 225 m. This distinction cited by the NWQG is arbitrary, the NWQG are just that, *guidelines* and it is necessary to consider the soil and lithological context of the catchment for a more applicable *region-specific criterion* as the NWQG specify e.g. East Gippsland, Bega Valley, and Sydney Basin for the lowland rivers guideline.

In the case of the Georges River, the river catchment drains areas of both outcropping Hawkesbury Sandstone and / or Wianamatta Shale. Streams that drain from the marine-derived Wianamatta Shale are naturally more saline.

Figure 4.1 below shows a very large fraction of the catchment of Georges River is mantled by outcropping Wianamatta Shale – a marine sediment, and that the river often runs through Quaternary sediments (fine clays) which would have largely eroded off Wianamatta Shale, the Triassic Hawkesbury Sandstone part of the catchment being less erosive. In addition, from its source to at least Wedderburn (where Shale outcrops strongly on both sides of the river) the river is naturally impacted by a number of ferruginous springs from the base of the Shale which raise salinity in, and immediately down river of, some pools. Salinity in the upper Georges River ranges naturally up to in excess of 1500 $\mu\text{S}/\text{cm}$ in prolonged dry weather or in the vicinity of springs or streams draining Wianamatta Shale without any discharges from the Mine (MWS&DB, 1985; Jarvis, 1997; Cardno Ecology Lab & Ecoengineers, 2010).

The results of PRP11 (Ecoengineers, 2012) indicated no acute ecotoxicity to a range of test organisms for Point 10 discharge water at $\text{pH}<9$ (refer **PRP 11 Section 1.1.2**). The mean salinity of the two Point 10 samples was $1860 \pm 52 \mu\text{S}/\text{cm}$. This is further evidence to suggest the lowland river NWQG salinity guideline of 2200 $\mu\text{S}/\text{cm}$ is more appropriate for the Point 10 discharge than the upland river NWQG guideline (350 $\mu\text{S}/\text{cm}$).

The tests used for PRP11 were acute tests and cannot rule out the potential for chronic effects, i.e. effects that may occur for exposures over a longer proportion of the test organism's life-cycle.

Nevertheless, the NWQG default trigger value of 2200 $\mu\text{S}/\text{cm}$ for lowland rivers in south-east Australia was clearly intended for the protection of low to moderately impacted ecosystems, partly because that part of Australia is the most densely populated, has a large proportion of agricultural land and/or a dominant lithological unit (affecting stream and river chemistry) being a marine or estuarine sediment e.g. East Gippsland, Sydney Basin. In independently reviewing the PRP10 studies (Cardno Ecology Lab & Ecoengineers, 2011), the well recognised Australian ecologist Dr. Ben Kefford noted that:

“The strongest conclusion that can be drawn from the program is that salinity is not the only issue associated with the discharge of the coal mine waters studied. Downstream of the discharge both pH and salinity increased.”

For these reasons we suggest it is appropriate to classify the upper Georges River, in respect of salinity, as a *south-eastern Australia lowland river*. Therefore we propose the NWQG default salinity trigger for lowland rivers in southeast Australia of 2200 $\mu\text{S}/\text{cm}$ should apply to the Upper Georges catchment.

Since November 2006 the salinity of water from Point 10 was in excess of 2200 $\mu\text{S}/\text{cm}$ 79% of the time, but Point 15 collected near the surface of BCD has been above 2200 $\mu\text{S}/\text{cm}$ only 42% of monitored occasions.

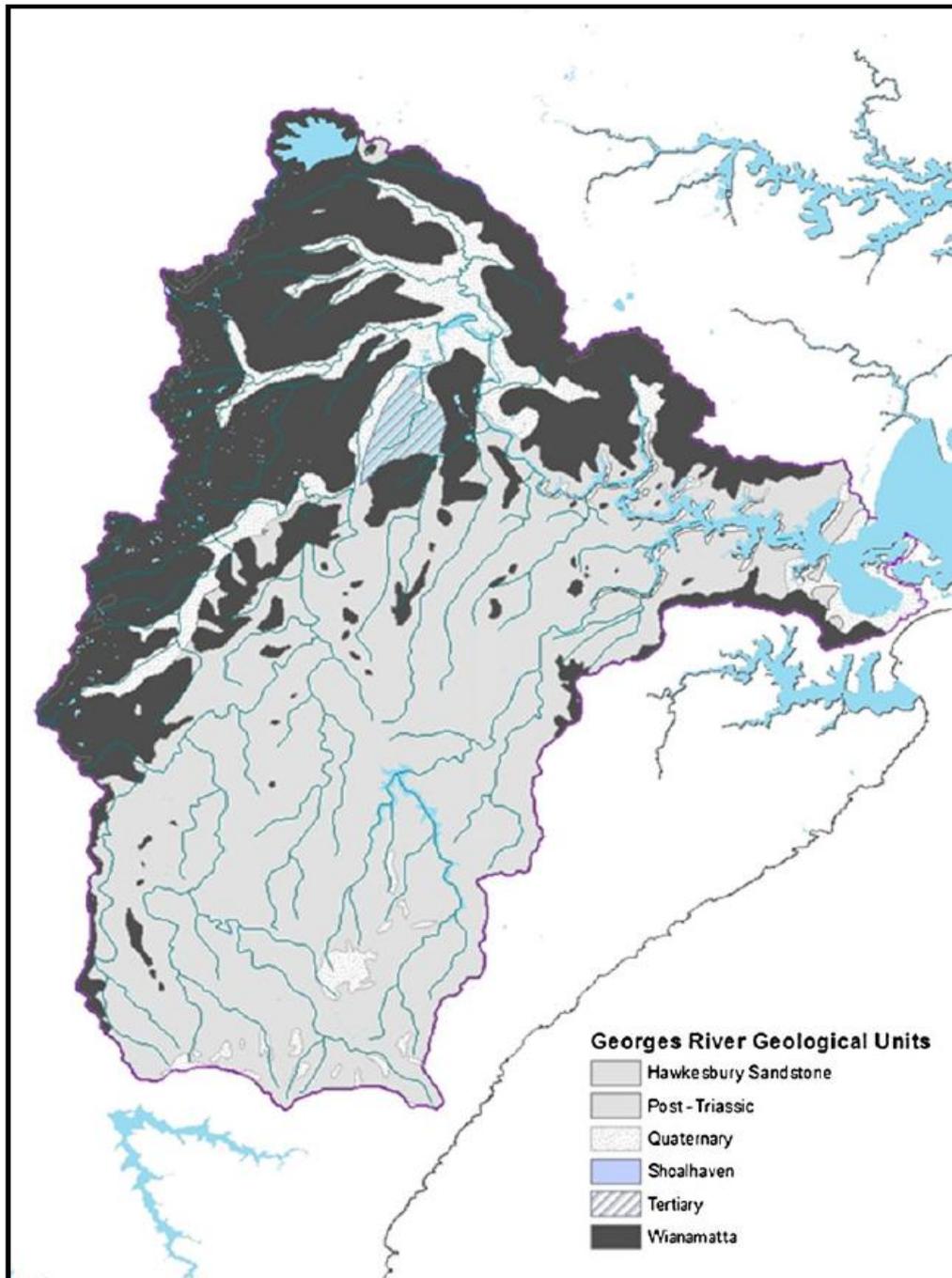


Figure 4.1: Georges River Catchment Lithological Units

Whilst salinity is known as a broad stressor of freshwater organisms, bicarbonate is a component of salinity that at high concentrations can exert a toxic effect (Cowgill and

Milazzo, 1991; Hoke et al., 1992; Mount et al., 1997). It is believed that the anion bicarbonate (HCO_3^-) species is most relevant to toxicity as opposed to the neutral NaHCO_3 ion-pair. The bicarbonate concentration is most accurately determined by speciation calculations using the total alkalinity (T.Alk.) as an input value.

Farag and Harper (2012) recently published toxicity data for bicarbonate effects on a wide range of North American aquatic organisms in two permanent rivers in Montana, US. They used the data to calculate a Criterion Continuous Concentration (chronic criterion) of 290 mg/L as HCO_3^- . OEH (2012) recently used that data to calculate trigger values from estimated No Observable Effect Concentration (NOEC) values and derived the following values in accord with the usual NWQG protocols:

- 95% species protection level: 225 mg/L HCO_3^-
- 90% species protection level: 261 mg/L HCO_3^-
- 80% species protection level: 319 mg/L HCO_3^-

The 95% species protection value estimated by OEH (2012) would translate to a measured EC value of only approximately 700 – 750 $\mu\text{S}/\text{cm}$ in the Point 10 water.

However, it is highly debatable whether such criteria should apply to the Georges River as there is absolutely no field evidence to suggest that bicarbonate is a recognisable stressor on the aquatic ecosystems of the Georges River.

Tippler et al. 2012 recently conducted a significant 2 year study of the Georges River supported by extensive field and laboratory water quality measurements. Streams in the Georges River catchment were sampled in spring 2009, autumn 2010, spring 2010 and autumn 2011. Their summary of results from the BIOENV procedure correlating invertebrate assemblage structure (class diversity) with physicochemical parameters (pH, EC, DO, Turbidity, HCO_3^- , CO_3^{2-} , Na, SO_4 , and Mg etc.) are shown in their Table 2 reproduced below.

Table 4.1: Correlation from the BIOENV procedure correlating with invertebrate assemblage structure

<i>k</i> variable	Bio-physical riparian variables contributing to maximum ρ	BIOENV maximum ρ ρ =rank correlation
4	RARC score, % EI, total nitrogen, calcium	0.650
5	RARC score, % EI, chloride, calcium, turbidity	0.646
3	RARC score, % EI, calcium	0.646
4	RARC score, % EI, calcium, turbidity	0.645
4	Chloride, calcium, RARC score, % EI	0.645
5	Turbidity, calcium, magnesium, RARC score, % EI	0.640
4	TKN, calcium, RARC score, % EI	0.639
5	Total nitrogen, magnesium, calcium, RARC score, % EI	0.638
3	RARC score, dissolved oxygen %, total nitrogen	0.637
2	RARC score, % EI	0.637

From streams in the Georges River catchment sampled in spring 2009, autumn 2010, spring 2010 and autumn 2011. Combinations of riparian variables (*k*) yielding the highest rank between variables (correlation ρ) are shown. *Bold* indicates the best combination (maximum ρ)

It can be clearly seen that, in the Georges River catchment, neither EC (as a measure of salinity) nor HCO_3^- were significantly ranked ahead of numerous other major water quality variables such as Total Nitrogen (TN), chloride (Cl), Calcium (Ca), turbidity, Magnesium (Mg) etc., as the driver of a reduced macroinvertebrate taxa-level diversity.

However, those parameters ranked highest were TN and Ca. Furthermore, it was also found that almost all of the TN-based impact could be ascribed to Total Kjeldahl Nitrogen (TKN), a laboratory analytical measure of both organic nitrogen (Org-N; generally considered non-ecotoxic except in rare circumstances) and total ammonia nitrogen ($\text{NH}_3\text{-N}$ or TAN; known to be partly ecotoxic). This strongly suggests that, other than Ca, the most significant driver reducing macroinvertebrate diversity in the Georges River catchment is likely to be un-ionized ammonia (as part of the $\text{NH}_3\text{-N}$).

In this connection, it is very important to appreciate that every single one of the now numerous laboratory ecotoxicological studies conducted on the NaHCO_3 -type weakly saline mine waters characteristic of the Southern Coalfield over more than 13 years has invariably shown that both chronic (e.g. water fleas, mayflies) and acute (e.g. rainbow fish, glass shrimp) toxicity increases with:

- increasing holding time of the water;
- increasing loss of dissolved CO_2 ; and
- increasing pH.

This effect has been observed in many studies from as far back as the NSW EPA (2000) study of the Elouera Colliery mine water (of EC only $\sim 1100 \mu\text{S/cm}$) to the most recent PRP11 studies (Ecoengineers, 2012; Ecotox Services Australasia, 2012a-d).

The OEH (2012) hypothesis essentially proposes that bicarbonate (HCO_3^-) was the principal driver of chronic or acute toxicity observed in such studies. However, it is noted that HCO_3^- concentrations in such waters **decrease** with increasing pH. For example, for a constant total carbonate alkalinity (Dissolved Inorganic Carbon; DIC) the mole ratio of HCO_3^- to DIC at pH 8.5 is about 0.96. This ratio falls steadily to about 0.82 at pH 9.5.

The loss/removal of CO_2 , with concomitant pH rise, often to in excess of pH 9.5, occurs frequently in many natural aquatic ecosystems wherever turbulence occurs or algal productivity increases. The principal driver of an aquatic ecotoxicity which increases with increasing pH cannot therefore be logically ascribed to HCO_3^- .

Similarly, it is well known that concentrations of the various cationic species of Al, Cu, Co, Pb, Ni and Zn known to be the drivers of ecotoxicity (Hofmann et al., 1995; Tessier and Turner, 1995; Paquin et al. 2002; Niogi and Wood, 2004) all **decrease** with increasing pH due to increased complexation by hydroxide ions (OH^-) in the case of Al and carbonate ions (CO_3^{2-}) in the cases of Cu, Co, Pb, Ni and Zn.

Therefore, the principal driver of an aquatic ecotoxicity which increases with increased pH also cannot be easily ascribed to any of the metals Al, Cu, Co, Pb, Ni and Zn (or Cd, Co or Mn).

Under such conditions, the principal toxicity driver needs to be a species or suite of species whose expected ecotoxicity should rise for some well defined chemical, biogeochemical or physicochemical reason(s).

It was realised after PRP11 that a good candidate is ammonia (NH_3), wherein the fraction of total ammonia comprised-of the ecotoxic un-ionized ammonia (NH_3) species rises markedly with increasing pH. It is noted that the NWQG value for total ammonia nitrogen ($\text{NH}_3\text{-N}$) is 0.18 mg/L at pH 9.0 and that the long term mean $\text{NH}_3\text{-N}$ in the Point 10 discharge water at the mean pH of 8.44 ± 0.30 at the one standard deviation level ($n = 1304$) is 0.16 ± 0.12 mg/L at the one standard deviation level ($n = 46$).

In terms of increased toxicity in laboratory ecotoxicity tests with extended periods (>48 hour) it is also relevant to note the potential ongoing actions of bacteria and light. These could cause mineralization of DON already present in water samples to ammonia (*ammonification*), increasing the ammonia concentration over a period of days (e.g. Sepers, 1981; Berman and Bronk, 2003). Even in the absence of a pH rise, this could perhaps increase the ammonia concentration to where ecotoxicity may be induced, especially in the longer ecotoxicity tests and especially where the water already contained a $\text{NH}_3\text{-N}$ level close-to or over say 0.180 mg/L.

The long term mean Total Kjeldahl Nitrogen (TKN; the sum of Dissolved Organic Nitrogen and Ammonia Nitrogen) in the Point 10 discharge water is 0.96 mg/L at a mean pH of 8.4 – a level twice that of the default NWQG value for $\text{NH}_3\text{-N}$ at pH 8.4 (0.480 mg/L).

It is also noted that none of the longer duration acute or chronic ecotoxicity tests conducted for PRP11 by Ecotox Australasia Pty Ltd or OEHL included check analyses for $\text{NH}_3\text{-N}$ both at the beginning and end of the tests, even despite the well-known tendency for ammonification of excreta to occur in such tests, much less some potential ammonification of DON contributed by the waters themselves.

It is also noted that in the ecotoxicological tests conducted by OEHL (2012) on various Point 10 discharge samples collected on 6 occasions between 14 May and 25 June 2012 observable acute effects on larval rainbow fish mostly occurred on the final day of the 4-day tests by which time the pH had simply been allowed to drift upwards without water renewals and any ammonification possible and un-ionized ammonia-based effect would have been maximal.

The studies of Johnson (2007) and Johnson et al (2007) in Wyoming streams clearly indicates that dissolved organic nitrogen can transform (variably due to seasonal effects) to ammonia both downstream of discharges but also during transport of water from stream to the laboratory due to these well known heterotrophic bacterial, and/or photochemical, ammonification effects (e.g.; Purvina et al. 2010; Koopmans and Bronk, 2002). Remarkably, Johnson (2007) specifically noted such effects might explain significant differences between her instream ecotoxicological findings and those of some other instream studies conducted at the same or very close by locations (Frag et al. 2007).

We question whether the findings of the later Frag and Harper (2012) studies, conducted as they were in the high latitude, northern hemisphere permanent streams and rivers of Montana and Wyoming, US context, should be applicable to the Georges River context or that bicarbonate ecotoxicity estimates derived from them (OEHL, 2012) are necessarily

applicable to the Georges River or indeed to any weakly saline aquatic ecosystems in continental Australia.

We emphasize that the NWQG (ANZECC/ARMCANZ, 2000a, b) strongly endorse the critical importance of use of site-specific and regional chemistry and geology during consideration of ecotoxicological or ecological effects.

5. DISCHARGE pH, TURBIDITY, AND OIL AND GREASE

The current 100 percentile discharge limits as per the current EPL 2054 are pH between 6.5 and 9.0, an upper limit of 50 mg/L total suspended solids (TSS), and 10 mg/L oil and grease (O&G).

The pH and O&G limits have historically been complied with by the Mine on 99% of sampling occasions.

The TSS limit has been complied with on 100% of sampling occasions.

Based on the results of PRP11 there is no evidence that these levels represent any environmental threat to Brennans Creek or the Georges River.

We propose that the current limits be adapted to account for statistical deviation, i.e. we propose that:

- a 90 percentile limits for pH be set at $6.5 < \text{pH} < 9.0$;
- a 90 percentile limit for TSS be set at 50 mg/L; and
- a 90 percentile limit for O&G be set at 10 mg/L.

Therefore, it is expected that Point 10 discharges could be compliant with the proposed pH, TSS, and O&G limits on greater than 90% of occasions.

6. TOTAL DISSOLVED SOLIDS,

Collectively, the major cations and anions together with some minor dissolved species such as silicate, nitrate/nitrite and fluoride etc., may be regulated by the setting of a Total Dissolved Solids (TDS) parameter. To an adequate level of precision in most waters:

$$\text{TDS} = \text{Na}^+ + \text{K}^+ + \text{Ca}^{+2} + \text{Mg}^{+2} + 0.6 \cdot \text{T.Alk.} + \text{Cl}^- + \text{SO}_4^{-2} + \text{SiO}_3^{-2} + \text{NO}_3^- + \text{F}^-$$

It has been found that, for BCD waters, TDS may be calculated with a good reliability from EC by multiplying the latter by the factor 0.600. This value is within the accepted range of such factors (0.55 – 0.70; APHA/AWWA/WEF, 1998).

Thus a proposed EC limit of (say) 2500 $\mu\text{S}/\text{cm}$ would be equivalent to a TDS limit of 1500 mg/L.

7. BIOLOGICAL AND CHEMICAL OXYGEN DEMAND

It is possible that there may be a desire to place a limit on the (5-day) Biochemical Oxygen Demand (BOD) and/or Chemical Oxygen Demand (COD) of the licensed discharge from BCD. Except for rare occasions when fugitive or natural suspended solids elevations may

occur in BCD e.g. due to algal blooming, both BOD and COD can be reliably estimated from the levels of DOC or TOC respectively plus TKN in BCD waters (at various levels). It is noted both COD and BOD are expressed in units of mg/L O₂ (oxygen) per litre.

Thus, to a good approximation, we can combine the potential carbonaceous and nitrogenous oxygen demands (APHA/AWWA/WEF, 1998) to estimate COD and BOD thus:

$$\text{COD} = (\text{TOC} \times 32/12) + (\text{TKN} \times 48/14)$$

and

$$\text{BOD} = (\text{DOC} \times 32/12) + (\text{Diss. TKN} \times 48/14)$$

For example, for a 90 percentile BOD limit the mean DOC of Point 10 (7±3 mg/L) and the mean Filt. TKN (0.96±0.52 mg/L) can be used to estimate, with acceptable precision a likely maximal value of (13 x 32/12) + (1.0 x 48/14) = 35 + 7 = 42 mg/L. An acceptable 90 percentile value would then be (say) 35 - 40 mg/L.

Similarly an acceptable 90 percentile COD value of the order of 50 mg/L can be derived from the TOC and Unfilt. TKN values

8. NITRATE

The NWQG ecotoxicity trigger value (protection of 95% of species) for nitrate is 0.7 mg/L. Historical records are not available for nitrate specifically, but records are available for laboratory measurements of NO_x-N which is a combined measure of nitrate and nitrite (expressed as nitrogen). In the comparatively well-oxygenated water of Point 10, it can be assumed that the majority of NO_x is present as nitrate. The 0.7 mg/L nitrate trigger value corresponds to a NO_x-N concentration of 0.158 mg/L.

Based on previous historical data, the mean plus two standard deviations of NO_x-N concentrations discharged of Point 10 water is 1.8 mg/L.

This concentration (1.8 mg/L) is below the concentration measured during PRP11 testing. During PRP11 no acute ecotoxicity was observed to four different test organism species, despite a measured NO_x-N concentration of 1.97 ± 0.59 mg/L (n = 2), which is well above the trigger value. The lack of ecotoxicity suggests that in the Point 10 discharge waters, site-specific factors mean that nitrate is not as ecotoxic as the trigger value implies.

9. AMMONIA

The NWQG limit for total ammonia is based on the concentration of the free (un-ionized) NH₃ concentration at a given pH value. The free NH₃ concentration increases markedly with increasing pH, hence toxicity also increases with increasing pH. Since this trigger value already takes into account ammonia speciation, it is appropriate to use this value for a quantified limit.

Note the NWQG 95% protection guideline is not considered protective of all Australasian species not present in Brennans Creek/Georges River e.g. New Zealand freshwater invertebrate species (Hickey and Vickers, 1994).

It is appropriate to choose the NWQG NH₃-N trigger value for water at pH = 9.00 since this pH value is the upper limit already imposed in EPL 2054. As discussed in Section 3, the NH₃-N trigger value at pH 9.00 is lower than trigger values at lower pHs and hence is the most protective of aquatic life.

10. ARSENIC

Arsenic occurs chiefly in two oxidation states, As(III) and As(V), with chemical varying properties. The NWQG default trigger value for protection of 95% of species (applying to slightly-to-moderately disturbed ecosystems) is 0.024 mg/L for As(III) and 0.013 mg/L for As(V). Normal laboratory measurements of As do not distinguish between these two species.

The speciation of As is dependent on, amongst other things, the redox conditions of the water. Well oxygenated systems such as rivers are expected to be dominated by As(V), whereas As(III) is more likely to dominate in anoxic groundwaters.

For that reason, the As(V) trigger value is more appropriate to Point 10 (or Point 15) since it discharges into a small creek where oxygenation will occur rapidly, no matter the redox status of the discharge. Using the As(V) trigger value is also more protective since it is the lower of the two values.

11. METALS, SPECIATION AND SORPTION MODELLING

The suite of metals identified as relevant to BCD-based water discharges from Points 10 or 15 is Al, Cd, Cu, Co, Pb, Ni, Mn and Zn. Of these Al needs to be considered somewhat differently as the geochemistry and mode(s) of bioavailability of Al are sometimes significantly different to the other metals. Of these Mn has not been considered further as its level of occurrence is invariably compliant under all circumstance with all NWQG trigger values (ANZECC&ARMCANZ, 2000a).

Modeling of metal speciation has been performed using both the Swedish Visual MINTEQ (version 3.0) model and the American PHREEQC version 2 model.

Visual MINTEQ was used with the default (largely USEPA MINTEQA2 version 4) inorganic database with the exception that, based on recent improvements in understanding of Ni solute speciation, an anionic Ni dicarbonate complex ($\text{Ni}(\text{CO}_3)_2^{2-}$) was added to the database (log K = 6.2; Baeyens and Bradbury, 2003). This species does not appear in the USEPA MINTEQA2 version 4 database of February 2006. The log K of the anionic monocarbonate species was also corrected to the currently accepted value. Organic modelling was performed using the NICA-Donnan database incorporated in Visual MINTEQ.

DOM in water exposed to coal and shales is generally higher in overall cation exchange capacity and phenolic groups than DOM from river or lake water, leading to a greater complexation capacity for some metals at near neutral to alkaline pHs where the phenolic groups lose protons.

Therefore we believe that organic complexation modelling using the Visual MINTEQ NICA-Donnan default database may well underestimate DOM complexation of some metals in a coal mining context as here.

This makes the metals speciation modelling using Visual MINTEQ conservative in respect of metals ecotoxicity, noting metal-DOM complexes are generally believed to not be bioavailable (e.g. Tessier and Turner 1995).

As a cross check of the speciation predictions using Visual MINTEQ (and the NICA-Donnan database for organic complexation of metals), we also conducted speciation modelling using the USGS PHREEQC version 2 model.

In this latter case we used the well known (PHREEQC version of) the Tipping and Hurley WHAM Version V database dated 2 February 2007 for organic metal complex modelling (Tipping, 2002; Guthrie et al. 2005) and modifying the log K of the anionic Ni dicarbonate complex ($\text{Ni}(\text{CO}_3)_2^{2-}$) (log K = 6.2; Baeyens and Bradbury, 2003) from the older value of 10.1. It was also assumed that the DOC in the water had 68% carbon content and a total number of carboxylate plus phenoxylate sites of 2.0 millimoles/mg in accord with the literature on humic acids leached from coal and shales.

We also assumed that the ~1.0 mg/L of Total Fe invariably in these waters is present as ~1.6 mg/L hydrous ferric oxide (HFO; also known as ferrihydrite or amorphous ferric hydroxide) with 0.2 millimoles/mg strong sites and 0.005 millimoles/mg weak sites (Dzombak and Morel, 1987).

Preliminary modelling showed that all of this Fe is present as insoluble colloidal material as the Saturation Index (SI) of the HFO (and also of goethite and hematite) was of the order of +2.5 or more in all waters collected at all levels in BCD. That is, we can safely assume that all fractions of the elements As, Cu, Ni, Pb and Zn adsorbed onto HFO are by definition present in the colloidal form and hence unavailable to contribute to ecotoxicity.

This approach differs from the Visual MINTEQ model which, by way of contrast, was set up to not allow any adsorption of these elements onto HFO-based colloids (in addition-to dissolved organic matter (DOM) complexation).

The exact 'fraction' of bioavailable metals is not known with certainty as there may be a number of mechanisms affecting bioavailability but it is generally believed to be due to cationic forms.

Summing the concentrations of all cationic species is a more conservative measure than simply considering the concentration of the free metal ion only.

In Table 11.1 below we compare the total cationic metal species estimated by various speciation modelling using PHREEQC and Visual MINTEQ as described above against the NWQG trigger values. Speciation modelling indicates that for Al, Cu, and Pb, the sums of all cationic species are trivial in comparison to the NWQG default trigger values.

In the absence of adsorption to colloidal HFO, the calculated cationic species total is similar to the trigger values (in the case of Zn) or well in excess (in the case of Ni) when the results from Visual MINTEQ are applied. However PHREEQC modelling including adsorption to colloidal HFO reduced the total cationic concentrations of Ni and Zn to approximately an order of magnitude less than the trigger values.

Table 11.1: Estimated cationic metal concentrations calculated by speciation modelling

Metal	PHREEQC Total cationic species (with HFO adsorption) (mg/L)	Visual MINTEQ Total cationic species (without HFO adsorption) (mg/L)	NWQG 95% Trigger Value (mg/L)
Al	0.000056	0.000052	0.055
Cu	0.0000061	0.0000021	0.0018
Ni	0.0039	0.041	0.011
Pb	0.00000097	0.0000045	0.0034
Zn	0.00092	0.0106	0.008

Based on this modelling, it is unlikely that the metal concentrations observed would exert any ecotoxic effect. It should be noted that the protective effect in respect of metals is a combination of adsorption onto particles, complexation of metals by organic matter (NOM), and complexation by inorganic ligands (chiefly carbonate).

12. ALUMINIUM

The NWQG trigger value (95% protection) for Al at pH > 6.5 is 0.055 mg/L. The chemistry of Al is complex in neutral to alkaline systems and it is necessary to consider site-specific factors in assessing potential toxicity.

Unlike many other metals for which the best predictor of toxicity are free cationic forms of the metal, Al bioavailability and ecotoxicity may be a combination of effects resulting from presence of the free ion, some monomeric Al forms (such as $\text{Al}(\text{OH})_2^+$) and polymeric forms such as Al_{13} . As Al polymerises further and forms colloidal and particulate species, it appears to be rendered non-ecotoxic (e.g. Gensemer and Playle, 1999).

It should be noted that the use of the water treatment coagulant Magnasol 572 downstream of the CPP contributes to elevated Al concentrations in Point 10.

At the pH of the Point 10 discharge (consistently > 8.0), the speciation of Al should be dominated by $\text{Al}(\text{OH})_4^-$. This was confirmed by speciation modelling which indicated approximately 98% of Al is in the anionic $\text{Al}(\text{OH})_4^-$ form. Even at a filterable Al concentration of 1.2 mg/L, the combined concentration of all other species is only 0.004 mg/L, well below the trigger value (0.055 mg/L). $\text{Al}(\text{OH})_4^-$ is not believed to be appreciably ecotoxic to aquatic organisms.

During PRP11, no ecotoxicity was observed to four different test organism species, despite an Al concentration 0.36 ± 0.01 (n = 2), again well above the trigger value of 0.055 mg/L. The lack of ecotoxicity suggests that most of the filtered Al is in a colloidal form or occurs as $\text{Al}(\text{OH})_4^-$, neither of which are appreciably ecotoxic.

In numerous previous monthly sampling campaigns, the filterable Al concentrations in Point 15 water have been 0.603 ± 0.182 mg/L ($n = 52$) (Table 3.1). The mean plus two standard deviations of Al concentrations discharged is 0.97 mg/L.

It is understood that the Mine is currently seeking to reduce its use of the Magnasol 572 coagulant with CPP wastewater which would have the effect of reducing the concentration of Al in BCD water.

13. COPPER, LEAD, NICKEL, ZINC, CADMIUM AND COBALT

In the context of the biogeochemistry of trace heavy metals such as Cd, Cu, Co, Ni, Pb, and Zn, it is very important to consider the role of metal speciation on bioavailability.

Ecotoxicity is widely held to be largely proportional to the concentration of the free metal cation, with sometimes contribution by other partly complexed cationic species (Tessier and Turner, 1995; Paquin et al. 2002; Niogi and Wood, 2004). In other words, the presence of specific chemical species and entities which reduce cationic species concentrations will cause a reduction in bioavailability.

Such parameters include pH, combination with DOM (Tipping and Hurley, 1992), carbonate, adsorption to colloids etc. (Dzombak and Morel, 1987; Davis and Kent, 1990).

According to the tiered management approach suggested in the NWQG, the effects of solution speciation and non-bioavailable forms should therefore be taken into account to assess the ecotoxicological risks (ANZEC&ARMCANZ, 2000a).

The Cu, Pb Ni, and Zn concentrations in BCD waters recorded during numerous previous monthly sampling campaigns are also summarised in Table 3.1 above.

In order to attempt to find appropriate quantitative limits for filterable metal concentrations for these metals we chose to include in the Visual MINTEQ and PHREEQC model the mean plus two standard deviations of long term discharged concentrations from Point 15.

13.1. Copper

Speciation calculations based on the water chemistry recorded over many years and using a filterable Cu concentration of 0.0076 mg/L indicated Cu speciation was dominated by complexes with DOM (0.0073 mg/L).

Simple inorganic species accounted for 0.0003 mg/L, well below the trigger value (0.0018 mg/L). Cu-DOM complexes are widely held to be non-ecotoxic. Therefore, modelling indicates that Cu ecotoxicity in this water is of very low risk.

In addition to the speciation calculations, and in keeping with the tiered approach of the Guidelines, ecotoxicity measurements were made as part of PRP11. During PRP11 no ecotoxicity was observed to four different test organism species, despite a filterable Cu concentration of 0.005 ± 0.000 mg/L ($n = 2$), which is slightly above the NWQG default trigger value. The lack of ecotoxicity in combination with the speciation described above is consistent with the finding that Cu in this water is significantly complexed by carbonate and DOM.

13.2. Lead

Lead concentrations in Point 10 and Point 15 water have historically been very low (0.0015 ± 0.0008 mg/L). During PRP11 no ecotoxicity was observed to four different test organism species. The filterable Pb concentration during that study was 0.002 ± 0.000 mg/L ($n = 2$), which is below the NWQG default trigger value. The lack of ecotoxicity is therefore not surprising.

13.3. Nickel

Speciation calculations using a filterable Ni concentration of 0.160 mg/L indicate that DOM complexation plays only a minor role in Ni speciation (0.010 mg/L) in Point 15 water.

Ni complexation was dominated by the uncharged NiCO_3 species (0.133 mg/L). However, the combined concentration of inorganic cationic Ni species was calculated as only 0.0038 mg/L, which is well below the trigger value of 0.011 mg/L.

This is consistent with the fact that, during PRP11 no acute ecotoxicity was observed to four different test organism species, despite a filterable Ni concentration of 0.105 ± 0.011 mg/L ($n = 2$), which is also well above the trigger value.

The lack of acute ecotoxicity in combination with the speciation calculations strongly suggests that the Ni carbonate complexes are not acutely ecotoxic.

13.4. Zinc

Calculations using a filterable concentration of 0.090 mg/L Zn indicated Zn speciation also was dominated by carbonate species (0.068 mg/L).

The calculated sum of inorganic, positively charged Zn species other than Zn carbonate species (including the potentially most ecotoxic free ion Zn^{2+} species) is 0.00089 mg/L, well below the NWQG default trigger value of 0.008 mg/L.

During PRP11 no ecotoxicity was observed to four different test organism species, despite a filterable Zn concentration of 0.033 ± 0.008 mg/L ($n = 2$), also well above the default trigger value in the NWQG.

As for Ni, the lack of ecotoxicity in combination with the speciation calculations suggests that the ecotoxicity of the Zn species is strongly diminished by carbonate complexation and to a lesser extent by organic complexation and adsorption to HFO colloids.

13.5. Cadmium, cobalt

It is noted that the regular monthly water quality monitoring, sampling and laboratory program operated as part of the current version of the West Cliff Water Management System (WMS) since 4 August 2004 does not include monitoring of the trace heavy metals Cadmium (Cd) and Cobalt (Co).

Level of both these metals, together with Chromium (Cr) and Molybdenum (Mo) in BCD waters were checked briefly in the period 2002 - 2003 and levels were found to be below the

NWQG default trigger values for protection of 95% of all aquatic species so were omitted from the subsequent monthly program.

However, we understand that more recently levels of filterable Co have risen to up to 6 times the NWQG default trigger value. This is probably due to a trend change in the lithology of the coal seam being mined and related shales over the last decade or so.

It is noted that the potential ecotoxicity of metals such as Co and Cd in particular is significantly moderated by carbonate complexation, organic complexation and adsorption to HFO in similar ways as Cu, Pb, Ni and Zn, however Cr, Mo and V behave differently being largely anionic.

It is therefore proposed that as part of a new Pollution Reduction Program an investigation be conducted of the levels of metals such as Co, Cd, Cr, Mo, Vanadium (V) in BCD waters.

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