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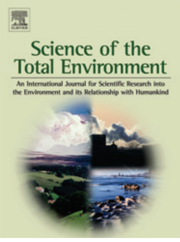

Processes of attenuation of dissolved arsenic downstream from historic gold mine sites, New Zealand

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ABSTRACT

Mine and processing sites in the mesothermal gold deposits of the Reefton gold field, New Zealand, generate extremely high dissolved As concentrations (up to 59 mg/L). Attenuation of these waters takes place by at least one of the three mechanisms: (1) precipitation of the secondary arsenic mineral scorodite, (2) chemisorption onto iron oxyhydroxide (HFO) and (3) dilution with regional catchment water. The presence and effectiveness of these mechanisms vary among the three studied catchments. A strong physiochemical control on arsenic attenuation was identified due to a chemical gradient within the gold field itself and processing methods, which can generate site specific arsenic minerals, such as arsenolite. Precipitation of scorodite only occurs in the presence of dissolving arsenolite, which is a roasting by-product present at two of the studied sites. Abundant HFO is generated in the pyritic mesothermal part of the gold field, and here chemisorption onto HFO is the dominant attenuation process. In the non-pyritic part of the gold field, HFO is mainly produced as a result of ankerite dissolution but only where sufficiently exposed mineralised rock is present. In the absence of significant adsorption sites, dissolved As is attenuated only via less effective dilution and ecosystem guidelines are exceeded over kilometres downstream from the mineralised zone until drainage waters are diluted by regional catchment water. Catchment morphology was identified as a major control on dilution.

Despite the presence of strong As point sources upstream, mine-related As contributes <10% to the regional As river load in all three catchments. On a regional scale As mobility across a wide range of pH regimes reveals a strong control of scorodite, which has already been observed locally.

1. Introduction

Mesothermal (orogenic) gold deposits are typically strongly enriched in arsenopyrite and arsenian pyrite (Goldfarb, 2005). These are excavated and processed with the gold ore, and deposited in waste rock piles and tailings. Percolating rainwater can facilitate oxidation and dissolution of As from the mine wastes and mine excavations and the dissolved As can be discharged into the environment with potentially toxic consequences for the downstream biota (Foy et al., 1978; Gebel, 1997; Loebenstein, 1993; Smedley and Kinniburgh, 2002; Turner, 1993). It is a worldwide occurrence that these elevated As concentrations decrease downstream via at least one of the three attenuation processes: (1) precipitation of secondary As minerals, such as scorodite (Ashley and Lottermoser, 1999; Borba et al., 2003; Craw and Nelson, 2000; Deutsch, 1997; Garcia-Sanchez and Alvarez-Ayuso, 2003; Krause and Ettel, 1988; Smedley and Kinniburgh, 2002; Vink, 1996; Williams, 2001), (2) chemisorption onto other solid phases, such as iron oxyhydroxides (HFO) (Belzile and Tessier, 1990; Foster et al., 1998; Hem, 1977; Jacobs et al., 1970; Majzlan et al., 2004; Pierce and Moore, 1982; Webster et al., 1994; Wilkie and Hering, 1996),

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(3) dilution with background waters. The environmental significance of dissolved As emanating from mines depends on the amount and spatial scale of these attenuation processes. However, it is difficult to distinguish among individual attenuation processes.

New Zealand's West Coast is renowned for its gold mining history. The most important deposits are in the Reefton gold field (Christie and Brathwaite, 2003; Rattenbury and Stewart, 2000), which hosts the Globe Progress Mine and the Blackwater mine (Fig. 1). These mining areas accommodate several strong point sources for As, which allow for easy tracing of the anomaly and its attenuation processes in relation to major ions. Arsenic anomalies originate from arsenopyrite in mine workings and from the secondary As minerals arsenolite and scorodite on processing sites (Haffert and Craw, 2008; Hewlett et al., 2005; Wilson, 2003).

This study uses these historic mine and associated ore processing sites to characterise attenuation processes and their underlying physiochemical controls in the site drainage until the As levels have been sufficiently attenuated for the water to be of drinkable quality. Fundamental differences in attenuation styles is caused by a marked difference in the arsenopyrite/pyrite ratio between the studied mining areas (Christie and Brathwaite, 2003). In the Blackwater deposits, pyrite is rare compared to arsenopyrite, and HFO is scarce and only associated with man-made structures. This makes it a suitable territory to observe the nature of As mobility in the absence of significant adsorption-based attenuation. Here, dilution becomes the most effective attenuation mechanism, and we describe the scale of the dilution process. This is then compared to As mobility from the pyritic mesothermal deposits at the Globe Progress Mine, where HFO is ubiquitous.

The impact of the As-rich mine residues on the stream catchment is then established on a regional scale. Despite differences in As attenuation between the two mining areas, downstream sources of As are mainly natural in all three studied catchments. Finally, possible controls of secondary As minerals on regional As mobility are investigated by consulting extensive As analyses from previous studies.

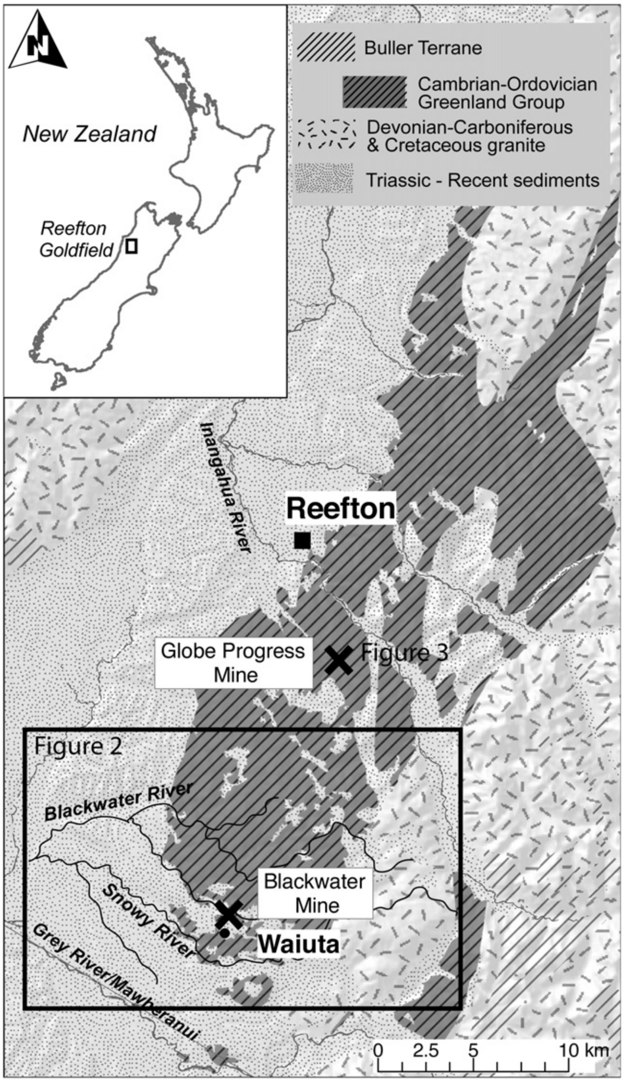


Fig. 1 – Location and geological setting of the Blackwater and Globe Progress Mine in the Reefton gold field.

2. General setting

2.1. *Basement geology*

The Reefton gold deposits are hosted within the oldest group of the Buller Terrane, namely the lower Palaeozoic Greenland Group (Cooper, 1974) (Fig. 1). The Greenland Group consists of alternating mudstones and sandstones with detrital quartz, rock fragments, muscovite, plagioclase and biotite. The latter two minerals have been largely altered to albite and chlorite, respectively, during greenschist facies metamorphism. Subsequent hydrothermal alteration of the sandstone has developed a mineral assemblage of K-mica, carbonate (dolomite–ankerite and ferroan magnesite–magnesian siderite, minor calcite), chlorite, pyrite and arsenopyrite (Christie and Brathwaite, 2003). The rocks have high acid neutralizing capacity (ANC), typically between 4 and 9 wt.% $CaCO_3$ (equivalent) (Hewlett et al., 2005), which generally exceeds the maximum potential acidity (MPA) (Haffert et al., 2006). The basement rocks are overlain locally by remnants of a Cretaceous–Tertiary sedimentary sequence (Suggate, 1957), which contains non-marine sections that include coal seams (Brunner Coal Measures), and marginal marine sediments that are locally calcareous and pyritic (Hewlett et al., 2005).

2.2. *Mineralised rocks*

Two endmember styles of mesothermal gold deposits can be identified in the Reefton gold field (Christie and Brathwaite, 2003; Maw, 2000). First, gold enrichment occurred in quartz veins in poorly veined, non-brecciated host rock. This type of deposit was mined at the Blackwater mine (Figs. 1 and 2), which consists essentially of one major quartz vein, the Birthday Reef (Christie and Brathwaite, 2003). Second, gold deposition occurred locally in clay-rich fault breccias of quartz vein and wall rock fragments (Christie and Brathwaite, 2003). These fault breccias make up the bulk of the ore reserves at Globe Progress mine (Fig. 1), which is characterised by multiple shear zones, quartz veins and abundant disseminated

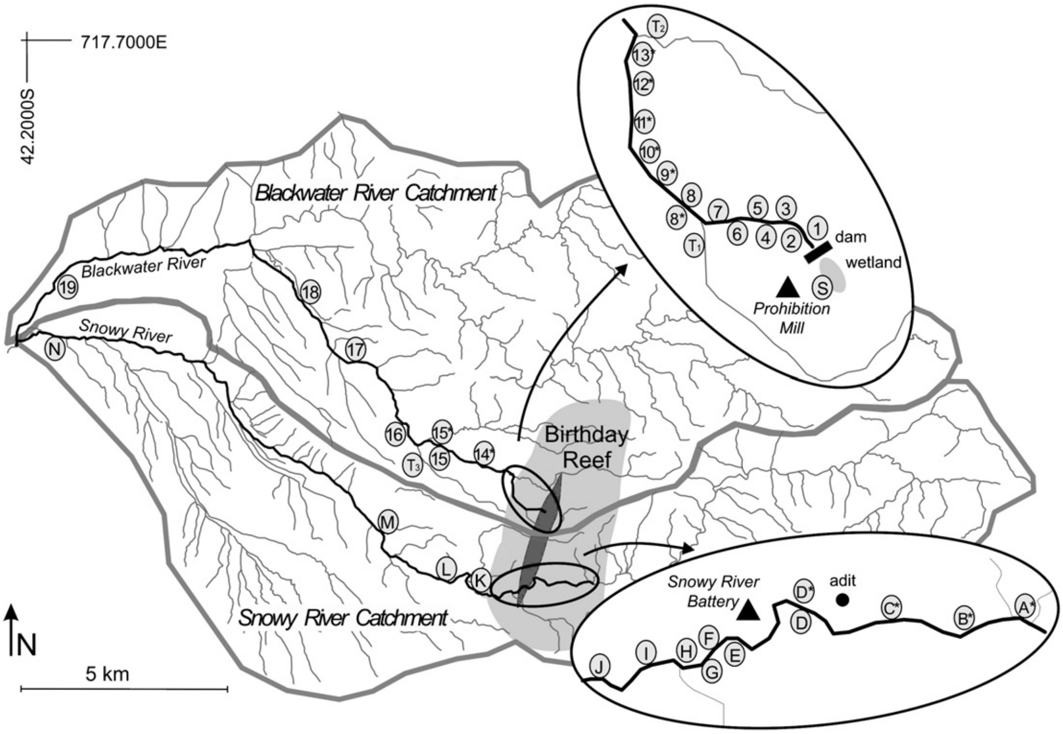


Fig. 2 – Sampling positions in the Blackwater and Snowy River catchments. The mineralised belt is added after Rattenbury (2000) (light shaded grey) and the Birthday Reef is added after Christie and Brathwaite (2003) (dark shaded grey).

mineralisation. Both mineralisation styles are enclosed in hydrothermally altered host rock, however, differences in structural setting and degree of alteration have produced a marked difference in the pyrite–arsenopyrite ratio between the Blackwater deposits and the remaining goldfield; Blackwater deposits include abundant arsenopyrite, and pyrite is rare. At the Globe Progress Mine, in contrast, pyrite is abundant and arsenopyrite is rare (Christie and Brathwaite, 2003; Hewlett et al., 2005).

2.3. *Topography and drainage*

The Birthday Reef, hosting the Blackwater mine, centres around the abandoned mine town of Waiuta, which is located on a plateau of moderate elevation (~400 m asl). The Waiuta area is dissected and drained by the Blackwater and Snowy River catchments (Fig. 2). The Blackwater catchment has an area of 100 km^2 and the majority of the drainage system overlies the Greenland Group metasediments. The upper reaches drain a granite body, whereas the lower part of the catchment drains mainly Triassic to Recent sediments (Fig. 1). The studied length of the drainage is 16 km. The upper 4 km of this distance are affected by water draining the mineralised belt (Fig. 2). The stream bed shows some regional HFO staining from weathering of mineralised stream cobbles.

The Snowy River catchment is slightly smaller with an area of ca. 70 km^2. It is different from the Blackwater catchment in that there is one principal river, the Snowy River, with numerous but relatively short tributaries from a steep terrain. It is joined towards the end by a relatively large tributary draining a plain south of the Snowy River. Similar to the Blackwater catchment, the Snowy River drains a granite body in the upper reaches. The middle section drains the Greenland Group rocks, which are overlain by Triassic to Recent sediments in the lower part of the catchment (Fig. 1). In this study the Snowy River was sampled over a distance of ca. 15 km, of which the upper 4 km are directly affected by the mineralised belt (Fig. 2). Like the Blackwater River stream bed, the Snowy River stream bed has some weak regional HFO staining from mineralised cobbles. Both rivers flow in an east–west direction and eventually join the Mawheraiti River, a major northern tributary of the Grey River/Mawheranui, which terminates at sea in Greymouth.

The Globe Progress mine area is drained by the Devils Creek and the significantly smaller Oriental Creek, which joins the Devils Creek at Progress Junction to the north–west of Globe Hill (Fig. 3). The catchment area upstream from Progress Junction is ~10 km^2 and is mostly underlain by the mineralised shear zone. Upstream of the Globe Progress mine, Devils Creek is joined by two small tributaries, which drain some of the Brunner Coal Measures, called the Alborn coalfield (Fig. 3) (Hewlett et al., 2005). Transported HFO from the Globe Progress mine and from the Alborn coalfield settled locally (>100 m) in stream beds. Devils Creek discharges into the Inangahua River, which reaches the sea at Westport as part of the Buller River.

The region is characterised by high orographic rainfall, averaging 2300 mm annually. Seasonal distribution of rainfall has spring and autumn maxima, and minima in late summer and midwinter (Mew and Ross, 1994). Rainfall introduces background concentrations of dissolved salts to the hydrological system via entrained marine aerosols (Craw and

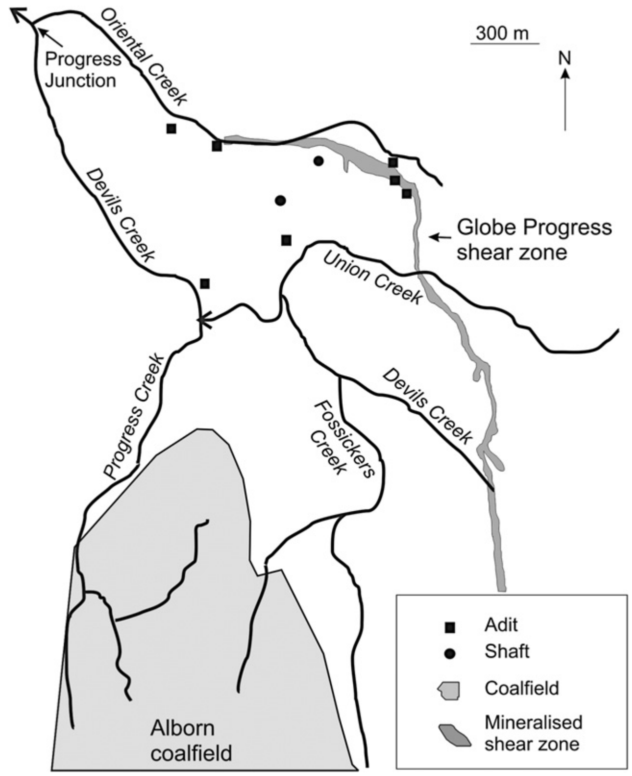


Fig. 3 – Map of the Devils Creek catchment above Progress Junction (after Hewlett et al., 2005). Shaft and adits of the historic Globe Progress mine are added as circles and squares, respectively.

Beckett, 2004; Nichol et al., 1997) The mean annual temperature is 12 °C, with prevailing westerly winds. Vegetation is dense, consisting of secondary growth beech forest and associated thick underbush. Original and present forest generated an organic layer, which overlies thin soils consisting of lithic material that is colluvial in places.

3. Site descriptions

Processing of arsenopyrite-rich ore took place at Blackwater Mine between 1908 and 1951 and has resulted in mine residues with extremely high As concentrations (up to 40 wt.% As). Arsenic mineralogy and mobility of these residues has been studied in detail by Haffert and Craw (2008). The main point source of As in the Blackwater catchment is the Prohibition Mill site. The site is located at the top of a hill at an elevation of ~560 m asl, which makes it unique in that water quality of the site drainage is not modified by input from surrounding terrains. Site run-off is collected in a wetland (~10 m wide, ~100 m long) which is constrained on the downstream side by a man-made dam (Fig. 2). The dam is composed of angular boulders of the mineralised Greenland Group. Water percolating through the dam emanates on the other side at the foot of a scree slope and eventually enters the Blackwater Creek (Fig. 2).

The wetland water contains extremely high dissolved As concentrations (up to 52 mg/L), which exceed the WHO drinking water guideline of 0.01 mg/L by 5200 times. The high dissolved As concentrations are generated by the dissolution of arsenolite (arsenic trioxide polymorph, As^{III}), which is a by-product of the arsenopyrite roasting process (Haffert and Craw, 2008). Arsenic trioxide is very soluble ($10^{-0.8}$ m, ~12 g/L As; Vink, 1996) and is still present as exposed crystals in the condenser tower of the roaster system and enclosed in the substrate surrounding the roaster. Substrate run-off has concentrations of up to 30 mg/L dissolved As, some of which is immobilised by the formation of scorodite ($FeAsO_4 \cdot 2H_2O$) before entering the wetland. The site pH is low (pH 4–5), caused by the oxidation of arsenite oxyanions produced during arsenolite dissolution (Haffert and Craw, 2008).

The Snowy River catchment includes the Snowy River Battery site and at least one known adit along the Birthday Reef. The battery site is positioned in a steep-sided valley adjacent to the Snowy River and, like the Prohibition Mill site, included a roaster system. Arsenic concentrations at this site are slightly lower than at the Prohibition Mill site reaching up to 26 wt.% in the site substrate. However, unlike the Prohibition Mill site, all the available arsenolite has dissolved at the Snowy River Battery site. As a consequence, dissolved As concentrations are controlled by scorodite solubility in the site substrate, which is two (at pH 7) to five (at pH 4) orders of magnitude lower than arsenolite solubility (Haffert and Craw, 2008). Circum-neutral run-off water from surrounding elevated ground neutralises any possible on-site acidification, resulting in circum-neutral site waters which drain directly into the Snowy River. Another significant point source of As to the Snowy River is the continuous discharge from an historic adit (~100 years old, Hancox, 1985), which joins the Snowy River approximately 150 m upstream of the Snowy River Battery.

The water chemistry of Devils Creek is significantly impacted by the Globe Progress Mine. This mine has operated historically between 1870 and 1920, and has recently (2007) reopened. The As discharges and attenuation from this mine and from the coal mine further upstream has been studied in detail by Hewlett et al. (2005). The main source of As in the Devils Creek catchment is the intensely mineralised rocks, which can contain up to 1 wt.% As in arsenopyrite and pyrite (Christie and Brathwaite, 2003) and can be released during oxidation. Abundant arsenic-rich HFO (up to 20 wt.%) is building up below historic adit entrances and can form aprons of up to 4 m thickness. A small fraction of dissolved As in the Devils Creek catchment stems from the coal field in the upper reaches, where ~0.01 wt.% As is present in pyrite (Hewlett et al., 2005).

4. Methodology

4.1. *Sampling*

Water samples were collected in May 2005, followed by a complementary sampling campaign in October 2005. Sample locations were selected to investigate the behaviour of As immediately after entering the aqueous environment, as well as the spatial scale of As attenuation. Accordingly, at the Prohibition Mill site samples were extracted at closely spaced intervals over a distance of 4 km starting at the creek emanating from the site. Further samples were taken at more widely spaced intervals from the Blackwater Creek, which comprises the Prohibition Mill site drainage. Thus, water derived from the Prohibition Mill site could be traced up to 15 km downstream (Fig. 2). Similarly, at the Snowy River upstream and downstream of the battery sample locations were positioned at close intervals covering an overall distance of approximately 4 km. At broader intervals, additional samples were extracted up to 15 km downstream of the battery (Fig. 2).

Water samples were filtered *in situ* (0.45 μm) and collected in acidified nitric acid-washed plastic bottles for dissolved As analysis. Simultaneously, a second unfiltered sample was collected for an anion/cation profile or, in the case of the complementing samples, solely for low sulphate analysis. Water sampling was accompanied by *in situ* pH, temperature and relative conductivity measurements with an Oakton PC10 electrode.

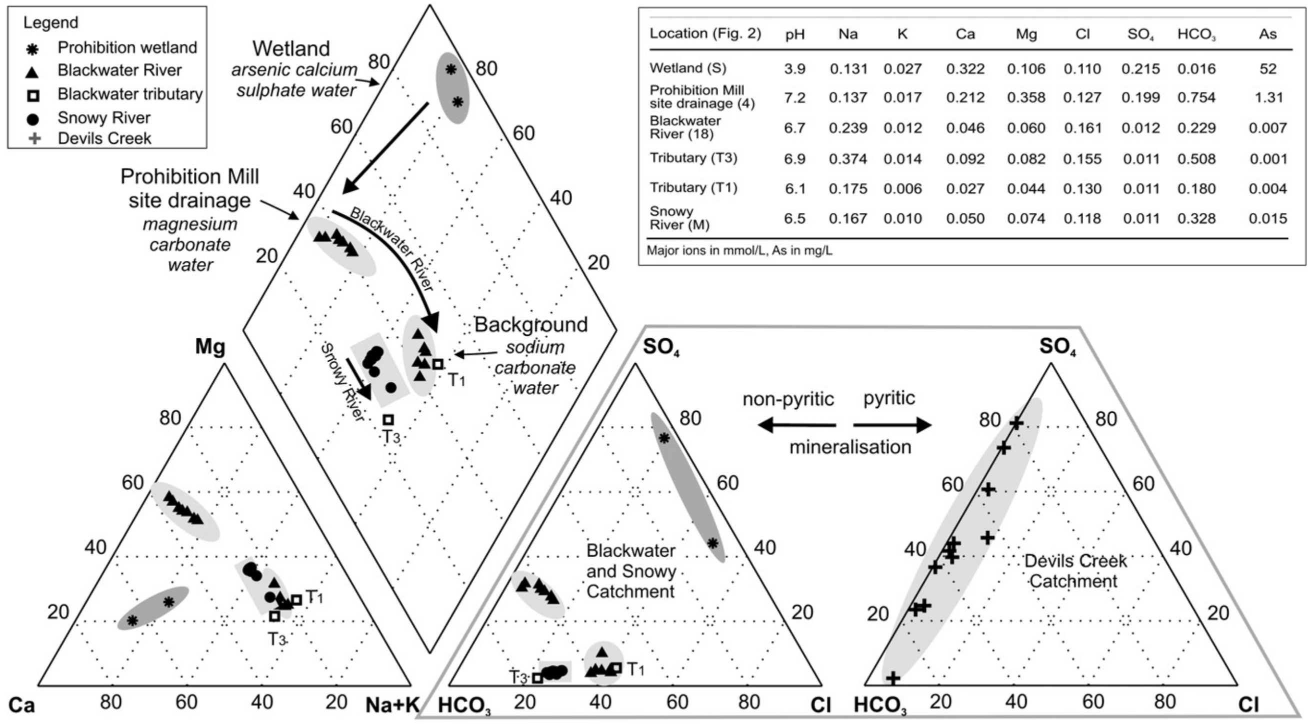
No sediment samples could be taken along the Prohibition Mill drainage because of steep terrain and consequent flushing of the stream bed. Conditions at Snowy River, however, allowed for sediment collection at several sample points.

Estimates of flow rates for small seeps and creeks were made by timing the collection of water flow in a container of known volume over a known period of time. In the case of larger streams and rivers, a floating object was timed over a known distance of near constant cross sectional area. Although crude, these methods provide better than order-of-magnitude estimates of flow rates (Hewlett et al., 2005).

4.2. *Analytical methods*

All water samples were analysed for dissolved As by ICP-MS at Hill Laboratories, Hamilton, New Zealand (detection limit 0.001 mg/L). These include a four point standard calibration curve (0.005, 0.010, 0.025, 0.050 mg/L), filter blanks and bottle blanks and a synthetic control reference standard per run. All blanks and standards are made with ultra pure, trace metal free water. At least one duplicate sample is run every 20 samples. Hill Laboratories also determined the anion/cation profile, including the following tests; pH, EC, alkalinity, bicarbonate, calcium, magnesium, hardness, sodium, potassium, chloride, sulphate, nitrate-N, nitrite-N, ion balance. Methods comply with the standard methods for the examination of water and waste water (APHA, 1998).

Samples possessing sulphate concentration close to the detection limit of the Hill Laboratories system (0.5 mg/L) and all supplementary samples were submitted for low level sulphate analyses (detection limit: 4.4 μeq/L) via ion chromatography at the NIWA atmospheric laboratory, Greta Point, Wellington. The chromatography conditions for sulphate anion are as described by Nichol et al (1997). Samples were analysed using clean-laboratory practice and injected directly with no sample clean up. Analytical accuracy has previously been tested through multi-laboratory inter-comparison conducted in conjunction with the GAW rainfall chemistry program (WMO/GAW, 2000). This method of low sulphate analysis proved to be better than 10%. (A. Marriner, personal communication). All of the above mentioned laboratories are internationally accredited laboratories (ISO17025).



Location (Fig. 2)	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3	As
Wetland (S)	3.9	0.131	0.027	0.322	0.106	0.110	0.215	0.016	52
Prohibition Mill site drainage (4)	7.2	0.137	0.017	0.212	0.358	0.127	0.199	0.754	1.31
Blackwater River (18)	6.7	0.239	0.012	0.046	0.060	0.161	0.012	0.229	0.007
Tributary (T3)	6.9	0.374	0.014	0.092	0.082	0.155	0.011	0.508	0.001
Tributary (T1)	6.1	0.175	0.006	0.027	0.044	0.130	0.011	0.180	0.004
Snowy River (M)	6.5	0.167	0.010	0.050	0.074	0.118	0.011	0.328	0.015

Major ions in mmol/L, As in mg/L

Fig. 4 – Piper Diagram of surface water analyses from the Snowy and Blackwater River catchments. Major ion data stems from the first sampling campaign (samples: S, 1–8, 15–19, T_1, T_3 for Blackwater River Catchment and D–N for Snowy River catchment). A table of major ion data of representative samples is included (number/letter in brackets are sampling positions, Fig. 2). A SO_4–HCO_3–Cl ternary diagram of Devils Creek catchment (after Hewlett et al., 2005) is added for comparison.

Stream sediment samples were oven dried at 45 °C and subsequently sieved to less than 120 μm, thus excluding quartz-rich material principally inactive in As mobilization and transport. A cut-off limit lower than 120 μm was not possible due to a lack of sediments in smaller grain size ranges. Samples were then analysed for total recoverable As and, in most cases Sb and Fe, by nitric/hydrochloric acid digestion (EPA 200.2, US-EPA, 1994) followed by solution analysis by ICP-MS (Hill Laboratories, Hamilton, NZ; detection limit 0.001 mg/L). Interference of $^{40}Ar^{35}Cl$ on ^{74}As analysis was corrected by measuring ^{77}Se and ^{82}Se and establishing the interference of $^{40}Ar^{37}Cl$ on ^{77}Se. This was then related to the $^{40}Ar^{35}C$ interference by adjusting for the natural abundance of both Cl isotopes.

4.3. Data from other sources

A collaborative research programme between CRL Energy, University of Canterbury, University of Otago and Landcare Research has been devised to assist with the planning of future mine developments. Part of this programme is a GIS database (Database for Assessment of Mine Environments, DAME) that compiles extensive surface water chemistry data as well as rock

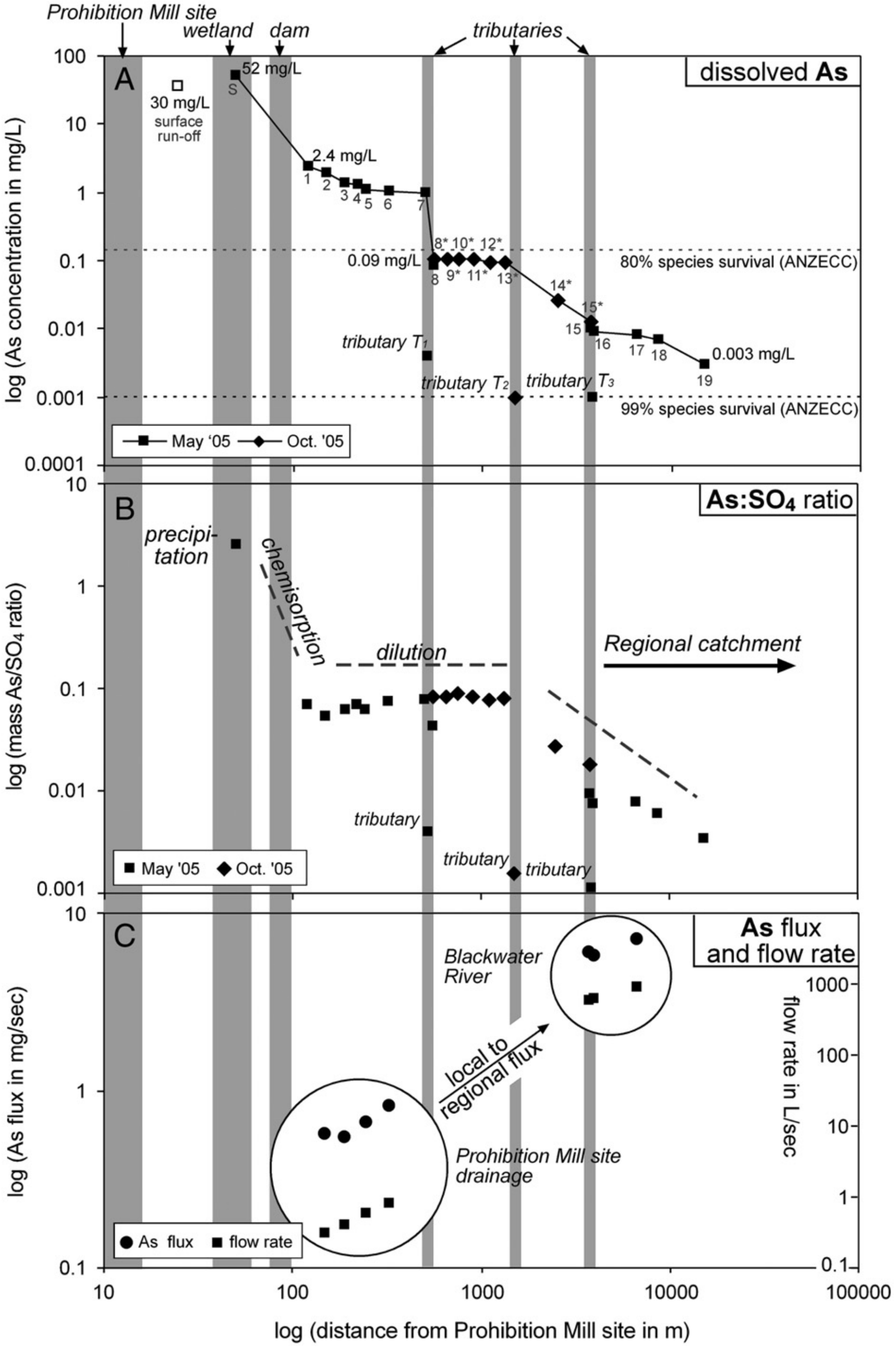


Fig. 5 – Prohibition Mill site drainage: dissolved As (A), As/S ratio (B) and As flux (C) versus distance.

chemistry data from mined and un-mined areas. The database for Westland includes the analyses of approximately 400 dissolved As (<0.45 μm) as well as total (unfiltered) As. Other work from the Otago Schist, NZ, has shown that in this setting the difference between filtered and unfiltered samples is insignificant (Wilson, 2003), therefore no distinction between the two methods is made in this part of the study.

Analyses from the Globe Progress mining area (Hewlett et al., 2005; Wilson, 2003) have also been incorporated into relevant parts of this study. These samples include groundwater, adit and surface water from the Devils Creek and its tributaries upstream of Progress Junction.

5. Results

5.1. *Major ions*

Within the samples from the Blackwater River catchment three hydrochemical facies were identified. Wetland water at the Prohibition Mill site is of the arsenic calcium sulphate type (Fig. 4) and is characterised by low pH (~3) and an electrical conductivity (EC) of ~170 μS/cm^2. This water is modified in the man-made dam to magnesium carbonate water through the interaction with well-exposed mineralised

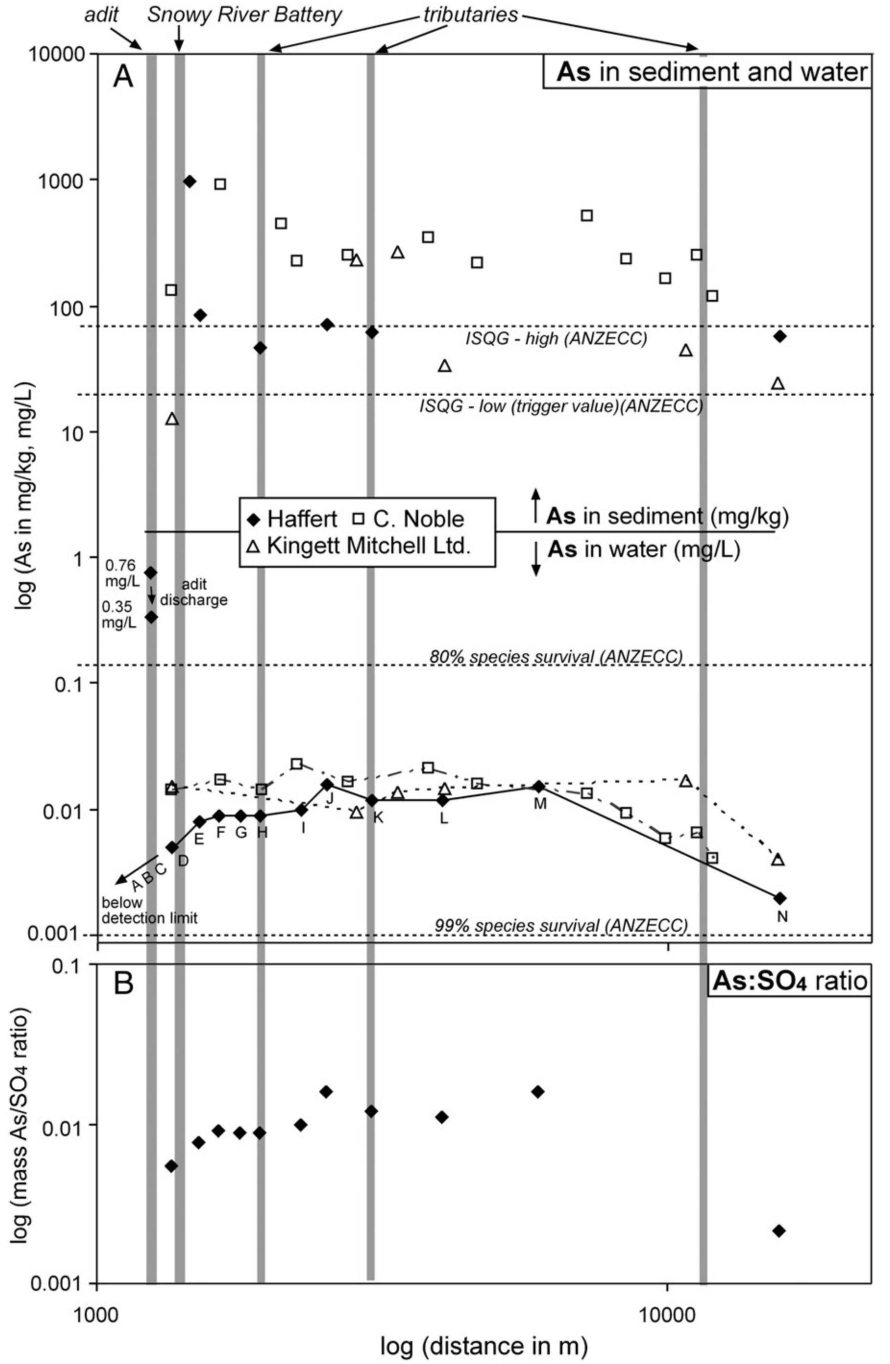


Fig. 6 – Snowy River catchment: As in sediment and dissolved As (A) and As/S ratio (B) versus distance.

host rock. This water possesses the highest EC encountered in this study (~200 μS/cm^2) at circum-neutral pH. The chemically anomalous signal emanating from the Prohibition Mill site prevails for 500 m downstream until a significantly larger tributary dilutes the site drainage water to the typical sodium carbonate background water (Fig. 4). This water type is encountered in all of the Snowy River and downstream Blackwater River samples and is characterised by circum-neutral pH, low TDS (~30 mg/L, calculated) and an approximate EC of 60 μS/cm^2.

Samples from the Devils Creek catchment are scattered across a range of hydrochemical facies. The situation is further complicated by the presence of the Alborn coalfield in the upper reaches of the catchment. In summary, like the Blackwater and Snowy River catchment, the Devils Creek catchment waters have high alkalinity, calcium, and magnesium (Hewlett et al., 2005). Many samples have significant sulphate concentrations as well, especially in adit and groundwater samples (Fig. 8).

5.2. *Arsenic concentrations*

Run-off draining the roaster complex and scorodite cemented substrate at the Prohibition Mill site contained 30 mg/L As (Fig. 5A). The wetland water, which drains most site run-off, possessed the highest As concentration encountered during this study (52 mg/L) and is close to one of the highest dissolved As concentrations (72 mg/L) published for mine waters worldwide (Williams and Smith, 2000). When the wetland discharge percolates through the man-made dam As concentrations drop by over an order of magnitude to 2.4 mg/L (Fig. 5A). Arsenic concentrations in the small creek emanating from the dam decrease steadily downstream. At the point where the stream discharges into a 10-times-larger creek, ~500 m downstream of the Prohibition Mill site, the As concentration has dropped by another order of magnitude to 0.09 mg/L. Further downstream, As concentrations continue to drop, which is especially pronounced at the confluence of tributaries (Fig. 5A). Despite the strong downstream decrease of As the Blackwater River still carries 0.003 mg/L As ~14 km downstream of the Prohibition Mill site and according to ANZECC (2000) the survival of 99% of the species is not guaranteed over the entire sampling extent (Fig. 5A).

Samples from the Snowy River catchment possess a comparatively small range of As concentrations (Fig. 6A). The highest As concentration (0.76 mg/L) was encountered in the discharge water from the adit upstream of the Snowy River Battery. Abundant iron oxyhydroxide precipitate covered the creek bed immediately downstream of the adit. At the point where the adit water discharged into the Snowy River As concentrations dropped to 0.35 mg/L. Snowy River water approaching the confluence with the adit water carried As concentrations below detection limit and increased to 0.007 mg/L downstream of the adit inflow and upstream of the Battery site. At ~50 m downstream of the Battery site the river carried 0.008 mg/L. Elevated As concentrations (0.008–0.016 mg/L) persist for ~5 km downstream of the Battery site, experiencing a slight increase with distance. This is especially pronounced ~1.2 km downstream of the site (Fig. 6A). Approximately 15 km downstream of the site, where the Snowy River is significantly diluted by water draining only non-mineralised bed rock, As concentrations drop below WHO drinking water levels to 0.002 mg/L (Fig. 6A). The dataset is in agreement with previous work undertaken on the Snowy River (Brown et al., 2003; Kingett, 2004; Noble, 2003), which shows continuously elevated As concentrations over most of the sampling distance, with a noticeable peak about 1.2 km downstream of the site. Approximately 10 km downstream of the site As concentrations drop to concentrations in the 10^{-3} mg/L range (Fig. 6A).

The few sediment analyses available from the Snowy River mirror the trend already observed in the water samples (Fig. 6A). Sediment just downstream of the site contains the highest As concentrations (978 mg/kg), which drop by over an order of magnitude ~150 m downstream from the site. Over the following 5 km As concentrations in sediments fluctuate between 47 mg/kg and 71 mg/kg.

Oriental Creek, a small tributary to Devils Creek, drains a catchment with several historic mine adits that discharge waters with up to 59 mg/L dissolved As (Figs. 3 and 7). The As concentrations decrease over metres or tens of metres as the adit discharge waters pass down into Oriental Creek (Craw et al., 2004; Wilson, 2003). Downstream of the Globe Progress Mine, Devils Creek has a significant dissolved As content at mean flow rate (0.14 mg/L) (Hewlett et al., 2005) just after the confluence with Oriental Creek (Progress Junction). In contrast, As concentrations in upstream coalfield waters are near to or below detection limits, similar to those upstream of gold mineralised zones (Hewlett et al., 2005).

5.3. *Arsenic flux*

Despite the elevated As concentrations (2.4 mg/L) leaving the Prohibition Mill site, the flow rate and consequent As flux are relatively low (~0.3 L/s and ~0.7 mg/s, respectively) (Fig. 5C). This is in contrast to the downstream environment where Prohibition Mill site drainage water has merged with regional catchment waters. At approximately 4 km downstream of the site, the Blackwater River carried ~600 L/s, and although As concentrations dropped to 0.01 mg/L the river transported approximately an order of magnitude more As (~6 mg/s) than the initial site discharge. The As flux remained relatively constant (6–8 mg/s) at least up to 7 km downstream from the site with a slight increase in flow rate (~800 L/s) (Fig. 5C).

In contrast, the Snowy River Battery is drained directly by the Snowy River which is of a similar size to the Blackwater River when approaching the Battery site. The adit upstream from the Battery site released ~3.5 L/s of water with an As flux of ~2.5 mg/s. The consequent As flux in the Snowy River downstream of the adit totalled ~4 mg/s. At 150 m downstream of the Snowy River Battery the flow rate and consequent As flux has increased to ~900 L/s and ~6 mg/s, respectively. Therefore, the Snowy River Battery contributed ~2 mg/s to the Snowy River As load. Over the following 3 km the flow rate and As flux further increased to ~1000 L/s and ~9 mg/s.

In the vicinity of the Globe Progress Mine, the Oriental Creek has typical flow rates between 0.1 and 1 L/s. Thus, in terms of flow rate, the Oriental Creek does not have a significant influence on Devils Creek, which has a mean flow

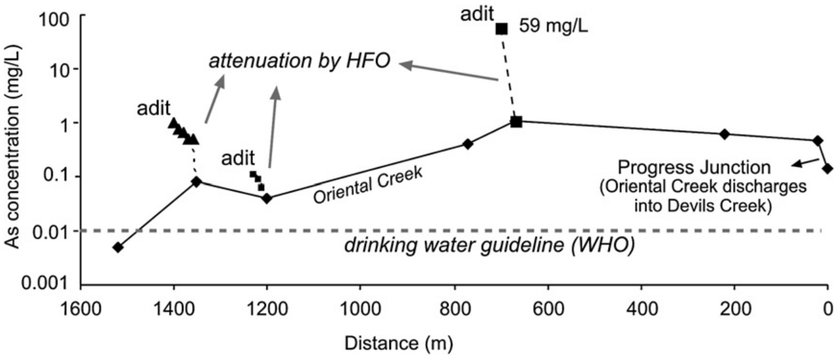


Fig. 7 – Example of arsenic variations downstream in the Globe Progress area (Oriental Creek, after Hewlett et al., 2005 and Wilson, 2003).

rate of ~230 L/s (Hewlett et al., 2005). The net flux of As from the mining area is ~30 mg/s, which is several orders of magnitude higher than estimated fluxed from most individual adits in the Globe Progress area, and 15 times higher than the most concentrated adit discharge (Hewlett et al., 2005). Hewlett et al. concluded that essentially all of this As flux comes from the gold mine area, but >90% of that flux is from natural sources.

6. Discussion

6.1. *Major ion variations*

A general feature of the background water of the Blackwater and Snowy River is the pre-eminence of HCO_3 (~260 μmol/L) in relation to relatively low SO_4 (~12 μmol/L), due to the occurrence of extensive carbonate alteration associated with the gold deposits (Fig. 4). The molar Ca/Mg ratio is close to 2:3, reflecting the dominance of Mg-bearing carbonates (ankerite, Fe-carbonate, magnesite) compared to Ca-bearing carbonates. The sum of the molar concentrations of Ca and Mg equals approximately half the HCO_3 concentrations; $[Ca]+[Mg]\sim 0.5\,[HCO_3]$. At the point where the river water is significantly diluted with water that has not been in contact with mineralised rock, the pH drops to 6.4 and Ca, Mg and HCO_3 decrease approximately by 20%, 30% and 20% respectively and Cl and K increase by approximately 20% and 30% respectively.

The low sulphate concentrations in these waters are consistent in both catchments and do not correlate with changes in As concentrations (Fig. 8). This indicates that in background waters, As and sulphate do not share the same source. Furthermore, sulphate in these waters increases with rainfall intensity, whereas As decreases (Fig. 8). Thus, in contrast to the anomalous water in the vicinity of the mineralised zone and in particular the Prohibition site, the low sulphate content in background water is derived principally from marine aerosols in rain water, rather than pyrite/arsenopyrite weathering.

In the anomalous Prohibition wetland water major ions are mainly controlled by gypsum and minor carbonate dissolution resulting in high SO_4 (216 μmol/L) and Ca (322 μmol/L) concentrations, followed by Na (131 μmol/L) and Mg (106 μmol/L) (Fig. 4). HCO_3 is comparatively low (16 μmol/L) and the molar Ca/Mg ratio is 3:1 reflecting the absence of significant carbonate dissolution. In the presence of Greenland Group carbonates HCO_3 concentrations would exceed Ca concentrations and the molar Ca/Mg ratio would be 2:3 as seen in the typical downstream catchment water.

When this water passes through the man-made dam it interacts with mineralised Greenland Group rocks and carbonate neutralisation and oxidation takes place. Simplified dissolution reactions for some minerals in these rocks are given in Table 1. Dissolution of carbonate minerals, such as dolomite–ankerite and siderite (Christie and Brathwaite, 2003) are reflected in the dataset by a 30% increase in Ca concentration (409 μmol/L), derived from the dolomite–ankerite series, and a seven-fold increase in Mg content (712 μmol/L). Bicarbonate increased by two orders of magnitude (1491 μmol/L) and the pH was neutralised to 7.7 (Fig. 4). The increase in sulphate (369 μmol/L) is due to the oxidation and dissolution of pyrite which is a minor component of the mineralised rocks. Na, K and

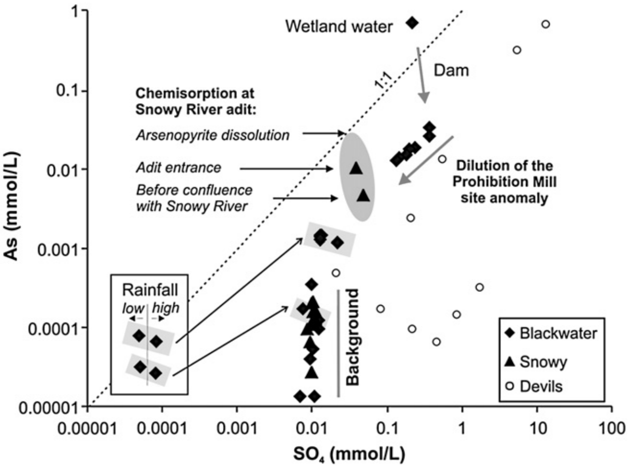


Fig. 8 – Dissolved arsenic versus sulphate in the Blackwater, Snowy River catchment (full symbols). Analysis from the Devils Creek catchment (hollow circles) are added (Hewlett et al., 2005). Two sampling positions (#8 and #15, Fig. 2) were sampled twice and the response of As and SO_4 to different rainfall intensity is shown in the bottom left corner.

Table 1 – Water quality modification and associated processes in the dam before water enters the Blackwater Creek

	(mg/L)	S	#1
Carbonate neutralization			
$CaMg(CO_3)_2 + 2H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$	Ca^{2+}	12.9	16.4
$FeMg(CO_3)_2 + 1/4O_2 + 5/2H_2O \rightarrow Fe(OH)_3 + Mg^{2+} + 2HCO_3^-$	Mg^{2+}	2.6	17.3
	HCO_3^-	1	91
	pH	3.9	7.7
Oxidation			
$FeS_2 + 15/4O_2 + 7/2H_2O + 4HCO_3^- \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H_2CO_3^0$	SO_4^{2-}	20.7	35.4
Arsenic removal			
Chemisorption with $Fe(OH)_3$	As	52.0	2.4

S = water above dam, #1 = water below dam.

Cl concentrations remained largely unaffected by the passageway through the dam.

The conservative/non-conservative behaviour of different analytes was investigated by applying Eq. (1) on the mixing of the Prohibition Mill site drainage creek (#7, Fig. 2) with the creek (T_1, Fig. 2) approximately 500 m downstream of the Prohibition Mill site. In Eq. (1), C refers to the concentrations of the subscripted water body and X_7 is the volume fraction of the Prohibition Mill site drainage creek contribution to the flow downstream of the confluence (#8, Fig. 2). The consistency ($\sigma = 0.002$) of X_7 values calculated using the major components SO_4, Ca, Mg and As suggests that these components have indeed mixed conservatively (Table 2).

$$X_7 = \frac{C_8 - C_{T1}}{C_7 - C_{T1}} \tag{1}$$

Devils Creek catchment water differs substantially from the Snowy and Blackwater River water, which are essentially carbonate waters draining non-pyritic mineralised rocks (Fig. 4). In the Devils Creek catchment, high sulphate concentrations from pyrite/arsenopyrite in mineralised rock and from the upstream coal field are competing with bicarbonates (Fig. 4). Chloride, predominantly derived from marine aerosols in precipitation, is comparatively minor.

6.2. *Processes affecting dissolved As*

A first assessment of the attenuation processes affecting waters from the Blackwater and Snowy River catchment was achieved by establishing the ratio between As and the conservative sulphate ion versus the sampling distance (Fig. 4B for the Blackwater catchment and Fig. 5B for the Snowy River catchment). In order to interpret this ratio accurately, the potential sources for As and SO_4 must be clearly defined. The Prohibition Mill site is a strong point source for As and sulphate, creating anomalies exceeding background levels by over 1000 and almost 100 times, respectively. The Snowy River Battery site is a strong point source for As, but not for sulphate, whereas the adit upstream of the site adds sulphate and As from arsenopyrite weathering. Diffuse As and sulphate, also from arsenopyrite weathering, enters the catchment downstream of mineralised bedrock. There are no significant As sources on a regional scale and sulphate is solely controlled by precipitation of marine aerosols.

6.2.1. *Precipitation and solubility of scorodite*

At the Prohibition Mill site the soluble roasting by-product arsenolite generates very arsenic-rich run-off (30 mg/L), which is partly trapped as a scorodite precipitate in the substrate (up to 30 wt.%) (Haffert and Craw, 2008). Scorodite will remain stable as long as arsenolite is available for dissolution. Once arsenolite dissolution ceases, dissolved As concentrations will drop and scorodite will become unstable (Haffert and Craw, 2008). This is the case at the Snowy River Battery site, the older of the two sites, where arsenolite is no longer available for weathering. Consequently, dissolved As concentrations are controlled by soluble scorodite and year-round precipitation provides abundant leachate for the transport of As from the substrate into surface waters (Haffert and Craw, 2008).

The control of scorodite on As mobility can also be observed on a regional scale. The DAME database provides an insight into the hydrochemistry of As under widely differing pH regimes and the relationship between pH and aqueous As concentration is plotted in Fig. 9. It shows that dissolved As concentrations are typically high at low pH (~3) and circum-neutral pH, whereas the intermediate pH range corresponds to low As concentrations (<0.001). This trend suggests that the dissolved As concentrations are controlled by the formation and solubility of the secondary As mineral scorodite. A solubility curve of scorodite (Krause and Ettel, 1988) is added to Fig. 9. Different approaches and thermodynamic data cause some discrepancy in the final position of the curve. However, the overall trend remains the same among different authors (Zhu and Merkel, 2001), matching the trend for maximum dissolved As concentrations. The strong control of scorodite on the dissolved As output

Table 2 – Mixing calculations from a confluence along the Prohibition Mill site drainage which show that Ca, Mg, SO_4 and As behave conservatively

(mg/L)	Ca	Mg	SO_4	As
#7	6.08	6.4	12.6	0.957
#8	1.49	1.52	2	0.086
T_1	1.08	1.07	0.99	0.004
X_7	0.082	0.084	0.087	0.086

The calculation is explained in the text. Sample positions (#7, #8, T_1) are shown in Fig. 2.

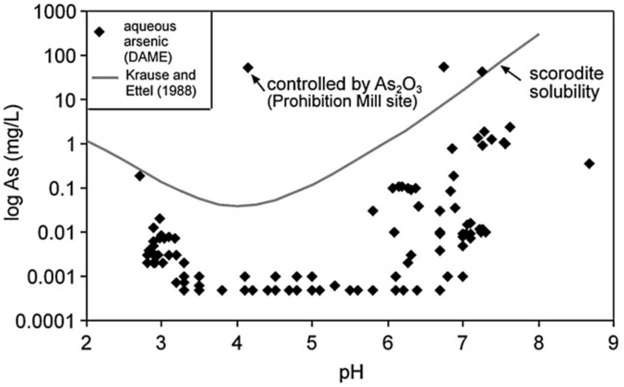


Fig. 9 – Aqueous arsenic concentrations versus pH. Data are taken from the DAME database. Scorodite solubility is added after Krause and Ettel (1988).

concentration under oxidizing conditions has also been noted in other cases (Ashley and Lottermoser, 1999; Borba et al., 2003; Craw and Nelson, 2000; Deutsch, 1997; Garcia-Sanchez and Alvarez-Ayuso, 2003; Krause and Ettel, 1988; Smedley and Kinniburgh, 2002; Vink, 1996; Williams, 2001).

6.2.2. *Chemisorption onto HFO*

From Fig. 4B it becomes evident that effective As removal occurs locally in the man-made dam at the Prohibition Mill site. Major modifications of the water quality through interaction with mineralised Greenland Group rocks in the dam take place, as previously discussed, and include carbonate neutralisation and oxidation. More important with respect to As attenuation, however, is the liberation of Fe during carbonate dissolution (Table 1). Due to the low solubility of Fe at circum-neutral pH, Fe transforms directly into HFO. Another source of Fe to the water percolating through the dam is the oxidation of pyrite. Pyrite is relatively rare in this part of the Reefton gold field and has a lesser impact via oxidation reactions on the water quality compared, for example, to the Globe Progress area (Hewlett et al., 2005). The oxidation of pyrite is a complex process that can involve a number of reactants and products under various conditions. When sufficient carbonate is present to maintain near-neutral pH conditions, the products are HFO precipitate and dissolved sulphate and bicarbonate (Nicholson, 1988) (Table 1). The HFO produced during carbonate and pyrite dissolution, has a high reactivity and surface area and is well known to be an efficient scavenger of As (e.g. Belzile and Tessier, 1990; Foster et al., 1998; Hem, 1977; Jacobs et al., 1970; Majzlan et al., 2004; Pierce and Moore, 1982; Webster et al., 1994; Wilkie and Hering, 1996), especially naturally-precipitated HFO from mine sites (Bowell, 1994; Roddick-Lanzilotta et al., 2002; Swedlund and Webster, 1999) and at a pH between 5 and 7 (Bowell, 1994; Xu et al., 1991). At present the dam induces a 20 fold decrease in dissolved As concentrations after more than 50 years of existence (Table 1). The precise mechanisms have been described elsewhere (e.g. Calvert and Price, 1977; Roddick-Lanzilotta et al., 2002) and may involve co-precipitation, adsorption, surface complex formation, ion exchange and lattice penetration (Ottesen and Theobald, 1994), here described as *chemisorption*. The dam is a field example of As attenuation by siderite dissolution, which was investigated in detail in a laboratory setting by Wang and Reardon (2001).

Chemisorption also takes place at the adit entrance upstream of the Snowy River Battery site, where HFO covers the creek bed for several metres downstream of the entrance. Adit discharge waters carry 0.757 mg/L As and have an As/SO_4 ratio just below the expected 1:1 molar ratio for arsenopyrite dissolution (Fig. 8). Thus, some As has already been removed further upstream from the adit entrance. Further removal takes place through chemisorption onto HFO below the adit entrance which is confirmed by another drop in the molar As/SO_4 ratio (Fig. 8). By the time the adit water approaches the Snowy River, As concentrations have halved to 0.35 mg/L.

At the Snowy River Battery site, a comparable mechanism to immobilise dissolved As from scorodite dissolution is not in place, and drainage water directly enters the Snowy River. However, the Snowy River acquires anomalously high As values in stream sediment when passing the Snowy River Battery. This is potentially caused by (1) erosion of processing residues into the River, in which case they act as a source of As, contributing to the increase in As/S ratio (Fig. 6B); and/or (2) As-rich subsurface seepage and ephemeral surface run-off, which is co-precipitated with HFO upon neutralisation with Snowy River water and would counteract the shift in As/S ratio (Fig. 6B).

In contrast to the Blackwater and Snowy River, HFO in the Devils Creek catchment is ubiquitous and visible on outcrops of mineralised rocks. More importantly it is abundantly present suspended in discharging adit waters and HFO builds up extensively below adit entrances and as a precipitate in stream beds (Hewlett et al., 2005). Chemisorption of As by HFO is a pivotal process in the Globe Progress area because it efficiently attenuates As concentrations in As-rich adit discharges by orders of magnitudes before it reaches the Oriental Creek (Fig. 7).

6.2.3. *Dilution*

Despite the substantial removal of dissolved As by the man-made dam at the Prohibition site, the creek emanating from the bottom of the dam is still significantly enriched in As (2 mg/L). The As/SO_4 ratio of this water remains approximately constant for almost 4 km downstream of the Prohibition Mill site, indicating that no significant As removal from the water phase occurs and attenuation takes place exclusively by dilution (Fig. 5B). The attenuation via dilution is less effective compared to the removal of As from the water phase by, for example, HFO and thereby allows elevated As signals to persist further downstream. The ANZECC (2000) threshold value for the survival of 80% of species is still exceeded by at least one order of magnitude 500 m downstream of the Prohibition Mill site. Arsenic concentrations drop significantly when diluted with major tributaries. However, As levels remain over an order of magnitude above the ANZECC threshold for 99% species survival over the following 4 km (Fig. 5A). Further downstream, the effect of the Prohibition Mill site drainage and mineralised rock weathering become diluted by regional catchment water. At this point sulphate concentrations merge with the regional background levels, which are controlled by marine aerosols in rainwater rather than by the

Prohibition Mill site anomaly or arsenopyrite weathering. Sulphate concentrations do not decrease below the regional background levels but arsenic concentrations continue to drop because of ongoing dilution. This results in an overall drop in the As/SO_4 ratio, which is linked to dilution, not arsenic chemisorption processes.

The Snowy River, a major stream, carries As concentrations below detection limit when approaching the mineralised zone (Fig. 6A). An increase in As concentrations and As/SO_4 ratio occurs over the mineralised zone and with the adit inflow just upstream of the Snowy River Battery site (Fig. 6A and B). Downstream of the Snowy River Battery site attenuation takes place mainly by dilution similar to the Blackwater catchment, which is reflected in the relatively constant As/S ratio for about 4 km (Fig. 6B). Sulphate is constant over the entire sampling distance at 10^{-2} mmol/L (Fig. 8), whereas As fluctuates between $7 \cdot 10^{-5}$ mmol/L (upstream of the battery site, position D in Fig. 2) and $2 \cdot 10^{-4}$ mmol/L (~1 km downstream of the battery site, position J, Fig. 2). The apparent increase in As over the sampling distance can be attributed to the dissolution of arsenopyrite and scorodite. If arsenopyrite dissolution causes the observed arsenic increase in the 10^{-4} mmol/L range, sulphate concentrations should experience the same molar increase and, therefore, should not cause a shift in the As/SO_4 ratio. However, the expected increase in sulphate from arsenopyrite weathering (10^{-4} mmol/L range) is insignificant compared to the background marine-derived sulphate in the river (10^{-2} mmol/L range). Thus, sulphate concentrations remain nearly constant downstream and the As/SO_4 ratio simply mirrors fluctuations in As concentrations in the Snowy River. Furthermore, in contrast to the Blackwater catchment, the Snowy River catchment has one main stream, the Snowy River, with numerous but small tributaries. These tributaries do not alter the water quality significantly, and As concentrations remain elevated (> 0.01 mg/L) over 4 km downstream. An anomalous peak exists about 1 km downstream of the site, which is reflected in the water and sediment data by an increase of 0.006 mg/L and 24 mg/kg, respectively (Fig. 6A). This could be due to another unknown As source, such as an adit or a sudden change in flow regime causing suspended As-rich matter to settle. This could then act as an anomalous source for dissolved As. As concentrations drop by another order of magnitude to below the WHO drinking water levels (0.01 mg/L) at ~5 km downstream of the Birthday lode, which is again mirrored by the As/SO_4 ratio.

6.3. *Local versus regional As flux*

The high rainfall at Reefton combined with the high relief ensures that weathering mineralised rocks are constantly flushed, yielding diffuse but substantial, As fluxes. The Prohibition Mill site is a potent point source for environmental As, contributing 0.7 mg/s to the Blackwater catchment (Fig. 4C). However, once the Prohibition Mill site drainage enters the regional catchment, background As contributions (~6 mg/s) overshadow the effect of the Prohibition Mill site (Fig. 4C). Thus the effect of the Prohibition Mill site is only significant on a local scale and elevated As levels (>0.01 mg/L) in the regional Blackwater catchment are mainly naturally derived.

Similarly, the Snowy River carries a large volume of water with relatively low concentrations of As (~0.01 mg/L) resulting in continuously high As flux (~9 mg/s). Contributions from the Snowy River Battery (~2 mg/L) and nearby adit (~2.5 mg/L) are noticeable but background As contributions are at least equally important.

Hewlett et al. (2005) noticed the same trend in the downstream Devils Creek. Here, As discharges from the Globe Progress area are mainly (>90%) coming from sources other than mine discharge sites. For example, percolating water can readily leach As from mineralised rock that is exposed through much of the Devils Creek catchment. Furthermore, natural seeps from mineralised rocks with high dissolved As concentrations have also been documented in the Devils Creek catchment (Hewlett et al., 2005). From the management perspective, the regional flux defines the lower limit for practical remediation of dissolved arsenic in mineralised areas. Individual sites should be remediated to discharge acceptably low dissolved arsenic concentrations in local streams. However, it is not plausible to require further remediation of major streams to below the natural regional arsenic flux levels.

6.4. *Control by mineralisation style*

Arsenic attenuation processes and consequent mobility depends largely on the specific geology of the area, which is evident when comparing the Globe Progress with the Blackwater Mine area (Table 3). Although the Globe Progress Mine has the same host rocks as the Blackwater Mine, mineralisation styles and consequent geochemistry differs significantly between the two deposits.

The extensive disseminated mineral deposits at the Globe Progress Mine contain abundant pyrite and to a lesser extent arsenopyrite. Natural weathering of the large mineralised rock volume results in a high downstream As flux (~30 mg/s) and elevated As concentrations (0.14 mg/L) in the Devils Creek (Table 3). The natural downstream flux from the Blackwater deposits is considerably smaller (5–6 mg/s), which can be expected from a significantly smaller mineralised rock volume principally consisting of one main lode (the Birthday Reef) (Table 3). When normalising the natural As flux against the mineralised rock volume, it becomes apparent that over 10 times more As is naturally derived from the Birthday Reef per km^3 rock volume, reflecting the high intensity of mineralisation in these deposits (Table 3). The deposits at the Globe Progress Mine are more widespread and yield less As per km^3.

In accordance with As flux values, the Blackwater deposits generate relatively low downstream As concentrations (0.01 mg/L), which are also influenced by waters that have not been in contact with mineralised rocks.

Mine sites in the Globe Progress area can produce very As-rich waters (up to 59 mg/L, Fig. 7) derived from arsenopyrite oxidation. Mine-related waters from the Blackwater Mine can be similarly high (52 mg/L), although these are generated by arsenolite dissolution. Arsenopyrite dissolution also generates elevated As levels at the Blackwater Mine, but do not exceed 1 mg/L (Snowy River adit). Attenuation of these As-rich waters from the Globe Progress mine is taking place in and adjacent to many mine sites by chemisorption onto abundant

Table 3 – Quantitative comparison of arsenic attenuation from the pyritic mesothermal Globe Progress Mining area and the mesothermal Blackwater mining area

Catchment	Blackwater River	Snowy River	Devils Creek
Deposits	Blackwater	Blackwater	Globe Progress
A Catchment area (km^2)	100	70	10
B Drained mineralised rock volume (km^3)	0.00027	0.00027	0.024
Mining sites			
C Maximum dissolved As (mg/L)	52	0.036	59
D Mining related As flux (mg/s)	0.7	4.5	4.6
Downstream environment			
E Dissolved As (mg/L)	0.01	0.01	0.14
F Flow rate (L/s)	600	900	230
G Total downstream flux (mg/s)	7	9	32
H Natural flux (mg/s)	6	5	27
I Relative natural flux (g/(s km^3))	22	17	1.1

(A) Inferred from map. (B) Calculated from strike length, depth and average lode width from Whetter (2006) for Globe Progress deposits and Christie and Brathwaite (2003) for Blackwater deposits. All of Globe Progress Deposits, located within a topographic high, are within the groundwater zone, whereas the depth of drainable Blackwater deposits is taken from the mining depth of 830 m. All of the deposits at the Globe Progress area are drained by the Devils Creek catchment, whereas the Blackwater deposits are drained to approximately equal parts by the Blackwater and Snowy River
(F) Flow rate measurements are crude but accurate within an order of magnitude Devils Creek flow rate from (Hewlett et al., 2005)
(I) Natural flux per km^3 mineralised rock: H/B.

HFO (Hewlett et al., 2005; Wilson, 2003). At the Blackwater Mine, HFO can occur locally in association with man-made structures, such as the adit or the man-made dam. However, its occurrence is very limited and attenuation mainly takes place via dilution downstream.

7. Conclusions

Mining and processing of arsenopyrite-rich ore to produce gold and to a lesser extent As trioxide at the Blackwater and Globe Progress Mine (Reefton gold field) has resulted in serious local contamination effects of site substrate, soil, and streams. Weathering and solution of As-bearing material is occurring and dispersion of As into the local ecosystem follows, especially as a result of rainfall events.

Our data show that underlying physiochemical controls play an important role in the attenuation of dissolved As in the Reefton gold field. These include geochemical gradients in the gold field itself and processing methods, which can generate site specific As minerals, such as arsenolite. Three attenuation mechanisms were identified in the catchments, where conditions allow. These operate in the spatial order downstream from the point sources: (1) precipitation of scorodite, (2) chemisorption to HFO and (3) dilution by tributaries.

Arsenic attenuation by precipitation of the secondary As mineral scorodite occurred in the substrate of the Prohibition Mill and Snowy Battery processing sites. This process immobilises, at least temporarily, some of the dissolved As from arsenolite dissolution. A strong control of scorodite on As mobility was also identified on a regional scale across a wide range of pH regimes.

Attenuation by chemisorption was found to depend strongly on the mineralogy of the bed rock. In the pyritic mineralised Greenland Group rocks of the Reefton gold field, such as the Globe Progress Mine, HFO from pyrite oxidation is ubiquitous and plays a pivotal role in As attenuation. In the non-pyritic mineralised rocks, such as the Blackwater deposits, HFO is mainly derived from ankerite dissolution, and only occurs where unnaturally large areas of mineralised rocks are exposed in adits or in the man-made dam composed of these rocks.

In the absence of significant adsorption sites, the anomalous hydrochemical signature generated by Blackwater mine sites currently exceeds ecosystem guidelines over 10 km downstream until it is diluted by regional catchment water. Furthermore, the process of dilution is strongly influenced by the morphology of the catchment. The Blackwater River is fed regularly by large tributaries, which causes rapid downstream dilution over the initial 4 km. The Snowy River catchment is comparatively narrow with small tributaries, and the anomaly generated by mine-related discharge and diffuse weathering from mineralised rock persists farther downstream (up to 10 km).

Nevertheless, in the downstream environment mine-related As contributions were relatively low in all three studied catchments, not exceeding 10% of the overall river load. Thus, our results suggest that in catchments with moderate relief and moderate rainfall, natural processes, particularly dilution and chemisorption, are sufficient to raise water quality. Rehabilitation, and expensive anthropogenic clean-up activity is unnecessary and unattainable for the downstream environment.

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