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Extended Abstracts

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Interactions of surface and ground waters

title: **Surface water-groundwater interaction in the fractured sandstone aquifer impacted by mining-induced subsidence: 2. Hydrogeochemistry**

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ABSTRACT

Hydrochemical data from the Waratah Rivulet a small stream in the Southern Coalfield, New South Wales (NSW), Australia, shows significant changes in water chemistry and quality along the rivulet. These changes are as a result of impact of mining induced-subsidence on water resources. The higher salinity and concentrations of major ions and metals are related to water-rock interaction, which causes the dissolution of carbonates, reductive dissolution of oxides and hydroxides, and oxidation of metal-sulphur minerals. The chemical composition of surface water changes from Na-Ca-Cl-HCO₃ type upstream to Ca-Na-HCO₃-Cl type downstream of the mining area. 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. Deterioration of water quality occurs through elevated concentration of metals and increased salinity, and aesthetic changes of the stream through precipitation of red/brown iron-oxides and hydroxides. The occurrence of metal precipitates and iron-oxidising bacteria is particularly evident where groundwater discharges through streambed cracking to surface water. Hydrogeochemical modelling shows that all surface water samples upstream, in mining area and downstream are undersaturated with respect to all cation and metal carbonate minerals and that all water samples are supersaturated with respect to iron and manganese oxides and hydroxides causing precipitation of these minerals as yellowish/orange-to-reddish/brownish precipitates.

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 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, et al., 2008).

ENVIRONMENTAL SETTING

The Waratah Rivulet catchment 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 compris-

es a gently deformed sequence of Triassic sandstone that forms the upper sequence of the Sydney Basin sediments.

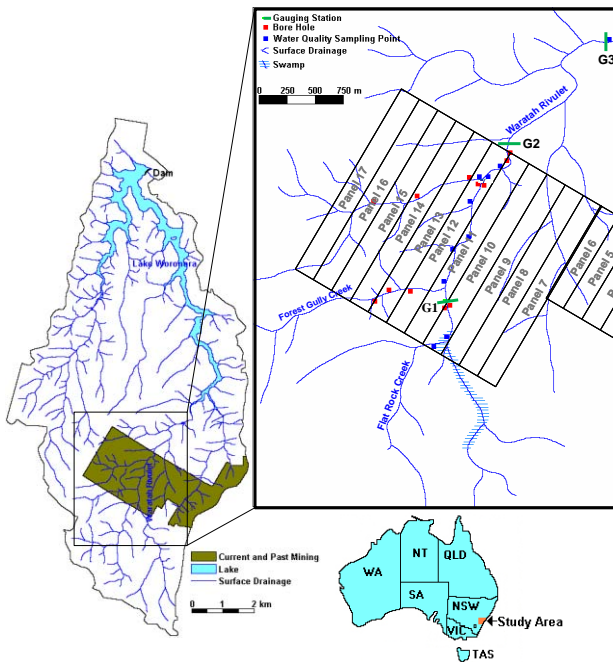


Figure 1. Location of the Waratah Rivulet catchment (left) and location of sampling points and longwall panels (right).

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. 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.

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 (Fig. 1). A reference point located in a tributary creek represents a pristine water quality environment. Groundwater quality samples were collected from recently drilled shallow bore holes 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 (Fig. 2). Chemical data shows that concentrations of major and minor elements are much higher in groundwater than in surface water. The higher concentrations are related to presence of well developed

and interconnected fracture networks in the mining-induced subsidence area and exposure of more rock strata to water-rock interaction, which causes dissolution of carbonates, reductive dissolution of oxides/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.

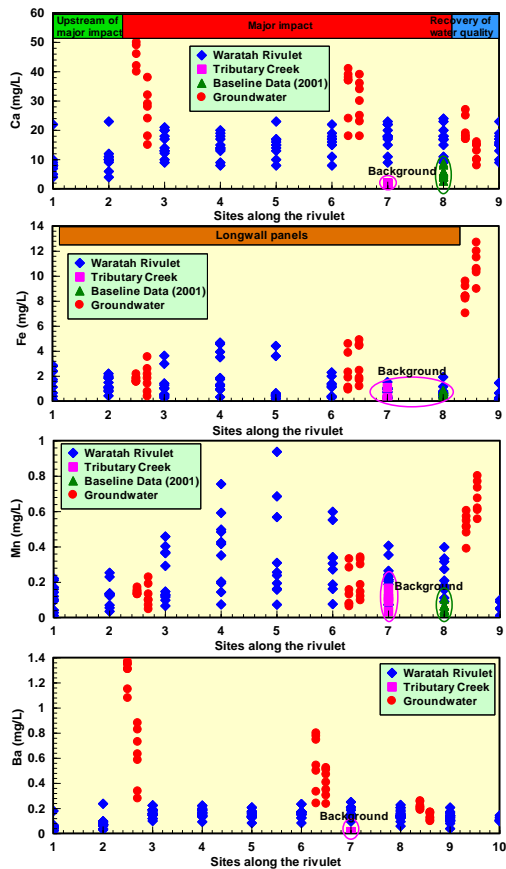


Figure 2. Variation of Ca, Fe, Mn and Ba concentrations along the Waratah Rivulet.

Deterioration of water quality occurs through elevated content of metals, increased salinity, and aesthetic changes of the creek channel through precipitation of yellowish/orange and reddish/brownish iron oxides/hydroxides. The occurrence of metal precipitates and iron-oxidising bacteria is particularly evident where groundwater discharges to surface water through streambed cracking. 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.

Infiltrating fresh, acidic of low concentration rainwater rapidly changes its chemical composition in contact with rock matrix. Concentrations of Fe and Mn initially rise in surface flow as groundwater discharges from the subsurface. This 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. However a few hundred metres downstream dissolved metal concentrations decrease as Fe and Mn are removed from aquatic system and precipitate as oxides and hydroxides, causing orange/red to brownish stains in the creek channel. These stains on the streambed and thick mats of iron/manganese-oxides/hydroxides floating on surface water are present until the next rainfall event which dissolves precipitates by slightly acidic runoff. This process 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 causing further contamination downstream, mostly in the Woronora storage.

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. 3).

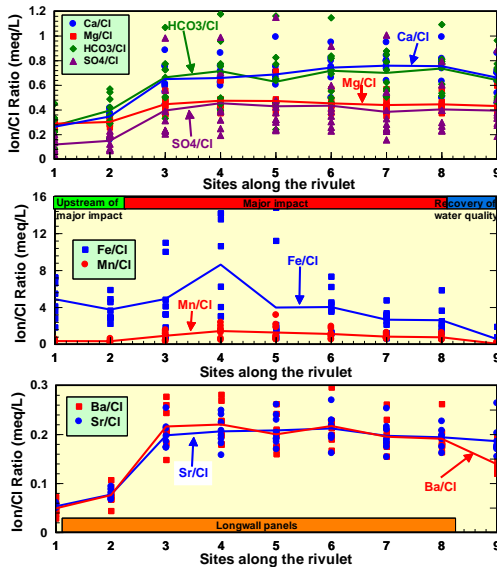


Figure 3. Ion/chloride ratio along the Waratah Rivulet (continuous lines represent average values for each ratio)

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 alumin-

silicates 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. Hydrogeochemical modelling has shown that surface water is undersaturated with respect to carbonate minerals (Fig. 4). These minerals are dissolved from the rock mass and the addition of Ca, Mg, Sr, Zn, Mn, Ba, Fe and HCO_3 into the aquatic system occurs, significantly increasing the concentration of these elements in groundwater and surface water. All sulphate minerals are undersaturated; except barite which is in equilibrium in aquatic system. All iron oxide/hydroxide (Fig. 4) and manganese-oxide/hydroxide-minerals are strongly supersaturated, including magnetite, hematite, maghemite, goethite, lepidocrocite and ferrihydrite, hence precipitation of these minerals quickly remove iron from the aquatic system.

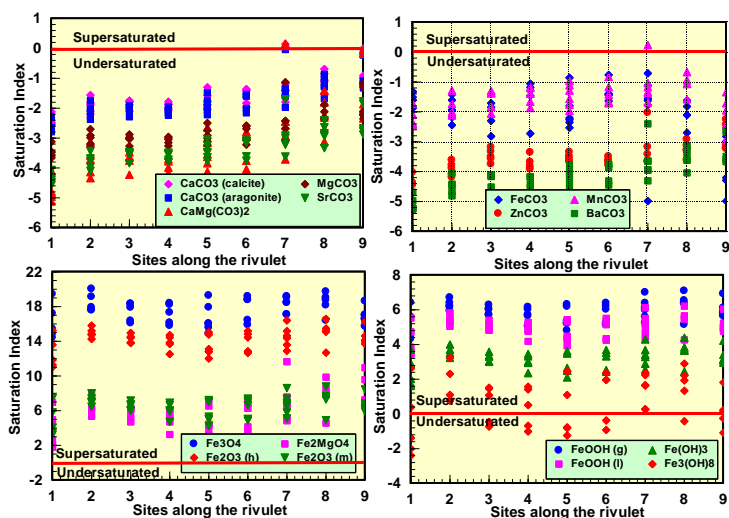


Figure 4. Saturation indices with respect to carbonates and iron oxides/hydroxides along the Waratah Rivulet.

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. 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 presence of fractures.

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.

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