IMPACT OF COAL AND COAL SEAM GAS INDUSTRIES ON AQUATIC ENVIRONMENTS

Submitted by

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This thesis is presented for the degree of Doctor of Philosophy

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Declaration

I certify that the work in this thesis entitled "Impact of coal and coal seam gas industries on aquatic environment" has not previously been submitted for a degree nor has it been submitted as part of requirement for a degree to any university or institution other than Macquarie University.

I also certify that the thesis is an original piece of research and it has been written by me. All help and assistance that I have received in my research work and the preparation of the thesis itself have been appropriately acknowledged.

In addition, I certify that all information sources and literature used are indicated in the thesis.

Aal-e ALI (Student id# 43535305)

Date: 10 May 2018

"Verily, all things have We created in proportion and measure."

"O believers do not forbid the good things God has made lawful for you; and do not transgress. Surely God does not love transgressors"

(Holy Quran 54:49 & 5:87)

Acknowledgements

All praise is to God who is most merciful and most beneficent. By His grace, this work has come to completion. I am grateful to my family for their encouragement and faith in my pursuance. I thank them for their support.

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Dedication

To my beloved family and environmentalists

Table of Contents

Abstract

Energy generation and its resource utilization involves processes like the extraction of coal and coal seam gas (CSG) which generate produced water causing possible surface water, groundwater, and sediments pollution. This study aimed on the environmental impact evaluation along with the sustainable developments, particularly in field of coal and coal seam gas production. The study reports the impact of produced water and discharges from coal and coal seam mine's activities on high conservation environments. The objective of the thesis was to investigate chemical contamination of water and sediment along with the composition of / bioaccumulation in inhabitant macroinvertebrates and chlorophyll. The outcome of the objectives was taken as indicators of industrial pollution and environmental impairment.

Extensive review precipitated into identifying the gaps in the reported work on the direct or indirect effects on sustainability of environment under continuous growth in energy consumption and coal and coal seam gas production. The water samples upstream and downstream from the discharge points were tested for water quality index (WQI) in comparison of national maximum admissible concentration (MAC) and their corresponding environmental impacts. Higher contamination of downstream samples was investigated for its toxicity and was used as an additional tool to assess water quality. The assessment culminated into newly proposed Environmental Water Quality Index (EWQI). 'Total Points' from 'Agency for Toxic Substances and Disease Registry (ATSDR)' being the basis for calculation validated EWQI as better index for impact evaluation. EWQI led to better trend in the impact evaluation of coal and coal seam gas mining activities on surface water quality. Similarly, the sediment samples were analysed for their size exclusion behaviour and contaminants adsorption. The contaminant analysis output was

scrutinised on the basis of sediment quality guideline value (SQGL) for impact evaluation. It was also subjected to impact exploration by finding mean effective range median quotient (ERMQ) and environmental toxicity quotient (ETQ). The contaminants' toxic effect was investigated on the inhabitant invertebrates' taxa, bioaccumulation and chlorophyll.

The study revealed that impacted water downstream of the mine discharge points contained higher metal content than the upstream reference locations above the Australia and New Zealand Environment Conservation Council and international water quality guidelines for freshwater stream. The major outliers to the guidelines were aluminium (Al), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn). Toxicology indices of metals present in industrial discharges were used as an additional tool to assess water quality which lead the newly proposed Environmental Water Quality Index (EWQI) to better trend in the impact evaluation of coal and coal seam gas mining activities in environmental and health impact assessment.

Various contaminants were measured to determine the sediment quality and arsenic, nickel, and zinc were found exceeding the Australian and New Zealand Environment and Conservation Council (ANZECC) guidelines. Degree of contamination (C_d), geoaccumulation index (I_{geo}), enrichment factor (EF), pollution load index (PLI) and sediment environmental toxicity quotients' increment in downstream sediment with the toxicology indices of metals present were used as tool to compare the level of environmental impact. Coal mining impacts were found to be substantially more than the coal seam gas production impact, mainly attributed to the different wastewater discharge licensing requirements which can be used as an additional model to assess the contribution of industrial and mining activities on aquatic environments.

Investigation of macroinvertebrates and chlorophyll as indicators of industrial pollution and environmental impairment revealed change in abundance, taxonomic richness, and pollution sensitive macroinvertebrate groups. Aquatic invertebrates can absorb metals from water and they can serve as an indicator of ecotoxicological impacts of mining. A statistical evaluation of aquatic life and correlation of contaminant with the presence of community in ecosystem was assessed. A non-uniformity in the changes were observed indicating difference in tolerance level of different invertebrates.

Finally, investigating the metal content in macroinvertebrates as indicators of pollution and environmental impairment revealed that certain metals were elevated within some of the aquatic invertebrate species indicating the presence of metal contamination as a function of both the ability of an individual species to regulate the metal intake and the concentration of metals in the environment. Elemental composition correlation indicated the phenomenon of filtering out Cr, Mn, Fe, Ni, and As for invertebrate survival. Certain metals, such as Al, Ti and Zn, were found to be in higher quantity in the invertebrates collected downstream the mining discharge locations.

The objective of this thesis was to substantiate the effect of coal and coal seam gas production on the environment. The possibility of the environmental impairment with the type of processes involved in the production, waste generation and their disposal procedure were studied. The study provides the novel ideas for the need of thorough monitoring and licencing procedures for the sustainable industrialization. A baseline of the industrial constituents was established to understand geochemical process, resource utilization, and need for the revision of the coal mine run off management. The need for implementation of robust monitoring procedure was concluded.

List of Publications

The following is a list of publications derived from this thesis with declaration of authorship contributions outlined in Appendix C.

Journal Articles

A. Ali, V. Strezov, P. Davies and I. Wright *Environmental impact of coal mining and coal seam gas production on surface water quality in the Sydney basin, Australia.* Environmental Monitoring and Assessment (2017) 189: 408, DOI 10.1007/s10661-017-6110-4.

A. Ali, V. Strezov, P. Davies and I. Wright *River sediment quality assessment using sediment quality indices for the Sydney basin, Australia affected by coal and coal seam gas mining.* Science of the Total Environment (2018) 616: 695, DOI: 10.1016/j.scitotenv.2017.10.259.

A. Ali, Daniel R. Sloane and Vladimir Strezov *Aquatic life and environmental impairment by coal mine discharge in the Sydney region*, International Journal of Environmental Research and Public Health, (2018), 15: 1556.

Aal-e Ali, Grant C. Hose, Peter J. Davies, Armand J. Atanacio, Vladimir Strezov *Effect of coal and coal seam gas mining on elemental composition of aquatic invertebrates in the Sydney region* (To be submitted)

Peer-reviewed Conferences

A. Ali, V. Strezov, P. Davies, I. Wright, T. Kan *Impact of Coal Mining on River Sediment Quality in the Sydney Basin, Australia,* International Journal of Environmental, Chemical, Ecological, Geological and Geophysical Engineering Vol:11, No:4, 2017 pp 273-242. World Academy of Science, Engineering and Technology 19th International Conference on Environment and Water Resource Management (ICEWRM 2017) April 18 – 19, 2017, Paris, France.

A. Ali, Grant C. Hose, V. Strezov *Coal mine discharge impacts on aquatic invertebrates in the Sydney region,* ISER- 206th International Conference on

Chemical and Environmental Science (ICCES) Brisbane, Australia 4th-5th August 2017.

Introduction

1.1 Problem Statement

United Nations General Assembly adopted a resolution (A/70/L.I) on 25 September 2015 titled "Transforming our world: the 2030 Agenda for Sustainable Development" (UN, 2015). Based on the resolution United Nation has made a call for all countries to protect the planet in due process of development and prosperity, which is called 'Sustainable Development Goals (SDGs)' (Lu et al., 2015). United Nations Framework Convention on Climate Change is the primary international, intergovernmental forum for negotiating the global response to climate change which outlined 17 Sustainable Development Goals as follows:

Goal 1. End poverty in all its forms everywhere

Goal 2. End hunger, achieve food security and improved nutrition and promote sustainable agriculture

Goal 3. Ensure healthy lives and promote well-being for all at all ages

Goal 4. Ensure inclusive and equitable quality education and promote lifelong learning opportunities for all

Goal 5. Achieve gender equality and empower all women and girls

Goal 6. Ensure availability and sustainable management of water and sanitation for all

Goal 7 Ensure access to affordable, reliable, sustainable and modern energy for all

Goal 8. Promote sustained, inclusive and sustainable economic growth, full and productive employment and decent work for all

Goal 9. Build resilient infrastructure, promote inclusive and sustainable industrialization and foster innovation

Goal 10. Reduce inequality within and among countries

Goal 11. Make cities and human settlements inclusive, safe, resilient and sustainable

Goal 12. Ensure sustainable consumption and production patterns

Goal 13. Take urgent action to combat climate change and its impacts*

Goal 14. Conserve and sustainably use the oceans, seas and marine resources for sustainable development

Goal 15. Protect, restore and promote sustainable use of terrestrial ecosystems, sustainably manage forests, combat desertification, and halt and reverse land degradation and halt biodiversity loss

Goal 16. Promote peaceful and inclusive societies for sustainable development, provide access to justice for all and build effective, accountable and inclusive institutions at all levels

Goal 17. Strengthen the means of implementation and revitalize the Global Partnership for Sustainable Development

A careful monitoring approach has been placed by UN Secretariat through International Money Fund, Organization for Economic Co-operation and Development, and the World Bank (UN, 2004,). However, individual countries are taking different approach suitable to their circumstances to achieve the sustainability goal (Wellmer and Becker-Platen, 2002). Sustainable development in mineral industries are achieved by putting all the SDGs in place with emphasis on seven of them (de Mesquita et al., 2017). Australia is one of the active countries when it comes to environment. A 'No New Coal Mine' campaign was launch by non-government organization to make sure that the SDGs are implemented (TAI, 2017). Although China and USA adopted temporary ban on new coal mine, India and Australia did not.

It is matter of great concern that increasing energy demand is causing compromises in environmental sustainability through energy resource production (Berge et al., 2015; Wang et al., 2017; Sarkis and Zhu, 2018). Conventional fossil fuel is still in extensive use causing environmental impacts (de Vallejuelo et al., 2017; Baykara, 2018) despite commitments for transition to low carbon energy sources (Hildingsson & Johansson, 2016; Shen and Xie, 2018). It has been estimated that the demand for coal production may increase 90% by 2022 (IEA, 2017). Energy produced by coal is 60% of the total energy production in Australia. The seams present in coal bed are filled with gas called coal seam gas (CSG) which are also extensively being used as energy source. It is expected that half of all natural gas produced in United States will come from unconventional sources by 2030 (EIA, 2007). CSG gases are trapped in underground coal seams which are taken out by drilling and used as energy source. To release the gas trapped in the coal seams variety of chemicals and techniques are used which cause potential hazard to the human health and environment (Navi et al., 2015). A typical water lifecycle is illustrated in Figure 1.1.

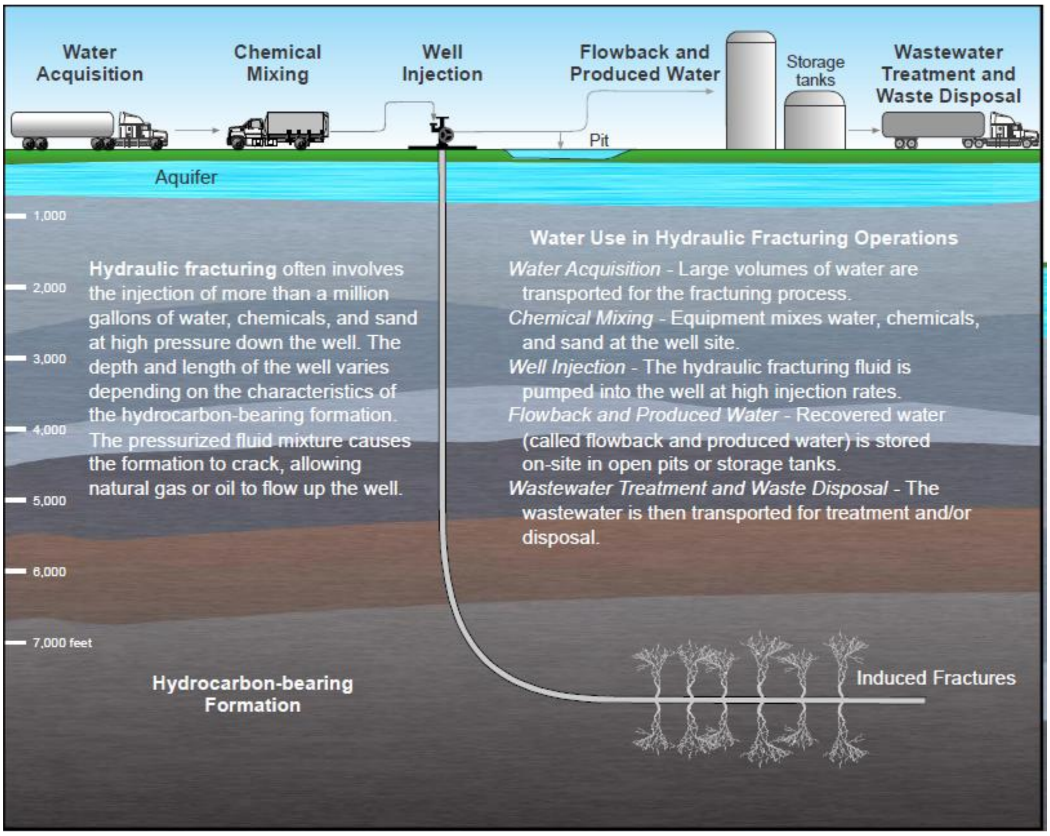

Figure 1.1: Water life cycle in hydraulic fracturing (USEPA, 2011).

Coal seam gas (CSG) is one of the most attention seeking energy resources (Hamawand et al., 2013). Its production process generates significant amounts of produced water, which comes out on the surface and increases the possibility to mix with and contaminate the surface water (He et al., 2018; Hildenbrand et al., 2018). The contamination could occur through surface spill or run-off due to variety of failures in the process. The possible population exposure pathway to the mine water is depicted in Figure 1.2, where contaminated water comes to the environment either directly or through the leakage during treatment process.

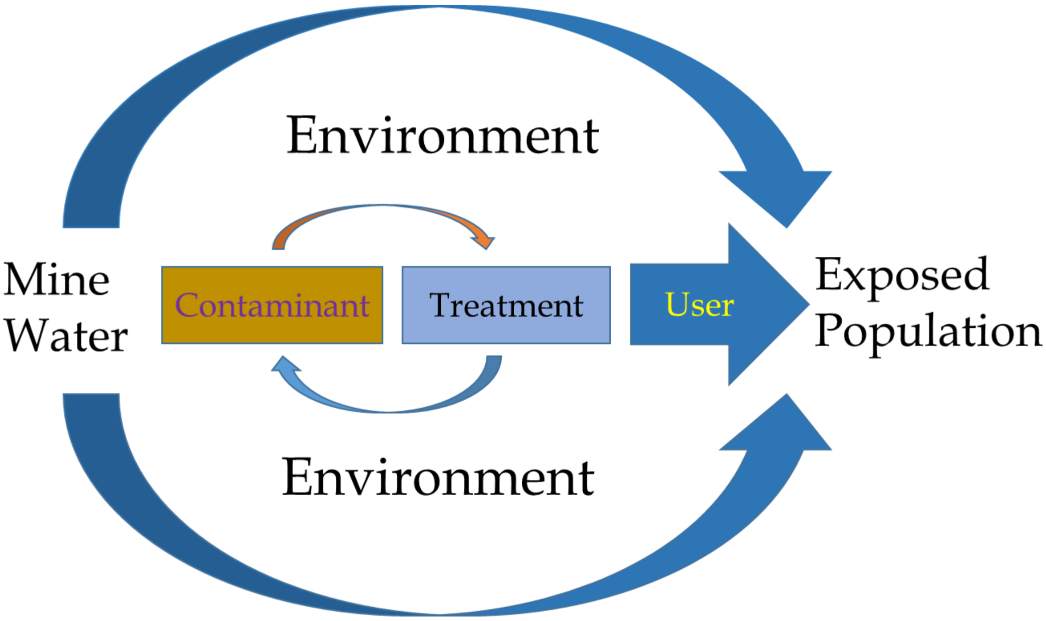

Figure 1.2: Mine water exposure pathway

Mine water is classified into three categories based on Global Acid Rock Drainage (GARD) Guide, which is tabulated in Table 1.1 with its description (Opitz and Timms, 2016). Mineral Council of Australia (MCA) being part of Water Accounting Framework (WAF) took a more all-inclusive approach to classify into three groups based on chemical parameters like pH, TDS, toxic constituents, and biochemical constituents, which is tabulated in Table 1.2 with the description (MCI, 2014).

Table 1.1: The GARD Guide mine water classification (Verburg et al., 2009)

GARD Guide classification	Class description	Thresholds
Acid Rock Drainage / Acid and Metalliferous Mine Drainage	• Acidic pH • Moderate to elevated metals • Elevated sulphate	• pH < 6
Neutral Mine Drainage (NMD)	• Near-neutral to alkaline pH • Low to moderate metals • Low to moderate sulphate	• pH > 6 • Sulphate < 1,000 mg/L • TDS < 1,000 mg/L
Saline Drainage (SD)	• Neutral to alkaline pH • Low metals (only moderate Fe) • Moderate sulphate, Mg and Ca	• pH > 6 • Sulphate > 1,000 mg/L • TDS > 1,000 mg/L

Some classifications are based on mine water chemistry related to distance from pollutant formation, based on deposit, chemical-ecological classification, environmental pressure based classification, and other, which were used to establish an environmental quality index (EQI) (Banks and Banks, 2001; Davies et al., 1997; Puura and D'Alessandro, 2005). In Australia some mines have developed site specific trigger values based on ecotoxicity study of local invertebrates which has been compiled in ANZECC 2000 (Heritage, 2012)

Hydraulic fracking, a technology used for CSG production, causes local and regional stress on the ground in many ways, especially subsidence and frictional instability towards earthquakes (Segall, 1989). The earthquake link to fracking was evident in the studies, which led USEPA to recommend a moratorium on fracking water injection in earthquake prone areas (Bushkin-Bedient et al., 2018). Coal production and coal seam gas (CSG) production both are associated with the negative impacts on environment through the water, sediment and air contamination (Choudhury et al., 2017; Silva et al., 2017; Shang et al., 2018). The impact risk could be through transportation spill, drilling site discharge, casing failure, fracture leak to aquifer, wastewater discharge, and other mechanisms. It has been reported that more than 2500 hydrofracking products are in market to increase the productivity of CSG, which are known to affect respiratory, gastrointestinal, neurological, immune, cardiovascular, renal and endocrine systems (Waxman et al., 2011; Holloway, 2018). Sulphur containing materials encounter moisture and air during the mining process generating sulfuric acid known as acid mine drainage (AMD) which dissolves rocks generating contaminant metal ions. All the contaminants may end up in surface water and may be settled with the sediment as a contaminant storage adversely affecting inhabitants.

Table 1.2: The WAF mine water classification (MCA 2014)

WAF classification	**Class description**	**Thresholds**
Category 1 High water quality	Minimal effort necessary to achieve drinking water quality	• pH = 6 – 8.5, TDS < 1,000 mg/L • No turbidity after sedimentation, no/traces of pesticides/herbicides or harmful constituents • Coliforms < 100 cfu/100ml
Category 2 Medium water quality	Moderate treatment necessary for individual constituents	• pH = 4 – 10, TDS = 1,000 – 5,000 • Coliforms > 100 cfu/100ml
Category 3 Low water quality	Significant treatment necessary to achieve satisfactory water quality	• pH < 4 or > 10, TDS > 5,000 mg/L

Energy resource production being hazardous caught attention of environmentalist and researchers. NSW Government put all the precautionary measures by evaluating the chemicals used by the year 2012 (DEE, 2017)

1.2 Aims and oobjectives of the study

The aim of the study is to achieve benchmark of chemical constituents at individual sites due to mine water discharge and its effect on inhabitants. The objectives of this thesis are to study:

(i) The impact of coal and coal seam gas production on surface water quality

(ii) Sediment quality impairment by coal and coal seam gas industries and

(iii) Mine impact assessment using macroinvertebrates taxa and metal content.

1.3 Outline of the thesis

The thesis is outlined as thesis by publication with four chapters in addition to the Introduction, Literature Review, Conclusions, and Recommendations chapters starting from Chapter 1 as introduction. Furthermore, two conference papers and declarations are added to these 7 chapters as appendices.

Chapter 2 is a review of the environmental concern and the processes involved in production of coal and coal seam gas. A progressive development in the production technique and its commercial and environmental concerns were discussed. This included the possible physical and chemical disturbances caused by hydraulic fracking processes to the natural seams and aquifers. Based on the environmental, social and economic three-dimensional approaches of sustainability recommended by International Union for Conservation of Nature (IUCN), the industrial development, and its impact on the environment and inhabitants was reviewed. The present and future of energy generation and use of coal and coal seam gas for its production were highlighted with the available statistical data to reflect the environmental impact with the growing energy demand. The emphasis was given to the long-term effect on the resource, vegetation, land, inhabitants, atmosphere, and human health.

Chapter 3 accounts experimental work of the impact of coal and coal seam gas production on the water quality. Variety of water quality indices of different international and national standards were applied to the surface water collected from the stream before the industrial discharge mixed with the stream. Based on the toxicity of contaminants and human health a new environmental water quality index (EWQI) was proposed. This chapter was published as an article A. Ali, V. Strezov, P. Davies and I. Wright *Environmental impact of coal mining and coal seam gas production on surface water quality in the Sydney basin, Australia.* Environmental Monitoring and Assessment (2017) 189: 408, DOI 10.1007/s10661-017-6110-4.

Chapter 4 represents an experimental evaluation of sediment of the same study area where surface water was studied. Considering the sediment as temporary reservoir of contaminant its quality was assessed with the sediment quality guideline values (SQGVs) and the health concern based on effective range low/median (ERL/ERM) trigger values and threshold/probable effect level (TEL/PEL). The work was published as A. Ali, V. Strezov, P. Davies and I. Wright *River sediment quality assessment using sediment quality indices for the Sydney basin, Australia affected by coal and coal seam gas mining.* Science of the Total Environment (2018) 616: 695, DOI: 10.1016/j.scitotenv.2017.10.259.

Chapter 5 related the experimental evaluation of the effect of change in the water and sediment quality on the taxa. The statistical changes of variety of invertebrates were studied and correlation was revealed. The chapter is ready for the publication as A. Ali, Daniel R. Sloane and Vladimir Strezov *Aquatic life and environmental impairment by coal mine discharge in the Sydney region*, International Journal of Environmental Research and Public Health, (2018), 15: 1556. Chapter 6 reveals the result of elemental composition of the biota. A possible bioaccumulation trend with the change in the environment due to coal and coal seam gas production. This chapter has been submitted for the publication as Aal-e Ali, Grant C. Hose, Peter J. Davies, Armand J. Atanacio, Vladimir Strezov *Effect of coal and coal seam gas mining on elemental composition of aquatic invertebrates in the Sydney region,* Chapter 7 provides the limitations, conclusions and recommendations signposted by the study.

Appendix A represents an evaluation of sediment by Fourier transform infra-red spectroscopy (FTIR) and thermogravimetric analyser (TGA) along with chemical contamination analysis. The work was published as A. Ali, V. Strezov, P. Davies, I. Wright and T. Kan *Impact of Coal Mining on River Sediment Quality in the Sydney Basin, Australia*. International Journal of Environmental, Chemical, Ecological, Geological and Geophysical Engineering Vol:11, No:4, 2017, World Academy of Science, Engineering and Technology, ICEWRM 2017 : 19th International Conference on Environment and Water Resource Management, April 18-19, 2017 Paris, France. (scholar.waset.org/1999.6/10006635)

Appendix B is related to the environmental impact evaluation based on the taxa changes. The chapter was published as Aal-e Ali, Grant C. hose and Vladimir Strezov *Coal Mine Discharge Impacts on Aquatic Invertebrates in The Sydney Region*, in Proceedings of International Society for Engineers and Researchers (ISER), International Conference on Chemical and Environmental Science. Date 4th-5th August, 2017, Venue: Brisbane, Australia. ISBN: 978-93-86083-34-0

Appendix C is graphic presentation of the site locations and sampling which were not included in publications.

Appendix D is declaration of authorship contribution in all the research publications.

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A Review of Impact of Coal and Coal Seam Gas Industries on Aquatic Environment

2.1 Introduction

All industrial development should be restricted to the development that meets the needs of the present without compromising the ability of future generations to meet their needs. It should follow the International Union for Conservation of Nature (IUCN) proposed three-dimensional approach of sustainability based on environmental, social, and economic approaches. Sustainable development should demonstrate the three objectives integrated to keep the balance called circle of sustainability (Figure 2.1).

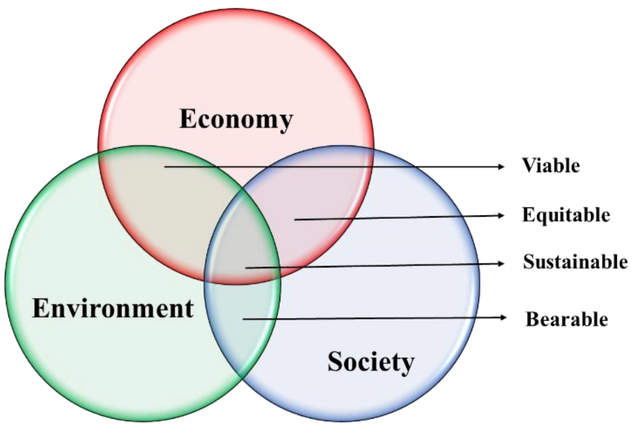

Figure 2.1: Circle of sustainability

It is necessary to study the reasons behind the industries, detail of the industrial processes, environmental impact of the processes, mechanism of the impact, and possible change in processes for the rectification of environmental impairment to maintain sustainable environment. It is important to record the processes and findings in continuation with the industrialization to achieve sustainable environment and human health.

One of the major sectors that define industrial development is the energy sector. Continuous growth in energy resource utilization, industrialization, and other anthropogenic activities contribute to more than 50% of change in the earth surface (Gao et al., 2017). To meet all the energy needs, the conventional fossil fuel, such as coal and natural gas, are still used for required energy generation (Chong et al., 2016) despite the international commitments to develop renewable energy sources to reduce the environmental threat from global warming and climate change (Hildingsson and Johansson, 2016). Global industrialization and urbanization has resulted in continuous increase in the energy demand causing exponential increase in energy resource production. Energy resources, like coal and coal seam gas (CSG), productions are associated with many environmental and health concerns (Phelan et al., 2017; Gao et al., 2017). It is evident that the increase in global coal consumption has increased by 64% in the period from 2000 to 2014. Furthermore, the coal consumption is expected to supersede the natural gas consumption by 2020 (IEA, 2015). In Australia coal is used to produce 60% of total energy generation which is further expected to grow by 42% in the period from 2015 to 2050. Beside coal production coal seam gas production has been exponentially increasing with time to meet the energy demands. Developing world economies led by China anticipate almost 90% of demand growth due to annual predicted consumption of 4,000 billion cubic meters (bmc) by 2022 (IEA, 2017). China alone would need 40% of global demand growth. US is taking the gas scenario as the second wave of the shale revolution and a tremendous increment in the production is expected to the level of 40% of global production growth. However, this growth is expected to be initially led by Australia and a thorough study of environmental impacts is highly recommended. Although the renewable energy consumption is expected to increase by 2%, the conventional gas production increment is expected to increase by 2.7% a year (BREE, 2014). It is known that the use of fossil fuels is harmful for the flora and fauna of the surrounding environment as the production and processing plants of these fuels emit pollutant gases and excrete hazardous effluents which contaminate the nearby water bodies, significantly affecting the aquatic organism.

Coal production and mine fire generate pollutants like polynuclear aromatic hydrocarbon (PAH) (Hofmann et al., 2007), methane gas (Beckmann et al., 2011), carbon monoxide, sulphur and nitrogen oxides (SO_X and NO_X) (Pandey et al., 2018), particulate matter (Richardson et al., 2018), and trace elements (Guo, 2018). Global warming caused by carbon dioxide and methane emissions is directly and indirectly linked to the coal mining and consumption. It is documented that the iron sulphide (pyrite) is abundant in coal deposits. It exists naturally in association with other elements, such as As, Bi, Cd, Co, Cu, Ga, In, Hg, Mo, Pb, Re, Sb, Se, Sn, Te and Zn (Spears et al., 1994). Presence of all constituents in downstream of the surface water could be used as indicator of leakage from the coal mine. Coal seam gas production generates significant amount of toxic water, contaminating the surrounding water bodies and sediments. It has been reported that these contaminated sites contain high sodium (Na^+), high bicarbonate (HCO_3^-), high chloride (Cl^-), low calcium (Ca^{2+}), low magnesium (Mg^{2+}), and low sulphate (SO_4^{2-}). In addition to this, sodium adsorption ratio (SAR) and high total dissolved solids (TDS) have also been in water contaminated by coal seam gas production (Wang et al., 2012). Depth and location of the coal seam also affects the change in the produced water (Hamawand et al., 2013). Produced water storage and transfer to transient channels have shown drastic changes in ecological and environmental conditions of the rivers and ponds (Sivanpillai & Miller, 2010).

Energy generation and water consumption are so interdependent that a term Water-Energy Nexus (Raucher et al., 2008) is used for the relationship which is seen in thermoelectric power generation, refining of fuels, biofuel production, hydraulic fracturing, waste water desalination, pumping, stripping, treatment, and distribution (Griffiths-Sattenspiel & Wilson, 2009; Rothausen & Conway, 2011). With this nexus the impact on water by energy generation is obvious, which is of extreme concern due to its importance in life. Produced water generated in coal seam gas and coal production are discharged into the waterways contaminating surface water and sediments (Alvarez et al., 2011; Nghiem et al., 2011) and, overtime, these waterways show rising acidity, high metal concentration, and inhospitable environments.

Moreover, coal mines release sulphur rich minerals into water which produces sulphuric acid after combining with atmospheric oxygen, contaminating the water and sediments considerably (Jacobs et al., 2014; Matsumoto et al., 2016; Choudhury et al., 2017). Water and sediment quality assessments have been carried out in variety of ways as individual contaminants analysis and their comparisons have been made with the published standards, water quality index, sediment quality guideline values (SQGVs), bioaccumulation, and inhabitants' population indices (Birch, 2018). The studies demonstrated that the aquatic inhabitants in contaminated water and sediments were adversely affected (Smith et al., 2009)(Vu et al., 2017). It has also been noticed that metal contamination has a great impact on the aquatic ecosystem as the heavy metals discharged by coal mines can be consumed by the living aquatic organisms (Mishra &

Shukla, 2016). The adsorbed metal on sediment (Alvarez et al., 2011) becomes the ultimate sink for trace metals and affects the living organisms on the coastal areas (Mokwe-Ozonzeadi et al., 2018). However, certain species have their own system to maintain the intake of contaminants and constant accumulation of trace metals in these species continues, irrespective of the available trace metals in the water system (Johnstone et al., 2016). Dissolved material in water has its own effect on the inhabitants' colony. It is reported that mine water salinity affects the algae and duckweed negatively (Smith et al., 2009). At the same time in some cases increase in salinity due to discharge can be tolerated by the taxa (Bailey et al., 2002). The varying scenarios may affect differently the invertebrate taxa which may lead to high or low abundances. It has been reported that salinity increment causes decrease in richness and density of invertebrates (Bunn & Davies, 1992).

The macroinvertebrate taxa do not show consistency in essential or non-essential trace element accumulation patterns for different sites (Karimi & Folt, 2006). Reportedly, coal waste exposes the aquatic invertebrates to large number of potentially toxic metals and metalloids (Rowe, 2014), which is considered as global environmental problem (Rath et al., 2009) due to their bioaccumulation in inhabitants (Rath et al., 2009). Bioavailable contaminants assessment (Corbi et al., 2011) and stream assessment (Worthen, 2002) can easily be pursued with the knowledge of living organisms because of the element and taxa specific pattern (Lavilla et al., 2010). Even closely related taxa differ in bioaccumulation pattern of trace elements (Poteat et al., 2013). This pattern also changes with the sediment grain size (Worthen et al., 2004). The pattern is now being used as tracer to investigate biomagnification of contaminants (Cui et al., 2011) and mesotrophic to eutrophic classification of impaired water with bacterial blooms indication (Bazán et al., 2014) based on trace element intake.

The proposed work is to evaluate the impact of coal and coal seam gas mining on water and sediment quality, assess the impact on taxa of inhabitants, and bioaccumulation of contaminants in biota. The water and sediment quality assessment would be made by calculating different indices related to water and sediment quality. Relatively improved new indices with more sustainability impact would be proposed based on the statistical evaluation of the findings and health hazard indicators.

2.2 Coal production

Coal is a predominant energy source in the world and worldwide coal production has continuously increased (Wang et al., 2018). Variety of energy sources were used with changing priority in different periods, however, coal had its evergreen priority all the time. Even after environmental awareness, sustainability problem, and green energy revolution, its production was exponentially increased since 2000 and its consumption is still the second highest to oil in comparison to all global primary energy resources (BP, 2017). Its production goes back thousands of years, for example, the use of coal has been reported by archaeological evidence as early as approximately 3490 BC in China (Dodson et al., 2014), however, its first user and period of use as energy source is not clear. It has been reported that Romans were making use of coalfields in Roman Britain in late second century (Smith, 1997), with its use increasing substantially with the Industrial Revolution. In Australia coal mining has been recorded since August, 1797 (Statistics, 1909). Machines were introduced in Australian coal mines in 1830s while proper training of mining technology in Australia started by establishing school of mine in 1870 (Birrell, 2005).

Coal is the leading energy source in most of the countries. The increase in coal consumption globally in the period from 2000 to 2014 was 64% (Council, 2016). Countries like China, India, Australia, Indonesia, South Africa, and Poland heavily rely on coal for electricity production. Coal is selectively extracted by either open cut or underground methods depending on the depth of coal availability. Nearly 50% of world's deposits are flat and of commercial importance, with very few seams of even thickness and wide horizontal spread which is convenient for open cut mining (Council, 2016). When coal is nearer to the surface, it is more convenient and economic to extract by open cut mining method (Patterson, 2016). In contrast, complicated faults containing deposits with numerous irregular seams at varying depth are more conveniently extracted by underground mining. The ground above the coal seam, called over burden, is removed using earthmoving equipment after blasting into the drilled holes in the ground. The coal strip exposed after the overburden removal, called block, is again drilled and blasted depending on its hardness. The blasted coal is directly loaded for transportation (Hitzman et al., 2007). This technique recovers almost 90% of the coal deposit. Underground mine is preferred when the coal strips are deep underground and removal of burden is uneconomical. There are two major techniques used in underground mining, Room-and-Pillar Mining and Longwall mining. Room-and-Pillar Mining (bord and pillar) is simply the extraction of coal by making space and leaving the block of coal pillar to support the roof. This technique is used only up to 1,000 feet deep mining as it needs to leave larger pillars to support the roof. This extracts coal by creating parallel tunnels and cutting them at right angles by tunnelling, leaving the pillars to hold the roof. Bord and pillar system of extraction was introduced in 1828 and not much technological advancement was made until Australian Kerosene Oil and Mineral Company Limited introduced long wall mining system in 1880 (Davies & Lawrence, 2015).

Longwall mining can be considered as the second phase of the bord and pillar mining, where a large block of coal is totally removed and the mine roof is allowed to collapse. This allows for higher productivity and higher coal recovery. However, a large initial budget for the advanced equipment and subsidence development (Wright et al., 2015) can be considered as a disadvantage of this technique. Roof top collapse is a safety hazard as many casualties have been reported in the past (Shi & Xi, 2018). Nearly 47% of mine casualties are due to roof collapse. Mining method, mine location, coal bed, rock strength, roof span, seasonal patterns, seam height and mine size all affect the roof collapse. However, the roof support technique was the most frequent cause of the collapse. Intrinsic and standing supports are used to minimise the accidents (Mark & Barczak, 2000). Roof support depends on the conditions and it may perform with different outputs depending on ground, applied load, and support characteristics. Roof fall rates are higher in deeper mines in general, probably due to larger stress. Geological variation, horizontal stress, overwide intersection, and quality of roof bolt installations are important factors affecting the roof stability (Molinda et al., 2000).

Coal body varies in individual piles and seam thickness. In opencast (open cut) mining the seam thickness of 0.5 to 1.0 m is considered as workable, otherwise drilling and blasting would lead to additional cost. A study of Surat Basin indicated the average coal bed of less than 30 cm and seam thickness of up to 10 metres has a deposit of over 2500 metres (Morris & Martin, 2017; Exon, 1976). The structure continuity cannot be assured as its quality may degrade from coal to clay rich facies. Inter-relationship and connectivity of facies are important structures to understand the safety precaution in mining processes. The deposition in alluvial plain has been reported to be in the form of sandstones, siltstones, claystones, carbonaceous mud stone, and coals. The origin of coal and the processes involved have been studied to facilitate the decision making for mining investments. Coals are classified by rank which is simply a degree of transformation and can be considered as measure of coal's age. With time, the transformation takes place from its original state to the product with more heating value and higher fixed carbon content. Volatile matter content decreases with time and carbon fixation. The coal found in wetland environments are groundwater fed and called rheotrophic (Keddy, 2010). In Australia, coal was formed in the Middle Jurassic period, Aalenian Bathenian, and Callovian Kimmeridgian (Martin et al., 2013). Most of these coals are bituminous, perhydrous, and of low rank having high volatile content (Scott et al., 2007). For gas production perspective connectivity integration is of high importance which has special relation with depositional system in which geometric elements and facies association leads to guiding static geomodels. In Australia several seams exceeded 67.4 km^2 of block boundary and a large gas reserves are trapped in the coals.

The ten largest coal producing countries are China, India, United States, Australia, Indonesia, Russia, South Africa, Germany, Poland, and Kazakhstan. China's production was estimated to be 3.2 billion tonnes annually, India's 708 million tonnes, United States' 683 million tonnes and Australia's 509 million tonnes, which is 10% of world production by approximately 100 private mines (EnerData, 2017). The major consumption of coal for energy generation is in Southeast Asia and coal energy mix projection depicted in Figure 2.2 indicates the coal consumption increment to exceed the natural gas consumption by 2020 (IEA, 2015). Coal consumption for electricity generation in Australia has always been high and more than 60% of electricity is generated by coal causing significant environmental impacts. Land disturbance, mine subsidence, dust and noise pollution, and rehabilitation problems are the major concerns of coal production.

Australia has surplus of coal in comparison to its needs and has continuously increased its production to meet the market demand of increasing economies of Asia. Energy consumption in Australia is expected to grow 42% in the period from 2015 to 2050 with electricity growth expected to be 30% (BREE, 2014). Coal is recorded for the 62% of total electricity generation in Australia which is expected to rise to 70%. Coal is going to remain the highest energy resource for the near future with the increment in use of 0.8% per year.

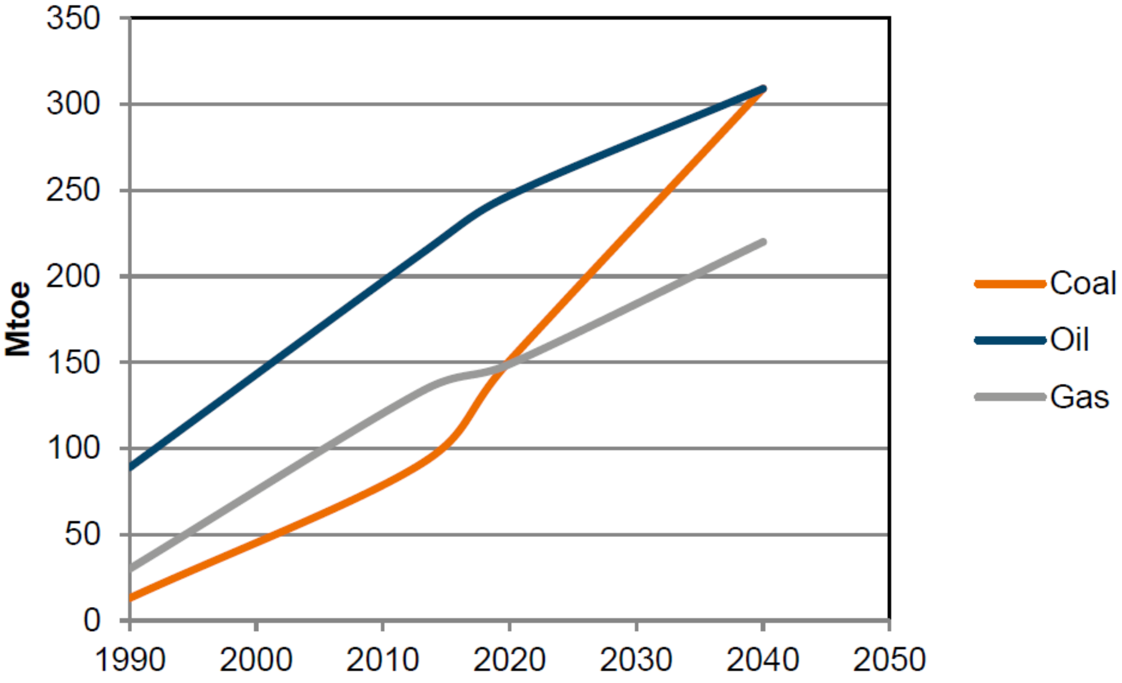

Figure 2.2: Primary energy demand by fossil fuel in Southeast Asia, 1990-2040. Source: (IEA, 2015)

Many environmental considerations have emerged due to global energy consumption. Historic evidence of the environmental impacts from coal mining and nuisances to neighbours has been recorded as early as in 1620 (Levine & Wrightson, 1991). Coal production and mine fire generates pollutants like polynuclear aromatic hydrocarbons (PAHs) (Hofmann et al., 2007), methane gas (Beckmann et al., 2011), carbon monoxide, sulphur and nitrogen oxides (SO_X and NO_X) (Pandey et al., 2018), particulate matter (Richardson et al., 2018), and trace elements (Guo, 2018). Global warming caused by carbon dioxide and methane emissions is directly and indirectly linked to the coal mining and consumption. Water and sediment contamination studies have been taken as environmental impact evaluation in due course of global research. A report published by the Chief Scientist of Australia found coal mining resulted in the complete transformation of the Australian eco-systems, modulating vegetation, food-chain topologies, and geomorphology among other factors that resulted in environmental and economic burden, shown in Figure 2.3 (Water NSW, 2018).

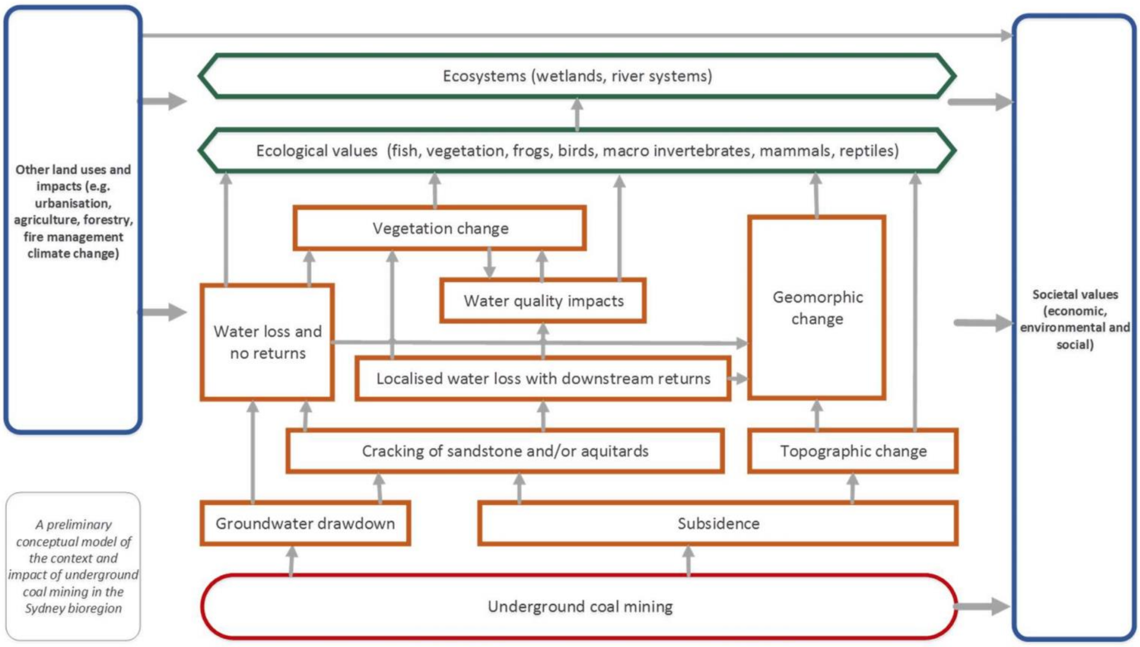

Figure 2.3: Impacts of underground coal mining Source: (Water NSW, 2018)

The levels of heavy metals in river sediments are being used to determine the contribution of key social and political events on environment by reconstructing with the changes in metal concentration in sediments (Wang et al., 2015). Environmental and social impacts associated with the mining industry remain impacted by both current and abandoned mines, where rehabilitation and mine closure has not been undertaken adequately. The minerals present in the mines can be dissolved and transported away from the site when exposed to stormwater or groundwater, impacting adversely on downstream waterways (Younger, 2004).

A literature review of underground mining beneath catchments and water bodies report that the impact of coal mines are seen in the increment of iron, manganese, aluminium, sodium, calcium, barium, chloride and sulphate in surface water (NSW, 2016). The coal washery rejects order 2014 allows maximum average concentration of contaminants other attributes in the washery as listed in Table 2.1. This indicates that surface water is under threat of a substantial amount of contaminant.

2.3 Coal seam gas (CSG) production

Composting natural gas in the coal seam was initially identified in the early nineteenth century in the coal mining areas in Australia which used to be vented during the mining process. Attention was paid in the 1950s and drainage holes were used in 1970s for venting which finally ended in collecting and developing a separate coal seam gas (CSG) industry in the early 1980s. The motivation for collection of the gas was mainly based on reduction of three complications faced by the mining industries. Firstly, there had been thousands of reported fatalities due to mine explosion caused by methane presence (USDOL, 2015; Yueze et al., 2017).

Table 2.1: The absolute maximum concentration or other value of that attribute in any coal washery rejects

S. No.	Chemicals and other attributes	Absolute maximum concentration (mg/kg 'dry weight')
1.	Mercury	1
2.	Cadmium	1
3.	Lead	100
4.	Arsenic	20
5.	Chromium (total)	150
6.	Copper	100
7.	Nickel	80
8.	Selenium	5
9.	Zinc	200
10.	Electrical Conductivity	2 dS/m
11.	pH	7 to 12
12.	Combustible content	40%
13.	Sulphur	1%

The collection would reduce the explosion possibility by reducing its concentrations. Secondly, collection of methane helped improve the mine economy by reducing the cost of venting and earning revenue by gas utilization. Thirdly, it was beneficial to reduction of global warming caused by venting coal seam methane gas to the atmosphere. In the same period substantial work was in progress in USA for the collection of coalbed methane gas and several technological developments were in progress (Wilson et al., 1995) which led to production trials in Australia in 1988 and finally to commercial production in 1996 in the form of liquified natural gas (LNG). Different names, like sour gas, light gas, shale gas and coal bed methane are in use for description of the natural gas. In Australia it is commonly called coal seam gas (CSG) which is adsorbed methane gas in the semi liquid state in the pores of coal (coal seams).

United States Environmental Protection Agency (USEPA) reported the liberation of 29 to 41 x 10^9 m^3 of methane annually from underground coal mining during the coal seam gas mining developments and out of which they were able to utilise 2.3 x 10^9 m^3 of methane as fuel. In Australia 594 to 1,162 x 10^6 m^3 of methane was liberated and only 70 to 122 x 10^6 m^3 were used for energy generation (USEPA, 1994; IEA Board, 1994). Methane is a major greenhouse gas and is hazardous to the environment when vented to atmosphere. It was found that 90% of global methane was caused by ten large coal mining activities. Even after feasibility assessment it was lack of finance which was preventing the gas collection project. It was predicted that it will never be possible to completely eliminate the methane gas emission from coal mining due to technical, economic and institutional barriers (Diamond, 1995). However, its commercial value compelled a successful growth in the natural gas production and a fundamental transformation is being observed in the natural gas market.

The gas industry has taken over the power sector in countries like China, USA, developing Asian countries and Middle East countries. It is so drastic demand-based transformation that it is considered as the second wave of liquefaction of gases in countries like Australia and USA. A rising demand in countries like China, India and Pakistan is predicted to have more demand than production of natural gas depicted in Figure 2.3. Developing world economies led by China anticipate almost 90% of demand growth due to annual predicted consumption of 4,000 billion cubic meters (bmc) by 2022 (IEA, 2017). China alone would need 40% of global demand growth. US is taking the gas scenario as the second wind of the shale revolution and a tremendous increment in the production is expected to the level of 40% of global production growth. However, this growth is expected to be initially led by Australia and a thorough study of environmental impact is highly recommended. Although the renewable energy consumption is expected to increase by 2%, the conventional gas production increment is expected to increase significantly by 2.7% a year (BREE, 2014).

Natural gas in Australia is mainly coal seam gas (CSG) naturally trapped by water or pressure in the seams of underground coals (Guo & Kantzas, 2007). CSG can be taken out of the seams by drilling well in the coal seam and pressurising it by water with required material solution according to circumstances. This production process known as hydraulic fracturing creates passages in the seams allowing the gas flow out to the surface and compressor to liquefy and store (Shen et al., 2011). In the process, the extracted water, called 'produced water' is stored for further reuse or treatment. The quantity of produced water is large and if chemicals are used to facilitate the gas extraction it can impact the surface water quality if not managed properly. The produced water affects the ground water and produces greenhouse gases in the production process (Xu & Zhu, 2010). It causes the increment of salts in the environment, declines the groundwater level, changes the surface water flow and degrades the quality of both groundwater and surface water (Clarke, 1996; Cheung et al., 2010). The environmental issues are numerous with the effect on the resource, habitation, vegetation, atmosphere, and land considered as immediate environmental impacts (Clarke, 1996; Xiaoying & Xianbo, 2009). Australian legislation does not automatically allow land owner to own the mineral resource underneath and therefore, the conflict of use and control of land arises. The conflict leads to less controlled environmental management resulting landscape salinity and alkalinity (Biggs, 2011).

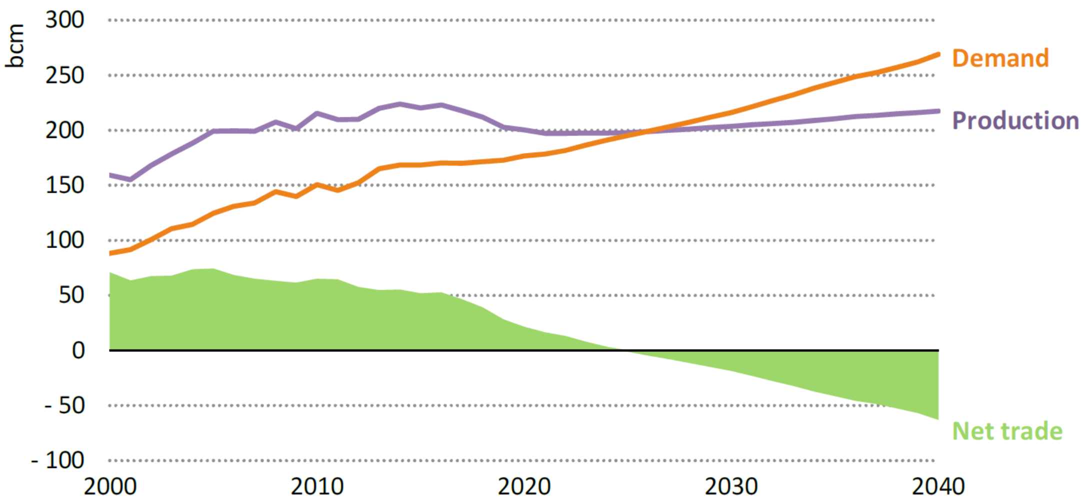

Figure 2.4: Natural gas balance prediction scenario in Southeast Asia. Source IEA 2017 (IEA, 2017)

Australia is a drought prone country with 70% of arid or semi-arid landscape which makes sustainability of water resources of high concern. Although the contamination composition of Australian produced water is not well reported, the global record shows high sodium (Na^+), high bicarbonate (HCO_3^-), high chloride (Cl^-), low calcium (Ca^{2+}), low magnesium (Mg^{2+}), low sulphate (SO_4^{2-}), high sodium adsorption ratio (SAR) and high total dissolved solid (TDS) (Wang et al., 2012). Depth and location of the coal seam also affect the change in the produced water (Hamawand et al., 2013). Produced water storage and transfer to transient channels have shown drastic changes in ecological and environmental conditions of the rivers and ponds (Sivanpillai & Miller, 2010). In Australia a proper treatment of produced water is part of the process which is commonly done by reverse osmosis (Averina et al., 2008) in association with various chemical and ion exchange pre-treatments (Millar et al., 2016). Scaling and fouling due to ions like Ca^{2+}, Mg^{2+}, barium (Ba), silica (SiO_2), fluoride (F^-), SO_4^{2-}, bicarbonate alkalinity as $CaCO_3$, and boron (B) disturbs the process and continuous production and treatment leads to inadequate treatment (Henthorne & Boysen, 2015). Additionally, untreated water release to the surface is also environmental concern (Wang et al., 2012).

Hydraulic fracturing is involved in the production process to increase the output, with a suitable chemical composition of pressurising fluid used for further improvement in output. The USEPA has identified more than 1000 possible chemicals used in hydraulic fracking fluids (US EPA, 2012). It has also been mentioned that more than 75% of the chemicals have health implications as they may affect the respiratory and gastro intestinal system. Nearly half of the chemicals could affect the neurological, immune, cardiovascular, and renal systems. 37% of the chemicals could affect the endocrine system. Another investigation has revealed that the leading companies have used more than 2500 hydro-fracking products (Waxman et al., 2011). In Australia, very limited products of around 113 are in use with strict regulations in place (DEE, 2017a; DEE, 2017b).

During mining processes variety of materials are consumed, processed, and washed away as a discharge in the form of produced water. Although the water discharged into the creeks and waterways is diluted in the downstream flow, a continuation in discharge leads to persistence of contaminants in waterways. Water and sediment quality can be compromised due to coal and coal seam gas mining activities. During the production, coal washing and groundwater seepage into underground mines generate contaminated wastewater. Sulphur containing material in mine encounters water which naturally generates sulphuric acid, termed as acid mine drainage (AMD) (Jacobs et al., 2014; Choudhury et al., 2017). Sulphuric acid production causes dissolution of rocks generating metal ions and subsequently contamination of water and sediments (Matsumoto et al., 2016). AMD causes seasonal variation in microbial community (Hao et al., 2017). Alkaline dozers are used to reduce the acidity and dissolved metals from the acid mine drainage, but the improvements were shown as non-linear (Johnson et al., 2014).

In additional to traditional coal mining activities, coal seam gas (CSG) extraction, as significant source of energy, has added its own environmental concerns (Morgan et al., 2016). More than 2500 hydro fracking chemical products available on the market to facilitate the extraction of gas from coal and shale seams (Waxman et al., 2011) have presented new environmental exposure risks to water and sediments in combination with the geogenic contaminant mobilization from coal seams, which raise potential public health concerns (Yost et al., 2016). Water production quantity is dependent on geological formation of basin as well as it is unavoidable process with the coal and CSG production (Nghiem et al., 2011). Water quality evaluation data is important to maintain sustainable environment. A comprehensive method of quality assessment based on selecting water sources for human consumption, wastewater monitoring, water classification, and evaluation of pollution needs to be implemented for assurance of sustainability (Najar & Khan, 2012). Contamination of water further impacts sediments of ponds creeks and rivers which act as long-lasting source of contamination hazard to the living organism (Alvarez et al., 2011). If the produced water from coal mine or coal seam gas mine is discharged with inadequate treatment, it will contain contaminants that will subsequently impact downstream waterways and sediments. Accumulation of excessive contaminants due to continuous loading into the waterway will serves as pollution source and impact the ecosystem (Wright et al., 1995; Belmer et al., 2015; Wright & Ryan, 2016).

2.4 Water quality impairment

Discharge of mine water on surface and groundwater supplies has been the major area of environmental and health concerns from coal mining and CSG extraction (Post

& Baker, 2017), causing degradation of the ecosystems (Hastings, 2017). Coal and coal seam, as the major sources of energy (Werner et al., 2017), compel the assessment of water quality which can be achieved by implementing monitoring programs (Massoud et al., 2010). The water quality assessment can easily be achieved by comparing to published standards and guidelines (De Rosemond et al., 2009). Inconsistent parameters monitoring between the countries make it difficult to compare the studies of different countries, in addition, different standards designed for various applications make it more unbalanced for a comprehensive study. The variety of standards and test parameters makes the presentation a bulky compilation of result and to comprehend its outcome at a glance is difficult, therefore, a simple expression of surface water quality is articulated by a representative number, called water quality index (WQI) which is a mathematical calculation of a single value from various test results. In other words, WQI is an aggregation calculated from variety of water quality parameters which was first applied in USA in the early sixties (Ott, 1978).

The WQI can be used to compare the field samples of upstream to the possible contamination point or unimpacted water stream (geogenic) to the downstream of the contamination point or impacted water stream (anthropocentric) (Şener et al., 2017) to provide an assessment to establish surface water quality classification (Lermontov et al., 2011; Boyacioglu, 2009). It has been reported that WQI is the best among all the innovated methods to present the water quality (Hosseini-Moghari et al., 2015). The index can help assess the possible uses of surface water and assess pollution (Van der Hoven et al., 2017) which helps to evaluate the environmental impacts of industrial discharges (Amadi, 2011). A possible correlation between WQI and aqua cultural activities (Ferreira et al., 2011), urban impact assessment (Kannel et al., 2007), and ecosystems health (Alobaidy et al., 2010) were studied to assess the comprehensive environmental impact assessment by industrialization.

Toxic effect of heavy metals and its continuous discharge from the industries has become concern in the developing world (Chakraborty et al., 2009). The extensive global industrialization and deterioration of water quality compelled the United Nations Environment Programme (UNEP, 2000) to devote discussions on water quality and trace metal impacts to human health and the environment (Venkatramanan et al., 2015). Variety of metal contamination by coal mining and related industries' produced water has elevated the concentrations of trace metals which have been linked to variety of health concerns. Presence of elevated antimony in water was linked to increase in blood cholesterol (EPA, 2016). It was observed that population near coal mine has high cardiovascular disease (CVD) mortality rates which could be because of the elevated antimony in water (Esch & Hendryx, 2011). Arsenic was linked to cancer mortality (Hendryx et al., 2010), while barium causes reduction in life expectancy by more than five years (Veugelers & Guernsey, 1999). With the concern of metal content in the water, a number of indices related to metals have also been introduced to understand the water quality (Brraich & Jangu, 2015). Degree of contamination (C_d) assessment relating to the quality of water to human health risk was calculated and reported (Backman et al., 1998; Prasanna et al., 2012) along with the heavy metal potential index (HPI) (Mohan et al., 1996; Reddy, 1995) and heavy metal evaluation index (HEI) (Edet & Offiong, 2002) to provide better adequacy to the water quality assessment. Environmental impact assessment internationally remained in practice by comparing the findings with published standards. Australian and New Zealand Environment and Conservation Council (ANZECC) guidelines for fresh water, United States Environmental Protection Agency (USEPA) maximum admissible concentration, Canadian maximum admissible concentration, and World Health Organization (WHO) Health for fresh water are well known among them.

2.5 Sediment quality impairment

Contaminants in the water streams settle on sediments with time impacting their quality, which requires evaluation of industrial impact on the sediments. The trace metals from the mining discharge associated with fine grains of the sediments become long-term source of pollution causing loss of inhabitant species (Stone & Droppo, 1996). Like water, sediment quality assessment also starts with simple comparison of the concentrations of individual contaminants with the national and international published standards. The assessment should carry a combination of investigations which can represent many of the qualities, like sediment chemistry with bioavailability, toxicity, bioaccumulation, and benthic community structure and function. The concepts of particle size affecting contaminants bioavailability, and bioavailability affecting bioaccumulation and toxicity, makes it a complex problem of environmental impairment evaluation based on sediment quality which makes the sediment quality an imperative evaluation study parameter. A thorough investigation of the potential toxicity, persistence, bioaccumulation, and fate and transport of the contaminants is essential. Metals can be inactive in the sediment and form conservative pollutants (Liu et al., 2007) which can later be released into the water stream due to disturbances (Agarwal et al., 2005) which further affect the ecosystem (Chow et al., 2005; Hope, 2006).

Multiple assessment approaches have evolved with an increased understanding and analytical tools. Before any chemical toxicity testing it is essential to manipulate the sample and remove the large particles and debris, perform separation of indigenous biota, and homogenization (Chapman et al., 2002). The most fundamental and initial approach of evaluation has always been the analysis of bulk chemical contamination of an individual contaminant in the sediment (Gambrell et al., 1983). This is a simple measurement of baseline contamination at specific location. There are marginally varying semi-quantitative approaches, like triad of chemistry, ecology and ecotoxicology, to evaluate the quality of sediments (Stevenson & Chapman, 2017). Organic contaminants have played a major role in the sediment evaluation especially for the effect of localised heterogeneity (Guerrero et al., 2003). The living organisms have different burrowing and feeding behaviour of sorting particles, enriching or depleting organic matter, and injecting of oxygen to sediment which is now being taken as parameters for the sediment evaluation (Stockdale et al., 2009; Simpson & Batley, 2003). A quality evaluation can be achieved by finding the relationship between chemical contaminants and ecotoxicity (Long & Chapman, 1985). Certain specific stressor indicators to an ecosystem can be taken as quality indicator to evaluate the sediment quality for specific assessment approach (Jorgensen et al., 2016). Sediment quality has been evaluated by finding a relationship between chemical contaminants and ecotoxicity (Long & Chapman, 1985). Parameters, like pH, redox potential, pore-water iron, dissolved oxygen, electrical conductivity (EC), salinity, turbidity, particle size, acid volatile sulphide (AVS) and temperature are essential for monitoring sediment quality, however, particulate metals, organometallics, inorganics and organics are the decision-making parameters for sediment quality (Chapman, 1989).

The fraction of contaminants available for uptake by an organism of interest is important parameter to define the quality of sediments. This uptake characteristic of bioavailability is direct indicator of biological effect which relates to the chemical behaviour of the contaminant (Simpson & Batley, 2007). This approach of bioavailability has revealed that the toxicity of the sediment depends on the specific chemical binding of the contaminants to the sediment. Further studies have established a relationship between bioavailable metals and sediment toxicity to the extent of high mortality risk often involving target species (Rosado et al., 2016). Equilibrium partitioning theory (EqP) based approach, like chromium (Cr), where trivalent chromium (Cr^{3+}) is relatively non-toxic comparing to hexavalent Cr^{6+} is considered along with other partition parameters (Maruya et al., 2012). A potential ecological risk index (PERI) with the toxic substances has also been used to assess the sediment contamination (Hakanson, 1980).

When continuous bioaccumulation reaches a point where it causes adverse effect on biota, the sediment is considered as polluted. Pollutants could be organic or inorganic materials used in the coal and CSG industries. Comparison of total concentration of contaminants in sediments before and after industrialization plays an important role in assessment of the impact of industrialization on sediment quality. A range of guideline values for the contaminants in sediment are reported (Bunchman, 2008) also internationally known as sediment quality guideline values (SQGVs). Australia and New Zealand collectively published SQGVs with the water quality guidelines in 2000 (ANZECC, 2000) which was revised in 2007 (Simpson et al., 2007), in 2013 (Simpson et al., 2013), and further amendments made for copper and zinc in 2017 (NIWA, 2017).

Trace metals have been extensively studied for health issues for which a trace metal pollution index was established to assist identify metals and their concentrations with potential to impact environmental health. Many indicators, like the degree of metal enrichment in sediments (Hahladakis et al., 2013), degree of contamination (C_d) (Hakanson, 1980), modified degree of contamination (mC_d) (Abrahim & Parker, 2002), geoaccumulation index (Abrahim & Parker, 2002), enrichment factor (EF) (Ergin et al., 1991), and pollution load index (PLI) (Tomlinson et al., 1980) were applied for assessment of sediment quality. Based on the sediment quality guideline values (SQGV) published by ANZECC/ARMCANZ, effective range low/median (ERL/ERM) trigger values (Long & MacDonald, 1998), and threshold/probable effect level (TEL/PEL) were also calculated and used for evaluation of environmental impairment by industrial contamination of sediments (McCready et al., 2006).

2.6 Aquatic ecological impact

Basin natural capacity evaluation is important for achieving overall sustainability. U.S. Environmental Protection Agency (USEPA) proposed Soil and Water Assessment Tool (SWAT) of six important components, which include two important study points of aquatic inhabitant condition and biological condition. Aquatic ecological impact of mine wastewater is evident in the literature (Smith et al., 2009) which makes the industrial discharge an important ecological problem. The wastewater quality, geochemistry and metal contamination causes long distance impact on the ecosystem (Wright et al., 2017). Different heavy metals discharged by coal mines can be consumed by the living aquatic organisms (Mishra & Shukla, 2016). As adsorbed metal on sediment (Alvarez et al., 2011) becomes ultimate sink for the trace metals it affects the living organisms on the coastal areas. Metals exist in sediments in various geochemical phases and are controlled by the chemistry and hydrology of stream water. When metals are mobilised, they impact the ecosystem form and function. Even at low level contamination, the trace metals affect the flora and fauna, which can then enter the food chain through bioaccumulation (Bazrafshan et al., 2016), also impacting human health (Allinson et al., 2015). It has been demonstrated that Pb, Zn, As, Cr and Ni have negative influence on the ecological status of the river basins (Thomas et al., 2016).

Aquatic ecological impact of mine wastewater is evident in the literature (Smith et al., 2009)(Sievers et al., 2018; Wright et al., 2017). The increment of trace metals in the discharged water was observed previously in the downstream sediment and surface water from the mining activities (Abraham & Susan, 2017). It is critical to know that the contaminants which may not be directly in water but remain attached to the sediments and certain trace metals which are not permanently bonded in the sediment get released in the water under different conditions (Caille et al., 2003). Some of them (Mo, Cr, Zn, Se, Co, Fe) are used in the biological functions and are not harmful in low concentrations but those which are not essential for the biological use (Pb, Hg, Cd, As, Ni) can be toxic even at very low concentrations (Pagenkopf, 1983). Inhabitants have their own way of living and reacting to the environment. Certain species have their own system to maintain the intake of contaminants and constant accumulation of trace metals in these species continues irrespective of the available trace metals in the water system (Johnstone et al., 2016). Dissolved material in water has its own effect on the inhabitants.

It is reported that mine water salinity affects the algae and duckweed (Smith et al., 2009). At the same time in some cases increase in salinity due to discharge can be tolerated by the taxa (Bailey et al., 2002). The varying scenarios may affect differently the invertebrate taxa which may lead to high or low abundances. It has been reported that salinity increment causes decrease in richness and density (Bunn & Davies, 1992).

Inhabitants have their own characteristic affinity towards the available trace nutrients. The varying behaviour can go to any extent and in any positive or adverse trend, such as available evidence of acidophilic bacteria, which causes coal to leach and form low pH drainage by its metabolic activity (Baruah & Khare, 2010). This varying trend may lead to varying taxa structure with the changing environmental condition and due to variety of behavioural changes macroinvertebrates in a river ecosystem can be used as a tool for assessment of water quality and industrial impact (Andersen et al., 2016). Macroinvertebrates can also be used as anthropogenic adverse effect indicator on aquatic systems (Kaboré et al., 2016). Impact of wastewater discharge on water, sediment, and damage to aquatic ecosystems may have some correlation and can form a kind of relative aquatic river health indicator for environmental studies. The role of an organism in its environment, called niche, has a major importance in environmental impact evaluation. Variety of niche widths were studied for inhabitant's place of living and their functionality or functional role in the environment (Kennedy et al., 2017). It is evident from the literature that species densities are high when there is scarcity in distribution which is one of the most robust patterns in macroinvertebrates (Blackburn et al., 2006). It is also evident that due to low extinction rate, locally abundant species have high chance of filling the gaps and becoming more abundant (Hubbell, 1997).

The industrial activity disturbs the flux of biological community (Ding et al., 2017). Therefore, diversity estimates of benthic macroinvertebrates are used worldwide as stream health indicators and consequently an environmental impact assessment tool (Jackson & Fuereder, 2006). Many cases have been reported to be very tolerant to the environmental disturbances caused by industrialization (Davey et al., 2012), however, tolerance by certain species (Mayor et al., 2015) and even benefit from the environmental degradation is also reported (Tolkkinen et al., 2015). Regional occupancy and local abundance of macroinvertebrates are a characteristic pattern (Hanski, 1982) which has been documented for various group of organisms (Tales et al., 2004; Heino, 2005;

Soininen & Heino, 2005; Heino & Virtanen, 2006). Heavy metal resistance has been observed in mining environments (Ledin & Pedersen, 1996), indicating the potential of specific microorganisms to have internal bioremediating mechanisms. Heavy metals may be extracted or removed from the waterways with the implementation of algae and bacteria, which have shown positive effects on mine wastewater. Despite the ability to survive in the presence of similar contaminants, the physiology and the metabolism of the bacteria are compromised (Lima e Silva et al., 2012). The impact on biodiversity ecosystem is in both aquatic and terrestrial environment (Tilman et al., 2001). Effect of acidity or changing pH value or trace element have shown detrimental effect on microbial diversity and ecosystem functionality (Simon et al., 2009). It has also been reported that naturally changing lower pH and higher metal content does not harm the ecosystem to the extent as man made changes in the same parameter does (Schmidt et al., 2012).

2.7 Trace element accumulation in taxa

It is reported that aquatic invertebrates consume and accumulate trace metals in varying concentrations across taxa. In presence of certain trace metals, the process of uptake of other trace metals by inhabitants are reduced. Even the processes, like photosynthesis, are affected (Volland et al., 2014). This process of selective nutrients uptake of trace metals in presence of others affects in both ways of increasing or decreasing the damage to plants. Eventually, bioavailability of trace metals affecting the inhabitants are seen altering the macroinvertebrate assemblages in various forms (Mykrä & Heino, 2017). Trophic metal transfer is one of the crucial roles of aquatic invertebrates which accumulates pollutants by food intake (Fisher & Reinfelder, 1995). Certain metals are considered as homeostatic as they are needed for certain physiological functions, while others are nonessential which are metabolically controlled by invertebrates (Fisher, 2002). With this concept, depending on the environmental condition the nutrients intake increases (Bode et al., 2015) and decreases (Frangoulis et al., 2004) or is recycled (Bode & Varela, 1994) which can be used as the indicator for environmental impact evaluation comparison of bioaccumulation with the change in macrobian species. Some species are carnivorous (Turner, 1978) some are omnivorous (Lillelund, 1971) and can be distinctive of pollution accumulation (García-Flor et al., 2008).

No macroinvertebrate taxa show consistency in essential or non-essential trace element accumulation patterns for different sites (Karimi & Folt, 2006). Reportedly, coal waste exposes the aquatic invertebrates to large number of potentially toxic metals and metalloids (Rowe, 2014), which is considered as global environmental problem (Rath et al., 2009) due to its bioaccumulation in inhabitants (Rath et al., 2009). This provides an excellent opportunity for investigation of trace elements and taxa specific pattern of bioaccumulation. Bioavailable contaminants assessment (Corbi et al., 2011) and stream assessment (Worthen, 2002) can easily be pursued with the knowledge of living organisms because of the element and taxa specific pattern (Lavilla et al., 2010). Even closely related taxa differ in bioaccumulation pattern of trace elements (Poteat et al., 2013). This pattern also changes with the sediment grain size (Worthen et al., 2004). The pattern is now being used as tracer to investigate biomagnification of contaminants (Cui et al., 2011) and mesotrophic to eutrophic classification of impaired water with bacterial blooms indication (Bazán et al., 2014) based on trace element intake. It is important to understand the pollution dynamics of environment as trace element bioaccumulation, biomagnification and bioavailability in the ecosystem is enhanced. It has been reported that the route of human exposure to metals and metalloids is 90% through bioaccumulation in comparison to inhalation and dermal contact (Griboff et al., 2017).

It is highly important to investigate the metal accumulation into the macroinvertebrates for the impact evolution of environmental impairment due to mining industries around the water streams. The macroinvertebrates are valuable indicators of metal exposure (Van Ael et al., 2015) due to their bioaccumulation ability of essential and non-essential metals present in the surrounding environment (Bervoets et al., 2016) and provide a valuable tool for the assessment of anthropogenic environmental impairment.

2.8 Conclusion

This study reviewed the emissions of chemical constituents derived from coal and coal seam gas mining activities in water, sediment, and invertebrates to achieve the data of reduction of their quality towards exceeding limits of guidelines. Water quality, sediment quality, inhabitant's taxa, and bioaccumulation were swotted to establish a benchmark for individual sites and find gaps for future change in their quality and indexing to evaluate the sustainability of the environment. The review of coal production techniques and waste generation revealed the need of further monitoring study of the chemical composition using the techniques compiled in this chapter. Further data on regular monitoring of discussed parameter is required to fill the gaps in monitoring for the environmental impact evaluation. Parameters used in the review study are insufficient to ascertain the concluding remarks and needs to be expanded to achieve the better judgement. A thorough study of single parameter like salinity was performed in the study region which needs to be extended to all the possible discharge constituents. The ANZECC guideline data available in the review was only a fraction of the discharged chemical composition in the study area. A discrepancy in literature on the effect of the discharged chemical on its inhabitants was felt as relationship between the discharged material and biota was found to be lacking. This review has identified gaps in the quality parameters of water, sediment, and inhabitants and need of further research was felt to ascertain environmental sustainability and environmental impact evaluation.

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Environmental Impact of Coal Mining and Coal Seam Gas Production on Surface Water Quality in the Sydney Basin, Australia

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Abstract

The extraction of coal and coal seam gas (CSG) will generate produced water that, if not adequately treated, will pollute surface and groundwater systems. In Australia, the discharge of produced water from coal mining and related activities is regulated by the state environment agency through a pollution licence. This licence sets the discharge limits for a range of analytes to protect the environment into which the produced water is discharged. This study reports on the impact of produced water from coal mine activities located within or discharging into high conservation environments, such as National Parks, in the outer region of Sydney, Australia. The water samples upstream and downstream from the discharge points from six mines were taken and 110 parameters were tested. The results were assessed against a water quality index (WQI) which accounts for pH, turbidity, dissolved oxygen, biochemical oxygen demand, total dissolved solids, total phosphorus, nitrate nitrogen and e-coli. The water quality assessment based on the trace metal contents against various national maximum admissible concentration (MAC) and their corresponding environmental impacts was also included in the study which also established a base value of water quality for further study. The study revealed that impacted water downstream of the mine discharge points contained higher metal content than the upstream reference locations. In many cases the downstream water *was above the Australia and New Zealand Environment Conservation Council and international water quality guidelines for freshwater stream. The major outliers to the guidelines were aluminium (Al), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn). The water quality index (WQI) of surface water at and downstream of the discharge point was lower when compared to upstream or reference conditions in the majority of cases. Toxicology indices of metals present in industrial discharges were used as an additional tool to assess water quality and the newly proposed Environmental Water Quality Index (EWQI) lead to better trend in the impact of coal and coal seam gas mining activities on surface water quality when compared to the upstream reference water samples. Metal content limits were based on the impact points assigned by the Agency for Toxic Substances and Disease Registry, US. For environmental and health impact assessment the approach used in this study can be applied as a model to provide a basis to assess the anthropogenic contribution from the industrial and mining activities on the environment.*

Keywords: Water quality index; coal mine; coal seam gas; environmental impact; surface water.

3.1 Introduction

Coal is a predominant energy source in Australia and worldwide coal production has exponentially increased since 2000 (Outlook, 2008). Coal is extracted by either open cut or underground methods, while coal seam gas (CSG) is extracted from underground seams through a connection of wells. Each of these extraction methods has an environmental impact (Dhar, 1993; Hawke, 2009). One of the major areas of environmental and health concerns from coal mining and CSG extraction is the impact of mine water discharge on surface and ground water supplies (Dhar, 1996; Johnson, 2003; Younger, 2004; Tiwary & Dhar, 1994). Produced water disposal from coal mining activities into local waterways can cause degradation of the ecosystems (Jarvis & Younger, 1997; Tiwary, 2001; Pond, 2010) and is also known to affect public health (Health, 2010). Nonetheless, fossil fuels are attributed to providing the majority of energy that has supported the economic growth across most countries (Drew, 2014; Ball et al., 1965; Nematollahi et al., 2016) which makes the water quality assessment related to mining an essential part of water resource management (Banerjee & Srivastava, 2009). The quality of river water is controlled by both geogenic and anthropogenic activities (Huang et al., 2010), which can be quantified through carefully designed and implemented monitoring programs (Massoud et al., 2010).

Surface water quality can be assessed by comparing to predetermined standards and objectives (De Rosemond et al., 2009). These standards and objective are not comprehensive (Kannel et al., 2007) and therefore a simple expression of surface water quality is often articulated by a representative number, which is called water quality index (WQI). An index is a mathematical mean of calculating a single value from various test results. WQI can be used for a range of purposes including: 1) comparison of the geogenic (or pre impacted) to anthropocentric (impacted) streams to assess environmental impact of various activities (Ferreira et al., 2011; Dubé et al., 2006; Lumb et al., 2006; Khan et al., 2005; Khan et al., 2003; Lumb et al., 2011; De Rosemond et al., 2009); 2) to provide an assessment against water quality objectives (Debels et al., 2005; Cash & Wright, 2001); 3) to establish surface water quality classification(Lermontov et al., 2011; Boyacioglu, 2009); 4) to assess the beneficial use of surface water (Said et al., 2004) and pollution (Zhang & Zhang, 2007; Kannel et al., 2007; Bakan et al., 2010; Akkoyunlu & Akiner, 2012): 5) to assess the environmental impacts of dumping sites (Amadi, 2011), aqua cultural activities (Ferreira et al., 2011), urban impact assessment (Kannel et al., 2007), and ecosystems health (Jawad A H M et al., 2010).

Internationally, the United Nations Environment Programme (UNEP, 2000) notes that there is worldwide deterioration in water quality, including trace metal impacts to human health and the environment (Klavinš et al., 2000; Mofarrah & Husain, 2011; Venkatramanan et al., 2015; Dahunsi et al., 2014; Mendiguchía et al., 2007; Kidd et al., 2007; Bhattacharya et al., 2015; Krishna et al., 2009). For coal mining and related industries produced water containing elevated concentrations of trace metals have been linked to a range of health concerns. For example: 1) elevated levels of antimony have been linked to increase in blood cholesterol (EPA, 2016) and high cardiovascular disease (CVD) mortality rates near coal mining areas (Esch & Hendryx, 2011), 2) arsenic linked to cancer mortality (Hendryx et al., 2010),

3) barium causing reduction in life expectancy by more than five years (Veugelers & Guernsey, 1999).

Cost effective ways of monitoring water quality parameters are needed to help control and manage the impact. A trace metal pollution index may assist in this regard where multiple metals are known to impact environmental health. There are multiple water-quality index systems in practice (Sutadian et al., 2016). Currently, there is no water quality indicator that incorporates the relative toxicity of the trace metals in the assessment. In addition, the use of an index which incorporates pollution from industrial activities, such as mining, has not been well developed and further study is required to correlate the indices used for environmental monitoring. A more comprehensive index system comparing to WQI (used for domestic water) can be recommended for the coal-mine impact assessment after analysing individual cases across the board. WQI considers only limited parameters for estimating water quality and does not exhaust all potential impacting properties, including toxicity of metals. For this reason, in this study the contamination index (C_d), heavy metal evaluation index (HEI) and heavy metal potential index (HPI) were estimated and a new comprehensive trace element toxicity index (TETI) and a new environmental water quality index (EWQI) were propose. This study investigates application of WQI and presents an assessment of water quality parameters and trace metal toxicity of coal seam gas and coal mining activities on surface water quality

3.2 Materials and methods

3.2.1 Study area and site description

The study focused on two mining regions located to the west and south-west of Sydney, New South Wales, Australia. The Blue Mountains study area is located 85 to 140 km inland from Sydney and sampling was focused on reference streams and coal mines in the Coxs, Wollangambe and Grose Rivers. They are small, shallow and fast flowing upland streams. Their elevation ranges from 460 to 1,093 m above sea level. It is a rocky and relatively inaccessible area with very limited access via walking trails (Macqueen, 2007). Major study area is undisturbed wilderness within the Greater Blue Mountain World Heritage area (Government, 2000). The mines included as part of this study were the Canyon, Clarence and Springvale Collieries.

Canyon Colliery operated from 1920s to 1997 (Government, 2001; Macqueen, 2007) and this abandoned mine continuously discharges into Dalpura creek which shortly flows into Grose River. Clarence Colliery, an underground mine with a pit top adjacent to Wollangambe River which occasionally causes collapse of coal fines into the river (Cohen, 2002). It discharges 13.8 million litres of produced water each day. Springvale colliery (Centennial Coal Pty Ltd.) uses 20725 mega litre water per day and licenced for discharging maximum 30,000 kL/day into dams (LTD, 2013).

The second region is located 60 to 120 km southwest of Sydney in the Georges and Bargo River catchments. The locations of interest included: West Cliff Colliery which discharges into Brennans Creek and further downstream to Georges River; and Tahmoor Colliery which discharges in Bargo River and affects other creeks, including Redbank Creek, due to underground mining causing subsidence. Brennon Creek is a rocky uneven waterway carrying mainly waste released from Westcliff Colliery. Produced water sample was collected from 50 meter before it falls into Georges River nearly 500 metre distance from the storage pit. Upstream and downstream samples were collected from a distance of 50 meter from the merger point of Brennans Creek to the Georges River. The creek and river depth was less than a meter and width 3-4 metre. Tahmoor Colliery is an underground coal mine operating since 1979 under approval to begin longwall mining in 1986 (Coal, 2014) and produces water disposal under the Protection of the Environment operations (1997) Act. Approximately 2500 kilolitre water seep into mine which is pumped out to the surface and discharged following the contract monitoring of the produced water. The upstream of Redbank Creek was above Longwall 26 with sandstone bedrock having apparent fracturing where some groundwater flow remerged in the creek as surface water. The downstream sample was taken from large stream pool above the ‘Longwall 27’ 100 m downstream. Bargo River upstream sample was taken from 1 kilometre (km) above the coal mine discharge point and downstream from the approximately 2 km below the discharge point.

The coordinates and details of the sampling locations are listed in Table 3.1. Sample location points are further depicted in Figure 3.1 and Figure 3.2. Three different colours were used to indicate the upstream, downstream and discharge sampling locations. In the Blue Mountains region, the sampling locations can be divided into three areas of study (Figure 3.1). Study area 1 covered the Ash Dams, Angus Place, Sawyers Swamp and Springvale coal mines and used an upstream location at the Coxs River as the reference site. Study area 2 sampled downstream of the licenced discharge point from the Clarence coal mine and included upstream reference sites on the Wollangambe River. The third study area covered the Canyon coal mine which discharges water into Dalpura Creek. The south-western Sydney region was divided into four study areas 4, 5, 6 and 7 (Figure 3.2). Area 4 was selected to assess the impact of the West Cliff Colliery on Georges River and Brennans Creek, area 5 to assess the impact of Tahmoor coal mine on Bargo River, area 6 to assess the impact of subsidence caused by underground mining on the quality of water of Redbank Creek and area 7 was selected to study the impact on the Nepean River of coal seam gas production. All the sites were expected to have impact of mining and monitoring licences were issued to the mining companies with condition of monitoring. However, very limited parameters were monitored. Most of the work in this region was based on impact on the inhabitants and their colonies before our propose work (Wright et al., 1995; Growns et al., 1995).

Table 3.1: Sample and site identification.

Study Area	Mines	Sample collection site	Coordinates		Site I.D.
1	Ash Dam, Angus Place and Springvale	Coxs River, upstream	33°18'0.64"S	150° 5'49.30"E	W1
		Sawyers Swamp, downstream	33°22'50.74"S	150° 5'11.63"E	W2
		Sawyers Swamp, upstream	33°23'37.40"S	150° 7'28.12"E	W3
		Springvale discharge	33°24'6.55"S	150° 5'39.55"E	W4
2	Clarence Coal Mine	Wollangambe River, upstream	33°27'19.94"S	150°15'26.64"E	W5
		Wollangambe River, downstream	33°27'53.63"S	150°15'49.68"E	W6
		Wollangambe River, discharge	33°27'52.26"S	150°15'33.73"E	W7
3	Canyon Coal Mine	Dalpura creek, upstream	33°32'24.67"S	150°18'22.19"E	W8
		Dalpura creek, downstream	3°32'27.75"S	150°18'25.71"E	W9
		Dalpura creek, further downstream	3°32'18.58"S	150°18'5.55"E	W10
4	West Cliff Colliery Appin	Georges River, upstream	4°12'13.46"S	150°47'52.74"E	S1
		Georges River, downstream	4°12'17.25"S	150°47'55.89"E	S2
		Brennans creek discharge	4°12'16.11"S	150°47'57.48"E	S3
5	Tahmoor Coal Mine	Bargo River, Tahmoor, upstream	4°14'12.11"S	150°34'46.02"E	S4
		Bargo River, Tahmoor, downstream	4°14'58.47"S	150°36'25.37"E	S5
6	Tahmoor Coal Mine	Redbank creek, Picton, upstream	4°11'56.19"S	150°35'22.02"E	S6
		Redbank creek, Picton, downstream	4°11'53.32"S	150°35'29.04"E	S7
7	Coal Seam Gas	Nepean River, Menangle (up)	34° 7'7.01"S	150°44'30.94"E	S8
		Nepean River, Spring farm (down)	34° 4'46.19"S	150°44'30.07"E	S9
		Nepean River, Belgenny oval (further down)	34° 4'8.43"S	150°41'59.18"E	S10

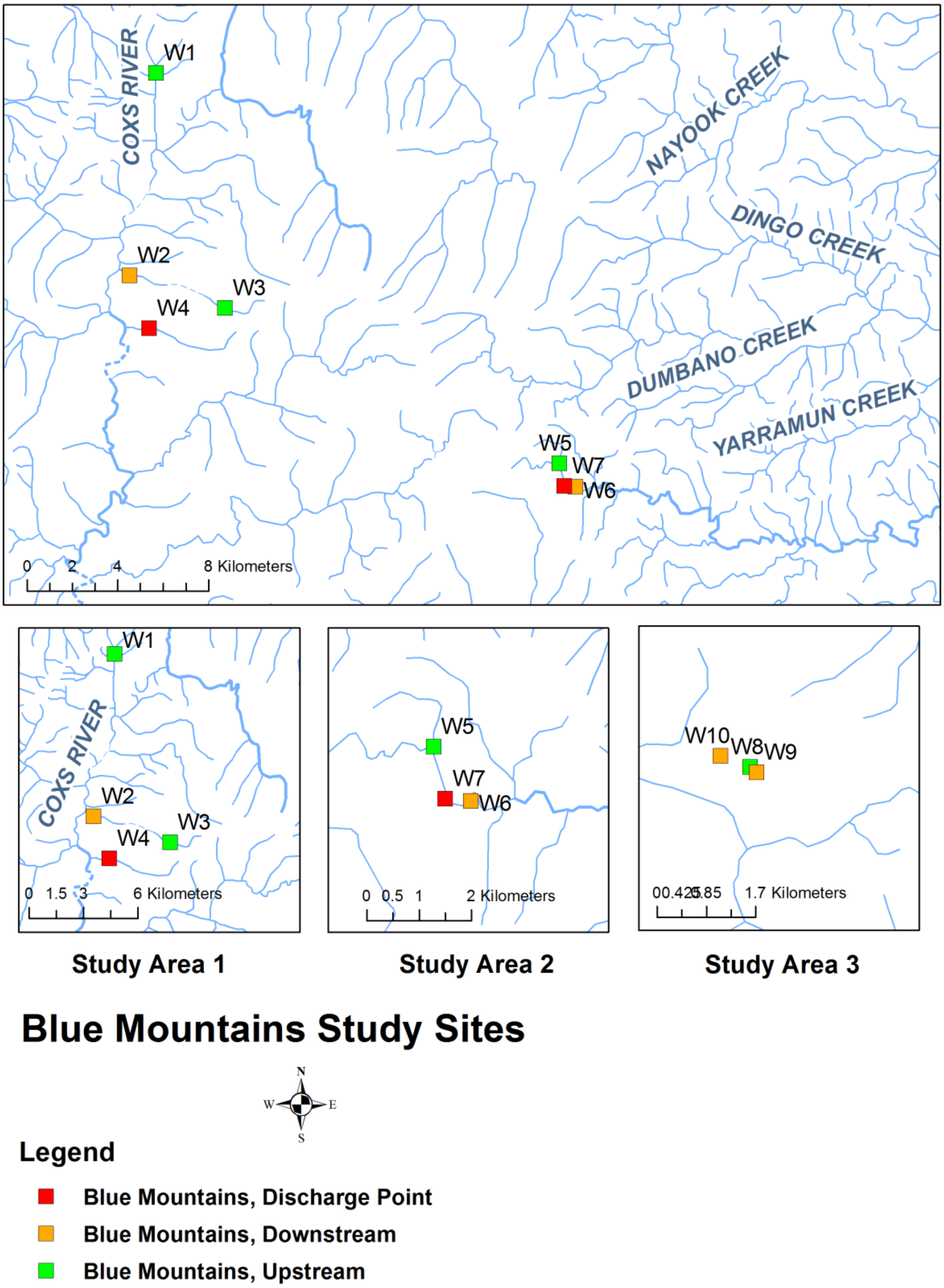
COXS RIVER
W1
W2
W3
W4
NAYOOK CREEK
DINGO CREEK
DUMBANO CREEK
YARRAMUN CREEK
W5
W7
W6
0 2 4 8 Kilometers
W1
COXS RIVER
W2
W3
W4
0 1.5 3 6 Kilometers
W5
W7
W6
0 0.5 1 2 Kilometers
W10
W8
W9
1.7 Kilometers
Study Area 1
Study Area 2
Study Area 3
Blue Mountains Study Sites
N
W
E
S
Legend
Blue Mountains, Discharge Point
Blue Mountains, Downstream
Blue Mountains, Upstream

Figure 3.1: Blue Mountain sampling locations

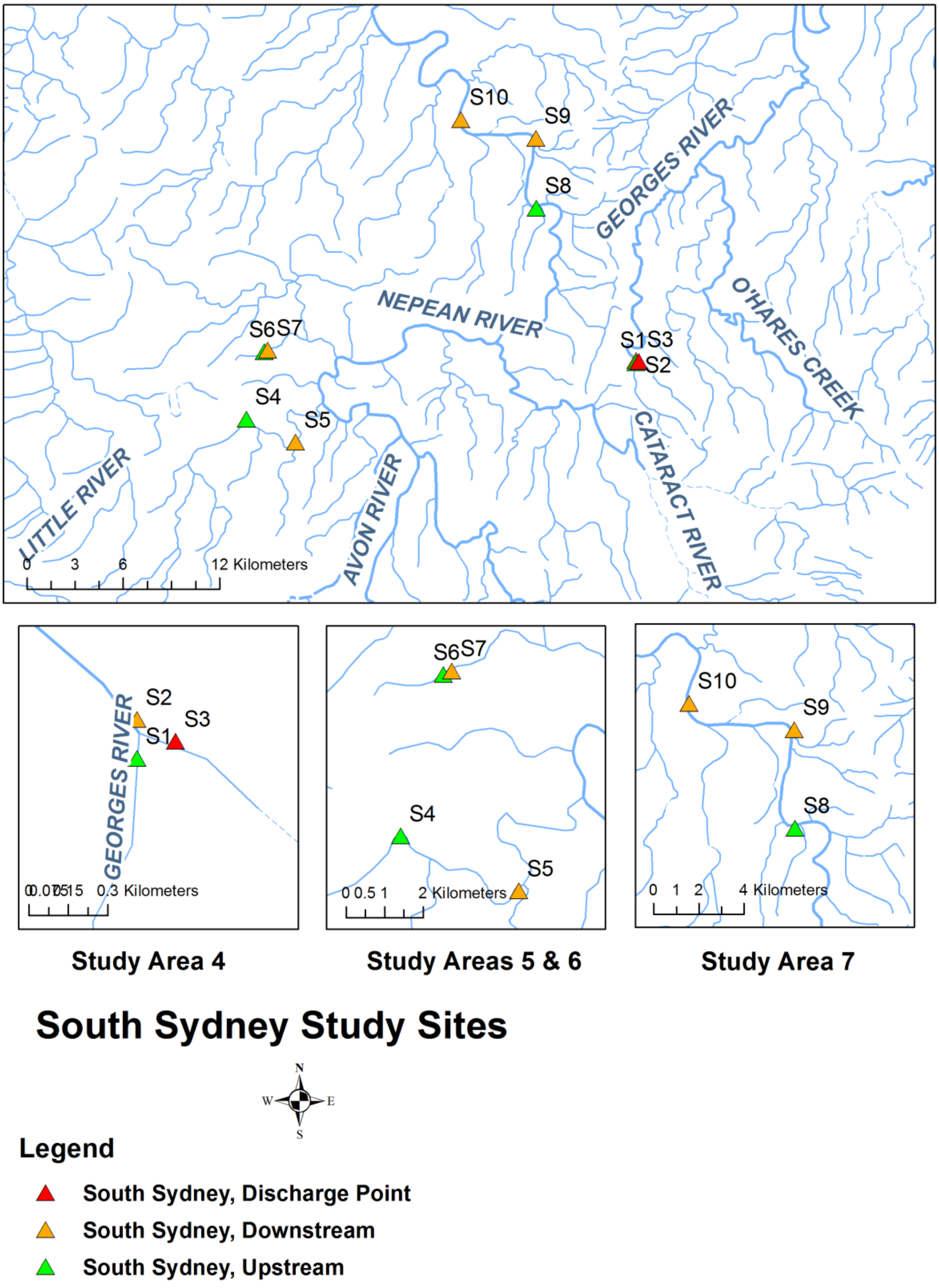

Figure 3.2: South Sydney sampling locations

3.2.2 Sampling and analysis

The samples taken upstream and downstream of the mining discharge points were of major interest for this study. Very limited study of contaminants like pH, electrical conductivity (EC), total dissolved solid (TDS), oil and grease, filterable iron and filterable manganese in selected area was reported for licencing. A sampling campaign was performed in each location with the aim to compare water quality of the selected rivers close to the mining discharge and downstream locations with the upstream location. The sampling campaign was designed to perform indicative assessment of the impact of mining on the rivers and also to compare different water quality assessment indices and their suitability to estimate water quality impacts of the mining activities. Variety of tests listed in Table 3.4 and Table 3.5 were performed for the study. Samples were collected between July 2014 and September 2015. A minimum of three samples were collected in one litre bottle at each location listed in Table 3.1 and the analysis was performed on a composite sample. Sample collection was performed under the guidelines described in the methods listed in Table 3.2 and procedures outlined by the instrument suppliers. Samples for biological oxygen demand (BOD), total dissolved solids (TDS), turbidity, nitrogen and phosphate were collected in clean screw capped polypropylene bottles without any preservatives. Samples for trace element analysis were collected in pre-cleaned and nitric-acid acidified screw capped polypropylene bottles. The trace elements tested for this study included all alkali metals, alkaline earth metals and most of the transition metals, metalloids and polyatomic non-metals. Sulfuric acid acidified polypropylene bottles were used for testing the total phenols, chemical oxygen demand (COD), total nitrogen and bottles were used for testing the total phenols, chemical oxygen demand (COD), total nitrogen and ammonia nitrogen. All the analyses were performed in compliance with the techniques outlined in Standard Methods (Eaton et al., 2005).

On-site measurements of pH, dissolved oxygen (DO), temperature and pressure were performed using an YSI Professional Plus Instrument. This was calibrated prior to each sampling day. Five replicated measurements were taken for the quality purpose on each sampling site. E-coli was analysed following the

USEPA approved IDEXX Laboratories produced Colilert test kit procedure (Croteau et al., 1999). All the remaining inorganic, organic and standard water quality parameters were analysed by the National Association of Testing Authorities (NATA), Australia accredited Envirolab Services (Envirolab Services, 2015). The samples were filtered in laboratory before testing for the dissolved parameters in compliance to the approved methods. The analytical procedures used in this study, listed in Table 3.2 were based on the Standard Method (Eaton et al., 2005), USEPA method, National Environment Protection (Assessment of site contamination) Measure (NEPM B1) method and in-house methods approved by NATA.

Table 3.2 Test methods used for the analysis of water quality parameters.

S. No.	Analytical parameter	Reference Method
1.	Turbidity	APHA 2130B
2.	Biological Oxygen demand (BOD)	APHA 5210D
3.	Chemical oxygen demand (COD)	APHA 5220C
5.	Nutrients suit – Nitrogen	YSI Professional Plus, APAH 4500, USEPA method 351.2,
6.	Trace elements	USEPA 200.8, USEPA 3005A, USEPA 6020A, USEPA 7471A and APHA 3125
7.	Dissolved gases	GC-FID using method USEPA SOP RSK175

3.2.3 Water quality

Sample water quality was assessed, and the quality indices were calculated as outlined below:

3.2.3.1 Water quality index (WQI) calculation

The WQI incorporated the results of nine parameters including temperature; dissolved oxygen; pH, nitrate; turbidity; total dissolved solids (TDS); total phosphorous; biological oxygen demand (BOD); and e-coli (Abbasi & Abbasi, 2012). This index is a product of Q-value and weight factor where Q indicates the level of the water quality relative to any single parameter and the weight factor represents the relative importance to that single parameter to the overall water quality:

$$WQI = \sum W_X Q_X = W_{Temperature}Q_{Temperature} + W_{DO}Q_{DO} + W_{pH}Q_{pH} + W_{Nitrate}Q_{Nitrate} + W_{Turbidity}Q_{Turbidity} + W_{TDS}Q_{TDS} + W_{Phosphate}Q_{Phosphate} + W_{BOD}Q_{BOD} + W_{E\text{-}coli}Q_{E\text{-}coli}$$

The WQI produces a relative score with a maximum value of 100. Water quality can be described as excellent (100-91), good (90-71), medium (70-51), bad (50-26) and very bad (25-0) (Nikoo et al., 2011).

3.2.3.2 Contamination Index (C_d)

The C_d relates the quality of water to human health risk and was calculated (Backman et al., 1998; Prasanna et al., 2012) as:

$$C_d = \sum_{n=1}^{n} C_{fi}$$

where $C_{fi} = C_{Ai}/C_{Ni} - 1$; C_{fi}, C_{Ai} and C_{Ni} represents contamination factor, analytical value and upper permissible concentration of the ith component respectively and N denotes normative value (Edet & Offiong, 2002) and hence C_{Ni} is taken as maximum allowable concentration (MAC).

The calculated values are grouped into low (C_d <1), medium (C_d =1-3) and high (C_d >3) contamination (Backman et al., 1998).

3.2.3.3 Heavy metal pollution index (HPI)

HPI represents the amount of heavy metals in the water and is inversely proportional to the recommended standard (S_i) for each parameter (Mohan et al., 1996; Reddy, 1995). It is calculated by

$$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i}$$

where Q_i is sub-index and W_i is unit weight of the ith parameter respectively and n is number of parameter considered. The sub-index (Q_i) can be calculated by:

$$Q_i = \sum_{i=1}^{n} \frac{[M_i - I_i]}{(S_i - I_i)} \times 100$$

where M_i, I_i and S_i are the analysed, ideal and standard value of the i^{th} parameter and the negative sign (-) denotes numerical difference only. The proposed index has a critical value of 100 for drinking water.

3.2.3.4 Heavy metal evaluation index (HEI)

HEI also describes water quality condition in response to anthropogenic heavy metals and was calculated by (Edet & Offiong, 2002):

$$HEI = \sum_{i=1}^{n} \frac{H_c}{H_{mac}}$$

where H_c is monitored value and H_{mac} is maximum admissible concentration (MAC) of i^{th} parameter.

The HEI values are grouped into low contamination (HEI < 400), medium contamination (HEI = 400-800) and high contamination (HEI > 800) (Edet & Offiong, 2002).

Table 3.3: Australian and international standard and / or guidelines for freshwater ecosystem. Unit of measure is µg/L.

Sample	**ANZECC Trigger level Fresh Water**	**US EPA (MCL)**	**CANADA (MAC)**	**WHO Health**
Aluminium	55	200	200	
Arsenic	13	10		10
Boron	370			300
Barium		2000	1000	700
Cobalt	1			
Copper	1.4	1300	1000	2000
Iron	300	300	300	
Mercury	0.06	2	1	1
Manganese	1900	300	50	500
Molybdenum	34	100		70
Nickel	11	100		20
Lead	3.4	15	10	10
Antimony		6	6	5
Zinc	8	5000		

MAC = Maximum admissible concentration
MCL = Maximum concentration limit

3.2.4 Environmental impact assessment

The environmental impact assessment was performed by comparing a comprehensive list of results of samples upstream of the mine discharge and the downstream of the produced water discharge point. Data was compared with the available trigger values recommended by Australian and New Zealand Environment and Conservation Council (ANZECC) guidelines for fresh water and with internationally published guidelines including United States Environmental Protection Agency (USEPA) maximum admissible concentration, Canadian maximum admissible concentration and World Health Organization (WHO) Health for fresh water. All the comparative standard guidelines are listed in Table 3.3.

A novel environmental water quality assessment index is proposed in this study. This index was calculated by multiplying the concentration of each contaminant measured in the water samples with the corresponding hazard intensity to determine the water quality impact. The hazard intensity of each parameter was determined according to the Toxicological Profiles of the Priority List of Hazardous Substances prepared by the Agency for Toxic Substances and Disease Registry (ATSDR), the Division of Toxicology and Environmental Medicine, Atlanta, USA (ASTDR, 2015). The ranking in the hazardous substance priority list is based on three criteria, which are combined to result in total score.

Total score (TS) = NPL frequency + Toxicity + Potential for human exposure

(1,800 maximum points) (600 points) (600 points) (300concentration + 300 exposure)

Each trace element detected was multiplied by its total score and products were added to calculate the trace element toxicity index (TETI). The water quality index (WQI) was divided by calculated TETI to achieve and propose an environmental water quality index (EWQI).

Environmental water quality index (EWQI)

$$= \frac{\mathrm{WQI}}{\sum_{i=1}^{n} C_i * TS_i}$$

where WQI = water quality index

C_i = concentration of individual trace element

TS_i = Total Score (Agency for Toxic Substances and Disease Registry) of individual trace element.

3.3 Results and discussion

The water quality and WQI for each site are presented in Table 3.4 with upstream data highlighted in green colour. The DO value of the water ranged from 54.8 % to 108.3 % and the results comparing up and downstream sites suggest the DO levels are not adversely impacted by the mining activities. Result for pH indicate that pH levels downstream of the mine are generally higher than reference sites. Most of the streams in the study catchment reported naturally low pH levels (Wright, 2012). As part of the NSW environmental pollution licence requirements each of the mines in the study are required to manage their acid mine drainage and consequently discharge at levels typically higher than found in the natural receiving streams. EC at all upstream sites is significantly lower when compared to the discharge points (Table 3.4). Nepean River samples (S8, S9 & S10) showed very little changes in EC values and pH values. The turbidity levels in upstream samples were found to be generally lower than the downstream samples. Few of the downstream samples indicate the turbidity in the examined samples (W7, S7) is higher than the ANZECC guidelines, which should be in the order of 1-20 NTU for lakes and reservoirs. Total dissolved solids (TDS) and salinity are lower in all upstream samples than downstream counterparts.

The WQI reported stream water quality above and below the mine discharge as good with the exception of the Sawyers Swamp (W3) site, upstream of the mine discharge point. (Table 3.4). WQI calculation takes the weight factor of the selected parameters and is designed to validate overall water quality for domestic use where DO and *E-coli* have greater significance (Rincón & Pulgarin, 2005). In certain cases water quality falling in the same category might give better picture by the index number representing the actual quality of water. Lower WQI at W3 was caused by low DO and presence of *E-coli*. Naturally acidic water of Coxs River (W1) adversly affected the WQI. The WQI in all sampling locations decreased in the mining discharge sampling points, except for Bargo River (S5). The presence of *E-coli* in the upstream sample, S4, and neutral pH value of downstream, S5, reversed the trend. Source of *E-coli* could be native animals or farming as there are no sewerage treatment plants (STPs) upstream of this site. Similar WQI at S8, S9 and S10 indicates the lowest impact of CSG activity on the Nepean River which is because of the fact that each of the CSG wells collects its produced water in an above ground tank and sent to water treatment rather discharging directly to the stream. The changes observed in the discharge and downstream locations were mainly incremental in either metal content, TDS or conductivity. Each of these three parameters is interrelated.

3.3.1 Trace elements

In total 65 trace elements were analysed from each of the sample sites (see Table 3.5 for detected elements) by ICPMS. Na, S, Ca, Mg, Fe, K, Si, Al, Mn, Sr, Li, Zn, Ni and B were recorded in all samples. Upstream samples, or reference samples, were found with lower concentration than the downstream samples. All coal mine discharge downstream samples had concentrations of sodium from 270 mg/L to 800 mg/L, while upstream samples had concentrations ranging from 29 mg/L to 44 mg/L indicating very low background levels and a substantial impact of the release of salts from the coal mine produced water. Elevated level of sodium, sulphur, barium, lithium, and nickel in the downstream in all seven study areas is attributed to coal mines. At Sawyers Swamp (W2) and at the downstream discharge sampling points W3, W7 and S3 high aluminium levels were detected. The ANZECC trigger value for aluminium in freshwater is 55 µg/L and, except for a few samples from the Blue Mountains area (W1, W6 W9, & W10), all had higher than the trigger concentrations of aluminium, including the upstream samples. The upstream reference for Coxs River (W1) had only 40 µg/L of aluminium, however, the creek falling into the river (W3) carried 9700 µg/L of aluminium, however, the creek falling into the river (W3) carried 9700 µg/L of aluminium. Sawyers Swamp (W2), which connects to Coxs River yielded a measurement of 840 µg/L of aluminium. Wollangambe downstream (W7) exhibited more than three times the aluminium concentration than the upstream sample (W5) confirming the mine impact. High concentration of antimony was also detected near West Cliff colliery (S2 & S3).

Table 3.4 Water quality index parameters.

Testing Parameter	Unit	Weight Factor for WQI	Measurement Uncertainty %	Study Area 1				Study Area 2			Study Area 3			Study Area 4			Study Area 5		Study Area 6		Study Area 7		
				W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Temperature	°C	0.1	±0.2°C	10.3	18.1	9.5	8.7	9.3	8.5	13	7.6	7.8	15.2	9.5	9.3	9.3	9.6	9.6	9.2	10.4	10.5	10.3	10.2
DO%	%	0.17	2	60.1	90.1	54.8	81.4	99.3	93	94.3	86.7	87.8	57.3	92.6	81.7	90	108.3	93.6	75.6	65.5	97.3	97.2	97.2
pH		0.11	±0.2 units	5.1	8.59	4.92	8.02	7.49	8.08	8.58	7.17	8.81	5.08	7.91	8.7	8.68	7.75	8.6	7.52	6.99	7.5	6.5	7.3
NO_2	mg/L	0.1	13	0.17	0.89	0.15	0.47	0.06	0.14	0.24	0.05	0.14	0.15	0.46	1.6	1.64	0.54	1.37	0.73	3.76	0.6	0.6	0.62
Turbidity	NTU	0.08	12	0.7	10.6	1.7	8.7	2.9	0.5	81	0.4	0.8	4.2	1.6	8.1	12	4.6	5.6	2	300	4.1	23	2.8
Total Dissolved Solids	mg/L	0.07	11	21	710	27	270	20	190	42	12	67	85	170	1000	1300	100	540	180	820	130	120	110
Phosphorus	mg/L	0.1	18	<0.05	<0.05	<0.05	0.09	0.05	0.05	0.1	0.2	0.08	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
BOD	mg/L	0.11	15	<5	<5	48	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
E-Coli	mpn	0.16		<1	17.8	11.1	5.3	2	<1	<1	<1	<1	<1	1	2	2	12.4	1	<1	<1	2	<1	7.5
Conductivity	µS/cm		0.5	31.6	1116	39.4	471	22.3	39.1	260	21.3	101.6	227.8	241.8	1483	1718	158.5	720	263.5	1363	153.7	120	190.2
Water Quality Index WQI				76	73	68	78	77	88	76	84	83	71	88	78	78	82	83	85	71	85	84	83
Water Quality*				G	G	M	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G
Contamination index (C_d)				-2	8	792	-4	-2	-3	-2	-3	-1	-1	-2	1	4	0	-4	-2	112	-2	-3	-3
Contamination Level				Low	High	High	Low	Low	Low	Low	Low	Low	Low	Low	M	High	Low	Low	Low	High	Low	Low	Low
Heavy metal Evaluation index (HEI)				2.8	19.9	1138	6.1	2.6	38.1	22.5	0.9	104.8	134.0	7.5	54.8	68.6	10.0	20.7	1.9	227.3	4.6	4.2	4.1
HEI Level				Low	Low	High	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low	Low
Heavy metal Potential index (HPI)				1.9	54.8	189.6	10.7	1.4	3.7	1.2	1.2	8.1	82.0	5.5	14.4	21.2	1.6	29.0	1.3	4.1	1.7	1.9	1.8
HPI Level				CI	CI	ACI	CI	CI	CI	CI	CI	CI	CI	CI	CI	CI	CI	CI	CI	CI	CI	CI	CI
Trace Element Toxicity Index (TETI)				70	4378	8615	11174	394	11892	1037	309	3780	6932	2017	6199	6486	842	2562	2064	5169	797	818	891
Environmental Water Quality Index (EWQI)				1.088	0.017	0.008	0.007	0.196	0.007	0.074	0.272	0.022	0.010	0.043	0.013	0.012	0.097	0.032	0.041	0.014	0.107	0.102	0.093

* G = Good, M = Medium, CI = within critical index value and ACI = above critical index value.

Arsenic, which has the highest toxicity ASTDR value, was found to be above the ANZECC trigger value of 13 µg/L for Sawyers Swamp (W2 = 19 µg/L). Boron in the Blue Mountains area did not show elevation in discharge, however, West Cliff colliery and Bargo River in Tahmoor (S3 & S6) recorded double the concentrations comparing to the downstream locations. Though lower than the ANZECC trigger value, Zn was highly elevated in downstream locations, except for West Cliff colliery (S2 & S3) confirming mine impact.

It is important to note that the iron levels are of particular interest to water supply authorities and it can affect taste and colour. As study contained many sites within Sydney's drinking water catchment (Birch et al., 2015) this may present future management issues for the water authority. Iron has ANZECC guidelines trigger value of 300 µg/L, while the concentrations in the studied samples had up to 210,000 µg/L. Sawyers Swamp sample downstream of discharge (W3) had iron concentration almost 500 times above the sample collected from Coxs River (W1). The trend of iron in the West Cliff colliery (S1, S2 & S3) and Tahmoor coal mine Bargo River (S4 & S5) did not show any impact of the mine. The manganese trigger value was exceeded at the Redbank Creek site (S7). Molybdenum, nickel, lead, rubidium, antimony, titanium, uranium, vanadium are rarely detected in the samples, however, there is evidence of these metals in all downstream samples (W6, W7, W9, W10, S2, S3, S5 & S7) indicating impact of the mine discharge. Strontium and barium are not listed in the ANZECC trigger guidelines but their high presence in the downstream samples is a concern as a substantial amount is registered in W6, W7, W9, W10, S2 S3, S5 and S7.

3.3.2 Comparative assessment of indicators of water quality

Table 3.4 presents the results of the five indices used to assess the quality of water released from the coal mine and CSG activities. The WQI of the study areas 3, 4, 5 and 6 clearly show the impact of coal and CSG activities on the downstream environment. In two cases (W6 and S5) the WQI suggests the quality of produced water is better than the upstream or reference water quality. This is likely due to the presence of e-coli from domestic or native animals in the upstream (S4) and neutral pH value of the downstream location (S5), impacting the trend of the index.

Table 3.5: Analysis of trace elements in water samples.

Study area		Measurement Uncertainty %	1				2			3			4			5		6		7		
Sample location			**W1**	**W2**	**W3**	**W4**	**W5**	**W6**	**W7**	**W8**	**W9**	**W10**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
Analytes	**DL**		**U**	**D**	**U**	**D**	**U**	**D**	**DP**	**U**	**D**	**DD**	**U**	**D**	**DP**	**U**	**D**	**U**	**D**	**U**	**D**	**DD**
Sodium	0.5 mg/L	17	4.7	370	4.1	84	3.8	3.6	5.3	3.9	3.2	3.5	44	680	800	29	270	41	390	32	35	40
Potassium	0.5 mg/L	18	1.2	13	0.9	7.4	0.6	5.2	2.7	<0.5	1.9	2.7	1.8	4	4.2	2.3	11	10	3.6	2.5	2.8	2.9
Calcium	0.5 mg/L	15	<0.5	5	0.8	17	<0.5	37	1.9	<0.5	4.7	13	15	8.6	7.2	3.1	9.5	9.9	13	4.3	4.9	5.4
Magnesium	0.5 mg/L	12	<0.5	3.6	1.1	11	<0.5	11	0.9	<0.5	6.4	15	4.5	3.6	3.5	4.7	7.9	12	37	4.2	4.6	5.1
Sulphur	0.5 mg/L	-	<0.5	11	2.2	35	0.9	37	2.2	0.7	9.3	20	5.5	16	16	2	2.5	5.8	9.1	1.8	1.9	2.1
Silicon	0.2 mg/L	17	3.9	4.6	6	4	2.4	2.8	3.1	1.6	3.4	3.3	2.2	3.1	3.2	2.4	2.5	3.1	5.9	1.3	1.7	1.3
Aluminium	10 µg/L	18	40	840	9700	120	80	20	250	100	10	40	80	540	660	110	120	90	60	110	90	100
Arsenic	1.0 µg/L	16	<1	19	4	<1	<1	<1	<1	<1	<1	<1	<1	8	9	<1	12	<1	<1	<1	<1	<1
Boron	5.0 µg/L	20	7	78	18	28	9	10	9	10	9	12	27	56	63	19	34	49	16	14	15	14
Barium	1.0 µg/L	10	12	37	130	33	10	25	18	5	25	32	66	390	480	18	1400	54	270	87	92	92
Cobalt	1.0 µg/L	21	<1	13	52	<1	<1	15	8	<1	25	9	<1	3	4	1	7	<1	37	<1	<1	<1
Copper	1.0 µg/L	24	<1	<1	14	1	<1	<1	2	<1	1	<1	<1	5	5	<1	<1	<1	<1	<1	<1	<1
Iron	10 µg/L	13	430	730	210000	260	240	85	270	26	340	410	730	450	570	1200	520	180	33000	440	410	400
Mercury	0.05 µg/L	16	<0.05	<0.05	0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Lithium	1.0 µg/L	-	<1	170	2	35	<1	20	<1	<1	15	20	20	290	330	1	500	<1	29	25	30	34
Manganese	5.0 µg/L	19	20	170	1200	130	49	230	92	12	400	80	94	39	39	120	36	29	2300	41	33	29
Molybdenum	1.0 µg/L	13	<1	42	<1	2	<1	<1	<1	<1	<1	<1	<1	46	55	<1	8	<1	<1	<1	<1	<1
Nickel	1.0 µg/L	20	<1	13	16	3	<1	66	36	<1	190	260	3	86	110	2	31	<1	32	2	2	2
Lead	1.0 µg/L	13	<1	1	10	<1	<1	<1	<1	<1	<1	<1	<1	3	3	<1	1	<1	<1	<1	<1	<1
Rubidium	1.0 µg/L	-	<1	<1	<1	<1	<1	16	1	<1	<1	<1	3	5	5	3	25	7	7	6	6	6
Antimony	1.0 µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	12	14	<1	1	<1	<1	<1	<1	<1
Strontium	1.0 µg/L	14	5	22	18	84	4.4	76	9.1	3.4	18	50	75	230	270	23	290	140	97	47	53	59
Titanium	1.0 µg/L	-	<1	7.7	18	1.6	<1	<1	3.4	<1	<1	<1	<1	7.9	13	1.5	1.9	2	1.1	2	1.6	2.9
Uranium	0.5 µg/L	15	<0.5	0.7	1.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	6.5	7.7	<0.5	2.1	<0.5	<0.5	<0.5	<0.5	<0.5
Vanadium	1.0 µg/L	13	<1	<1	26	<1	<1	<1	<1	<1	<1	<1	<1	16	18	<1	<1	<1	<1	<1	<1	<1
Zinc	1.0 µg/L	22	3	23	49	12	6	55	41	3	340	320	50	26	21	6	30	3	88	4	3	4
Zirconium	1.0 µg/L	-	3	23	49	12	<1	<1	<1	<1	<1	<1	<1	5.6	6.5	<1	2.3	<1	<1	<1	<1	<1

*U= upstream, DL = detection limit, D = downstream, DP = discharge point and DD = further downstream

The samples collected in the Blue Mountains region generally showed low contamination C_d index with the exception of the high level reported for Sawyers Swamp (W2 and W3) (Table 3.5). In the Sydney south study area Tahmoor, Redbank Creek sample after the subsidence (Wright et al., 2015) (S7) had high contamination with iron, manganese and zinc and consequently the index (C_d) was also found high. Although the discharge point samples had low contamination categories, the numerical index values indicated the higher contamination of produced water samples than the upstream location, except in case of Bargo River (S4). This may be the case because the S4 sampling location was collected where stream flow resurfaces from the subsidence area raising the iron level and consequently the contamination index. All the other samples in the Blue Mountains area (W4. W5, W6, W7, W8, W9 & W10) had low C_d index.

The heavy metal evaluation index (HEI) reports that all samples, except for W3, were classified as low pollution, while W3 was a high polluted sample, which was found to be in accordance to the WQI and C_d. Although HEI at locations W8 and S7 indicated low pollution level, the index is higher than in the other sites and compares with high C_d index and low WQI. The heavy metal pollution index (HPI) is based on the composite influence of the individual heavy metals on the overall water quality (Mohan et al., 1996). The critical condition arises if the index reaches the value of 100. It is only Sawyers Swamp (W3) which exceeded the index value of 100, while all other samples were in the category below the critical index value. The estimated high metal pollution of the W3 sample coincided with the related HEI. Although only W3 exceeds the critical value, elevated HPI was estimated for W2 and W10.

The results identify the various indices do not consistently predict the impact of mine produced water in the receiving streams. This highlights the indices are designed to reveal different attributes in the water quality and thus points to the importance to look more broadly at the background conditions and water chemistry While the WQI considers wider impact of nutrient, pH and biological pollution on the water quality, it ignores the toxicology of the metals present in the dissolved solids. Additionally, the individual toxicological and environmental impacts of the elements present in the dissolved solids are not well depicted by the C_d, HEI and HPI. For this reason a separate new index based on the elemental toxicological impact is additionally proposed in this work, which is termed trace element toxicity index (TETI). This index is recommended for inclusion in environmental impact evaluation as it provides intensity of the contaminants to the environment in terms of total toxic environmental impact. Appendix 3.1 gives the individual toxicological estimates for the elements based on their concentrations measured in each location and the relative toxicological weight. The results indicated sulphur had the highest impact on the toxicological profiles of most sites, followed by aluminium, manganese, barium, strontium and zinc. W1, W3, S2, S3 and S7 also reported methane as a significant impact on the quality. For sites W9 and W10, sulphur, manganese, zinc and nickel had substantial toxicological values. According to TETI the locations downstream and mine discharge points had higher index values than the upstream locations, for all sampling sites. The highest risk carrying sites were Wollangambe River and Springvale discharge points W6 and W4, followed by W3, W10, S3, S2, S7 and W2.

The newly proposed TETI index will only be applicable for toxic elements in the water, while it does not consider the other fundamental water quality parameters used for WQI calculation. In order to incorporate an all-inclusive water quality parameter, a new Environmental Water Quality Index (EWQI) is proposed which includes WQI and TETI indices. The trend shown by the newly proposed EWQI gives very clear trend in the impact of coal and coal seam gas mining activities on surface water quality when compared to the upstream reference water samples. EWQI, which is higher for better water quality, clearly indicates that all reference water upstream samples had higher EWQI ranging between 0.04 and 1.088, comparing to the downstream samples which were as low as 0.07 for W4 and W6, due to significant sulphur concentrations. Considering no other index accounted for the toxicological profile of the sulphur, these two sites were classified as sites with good water quality in all other indices. Sulphur is considered a primary tracer of coal (Puig et al., 2008), and should be investigated to evaluate the impact of coal related activity on environment or inhabitants. The newly proposed EWQI also indicates significantly higher impact on surface water quality from coal mining comparing to coal seam gas mining. The EWQI of the downstream locations in the coal mining sites were in the range of, as low as, 0.6% (W4) to 37% (W7) of the corresponding background upstream EWQI values, with the average EWQI being only 8% of the reference sites. This means that the downstream water exhibits an average 92% degradation in the water quality comparing to the upstream sites due to the coal mining activities. The CSG downstream location showed EWQI values from 28% to 95% of the background upstream EWQI values with median degradation in water quality at 49%. This further indicated the collection of CSG produced water on the surface for treatment rather direct release to the stream.

The newly proposed EWQI, a comprehensive representation of impact fallen into the same level for W3, W4 and W6 (0.008, 0.007 and 0.007 respectively) which was not possible with any of the indices discussed above. WQI considered W4 better than W3 and W6 even better than W4 which in reality was not true because of the missing high impact of sulphur on W6 and W4. Similarly, C_d, HPI and HEI have indicated a very high index for W3 in comparison to W4 and W6 because of the desirable concentration of limited metals only and missing other parameters included in total score of EWQI calculation. WQI of W4, W5, W6, W7, W8, W9, W10, S1, S2, S3. S4, S5, S6, S7, S8, S9, and S10 all came under same category of good water quality. Similarly, HEI was low and HPI within critical value for all the above samples while EWQI of W5 was 28 times of W6, W8 was 27 times of W10 and S1 was 3.6 times of S3. This difference in the value of newly proposed EWQI has opened a new chapter in the indices of impact assessment. It will bring future statistical research work forward to evaluate and assign the different ranges of EWQI for impact assessment based on the inhabitants' survival statistics.

3.4 Conclusion

This study examined the extent of chemical constituents derived from coal and coal seam gas mining activities and their impacts on surface water. Environmental impacts of increased pollutants from both past and present mining activities in the region are associated with reduction of water quality and resource depletion. Variety of water quality encountered in the coalfield provides a baseline for geochemical understanding, and a sustainable remedial system can be designed for the future resource utilization. Trace level of contaminants in Nepean River rules out the major risk associated with CSG production as the impact of CSG activity across the overall catchment was minor. The measured trace metal concentration established a benchmark for individual sites for future change in the water quality and indexing. The study further proposed an all-inclusive environmental water quality index (EWQI) which accounts for the standard water quality index and the environmental toxicology of the dissolved toxic metals in the water. This is a more comprehensive tool for water quality assessment and evaluation of impacts of industrial activities on surface waters. This will open a new chapter of statistical inhabitant study with respect to EWQI range. This research work points out on the need for revision of the conditions of coalmine run off management and recommends the compulsion of regular monitoring of produced water and natural resources in the region. It is evident that the current regulatory approach may need to consider inclusion of appropriate tools and measures for achieving a more sustainable environment. Future studies may investigate metal solubility and mobility as well as metal association with particle sizes and their impact on mobility.

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Appendix 3.1: Environmental Impact Assessment based on concentrations and relative toxicity of trace elements, according to the ASTDR

Study area				1				2			3			4		5		6		7	
Location number	**ATSDR Total Points**	**W1**	**W2**	**W3**	**W4**	**W5**	**W6**	**W7**	**W8**	**W9**	**W10**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
Sulfur	310		3410	682.00	10850	279	11470	682	217	2883	6200	1705	4960	4960	620	775	1798	2821	558	589	651
Aluminium	686	27.4	576	6654	82.3	54.9	13.7	171.5	68.6	6.86	27.4	54.9	370	453	75.5	82.3	61.7	41.2	75.5	61.7	68.6
Arsenic	1672		31.8	6.69									13.4	15.0		20.1					
Boron	438	3.1	34.2	7.88	12.3	3.94	4.38	3.94	4.38	3.94	5.26	11.8	24.5	27.6	8.3	14.9	21.5	7.01	6.13	6.57	6.13
Barium	802	9.6	29.7	104	26.5	8.02	20.1	14.4	4.01	20.1	25.7	52.9	313	385	14.4	1123	43.3	217	69.8	73.8	73.8
Cobalt	1012		13.2	52.6			15.18	8.10		25.3	9.11		3.04	4.05	1.01	7.08		37.4			
Copper	806			11.3	0.81			1.61		0.81			4.03	4.03							
Mercury	1459			0.09																	
Lithium	422		71.7	0.84	14.8		8.44			6.33	8.44	8.44	122	139	0.42	211		12.2	10.6	12.7	14.3
Manganese	798	16.0	136	958	104	39.1	184	73.42	9.58	319	63.8	75.0	31.1	31.1	95.8	28.7	23.1	1835	32.7	26.3	23.1
Molybdenum	442		18.6		0.88								20.3	24.3		3.54					
Nickel	996		12.9	15.9	2.99		65.7	35.9		189	259	2.99	85.7	110	1.99	30.9		31.9	1.99	1.99	1.99
Lead	1529		1.5	15.3									4.59	4.59		1.53					
Antimony	601												7.21	8.41		0.60					
Strontium	804	4.0	17.7	14.5	67.5	3.54	61.10	7.32	2.73	14.47	40.20	60.30	185	217	18.5	233	113	78.0	37.8	42.6	47.4
Titanium	481		3.7	8.66	0.77			1.64					3.80	6.25	0.72	0.91	0.96	0.53	0.96	0.77	1.39
Uranium	831		0.6	1.00									5.40	6.40		1.75					
Vanadium	650			16.9									10.4	11.7							
Zinc	915	2.7	21.0	44.8	11.0	5.49	50.3	37.5	2.75	311	293	45.8	23.8	19.2	5.49	27.5	2.75	80.5	3.66	2.75	3.66
Methane	953	6.7		20.0									11.4	60.0				7.62			
Total of ATSDR multiple		70	4378	8615	11174	394	11892	1037	309	3780	6932	2017	6199	6486	842	2562	2064	5169	797	818	891

ATSDR = Agency for Toxic Substances and Disease Registry,
EIA = Environmental Impact Assessment Index equivalent to Arsenic

River Sediment Quality Assessment Using Sediment Quality Indices for the Sydney Basin, Australia Affected by Coal and Coal Seam Gas Mining

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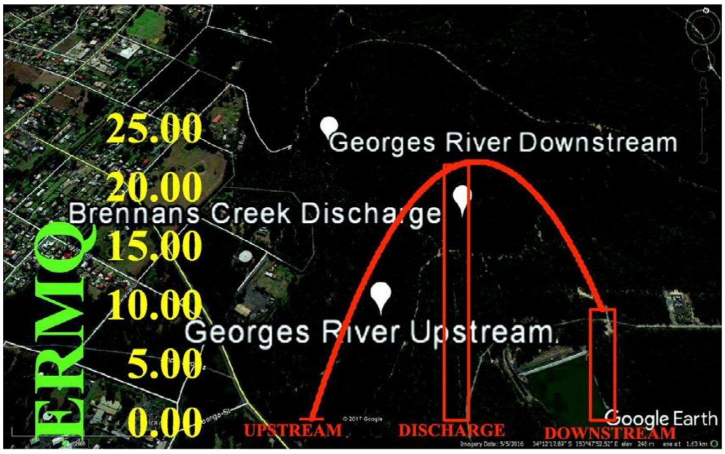
Highlights

- Trace elements were analysed to study the quality of sediments affected by mining.
- Significant increment was determined in contaminants near coal mine discharge.
- Degree of contamination of the sediments was determined using sediment quality indices.
- New environmental toxicity quotient (ETQ) was proposed in this study.

Graphical Abstract



Abstract

Coal mining activities in the Sydney basin have been historically associated with significant environmental impacts. The region is facing more recent coal seam gas extraction activities and the synergetic environmental impacts of the new mining activities are still largely unknown. The aim of this study was to provide environmental assessment of river sediments comparing upstream to downstream areas relative to industrial-discharge sites associated with coal and coal-seam-gas extraction within the Sydney basin. Various contaminants were measured to determine the sediment quality according to the Australian and New Zealand Environment and Conservation Council (ANZECC) guidelines. Arsenic, nickel and zinc were the main sediment contaminants in downstream samples exceeding the ANZECC guidelines. Degree of contamination (C_d), geoaccumulation index (I_{geo}), enrichment factor (EF), pollution load index (PLI) and sediment environmental toxicity quotients' increment in downstream sediment were estimated for the studied areas. Toxicology indices of metals present in the sediments near industrial discharge sites were used as an additional tool to compare the level of environmental effects with their increment. The study revealed that the sediments from coal mining sites were highly affected by increased concentrations of manganese, zinc, cobalt, nickel and barium. The sediments associated with coal mining activities were found to be substantially more affected than the sediments near coal seam gas production sites, mainly attributed to the different wastewater discharge licensing requirements. The approach applied in this study can be used as an additional model to assess the contribution of industrial and mining activities on aquatic environments.

Key words: Coal mine; environmental effect; produced water; sediment quality guidelines value (SQGV); mean effective range median quotient (ERMQ); environmental toxicity quotient (ETQ).

4.1 Introduction

Increasing demand for energy resources is continuously affecting our environment with fossil fuel energy sources, such as coal and natural gas, which are still experiencing exponential demand (Chong et al., 2016) despite international commitments to transition to low carbon energy sources (Hildingsson and Johansson, 2016). Coal and coal seam gas (CSG) mining and related activities are associated with a range of health and environmental concerns (Phelan et al., 2017; Tiwari et al., 2017). Coal mining is frequently associated with acid mine drainage (Jacobs et al., 2014; Choudhury et al., 2017), which results from oxidation of sulphide bearing rocks to produce sulphuric acid in the presence of atmospheric oxygen and water. Sulphuric acid produced in this process causes dissolution of rocks, generating metal ions and subsequently contamination of water and sediments (Matsumoto et al., 2016). In additional to traditional coal mining activities, coal seam gas (CSG) extraction has emerged as a significant source of energy with its own environmental concerns (Morgan et al., 2016). It has been reported that more than 2500 hydro-fracking chemicals are in the market to facilitate extraction of gas from coal and shale seams (Waxman et al., 2011). This variety of fracking chemicals, which are regulated to varying degrees, present new environmental exposure risks to water and sediments. In combination with the mobilization of geogenic contaminants from coal seams, the fracking compounds raise potential public health concerns (Yost et al., 2016).

Studies are now attempting to reconstruct the levels of heavy metals in river sediments to determine the key social and political events contributing to changes in metal concentration in sediments (Wang et al., 2015). Environmental and social impacts associated with the mining industry apply to both current and abandoned mines, where rehabilitation and mine closures have not been adequately taken. Minerals associated with mine wastes dissolve and result in an abrupt increase in dissolved acidity, called acid generating salts (Wright et al., 2015). Fine sediments (< 63um), produced by the flows and settlement usually have the most contaminating effects due to the greater surface area and access to more binding sites. The acid generating salts affect water and sediments by geochemical processes which can occur over a period and distance from the mine discharge. Underground longwall coal mine activity removes coal seams causing movement and fracture of geological strata which generates surface subsidence. Water can flow through the subsidence, dissolve the contaminants, transporting them through surface and subsurface flows and subsequently deposit in sediments downstream from the mine. Soil heaps linked to both underground and surface coal mines, which originally contain coarse fragments of rock, can change to a mass of disaggregated mud and sand due to weathering. The muds and sands can escape from a mine site typically associated with an engineering failure and can enter waterways. Discharge of mine wastewater from a site, if not adequately treated, will contain contaminants that will subsequently affect downstream waterways and sediments. Accumulation of excessive contaminants due to continuous loading into the waterway will serve as pollution source and damage the ecosystem (Wright et al., 1995; Belmer et al., 2015; Wright and Ryan, 2016). The continuous accumulation of contaminants may reach a point where it causes an adverse effect on biota and the sediment is considered as polluted. Biotransformation and desorption of these contaminants are very slow. Even at low level contamination, the metals affect the flora and fauna, which can then enter the food chain through bioaccumulation (Bazrafshan et al., 2016). Sediment quality assessment, therefore, is an essential environmental management consideration for coal and related mining activities.

There are different approaches to assess the sediment quality and these have evolved with an increased understanding and improved analytical tools. Bulk chemical contamination of an individual contaminant was the initial approach to evaluate sediment quality (Gambrell et al., 1983). A relationship between chemical contaminants and ecotoxicity has been applied to evaluate sediment quality (Long and Chapman, 1985; Jørgensen et al., 2016). A potential ecological risk index (PERI) with the toxic substances has also been used to assess the sediment contamination (Hakanson, 1980). A number of studies have also focused on the relationship between sediment contamination and toxicity response through the bioavailability of the contaminants (Chapman, 1989; Adams et al., 1992; Amato et al., 2016). Knowledge of the total concentration of contaminants in sediments plays an important role in the assessment of the sediment quality. It is essential that the contaminants analysed at an industrial site are compared with a reference site to achieve environmental assessment, as this can account for the natural or background conditions preceding the industrial or mining activity. A metal pollution index may assist in this regard where metals are known to affect environmental health. This study focussed on anthropogenic effects of coal and coal seam gas industries on the river sediments using pollution indicators, including the degree of contamination, geoaccumulation index, enrichment factor (EF), pollution load index (PLI), and the pollution status determined through the sediment quality guidelines (SQGs). Previous study (Ali et al., 2017) identified significant impact of the coal mining activities on surface water quality but did not discuss the impact these activities have on the sediment quality. The objective of this research was to study the effect of coal and coal seam gas mining in the Sydney basin on the river sediment quality and develop an environmental assessment index capable of quantifying the environmental effects of mining activities on the downstream river sediments.

4.2 Materials and methods

4.2.1 Study area and site description

Two regions were selected for this study consisting of: (i) Western Sydney region of the Blue Mountains located 85 to 140 km west and (ii) the Southern Sydney region located 60 to 120 km southwest of Sydney because of extensive coal and, to a lesser extent, coal seam gas mining activities. Four coal mines of interest (Canyon, Centennial, Angus Place and Springvale collieries) affecting the water resources were selected for the study. These mines are discharging their wastewater into the natural resources which could significantly affect the environment and need monitoring. These mines discharge to Coxs, Wollangambe and Grose rivers, Dalpura Creek, and Sawyers Swamp, respectively, and are located in the Western Sydney region of the Blue Mountains. They are shallow and fast flowing upland streams at elevations from 460 to 1,093 m above sea level. These sites are rocky and difficult to access. The mines started operating in this area in the early 1900s and few have closed, such as the Canyon mine, which closed in 1997 (Macqueen, 2007).

Four study areas 4, 5, 6 and 7 were selected for the Southern Sydney region. Study area 4 to determine the effect of West Cliff Colliery on Georges River and Brennans Creek, area 5 for the effect of Tahmoor coal mine on Bargo River, area 6 for the effect of subsidence caused by underground mining on the quality of sediment of Redbank Creek and area 7 was selected to study the effect of coal seam gas production on the sediment quality of Nepean River. West Cliff and Tahmoor collieries discharge to Brennans Creek, Redbank Creek, Georges and Bargo Rivers. Samples were collected from the Nepean River to assess the impact of a coal seam gas (CSG) production site in the Southern Sydney region. The sampling location points are shown in Figure 4.1. The sediment samples were collected from the locations before and after the produced water discharge points.

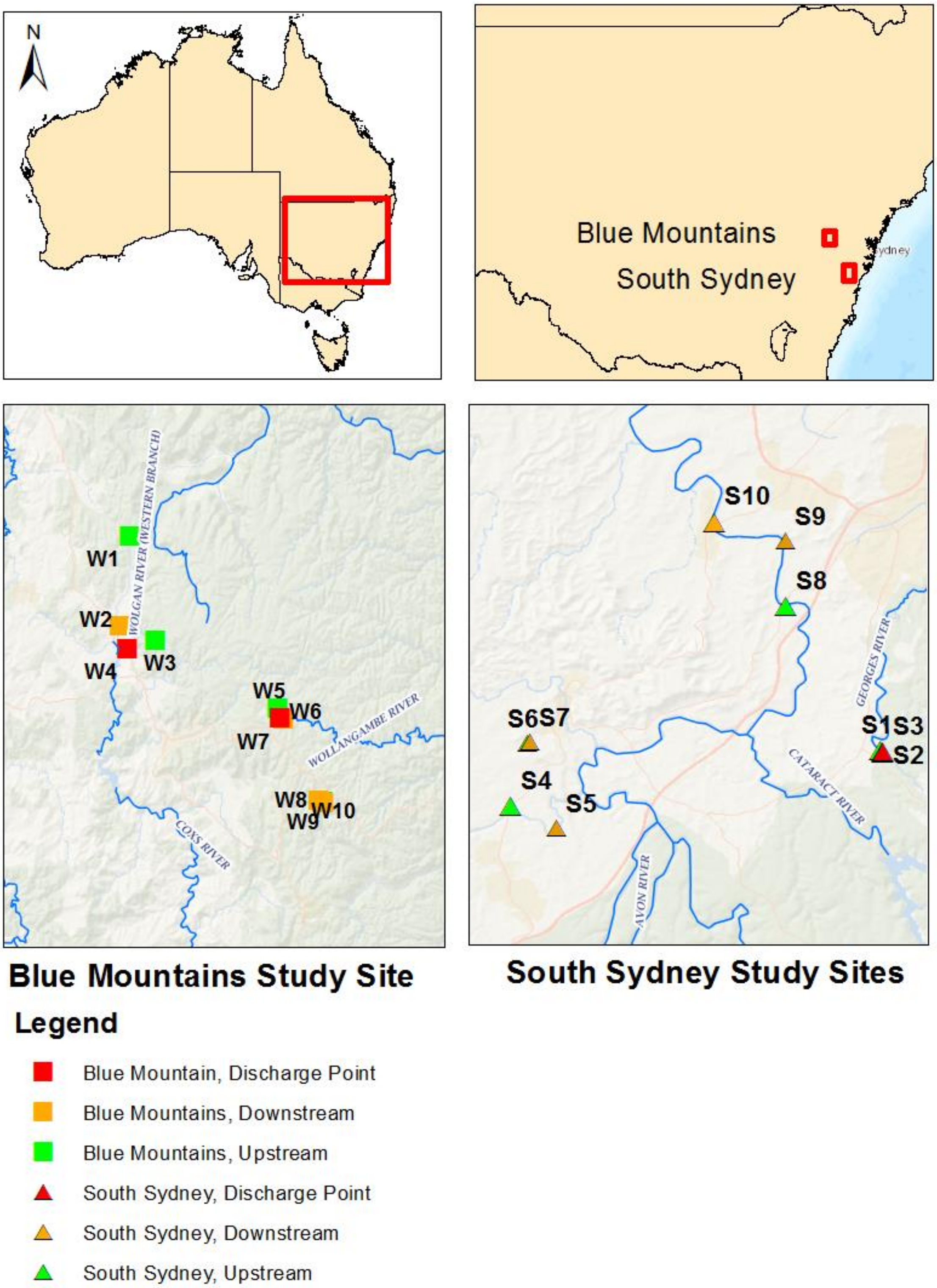


Figure 4.1. Map of the sampling locations.

4.2.2 Sampling and analysis

The sampling points were randomly selected depending on the access to the representative stream of discharge of the mine to the creek or river before and after the mine discharge. Sediment samples grabbed from the surface in triplicates were collected from an area within 1 m^2 in clean screw capped 250 gm glass jar without any preservatives from the sampling points shown in Figure 4.1 in the period between July 2014 and September 2015.

A composite dry weight sample for each site was used for analysis of the alkali metals, alkaline earth metals and most of the transition metals, metalloids and polyatomic non-metals. The standard sediment quality parameters were analysed by an external laboratory accredited through National Association of Testing Authorities (NATA) and following the standard reference methods USEPA 200.8, USEPA 6020A, USEPA 7471A, USEPA 3051A, and APHA 3125.

For particle size analysis a gravel free sample sieved to < 2.0 mm was dispersed in water and passed through laser detection on Malvern Mastersizer 2000 with a 300RF lens. An average of two readings were performed for calculation of the grain size range. All sediments were classified into three groups, clay with particle size from 0.01 to 2.0 μm, silt with particle size from 2.0 to 62.5 μm, and sand with particle size from 62.5 to 2000 μm. The particle size distribution was determined with a built-in Malvern software based on the standard procedure (Sperazza et al, 2004).

4.2.3 Pollution indicators

A number of indicators were applied for environmental assessment, including the degree of metal enrichment in sediments (Hahladakis et al., 2013), degree of contamination, geoaccumulation index, enrichment factor (EF) and pollution load index (PLI), which are commonly used for environmental assessment. The sediment quality guideline values (SQGV) published by the Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand (ANZECC, 2000), effective range low/median (ERL/ERM) trigger values, and threshold/probable effect level (TEL/PEL) were also used to evaluate the degree of contamination (C_d) and modified degree of contamination (mC_d).

Calculated contamination factor (C_f) for pollutants is used as the basis for representation of the degree of contamination (C_d) which is calculated as:

$$C_f^i = \frac{M_x^i}{M_b^i}$$

Where M_x represents the concentration of individual metals in the sediments and M_b is the baseline concentration of each metal in the sediment. The sum of all contamination factors is considered as a degree of contamination (Hakanson, 1980):

$$C_d = \sum_{i=1}^{n} C_f^i$$

The equation proposed by Hakanson (1980) had a limitation, as the equation does not account for the number of contaminants. For this reason, the degree of contamination index was modified by Abrahim & Parker (2002) as:

$$mC_d = \frac{\sum_{i=1}^{n} C_f^i}{n}$$

where n is the number of analytical parameters. Based on the modified degree of contamination mC_d, the sediment contamination can be classified as very low, low, moderate, high, very high, extremely high, and ultra-high with respective range of <1.5, 1.5 to <2, 2 to <4, 4 to <8, 8 to <16, 16 to <32, and >32.

4.2.4 Geoaccumulation index (I_{geo})

The geoaccumulation index is another relative contamination assessment of sediments proposed by Muller in 1969 (Abrahim and Parker, 2002), estimated according to the equation:

$$I_{geo} = log_2 \left(\frac{C_n}{1.5 * B_n}\right)$$

where B_n and C_n are baseline concentrations and measured concentrations of affected sediments, respectively. Based on I_{geo} the pollution status varies from unpolluted, unpolluted to moderately polluted, moderately polluted, moderately to strongly, strongly, strongly to extremely strongly, and extremely polluted status with respective range of <0, 0-1, 1-2, 2-3, 3-4, 4-5, and >5. The baseline values for the geoaccumulation index were determined from the upstream results of the sediment analysis.

4.2.5 Enrichment factor (EF)

The enrichment factor of the metals in sediments was estimated according to Ergin et al. (1991):

$$EF = \frac{\left(\frac{M}{Fe}\right)_{sample}}{\left(\frac{M}{Fe}\right)_{background}}$$

Where $\left(\frac{M}{Fe}\right)_{sample}$ is the ratio of metal and iron concentration of the sample and $\left(\frac{M}{Fe}\right)_{background}$ is the same ratio for the background sample. The upstream samples of each site were considered as background samples.

4.2.6 Pollution load index (PLI)

The number of times of increase in heavy metal concentration in the sediment relative to the background concentration is known as pollution load index (PLI). PLI gives a collective indication of the overall heavy metal concentration levels and is obtained as a concentration factor (CF) according to Tomlinson et al (1980):

$$CF = C_{metal} / C_{background\ value}$$

$$PLI = PLI = \sqrt[n]{(CF1xCF2xCF3x \ldots \ldots . xCFn)}$$

where CF = contamination factor, n = number of metals, C_{metal} = metal concentration in polluted sediments and $C_{Background\ value}$ = background value of that metal.

4.2.7 Sediment quality guidelines (SQG)

Sediment quality guidelines are representation of concentration limits of contaminants in sediments (Hinkey and Zaidi, 2007; Violintzis et al., 2009), developed by the National Oceanic and Atmospheric Administration (NOAA) after collection and investigation of large chemical and biological data (McCready et al., 2006). ANZECC (2000) applies the terminology of sediment quality guideline values (SQGVs) based on the contaminants' biological effect on inhabitants. This was achieved by statistical data evaluation of concentrations and toxicity (Smith et al., 1996). Two SQGVs are mentioned in the ANZECC guidelines. One is recommended SQGVs, also called effective range low/median (ERL/ERM) trigger values, representing the threshold value to trigger an adverse effect. The second is upper SQGV or a high value representing the high probability of effect, called threshold/probable effect level (TEL/PEL). An effective measure of toxicity can be evaluated by a mean quotient defined with:

$$\text{Effective range median mean quotient ERMQ} = \frac{\sum_{i=1}^{n} M_i/ERM_i}{n}$$

where M_i is concentration of element i in sediment and ERM_i is lower SQGV for element i

$$\text{Probable effect level mean quotient PELQ} = \frac{\sum_{i=1}^{n} M_i/PEL_i}{n}$$

where M_i is concentration of element i in sediment and PEL_i is upper SQGV for element i. The ERMQ value of <0.1, 0.11 to 0.5, 0.51 to 1.5 and >1.5 are respectively related to 12, 30, 46 and 74% toxicity of amphipod survival bioassays (Long and MacDonald, 1998). Similarly, PELQ of <0.1, 0.11 to 1.5, 1.51 to 2.3 and > 2.3 are in accordance to 10, 25, 50 and 76% of toxicity (McCready et al., 2006). The ERMQ and PELQ were calculated in this work for all collected sediment samples following the ANZECC guidelines.

4.2.8 Sediment environmental toxicity quotient

A novel sediment quality assessment quotient is proposed in this study calculated by multiplying the concentration of each contaminant measured in the sediment samples with the corresponding hazard intensity to determine the sediment quality based on toxicity. The hazard intensity of each parameter was determined according to the Toxicological Profiles of the Priority List of Hazardous Substances prepared by the US Agency for Toxic Substances and Disease Registry (ATSDR) the Division of Toxicology and Environmental Medicine, Atlanta, USA (ASTDR, 2015). Each detected element was multiplied by its total score (TS), divided by the highest TS assigned by ATSDR and results were added to calculate the elemental toxicity of the sediments. The proposed environmental toxicity quotient (ETQ) was determined by dividing the elemental toxicity by the total number of parameters. ETQ can be represented by the equation:

$$ETQ = \frac{\sum_{i=1}^{n} TS_i * C_i/TS_{As}}{n}$$

where C_i is the measured concentration of a specific element and n is the number of the analysed elements. TS_i is the total score for each element and TS_{As} is the total score of arsenic, which has the highest TS published by the Agency for Toxic Substances and Disease Registry (ATSDR).

4.2.9 Statistical analysis

The tabulated data was analysed using IBM SPSS v.23.0 (2015) statistical software. The variance analysis was performed by Mann-Whitney U test (McKnight & Najab, 2010), which was preferred over the other normality tests because of the smaller sample size and higher statistical power of the software for detecting deviance from normality test. An asymptotic significance was displayed to the level of 0.05 value of p.

4.3 Results

The sediment analysis results for each site are presented in Table 4.1. The sediment sample was found to be sand based in general, except for some locations in the Blue Mountains where silt had a noteworthy percentage (W2=14.6, W4=49.3, W5=32.4, W7=14.4, W9=25.4 and W19=49.6 %). The Blue Mountains area showed high total organic carbon content. Although the phosphorous (P) content ranged from zero to 440 with mean value of 172.5 mg/kg in downstream sample and from 20 to 550 with mean value of 101.25 mg/kg in upstream, it was found that there was no significant change in the concentration from upstream to downstream locations. The ammonia as N analysis identified a substantial increase in nitrogen discharge from the closed Canyon coal mine discharging into Dalpura Creek (W9 and W10). The elevated N levels (up to 2 orders of magnitude) may affect the downstream aquatic systems, however, the trend is inconsistent especially in South Sydney Bargo River and Redbank Creek (S5 and S7).

The sediment samples were analysed for 37 elements in total for each of the sample sites and the positively detected elements are presented in Table 4.1. Al, As, Ba, Ca, Cr, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Si, Ti, U, and Zn were recorded in all sediment samples. The upstream (U) samples, identified as the shaded columns in Table 4.1, reported lower concentrations of the elements than the samples collected downstream of the coal mine or CSG wastewater discharge points with reasonable exceptions of Bargo River (S4 and S5) and Redbank Creek (S6 and S7). In general, the change from upstream to downstream was significant in case of aluminium ($p=0.02$), barium ($p=0.01$), copper ($p=0.007$), lead ($p=0.02$), sulphur ($p=0.047$), uranium ($p=0.01$), calcium ($p=0.007$), potassium ($p=0.01$) and magnesium ($p=0.012$), however, the changes in chromium, cobalt, iron, manganese, nickel, silicon, titanium, zinc and sodium were substantial at individual sites. Aluminium was in the range of 190 to 5,800 mg/kg with average of 2,172 mg/kg in upstream and from 1,300 to 27,000 with average of 6,633 mg/kg in the downstream samples. The upstream reference for Dalpura Creek (W8) had only 190 mg/kg of aluminium, however, the creek falling into the river (W3) carried 12,000 mg/kg of aluminium. Arsenic was found to be above the ANZECC trigger value (SQGV) of 20 mg/kg for Sawyers Swamp (W2 = 41 mg/kg), Springvale (W4 = 26 mg/kg) and Dalpura Creek (W9 = 28 mg/kg) ranging from zero to 16 with average of 3 mg/kg in the upstream and from zero to 41 with average of 10.2 mg/kg in the downstream samples. Barium, with significant increment ranging from 1 in the upstream to 610 mg/kg in the downstream sample, was above the trigger value (300 mg/kg) in the downstream samples at Springvale and Dalpura Creek. Cadmium in Swayer Swamp and Dalpura Creek (W2 = 2 mg/kg & W9 = 2 mg/kg) was also higher than the trigger value of 1.5 mg/kg SQGV. Nickel is highly elevated in the Blue Mountains area (W2 = 210 mg/kg, W4 = 59 mg/kg, W7 = 53 mg/kg W9 = 2300 mg/kg, and W10 = 870 mg/kg) with concentrations in the sediments above the trigger value of 21 mg/kg.

Calcium, potassium, and magnesium were significantly higher in the downstream samples comparing to the upstream samples with $p=0.007$, 0.01 and 0.012 respectively. Sodium concentrations in the upstream samples were in the range of zero to 350 mg/kg comparing to 20 to 2,200 mg/kg in the downstream locations indicating very low background levels and a substantial effect of the release of salts from the coal mine produced water. Elevated levels of sodium, potassium, calcium, sulphur, cobalt, iron, barium, and nickel in the downstream locations across most study sites were detected and are indicative of the coal mining activities.

The sample collected from Coxs River (W1) was well under the ANZECC limit of SQGV and could be considered as upstream site to compare with Sawyer swamp (W2) and Springvale (W4) downstream sites. The downstream of Sawyer Swamp and Springvale show most of the listed contaminants above the limit, like arsenic in Sawyer Swamp (W2) 42 mg/kg and 26 mg/kg in Springvale (W4), while nickel was 210 mg/kg and 49 mg/kg, and zinc was 650 mg/kg and 380 mg/kg respectively. The contamination of Sawyer swamp is higher than that of Springvale. In addition to the listed contaminants all other analysed parameters were significantly high in downstream samples. Study area 2 of Wollangambe River was affected by the occasional collapse of Centennial coal mine waste. This river is known for its wilderness with the upstream being indicative of very clean sediment while the downstream and discharge points were well above the SQGV for nickel (W6=240 mg/kg, W7=320 mg/kg, W9 = 2300 and W10=870) and zinc (W2=650, W5= 380, W6= 340 mg/kg, W7=760 mg/kg, W9= 3500, W10= 1800). This has indicated that the waste piling at the mining site occasionally disturbs the environment

Table 4.1: Sediment quality parameters detected in a composite sample of triplicate sampling (mg/kg) *

Study area		Precision	SQGV	Study Area 1				Study Area 2			Study Area 3			Study Area 4			Study Area 5		Study Area 6		Study Area 7		
				Coxs River	Sawyers Swamp		Springvale	Wollangambe River near Centennial Coal's Waste			Canyon Mine Dalpura Creak			Georges River and Brennans Creek Appin			Bargo River _Tahmoor		Redbank Creek Picton		Nepean River		
Sample location				W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Sample location				W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Analytes	**DL**			**U**	**D**	**U**	**D**	**U**	**D**	**DP**	**U**	**D**	**DD**	**U**	**D**	**DP**	**U**	**D**	**U**	**D**	**U**	**D**	**DD**
Silt (%)				0.0	14.6	3.5	49.3	32.4	3.7	14.4	0.0	25.4	49.6	1.5	0.0	0.4	0.8	0.9	2.2	0.5	0.0	2.3	1.1
Sand (%)				100.0	85.0	96.5	47.1	66.5	96.3	85.4	100	73.2	47.6	98.5	100.0	99.6	99.2	99.2	97.8	99.5	100.0	99.7	98.9
Total Nitrogen	10	1.16		32000	3900	690	5900	140	170	610	67	3600	6900	75	39	90	240	77	240	43	66	250	220
TOC	200	3.24		1100	34000	21000	82000	390000	130000	90000	700	18000	130000	7000	2900	7700	15000	1100	7200	800	800	9600	4600
Ammonia as N	0.5	7.4		2.2	17	1.9	13	1.3	1.4	3	1.8	100	48	0.9	1.3	2.4	11	2.9	4.3	1.1	3.5	7.1	4.2
Phosphorus	10	5.75	2000	440	360	40	490	<10	<10	40	<10	60	550	10	20	20	70	100	210	40	30	140	80
Aluminium	1	7.36		5800	27000	1500	8200	270	910	1500	190	12000	6500	1100	1600	5200	3000	1300	4000	1500	990	4500	2600
Arsenic	4	5.03	20	16	41	<4	26	<4	<4	<4	<4	28	18	<4	<4	<4	<4	9	8	<4	<4	<4	<4
Barium	1	5.5	300$	120	220	23	610	3	33	25	1	510	260	25	23	45	17	90	27	20	18	100	40
Chromium	1	5.69	80	8	10	2	9	<1	1	2	<1	1	10	2	2	3	4	6	16	31	2	7	5
Cobalt	1	5.21	50$	66	180	3	51	<1	310	230	<1	3600	470	<1	<1	1	3	4	4	3	<1	5	2
Copper	1	5.51	80	5	17	2	22	<1	2	4	<1	87	180	2	2	2	2	30	7	3	<1	5	3
Iron	1	7.59		300000	27000	9200	21000	900	2500	6600	870	360000	310000	4000	4300	3100	5800	13000	33000	9700	2400	10000	5200
Lead	1	5.34	50	6	24	3	23	<1	3	4	<1	37	130	2	3	3	5	4	11	4	2	6	4
Manganese	1	6.85	500$	3200	3800	64	8600	160	2400	2500	2	38000	4700	31	64	210	180	290	120	100	49	230	45
Nickel	1	5.66	21	13	210	2	59	<1	240	320	<1	2300	870	1	1	2	3	4	6	21	1	5	3
Sulphur	10	6.86	600$	1600	4700	130	1600	10	70	210	<10	2400	2900	30	70	240	70	50	70	40	20	120	80
Silicon	10	5.74		1800	380	80	730	70	120	500	110	8000	1500	10	240	20	20	10	10	10	50	60	20
Titanium	1	5.05		17	25	4	8	1	3	9	2	2	39	3	16	120	8	41	15	10	10	8	6
Uranium	0.1	7.92	23$	0.6	2.7	0.2	0.9	<0.1	0.3	0.4	<0.1	9.8	18	0.2	0.2	0.7	0.2	0.2	0.2	0.1	<0.1	0.3	0.3
Zinc	1	5.55	200	43	650	8	380	1	340	760	<1	3500	1800	5	7	21	20	47	33	17	4	20	11
Calcium	5	7.57		830	17000	61	3900	8	380	570	<5	1300	3500	220	2500	14000	460	650	570	1800	130	670	190
Potassium	10	7.7		320	1100	50	1200	20	30	70	10	2300	800	110	140	250	110	100	270	120	100	340	200
Magnesium	5	6.85		520	990	30	810	8	40	120	<5	480	1300	140	480	1800	270	670	460	290	82	370	170
Sodium	10	7.91		350	2200	10	860	<10	<10	<10	<10	210	60	300	190	100	80	110	180	110	20	60	40

*U = upstream, D = downstream, DP = discharge point, DD = further downstream, DL = method detection limit, TOC (Total Organic Carbon) and SQGV is sediment quality guideline value ($ Department of Environment and Conservation ecological investigation level) , highlighted green columns represent upstream or background sites to a very high extent. The trigger SQGV value of zinc is 200 mg/kg and five sites reported elevated levels of zinc above this value, including W2, W4, W5, W7, W9, and W10. However, in the South Sydney area the zinc values had relatively low difference between the upstream and downstream locations with exception of the reverse trend in the Redbank Creek (S6).

Subsidence has been observed in Redbank Creek due to underground mining (Wright et al., 2015). Water flowing through the subsidence resurfaces at the sampling point and a high value of nickel at S6 upstream sample was detected that can be attributed to contamination of resurfaced water. Iron concentrations were found to be high in all cases which is natural geology of the area (Pickett, 2003) and varied from 870 mg/kg to 300,000 mg/kg in the upstream and from 3,100 to 36,000 mg/kg in the downstream locations. Iron does not have ANZECC guidelines trigger value but in several cases of downstream samples (W5, W7, W9 and W10) the concentrations of iron ranged over 30% of the sediment chemistry.

The elemental enrichment factors, shown in Supplementary Table 4.1, were found to be the highest in the downstream samples for all elements in Sawyers Swamp (W2), followed by Springave (W4). Delpura Creek (W9 and W10) exhibited higher enrichment in the downstream samples for Co, Mn, Ni and Zn, Brennans Creek (S2 and S3) for Ti, Mg, Mn and Zn, redbank Creek (S7) for Ni and Tahmoor (S5) for Co.

The environmental assessment based geoaccumulation index (Igeo), presented as Supplementary Table 4.2, showed unpolluted to moderately polluted sediment quality above and below the mine discharge in the South Sydney area. The Blue Mountains area had few parameters above the extremely polluted status (>5) including Sawyer Swamp downstream (W4) with Mn = 6.5, Na = 5.8 and Zn = 5.0, Wollangambe River with Zn = 7.8 (W6) and 9.0 (W7) and Dalpura Creek, which was most affected with Mn = 13.6 (W9) and 10.6 (W10), Zn = 11.2 (W9) and 10.2 (W10), Co = 11.2 (W9) and 8.3 (W10), Ni = 10.6 (W9) and 9.2 (W10), as well as Al, Ba, Cu, Pb and Mg.

Table 4.2 summarises and compares the sediment quality indices for all sites. The modified degree of contamination mC_d data for each of the Western Sydney Blue Mountains sites indicates sediment contamination from the respective coal mines. mC_d values ranged from ultra-high (Centennial W7, Canyon W9, W10 and Angus Place mine

Table 4.2: Sediment quality Indices*

Study area	Study Area 1				Study Area 2			Study Area 3			Study Area 4			Study Area 5		Study Area 6		Study Area 7		
Sample location	**W1**	**W2**	**W3**	**W4**	**W5**	**W6**	**W7**	**W8**	**W9**	**W10**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
Stream	**U**	**D**	**U**	**D**	**U**	**D**	**DP**	**U**	**D**	**DD**	**U**	**D**	**DP**	**U**	**D**	**U**	**D**	**U**	**D**	**DD**
Modified degree of contamination mC_d	1	4.5	1	24.9	0.59	20	42	1	1393.3	372.7	0.9	2.9	7.4	1	2.3	1	0.8	1	3.8	2.1
Pollution load index (PLI)	1	4.7	1	12.3	1	1.1	1.2	1	75.2	108.7	1	1.1	1.6	1	2.2	1	0.8	1	3.3	2.2
Mean effective range median quotient ERMQ	0.32	2.69	0.08	1.15	0	2.21	3.2	0.05	21.75	9.47	0.06	0.07	0.09	0.10	0.25	0.23	0.30	0.06	0.14	0.1
Mean probable effect level quotient PELQ	0.11	1.07	0.02	0.44	0.0004	0.91	1.3	0.01	8.94	3.78	0.02	0.02	0.03	0.03	0.08	0.07	0.10	0.02	0.04	0.03
Environmental toxicity quotient (ETQ)	121.8	186.0	4.1	339.0	5.6	120	140	0.1	1711.1	314.9	2.6	4.1	12.7	8.7	18.7	10.2	7.8	3.0	13.8	4.5

*U = upstream, D = downstream, DP = discharge point, DD = further downstream, DL = method detection limit and highlighted green columns represent upstream or background sites

Modified degree of contamination mC_d range: <1.5 very low, 1.5 to <2 Low, 2 to <4, Moderate, 4 to <8 High, 8 to <16 very high, 16 to <32 extremely high, and >32 ultra-high

Mean effective range median quotient ERMQ range: <0.1 results 12% toxicity of amphipod survival bioassays, 0.11 to 1.5 results 30% toxicity of amphipod survival bioassays, 1.51 to 2.3 results 46% toxicity of amphipod survival bioassays, and > 2.3 results 74% toxicity of amphipod survival bioassays

Mean probable effect level quotient PELQ range: <0.1 results 10% of toxicity, 0.11 to 1.5 results 25% of toxicity, 1.51 to 2.3 results 50% of toxicity, and > 2.3 results 76% of toxicity

W2), extremely high (Springvale mine W4, Centennial W6), very high (W1) to very low (W3, W5, W8). The data from the South Sydney region indicates that mC_d of all downstream sediments were in the moderate to very low degree of contamination, except for the discharge point of Westcliff colliery (S3 = 7.4), which had a high degree of contamination. The Dalpura Creek upstream sediment (W8) was sandy with continuous flow of natural water and was found to have the least degree of contamination. Accounting for the mC_d index the degree of contamination downstream of Dalpura Creek had the highest degree of contamination (W9 = 1393 and W10 = 373), well above the threshold for the ultra-high degree of contamination (>32). The high and ultra-high degree of contamination of the sediment clearly indicated deterioration of the downstream sediment due to coal mine discharge. Dalpura Creek downstream (W9 and W10) was found to be extremely polluted for most parameters. This creek receives untreated water continuously from the closed Canyon coal mine and this creek then flows into the Grose River located within a world heritage area (Macqueen, 2007). The results for this site highlight the inadequate mine closure and associated regulatory processes and will continue for the near future to have an ongoing and detrimental environmental effect. The upstream Dalpura Creek (W8) sediment comprised of sands derived from weathering of the Hawkesbury sandstone and reported the least concentration of metal contamination. The relative difference in metal concentrations between the very clean (upstream) and contaminated (downstream) sites resulted in the highest pollution value, further emphasising the ongoing and legacy effects due to this closed and unregulated mine wastewater discharge.

4.4 Discussion

4.4.1 Mining impact on sediment quality

All the three sampling sites in the South Sydney area near coal seam gas (CSG) production industries reported lower degree of contamination, ranging between low and moderate when compared to the coal mine sites, which ranged above ultra-high degrees of contamination of the sediments. A similar trend was observed in the case of enrichment factor (EF), except in case of West Cliff mine sites. The CSG activity in the South Sydney catchment does not discharge directly to waterways with their produced water collected in above ground tanks and disposed off-site as part of their pollution licence condition under the Petroleum (Onshore) Act 1991 by the Division of Resources and Energy in NSW Trade & Investment. The differing method of wastewater disposal undertaken by the CSG production at this site also reflects the relative 'dry' coal seams within this area that impact on the volume of produced water generated through the extraction process. The implications mean that produced water can be collection, contained and disposed off-site, an approach that is not suitable for most CSG activities (Davies et al., 2015).

The effective range median mean quotient (ERMQ) and probable effect level quotient (PELQ) were calculated based on the measured concentration levels relative to the trigger SQGVs and probable SQGVs of the ANZECC guidelines. The mean quotient was used to determine the indicative toxicity of the sediments. The estimated ERMQ suggests the sediments from downstream Sawyers Swamp (W2), Wollangambe (W7) and Dalpura Creek (W9 & W10) were above 46% of the warning level. This result indicated a standout site of the Canyon mine followed by Sawyer Swamp, Springvale and Angus Place mines. Moreover, the certainty of more than 76% of toxicity effect on the amphipod survival bioassays was determined by the PELQ index for the downstream Dalpura Creek sediment samples (W9 & W10) confirming the possible large effect on the inhabitants in the area.

All the sediment samples from South Sydney were well below 30% of the warning level of ERMQ and below 10% of PELQ of toxicity effect. This suggests the treatment of the produced water before the discharge is more effective at removing contaminants when compared to the mining operations in the Blue Mountains area. The comparative values of PELQ also shows lower environmental effects in the South Sydney area of coal and coal seam gas production, comparing to the Blue Mountains region. This could be due to better surveillance in South Sydney than at difficult-to-access Blue Mountains sites. Lower environmental effects in the CSG production area is indicating the strict licencing of the CSG production which needs proper storage, transportation and treatment before discharge.

4.4.2 Developing environmental assessment index

When different sediment quality indices are compared, some level of discrepancy is observed between them. While the modified degree of contamination (mC_d) showed very low degree of contamination for W1 (Table 4.2), the ERMQ and PELQ showed 30% and 25% toxicity, respectively. In case of W2, PELQ showed 25% toxicity only, while ERMQ estimated 74% toxicity of amphipod survival bioassays and mC_d indicated high level of toxicity. For samples W4 and W6 PELQ identified only 25% toxicity while mC_d estimated extremely high degree of contamination. It was only in case of ultra high toxicity identified by mC_d for W9 and W10 locations that both ERMQ and ETQ showed the highest toxicity. Differences in identifying the risks associated in the moderate to high contamination sites between different indices prompts on the importance to initiate an all-inclusive environmental quality index, which will take into consideration both human and environmental toxicity. For this purpose, an environmental toxicity quotient (ETQ) is proposed in this work, which is directly derived from the absolute toxicity effect of each chemical compound in the sediment and can provide a more reliable data for the environmental assessment of the sediments.

The newly proposed ETQ considers the overall toxicity parameter of each element as a total score (TS) published by the Agency for Toxic Substances and Disease Registry (ATSDR), as shown in Supplementary Table 4.3. In case of sample W1, where mC_d failed to identify any risk, but the other indices (ERMQ and PELQ) indicated levels of toxicity, ETQ was calculated at 121.8, which is similar to location W6 (ETQ=120), where mC_d suggests extremely high contamination and both ERMQ and PELQ also indicate different levels of toxicity. In case of locations W9 mC_d identifies ultra high level of contamination, ERMQ and PELQ suggest the highest level of toxicity, and ETQ also showed the highest value amongst all sites. Sample W4 had high ETQ score at 339, which was in a similar range to W10 (ETQ=315) although mC_d categorised both sites in different levels of pollution. According to the estimates in this work, the following pollution ranges can be assigned for ETQ, <10 low, 10-50 moderate, 50-100 high, 100-300 very high and >300 extremely high. Following these criteria, three sites (W4, W9 and W10) fall into category of extremely high pollution, four locations (W1, W2, W6 and W7) are categorised as very high polluted sites, while four sites (S3, S5 and S6 and S9) are in the moderately polluted range. In case of S3 mC_d categorises this site as highly polluted, while ETQ assigns moderate pollution, which is an average recommendation if also accounting the estimates by ERMQ and PELQ, both indicating low level of toxicity for this site. The main elements of concern identified by the ETQ in the order of importance were Mn, Zn, Co, Ni and Ba (see Supplementary Table 4.3). When comparing between different study areas, ETQ indicates that in all coal mining sites the sediments at the discharge and downstream locations had higher ETQ, except for Redbank Creek (S7) which was contaminated due to subsidence. In case of coal seam gas production, where discharges go into a holding tank and disposal is off-site in a registered wastewater treatment plant, the ETQ values for the downstream locations were lower than for the coal mining locations.

4.5 Conclusions

The chemical contamination and toxicity increments in river sediments up and downstream from coal and coal seam gas mining sites in outer Sydney metropolitan areas were investigated in this study. The results revealed that the sediment quality, specifically for arsenic (As), nickel (Ni) and zinc (Zn) in downstream coal mining discharge locations exceeded the ANZECC guideline limits for sediments. The Blue Mountains locations to the west of Sydney were more polluted than the southern Sydney mines. This may be attributed to the specific geochemistry of the coal seams but is most likely a result of pollution control strategies being less effective at metal removal. The abandoned Canyon coal mine has no treatment and provides evidence for the need for greater attention to mine closure processes, coupled with regulatory intervention. The study indicated higher environmental contamination in the sediments for locations near coal mining, comparing to the predominantly coal seam gas production activities. This reflects the specific licencing of the CSG operation that enables the collection and off-site disposal via a wastewater treatment plant, unlike the discharge to stream methods allowed for coal mines. A baseline for the concentration of contaminants in sediments is also provided in this study. Aluminium, cobalt, copper, magnesium, nickel and zinc were found to be the major contributors to sediment contamination from the coal mining industries. The study revealed some discrepancies in the sediment quality indices in the estimated ecological and toxicological effects, leading to the proposal of a new environmental toxicity quotient (ETQ). The newly proposed ETQ was found to be more contemplative for environmental assessment than the other indices. This study recommends that the ETQ method could supplement existing pollution licencing and eco-toxicological management to evaluate the impairments of point source discharges, where suitable up and down-stream monitoring is available.

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Aquatic Life and Environmental Impairment by Coal Mine Discharge in the Sydney Region

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Abstract

Coal and coal seam gas mining has been shown to affect water and sediment quality in the proximity of the mining area. An increment of aluminium (Al), iron (Fe), manganese (Mn), nickel (Ni), zinc (Zn) in water and sediments with substantial difference in community structure was observed in the upstream and downstream of mine discharge. The objective of this study is to assess the impact of coal mining on the Sydney environment by investigating macroinvertebrates and chlorophyll as indicators of industrial pollution and environmental impairment. The sampling was conducted between July 2014 and September 2015. The study revealed change in abundance, taxonomic richness, and pollution sensitive macroinvertebrate groups. A statistical evaluation of aquatic life was performed and a correlation of contaminant with the presence of community in ecosystem was studied. The environmental sustainability of river and stream with water chemistry affecting biological system was assessed. A non-uniformity in the changes were observed indicating difference in tolerance level of different invertebrates.

Keywords:
Aquatic Life, Environmental Impairment, Coal Mine, Ecosystem, Macroinvertebrate, Industrial Pollution, Stream Invertebrate Grade Number – Average Level (SIGNAL)

5.1 Introduction

Rapid development with growing energy consumption has resulted in exponential production of resources for energy generation, such as coal and natural gas (Gilbert and Sovacool, 2017). During mining a variety of materials are consumed, processed, and might get washed away as discharge in the form of produced water. Although the water discharged into the creeks and waterways is diluted in the downstream flow, a continuation in discharge leads to persistence of contaminants in waterways. Water and sediment quality can be compromised due to coal and coal seam gas mining activities (Ali et al., 2017; Ali et al., 2018). During the production, coal washing and groundwater seepage into underground mines generate contaminated wastewater. Sulphur containing material in mine comes in contact of water which naturally generates sulphuric acid, termed as acid mine drainage (AMD), which can dissolve harmful metals and metalloids from surrounding rocks and increase the water contamination level (Liu et al. 2017). Alkaline dozers are used to reduce the acidity and dissolved metals from the acid mine drainage but the improvements were shown as non-linear (Johnson et al. 2014). Sulphur is also used as a primary tracer of coal, with various metal ratios in the coal being used as fingerprints to determine the source (Chou, 2012).

The wastewater discharged from coal mines in the water streams can compromise water quality, geochemistry and metal contamination (Ali et al., 2017; Ali et al., 2018) (Chapter 3 and 4), causing long distance impact on the ecosystem (Wright et al. 2017). Different heavy metals discharged by coal mines can be consumed by the living aquatic organisms (Mishra and Shukla 2016). Aquatic ecological impact of mine wastewater is evident in the literature (Venkateswarlu et al. 2016; (Somers et al., 2018), however the correlation of the impact with multiple parameters including water quality indices, sediment quality indices and individual contaminants concentration are still not available.

Low soluble trace metals can be easily adsorbed in sediments and this continuous process yields to high accumulation of contaminants (Alvarez et al. 2011). Due to sediments being ultimate sinks for the trace metals, living organisms on the coastal areas may also be affected by the poor sediment quality. Certain trace metals which are not permanently bonded in the sediment can be released in the water under different conditions (Wang et al. 2016). Some of them (Mo, Cr, Zn, Se, Co, Fe) are used in the biological functions and are not harmful in low concentrations but those which are not essential for the biological use (Pb, Hg, Cd, As, Ni) can be toxic at very low concentrations (Pagenkopf 1983). The trace metals can be accumulated in the body of the biota and finally end up in the food chain and affect human health (Allinson et al. 2015).

It has been reported that there are certain species which have their own system to maintain the intake of contaminants and there is constant accumulation of trace metals in these species irrespective of the available trace metals in the water system (Johnstone et al. 2016; Gzyl et al., 2017). In some cases, such as increase in salinity due to discharge, can be tolerated by the taxa (Bailey et al., 2012; Zhao et al., 2018). It is reported that mine water salinity affects the algae and duckweed (Smith et al. 2009). Invertebrates can be affected and lead to high densities i.e. abundance per square area of stone and low richness by salinity increment (Bunn and Davies 1992). The increment of trace metals in the discharged water was observed previously in the downstream sediment and surface water from the coal mining activities in the Sydney region (Ali et al. 2017b). There are acidophilic bacteria which causes coal to leach and form low pH drainage by its metabolic activity (Baruah and Khare 2010). Inhabitants have their characteristic affinity towards the available trace nutrients. In presence of certain trace metals, the process of uptake of other trace metals by inhabitants are reduced. Even the processes, including the photosynthesis, are affected (Volland et al. 2014). The process of selective nutrient uptake of trace metals in presence of others affects in both ways of increasing or decreasing the damage to plants. Eventually, bioavailability of trace metals affecting the inhabitants are reflected in diverse forms. It is reported that aquatic invertebrates consume and accumulate trace metals in varying concentrations across taxa.

Due to variety of behavioural changes macroinvertebrates in a river ecosystem can be used as a tool for assessment of the water quality and industrial impact (Andersen et al. 2016). They can be applied as anthropogenic adverse effect indicator on aquatic systems (Kaboré et al. 2016). Impact of wastewater discharge on water, sediment and damage to aquatic ecosystems may have some correlation. The aim of this work is to investigate the changes in the ecology of rivers by analysis of chlorophyll and invertebrates in the area affected by the produced industrial discharge from coal mining activities and in the less affected areas before the discharge points.

5.2 Material and methods

5.2.1 Study area and site description

The selected study site in this work was located 60 to 120 km southwest of Sydney, Australia. Two mines in the region were selected for this study, one was West Cliff Colliery which discharges into Brennans Creek and then to Georges River, and the other was Tahmoor Coal mine discharging into the Bargo River. The coordinates and details of the sampling locations are listed and illustrated in Table 5.1 and Figure 5.1. The samples were collected from the locations before (upstream) and after (downstream) the produced water discharge points. The sampling points were selected the same as in the previous study (Ali et al. 2017) because the water quality in the upstream and downstream of the mine discharge was investigated and indices were already calculated and reported for the assessment of water quality.

Table 5.1 Sample and site identification.

S. No.	Mines / Industry	Sample collection site	Coordinates		Site I.D.
1	West Cliff Colliery Appin	Georges River, Appin, upstream	4°12'13.46"S	150°47'52.74"E	S1
		Georges River, Appin, downstream	4°12'17.25"S	150°47'55.89"E	S2
2	Tahmoor Coal Mine	Bargo River, Tahmoor, upstream	4°14'12.11"S	150°34'46.02"E	S4
		Bargo River, Tahmoor, downstream	4°14'58.47"S	150°36'25.37"E	S5

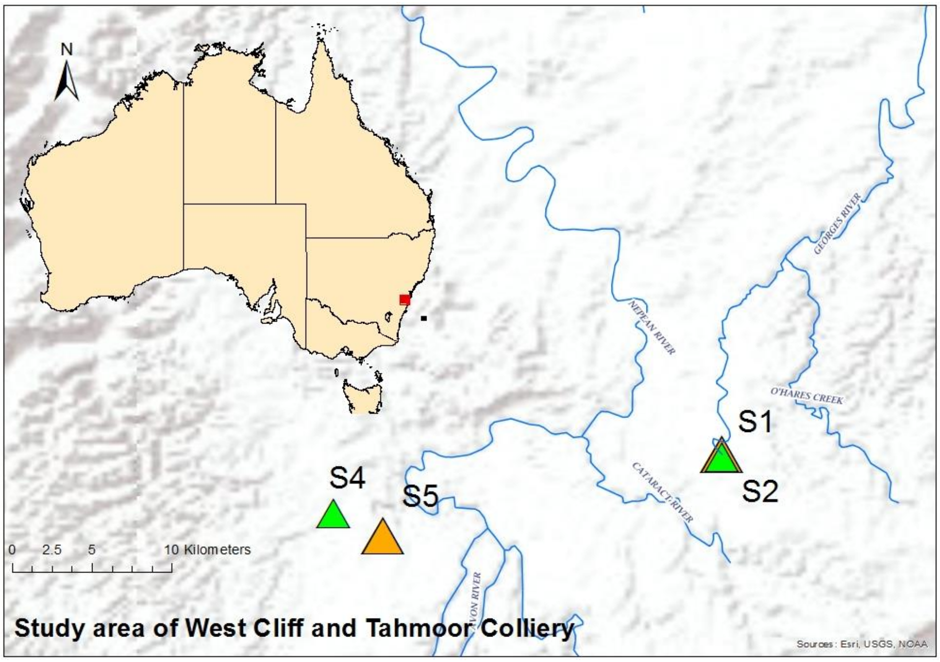

Figure 5.1:Sampling locations in South Sydney area for West Cliff and Tahmoor colliery.

5.2.2 Sampling and Analysis

The aquatic macroinvertebrate samples were collected from both upstream and downstream locations to the coal mine waste discharge points. The study was carried out in October 2016. Two types of samples were collected for this study, (i) stone scratched samples for chlorophyll-A analysis, and (ii) stone scrubbed samples for benthic macroinvertebrate analysis. A standard 18″ rectangular frame with mesh size 500 µm net was used for the sampling of invertebrates. Six randomly selected benthic macroinvertebrate samples were collected from coble riffle available in the area within 10-meter distance of each site using a 'kick sampling' method. In this method, the sampling net was placed at the bottom and the stream was disturbed before the net to let invertebrates come out of their colony and get trapped in the net (Tyufekchieva, 2011). The samples collected were transferred to small jars and stored in ice esky.

The second technique of sample collection for the study was by scrubbing and scratching of the stone to examine the biota on a rock for the abundance and type of biota. Invertebrates and chlorophyll-A were taken from randomly selected rocks which were removed from the river at sites above and below the mine water discharge. The rocks of a size like a football were removed from the stream bed and placed into a 500 μm mesh net while still under water. The net was placed immediately downstream of the rock to capture any animals dislodged during rock removal. The rocks were taken to the river bank and rock and contents of the net placed into a plastic tray for processing. A 3 cm by 3 cm template was used twice for collection of the chlorophyll from a rock sample. The template was placed on the rock and carefully scrapped the algae and biofilm of entire area of rock within the template and rinse transferred to a jar using a wash bottle. The jar containing the algal scraping was wrapped in aluminium foil to avoid light exposure and placed in a portable cooler. Sampling to examine the biota on a rock for the abundance and type of biota was performed on the same stone where chlorophyll samples were scratched from. The rocks were thoroughly scrubbed and washed in the tray along with the net. It was visually inspected to ensure all animals were removed. All animals were transferred into a clean plastic jar and frozen until later analysis in the laboratory.

For chlorophyll-A analysis the samples were filtered first through a Whatman 42 membrane filter. The filter membranes were kept in acetone at 4°C for 24 hours in the dark. The acetone solution was then analysed for chlorophyll-A by measuring absorbance at 750, 664, 647 and 630 nm using a Hach portable spectrophotometer. Calculation of the chlorophyll concentration was performed according to the standard procedure described elsewhere (Wright et al. 2005).

The abundance and type of invertebrates from the rock were examined, sorted, identified and enumerated under a high resolution microscope following the guidelines of Environmental Protection Agency (Gerritsen et al. 1998). The invertebrates were identified to family level, where possible, apart from Chironominae which were identified to subfamily. Oligochaetes and mites were identified to class only. The invertebrates collected were analysed for their abundance, density, and richness. The abundance was described as number of animals collected on each rock and the density was calculated as number of animals collected on each rock divided by the size of the rock. Richness was the number of different invertebrate taxa collected on each rock.

The surface area of each rock was estimated by covering the rock in a single layer of aluminium foil and calculating the area from the mass of the foil based on a standard curve. The abundance, richness of invertebrates, densities of invertebrates and chlorophyll-A on rocks collected upstream and downstream from discharge points were compared using a 1-way analysis of variance. Assumptions of normality and homogeneity of variance were determined using q-q plots and plots of residuals. The significance level (α) for these analyses was 0.05. Analyses were done using Minitab v17, IBM SPSS Statistics 24, and Past 3 software.

5.2.3 Stream Invertebrate Grade Number – Average Level (SIGNAL)

Stream Invertebrate Grade Number – Average Level (SIGNAL) is macroinvertebrate scoring system for samples from Australian River (Tyufekchieva, 2011). It can indicate the pollution type and the factors affecting the invertebrate community which helps in deciding the condition of the river or the river health. A higher SIGNAL-2 score is related to higher water quality indicating low salinity, turbidity, nutrient (e.g. nitrogen and phosphorus) contents and a high content of dissolved oxygen (Chessman 2003). The SIGNAL-2 score was calculated by identifying the invertebrates to the family level. Each type of invertebrates is assigned a 'grade number between 1 and 10 and their abundance have weight factors accordingly. The SIGNAL score is calculated as:

$$\text{SIGNAL score} = \frac{\text{Total of grade } \times \text{weight factor}}{\text{Total of weight factor}}$$

5.2.4 Statistical Analysis ANOVA

This is a simple test of analysing mean and variance among and between the groups. This could be one-way ANOVA or two-way ANOVA depending on the number of variables compared to other variables. Our analysis of the abundance of invertebrates for its significance was performed on one-way ANOVA using Minitab v17, IBM SPSS Statistics 24, and Past 3 software. The quality data were compared between sites and stream levels to analyse the normality and homogeneity of variance to find its significance.

5.2.5 Simpson's Dominance Index (D)

Formation of continuous progression from dominants through intermediates to rare species by arranging the communities in a sequence from most to least important generates dominance index. It directs towards submissive and aggressive behaviour between two members of all possible paired combination of animals in the group. This index takes species richness and the abundance of individuals within each species into account to determine how uneven a biological community is. This index is calculated from pooled samples at each site to yield a value between 0 and 1. This value represents the probability that two randomly selected individuals will be from the same species. Therefore, a probability of 1 means that all individuals at a site belong to the same species and a value of 0 indicates that individuals are evenly distributed amongst all species from a community. The following equation calculates this index (Hill 1973):

$$D = \sum_i \left(\frac{n_i}{n}\right)^2$$

where n_i is number of individuals of taxon i.

5.2.6 Similarity Indices

Numerous similarity indices are used to measure similarity among the communities. Two suitable indices were considered for this study. Jaccard's similarity index and Bray-Curtis dissimilarity index.

Jaccard's similarity index is used to assess similarity between biological communities based on presence and absence of taxa. In this comparison of two sets (communities), the intersection (taxa common to both communities) is divided by the union (total combined taxa from both communities) to yield the similarity index. The following equation represents this:

$$J(A,B) = \frac{|A \cap B|}{|A \cap B|} = \frac{|A \cap B|}{|A|+|B|-|A \cap B|}$$

where A and B are two sets of communities (Jaccard 1912)

Bray-Curtis dissimilarity index differs from Jaccard's similarity. In addition to presence and absence, Bray-Curtis takes abundance of individuals within taxonomic groups into account. Bray-Curtis similarity returns a value between 0 and 1 where 1 means two sets do not share any similarity with each other at all and 0 means two sets have same composition. It is represented as:

$$BC_{ij} = 1 - \frac{2C_{ij}}{S_i+S_j}$$

where S_i and S_j are number of specimen counted for set 'i' and set 'j' respectively and C_{ij} is sum of the specimen common in both set of species (Bray and Curtis 1957).

5.3. Results and discussion

At both sites, the density of chlorophyll on rocks was not statically significant ($p>0.05$), however, it was observed that the chlorophyll abundance on rocks were higher in areas downstream of the mine discharge points (Figure 5.2). Statistical evaluation of chlorophyll-A revealed that there was a very significant change in chlorophyll-A density with the change in stream type ($p = 0.028$, $F = 510.7$, and $df = 1, 1$). Chlorophyll-A also showed a significant change with the change in site location ($p = 0.026$, $F = 580.5$, and $df = 1, 1$) which means the change in the chlorophyll-A content in West Cliff was significantly different from chlorophyll-A content of Tahmoor. It was 558 µg/m^2 in upstream of West Cliff while it was 1551 µg/m^2 in case of upstream of Tahmoor. This indicated that the environment itself was affecting differently for the survival of chlorophyll-A even before the discharge point. However, the difference between upstream and downstream of West Cliff was more than 2.6 times while that in Tahmoor was more than 1.6 times indicating that the downstream environment was more suitable for chlorophyll-A at both the sites.

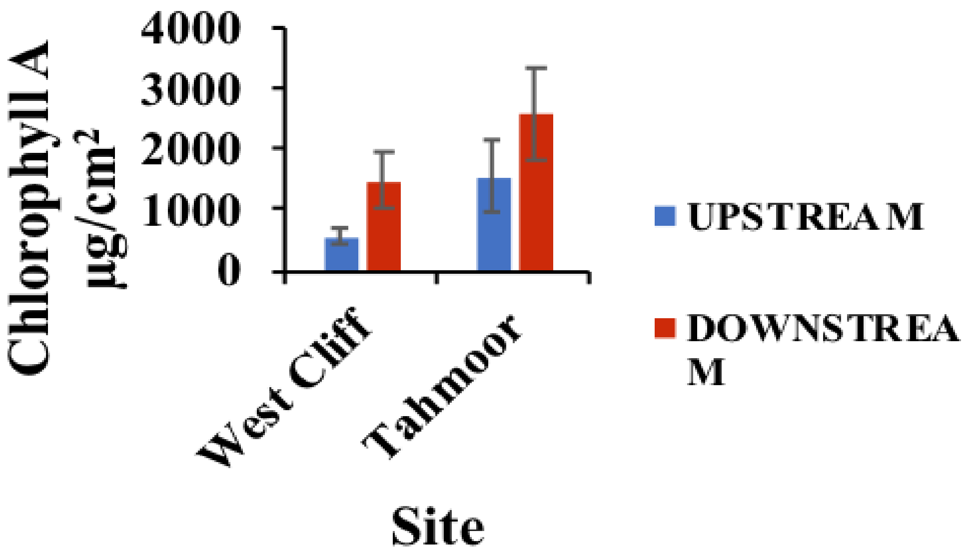

Figure 5.2: Mean (±SE) chlorophyll-a densities on rocks collected from upstream and downstream of mine water discharge points at Georges River (West Cliff Mine) and Bargo River (Tahmoor Mine). N=6

There was significantly greater invertebrate abundance on rocks downstream of the West Cliff mine discharge point compared to the upstream sampling location (p=0.015) (Figure 5.3). The greater abundance of invertebrates downstream of the Westcliff mine discharge may reflect habitat rather than water quality differences as a result of mine discharge (Stewart et al. 2000). Apparently, the flow velocities and water volume were both greater at downstream than upstream sites. There was no significant upstream to downstream difference in invertebrate abundance at Tahmoor, however, a small decrease in the invertebrate abundance was observed in the downstream location.

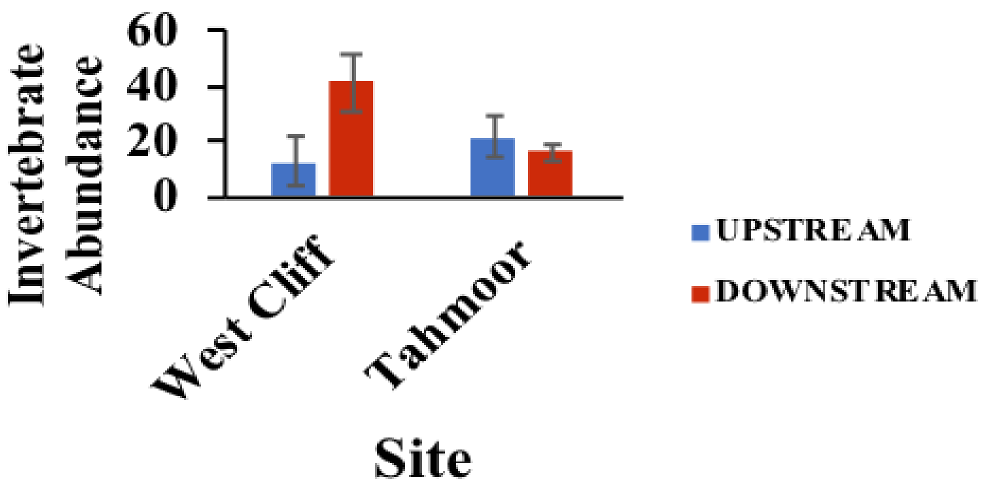

Figure 5.3: Mean (±SE) invertebrate abundance on rocks collected from upstream and downstream of mine water discharge points at Georges River (West Cliff Mine) and Bargo River (Tahmoor Mine). P=0.015.

Density of the invertebrates, shown in Figure 5.4, was evaluated by abundance per unit area of the rock and the results contrasted with each other on both sites. Although the results were statistically insignificant, they showed increment in the downstream of West Cliff site. On the other hand, the downstream of Tahmoor site had lower invertebrate density comparing to the upstream sampling site. Decrease in density of the invertebrates in Tahmoor downstream can be considered as indicative of halo-sensitive invertebrates in the area (Pauletti et al. 2010). There was no significant difference in density (abundance/rock size) at either site.

Invertebrate richness was not significantly different between upstream and downstream locations in either of the rivers ($p>0.05$), (Figure 5.5), however, there was an apparent increase in richness in the downstream of both West Cliff and Tahmoor sites suggesting the nutrient level is within the threshold limit of contaminants for the survival of the species. Invertebrate richness is in accordance to the expectation as proposed Environmental Water Quality Index (EWQI) of these sites (Ali et al. 2017b) have indicated that the downstream of the water quality is less hazardous to the health. This further gives strength to the proposed Environmental Water Quality Index (EWQI) as important index for the impact study. The change in assemblage in the downstream of Tahmoor and its relevance to the detected metal pollution (Ali et al. 2017b) has come to its agreement with the fact that changes in assemblage can be considered as relevant indicator of stream pollution (Demars et al. 2012).

A scoring system of macroinvertebrate (Water Bug) in Australian rivers called 'Stream Invertebrate Grade Number – Average Level' (SIGNAL) which indicates the water quality of the inhabitants collected was calculated. SIGNAL-2 values were compared between sites (West Cliff and Tahmoor) and between stream locations (upstream and downstream) to elucidate differences between these groups. The statistical assumptions for the valid application of analysis of variance (ANOVA) include normality and homogeneity of variances. These assumptions were tested with the Shapiro – Wilk test (Shapiro and Wilk 1965) and Levene's test (Levene 1960) respectively.

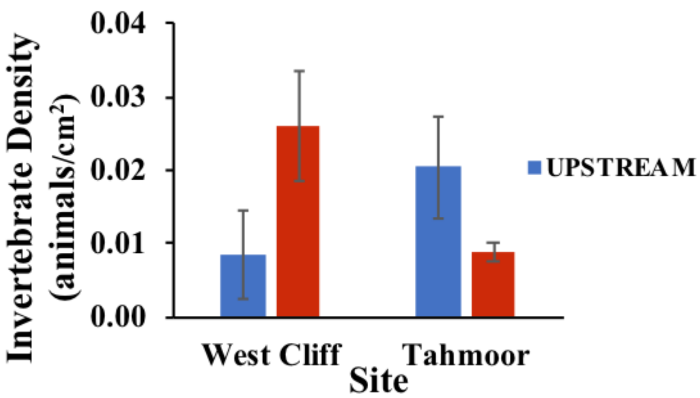

Figure 5.4: Mean (±SE) density of invertebrates on rocks collected from upstream and downstream of mine water discharge points at Georges River (West Cliff Mine) and Bargo River (Tahmoor Mine).

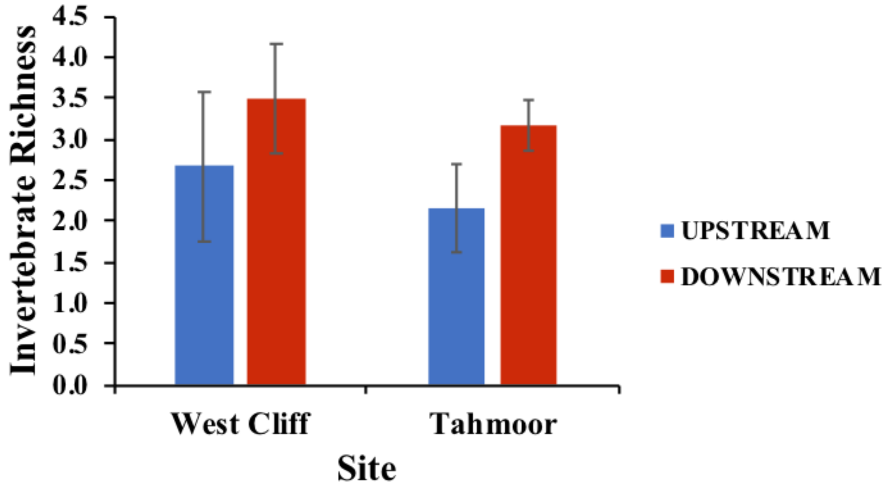

Figure 5.5: Mean (±SE) invertebrate richness per rock collected from upstream and downstream of mine water discharge points at Georges River (West Cliff Mine) and Bargo River (Tahmoor Mine).

The Tahmoor site (TC) was found to violate normality (0.632, df = 12, p = <0.001) while the West Cliff site (WC) accepted the null hypothesis of normality (0.923, df = 12, p = 0.311). The null hypothesis of homogeneity of variance by Levene's test was met across sites (0.358, df = 1,22, p = 0.556). ANOVA is robust to violations of normality, provided that the homogeneity of variance assumption is met (Quinn and Keough 2007). Therefore, the application of ANOVA was justified to compare sites based on SIGNAL-2.

Upstream and downstream SIGNAL-2 values were then assessed to ascertain whether they met the assumptions of ANOVA. Downstream SIGNAL-2 accepted the null hypothesis of normality (0.927, df = 12, p = 0.347) while upstream violated normality (0.805, df = 12, p = 0.011). Once again, the null hypothesis of homogeneity of variance by Levene's test was met (0.087, df = 1, 22, p = 0.770), thus allowing the application of ANOVA to compare SIGNAL-2 between stream locations. The increment in the SIGNAL-2 score downstream of both West Cliff and Tahmoor is again in accordance to the Environmental Water Quality Index (EWQI) of these sites (Ali et al. 2017b).

There was a statistically significant difference in SIGNAL-2 scores between West Cliff and Tahmoor sampling sites (F = 6.626, df = 1, 22, p = 0.017; Figure 5.6). West Cliff (M = 4.318, SD = 0.808) had a significantly higher mean SIGNAL-2 score than the

Tahmoor site (M = 3.438, SD = 0.868). This is indication of better water quality at West cliff than at Tahmoor which is in accordance to the Environmental Water Quality Index (EWQI) reported on these two sites (Ali et al. 2017b). Although downstream locations displayed higher mean SIGNAL-2 score (M = 4.036, SD = 0.979), than upstream locations (M = 3.72, SD = 0.903) for both sampling sites, there was no statistically significant difference in the mean signal-2 score between the upstream and downstream locations (F = 0.675, df = 1, 22, p = 0.420; Figure 5.6).

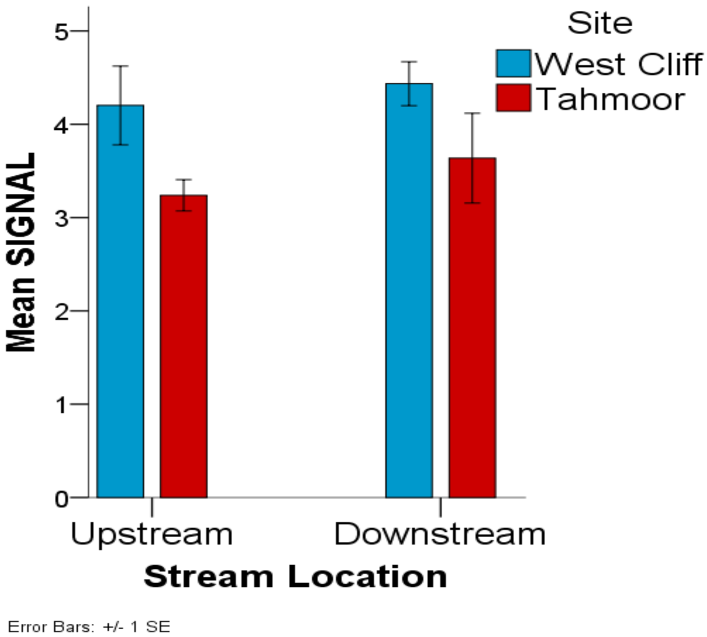

Figure 5.6: SIGNAL-2 based on the invertebrates counted in West Cliff and Tahmoor mine discharge area

The macroinvertebrate dominance analysis of each site was carried out by pooling the subgroups of Chironominae (purple and lower) into Chironominae and subgroups of Elmidae (Elminae Adult and Larvae) into Elmidae. The results are shown in Figure 5.7. Tahmoor upstream location had the most uneven community, followed by West Cliff downstream, Tahmoor downstream and West Cliff upstream location, which had the most even community. There was no consistent effect of the discharge on macroinvertebrate dominance, as there was an increase in dominance at the West Cliff downstream location, whilst a decrease at the Tahmoor downstream location.

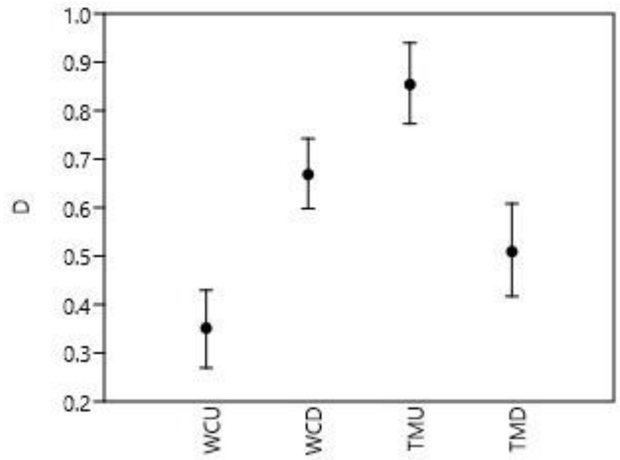

Figure 5.7: Simpson's dominance index by site and stream location. WCU = West Cliff Upstream. WCD = West Cliff Downstream. TMU = Tahmoor Upstream. TMD = Tahmoor Downstream

Jaccard's similarity index, shown in Figure 5.8, was used to assess similarity in taxa present in invertebrate communities at the sampling sites both for upstream and downstream of the mine discharge location. It was determined that the present taxa of the invertebrate communities were more dependent on the location relative to the mine discharge points (upstream or downstream) than the sites (i.e. West Cliff or Tahmoor). Therefore, this study reveals that mine discharge location is more relevant to presence and absence of a specific invertebrate taxa than the location, within the broad geographic region of Sydney region. The upstream locations for both sites exhibited the closest similarity (Jaccard = 0.556), whilst the downstream locations were less similar from one another (Jaccard = 0.214).

Within the sites, West Cliff upstream location was closer to the West Cliff downstream (Jaccard = 0.333) than Tahmoor upstream was to Tahmoor downstream location (Jaccard = 0.25). Therefore, the Tahmoor mine discharge appears to be exerting a greater effect on invertebrate community composition than at West Cliff mine, at least in terms of the presence/absence of taxa. This may reflect differences in the response of taxa to the various pollutants discharged at each site or the taxa originally found at each site.

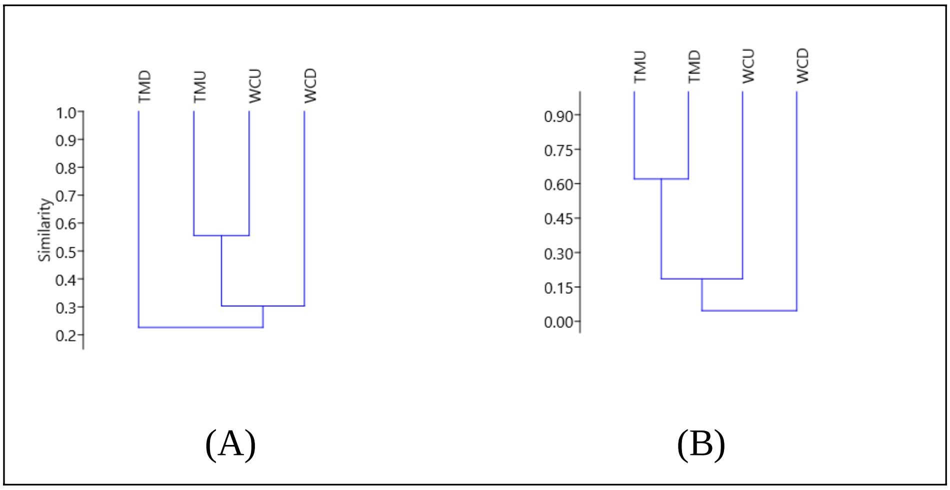

Figure 5.8: Jaccard's similarity index (A) Cophenetic correlation coefficient = 0.9839 and Bray-Curtis dissimilarity index (B), Cophenetic correlation coefficient = 0.9894

The Bray-Curtis dissimilarity index which takes presence/absence and abundance into account, displayed a different relationship to Jaccard. Bray-Curtis is a dissimilarity index where a value closer to 0 indicates greater similarity between groups. Once abundance of individuals within taxonomic groups was included in the dissimilarity algorithm, stream locations continued to exert a greater influence on macroinvertebrate community composition than site. This effect was particularly prevalent at Tahmoor, where upstream and downstream locations were highly dissimilar (Bray-Curtis = 0.620), whereas West Cliff upstream and downstream were more similar (Bray-Curtis = 0.106). Therefore, it appears that mine site pollution affects macroinvertebrate community composition at Tahmoor more than West Cliff, although greater replication of physiochemical sampling and macroinvertebrates would be required to confirm this.

Percent relative abundance of each taxon was calculated for each site and stream location and the result is summarised in Figure 5.9. At West Cliff, relative abundance of Simulidae increased at the downstream site (81%) compared to the upstream site (52.7%). Tipulidae, which was not present upstream, made up 8.9% of downstream invertebrates. Conversely, Chironominae decreased from 18.92% upstream to 7.692% downstream. Tanypodinae, which was present at the same proportion as Chironominae upstream (18.92%) did not appear downstream. Leptophlebiidae and Leptoceridae were rare taxa upstream (2.7% each) and were not found downstream.

At Tahmoor, Chironominae made up most of the invertebrate community upstream (92.31%), although this taxon was found in lower relative abundance downstream (60.61%). However, an increase in both sub-groupings of Chironominae (termed here as Chironominae lower and Chironominae purple), which were not found upstream, were found downstream at 5.05% and 2.02% respectively. Similarly, a subgroup of Elminae (here termed Elminae L or Larvae) which were only found upstream at 0.77% relative abundance, were found downstream at 19.19%.

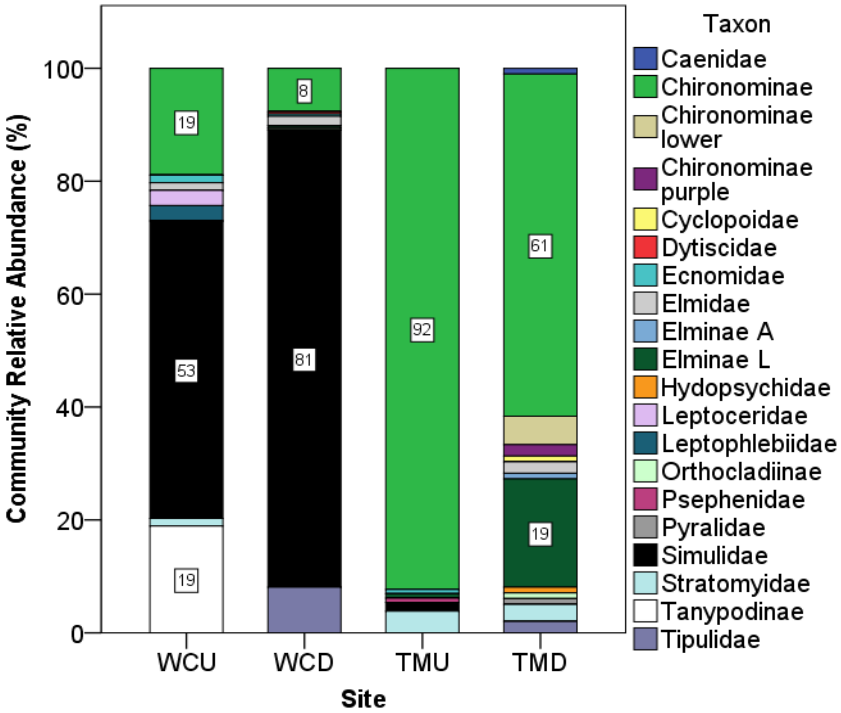

Figure 5.9: Relative abundance of invertebrate communities. WCU = West Cliff Upstream, WCD = West Cliff Downstream, TMU = Tahmoor Upstream, TMD = Tahmoor Downstream

If West Cliff and Tahmoor upstream environments are taken to be representative indicators of background macroinvertebrate communities at these sites, these are distinct even without the influence of mine site pollution. At West Cliff upstream, this community is dominated by Simulidae at 52.7% relative abundance, increasing to 81% downstream, which suggests that this taxon is more tolerant to toxic conditions than other co-occurring taxa and/or that it had a greater capacity to adapt, perhaps due to a presumably larger gene pool to draw upon which is inferred from its high relative abundance.

In contrast, Simulidae only made up 1.5% of the upstream community at Tahmoor, and were not found downstream. Instead, the Tahmoor upstream community was dominated by Chironominae at 92.3%. This declined substantially downstream, to 60.6%, although Chironominae remained the dominant taxon.

A correlation between the measurements conducted in this work with the water quality parameters studied in Chapter 3 for the same locations (Ali et al., 2017) is presented Appendix 3.1. It was found that richness of invertebrates increases with pH, nitrate, dissolved solids, conductivity, and heavy metal potential index (HPI) indicating basic medium with nutrients favours the richness of invertebrates. However, it was found that the dissolved oxygen and the Environmental Water Quality Index (EWQI) were inversely related to the richness indicating that higher oxygen does not favour the richness. EWQI, an indicator of adverse effect on living organisms, has clearly indicated the inverse trend in richness, SIGNAL, average sensitivity grade and density of invertebrates. The water quality index is also indicating inverse trend to the invertebrate richness indicating that bad water quality to a certain degree is favourable for the invertebrate's life. This is also evident with the contamination index (C_d) directly related to the invertebrate density and abundance. Based on this, it can be concluded that in less contaminated water a low number of sensitive species are present, but in highly contaminated water a high number of tolerant species of invertebrates are observed. This statement is more supported by the finding that the richness increment with pH is reversed in case of average sensitivity grade, additionally more sensitivity average was in accordance to the water quality index indicating that more sensitive species are more populated in better water quality. An increment in the invertebrate density and chlorophyll content was directly related to the nitrate concentration (Ali et al. 2017) confirming the nutrient property of nitrate in the environment.

Previous studies have consolidated that the wastewater runoff from West Cliff Colliery has contaminated the groundwater, with contamination levels high enough to be considered as water pollution (Wright, 2012). This coincides with abnormal increase in subsidence above longwall panels (Gale, 2012) with a drastic collapse of macroinvertebrate numbers (Wright, 2009). With studies showing a greater absorption of particles with increasing surface area (Engates et al. 2011) it can be concluded that the fines from the coal mines may play a role in this topographical change. This change may be determined to be as a result of a positive feedback loop, where mobility of metals is microbially mediated to groundwater, with the resulting minerals contributing to further mobilization (Haque ey al., 2008).

5.4 Conclusion

The comparative study of chlorophyll and invertebrates in upstream and downstream locations of two coal mines resulted in an inconsistent trend at different locations which indicated the chlorophyll and invertebrate do not behave identically to the contaminants in the environment for their survival. However, nutrient content in the environment affects both in the same manner. The study observed that the discharge from coal mines may alter the macroinvertebrate assemblages, as the most contaminant tolerant species were more prevalent in the downstream discharge locations. The invertebrate abundance was limited to the non-nutrient contaminants only. It was seen that a single parameter in water quality could not be used to establish the trend in impact as variety of factors and concentration limits influence the trend. This behaviour also suggested that default guidelines may not necessarily be equally affecting the variety of taxa and other environmental factors may be playing with abundance and distribution of biota. Diverse assemblages have suggested of pollution sensitive taxa and essence of sustainable development approach for the industrialisation. The measures to control pollution sources should be essential part of development. The approach used in this study aims to provide information to assess the impact of mining industries on aquatic life. It helps enable systematic conservation plan. This study suggested that future environmental management plan should include the taxa comparison with other monitoring parameters.

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Effect of Coal and Coal Seam Gas Mining on Elemental Composition of Aquatic Invertebrates

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Abstract

Coal and coal seam gas (CSG) mining have significant impact on water and sediment quality of the rivers and streams in the proximity of mining areas through increased metal deposition. Aquatic invertebrates can bioaccumulate metals from water and they can serve as an indicator of ecotoxicological impacts of mining. The objective of this study was to assess the impact of coal mining on the aquatic environment by investigating the metal content in macroinvertebrates as indicators of pollution and environmental impairment. The results revealed certain metals were elevated within some of the aquatic invertebrate species indicating the presence of metal contamination is a function of both the ability of an individual species to regulate the metal intake and the concentration of metals in the environment. The types of invertebrates were identified for their characteristics of changing elemental composition with environmental conditions, and blockage of excess uptake of elements by their receptors. Elemental composition correlation indicated the phenomenon of filtering out Cr, Mn, Fe, Ni, and As for invertebrate survival. Certain metals, such as Al, Ti and Zn, were found to be in higher quantity in the invertebrates collected downstream the mining discharge locations when compared to upstream populations. The results also indicate that the invertebrates may not be capable of regulating the intake of Al, K and Mn.

6.1 Introduction

Coal and coal seam gas are critical to the energy needs of Australia and many countries, yet the extraction of these resources comes at a cost to the environment (Carlson and Adriano 1993, Hamawand et al. 2013), particularly where produced waters are discharged to natural waterways. Ali et al reported higher metal concentrations in the sediment (Chapter 4) and surface water (Chapter 3) at sites receiving water from coal mining and coal seam gas extraction industries (Ali et al., 2017; Ali et al., 2018). In-stream sediments contain the largest reservoir of metals (Demirak et al. 2006) and can contribute to the impairment of aquatic ecosystems (Lainé et al. 2014). Effect of coal seam gas and coal production on surface water correlates with the natural mine structure. Geological studies have shown a range of cations (Dahm et al. 2011), with the elements of environmental concerns in the industrial areas found to be Mg, Al, Fe, Sr and Ba (Ali et al., 2017; Alley 2011). Although preventive measures have been taken, the accidental spills and surface water contamination still occurs in Australia (Davies et al. 2015). Toxic leachates are generated in the mining area through complex natural weathering termed acid mine drainage (AMD). This process facilitates contamination of water system with toxic metals by their dissolution (Roy et al. 2017), although mine discharge is not always acidic (Banks et al. 2002). Large quantities of solid waste are also generated during the mining process and even from abandoned mines which contribute to metal contamination of the aquatic system (Bird et al. 2010). It is known that metals exist in sediments in various geochemical phases causing long-term effect. When the metal is released in a mobile phase it affects the ecosystem.

The impact of coal mines on aquatic ecosystems has been reported as early as 1960s (Reish and Gerlinger 1984). Aquatic invertebrates are able to accumulate metals from any available source, such as sediments, dust, aerosols, runoff and industrial discharge (Goodwin et al. 2003). Freshwater invertebrates are food for the aquatic life which become source of cycling the contaminants and bioaccumulation. The invertebrates play crucial role in the ecosystem and therefore can be used as indicators of stream health (Batty et al. 2010). Mine activities can bring wide range of impacts on the abundance of taxa and biodiversity due to metal contamination of the water stream (Hirst et al. 2002). The importance of the metal content has gained critical role with European Commission making it mandatory to determine the bioavailable concentrations of Cd, Pb, Hg and Ni in the water (Mills et al. 2014). Some metals are essential for the living organisms, but their excess could be toxic to biota (Newman 2009) and the change in abundance and diversity in aquatic invertebrates may relate to the metal pollution in aquatic ecosystem (De Jonge et al. 2008). The metal accumulation may even be fatal to the organisms (Langston 1990). The toxicity of the metals, their bioavailability, interaction between metals, and effect of metal mixture are all relevant to the aquatic invertebrate life (López-Doval et al. 2012). Changes in assemblages and distribution of benthic macroinvertebrates can be taken as mean of evaluation of anthropogenic influence and pollution stress (Saha et al. 2007).

The bioavailability of the contaminants depends on variety of (Yujun et al. 2008; Mwedzi et al. 2016) environmental factors, such as metal content in surrounding water and its hardness, ionic state of the metal and the presence of organic matter (Solà and Prat 2006). Bioaccumulation can place long term adverse effect of toxicity which can lead to the change in aquatic ecosystem (Johnson et al. 2011). Variety of aquatic invertebrates can accumulate metals in accordance with their changing bioavailability which could be used for the study of aquatic life. Local environmental conditions can be well represented by the benthic lifestyle of macroinvertebrates which can be used as reliable indicators of biological stress. Very limited work has been published on the change in assemblage and its relevance to the detected metal pollution (Demars et al. 2012; Stark, 1998; Langston, 2017) and can be considered as relevant indicator of stream pollution. Variety of work on aquatic ecosystem like Stream Investigation Number Average Level (SIGNAL) (Growns et al. 1995), ionic water chemistry due to disposal of coal mine water (Wright et al. 2011), abundance of macroinvertebrates living in the disposal stream (Wright and Burgin 2009), and degradation effect of water quality on macroinvertebrates (Tippler et al. 2012) have been in extensive studies. The effect of coal seam gas production has also been reported indicative to the stream water contamination and lethal to aquatic life. However, bioaccumulation of the metal contaminants in macroinvertebrates has not been extensively studied and many gaps remain to ascertain it as an additional ecotoxicological indicator of the impact of coal mining. Heavy metals are also serious problem for the human health (Cao et al. 2014; Hannon 2014, Stankovic et al. 2014, Wongsasuluk et al. 2014) and if they accumulate in the ecosystem there is a strong probability for their impact on human health, which compels the importance to evaluate the metal content in the inhabitants of the affected rivers.

The aim of this work is to study the bioaccumulation of contaminants in invertebrates near coal and coal seam gas mining discharge sites to assess the correlation of water and sediment metal concentrations with the bioaccumulation in various orders of aquatic macro invertebrates; investigate the suitability of environment for bioaccumulation. It will investigate the water and sediment quality parameter's relationship with the composition of invertebrates. The study would also introduce using the advances Proton induced X-ray emission (PIXE), a technique capable of measuring the elemental composition of a small quantity of macroinvertebrates, which are in low availability rates in the contaminated sites.

6.2. Material and methods

6.2.1 Study area and site description

The sites selected for this project were West Cliff Colliery and Tahmoor Coal mine and the coal seam gas (CGS) production sites within the Nepean River catchment area located 60 to 120 km southwest of Sydney, Australia (Table 6.1 and Figure 6.1). West Cliff Colliery discharges into Brennans Creek and then to Georges River, while Tahmoor Coal mine discharges into the Bargo River. For the CSG mining area, the selected location was the river travelling through the CSG production sites in the Camden area (Figure 6.1). The samples were collected from the locations before (upstream) and after (downstream) the coal and CSG produced water discharge points. Though the CSG produced water are not directly discharged into the Nepean River but the study would investigate the possible contamination associated with the leaks or aquifer interplay during CSG production. The selected sampling points were the same as in the previous (Chapter 3 and Chapter 4) studies (Ali et al., 2017; Ali et al., 2018) where water and sediment quality impairment in the downstream of the mine discharge were easily observed.

6.2.2 Sampling and analysis

The macroinvertebrate samples were collected from each site in October 2016. At each site six rocks (a-axis approx. 20 cm) were haphazardly selected from a slow flowing area of the river with depth approximately 50-100 cm. A 500 µm-mesh net was placed downstream of the rock and the rock placed into the net and carried to the river bank. Each rock was placed in a plastic tray and scrubbed to remove all invertebrates which were subsequently collected in a clean plastic jar and frozen until later analysis in the laboratory. Six samples were collected at one site within a 10-meter diameter. The types of invertebrates from the rock were examined and identified under a high-resolution microscope following the guidelines of Environmental Protection Agency (Gerritsen et al. 1998). The invertebrates were identified to family level, where possible, apart from Chironominae which were identified to subfamily. Oligochaetes and mites were identified to class only. Due to small quantity of invertebrates collected and classified to the family level the elemental analysis was undertaken using a composite sample of aquatic invertebrates collected from the six samples was prepared for the Proton induced X-ray emission (PIXE) and particle induced gamma-ray emission (PIGE) analysis (Cohen et al. 1996).

Table 6.1 Sample and site identification.

Mines / Industry	**Sample collection site**	**Coordinates**		**Site I.D.**
West Cliff Colliery Appin	Georges River, Appin, upstream	4°12'13.46"S	150°47'52.74"E	WCU (S1)
	Georges River, Appin, downstream	4°12'17.25"S	150°47'55.89"E	WCD (S2)
Tahmoor Coal Mine	Bargo River, Tahmoor, upstream	4°14'12.11"S	150°34'46.02"E	TMU (S4)
	Bargo River, Tahmoor, downstream	4°14'58.47"S	150°36'25.37"E	TMD (S5)
Coal Seam Gas (CSG) industries	Nepean River, Menangle (up)	34° 7'7.01"S	150°44'30.94"E	CSGU (S8)
	Nepean River, Spring farm (down)	34° '46.19"S	150°44'30.07"E	CSGD (S9)

6.2.2.1 Metal analysis

PIXE is a non-destructive analytical technique where charged particles with high energy are bombarded and the ejection of electrons from inner orbital takes place compelling outer electrons to fill in the inner orbital causing x-ray emission which are characteristic of element and can be used for the elemental analysis. PIGE is also a non-destructive analytical technique where protons with high energy penetrate to the nucleus by overcoming to the Coulomb force resulting in nuclear reaction generating high energy gamma ray emission from the nucleus used to fingerprint the elemental composition which can be used for the elemental concentration.

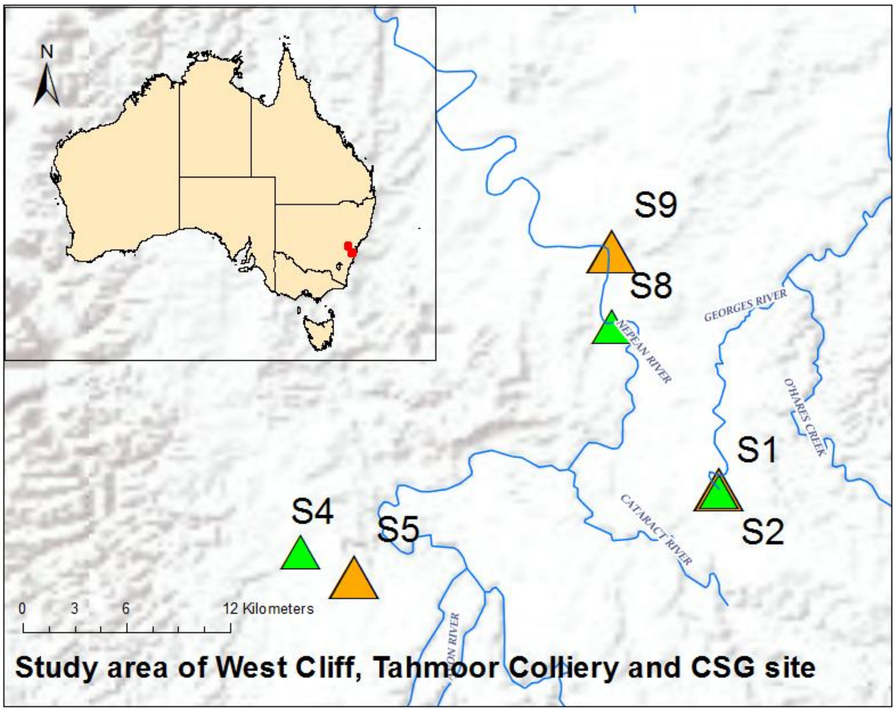

Figure 6.1: Sampling locations in South Sydney area for West Cliff and Tahmoor colliery

Samples were transferred to 2 mL vials with glass beads called Precellys® Lysing Hard Tissue Homogenizing Kit specially designed for crushing and homogenizing the hard tissues. The samples in vial were dried overnight under vacuum at 70°C and crushed by using 'Bertin INSTRUMENTS' Precellys® 24 automated homogenizer at 6500 rpm for 30 seconds. The samples were again placed under vacuum at 70 °C over night to ensure complete drying and then they were crushing to a fine powder by repeating the crushing by 'Bertin INSTRUMENTS' Precellys® 24 automated homogenizer at 6500 rpm for 30 seconds.

Each fine powder sample was subsequently deposited onto 25 mm diameter stretched Teflon filter substrates (PALL scientific) for elemental analysis using accelerator-based ion beam analysis (IBA) at the Centre for Accelerator Science at the Australian Nuclear Science and Technology Organisation (ANSTO). The stretched Teflon filters have a 3 µm pore size, 200 µg/cm^2 thickness and a defined circular deposition diameter restricted to 17 mm using a mask. The total deposited mass of each sample was determined by weighting each filter before and after deposition using a NATA calibrated Mettler Toledo MX5 microbalance (readability ±1 µg) under standard maintained laboratory conditions of 22 ± 5°C and relative humidity of 50 ± 10%.

Each filter was analysed using a combination of Proton Induced X-ray Emission Analysis (PIXE) and Proton Induced Gamma-ray Emission (PIGE) analysis. Their calibration was performed using thin film reference standards (Micromatter Pty Ltd) certified by mass to ±5%. PIXE and PIGE were performed with a 10 mm diameter proton beam of 2.5 MeV energy, 10 nA ion beam current and charge collection of 3µC.

The result measured by the instrument was in µg/cm^2 which was converted to µg/mg by taking into account the total sample area and the total amount of the sample on the filter. The method detection limit (MDL) of the instrument was as follows:

Element	Al	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni	Zn	As
MDL µg/cm^2	0.045	0.027	0.017	0.016	0.014	0.017	0.010	0.008	0.010	0.007	0.009	0.008	0.010

A technique for investigating two continuous quantitative variables known as Pearson Correlations was applied to the elemental content in invertebrates. A general linear model (GLM) analysis of the metal content for all collected invertebrates was conducted using 'IBM SPSS Statistic 24' software by maintaining the stream location and invertebrate type as fixed factors and site as a random factor to find the impact variation with site change. The significance level (α) for these analyses was 0.05

6.3 Results and discussions

Invertebrates were analysed for aluminium (Al), arsenic (As), calcium (Ca), chlorine (Cl), chromium (Cr), iron (Fe), manganese (Mn), nickel (Ni), phosphorus (P), potassium (K), sulphur (S), titanium (Ti) and zinc (Zn) composition in upstream and downstream biota using metal analysis PIXE method described above. The analytical results are tabulated in Table 6.2.

The elemental content varied inconsistently in different invertebrates in both cases of upstream and downstream locations (Table 6.1). Some animals exhibited different concentration of an element collected from two different locations, including the locations of uncontaminated water. Aluminium (Al) content in Ecnomidae collected from the upstream of West Cliff colliery was 422.5 µg/mg while the it was only 131.5 µg/mg in Ecnomidae collected from near Tahmoor colliery. Similarly, the Al content decreased from 422.5 µg/mg upstream to to 358.5 µg/mg downstream of West Cliff while it increased downstream from 131.5 µg/mg to 205.3 µg/mg near Tahmoor colliery.

Phosphorus (P), sulphur (S), potassium (K), titanium (Ti), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni) and arsenic (As) concentrations increased from upstream to downstream at West Cliff and Tahmoor. Conversely, aluminium (Al), chlorine (Cl), calcium (Ca), manganese (Mn), iron (Fe) and zinc (Zn) were decreased downstream of West Cliff but increased downstream of Tahmoor. This has indicated that metal content increase was caused by the discharged metals into the stream. The inconsistency between West Cliff downstream and Tahmoor downstream could be due to metal filtering out capacity of invertebrates. In the case of Tahmoor, the contamination combination in stream could have exceeded the filtering out capacity and have compelled the intake by invertebrates.

In contrast to higher levels of elemental composition in downstream Economidae of West Cliff, certain elements, including Cl, Ca, Mg, Fe and Zn showed higher concentrations in upstream invertebrates. This could be due the organism's ability to metabolise or properly excrete the specific ions. Selective pressure action of controlling mechanism of metamorphosis may have also favoured this trend (Hadfield 2000). Interestingly, this deviation in trend was not observed in Tahmoor, which leads to the possibility of a second source of pollution in the West Cliff area. Higher elemental level in downstream provides evidence of facilitation of intake by site contamination of polluted waterways, particularly in Tahmoor, except in the case of calcium which is part of the invertebrate itself. It suggested that Economidae has an internal mechanism that allow safe metabolism and secretion of the cation, however, due to considerably higher levels of metals in West Cliff, this cannot be the case. An alternative hypothesis could be that there is a second calcium enricher be it due to human waste or from naturally occurring deposits in the sediment.

Table 6.2: Parameters detected in a composite sample of six samples of invertebrates. (µg/mg) *

Invertebrate Type	Site	Al	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni	Zn	As
Economidae	WCU	422.5	115.2	76.8	132.7	76.8	3970.4	14.0	10.5	31.4	1215.2	7.0	21.0	7.0
	WCD	358.5	285.2	211.9	80.3	190.8	476.1	27.1	87.4	20.1	524.3	33.1	16.1	22.1
	TMU	131.5	166.2	99.4	5.7	38.2	2179.4	22.9	408.9	35.4	1657.5	166.6	9.7	3.9
	TMD	205.3	762.7	493.0	8.1	139.8	5594.3	85.6	565.0	74.2	2444.8	240.0	29.3	16.3
Corixidae	WCU	324.1	274.4	98.2	59.9	145.7	6303.5	22.6	921.5	47.4	3798.8	356.8	16.9	51.9
	WCD	43.7	250.4	170.8	78.8	173.9	72.5	10.9	2.3	3.9	88.1	2.3	8.6	3.1
	TMU	198.8	311.4	116.9	22.5	81.3	2670.6	15.0	205.7	26.9	942.3	90.0	12.5	14.4
	TMD	61.8	270.9	183.0	7.3	45.6	1627.9	16.3	212.3	27.7	881.9	91.1	15.5	5.7
Chironominae	WCU	172.9	204.4	118.8	51.1	184.9	1748.2	1.5	129.3	7.5	574.2	60.1	28.6	16.5
	WCD	559.7	242.4	155.9	40.2	195.0	982.8	29.2	153.7	14.3	876.5	57.8	19.3	23.1
	TMU	23.2	26.0	14.6	2.4	11.6	197.5	2.5	26.1	5.0	140.9	12.9	1.9	0.8
	TMD	333.8	265.2	179.6	9.7	72.2	1990.0	55.2	160.2	54.6	1026.9	68.6	23.1	7.9
	CSGU	622.1	290.9	193.4	0.8	86.6	1141.6	42.0	224.5	50.4	1377.0	80.7	24.4	12.6
	CSGD	630.2	245.3	153.7	4.2	70.5	1877.9	102.9	282.0	46.5	1487.4	121.2	14.1	59.2
Caenidae	WCU	176.4	220.8	56.7	39.9	67.5	3024.4	18.4	188.6	38.3	1423.2	75.1	23.0	0.0
	WCD	916.6	326.9	216.7	31.0	199.3	513.0	74.7	35.9	13.2	626.1	21.9	34.7	23.1
Simulidae	WCU	179.3	96.9	47.7	34.7	50.6	2385.5	7.2	442.4	46.3	2105.0	170.6	2.9	10.1
	WCD	1179.9	278.2	242.0	15.0	254.4	435.4	54.8	32.7	19.4	729.5	13.2	34.4	3.5
Dytiscidae	WCU	17.5	277.1	202.8	83.7	290.1	76.1	3.1	3.1	5.4	87.7	1.3	21.9	0.9
	WCD	36.7	449.9	305.8	107.4	372.4	100.6	8.2	1.4	5.4	104.7	1.4	31.3	6.8
	TMU	89.6	418.3	68.2	8.1	33.6	3226.6	20.4	337.9	23.4	1381.2	129.3	5.1	5.1
	TMD	145.6	234.0	112.3	18.6	55.0	2782.6	27.1	379.6	35.6	1657.0	144.1	20.1	4.6
Hydrophilidae	WCU	35.5	341.9	218.5	56.0	362.5	44.7	3.5	1.4	7.1	122.7	0.7	19.9	7.1
	WCD	32.0	383.3	247.7	48.9	336.0	76.8	7.8	2.1	5.4	245.5	1.1	28.7	3.8
Acarinae	WCU	85.8	276.5	179.1	53.6	282.3	231.9	9.1	51.2	18.2	465.5	19.0	8.3	10.7
	WCD	136.6	137.6	99.4	32.1	100.4	177.8	10.0	75.3	9.0	538.3	35.2	15.1	5.0
Elmidae	WCU	90.2	209.9	134.9	50.3	214.6	729.4	4.7	119.7	16.1	985.8	50.3	19.9	7.6
	WCD	296.5	273.3	183.5	70.5	197.0	690.6	23.2	195.1	18.4	902.1	86.9	23.2	8.7

* Detection limits are explained in section 2.2 Material and methods.

The composition of Corixidae has indicated that only sulphur and chlorine concentrations increased from upstream to downstream locations, with very minor variations, while all the other metals were in decreasing order at West Cliff upstream to downstream locations. Presence of Al, Ca, Mn, Ni and As in the downstream invertebrates at West Cliff was negligible in respect to the upstream. Although the water and sediments did not show any substantial change in their quality (Ali et al., 2017; Ali et al., 2018), the invertebrate composition from upstream to downstream was significantly different . It is possible that the environment was allowing the invertebrates to manage their composition, and the invertebrate selected higher content of Al, Ca, Mn, Ni and As in the upstream. In case of Tahmoor, elemental presence is relatively consistent, with sulphur showing an increment from 116.9 to 183.0 μg/mg and Al, Cl and As were in decreasing order in the downstream. Rest of the metals followed very minor change and indicated a better elemental intake management by Corixidae in adverse condition of the Tahmoor downstream site. Possible reasons for this include the ability of the organism to safely metabolise these ions to secretion or have internal cellular mechanisms that block the excess uptake by cellular receptors (Ayangbenro and Babalola, 2017).

Trends in the metal contents of Caenidae and Simulidae were similar to each other except for arsenic which was not found in Caenidae upstream of West Cliff while the As in Simulidae was higher in upstream than downstream of West Cliff. Ca, Cr, Mn, Fe and Ni were high in upstream while Al, P, S, K, Ti and Zn were higher in downstream in both cases. Furthermore, upstream levels of Cl, Ca, Cr, Mn, Fe and Ni in Caenidae were considerably higher when compared to downstream measurements. This deviation was also observed with Cl, Ca and Fe levels in Ecnomidae in West Cliff as well as with Cl, Ca, Cr, Mn, Fe, Ni and As levels in Simulidae in West Cliff. It should be noted that Caenidae showed no amount of As upstream of the mine discharge site, but levels rose to 23.3 μg/mL downstream. It is in accordance to the arsenic level undetected in the upstream environment, hence, this result indicates that the contamination on site had increased arsenic levels (Ali et al., 2017) beyond the natural threshold for Caenidae in West Cliff downstream.

Dytiscidae showed all metal content in higher concentrations in downstream West Cliff. Similar trend was found in Tahmoor except for Ca which was slightly higher upstream. Ca, Ti, Cr, Fe and Ni all showed higher concentration levels downstream in Tahmoor when compared to West Cliff. This was not observed in any other organism, which indicates that it is not the local environmental pressure that is the main driver of this phenomena, but rather an internal mechanism unique to this organism (Dytiscidae).

Hydrophilidae was found to have most of the metals in almost the same amounts in both upstream and downstream locations for Ca, Ti, Fe and Cr. This almost even split was unobserved in other organisms except Acarinae and Elimidae. Acarinae resulted in most of the metal concentrations being higher upstream, contrary to Elmidae, for which almost all of the metals were found higher in the downstream West Cliff location.

In almost all studied organisms, Al, Ti, Ar and Zn showed low levels of presence in the upstream and higher in the downstream invertebrates, as expected (Bhattacharya et al. 1999). These four elements are prone to metabolic uptake and therefore should be more closely monitored. Multiple organisms consistently demonstrated higher levels of contamination upstream of the West Cliff site. This could be due to different environmental pressures, such as the downstream site has more contaminants drowning out ions that may be essential to the organism, or that the deposition point at West Cliff is releasing more pollutants.

When comparing the Chironominae collected from coal mine (West Cliff and Tahmoor) and the CSG production areas, as shown in Figure 6.2, it was found that the elements of Chironominae of CSG upstream were very high in comparison to Tahmoor upstream, while CSG downstream was almost the same as that of Tahmoor. On the other hand, CSG upstream and downstream samples both were alike that of West Cliff result. The Tahmoor upstream was very low in all the metals indicating the suitable environmental condition for Chironominae to release the elements. The difference between upstream and downstream of CSG was negligible which clearly indicated that the impact of the CSG production was negligible on Chironominae elemental composition, conversely a significant change was observed in case of Tahmoor coal mine production area.

Further analysis of correlation between the elemental content analysed in the invertebrates, as presented in the current work, and the elements reported in the water (Ali et al., 2017) and sediments (Ali et al., 2018) reported previously, revealed that there was no significant trend of relationship among any of the elements. This suggests that the invertebrates were able to adjust and had a filtering out system for certain metals. However, when investigating the correlation between the elements within the invertebrates (Table 6.3), important information was identified. For instance, the S content in the invertebrates was in good correlation (p=0.01) with P, K and Zn content in the invertebrates; Al with Ti, Cl with K, Ca and Zn; K with Cl, Ca and Zn; Ca with Cr, Mn, Fe and Ni; Ti with Mn, and As; Cr with Mn, Fe, As and Ni; Mn with Ca, Ti, Mn, Fe and Ni; Fe with Ca, Cr, Mn, Ni and As; Ni with Cr, Mn and Fe; As with Ti, Fe, Cr and Ni. All of these were highly correlated (p=0.01) and indicated that Ca, Cr, Mn, Fe, Ni and As are making significant change in the invertebrate content as one of them changes. It appears that if one of these elements is increased or decreased the invertebrate had to compensate this element by adjusting all other elements in the list.

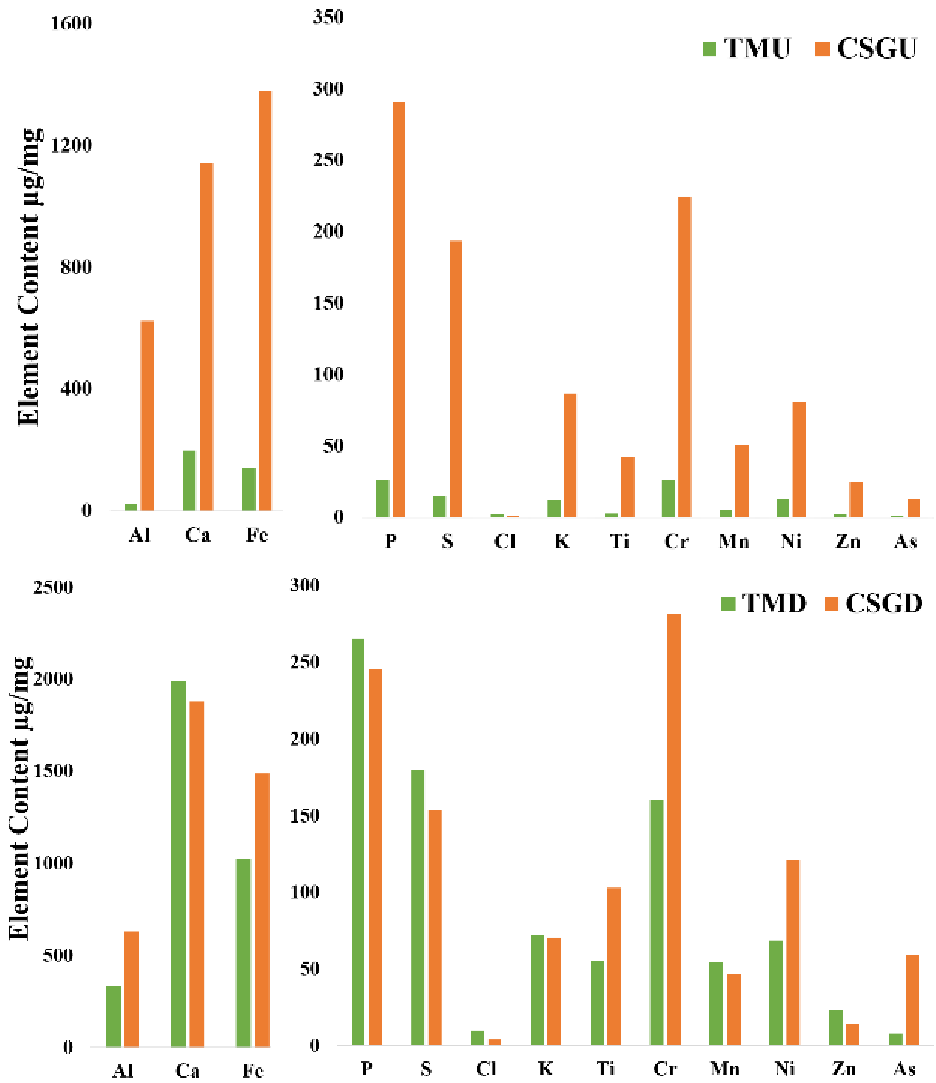

Figure 6.2: Trend in element content in Chironominae collected from upstream and downstream of CSG and Tahmoor

Elements present in invertebrates which correlated less significantly (p=0.05) with each other included Al with As and Zn; P with Ti and Zn; S with Ti; Cl with Ti and Mn; Ca with As; and As with Ca. Apart from these positive correlations, negative correlations were also observed in Cl with Ti and Mn; K with Ca, Cr, Mn, Fe and Ni. This indicated that strong presence of metal replaces the presence of Cl and K in the invertebrates. The correlation with the metal content in water and sediment has indicated that if Mn and Fe were higher, the invertebrates would reduce their Al and Mn uptake.

Table 6.3 Pearson Correlations of elemental content in invertebrates.

	Al	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni	Zn	As
Al	1	0.001	0.145	-0.192	-0.019	0.015	.665**	-0.011	0.209	0.146	-0.010	.460*	.381*
P	0.001	1	.854**	-0.060	0.365	0.256	.413*	0.198	0.281	0.137	0.219	.455*	0.099
S	0.145	.854**	1	0.056	.545**	-0.040	.444*	-0.054	0.160	-0.087	-0.028	.614**	0.047
Cl	-0.192	-0.060	0.056	1	.529**	-0.131	-.443*	-0.332	-.419*	-0.261	-0.343	0.181	-0.080
K	-0.019	0.365	.545**	.529**	1	-.493**	-0.194	-.438*	-.534**	-.472*	-.444*	.508**	-0.069
Ca	0.015	0.256	-0.040	-0.131	-.493**	1	0.274	.829**	.755**	.889**	.836**	-0.052	.377*
Ti	.665**	.413*	.444*	-.443*	-0.194	0.274	1	0.263	.590**	0.337	0.291	0.340	.547**
Cr	-0.011	0.198	-0.054	-0.332	-.438*	.829**	0.263	1	.716**	.953**	.998**	-0.194	.503**
Mn	0.209	0.281	0.160	-.419*	-.534**	.755**	.590**	.716**	1	.800**	.726**	-0.004	0.354
Fe	0.146	0.137	-0.087	-0.261	-.472*	.889**	0.337	.953**	.800**	1	.949**	-0.100	.509**
Ni	-0.010	0.219	-0.028	-0.343	-.444*	.836**	0.291	.998**	.726**	.949**	1	-0.179	.510**
Zn	.460*	.455*	.614**	0.181	.508**	-0.052	0.340	-0.194	-0.004	-0.100	-0.179	1	0.014
As	.381*	0.099	0.047	-0.080	-0.069	.377*	.547**	.503**	0.354	.509**	.510**	0.014	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

A statistical analysis of general linear model (GLM) of the metal content of all the collected invertebrate using IBM SPSS Statistic 24 keeping stream location and invertebrate type as fixed factor and site as random factor revealed that certain element in the invertebrates significantly changed with the change in location and change in type of invertebrate. Aluminium (Al) content significantly changed with change in upstream to downstream and from one invertebrate type to another (p = 0.007, F = 33.7, and df = 8, 3). Detailed analysis revealed that a significant change in Al content with invertebrate type in downstream measurements (p = 0.025, F = 14.62, and df = 8, 3). It also revealed that with the change from one site to another, invertebrates upstream consisted of significantly different amounts of Al (p = 0.05, F = 9.56, and df = 0.007). This was observed in all invertebrates, i.e. Al in Ecnomidae from West Cliff upstream location was 422.5 µg/mg but the same invertebrate in upstream of Tahmoor contained only 131.5 µg/mg of Al. Similarly, Corixidae and Chironominae have revealed that Al content differed in the upstream invertebrates from 324 µg/mg in West Cliff to 198.8 µg/mg in Tahmoor and to 622.1 µg/mg in Nepean river at Manangle, 172.9 µg/mg in West Cliff to 32.2 µg/mg in Tahmoor and to 630.2 µg/mg in Nepean river at Menangle respectively.

The change in Al content with the change in site locations, shown in Figure 6.3, revealed that the community of invertebrates at different places have different concentrations of Al. This demonstrates that with the change in environment the composition of invertebrate changed. The invertebrates were adaptable to the aluminium environment they lived. When Al was observed in the downstream of the discharge point, the content of Al significantly changed with the type of invertebrates. This indicated that the different type of invertebrates living in the same environment behave differently to the Al intake. Aluminium content in Ecnomidae in the downstream of West Cliff was 358.5 µg/mg and in the same water in Corixidae it was 43.7 µg/mg, Chironominae 559.7 µg/mg, Caenidae 916.6 µg/mg, Simulidae 1179.9 µg/mg, Dytiscidae 36.7 µg/mg, Hydrophillidae 32.0 µg/mg, Acarina 136.6 µg/mg, and Elmidae 296.5 µg/mg. Although differences in aluminium composition of different invertebrates was natural, the statistical evaluation was prominent in case of aluminium. Secondly, natural difference of Al content in different upstream invertebrates was not as prominent as for the downstream samples, indicating the effect of different discharge types from the mines.

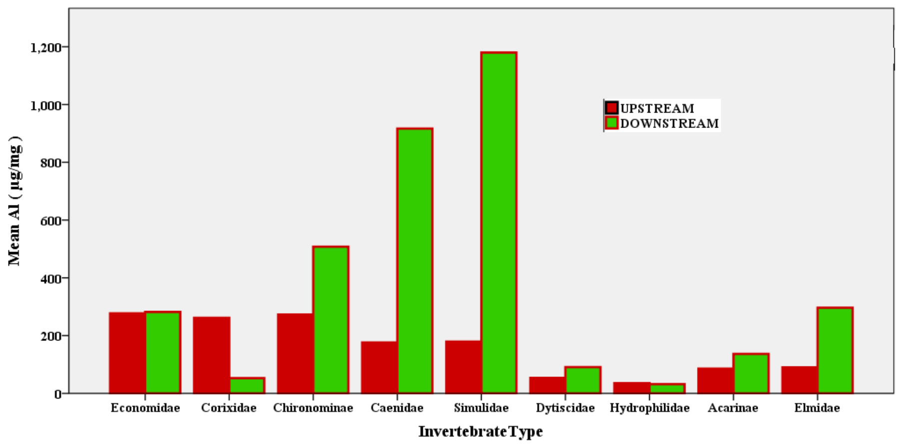

Figure 6.3: Mean aluminium content variation in the invertebrates upstream and downstream

Statistical evaluation of potassium (K) content in the invertebrates also indicated a significant change with the invertebrate type and change in stream type (p = 0.047, F = 9.27, and df = 8, 3), as shown in Figure 6.4. Manganese (Mn) showed a significant change with the change in site and stream (p = 0.037, F = 11.95, and df = 2, 3). The invertebrate downstream of both deposition sites exhibited significant change in the Mn content with the change in mine, meaning the change in the Mn content in the West Cliff downstream invertebrates was significantly different from Mn content in Tahmoor downstream samples (p = 0.024, F = 16.32, and df = 2, 3). Ecnomidae exhibited 20.1 µg/mg Mn in case of West Cliff while it was 74.2 µg/mg in case of Tahmoor. Similarly, Corixidae exhibited 3.9 µg/mg and 27.7, µg/mg Chironominae exhibited 14.3 µg/mg and 54.6 µg/mg, and Dytiscidae exhibited 5.4 µg/mg and 35.6 µg/mg in West Cliff and Tahmoor respectively.

There are changes in the elemental composition of the invertebrates with the change in environment, but its significance is very low in most of the cases. The significant change in case of Al, K and Mn indicated that the invertebrates were not able to regulate these elements in their system. On the other hand, the invertebrates well-regulated majority of the other elements.

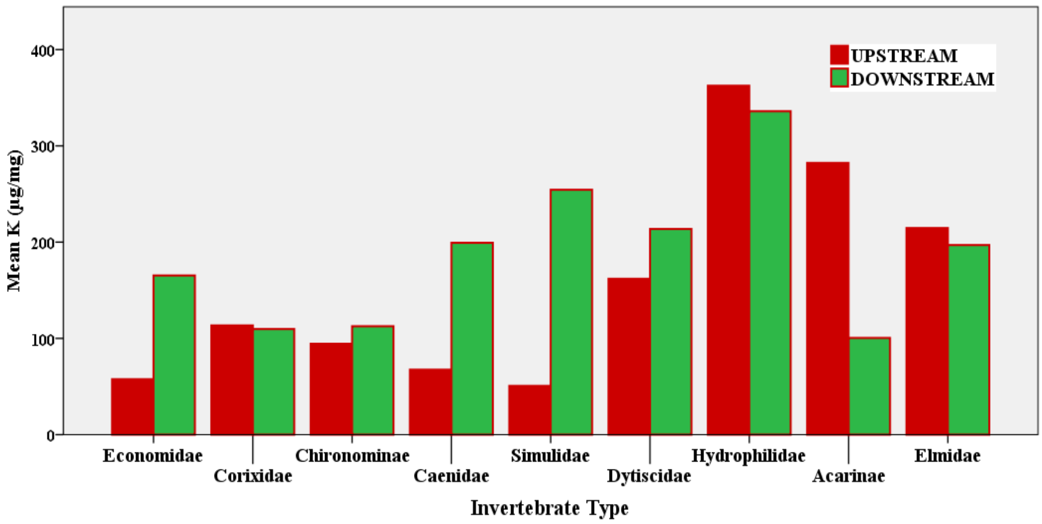

Figure 6.4: Mean potassium concentration variation in the invertebrates upstream and downstream.

6.4 Conclusions

The elemental composition of invertebrates collected from rivers before and after discharge locations of two coal and one coal seam gas mining sites were investigated in this work. Non-uniformity in the elemental composition was observed indicating difference in tolerance level of different invertebrates towards metal contamination. The change in invertebrate type exhibited significant change in elemental composition of the invertebrates. Similar trends in the metal content of Caenidae and Simulidae were identified. Safe metabolism and secretion of calcium with natural mechanisms to block the excess uptake was hypothesised in Ecnomidae which needs be further studied to confirm this hypothesis. The study suggested that the local environmental pressure did not play the main driver of metal accumulation, but an internal mechanism unique to the organism could have played the major role in the phenomena. It is hypothesised that the invertebrates can adjust themselves with filtering out the elements not in need. Ca, Cr, Mn, Fe, Ni and As made significant change in the invertebrates which had to compensate for the change in content for their survival. Al, Ti and Zn showed lower levels in upstream measurements when compared to downstream samples, indicating these four elements are prone to metabolic uptake and therefore should be more closely monitored. The invertebrates were found to be adaptable to the Al environment they lived and different type of invertebrates living in the same environment behave differently to the Al intake. The mechanism in the invertebrates to keep aluminium, potassium, and manganese with changing environment of upstream and downstream needs further monitoring.

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Conclusions and Recommendations

7.1 Conclusions

The objective of this thesis was to substantiate the effect of coal and coal seam gas production on the environment. The possibility of the environmental impairment with the type of processes involved in the production, waste generation and their disposal procedure was studied. The study provides the novel ideas for the need of thorough monitoring and licencing procedures for the sustainable industrialization. Comprehensive assessment of the impact of the coal seam and coal mining with the international quality parameters of water, sediments and inhabitants needs to be thoroughly implemented. The chemical constituents of the mining activities were examined and compared with the change in condition to evaluate the impact on the inhabitant's health. A baseline of the industrial constituents was established to understand geochemical process, resource utilization, and need for the revision of the coal mine run off management. The need for implementation of robust monitoring procedure was concluded.

The important consequent research outcome of this PhD research project is summarised as follows:

1. The literature review on "Impact of coal and coal seam gas industries on aquatic environment" established the study process to achieve a baseline of contaminants at individual sites for the emission of chemical constituents from coal and coal seam gas industries into water, sediment and invertebrates causing their quality impairment.
2. Water analysis concluded an empirical benchmark of chemical constituents at individual sites due to mine water discharge. Change in contamination intensity is easily detectable in the stream receiving the coal mine discharge. International water quality index (WQI) empirical result revealed the quality impairment caused by the coal mining.
3. Study revealed that the chemical constituent causing compromises with the water quality are more prominent in the coal mining area than that of coal seam gas

production suggesting the environmental sustainability with strict licencing policies of CSG production.

4. A new all-inclusive environmental water quality index (EWQI) based on health hazard was proposed. Total Points from Agency for Toxic Substances and Disease Registry were the basis for calculation. EWQI proved to be more designated parameter for future environmental impact evaluation.
5. The chemical contamination and toxicity increment in sediment exceeding ANZECC guideline limit due to mining discharge was revealed.
6. A health hazard signalling toxicity quotient study revealed the impairment of the sediment quality to the limit of trigger and threshold of the hazard. This inculcated the proposal of a new environmental toxicity quotient (ETQ). The newly proposed ETQ was found to be more contemplative of environmental impact than other indices.
7. Uncontrolled abandoned coal mines are more threatening to the environment than the mines under controlled operations. Continuous trace element build up and accumulation resulted in catalysing the natural process of quartz and clay formation in the sediment. There was indication of thermally high stability compounds discharge from coal mines as well.
8. Macroinvertebrate study revealed that other environmental factors affect the trend more than individual trend of contaminants on the abundance and distribution of biota as was shown by inconsistent trend in biota at different locations. Further study indicated that the default guidelines may not necessarily be equally affecting the variety of taxa. This independency of variety of taxa was also established by different trend in behaviour of chlorophyll and invertebrate towards the contaminants in the environment for their survival. However, nutrient content in the environment affects both in the same manner.
9. The local environmental pressure was not the main driver of metal accumulation phenomena in the invertebrates but it was hypothesized that an internal mechanism unique to the organism controlled the process, which resulted in non-uniformity in the elemental composition of different invertebrates. The overall inference from the study is that the effect of contaminants on the aquatic habitats is less severe than

expected from the calculations based on the ANZECC (2000) contaminants trigger values.

10. This study compiled the information to assess the impact of mining industries like coal seam gas production and coal mining on water, sediments, and aquatic life, and help enable systematic conservation plan.

7.2 Limitations

There are some limitations of this work, which are listed below:

1. The findings may not be able to be generalised due to the specific nature of this study.
2. The sensitivity of the equipment was restricting the generalization of the findings.
3. Because of difficulty getting permission to access the CSG site monitoring wells, underground water contamination study could not be included in the scope of this thesis work.

7.3 Recommendations

The thesis accomplished a comprehensive study on the prerequisites for the assessment of anthropogenic environmental impact of coal seam gas and coal production industries. However, filling the entire gaps emerging during the study still remains persistent to achieve the sustainability of environment. Following recommendations would further enhance the thesis achievements:

1. An independent monitoring schedule is highly recommended to be in place to avoid uncontrolled continuous environmental impact compromises. The plan of a thorough revision of the conditions of coalmine run off management should be implemented under the government supervision to avoid conflicting interest of mining industries.

2. The pollution control strategies being less effective at metal removal, the proposed environmental water quality index (EWQI) should be included in monitoring parameters to get health hazard reflection from the collected data. A statistical inhabitant study with respect to EWQI rang is highly recommend. A comparison of environmental impact of sediment's toxicity quotient (ETQ) on inhabitants trending would bring conclusive result for the future sustainable development.

3. A revised thorough mine closure processes with greater attention should be implemented to avoid uncontrolled continuous environmental sustainability compromises.
4. To avoid regulatory intervention discrepancy in the sediment quality indices in terms of the ecological and toxicological impacts the study recommends more contemplative proposed environmental toxicity quotient (ETQ) to supplement pollution licencing and eco-toxicological management in order to evaluate the impacts of a point source discharge where suitable.
5. Invertebrate abundance inconsistency could be of the interest to explore further into the composition of discharge into the waterways. Al, Ti, and Zn are prone to metabolic uptake and therefore should be more closely monitored.
6. The inability of the invertebrates to regulate aluminium, potassium and manganese to their original levels with changing environment recommends its regular monitoring in the invertebrates and establish the trend in tolerance limit or trigger value to ascertain the impact trend.

Impact of Coal Mining on River Sediment Quality in the Sydney Basin, Australia

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Abstract

The environmental impacts arising from mining activities affect the air, water and soil quality. Impacts may result in unexpected and adverse environmental outcomes. This study reports on the impact of coal production on sediment in Sydney region of Australia. The sediment samples upstream and downstream from the discharge points from three mines were taken and 80 parameters were tested. The results were assessed against sediment quality based on presence of metals. The study revealed the increment of metal content in the sediment downstream of the reference locations. In many cases the sediment was above the Australia and New Zealand Environment Conservation Council and international sediment quality guidelines value (SQGV). The major outliers to the guidelines were nickel (Ni) and zinc (Zn).

Keywords:

Coal mine, environmental impact, produced water, sediment quality guidelines value (SQGV).

A.1 Introduction

Exponential increase in the energy demand has made extensive use of fossil fuels (Zhang & Luo, 2015). Extreme interdependency of energy generation and water consumption has evolved the term Water-Energy Nexus (Raucher & Cromwell, 2008) which suggests that water used in and disposed of as part of energy generation would contain a variety of materials that eventually if not treated and disposed adequately would affect water and sediment quality in downstream environments. The nuisance of coal mining has been documented as early as 1620 (Levine & Wrightson, 1991). In Australia, coal was used by Aborigines for cooking purposes in pre-1788 era (Government) and was 'discovered' by Lieutenant John Shortland in 1797. The mining and export of coal began in 1799 and it remains the major source of energy and a key export commodity (Government). Coal is extracted in Australia by both open cut and underground methods. Wastewater is discharged under a pollution license issued by the State environment agency (Dhar, 1993) and is typically treated to manage acid mine drainage and dissolved minerals (Younger, 2004). The acidity caused by the geochemical process of mineral ion exchange and oxidative weathering from coal wastewater produces acid generating salt (AGS) which has become a significant parameter in sedimentology (Scott, 2003) due to the process of converting a spoiled heap of coarse fragment of rock from coal mine into disaggregated mud and sand. The weathering effect ends into layers of sediment deposits in natural process of storm and wind.

The discharge of coal mine wastewater and associated sediments to waterways are source of contamination. Contaminants may be associated with the sediment grains, which in turn can impact on flora and fauna and bioaccumulate (Bazrafshan et al., 2016). The sediment holding the inactive contaminants can release into the water due to disturbance and affect the ecosystem (Hope, 2006). It has become essential to study the sediment quality to effectively manage the environment.

There are always risks of environmental deterioration if a site goes under redevelopment or remediation. For a sustainable environment, an assessment of potential toxicity, bio-accumulation and fate of contaminants must be studied. Environmentalists are looking for the ways to incorporate the latest science into the assessment of contaminated sediments. Some technique works for the marine water sediment but may not equally work for the freshwater. In past, focus was more on costal marine environment and freshwater study was limited. A total chemical contamination analysis had always been a step forward to assess the contaminants. A sediment quality guidelines (SQGV) for contaminants have been proposed (Buchman, 1999) and Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand (The ANZECC/ARMCANZ 2000a) has published and revised these SQGVs for the assessment (Simpson et al., 2013).

Apart from bulk analysis of individual contaminants, sediment quality was evaluated by ecotoxicity (Long & Chapman, 1985). A bioavailability assessment approach and bioanalytical approaches were applied as an indicative tool for the quality assessment (Di Toro et al., 1991; Bergman et al., 2013). Bioavailability, which is the fraction of contaminants available for uptake by an organism of interest, is assessed by leaving the organism in the sediment in the laboratory. Bioanalytical approach is the analysis of endocrine disrupting chemicals (EDC) using mechanism based biological screening tools. Toxicity identification evaluation (TIE) for dissolved toxicants has also been tried for the sediment evaluation (Ho & Burgess, 2008). Bioaccumulation in the tissues of organisms with contaminated sediment was used as quality indicator for the sediment (Rainbow, 2007). Biomarker is a chemical or non-chemical response to single or multiple environmental stressors within an organism and was used for the quality assessment of sediment (Hook et al., 2014). Sediment contamination assessment by potential ecological risk index (PERI) of toxic substances and water analysis based on USEPA criteria with equilibrium partitioning (EqP) of contaminants was considered for certain period of time (USEPA, 1981). Ecosystem stressors were also applied to evaluate the sediments quality (Jørgensen et al., 2016). Having all the technological developments applied to evaluate the sediment it was always accepted that total contaminants analysis correlates with the sediment quality. This study revolves around analysis of different parameters of sediments near coal mining area in the Sydney basin, based on contaminants concentration.

A.2 Material and Methods

A.2.1 Study Area and Site Description

This paper covers three sites in Blue Mountain area of Western Sydney region located 85 to 140 km west of Sydney. Extensive coal mining activities in the region prompted the selection of the area where water resources were affected by three coal mines namely Canyon, Centennial, and Springvale collieries. These mines are affecting the quality of Coxs River, Wollangambe River, Grose River, Dalpura creek, and Sawyers Swamp's sediment quality. The Canyon Colliery was an underground coal mine operated from 1930 to 1997. Drainage shaft carries the drainage to Dalpura creek at high flow which contributes to 65% of the water flow in the upper Grose River. It has been reported that the water was highly contaminated with acid mine drainage (AMD) and after the closure of mine the ground water was continuously flowing through the mine to the Dalpura creek (Wright, 2009). The drainage falling into Wollangambe River comes from coal washing dewatering and surface storage at mine site of Clarence Colliery. Table A.1 shows the detail of the coordinates and sampling locations. Sample location points are further depicted in Figure A.1. This region has 150 years' history of coal mining activities (Macqueen, 2007). The sediment sampling locations were selected to represent sediment before and after the discharge points of industrial wastewater.

Table A.1: Sample and site identification

Study Area	Mines / Industry	Sample collection site	Sample identification	Coordinates	
1	Ash Dam, Angus Place and Springvale	Coxs River, upstream	W1	33°18'0.64"S	150° 5'49.30"E
		Sawyers Swamp, downstream	W2	33°22'50.74"S	150° 5'11.63"E
		Sawyers Swamp, upstream	W3	33°23'37.40"S	150° 7'28.12"E
		Springvale discharge	W4	33°24'6.55"S	150° 5'39.55"E
2	Centennial Coal Mine	Wollangambe River, upstream	W5	33°27'19.94"S	150°15'26.64"E
		Wollangambe River, downstream	W6	33°27'53.63"S	150°15'49.68"E
		Wollangambe River, discharge	W7	33°27'52.26"S	150°15'33.73"E
3	Canyon Coal Mine	Dalpura creek, upstream	W8	33°32'24.67"S	150°18'22.19"E
		Dalpura creek, downstream	W9	3°32'27.75"S	150°18'25.71"E
		Dalpura creek, further downstream	W10	3°32'18.58"S	150°18'5.55"E

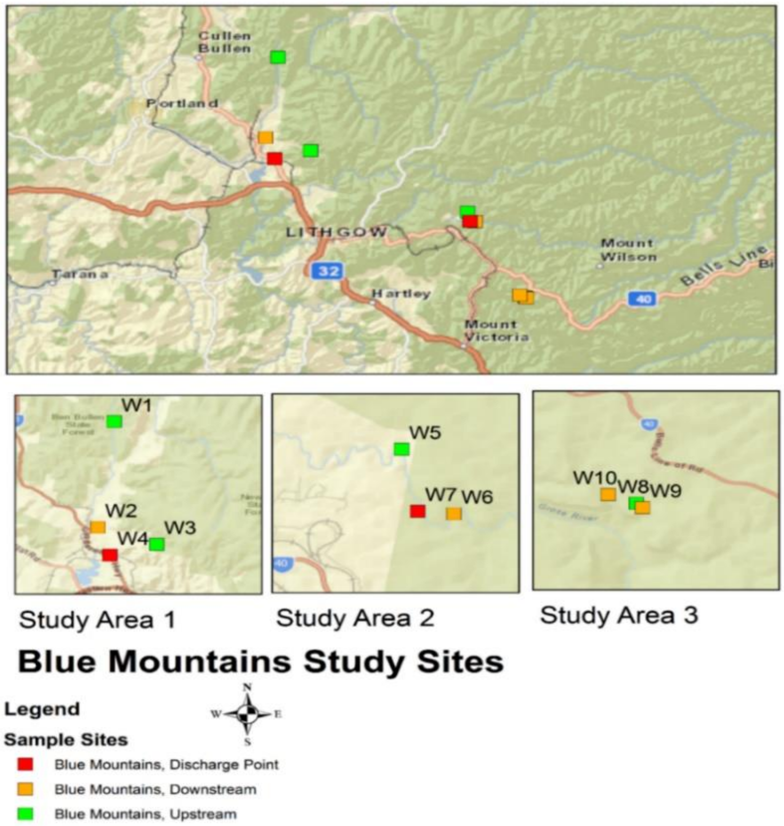

Figure A.1: Mapping nonlinear data to a higher dimensional feature space

A.2.2 Sampling and analysis

A clean screw capped glass jar was used to collect sediment samples from the surface of sampling points. Samples were kept in an ice box without addition of any preservatives during the period of July 2014 to September 2015 with the favorable weather for accessibility to the remote sites. A National Association of Testing Authorities (NATA) accredited external laboratory, Envirolab, was used for the analysis of samples. USEPA 200.8, USEPA 6020A, USEPA 7471A, USEPA 3051A, and APHA 3125 as standard reference methods were used for the analysis of sediment samples. The parameters analyzed by external laboratory for the study included polyatomic non-metals, most transition metals, alkali metals, and alkaline earth metals metalloids of interest.

Thermo-gravimetric and computer aided thermal analysis of sediments were performed using Mettler Toledo thermo-gravimetric analyzer (TGA/DSC 1 STARe system). Weight changes of the samples with the change in temperature was analyzed by using STARe software. The carrier gas nitrogen with flow rate of 20 mL/min was used for approximately 20 g of sample heated to the maximum temperature of 1000 ^{0}C at the rate of 10 ^{0}C/min.

Fourier transform infra-red spectroscopy (FTIR) was used to monitor the abundance of functional groups with the changing location of sediments. Nicolet 6700 FTIR spectrometer was used with 32 number of scans and spectral resolution of 4 cm^{-1}. Attenuated total reflectance (ATR) with a diamond crystal was used for the analysis.

A.3 Results and discussion

The sediment samples were analyzed for 37 trace element parameters. The results for each site are presented in Table A.2 with detectable elements only. Concentrations range of sodium in downstream samples varied from 10 mg/kg to 2200 mg/kg, while upstream samples had concentration ranging from undetected to 350 mg/kg. The increment sodium indicated a significant impact of the release of salts from the coal mine produced water. Study Area 3 revealed that many of the parameters which were not detected in the upstream sample were in very high concentration in the downstream sediment sample. Arsenic, cobalt, copper, lead, nickel, zinc, calcium, and magnesium were among those that exceeded the available SQGVs. Most of the study areas revealed elevated levels of sodium, cobalt, iron, barium and nickel in the downstream and indicated an effect of the coal mining activities. Sawyers Swamp (W2) and other downstream discharge sampling points W4, W6, W7, W9, and W10 showed high aluminum levels. Although the ANZECC guidelines do not report trigger values for aluminum in sediments, high concentrations of aluminum are of concern as Dalpura Creek falling into the river (W3) carried 12,000 mg/kg of aluminum which is a continuous process for years without any regulatory restriction.

Elevated concentration of nickel, calcium and potassium were also detected in most of the downstream sediment samples. The highly toxic substance, arsenic, was found to be above the ANZECC trigger value of 20 mg/kg for Sawyers Swamp (W2 = 41 mg/kg), Springvale (W4 = 26 mg/kg), and Dalpura creek (W9 = 28 mg/kg). Cadmium in Sawyer Swamp and Dalpura Creek were also higher than the trigger value of 1.5 mg/kg SQGV (W2 = 2 mg/kg & W9 = 2 mg/kg). Nickel was also highly elevated downstream of the Blue Mountains area (W2 = 210 mg/kg, W4 = 59 mg/kg, W7 = 53 mg/kg W9 = 2300 mg/kg, and W10 = 870 mg/kg) with concentrations in the sediments above the trigger value of 21 mg/kg. Zinc was highly elevated in many of the downstream locations. The trigger value of zinc SQGV is 200 mg/kg while the measured values in W2 = 650 mg/kg, W4 = 380 mg/kg, W5 = 360 mg/kg, W9 = 3500 mg/kg, and W10 = 1800 mg/kg were well above the trigger values. It is important to note that the iron levels were found to be very high in all cases and varied from 870 mg/kg to 300,000 mg/kg. Iron does not have ANZACC guidelines trigger value but in several cases (W1, W9 and W10) the concentrations of iron ranged over 30% of the sediment chemistry. Calcium, potassium, magnesium and sodium in the collected sediments exhibited strong contamination trends at the mine discharge locations. The results clearly indicated that the sediments in the vicinity of coal mines in the Blue Mountains area were subjected to higher environmental impact.

Table A.2**:** Sediment Quality Parameters.

Study area		**SQGV**	**Study Area 1**				**Study Area 2**			**Study Area 3**		
Sample location			**W1**	**W2**	**W3**	**W4**	**W5**	**W6**	**W7**	**W8**	**W9**	**W10**
Analytes	**DL (mg/kg)**		**U**	**D**	**U**	**D**	**U**	**D**	**DP**	**U**	**D**	**DD**
Total Nitrogen	10 mg/kg		32000	3900	690	5900	1800	2200	2000	67	3600	6900
Ammonia as N	0.5 mg/kg		2.2	17	1.9	13	0.5	3	2	1.8	100	48
Phosphorus	10 mg/kg		440	360	40	490	10	140	70	<10	60	550
Aluminium	1 mg/kg		5800	27000	1500	8200	800	5400	3800	190	12000	6500
Arsenic	4 mg/kg	20	16	41	<4	26	<4	<4	<4	<4	28	18
Barium	1 mg/kg		120	220	23	610	36	59	44	1	510	260
Calcium	5 mg/kg		830	17000	61	3900	260	360	250	<5	1300	3500
Chromium	1 mg/kg		8	10	2	9	<1	5	4	<1	1	10
Cobalt	1 mg/kg		66	180	3	51	310	5	59	<1	3600	470
Copper	1 mg/kg	80	5	17	2	22	2	21	7	<1	87	180
Iron	1 mg/kg		300000	27000	9200	21000	1800	10000	7600	870	360000	310000
Lead	1 mg/kg	65	6	24	3	23	2	13	7	<1	37	130
Magnesium	5 mg/kg		520	990	30	810	20	180	99	<5	480	1300
Manganese	1 mg/kg		3200	3800	64	8600	2800	160	750	2	38000	4700
Nickel	1 mg/kg	21	13	210	2	59	260	13	53	<1	2300	870
Potassium	10 mg/kg		320	1100	50	1200	40	290	130	10	2300	800
Sodium	10 mg/kg		350	2200	10	860	<10	40	20	<10	210	60
Sulphur	10 mg/kg		1600	4700	130	1600	100	380	210	<10	2400	2900
Silicon	10 mg/kg		1800	380	80	730	80	370	220	110	8000	1500
Titanium	1 mg/kg		17	25	4	8	3	15	8	2	2	39
Uranium	0.1 mg/kg		0.6	2.7	0.2	0.9	0.1	0.5	0.4	<0.1	9.8	18
Zinc	1 mg/kg	200	43	650	8	380	360	31	91	<1	3500	1800

D = downstream, DD = further downstream, DP = discharge point, and U= upstream, DL = detection limit

Figure A.2 represents general outlook to the trend in the presence of contaminants before and after the discharge point. The data was collected from the sediment samples of Dalpura creek. Upstream sample was clean sand and selected parameters Ni, Co and Zn were not detected in the sediment sample. The downstream sample was collected from close to the discharge point of the abandoned coal mine and further down sample was collected from a distant place to the discharge point. All the three contaminants selected in Figure A.2 are highly toxic and their sudden increment from absence to nearly 3500 mg/kg was found to be potentially highly damaging to the inhabitants.

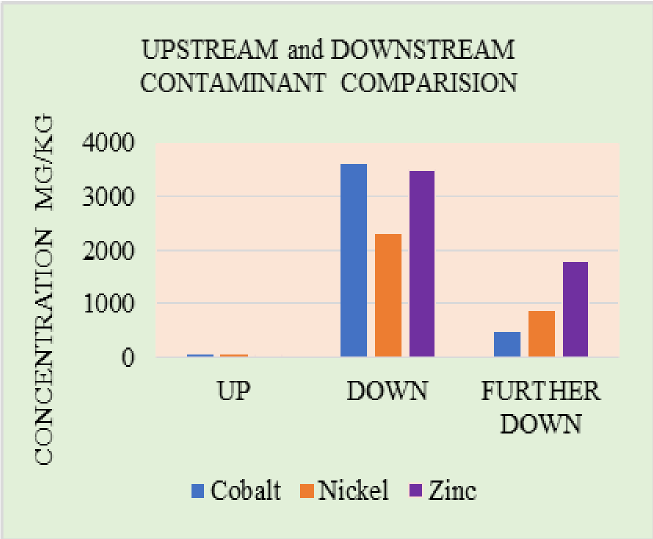

Figure A.2: Comparison of upstream to downstream contaminants in Dalpura creek sediments

Zinc deficiency has been an issue in the past but in recent research work it was found to affect the inhabitants adversely as it affects the enzymes that regulate RNA and DNA (Eisler, 1986). Cobalt poses adverse effect on kidney and eye sight and the magnitude of increment in the samples was considered a threat to the inhabitants (Paustenbach et al., 2013). Nickel is listed in the European Commission List, World Health Organization as Group 1 (human carcinogen) (Eisler, 1998) and its increment downstream was found to be very high.

High phosphorous presence can affect the biological productivity of freshwater ecosystem (Davis & Koop, 2006; Heathwaite, 2003). Downstream samples of Centennial coal mine (W6) and Canyon coal mine (W10) showed a significantly high presence of phosphorous, though the increment of phosphorous content in other downstream samples was not very high. Significant increment in nitrogen value of Canyon coal mine's Dalpura creek was also observed.

Figure A.3 shows the FTIR of the sediment samples. The side peak at 1162 cm^{-1} and a large peak centering at around 1060-1080 cm^{-1} for sample W1 are ascribed to quartz and aluminosilicate clay minerals (e.g., kaolinite), respectively. This information matched with the abundance of aluminum in the sediment analysis. Double peaks at 796 and 777 cm^{-1} correspond to the inorganic materials, such as clay and quartz minerals, while the peak at 692 cm^{-1} is attributed to anthophylitte. The existence of quartz is also confirmed by the peak at 467 cm^{-1} which is the result of Si-O and O-Si-O bending vibrations. This information revealed that the abundance of contaminants discharge had contributed in the natural process of quartz formation.

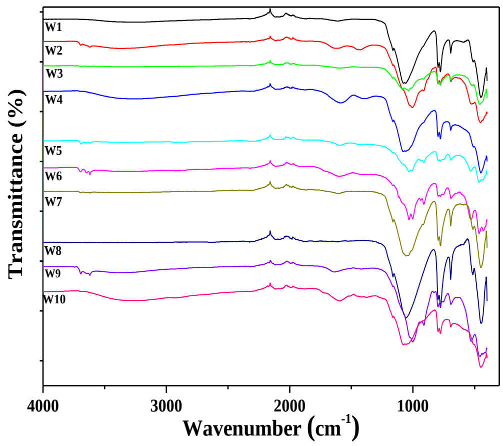

Figure A.3: FTIR of sediment samples from Blue Mountain area

The additional small peaks at 3619 cm^{-1} and 3696 cm^{-1} appeared in the IR spectrum of W2, which was related to Al-O–H stretching and Si-O and O-Si-O bending vibrations and/or Al-O–H (inter-octahedral), respectively. The peak at 1595 cm^{-1} became more intensive, demonstrating the increased content of Si–O–C bond. More intense bonding has indicated that the downstream sample has more minerals to form Si-O-C bonds. Similar results can be obtained when comparing W4 with W3, W6 with W5, and W9 with W8 respectively.

The mass loss of the samples when heated at 10°C/min are presented in Figure A.4. The differential thermogravimetry (DTG) analyses for samples indicated distinct discrete stages of degradation to reflect their thermal dynamics. Most of them are characterized by the initial loss of inherent moisture followed by the devolatilisation of primary volatiles. For instance upstream sample of Sawyer swamp, W3 illustrated initial DTG peak centered at 60-90 °C can be assigned to inherent moisture loss followed by a broad peak at 300-350 °C which started declining at 220 °C for water soluble materials.

Further temperature increment yielded a broader peak from 370°C through to 480 and slightly dipped at 450 °C which stabilized at 550 °C. At a temperature 620 °C another decline started yielding into a very sharp peak at 640-650 °C and finally got stable at 740 °C.

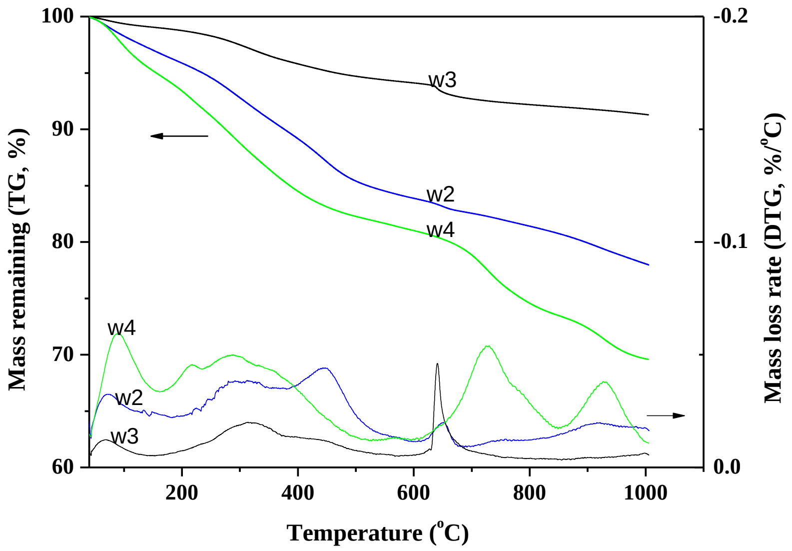

Figure A.4: DTG curves of sediments from Blue Mountain area

Downstream sample of the Sawyer swamp W2 initially exhibited the same pattern and the slight dip of W3 at 450 °C became a prominent peak reducing the size of sharp peak at 640-650 °C. When discharge point sample of Springvale was subjected to the DTG analysis an additional peak at 280 °C was observed and the sharp peak of W3 at 640-650 °C became more intense and broad which further showed a very prominent peak 940-960 °C indicating a highly stable compound.

A.4 Conclusions

This project enabled studying the chemical contaminants and toxicity increment in the sediment of Blue Mountain region near coal mine activities. The sediments have been seriously affected by the mine discharge breaching the ANZECC guideline limits. The exceedance of toxic elements to sediment quality guidelines value indicated the possible adverse contaminant-induced impact on resident benthic communities in the region. Geological time frame of continuous trace element build up and accumulation could have resulted in catalyzing the natural process of quartz and clay formation in the sediment which was confirmed by FTIR of the samples. TGA analysis indicated the discharge of thermally high stability compounds from coal mines or catalisation of their natural formation by discharged material. This work has provided a baseline of contaminants for the region, it has also provided quality data of the sediment. Based on the IR and TGA data regulatory authority can design remedial system for future resource utilization. This study revealed that an independent monitoring schedule should be in place to avoid uncontrolled continuous environmental impact compromises.

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Coal Mine Discharge Impacts on Aquatic Invertebrates in the Sydney Region

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Abstract

Our previous work has confirmed the impact of coal mine industries on the quality of water and river sediments in the Sydney basin region. Effluents generated from coal mine in some cases are highly contaminated with metals such as aluminium (Al), iron (Fe), manganese (Mn), nickel (Ni) and zinc (Zn), and other contaminants. The impact of mine and industrial activities on the river water ecosystems are investigated in this study. A substantial difference in community structure was observed above and below point of mine influence. Analysis also suggests that the mine water discharged affecting invertebrate communities in rivers above and below the discharge point has some relation with the heavy metal presence. The approach used in this study aims to provide information to assess the impact of mining industries on aquatic life and help enable systematic conservation plan.

B.1 Introduction

Rapid development with growing energy consumption has resulted in exponential production of resources for the energy generation (Chong et al., 2016). In the course of production processes variety of materials are consumed, processed and washed away as a discharge in the form of produced water. Though the water discharged into the creeks and waterways is diluted in the downstream flow, a continuation in discharge would lead to persistence of contaminants in waterways. It is a critical problem to maintain the water quality throughout the world due to toxicity and residue impact of industrialisation (Strady et al., 2017).

Water soluble contaminants are directly affecting the ecosystem. Low soluble trace metals can be easily adsorbed in sediments and this continuous process yields to high accumulation of contaminants (Alvarez et al., 2011). Due to sediment being ultimate sink for the trace metals (Ali et al., 2017a) living organisms on the coastal areas may be also affected by the poor sediment quality. Certain trace metals which are not permanently bonded in the sediment can be released in the water under different circumstances (Caille et al., 2003). Some of them (Mo, Cr, Zn, Se, Co, Fe) are used in the biological functions and are not harmful in low concentrations but those which are not essential for the biological use (Pb, Hg, Cd, As, Ni) can be toxic at very low concentrations (Pagenkopf, 1983). These trace metals can be accumulated in the body of the biota and finally end up in the food chain and affect human health (Allinson et al., 2015). It has been reported that there are certain species which have their own system to maintain the intake of contaminants and there is constant accumulation of trace metals in these species irrespective of the available trace metals in the water system (Johnstone et al., 2016). In some cases, such as increase in salinity due to discharge, can be tolerated by the taxa (Bailey et al., 2002). Mine water salinity affects the algae and duckweed (Smith et al., 2009). Invertebrates can be affected and lead to high densities i.e. abundance per square area of stone and low richness by salinity increment (Bunn and Davies, 1992). The increment of trace metals in the discharged water was observed previously in the downstream sediment and surface water from the coal mining activities in the Sydney region (Peralta-Videa et al., 2009). Inhabitants have their characteristic affinity towards the available trace nutrients. In presence of certain trace metals, the process of uptake of other trace metals by inhabitant are reduced. Even the processes including the photosynthesis are affected (Volland et al., 2014). This process of selective nutrients uptake of trace metals in presence of others affects in both ways of increasing or decreasing the damage to plant. Eventually, bioavailability of trace metals affecting the inhabitants are reflected in diverse forms.

Due to variety of behavioural changes macroinvertebrates in a river ecosystem can be used as a tool for assessment of the water quality and industrial impact (Andersen et al., 2016). They can be applied as anthropogenic adverse effect indicator on aquatic systems (Kaboré et al., 2016). The aim of this work is to investigate the changes in the ecology of rivers by analysis of chlorophyll and invertebrates in the area affected by the produced industrial discharge from coal mining activities and in the less affected areas before the discharge points.

B.2 Material and Method

B.2.1 Study Area and Site Description

The study was carried out in October 2016. The study site was South Sydney region located 60 to 120 km southwest of Sydney. Two mines of the region were selected for this study, one was West Cliff Colliery which discharges into Brennans Creek and then the Georges River, and the other was Tahmoor Coal mine discharging into the Bargo River. The coordinates and details of the sampling locations are listed and illustrated in Table B.1 and Figure B.1, respectively. The samples were collected from the locations before (upstream) and after (downstream) the produced water discharge points.

Table B.1: Sample and site identification.

S. No.	Mines / Industry	Sample collection site	Coordinates		Site I.D.
1	West Cliff Colliery Appin	Georges River, Appin, upstream	4°12'13.46"S	150°47'52.74"E	S1
		Georges River, Appin, downstream	4°12'17.25"S	150°47'55.89"E	S2
2	Tahmoor Coal Mine	Bargo River, Tahmoor, upstream	4°14'12.11"S	150°34'46.02"E	S4
		Bargo River, Tahmoor, downstream	4°14'58.47"S	150°36'25.37"E	S5

This study area of south Sydney was chosen for our previous study of water quality (Ali et al., 2017b). A trend of water quality in upstream and downstream of the mine discharge was investigated and indices were calculated for the assessment of water quality. Heavy metal potential index of the study is shown in Figure B.2 to find a correlation with the ecology of river.

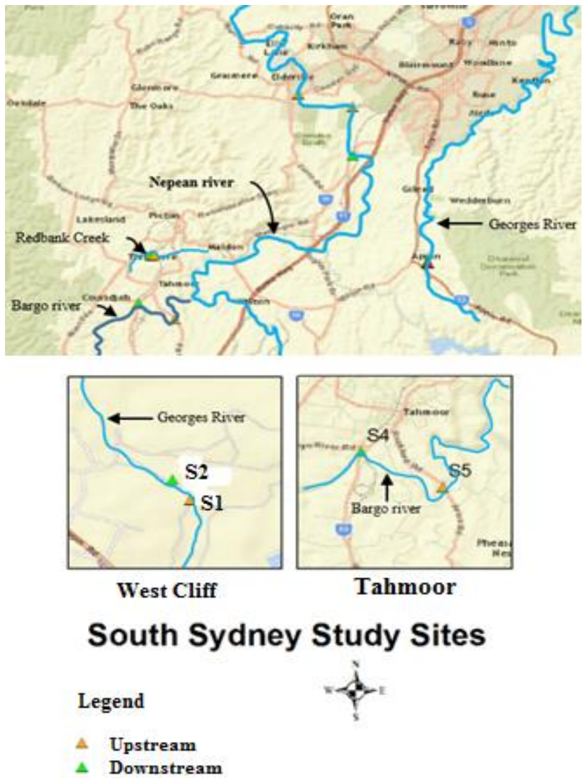

Figure B.1: Sampling locations of upstream and downstream of West Cliff and Tahmoor Colliery.

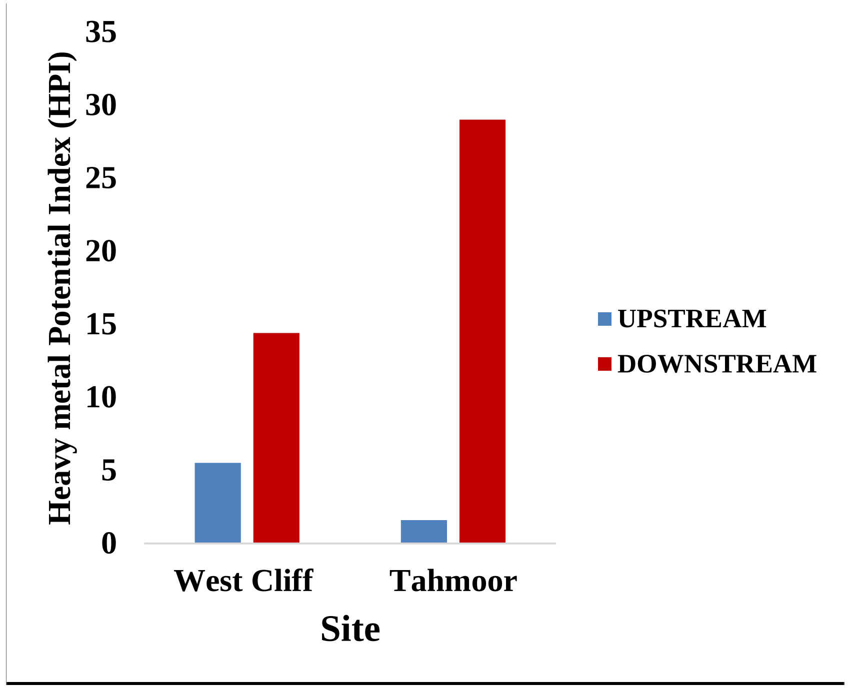

Figure B.2: Heavy metal potential index (HPI) of water samples collected from upstream and downstream of mine water discharge points on the Georges River (West Cliff Mine) and Bargo River (Tahmoor Mine) (Ali et al., 2017b)

B.2.2 Sampling and analysis

Samples of invertebrates and chlorophyll-A were taken from randomly selected rocks which were removed from the river at sites above and below the mine water discharge. Rocks of a size similar to a football were removed from the stream bed and placed into a 500 µm mesh net while still under water. The net was placed immediately downstream of the rock to capture any animals dislodged during rock removal. The rocks were taken to the river bank and rock and contents of the net placed into a plastic tray for processing. A 3 cm x 3 cm template was used twice for the collection of chlorophyll sample from a rock sample. The template was placed on the rock and carefully scrapped the algae and biofilm of entire area of rock within the template and rinse transferred to a jar using a wash bottle. The jar containing the algal scraping was wrapped in aluminium foil to avoid light exposure and placed in a portable cooler.

Samples were filtered and the filter membranes placed in acetone at 4 degrees for 24 hours in the dark. The absorbance of the acetone solutions was measured at 750, 664, 647 and 630 nm using a Hach portable spectrophotometer. Calculation of the chlorophyll concentration was performed according to the standard procedure described elsewhere (Wright et al., 2005). Samples were collected in clean screw-capped plastic jars. Sampling was performed to examine the biota on a rock for the abundance and type of biota. The rocks and net were washed in the tray and visually inspected to ensure all animals were removed. All animals were transferred into a clean plastic jar and frozen until later analysis in the laboratory. Invertebrates were identified and enumerated under a microscope following the guidelines of Environmental Protection Agency (USEPA, 1998).

The invertebrates were identified to family level, where possible, with the exception of Chironominae which were identified to subfamily. Oligochaetes and mites were identified to class only. The invertebrates collected were analysed for their abundance, density and richness. The abundance was described as number of animals collected on each rock and density was calculated as number of animals collected on each rock divided by the size of the rock. Richness was the number of different invertebrate taxa collected on each rock.

The surface area of each rock was estimated by covering the rock in a single layer of aluminium foil and calculating the area from the mass of the foil based on a standard curve. The abundance and richness of invertebrates and densities of invertebrates and chlorophyll-a on rocks collected upstream and downstream from discharge points were compared using 1-way analysis of variance. Assumptions of normality and homogeneity of variance were determined using q-q plots and plots of residuals. The significance level (α) for these analyses was 0.05. Analyses were done using Minitab v17.

B.3 Results and discussion

Figure B.3 displays the mean chlorophyll-a densities on rocks collected from upstream and downstream of mine water discharge points. At both sites, the density of chlorophyll on rocks was not statically significant ($p>0.05$), however, it was observed that the chlorophyll abundance on rocks were higher in areas downstream of the mine discharge points. It was expected to have adverse effect on the algae (Smith et al., 2009) but the result has shown that the downstream was more than that of upstream though insignificant. It indicates that the relationship of biota is not a simple many environmental factors play important role in abundance or concentration of species with chlorophyll-a.

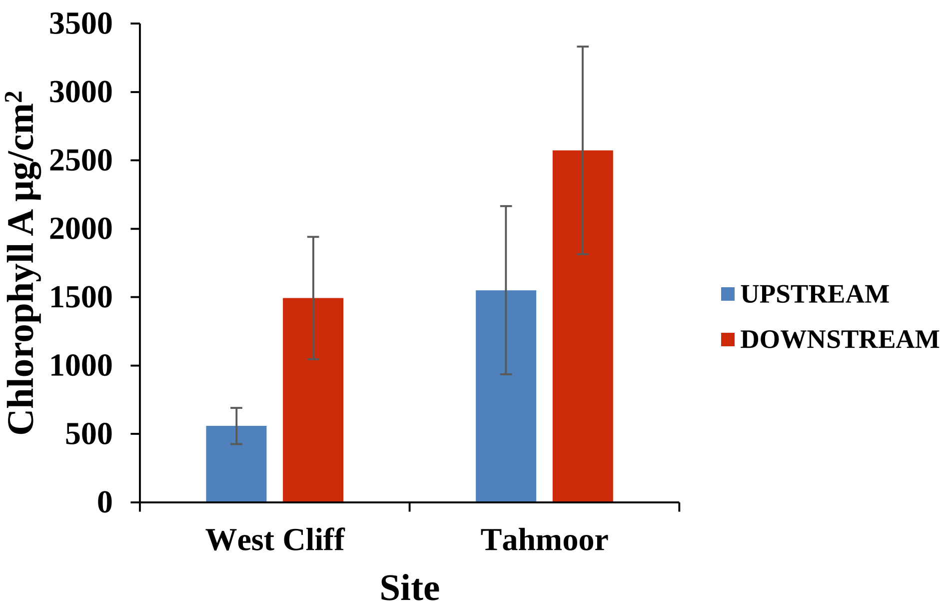

Figure B.3: Mean (±SE) chlorophyll-a densities on rocks collected from upstream and downstream of mine water discharge points at Georges River (West Cliff Mine) and Bargo River (Tahmoor Mine). N=6

Figure B.4 shows the mean invertebrate abundance on rocks collected from upstream and downstream of mine water discharge points. There was significantly greater invertebrate abundance on rocks downstream of the West Cliff mine discharge compare to upstream (p=0.015, Figure B.4). There was no significant upstream-downstream difference in invertebrate abundance at Tahmoor, however, a small decrease in the invertebrate abundance was observed. The greater abundance of invertebrates downstream of the Westcliff mine discharge may reflect habitat rather than water quality differences. Flow velocities and water volume were both greater at downstream than upstream sites, which is a direct consequence of the increased flow from the mine discharge.

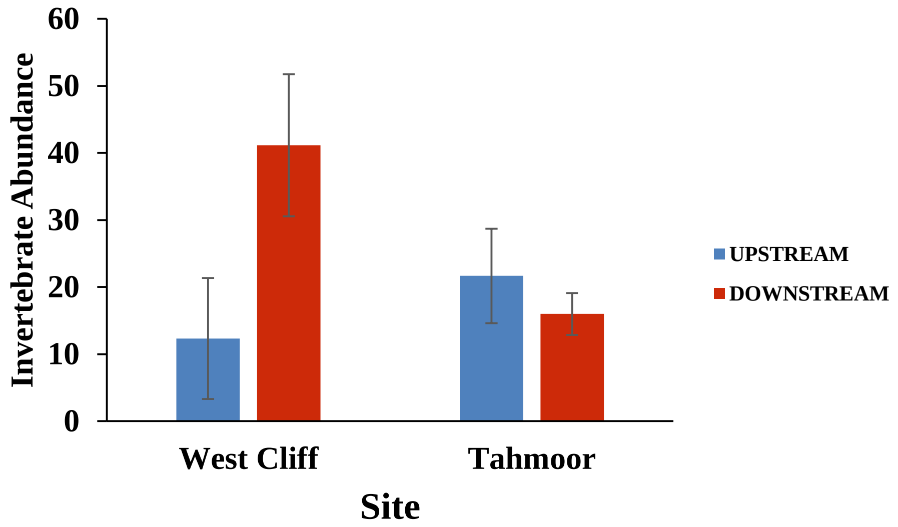

Figure B.4: Mean (±SE) invertebrate abundance on rocks collected from upstream and downstream of mine water discharge points at Georges River (West Cliff Mine) and Bargo River (Tahmoor Mine). P=0.015

The possibility of unhealthy discharge from the Tahmoor colliery activities cannot be ruled out as our previous work (Ali et al., 2017b) has indicated higher heavy metal potential index (HPI) in the downstream of the Tahmoor's Bargo River, as shown in Figure B.2. The HPI was 18 times higher in the Tahmoor colliery downstream comparing to the upstream sample, while in case of West Cliff downstream of Georges River it was about four times above the heavy metal potential index (HPI) of the upstream sample. The excess of HPI can be correlated to the lower abundance of the invertebrates, which needs further comparative study of invertebrates under nutrients with different HPI values. It is well known that the salinity may affect implicating decrease in number of taxa either directly, through osmotic stress, or indirectly through change in food resource. However, only a trigger value study could help in explaining the trend found in the presented work. This may need a toxic identification and evaluation procedure for effect intensity and significance. Having variable effect on biota, mine discharge needs a thorough study of nature and effect of the discharge water on inhabitants. There are some invertebrates which have very quick response to changes in water velocity and quality which might have contributed in the reverse trend in abundance of invertebrates and chlorophyll-A concentration.

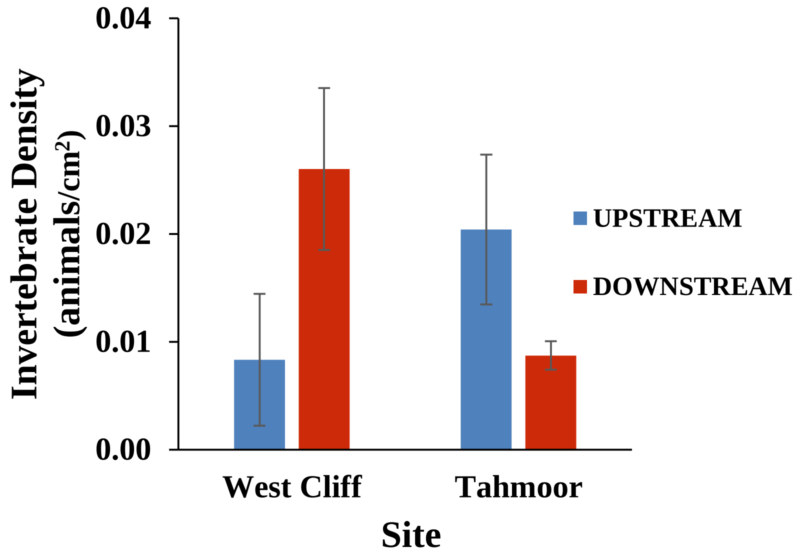

Figure B.5: Mean (±SE) density of invertebrates on rocks collected from upstream and downstream of mine water discharge points at Georges River (West Cliff Mine) and Bargo River (Tahmoor Mine).

Density of the invertebrates was evaluated by abundance per unit area of the rock and the result was in contrast to each other on both sites. Though it was statistically insignificant, it showed the increment in the downstream of West Cliff site. On the other hand, the downstream of Tahmoor site had lower invertebrate density comparing to the upstream sampling site. Decrease in density of the invertebrates in Tahmoor downstream can be considered as indicative of halosensitive invertebrates in the area. There was no significant difference in density (abundance/rock size) at either site.

The richness of the invertebrate is presented in Figure B.6. Invertebrate richness was not significantly different between upstream and downstream locations in either of the rivers (p>0.05).

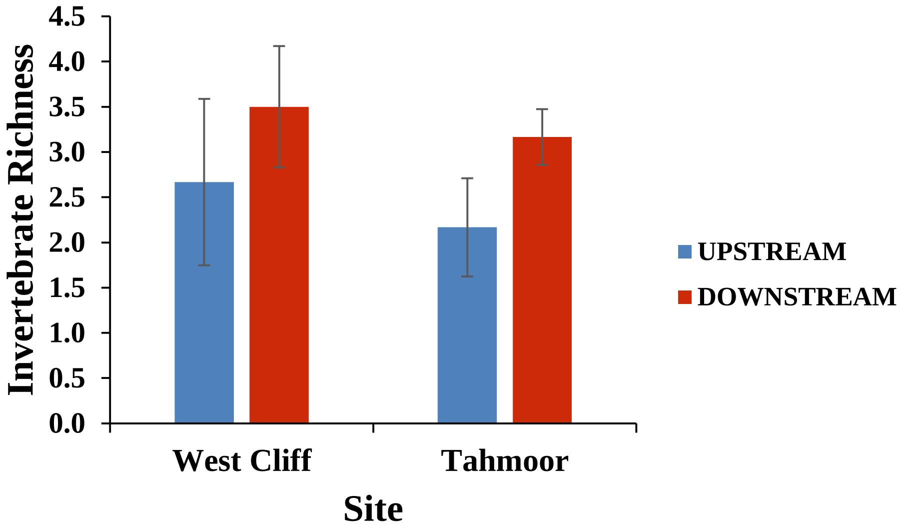

Figure B.6: Mean (±SE) invertebrate richness per rock collected from upstream and downstream of mine water discharge points at Georges River (West Cliff Mine) and Bargo River (Tahmoor Mine).

B.4 Conclusions

The comparative study of chlorophyll and invertebrates in upstream and downstream resulted in inconsistent trend at different locations which indicated the influence of other environmental factors on the biota. It was observed that the discharge may alter the macroinvertebrate assemblages. The invertebrate abundance inconsistency could be of the interest to explore further into the composition of discharge into the waterways. It was seen that a single parameter in water quality could not be used to establish the trend in impact and a study of tolerance limit or trigger value is suggested to ascertain the impact trend. This behaviour also suggested that default guidelines may not necessarily be equally affecting the variety of taxa. Other environmental factors may equally be playing with abundance and distribution of biota. Diverse assemblages have suggested of pollution sensitive taxa and essence of sustainable development approach for the industrialisation by formulating measures to control pollution sources.

Acknowledgment

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B.5 References

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Figures of Sampling Location

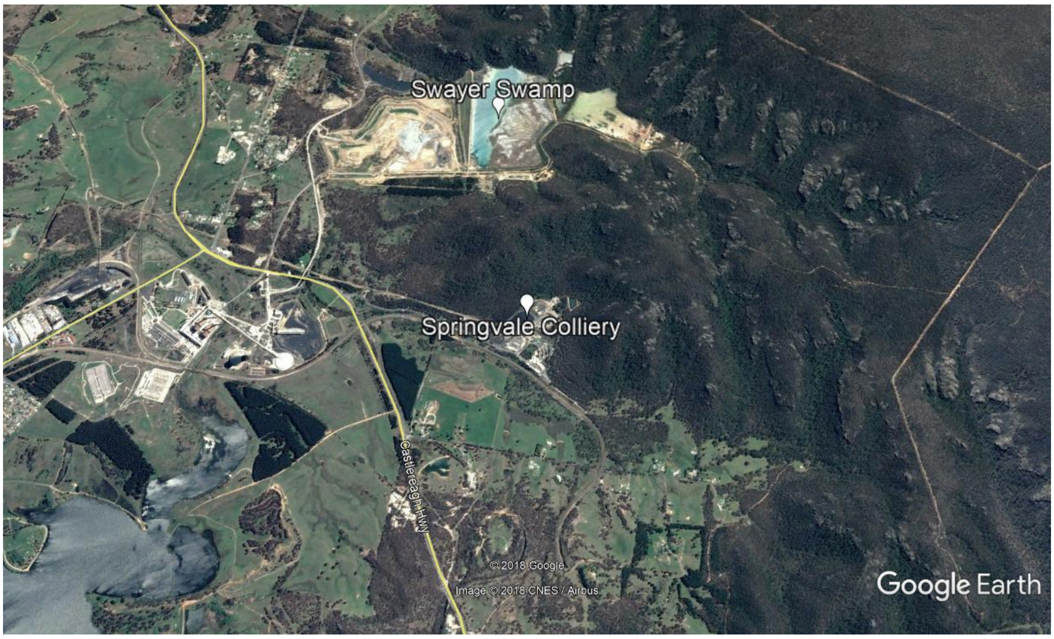

Figure C.1: Sampling Location at Coxs River near Springvale Coal Mine, Blue Mountains

Figure C.2: Sampling Location at Wollangambe River near Centennial Coal Waste, Blue Mountains

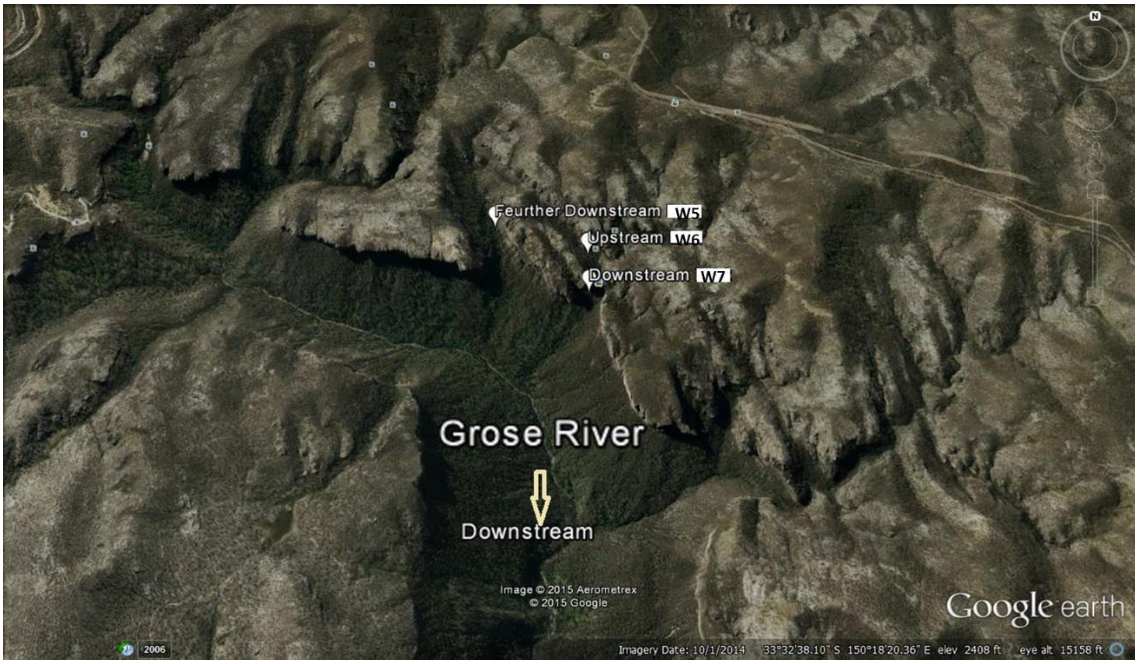

Figure C.3: Sampling Location at Dalpura Creek near Canyon Coal Mine, Blue Mountains

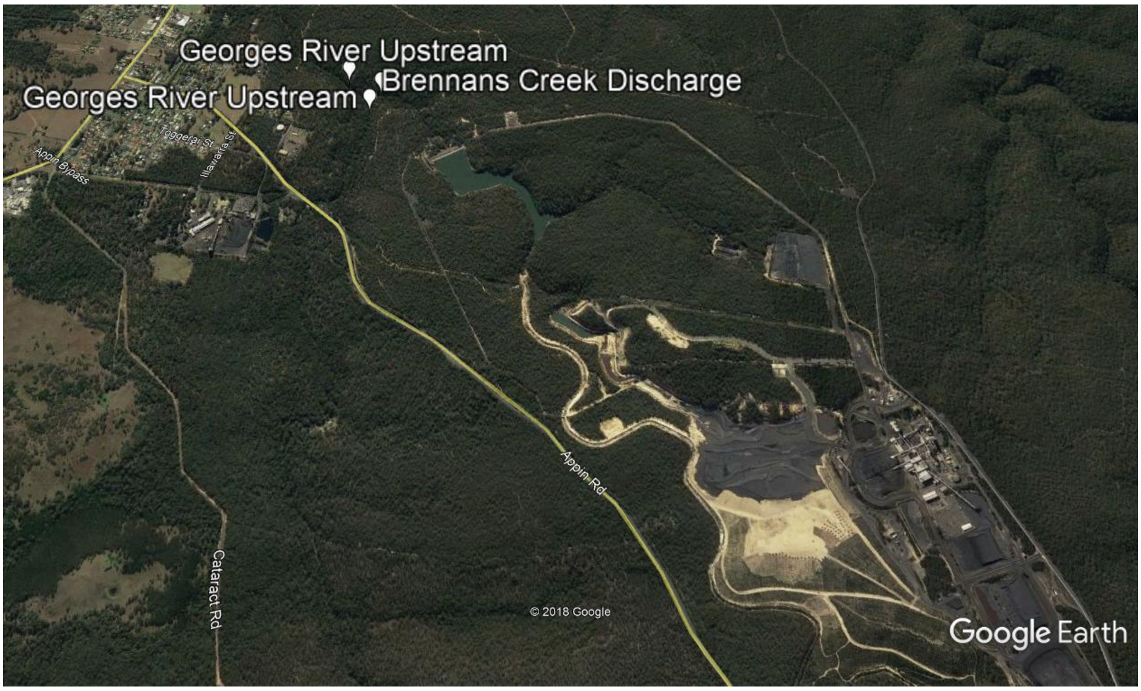

Figure C.4: Sampling Location at Georges River and Brennans Creek near West Cliff Colliery, Appin

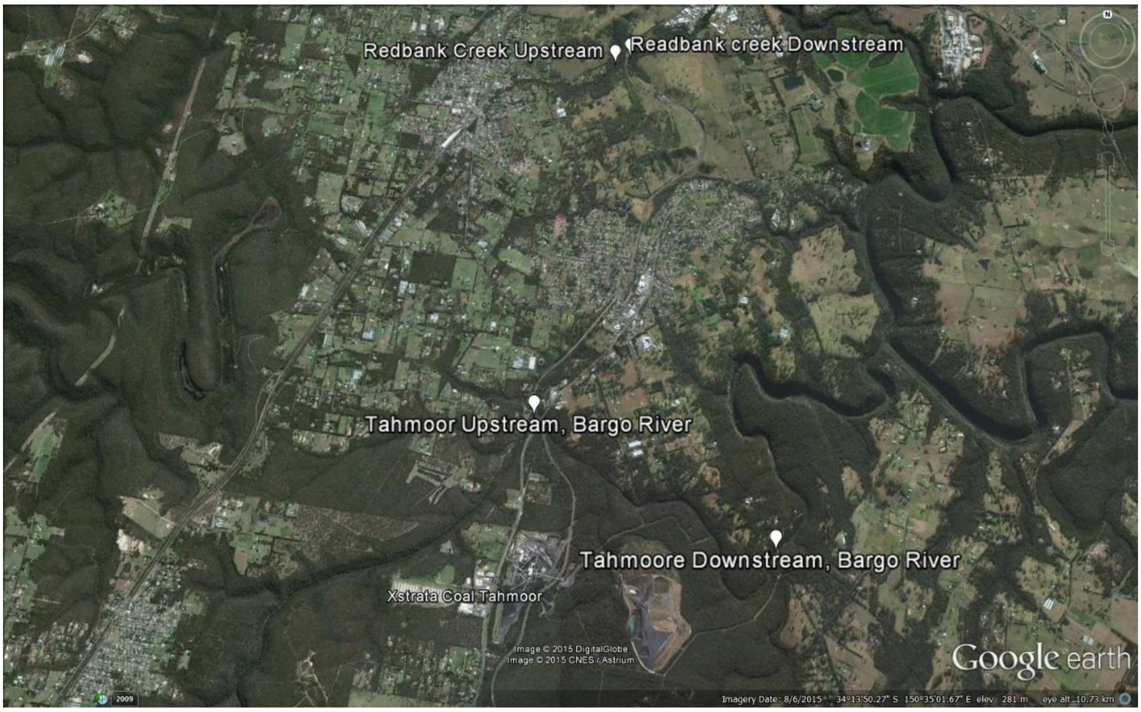

Figure C.5: Sampling Location at Bargo River near Tahmoor coal mine, Tahmoor and Redbank Creek, Picton.

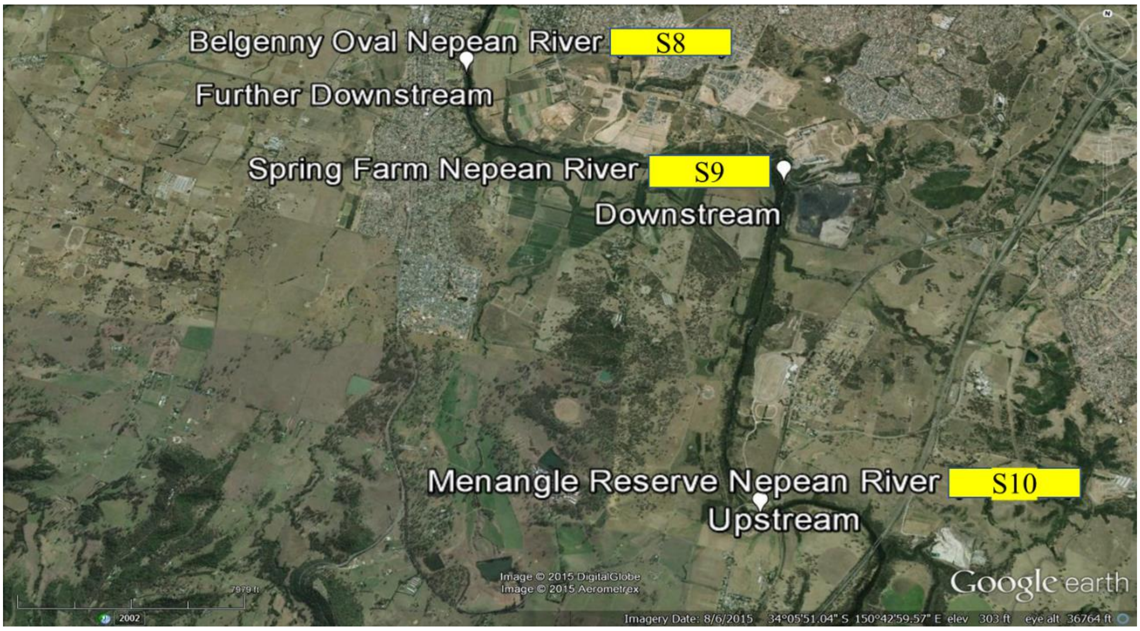

Figure C.6: Sampling Location at Nepean River near Tahmoor coal mine, Tahmoor and Redbank Creek, Picton.

Figure C.7: Continuous water discharge into Dalpura Creek from abundant Canyon Mine, Blue Mountains.

Figure C.8: A typical probe reading at Dalpura Creek, , Blue Mountains.

Figure C.9: Subsidence at Tahmoor coal mine, near Redbank Creek, Picton.

Figure C.10: CSG production site at Camden (Reference: Daily Telegraph).

Figure C.11: Preparation for macroinvertebrate sampling at Spring Farm.

Figure C.12: Macroinvertebrate sampling in Nepean River at Menangle.

Declaration of authorship contributions

Journal Articles

1. **Environmental impact of coal mining and coal seam gas production on surface water quality in the Sydney basin, Australia**

   Contributions to the paper were as follows:

   (87%) Aal-e Ali collected the water sample from Coxs River, Sawyer swamp, Springvale, Wollangambe River, and Dalpura Creek in Blue Mountains world heritage area in west of Sydney and Georges River, Brannons Creek Apin, Bargo River Tahmoor, Redbank Creek Picton, and Nepean River in South Sydney area. The analysis was carried out by a commercial laboratory, Envirolab. Few analyses were done in Macquarie University's laboratory. Aal-e Ali was the first author of the manuscript.

   (5.5%) Vladimir Strezov as the main supervisor with intuition into analytical work acted as a major reviewer of the manuscript.

   (5%) Peter Davies contributed as the co-supervisor during field sampling trip and sample collection. He also provided inputs to the manuscript in form of review.

   (2.5%) Ian Wright supported this work by providing guidance to reach the sampling locations and sample collection. He was also involved in the minor review of the article.

2. **River sediment quality assessment using sediment quality indices for the Sydney basin, Australia affected by coal and coal seam gas mining**

   Contributions to the paper were as follows:

   (85%) Aal-e Ali undertook the Sampling in Blue Mountains and South Sydney area, analytical work at Macquarie University laboratories and, managed outsourced analysis that was necessary. Aal-e Ali is the primary author of the manuscript.

   (10%) Vladimir Strezov acted in his capacity as the main supervisor with comprehension into analytical work and as a major reviewer of the manuscript.

(3%) Peter Davies provided support on the sampling and a limited review of the manuscript.

(2%) Ian Wright provided support on the guidance to the sampling location and a limited discussion on the manuscript.

3. **Aquatic life and environmental impairment by coal mine discharge in the Sydney region (Ready to be Submitted)**

Contributions to the paper were as follows:

(92%) Aal-e Ali collected the invertebrate's samples and analyzed for taxa in Macquarie University laboratories. Aal-e Ali was the first and corresponding author of this manuscript.

(5%) Vladimir Strezov as the main supervisor with insight into analytical work acted as a major reviewer of the manuscript.

(3%) Daniel Sloane contributed as the statistician during my data analysis. He also provided inputs to the manuscript in form of operating statistical software.

4. **Effect of coal and coal seam gas mining on elemental composition of aquatic invertebrates in the Sydney region (ready to be Submitted)**

Contributions to the paper were as follows:

(85%) Aal-e Ali undertook the sampling and analysis of invertebrate taxa work at Macquarie University laboratories and managed outsourced analysis that was necessary. Aal-e Ali is the primary and corresponding author of the manuscript.

(5%) Vladimir Strezov acted in his capacity as the main supervisor with insight into analytical work and acted as a major reviewer of the manuscript.

(5.5%) Grant Hose provided support on the methodology and taxa analysis of the invertebrates and acted as a reviewer of the manuscript.

(2.5%) Peter Davies provided support on the sampling and a limited review of the manuscript.

(2%) Armand J. Atanacio provided support on PIXE/PIGE analysis of the metal content in the invertebrates.

Peer-reviewed Conferences Articles

1. **Impact of Coal Mining on River Sediment Quality in the Sydney Basin, Australia**

   Contributions to the paper were as follows:

   (89.5%) Aal-e Ali collected the sample and undertook the analytical work in Macquarie University Laboratories and managed to outsourced analysis require. Aal-e Ali was the primary author and correspondent of the manuscript.

   (5%) Vladimir Strezov acted in his capacity as the main supervisor with insight into analytical work and acted as a major reviewer of the manuscript.

   (3%) Peter Davies provided support on the sampling and review of the manuscript.

   (1.5%) Ian Wright provided support on the guidance to the sampling location and discussion on the manuscript.

   (1.0%) Tao Kan provided support on the graphical presentation of the data analysis.

2. **Coal mine discharge impacts on aquatic invertebrates in the Sydney region**

   Contributions to the paper were as follows:

   (90%) Aal-e Ali undertook the sampling and analysis of invertebrate taxa work at Macquarie University laboratories. Aal-e Ali is the primary and corresponding author of the manuscript.

   (5%) Vladimir Strezov acted in his capacity as the main supervisor with insight into analytical work and acted as a major reviewer of the manuscript.

   (5%) Grant Hose provided support on the methodology and taxa analysis of the invertebrates and was a reviewer of the manuscript.