Changes of Water Quality in a Stream Impacted by Longwall Mining Subsidence

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Summary

Water quality along the Waratah Rivulet in the Woronora Catchment has been monitored during the last two years by the Sydney Catchment Authority. Water quality data shows changes in chemical composition due to cracking of riverbeds and rockbars, and diversion of surface water into subsurface routes in the Hawkesbury Sandstone aquifer. Water quality upstream of the longwall panels is comparable to nearly pristine water in creeks and rivers flowing in similar sandstone bedrock environments and to limited water quality data collected prior to mining. A segment of the Waratah Rivulet, where subsidence and cracking of riverbeds and rockbars has occurred, is causing surface water to be redirected into subsurface fracture systems, mix with groundwater already present in the aquifer and reappear downstream. This subsurface flow in the shallow fractured sandstone aquifer causes the chemical composition and water quality to change as an effect of water-rock interactions. Salinity, iron, manganese and many cation and anion concentrations increase, whereas oxygen is significantly depleted. Mobilisation of barium and strontium from the rock mass indicates fast chemical dissolution reactions between the subsurface flow and carbonate minerals. Other metals mobilised include zinc, cobalt and nickel. Subsurface water discharges from underground receptors downstream of the area impacted by longwall mining. The discharged water is rapidly oxidised by atmospheric oxygen, causing precipitation of iron and manganese oxides/hydroxides out of solution. Hydrogeochemical modelling indicates the dominant iron minerals precipitated out from the water are magnetite, hematite, goethite, lepidocrocite and ferrihydrite. The paper discusses changes in surface water and groundwater chemistry, the hydrogeochemical processes responsible for changes in water chemistry, as well as changes in water quality along the rivulet.

Key words: Longwall mining, surface water quality, groundwater quality, hydrogeochemistry

1. Introduction

Longwall mining may have a significant impact on surface and groundwater quality as a consequence of mining-induced subsidence and additional fracturing and development of cracks in riverbeds and rockbars. Surface water flowing through a river channel in a pristine environment is exposed to atmospheric oxygen and chemical reactions are relatively slow as rock materials and minerals are in a metastable equilibrium with water. Changes in chemical composition occur since fresh rock in fractures, that previously have had no contact with water, is exposed to surface water and groundwater. Rates of chemical reactions rapidly increase, mobilising large amounts of cations, anions and metals from the rock mass into the aquatic system. The concentration of these elements depends on the availability of soluble minerals and the initial chemical composition of surface run-off. Deterioration of water quality occurs through the elevated content of metals, mostly iron and manganese, increased salinity, and oxygen depletion, causing aesthetic changes in the river channel through precipitation of reddish/brownish iron-oxides/hydroxides and formation of

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algal blooms (Krogh, 2007). The occurrence of metal precipitates and iron-oxidising bacteria is particularly evident in creeks and rivers where groundwater interacts with surface water and discharges through riverbed and rockbar cracks (TEC, 2007). Iron- and manganese-oxidising bacteria commonly occur together with metal precipitates as thick floating mats in areas where groundwater discharges from fractured rock containing ironstones, iron/manganese carbonates, and oxides and hydroxides rich in iron and manganese compounds. As a result of these redox reactions, the level of dissolved oxygen declines as the component of groundwater in surface water increases, causing an impact to surface water aquatic ecology.

1.1. Surface Water

Diversion of surface water into subsurface flow as a result of riverbeds and rockbars cracking and fracturing intensifies the chemical reactions with geological material present in voids and fractures. Most of this geological material is exposed and connected for the first time to flowing, highly oxidised, fresh, recharged groundwater. As a result of this, rapid dissolution of carbonate minerals, weathering of aluminosilicate minerals, oxidation of metal compounds, and erosion of more resistant grains of sedimentary rocks such as quartz and feldspars, take place. Mobilised chemical elements and eroded sediments from the rock-mass are transported along fractures and bedding planes and may discharge back into surface waterways around or downstream of the longwall mining-induced impacted zone.

Several water quality indicators are above pre-mining levels, such as salinity, concentrations of major, minor and trace elements, metals, pH and gases, whereas dissolved oxygen is below pre-mining levels (TEC, 2007). During low flow baseflow-dominated conditions upstream of the mining area, the chemical composition of surface water is relatively stable with respect to electrical conductivity (EC), major and minor elements, and metals. Concentrations of various water quality indicators increase along the area impacted by subsidence, as the interaction between surface water and groundwater is enhanced by the diversion of water into the subsurface which after mixing with groundwater later reappears into the river channel downstream.

Downstream of the impacted area, the EC and concentration of non-reactive chemical elements is still elevated, however reactive metals such as iron and manganese react immediately with atmospheric oxygen dissolved in surface water causing precipitation and subsequent rapid decrease in concentration.

The occurrence of iron precipitates and iron-oxidising bacteria is particularly evident in creeks and rivers where surface cracking of riverbeds and rockbars causes groundwater to discharge to surface water. Iron and manganese bacteria commonly occur in the Hawkesbury Sandstone, and water seeping from rock fractures, joints, veins and bedding planes containing ironstones, iron/manganese carbonates, oxides and hydroxides rich in iron and manganese compounds, result in a reduction of dissolved oxygen. The mobilisation and flux of iron and manganese to surface waterways during subsurface flow is through the dissolution of siderite and rhodochrosite, and the oxidation of metal oxides and hydroxides (Jankowski and Spies, 2007). These metals reappear in higher concentration downstream of the mining impacted groundwater discharge zone, and are rapidly oxidised in contact with atmospheric oxygen. Changes in iron and manganese content in surface water are affected by a number of complex physico-chemical processes such as mixing of surface water and groundwater, changes in pH, redox reactions, microbial action, precipitation of oxides and hydroxides, and transformation reactions. During low flows, concentrations of iron and manganese are higher than during high flows, as baseflow discharge mostly contributes to river/creek flow.

Discharge of groundwater rich in iron and manganese to rivers and creeks causes the growth of large quantities of oxidising bacteria and the development of thick mats of iron/manganese-oxides/hydroxides during laminar flow conditions at low water stages. The bacteria grow thick mats of iron/manganese-oxides/hydroxides, which reduces the interstitial habitat, clogs the stream, reduces available food, and causes the development of toxicity through the decrease in oxygen content. Loss of native plants and animals occurs directly via iron toxicity, or indirectly via smothering when there are very high iron/manganese concentrations. However, high stages alter conditions from laminar to turbulent flow, and due to the presence of more acidic surface run-off, rapid chemical reactions dissolve and mobilise these precipitates, returning iron and manganese to the aquatic system.

The pH of surface waters during low flows is higher than during high flows. The pH during low flows is affected by baseflow discharge and is characterised by a slightly alkaline pH. Hydrogeochemical reactions involving weathering of aluminosilicate minerals, dissolution of carbonates (calcite and siderite), and redox processes elevate the pH of baseflow discharge. This relatively high pH is partially related to hydrogeochemical processes during subsurface flow and partially related to chemical reactions involving the interaction between surface water and iron/manganese-oxides/hydroxides mats. During high flows, the pH decreases and becomes more acidic from the contribution of rainwater and surface run-off. The pH rapidly decreases when the volume of flow increases. As rainwater in the Sydney region is acidic, with pH values between 3 and 6, it is expected that surface run-off will have similar pH values during rainfall events.

1.2. Groundwater

Hydrogeochemical and water quality studies of groundwater in coalfields around the world indicate that the high-extraction of coal through underground longwall mining affects the groundwater chemistry and quality of overlying aquifers (Booth, 2002; Booth and Bertsch, 1999; Booth et al., 1998). Subsidence causes contamination of groundwater by the development of acid mine drainage; increases sedimentation of fine material, rates of erosion, transport and sedimentation in the river channel, with associated turbidity impacts; deteriorates water quality due to the reduction in dissolved oxygen, as more groundwater is diverted to surface flow; and increases salinity, Fe, Mn, Al, Zn, and other metals released from the geological strata. The acidity of water not only increases due to recharge of more acidic rain water/surface run-off, but also by the oxidation of pyritic sediments, and mobilisation of Fe, Mn, Al, and other metals from the host rock (Jankowski et al 1998; Smith et al. 2002).

Where subsurface cracks and new fracture networks allow surface water to mix with flowing groundwater, the resulting mixture may enhance chemical processes during water-rock interactions. This mixed water has a much higher capacity for mobilising ions and metals from the geological material than the more equilibrated and mature groundwater, which is already present in the subsurface.

The extraction of coal and the subsequent cracking of geological strata surrounding the goaf may also liberate methane, ethane, carbon dioxide, hydrogen sulphide and other gases. Gases from the mine tend to diffuse upwards through cracks and fracture networks occurring in the strata, as well as through porous geological material. Some gases are trapped over long periods of time

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below the ground surface as an effect of biological and chemical reactions in the subsurface environment, with fracturing of near surface geological strata possibly resulting in the release of gases into the aquatic system. Released gases may escape and discharge into the atmosphere, or may dissolve in groundwater or surface water, enhancing chemical reactions with geological material.

These gas emissions are responsible for the deterioration of groundwater and surface water quality, and may sometimes cause pressure to increase, affecting groundwater discharge. In this situation, and during favourable topographical and structural geology conditions, discharge is under artesian pressure and groundwater can freely flow from fractures and joints. Gas emissions can result in localised plant death and dieback of riparian vegetation, as anaerobic conditions are created within the soil and surface waters with respect to increased toxicity of some gases. The groundwater pH increases when methane is emitted and decreases when carbon dioxide is emitted from the cracking of the geological strata surrounding the goaf.

Water that re-emerges downstream from subsurface flow is deoxygenated and may be heavily contaminated with the presence of toxic metals and increased salinity. The presence of toxic gases, together with oxygen depletion, may encourage the higher metal concentrations to persist in the reduced subsurface flow environment.

2. Environmental Setting

The Waratah Rivulet catchment is located approximately 45 km southwest of Sydney (Fig. 1). The elevation varies from around 360 m in the headwaters to 170 m where the rivulet enters Woronora Lake. The catchment is located in the southern part of the Sydney Basin. The geology of this area comprises a gently deformed sequence of Triassic sandstone that forms the upper sequence of the Sydney Basin sediments. The surface geological unit exposed through much of the Waratah Rivulet catchment area is the Hawkesbury Sandstone. This sandstone unit overlies other sandstones (Newport Formation, Bulgo and Scarborough Sandstones), claystones (Bald Hill and Stanwell Park Claystones) and shales (Wombarra Shale) of the Triassic Narrabeen Group. The total thickness of the Hawkesbury Sandstone exceeds 100 m, with the Narrabeen Group totalling more than 430 m in thickness. The mining occurs in the upper coal seam unit of the Permian Illawarra Coal Measures known as the Bulli Seam, which has a thickness of 3.2 – 3.6 m across the catchment area, and which underlies the Narrabeen Group.

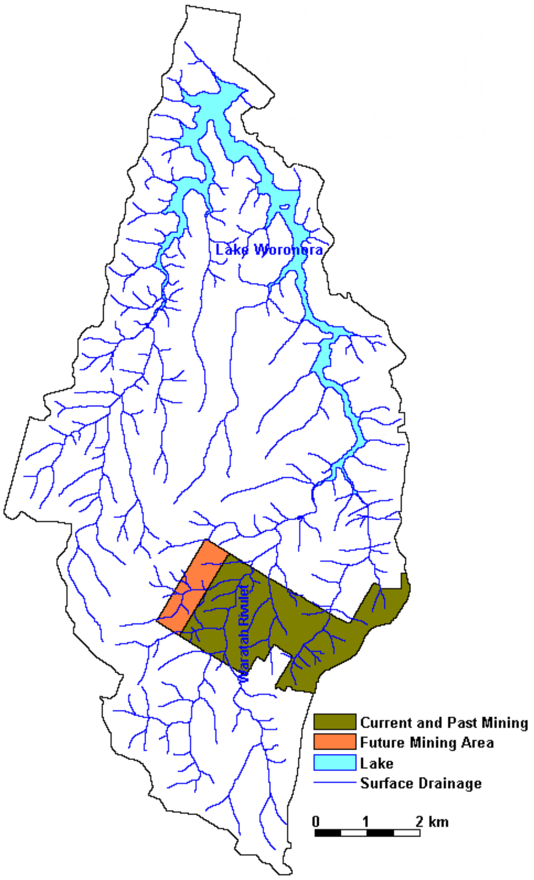

Figure. 1. Location of the Waratah Rivulet catchment.

The main surface waterway in the catchment is the Waratah Rivulet, which flows north and discharges into the Woronora Lake, one of Sydney's water supply system storages (Fig. 2). The longwall panels are located directly underneath the catchment and orientated in a southwest – northeast direction, 450 – 500 m below the ground surface (Fig. 2). Fourteen of the currently approved seventeen-longwall panels have been mined at the date of this paper, with a further three planned.

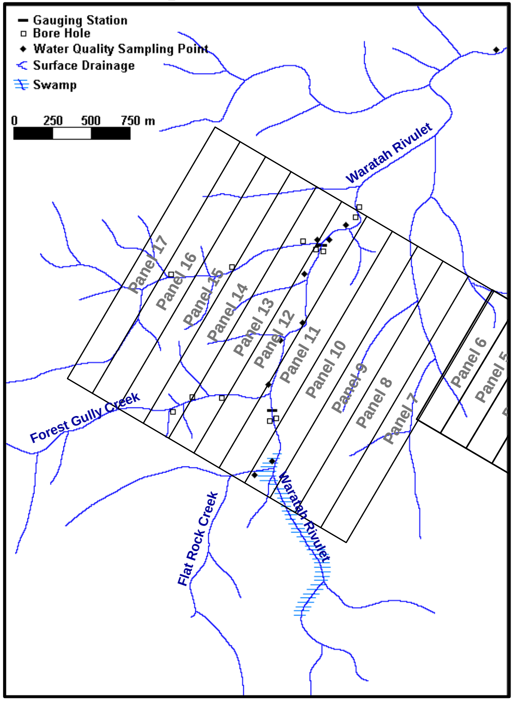

Figure. 2. Sampling points and location of longwall panels.

Waratah Rivulet has been severely affected by longwall mining-induced subsidence as evidenced by extensive fracturing of riverbeds, cracking of rockbars, ponding, loss of surface water into subsurface routes, leakage of rockbars, and declines in water quality. Monitoring of flow and surface water quality started in 2001, with a more comprehensive and detailed surface water and groundwater quality monitoring program established in 2005.

3. Methodology

Surface water sampling locations for water chemistry determination were set-up along the rivulet and are representative of areas upstream of the present mining, in the impacted part of the rivulet, and downstream of mining (Fig. 2). A reference point located in a tributary creek represents a pristine water quality environment. Groundwater quality samples were collected from recently drilled boreholes along the rivulet and along two main tributary creeks. These locations cover pristine and impacted areas (Fig. 2). General parameters and unstable elements were measured in the field, with major, minor, and trace elements and metals analysed in a laboratory from acidified and filtered water samples where required.

4. Results

To assess water quality, from 2005 the Sydney Catchment Authority began collecting surface water samples from the Waratah Rivulet, and in 2007 began collecting groundwater samples from boreholes drilled by Helensburgh Coal Pty Ltd. Water quality upstream of the longwall panels is quite similar to water flowing in creeks and rivers from pristine sandstone bedrock environments and to limited water quality data collected prior to mining (Table 1). Any elevated concentrations of major and trace elements could be related to previous mining in the headwaters of the Waratah Rivulet, where the Darkes Forest Colliery, during most of the twentieth century fully mined this area using partial and total extraction methods. Chemical data shows that concentrations of major and minor elements are much higher in groundwater than in surface water (Figs. 3 - 8). Also, higher concentrations are present in both water bodies when fracture networks are well developed in the mining-induced subsidence area. The EC of groundwater in the impacted area varies between 400-700 μS/cm. The pH varies from acidic, where metal-sulfur minerals are abundant, to slightly alkaline, where carbonate minerals are more abundant in the rock mass. Ca, Na, HCO_3 and Cl are the dominant ions in the groundwater system. The higher concentrations are related to well developed and interconnected fracture networks and exposure of more rock strata to water-rock interaction, which causes dissolution of

Table 1. Comparison of surface water quality from headwaters of the Waratah Rivulet with water quality from other sandstone terrains.

Sample	EC	pH	Ca	Mg	Na	HCO_3	SO_4	Cl	Fe	Mn	Al	Zn	Ba	Sr
	µS/cm		mg/L						µg/L					
Nattai River[1]	305	7.20	11	9	34	50	29	45	78	24	20	5	26	60
Upper Nepean River[2]	96	6.98	3	2	10	26	4	16	41	30	130	8	12	34
Doudles Folly Creek[2]	96	5.50	3	3	10	21	4	16	33	25	100	11	11	34
Waratah Rivulet (downstream 2001)[3]	186	6.10	8	5	21	48	10	32	370	30	20	32	NA	51
Waratah Rivulet (upstream)[4]	202	6.81	4	4	21	7	11	46	670	43	20	5	26	30

[1] Parsons Brinckerhoff Pty Ltd, 2006a.
[2] Parsons Brinckerhoff Pty Ltd, 2006b.
[3] Keyzer, 2001.
[4] Sydney Catchment Authority, 2006 (unpublished water quality data from the Waratah Rivulet).
NA – Not Analysed

carbonates, reductive dissolution of oxides and hydroxides, and oxidation of metal-sulfur minerals. These processes mobilise Ca, HCO_3, Fe, Mn, Ba, Sr and S (SO_4) from the rock mass.

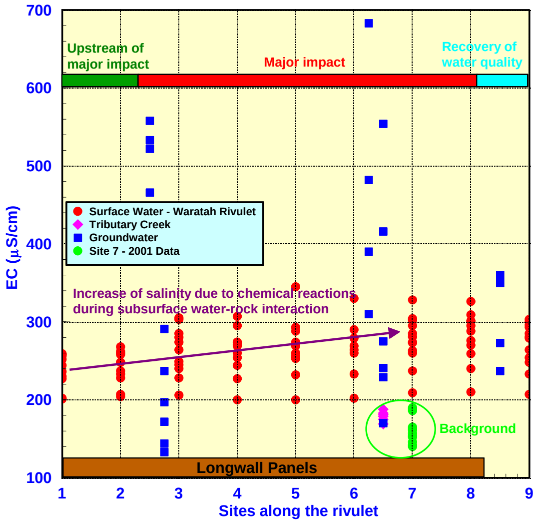

Figure 3. Variation of EC along the rivulet.

Comparison of chemical composition of surface water along the rivulet shows significant changes in water chemistry and quality (Figs. 3 - 8). Surface water flowing through the impacted area and downstream of the longwall panels have a much higher EC, pH, and content of major, minor, and trace elements, and significantly lower Eh and dissolved oxygen content compared to surface water flowing in the pristine environment (upstream of longwall panels, tributary creek, pre-mining data) (Figs. 3 - 8). The surface water chemistry in the rivulet shows significant changes in content and concentration over the 2 km length of the sampled channel. The salinity of surface water upstream of the subsidence area has low EC values ranging between 200 and 280 µS/cm. The salinity increases along the rivulet as more water re-emerges from the subsurface, with EC values between 260 and 340 µS/cm (Fig. 3). The pH upstream is slightly acidic, with a range of 6.5-7.1, increasing to pH 7.7 where subsurface water dominates surface flow. The chemical composition of surface water changes from Na-Ca-Cl-HCO_3 type upstream to Ca-Na-HCO_3-Cl type downstream of the mining area, resulting from high rates of chemical reactions during water-rock interaction, dominated by the dissolution of calcite and flux of Ca into surface water along the rivulet (Fig. 4). Elevated concentrations of Fe and Mn in surface water flowing through areas not impacted by mining are caused by baseflow discharge. The dominant minor elements in surface water that are mobilised during subsurface flow in the mining impacted area are Fe, Mn, Sr and Ba.

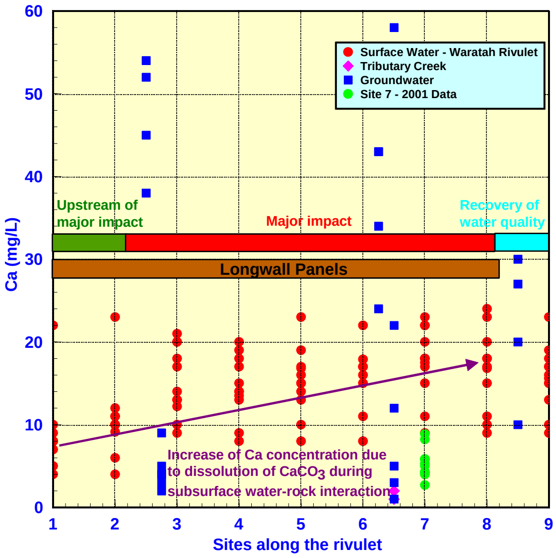

Figure 4. Variation of Ca along the rivulet.

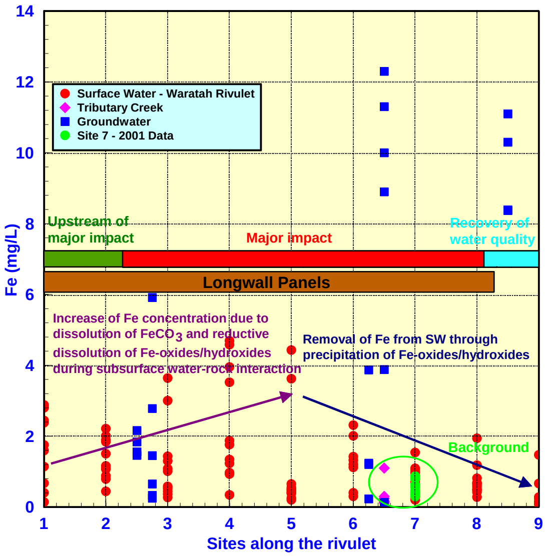

Figure 5. Variation of Fe along the rivulet.

The increase in salinity, ions, and metal concentrations are related to subsidence-induced fracturing below and around the riverbed channel, which increases the exposure of fresh rock to inflowing surface water.

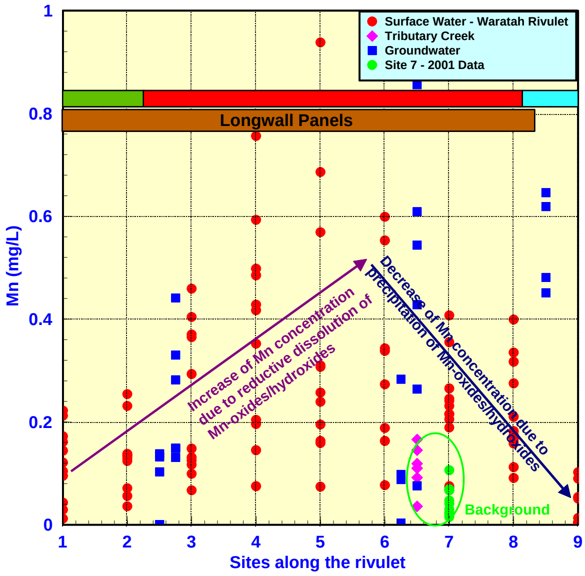

Figure 6. Variation of Mn along the rivulet.

Where subsurface cracks and new fracture and bedding plane networks allow surface water to mix with flowing groundwater, enhanced chemical reactions are likely to occur between water and rock. Deterioration of water quality occurs through elevated content of metals, increased salinity, and aesthetic changes of the river channel through precipitation of reddish/brownish iron oxides and hydroxides. The occurrence of metal precipitates and iron-oxidising bacteria is particularly evident where groundwater discharges to surface water through surface cracking. Chemical reactions increase the concentration of Ca, Na, Mg, HCO_3, Cl and SO_4 in water discharging from subsurface routes to the surface. The pH and HCO_3 increase due to dissolution reactions involving carbonate minerals such as calcite, siderite, rhodochrosite, strontianite and barite, which are the most abundant carbonates in the sandstone aquifer matrix. The presence of metal carbonates in the rock mass cause Fe, Mn, Sr and Ba to mobilise, significantly increasing concentrations of these elements downstream, where subsurface flow re-emerges at the ground surface. The highest rates of chemical reactions occur during and after rainfall events, when acidic rainwater with a pH of 3 – 6 and surface run-off infiltrate the subsurface system and mobilise metals from carbonate minerals.

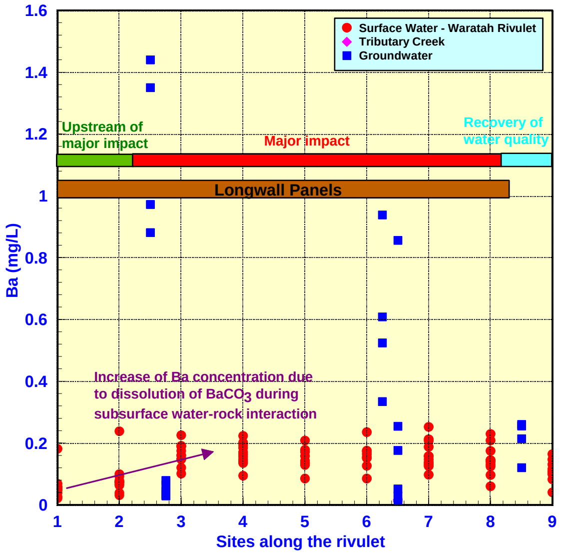

Figure 7. Variation of Ba along the rivulet.

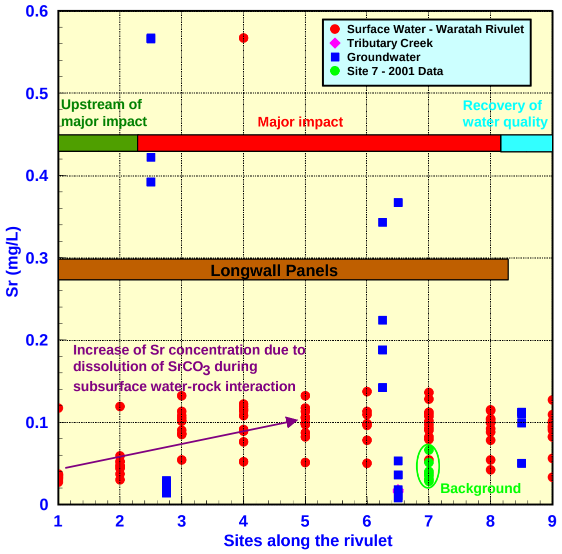

Figure 8. Variation of Sr along the rivulet.

Concentrations of Fe and Mn initially rise in surface flow as groundwater discharges from the subsurface. However a few hundred metres downstream, dissolved metal concentrations decrease as Fe and Mn oxides and hydroxides are precipitated, causing yellowish through to orange/red to brownish stains in the creek channel (Figs. 5 and 6). Discharge of groundwater rich in iron and manganese to the creek causes the development of thick mats of iron/manganese-oxides/hydroxides together with large quantities of iron oxidising bacteria during laminar flow conditions at low stages. The bacteria grow thick mats of iron/manganese-oxides/hydroxides, which reduces the interstitial habitat, clogs the stream, reduces available food, and causes the development of toxicity through decreased oxygen content. Loss of native plants and animals occurs directly through iron toxicity or indirectly via smothering.

Barium and strontium remain in solution and act as natural tracers that can be used to locate discharge points where groundwater re-emerges to the creek channel (Figs. 7 and 8). Both elements are present only in the rock matrix, unless they are mobilised during subsurface flow. Oxidation of traces of pyrite (FeS_2) during subsurface flow increases the concentration of iron and sulfate. Calcium, magnesium and bicarbonate are supplied from the dissolution of traces of the carbonate minerals calcite and dolomite, and water is generally undersaturated with respect to these minerals. Hydrogeochemical modelling has shown that carbonate minerals magnesite (Mg), strontianite (Sr) and siderite (Fe) are strongly undersaturated. These minerals are dissolved from the rock mass and the addition of Mg, Sr, Fe and HCO_3 into the aquatic system occurs, significantly increasing the concentration of these elements in groundwater and surface water. Only $CaCO_3$ was found to be slightly supersaturated in a few surface water samples, which originates from high-pH water transported through subsurface routes. Carbonate minerals of trace metals such as smithsonite (Zn), rhodochrosite (Mn) and witherite (Ba) are also undersaturated, keeping these metals in solution as long as oxidation does not remove them from the aquatic system. All iron oxide/hydroxide-minerals are strongly supersaturated, including magnetite,

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hematite, maghemite, goethite, lepidocrocite, ferrihydrite and magnesioferrite, which quickly remove iron from the aquatic system.

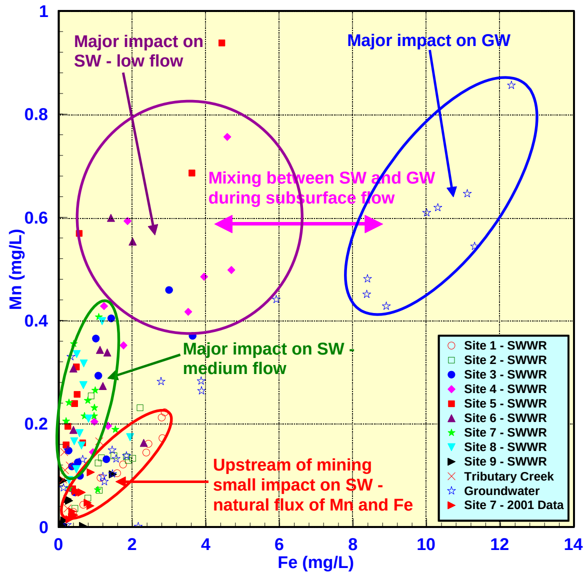

Figure 9. Relationship between Mn and Fe showing surface water–groundwater interaction.

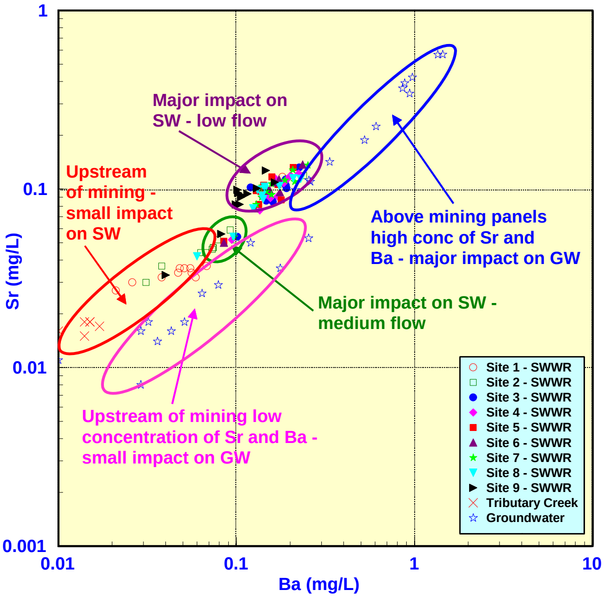

Figure 10. Relationship between Sr, and Ba showing surface water–groundwater interaction.

During rainfall events, acidic rain water and surface run-off with pH values ranging from 3 to 6 re-mobilises Fe and Mn oxides and hydroxides, eroding them from rocks and creek channels and returning these metals again into the aquatic system, causing further pollution downstream. During high water stages when turbulent flow prevails, iron mats are washed from pools and meanders where they have been immobile during low flow conditions, resulting in further contamination as they are dissolved in acidic conditions.

The highest correlation coefficient occurs for TDS and HCO_3, which indicates the main influence on TDS (and EC) is from the dissolution of carbonates; and the second highest correlation is between Ca and Sr, indicating high availability and mobilisation rates of these elements. High correlation between Ba and Sr indicates similar mobilisation rates of these ions from the rock mass.

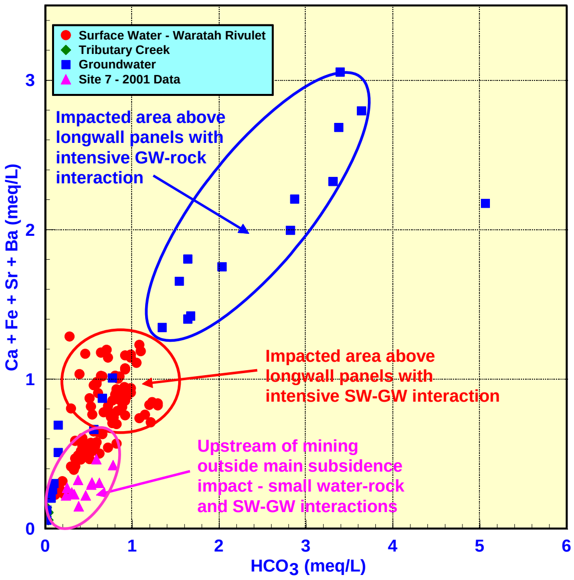

Figure 11. Carbonate system relationship between Ca + Fe + Sr + Ba versus HCO_3.

Interaction between surface water and groundwater can be interpreted on the basis of baseflow discharge data and hydrograph separation studies. The chemical composition of groundwater and surface water is used as a tool to show this interaction, as well as demonstrating the impact of groundwater chemistry on surface water quality. Mixing between re-emerging groundwater with flowing surface water changes the concentration of Fe and

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Mn in surface water (Fig. 9). As groundwater contains higher concentrations of Fe and Mn due to mobilisation from the rock mass during water-rock interactions, mixing of this groundwater with surface water causes higher concentrations than is present upstream of the mining area. These same processes are related to elevated concentrations of Sr and Ba (Fig. 10) in surface water after mixing with groundwater. As both Sr and Ba are present in very low concentrations in the natural surface water system, input from groundwater can provide insight about discharge locations and both are used as tracers to assess impacts of mining on water quality.

An almost straight relationship between Ca + Fe + Sr + Ba versus HCO_3 shows the dissolution of carbonates is the main source of the above chemical elements in the groundwater system (Fig. 11). The availability of carbonates in the rock mass and the pH of groundwater are responsible for the mobilisation of metals from the solid phase to the aquatic system.

5. Conclusions

Mining-induced subsidence alters the hydrological system of surface water and groundwater and intensifies surface water and groundwater connectivity. Increased water-rock interaction on the newly exposed rock in fractures, joints, veins, fracture zones and bedding planes mobilises chemical elements from the rock mass. This in turn increases the salinity of surface water, brings more metals into the surface waterways, and results in the deterioration of water quality. An understanding of the rates of chemical reactions and mobilisation of metals through dissolution, weathering, and redox processes should be established to assess water quality in mining impacted catchments. A full understanding of the impact on surface waterways and groundwater systems is needed before any remediation options to reduce loss of water into subsurface routes and minimise impact on water quality are considered.

6. Acknowledgements

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