

SURFACE WATER–GROUNDWATER INTERACTION IN THE FRACTURED SANDSTONE AQUIFER IMPACTED BY MINING-INDUCED SUBSIDENCE: 2. HYDROGEOCHEMISTRY

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Abstract. Water quality along the Waratah Rivulet in the Woronora Lake Catchment, New South Wales (NSW), Australia, has been monitored during the last three years by the Sydney Catchment Authority. Water quality data shows changes in chemical composition due to cracking of streambeds 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 streambeds and rockbars has occurred, is causing surface water to be redirected into subsurface fracture systems, mix with groundwater already present in the aquifer and partially 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 partially 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 in this environment goethite, lepidocrocite and ferrihydrite. The paper discusses changes in surface water and groundwater chemistry due to subsurface flow and water–rock interaction, the hydrogeochemical processes responsible for changes in water chemistry, as well as changes in water quality along the rivulet.

Key words: longwall mining, surface and groundwater chemistry, surface water–groundwater interaction, fractured aquifer, Australia.

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 streambeds 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 flowing water. Rapid changes in chemical composition occur since fresh rock in well developed network of fractures, joints and bedding planes

that previously have had no contact with water, is exposed to infiltrating surface water, groundwater and mixture of both. 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 present in the rock mass and the initial chemical composition of infiltrating surface water into subsurface routes. This causes deterioration of water quality through the elevated content of metals, mostly iron and manganese as well as

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aluminium, zinc, cobalt and nickel, increased salinity, and oxygen depletion, causing aesthetic changes in the river channel through precipitation of orange-reddish-brownish iron-oxides / hydroxides and formation of red and green algal blooms (Bullock, Bell, 1997; Jankowski, 2007; Jankowski, Spies, 2007; Krogh, 2007; Jankowski *et al.*, 2008). The occurrence of metal precipitates and iron-oxidising bacteria is particularly evident in creeks and rivers where groundwater interacts with surface water and baseflow discharges through streambed 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.

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 *et al.*, 1998; Booth, Bertsch, 1999; Booth, 2002). Where subsurface cracks and new fracture networks allow surface water to infiltrate a shallow aquifer, exposed fresh rock reacts rapidly with flow-

ing groundwater and chemical reactions are significantly enhanced during water-rock interactions. Deterioration of water quality occurs through elevated metal concentrations, increased salinity, and aesthetic changes to the stream through precipitation of red / orange / brown iron-oxides / hydroxides (Krogh, 2007). Chemical reactions increase the concentration of Ca, Na, Mg, HCO₃, Cl and SO₄ in water discharging from subsurface routes to streams. The presence of metal carbonates allow iron, manganese, zinc, strontium and barium to mobilise, significantly increasing the concentration 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 and surface run-off infiltrate the subsurface system and mobilise elements from carbonate minerals. Discharge of groundwater rich in iron and manganese to the stream 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 a decrease in oxygen content. Loss of native plants and animals may occur directly via iron toxicity, or indirectly via smothering when there are very high iron / manganese concentrations.

ENVIRONMENTAL SETTING

The Waratah Rivulet catchment in the Southern Coalfield, NSW, is located approximately 45 km southwest of Sydney (Fig. 1). The elevation varies from around 360 m a.s.l. in the headwaters to 170 m a.s.l. where the rivulet enters Woronora Lake, one of several Sydney's drinking water supply system storages. 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 Per-

mian 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.

The main surface waterway in the catchment is the Waratah Rivulet, which flows north and discharges into the Woronora Lake. The longwall panels are located directly underneath the catchment and orientated in a southwest–northeast direction, 450–500 m below the ground surface (Fig. 1). Seventeen of the currently approved nineteen-longwall panels have been mined at the date of this paper.

The Waratah Rivulet has been severely affected by longwall mining-induced subsidence as evidenced by extensive fracturing of streambeds, 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.

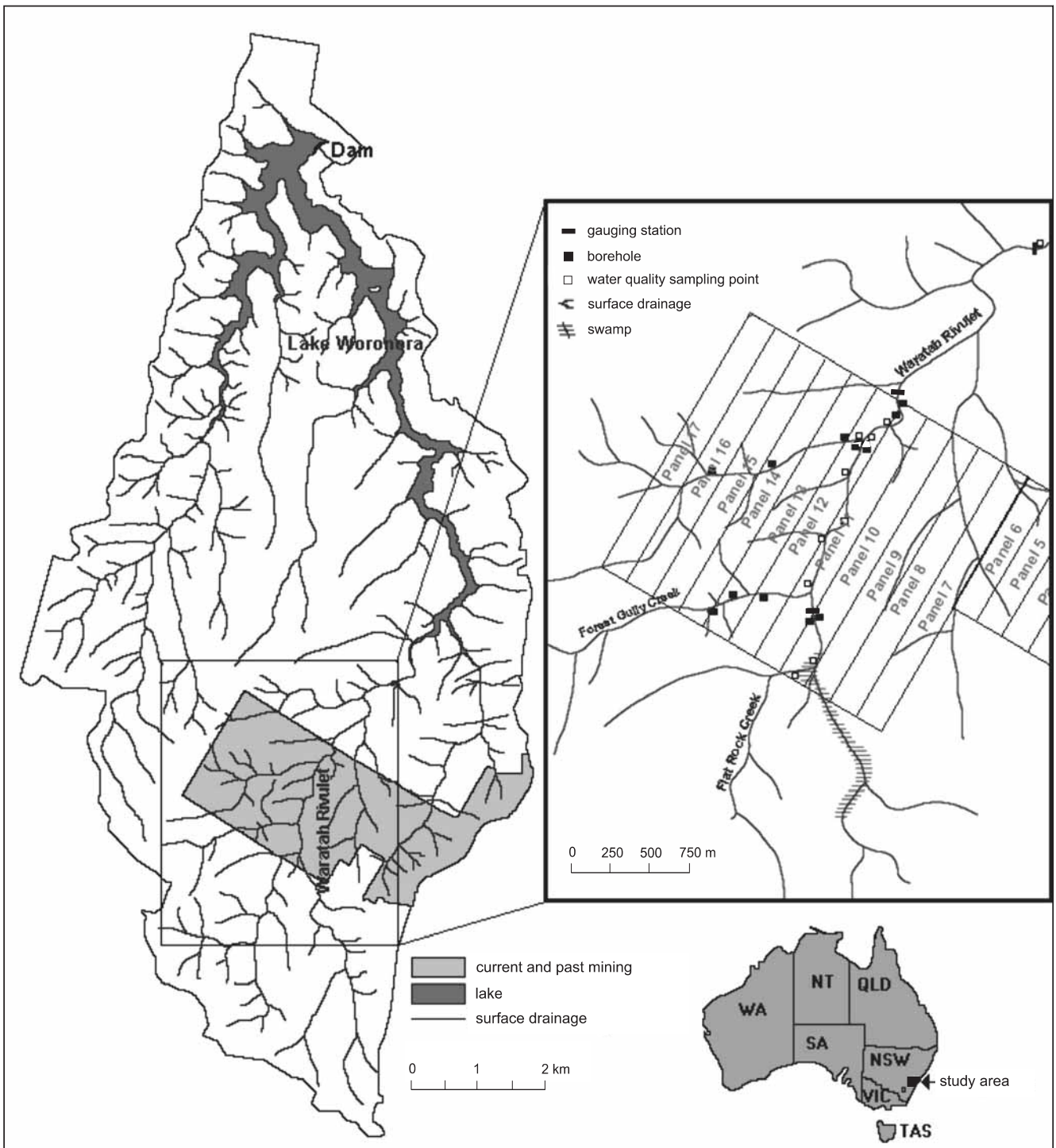


Fig. 1. Location of the Waratah Rivulet catchment (left) and location of sampling points and longwall panels (right)

RESULTS

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. A reference point located in a tributary creek represents a pristine water quality environment. Groundwater quality samples were collected from recently drilled shallow boreholes along the rivulet and along two main tributary creeks. These locations cover pristine and impacted areas (Fig. 1).

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 (Figs. 2, 3). Any elevated concentrations of major and trace elements could be related to previous board and pillar 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. 2, 3). 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 $\mu\text{S}/\text{cm}$. The pH varies from acidic, where metal-sulphur 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 carbonates, reductive dissolution of oxides and hydroxides, and oxidation of metal-sulphur minerals. These processes mobilise Ca, HCO_3 , Fe, Mn, Ba, Sr, S (SO_4) and other trace metals from the rock mass.

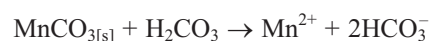
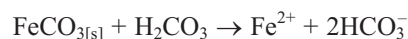
Comparison of chemical composition of surface water along the rivulet shows significant changes in water chemistry and quality. Surface water flowing through the impacted area and downstream of the longwall panels have a much higher EC, pH, and content of major, minor, and trace elements, and significantly lower Eh and dissolved oxygen content compared to surface water flowing in the pristine environment (upstream of longwall panels, tributary creek, pre-mining data). 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 $\mu\text{S}/\text{cm}$. The salinity increases along the rivulet as more water re-emerges from the subsurface, with EC values between 260 and 340 $\mu\text{S}/\text{cm}$. 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. 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. The increase in salinity, ions, and metal concentrations are related to subsidence-induced fracturing below and around the streambed channel, which increases the exposure of fresh rock to inflowing surface water.

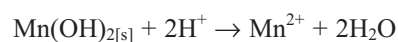
Where subsurface cracks and new fracture and bedding plane networks allow surface water to mix with flowing groundwater, enhanced chemical reactions are likely to occur between water and rock. Deterioration of water quality occurs through elevated content of metals, increased salinity, and aesthetic 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.

Concentrations of Fe and Mn initially rise in surface flow as groundwater discharges from the subsurface. Infiltrating fresh, acidic of low concentration rain water rapidly changes its chemical composition in contact with rock matrix. The plausible and most common chemical reactions in this type environment involving iron and manganese are:

Congruent dissolution of carbonates:



Congruent dissolution of hydroxides in an acidic environment:



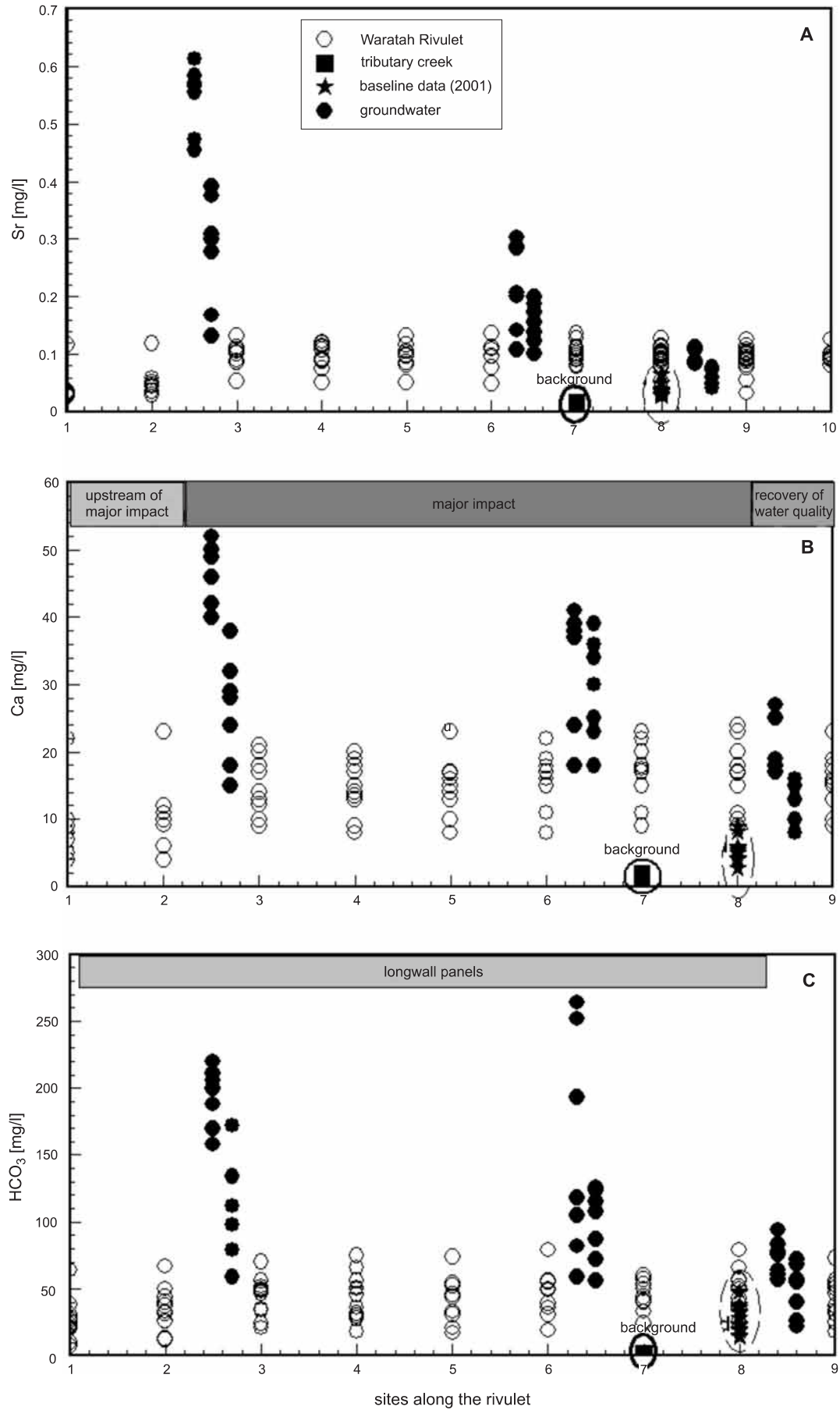


Fig. 2. Variation of strontium (A), calcium (B) and bicarbonate (C) concentrations along the Waratah Rivulet

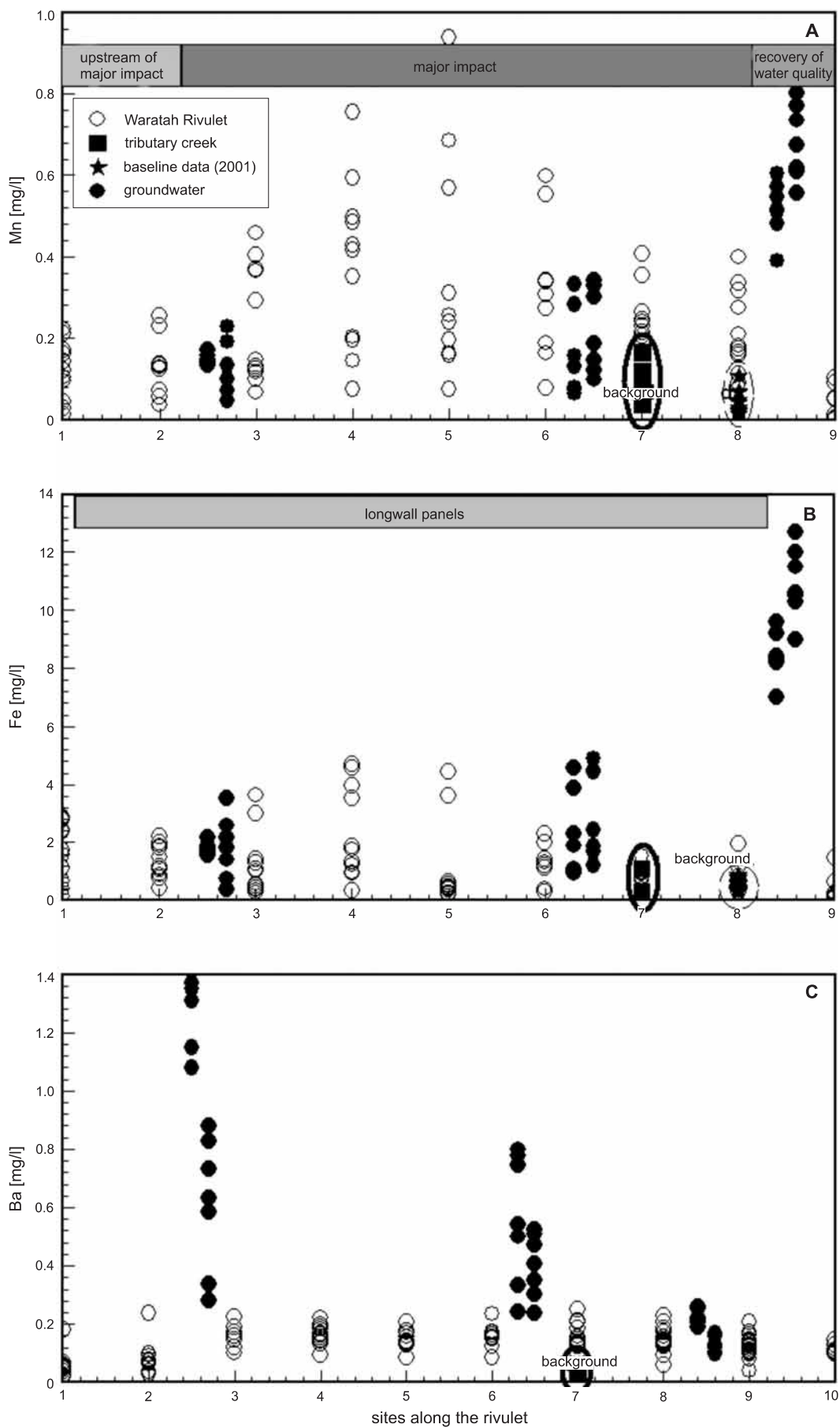
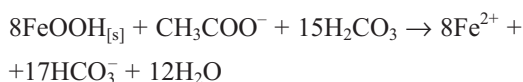
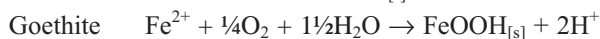
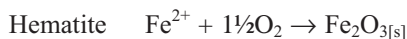


Fig. 3. Variation of manganese (A), iron (B) and barium (C) concentrations along the Waratah Rivulet

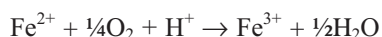
Reductive dissolution of goethite:



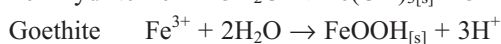
However a few hundred metres downstream dissolved metal concentrations decrease as Fe and Mn oxides and hydroxides are precipitated, causing yellowish through to orange/red to brownish stains in the creek channel. The possible chemical reactions removing iron and manganese from surface water can be precipitation of Fe^{2+} :



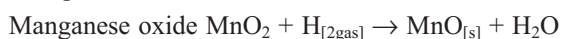
Transformation of Fe^{2+} to Fe^{3+} :



Precipitation of Fe^{3+} :



Precipitation of Mn^{2+} and Mn^{4+} :



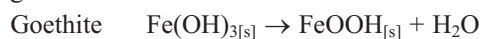
Manganese oxide-hydroxide



Manganese oxide



Transformation of aging ferric hydroxide amorphous to goethite:



Yellowish through orange/red to brownish stains on the streambed and thick mats of iron/manganese-oxides/hydroxides floating on surface water are present until the next rainfall event.

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.

DISCUSSION

Chloride ion in surface water along the rivulet as well as in groundwater has very uniform concentration. Input of Cl into aquatic system occurs through rainfall input containing this ion and originating from marine aerosols as groundwater chloride concentration is low due to freshwater depositional environment of sandstone and long term flushing of shallow subsurface by rainfall. Ion/chloride ratios have been calculated to assess changes of reactive ion concentrations versus conservative chloride ion (Fig. 4). Data shows significant increase of Ca and HCO_3^- relative to Cl indicating dissolution reaction of calcite, lesser increase of Mg from dissolution of traces of dolomite and weathering of aluminosilicates containing Mg. Oxidation of traces of pyrite/marcasite supply some SO_4 to aquatic system. High increase relative to concentration as well as to Cl occurs for Ba and Sr along the impacted part of the rivulet.

The PHREEQC – v. 2.11 computer program (Parkhurst, Appelo, 1999) was used to model the speciation and saturation indices of surface waters. Saturation indices were calculated using measured concentrations of elements at specific pH values and under oxidising conditions. The saturation index for a given mineral or solid phase is defined as $\text{SI} = \log(\text{IAP}/\text{K}_{\text{sp}})$, where IAP is the ion activity product in solution of the species involved in the dissolution/precipitation reaction and K_{sp} is the solubility product. The surface water is supersaturated with respect to given mineral if $\log \text{IAP}/\text{K}_{\text{sp}} > 0$; is undersaturated if $\log \text{IAP}/\text{K}_{\text{sp}} < 0$; and is at equilibrium if $\log \text{IAP}/\text{K}_{\text{sp}} = 0$.

Hydrogeochemical modelling has shown that carbonate minerals calcite, aragonite, dolomite, magnesite, strontianite

and siderite are undersaturated with respect to given minerals (Fig. 5). These minerals are dissolved from the rock mass and the addition of Ca, 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 slightly supersaturated in a few surface water samples that 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 (Fig. 5B), keeping these metals in solution as long as oxidation does not remove Zn and Mn from the aquatic system. Sulphate minerals such as gypsum, anhydrite and celestine are undersaturated, however barite is mostly in equilibrium in aquatic system suggesting that this mineral only slightly react with flowing through fractures groundwater. All iron oxide/hydroxide and manganese-oxide/hydroxide-minerals are strongly supersaturated (Fig. 6), including magnetite, hematite, maghemite, goethite, lepidocrocite and ferrihydrite, hence precipitation of these minerals quickly remove iron from the aquatic system. During rainfall events, acidic rain water and surface run-off with pH values ranging from 3 to 6 re-mobilises iron and manganese oxides and hydroxides, eroding them from the streambed and dissolving them from floating mats and returning these metals again to the aquatic system to cause further contamination downstream, mostly in the Woronora storage. 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.

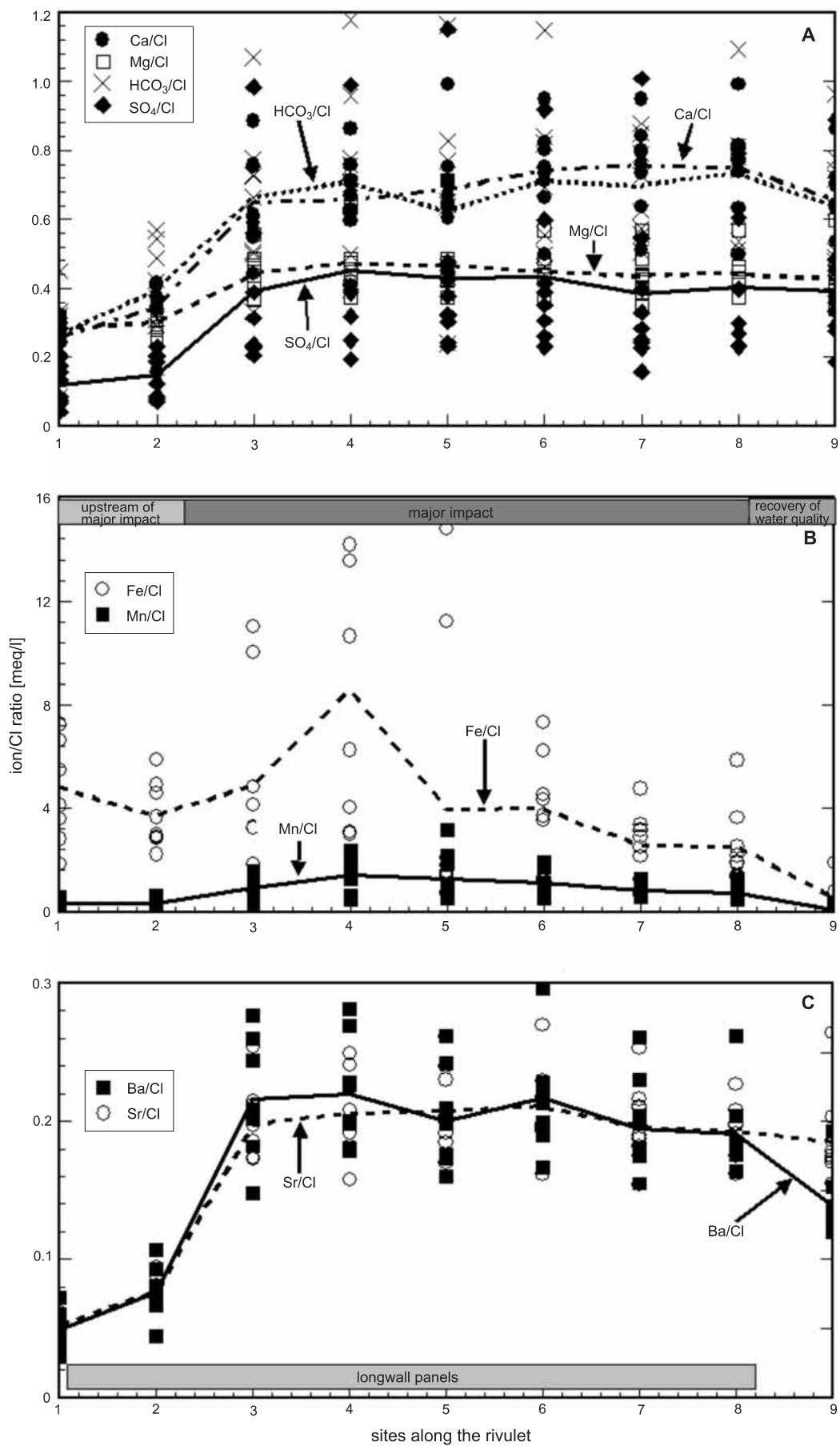


Fig. 4. Ion/chloride ratio along the Waratah Rivulet (continuous lines represent average values for each ratio)

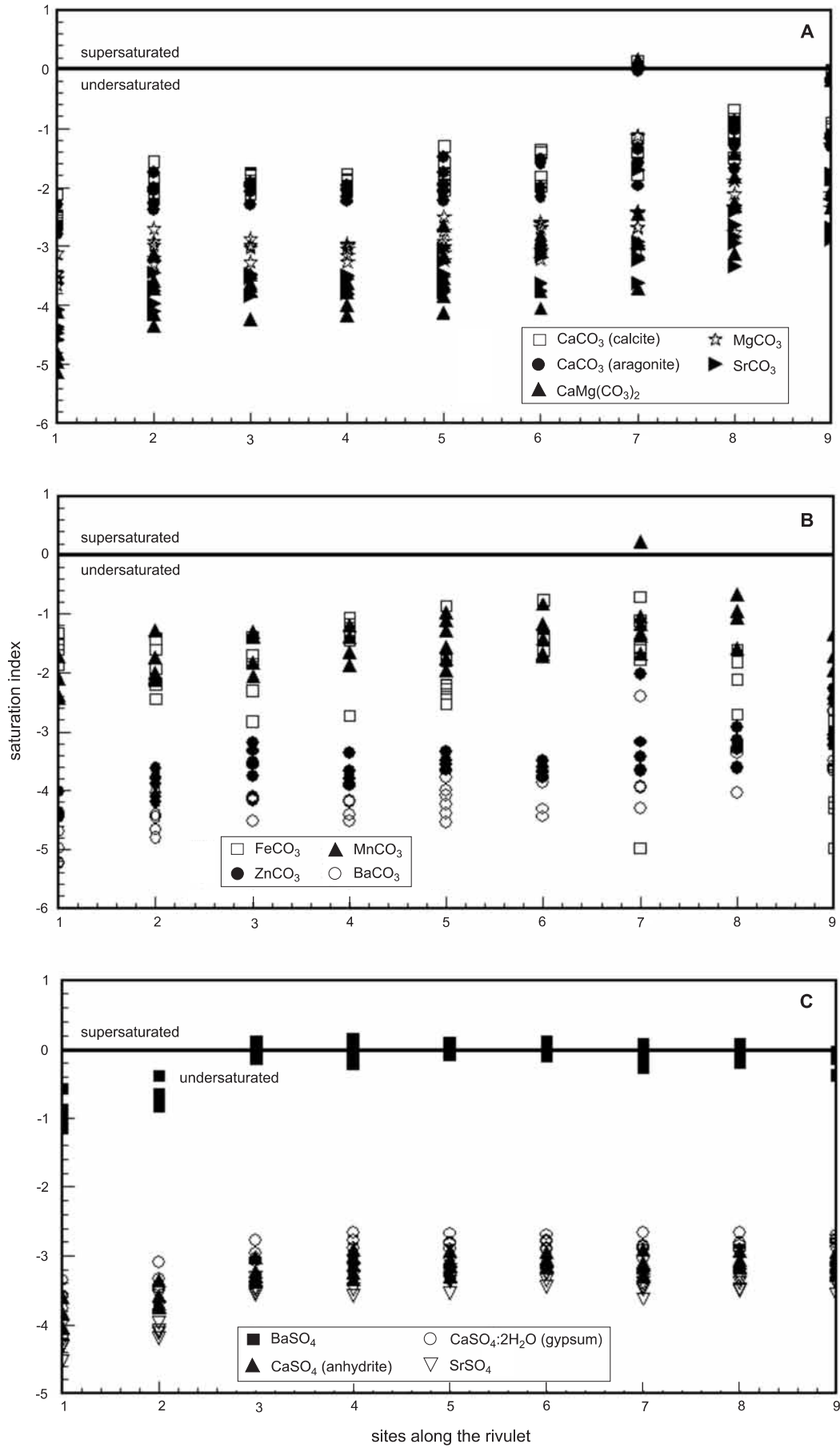


Fig. 5. Saturation indices with respect to carbonates (A, B) and sulphates (C) along the Waratah Rivulet

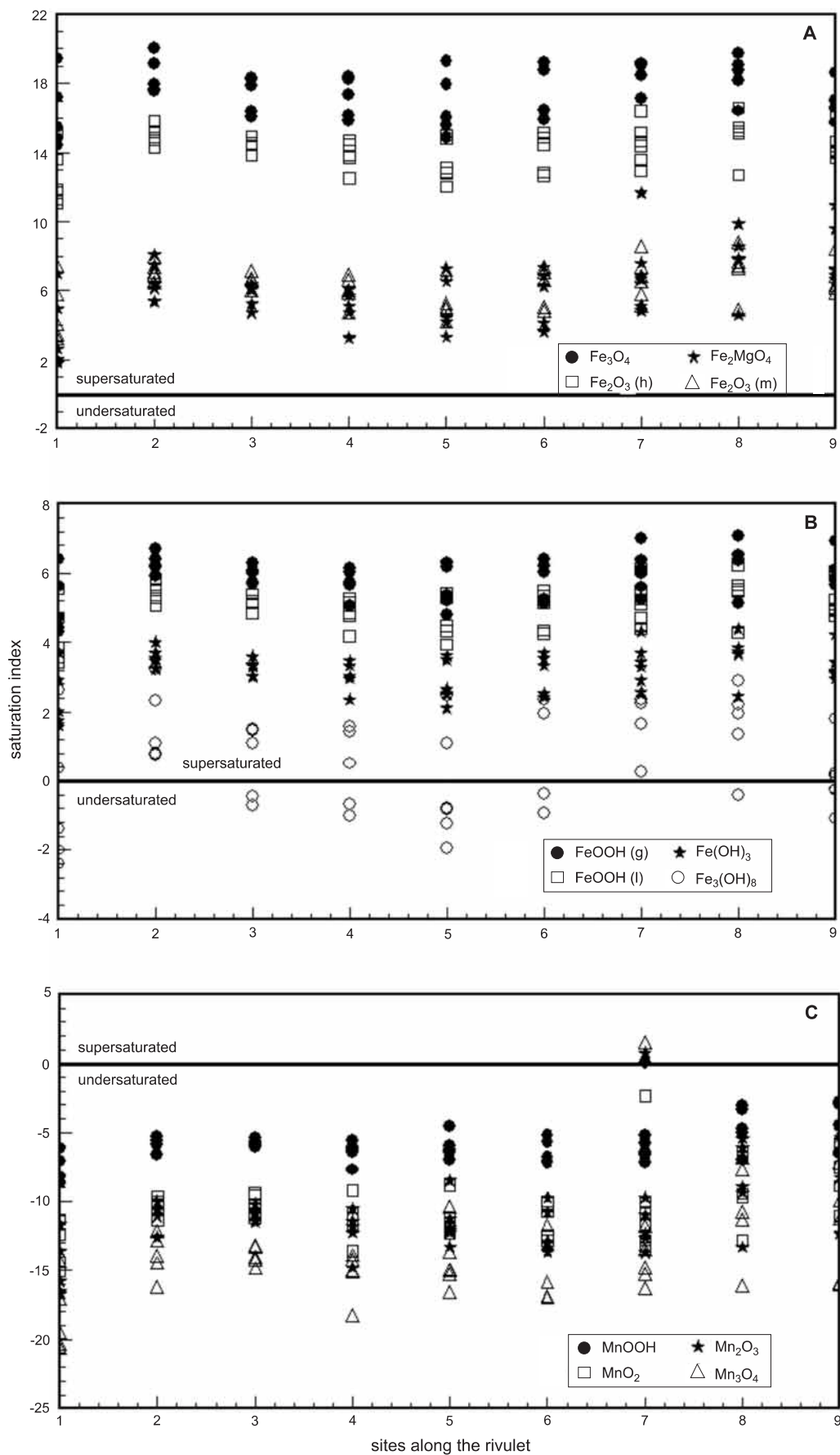


Fig. 6. Saturation indices with respect to iron oxides (A), iron hydroxides (B) and manganese oxides/hydroxides (C) along the Waratah Rivulet

CONCLUSIONS

Hydrochemical data from the Waratah Rivulet, a small stream in the Southern Coalfield, NSW, Australia, shows significant changes in water chemistry and quality along the rivulet. Surface water flowing through the mining-induced subsidence area and downstream of longwall panels has a much higher EC, pH and concentration of major, minor and trace elements, and significantly lower Eh and dissolved oxygen content compared to surface water flowing in a pristine environment (upstream of longwall panels, tributary stream, pre-mining data). The surface water chemistry in the rivulet shows significant changes in concentration over the 2 km length of the sampled streambed. The salinity of surface water upstream of the subsidence area is low, with EC values ranging between 200 and 280 $\mu\text{S}/\text{cm}$. The salinity increases along the rivulet as more water re-emerges from the subsurface, with concentrations between 260 and 340 $\mu\text{S}/\text{cm}$.

Concentrations of iron and manganese 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 orange / red to brownish stains on the streambed. The discharge of groundwater rich in iron and manganese to the rivulet 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. 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 rivulet. 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 sulphate.

Barium and strontium remain in solution and can act as natural tracers that can be used to locate discharge points where groundwater re-emerges to the creek channel. 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 sulphate. 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. 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.

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 Mn in surface water. 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 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 $\text{Ca} + \text{Fe} + \text{Sr} + \text{Ba}$ versus HCO_3 shows the dissolution of carbonates is the main source of the above chemical elements in the groundwater system. 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.

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. As the end of the Waratah Rivulet hydrological system is Woronora Lake all precipitated and dissolved iron and manganese ions flow into this storage. The total loading of Fe and Mn calculated from an average monthly flow and concentration data of iron and manganese into the Woronora Lake Reservoir for the period February 2002 to August 2009 was in the order of 15.4 and 4.0 tonnes of iron and manganese respectively. This loading does not take into account mining activities in the catchment and loading of iron and manganese to Woronora Storage prior to February 2002. 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.

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