

Heavy metal contamination of water column from a coal mine waste water discharge resulting in mobilisation of metal contaminants to riparian vegetation. Wollangambe River, Blue Mountains Australia.

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Abstract

This study investigates the mobilisation of heavy metal contaminants from the Wollangambe Rivers water column to one species of terrestrial riparian flora (*Acacia rubida*), from one regulated coal mine waste water discharge. The study was conducted at one upland stream (The Wollangambe River) found within the Blue Mountains region of Sydney, New South Wales Australia. Two sample sites were used for this study, one as a reference site upstream of Clarence Collieries waste water inflow to the Wollangambe River (W1). The second was located approximately 200m downstream of Clarence Collieries waste water inflow to the Wollangambe River (W3). Five replicated samples were taken from both sample areas. Plants were selected within a 10m lineal stretch of stream edge. Each replicated sample was delivered to a NATA accredited commercial laboratory (EnviroLab Sydney) and analysed for 10 metals (Aluminium, Arsenic, Beryllium, Cadmium, Cobalt, Molybdenum, Nickel, Strontium, Thallium and Zinc). Results found statistical differences between nine of the ten heavy metals when compared between sample locations (upstream and downstream). This study has shown that one coal mine waste water discharge appears to have allowed an avenue for increased heavy metal concentrations within the Wollangambe Rivers water column to mobilise to riparian vegetation found within the terrestrial environment. The implications that the licensed waste water discharges contaminants are mobilising to terrestrial riparian vegetation is of major concern. It is recommended that further research should be undertaken by the NSW EPA to better assess the implications of heavy metal mobilisation to the terrestrial environment from EPL protected waterways. If in fact heavy metal contaminants are leaving the water column of their receiving waterways and mobilising to the terrestrial environment, serious long-term legacy pollutant impacts may persist.

Key words

Bioaccumulation, heavy metal bioaccumulation, flora, native flora, coal mine wastewater, Blue Mountains National Park, Wollangambe River.

Introduction

Coal mining practices are well documented as contributors to an array of differing environmental problems including air pollution, fire hazards, ground subsidence or deformation, surface and or ground water pollution. Surface water pollution is a major environmental problem associated with coal mining and it occurs through the discharge of mine waters that are contaminated by various disturbances associated with mining practices (Jarvis and Younger 1997, Johnson 2003, Pond et al. 2008). Water pollution from coal mining occurs as large volumes of surface and groundwater are required to be removed from most underground coal mines. This is generally achieved through the pumping of water to the surface as surface and groundwaters infiltrate the mine shafts from the local geological sub-strata and subsequently accumulates in the underground mine workings. Without this, groundwater would flood most sections of the underground mining operation (Jarvis and Younger 1997, Younger 2004).

Coal mine waste water will often be contaminated due to the disturbance of the local geology associated with mining activities. The exact nature of the water contamination will vary depending on local factors such as groundwater geochemistry, hydrology and mineralogy of the local strata. In addition to the physical activity of the mining operation and the removal of the waste water, other activities will also often contaminate water used throughout a mining plant which can include; coal washing and the inclusion of other wastes generated by the surface operation at the mine such as sewage wastes (Younger 2004).

The Wollangambe River flows entirely within the Greater Blue Mountains area some 90km west of the Sydney CBD and for most of its flow it resides within the World Heritage Greater Blue Mountains National Park and is a protected tributary of the Colo River, a declared wild river. In the year 2000, the Greater Blue Mountains National Park was inaugurated into the World Heritage List due to its diverse natural values (Australian Government, Department of the Environment, Water, Heritage and the Arts 2012). The Wollangambe Rivers headwaters researched in this study lies within the Western section of the Greater Blue Mountains World Heritage National Park bordering the Wollemi National Park and the Gardens of Stone National Park. The Wollangambe River flows from Newnes Junction at an elevation of some 1050m above sea level. It continues through pristine wilderness over a distance of near 60km until it joins the Colo River at an approximate elevation of 50m above sea level (Department of Environment and Climate Change 2009).

In recent years, the concern about impacts of toxic metals in global ecosystems has reached unparalleled heights. Exponentially, increasing industrial and mining activities have led to further environmental pollution through wastes produced by these activities. Heavy metals from mining and industrial activities, when released to the environment, have the potential to accumulate within biota at toxic concentrations and cause chronic ecological impacts in ecosystem food chains (Sericano et al. 1995, Ashraf et al. 2011). Metal pollution is a global environmental issue and has been for many decades and when mobilised metal pollutants can enter waterways indirectly through land runoff. In many cases metal pollutants are directly discharged into waterways from anthropogenic activities. Many of these metal pollutants become absorbed to suspended particulates within the water column. Once absorbed to these suspended particulates the metal contaminated suspended particulates eventually deposit into waterway sediments often remaining indefinitely (Neff 1984, Wang and Rainbow 2008).

Aquatic ecosystems are often more highly sensitive to heavy metal contamination from anthropogenic activities, especially as waterways are often used as sources of discharge of many anthropogenic industrial wastes (Allen et al. 1993). Heavy metal contamination within aquatic environments can persist for much longer than terrestrial organic pollutants. This is due to the lack of biodegradation function of heavy metals in aquatic ecosystems in comparison to terrestrial ecosystems (Ashraf et al. 2011). Metal bioaccumulation has been linked to many differing mining activities within many aquatic flora and fauna species (Hill et al. 2000; Amish and Cowx 2000; Reash et al.; Otter et al. 2012;) and terrestrial flora (2006; Wislocka et al. 2006; Durães et al. 2014; Nawad et al. 2015; Maiti et al. 2015).

Methods

This study was conducted at one upland stream (The Wollangambe River) found within the Blue Mountains area of Sydney, New South Wales Australia. Two sample sites were used for this study, one as a reference site upstream of Clarence Collieries waste water inflow to the Wollangambe River (W1). The second was located approximately 200m downstream of Clarence Collieries waste water inflow to the Wollangambe River (W3). Five samples (whole plants) were taken from both sample areas. Plants were selected within a 10m lineal stretch of stream edge. All of the foliage was removed from each plant sampled at the Western Sydney University laboratory and stored in separate sample containers. Each replicate sample container was delivered to a NATA accredited commercial laboratory (EnviroLab Sydney) and analysed for 10 metals (Aluminium, Arsenic, Beryllium, Cadmium, Cobalt, Molybdenum, Nickel, Strontium, Thallium and Zinc). One species of Wattle (*Acacia rubida*) was used for this study as it was found to grow in abundance within the riparian zone of each sample location.

The ten metals analysed have been found to be in higher concentrations within the water column and river sediments at the same downstream sample location in previously published and currently submitted manuscripts of the authors of this study, with seven of the metals being statistically different for both water column and river sediment when compared between upstream and downstream sample locations. For instance, Cadmium, Cobalt, Molybdenum and Nickel have been recorded as below laboratory detectable limits within the water column upstream of the coal mine waste water inflow whilst only Cadmium and Molybdenum remain below laboratory detectable limits downstream of the coal mine waste water inflow. In contrast, river sediment concentrations upstream record Cadmium, Cobalt and Molybdenum below laboratory detectable limits whilst all of the metals are detectable downstream of the coal mine waste water inflow. Univariate data analysis was used to compare metal concentrations between samples collected upstream of the coal mine waste water inflow to samples collected downstream. This was performed using Students t-test.

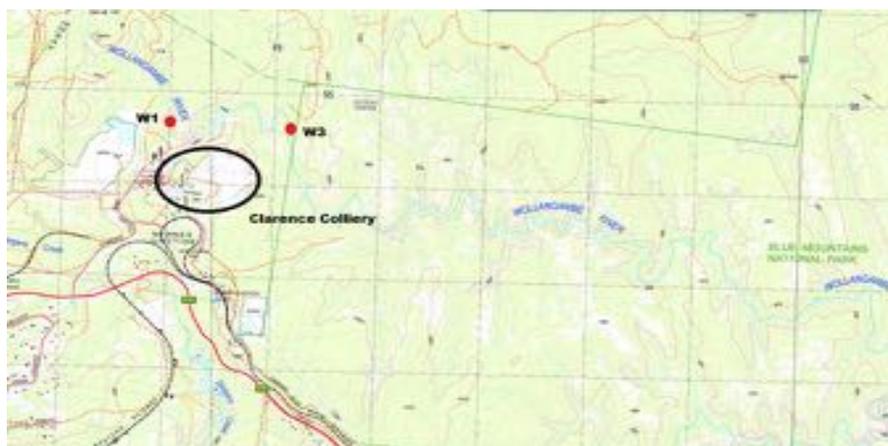


Figure 1. Map of sample locations W1 (upstream) and W3 (downstream). W1 is located approximately 200m upstream of the Clarence Colliery waste water inflow whilst W3 is approximately 200m downstream of the inflow (Colliery circled) (NSW Six Maps 2017).

Results

Results from plant tissue samples (*Acacia rubida*) show that nine of the ten metals analysed were found to be statistically different between upstream and downstream sample locations with all nine increasing downstream of the coal mine waste water discharge. Arsenic was not recorded to be statistically different (Table 1).

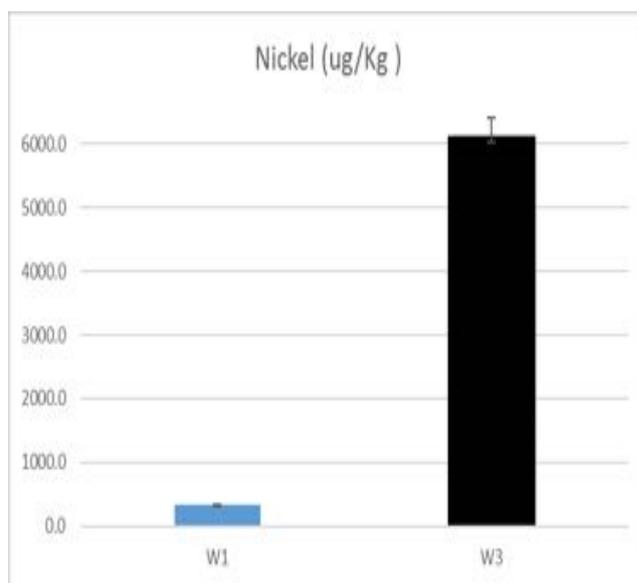
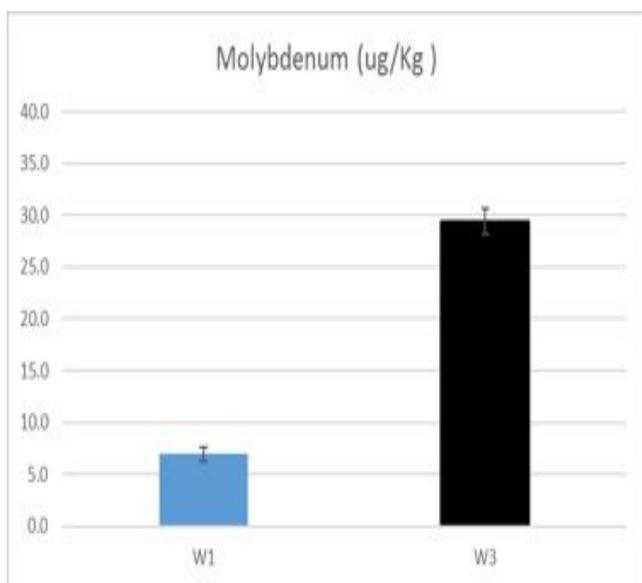
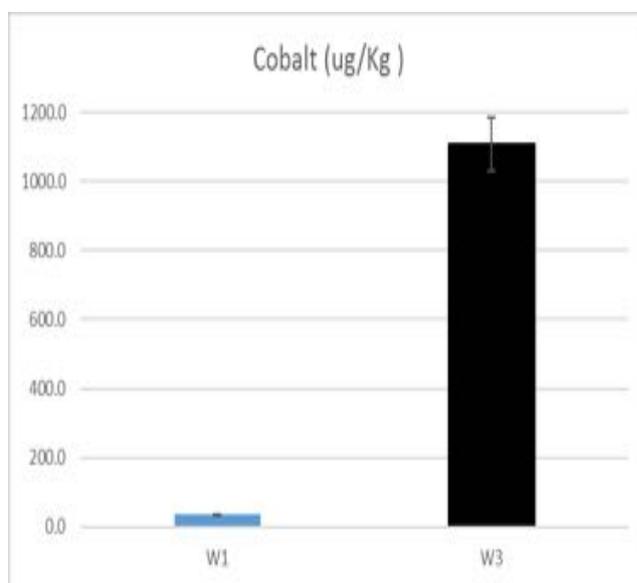
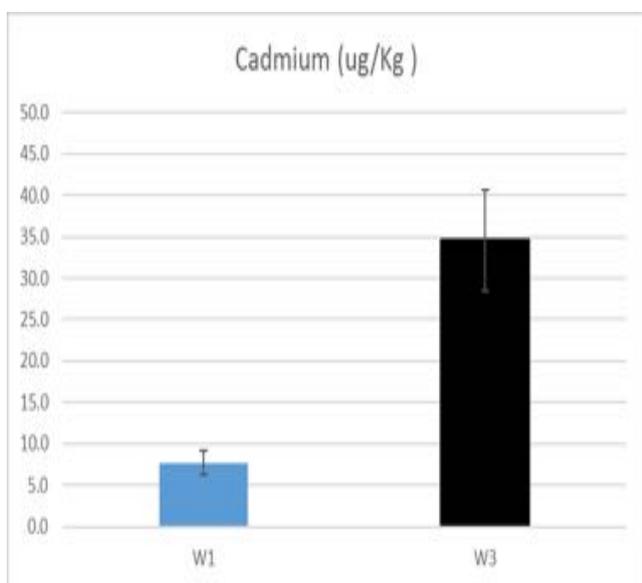
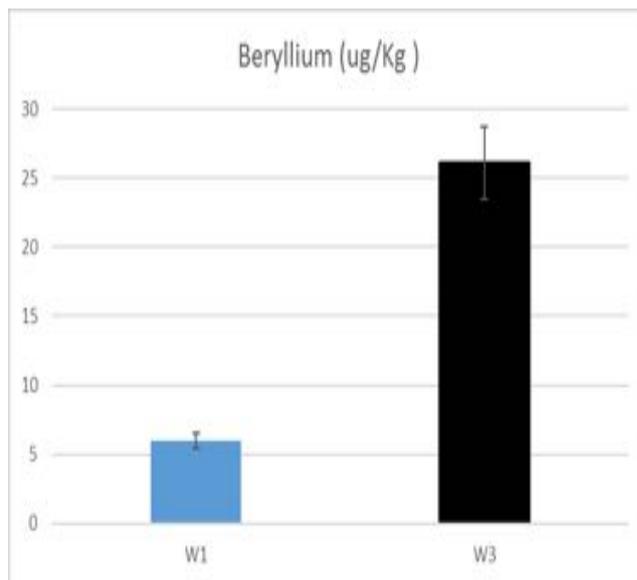
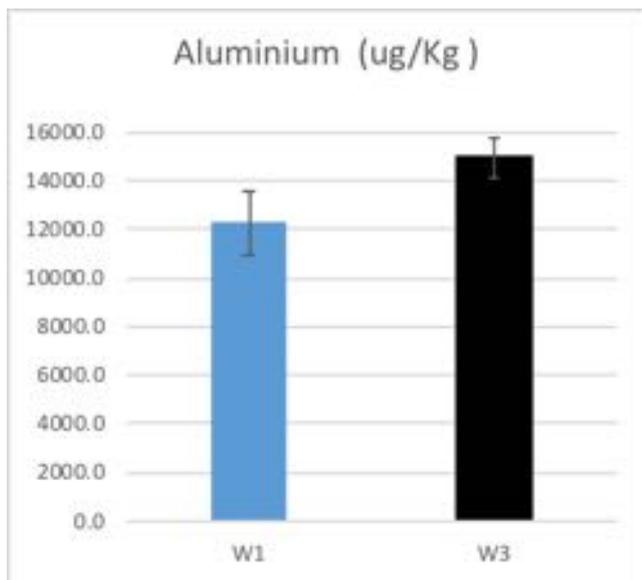
Aluminium increased from a mean of 12253 ug/Kg upstream of the mine waste water inflow to a mean of 14949 ug/Kg downstream ($p=0.009$). Upstream aluminium ranged from 10646 to 13752 ug/Kg whilst downstream ranged between 13965 and 16102 ug/Kg (Table 1 and Figure 2). Beryllium increased over 4 times from a mean of 6.0 ug/Kg upstream of the mine waste water inflow to a mean of 26.1 ug/Kg downstream ($p=3.73E-05$). Upstream beryllium ranged between 5.3 and 6.5ug/Kg whilst downstream beryllium ranged between 24.5 and 27.5 ug/Kg (Table 1 and Figure 2). Cadmium recorded increases over 4 times downstream of the coal mine waste discharge. Upstream recorded a mean of 7.7 ug/Kg in comparison downstream cadmium was recorded at 34.6 ug/Kg downstream ($p=0.0001$). Upstream cadmium ranged from 6.4 to 9.7 ug/Kg whilst downstream ranged between 26.0 and 41.9 ug/Kg (Table 1 and Figure 2). Molybdenum increased over 4 times from a mean of 6.9 ug/Kg upstream of the mine waste water inflow to a mean of 29.4 ug/Kg downstream ($p=1.89E-08$). Upstream molybdenum ranged from 6.0 to 7.4ug/Kg whilst downstream ranged between 27.8 and 31.2ug/Kg (Table 1 and Figure 2).

Strontium nearly doubled in concentrations downstream of the coal mine waste water inflow from a mean of 13917 ug/Kg upstream of the mine waste water inflow to a mean of 21827ug/Kg downstream ($p=0.001$). Upstream strontium ranged between 12422 and 15003 ug/Kg whilst downstream ranged between 17719 and 24608 ug/Kg (Table 1 and Figure 2). Thallium increased over 4 times from an upstream mean of 13.2 ug/Kg to a mean of 60.3 ug/Kg downstream ($p=0.0001$). Upstream thallium ranged from 10.7 to 16.9 ug/Kg whilst in comparison downstream thallium ranged between 44.5 and 74.5ug/Kg (Table 1 and Figure 2). Zinc recorded increases over 7 times downstream of the coal mine waste discharge which is the third greatest increase of this study. Upstream recorded a mean of 6756 ug/Kg whilst in comparison downstream zinc was recorded at a mean of 51914 ug/Kg downstream ($p=1.64E-05$). Upstream zinc ranged from 6264 to 6152 ug/Kg whilst downstream ranged between 46541 and 56932 ug/Kg (Table 1 and Figure 2). Nickel increased over 18 times downstream of the coal mine waste water discharge which is the second greatest increase of metal concentrations in this current study.

Nickel increased from a mean of 336 ug/Kg upstream of the mine waste water inflow to a mean of 6110 ug/Kg downstream ($p=8.18E-07$). Upstream nickel ranged from 333 to 338 ug/Kg whilst downstream ranged between 5799 and 6498 ug/Kg (Table 1 and Figure 2). Cobalt increased over 30 times below the coal mine waste water discharge which is the greatest increase found in this study. Cobalt increased from a mean of 35.1 ug/Kg upstream of the mine waste water inflow to a mean of 1110 ug/Kg downstream ($p=3.33E-06$). Upstream cobalt ranged from 34.0 to 36.8 ug/Kg whilst downstream cobalt ranged between 1021 and 1131 16102 ug/Kg (Table 1 and Figure 2).

Table 1. Heavy metal parameters, sample locations, T-statistic, p value, range and mean for plant tissue results (*Acacia rubida*). All metals are measured in ug/Kg.

Plant tissue results	t-stat	p value	Upstream		Downstream		Percent increase
			Mean	Range	Mean	Range	
Aluminium	3.83	0.009	12253	10646-13752	14949	13965-16102	22%
Beryllium	16.7	3.73E-05	6	5.3-6.5	26.1	24.5-27.5	335%
Cadmium	9.57	0.0001	7.7	6.4-9.7	34.6	26.0-41.9	349%
Cobalt	30.7	3.33E-06	35.1	34.0-36.8	1110	1021-1131	3060%
Molybdenum	34.7	1.89E-08	6.9	6.0-7.4	29.4	27.8-31.2	326%
Nickel	43.7	8.18E-07	336	333-338	6110	5799-6498	1718%
Strontium	5.63	0.001	13917	12422-15003	21827	17719-24608	57%
Thallium	8.99	0.0001	13.2	10.7-16.9	60.3	44.5-74.5	357%
Zinc	20.6	1.64E-05	6756	6264-6152	51914	46541-56932	668%



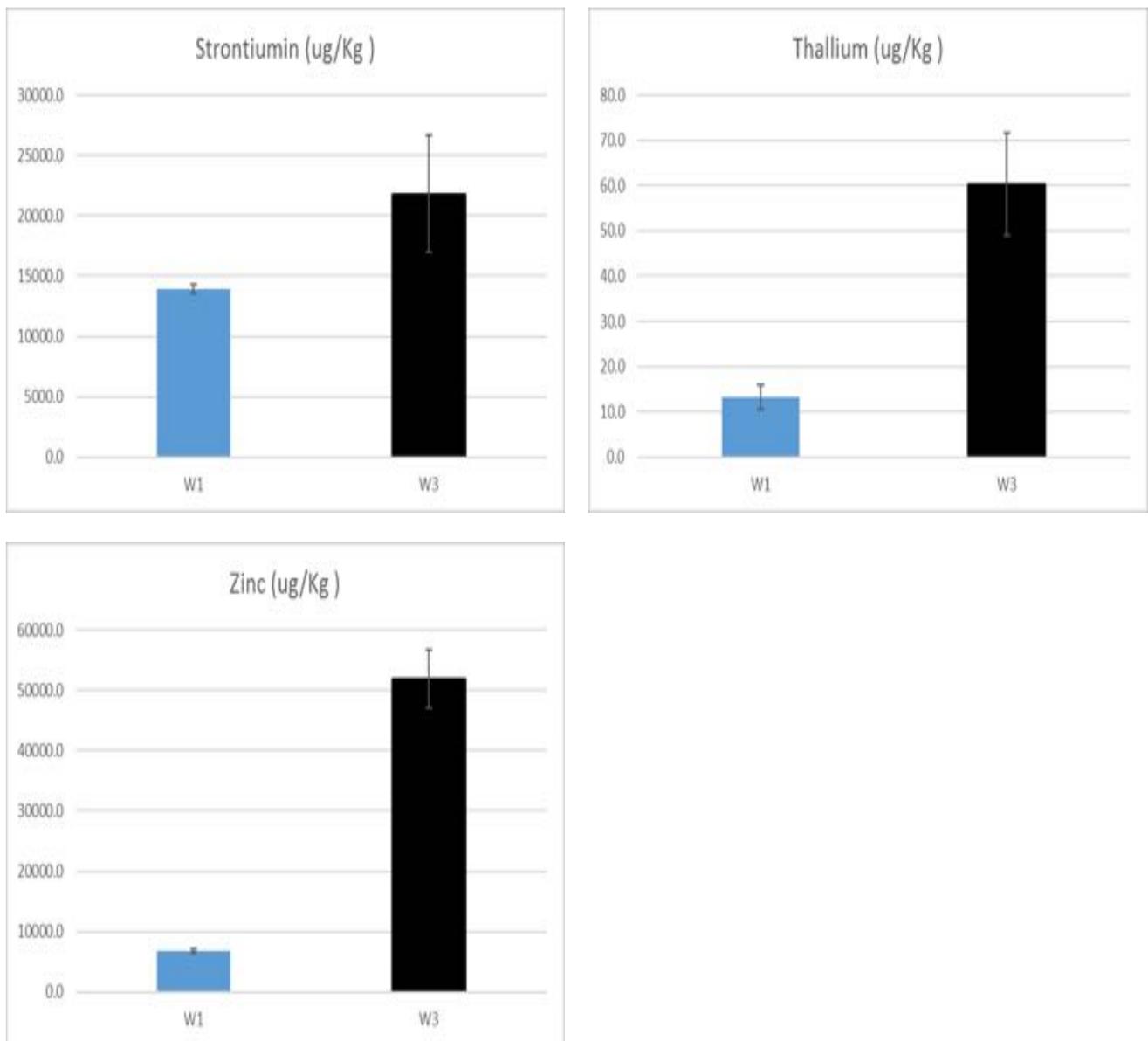


Figure 2. Mean plant tissue results (*Acacia rubida*). Blue is upstream (W1) of the coal mine waste water inflow and black is downstream (W3).

Discussion

This study has shown that one coal mine waste water discharge appears to have created an avenue for increased heavy metal concentrations within the Wollangambe Rivers water column to mobilise to riparian vegetation found within the terrestrial environment. This study could be the first to investigate the mobilisation of metals from a regulated coal mine waste water discharge to terrestrial growing riparian vegetation (*Acacia rubida*). The results of this current study show that there is a strong likelihood that heavy metal concentrations linked to one coal mine waste water discharge are mobilising and being bioaccumulated by one species of riparian vegetation (*Acacia rubida*). The implications of this regulated water column pollution mobilising out of the aquatic environment shows a major contamination issue from the coal mine discharge that is not assessed or managed by Environmental Protection Licenses.

This research has allowed for a better understanding of the broader impacts of the heavy metal contaminants from Clarence Collieries coal mine waste waters being discharged to the Wollangambe River are having on the surrounding terrestrial environment. The implications that the licensed waste water discharge is mobilising to terrestrial riparian vegetation is of major concern. The Environment Protection License process is designed to protect the aquatic environment of waterways which receive coal mine waste waters. Discharge limits set by EPL's stipulate levels of pollutants within the water column of a receiving waterway but do not take into account the surrounding terrestrial environment. Setting pollutant limits to EPL's may well be meaningless if the heavy metals are able to mobilise and bioaccumulate within terrestrial riparian vegetation. This represents a discord in the EPL process which is unsatisfactorily protecting the greater environment from coal mine waste water discharges.

There are many studies investigating water column pollution from metal contamination from a broad range of mining activities. Many investigate the links between metal mining impacts on water chemistry, river sediments and aquatic flora and fauna. The majority of these studies have found that impacted sample locations, from an array of differing metal mining activities, have increased heavy metal contamination of waters and soils worldwide. These heavily contaminated waters and soils have been reported to have increased the metal concentrations within many differing terrestrial and aquatic flora and fauna species (Neff 1984, Sericano et al. 1995, Hill et al. 2000; Amish and Cowx 2000, Wang and Rainbow 2008, Ashraf et al. 2011).

Studies have been conducted on the impacts of metal bioaccumulation from other coal mining activities on terrestrial and aquatic plant and fish tissue with very few investigating the bioaccumulation of metals from regulated coal mine waste water discharges. The majority of the studies have provided evidence to suggest that increased bioaccumulation of metals is occurring in areas subject to current or past coal mining surface working activities (Papagiannis et al. 2004, Atkinson et al. 2007, Ebrahimi 2009, Bharti and Banerjee 2011, Otter et al. 2012, Durães et al. 2014).

Maiti et al. (2015) found the metals Iron, Manganese, Zinc, Copper, Cadmium and Nickel were bioaccumulating in their study of trees growing in coal mine spoils. This is similar to this current study although the order of increase was differing with Nickel and Zinc being two of the three highest recorded increases. Nawad et al. (2015) reported statistically higher concentrations of cobalt in soil and plant material in their study of heavy metal bioaccumulation from chromite mining activities in Pakistan. This is similar to this current study with cobalt found to be the greatest increased metal concentration recorded. Telford et al. 2009 found that riparian vegetation growing along the banks of Bakers Creek, Hillgrove New South Wales Australia recorded antimony concentrations 2 to 3 times higher than riparian vegetation within non-mine impacted sites. These findings suggest that in the right conditions water column pollutants, naturally occurring or not have the ability to be accumulated by terrestrial flora.

Belmer et al (2014) and Wright et al (2017) found water column concentrations of Zinc and Nickel increased in the Wollangambe River downstream of the coal mine waste water discharge investigated in this study. They found that Nickel increased 9311% (Belmer et al 2014) and 15117% (Wright et al 2017) within the Wollangambe Rivers water column. Zinc was found to increase downstream 2571% (Belmer et al 2014) and 2400% (Wright et al 2017).

This study found that Aluminium and Strontium within plant tissue samples (*Acacia rubida*) increased by 22% and 57% which are conservative increases in percentage compared to many of the other metals. Beryllium, Cadmium, Molybdenum, Thallium and Zinc increased within plant tissue sampled (*Acacia rubida*) by 335%, 349%, 326%, 357% and 668%. With much larger increases within plant tissue samples (*Acacia rubida*) for Cobalt and Nickel, increasing by 3060% and 1718% respectively.

Recommendations

It is recommended that further research should be undertaken by the NSW EPA to better assess the implications of heavy metal mobilisation to the terrestrial environment from EPL protected waterways at both actively mined (treated waste water) and inactively mined (untreated waste water). If in fact heavy metal contaminants are leaving the water column of their receiving waterways and mobilising to the terrestrial environment, serious long-term legacy pollutant impacts may persist. Of equal concern is if in fact these water column heavy metals are becoming terrestrial pollutants within terrestrial vegetation the bioaccumulation may be wide spread as these terrestrial flora species are food sources for many more terrestrial fauna species.

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References

- Allen H E, Perdue E M and Brown D S (1993). *Metals in Groundwater*. Lewis Publishers. pp 437.
- Amisah S and Cowx I G (2008). Impacts of abandoned mine and industrial discharges on fish abundance and macroinvertebrate diversity of the upper River Don in South Yorkshire, UK. *J Freshwater Ecology*, vol 15, 237-49.
- Ashraf M A, Maah M J and Yusoff I (2011). Bioaccumulation of Heavy Metals in Fish Species Collected from Former Tin Mining Catchment. *International Journal of Environmental Research*. vol 6 (1) pp 209-218.
- Australian Government, Department of the Environment, Water, Heritage and the Arts (2012). *Australia's world heritage places, Greater Blue Mountains National Park*.
- Belmer N, Tippler C, Davies PJ, and Wright IA (2014) Impact of a coal mine waste discharge on water quality and aquatic ecosystems in the Blue Mountains World Heritage Area, in Viets, G, Rutherford, I.D, and Hughes, R. (editors), *Proceedings of the 7th Australian Stream Management Conference, Townsville, Queensland*, Pages 385-391.
- Department of Environment and Climate Change (2009). *The Vertebrate Fauna of the Wollangambe and Upper Wolgan area*, Department of Environment and Climate Change NSW, Hurstville.
- Durães N, Bobos I, Ferreira da Silva E and Dekayir A (2014). Copper, zinc and lead biogeochemistry in aquatic and land plants from the Iberian Pyrite Belt (Portugal) and north of Morocco mining areas. *Environmental Science Pollution Research*. vol 22 pp 2087–2105. DOI 10.1007/s11356-014-3394-6.
- Ebrahimi M and Taherianfard M (2009). Concentration of four heavy metals (cadmium, lead, mercury, and arsenic) in organs of two cyprinid fish (*Cyprinus carpio* and *Capoeta* sp.) from the Kor River (Iran). *Environmental Monitoring Assessment*. vol 168, pp 575-585. DOI 10.1007/s10661-009-1135-y
- Hill B H, Willingham W T, Parrixh L P and McFarland B H (2008). Periphyton community responses to elevated metal concentrations in a Rocky Mountain stream. *Hydrobiologia*, vol 428, 161-9.
- Jasonmith J F, Maher W, Roach A C and Krikowa F (2008), Selenium bioaccumulation and biomagnification in LakeWallace, New SouthWales, Australia. *Marine and Freshwater Research*. vol 59, pp 1048-1060
- Johnson D B (2003). Chemical and microbiological characteristics of mineral spoils and drainage waters at abandoned coal and metal mines. *Water, Air, and Soil Pollution*. vol 3, pp 47-66.
- Kolaříková K, Stuchlík E, Liška M, Horecký J, Tátosová J, Hardekopf D, Lapšanská N, Hořická Z, Hovorka J, Mihaljevič M, Fuksa J K and von Tümpling W (2012). Long-Term Changes in the Bioaccumulation of As, Cd, Pb, and Hg in Macroinvertebrates from the Elbe River (Czech Republic). *Water Air Soil Pollution*. vol 223, pp 3511-3526. DOI 10.1007/s11270-012-1129-1

- Maiti S K, Kumar A and Ahirwal J (2015). Bioaccumulation of metals in timber and edible fruit trees growing on reclaimed coal mine overburden dumps. *International Journal of Mining, Reclamation and Environment*. vol 30 (3). pp 231-244. DOI: 10.1080/17480930.2015.1038864.
- Miller L L, Rasmussen J B, Palace V P, Sterling G and Hontela A (2013). Selenium Bioaccumulation in Stocked Fish as an Indicator of Fishery Potential in Pit Lakes on Reclaimed Coal Mines in Alberta, Canada. *Environmental Management*. vol. 52, pp72-84. DOI 10.1007/s00267-013-0038-4
- Nawab J, Khan S, Shah M T, Khan K, Huang Q and Ali R (2015). Quantification of Heavy Metals in Mining Affected Soil and their Bioaccumulation in Native Plant Species. *International Journal of Phytoremediation*, vol. 17, pp 801–813. DOI: 10.1080/15226514.2014.981246
- Neff J M (1984). Bioaccumulation of organic micro pollutants from sediments and suspended particulates by aquatic animals. *Fresenius' Zeitschrift für analytische Chemie*, vol 319 (2). pp 132-136.
- Papagiannis I, Kagalou I, Leonardos J, Petridis D and Kalfakakou V (2004). Copper and zinc in four freshwater fish species from Lake Pamvotis (Greece). *Environment international*. vol. 30, pp 357-362.
- Pond, G. J., Passmore, M. E., Borsuk, F. A., Reynolds, L. & C. J. Rose, (2008). Downstream effects of mountaintop coal mining: comparing biological conditions Using family – and genus-level macroinvertebrate bioassessment tools. *Journal of the North American Benthological Society*, vol 27, pp 717-737.
- Reash R J, Lohner T W and Wood K V (2006). Selenium and other trace metal in fish inhabiting a fly ash stream: implications for regulatory tissue thresholds. *Environmental Pollution*. vol 142, pp 397-408.
- Sericano J L, Wade T L and Jackson T J (1995). Trace organic contamination in the Americas: An overview of the US national status and trends and the international mussel watch programmes. *Mar. Pollution Bulletin*. vol 31, pp 214-225.
- Swansburg E O, Fairchild W L, Freyer B J and Ciborowski J H (2002). *Environmental Toxicology and Chemistry*. vol. 21 (12). pp 2675–2684.
- Telford T, Maher W, Krikowa F, Foster S, Ellwood M J, Ashley P M, Lockwood P V and Wilson S C (2009). Bioaccumulation of antimony and arsenic in a highly contaminated stream adjacent to the Hillgrove Mine, NSW, Australia. *Environmental Chemistry*. vol 6, Pp 133–143. doi:10.1071/EN08097
- Otter R R, Bailey F C, Fortner A M and Adams S M (2012). Trophic status and metal bioaccumulation differences in multiple fish species exposed to coal ash-associated metals. *Ecotoxicology and Environmental Safety*, vol 85, pp 30-36
- Wang X W and Rainbow P S (2008). Comparative approaches to understand metal bioaccumulation in aquatic animals. *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology*, vol 148, (4). pp 315-323.
- Wislocka M, Krawczyk J, Klink A and Morrison L (2004). Bioaccumulation of Heavy Metals by Selected Plant Species from Uranium Mining Dumps in the Sudety Mts., Poland. *Polish Journal of Environmental Studies*. vol 15 (5). pp 811-818.
- Wright IA, Belmer N and Davies P J (2017) Coal Mine Water Pollution and Ecological Impairment of One of Australia's Most "Protected" High-Conservation-Value Rivers. *Water, air and soil pollution*, Springer.
- Younger, P L (2004). Environmental impacts of coal mining and associated wastes: a geochemical perspective. Geological Society, London, Special Publication vol 236, 169-209.