

Quantification and controls on As distribution in Westland, NZ

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Abstract

The Greenland Group, Westland, can be characterised with respect to environmental issues by the application of a GIS database (DAME), and specific sampling campaigns. Waters draining gold mineralised areas have a distinctive chemistry characterised by neutral pH and arsenic as a trace element. The acid neutralising capacity (ANC) from carbonates usually exceeds the maximum potential acidity (MPA) from sulphides resulting in circum-neutral pH. These waters are readily distinguishable from waters draining coal mine related areas, which commonly have low pH (~4) and low As concentrations (~0.1 ppm). In contrast, dissolved arsenic mobilised from Greenland Group historic gold mining areas is up to 2.4 ppm. This As mobilisation is controlled by the secondary As mineral, scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). Maximum dissolved As concentrations increase with increasing pH, corresponding to the increasing solubility of scorodite with increasing pH. Dissolved As is attenuated by dilution, precipitation of scorodite, and/or adsorption to iron oxyhydroxide (HFO). Adsorption to HFO is an important attenuation mechanism in and adjacent to many mine sites. HFO is abundant at mine sites where pyrite was abundant in fresh rock, such as where the mineralised zone is dominated by disseminated pyrite. Pyrite, and resulting HFO, are relatively rare where mineralisation occurred as well-defined quartz veins. Localised HFO occurs also where ankerite oxidises in host rocks. Arsenic output flux (ca. 25 g/day) from historic gold mine sites is commonly less than the natural background flux from mineralised rocks (>5000 g/day).

Keywords: West Coast, Arsenic, gold mining, pH, DAME database.

Introduction

Arsenic (As) is a trace metalloid which is of increasing environmental concern due to the growing awareness of its risk to plants, animals, and human health. Arsenic occurs naturally at an average crustal concentration of 1.5 mg/kg (Sparks, 1995). Mining activity can aid As mobilisation, which is especially pronounced in mesothermal gold deposits where As is commonly concentrated up to hundreds to thousands of times above the average crustal abundance (Hutchison and Ellison, 1992; Craw, 2001, Craw and Pacheco, 2002). The mining of New Zealand coal deposits and associated Acid Mine Drainage (AMD) is also known for weakly elevated As mobilisation (Black and Craw, 2001; Alarcon and Anstiss, 2002, de Joux and Moore, 2005).

In order to prevent or minimise mining related impacts on aquatic environments, 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 chemistry data from mined and un-mined areas. The purpose of this paper is to geochemically characterise Westland with respect to environmental issues by the application of the DAME database. Coal and gold have been mined on the West Coast of the South Island, New Zealand, since the 1860s (Brown et al., 2003). Historic mines were usually abandoned with little or no rehabilitation of the mine site or provision for the remediation of the potential metalloid-rich discharge and are therefore especially well known for elevated As

site output (Ainsworth et al., 1990; Baroni et al., 2000; Ashley et al., 2003). The database will be used to identify and quantify possible point-sources of aqueous As in Westland. Furthermore, differences between coal and gold mine related rock and water chemistry will be highlighted. Controls on As mobilisation and attenuation will be considered especially with respect to gold mineralised areas.

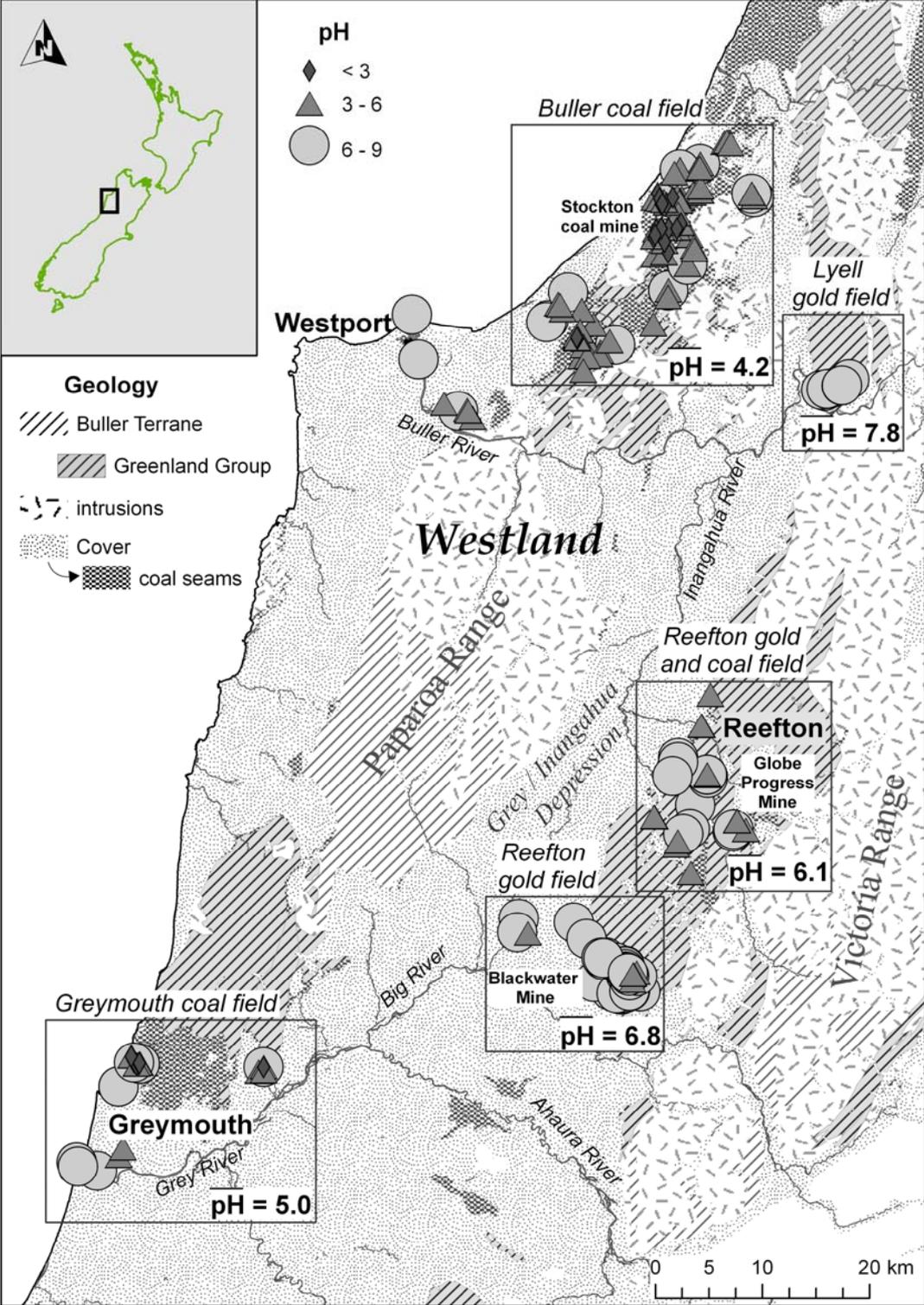


Figure 1. Geology and surface water pH of the West Coast, NZ (DAME database).

General Setting

Westland is a coastal region in the South Island of New Zealand on the western side of the Australian-Pacific plate boundary, the Alpine Fault. An outline of the major topographic features is depicted in Fig. 1. The area is confined on the eastern side by the Victoria Range, an inland mountain range (up to 1600 m asl), and to the west by the Paparoa Range, a coastal belt (up to 1485 m asl). In between these two mountain ranges lies a NNE trending valley, the Grey/Inangahua depression. This depression accommodates two main river systems, which drain the water flowing westward from the Victoria Range: the Grey River, which flows southwards and discharges into the sea by Greymouth, and the Inangahua River, which flows north where it joins the Buller River at Inangahua Junction. The climate of this region of New Zealand is characterised by very high annual rainfall with ~2300 mm in Westport and ~2900 in Hokitika. Mean annual temperature is approximately 12°C.

Geology

The basement Geology of the Westland region is dominated by the oldest group of the Buller Terrane, the Ordovician Greenland Group Fig. 1 (Cooper, 1989). The basement is weakly metamorphosed, quartzose, greywacke and argillite. In the Westland area these basement rocks have been folded into broad, NNE trending isoclinal folds (Cooper, 1989). The Greenland Group hosts mesothermal gold deposits the most of which are in the Reefton gold field (Rattenbury and Stewart, 2000; Christie and Brathwaite, 2003). The basement rocks are cut by a regional angular unconformity upon which rest the remnants of a Cretaceous-Tertiary sedimentary sequence, which was uplifted by a major change of tectonic activity (Kaikoura Orogeny), reducing cover across the region through erosion (Suggate, 1957). This sedimentary sequence ranges from the late Cretaceous Mawheranui Group to Quaternary gravels (Suggate, 1957). Part of the Mawheranui group are economic coal seams, the Paparoa Coal Measures, which are confined to north Westland, and the Brunner Coal Measures, which are widespread at the base of the Tertiary sedimentary sequence throughout the West Coast (Suggate, 1950).

Data processing

The DAME database comprises at present ca. 400 As analyses. In addition, approximately 1300 rock analyses were integrated in this study. Data handling and processing was conducted using Microsoft's Excel and Access software. For the illustrating and plotting of the data ArcMap, which is part of the ArcGIS software package (ESRI), was used.

In order to be able to illustrate and interpret the available pH data comprehensively, three pH categories have been defined. Arbitrary limits for each category were determined with the help of a histogram (Fig. 2). The histogram depicts two distinct pH groups with respect to pH. First, there is the circum-neutral to alkaline group forming the category ranging from pH 6 to 9. The second major group plots in the moderately acidic regime, ranging from 3 to 6. A third group is defined for the few waters possessing pH values below 3, thereby falling well below the natural range for surface waters.

The database includes the analyses of dissolved As (< 0.45 µm) as well as total (unfiltered) As. Other work from the Otago Schist, NZ, has shown that the difference between filtered and unfiltered samples is insignificant (Wilson, 2003) therefore no distinction between the two methods is made in this study. The As data are also grouped for the simplification and clarity of the presentation. Concentrations that fall below the WHO (1996) drinking water guideline of 0.01 mg/L form the first group. The second group ranges from 0.01 to 1 mg/L and can be considered as 'elevated' because samples contained in this group exceed the typical river

baseline concentration of As (~0.1-0.8 µg/L, Smedley and Kinniburgh, 2002) by orders of magnitude. The third group of samples exceeds 1 mg/L but stays below concentrations of 5 mg/L. 5 mg/L coincides with the typical upper limit of natural waters derived from As-rich provinces (Smedley and Kinniburgh, 2002). Waters containing more than 5 mg/L of As exceed the naturally possible range of As in river waters and form a fourth group.

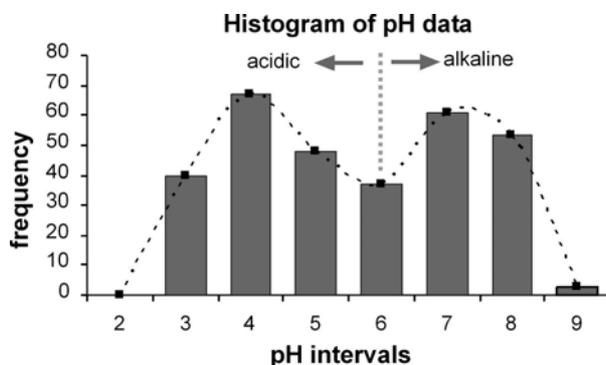


Figure 2. Distribution of pH data (DAME database)

River water chemistry and catchment geology are directly related. Of particular importance to this study is the relationship between geology and the water pH. The ability of the rock to produce acidity is generally expressed as the Maximum Potential Acidity (MPA). It is possible to determine MPA directly by one of several titrimetric approaches, but typically determinations are achieved by calculation from the pyritic sulphur content of the rock, using stoichiometric relationships (Sobek et al., 1978). It should be kept in mind that this method assumes that all the sulphur is present as pyrite, and complete oxidation and acid generation occurs. Thus MPA represents an upper limit on acid generation which is not necessarily reached. The MPA is balanced against the ability of the rock to neutralise acidic water, also called the Acid Neutralising Capacity (ANC) (Sobek et al., 1978). ANC determination is achieved by reacting a fixed mass of crushed rock with a known excess of concentrated hydrochloric acid while heating. The acidity remaining in the cooled, reacted fluid is titrated with a strong base back to pH 7, and compared with the initial acidity in order to determine the amount of protons consumed. The procedure does not discriminate among forms of neutralizers (carbonate minerals, exchangeable bases, and weatherable silicate minerals) and represents a theoretical maximum value for ANC.

Results

Geological controls on surface water chemistry

To illustrate the impact of economic stratigraphic units on surface water pH the sampling areas have been grouped according to their dominant commodities. Two sample areas have been defined to be influenced predominantly by coal deposits, the Buller and the Greymouth coalfields (Fig. 1), which contain the majority of the recoverable coal resource on the West Coast. The West Coast is also renowned for its gold mining history. The most important deposits are in the Reefton goldfield (see geology) which include the Blackwater mine and the Globe Progress Mine (Fig. 4). Within the general area of the Globe Progress Mine are also the Reefton coalfields which include a number of small historic opencast and underground mines and about eight active mines. Another smaller gold field, the Lyell gold field, is located farther north (Fig. 1).

Surface water pH and rock chemistry

The total range of pH recorded was from below 3 to over 8. Samples from the Greymouth and Buller coalfields have low pH, averaging 5.0 and 4.2 respectively (Fig. 1). These areas also include the widest range of pH values, comprising several occurrences of the lowest pH category (pH < 3). Samples from the Blackwater Mine area (Reefton gold field) and the Lyell gold field have circum-neutral pH, averaging 6.8 and 7.8, respectively. All samples from the Lyell goldfield fall into the circum-neutral to alkaline pH category (pH 6 - 9). The Blackwater Mine area is also dominated by waters from the circum-neutral to alkaline regime but includes some samples from the intermediate pH category (pH 3 – 6). In summary, coal mining related areas are drained predominantly by acidic water, whereas the mineralized Greenland Group areas generate circum-neutral waters. If an area includes both types of deposits, gold and coal, the average pH falls in between the typical pH of the two endmembers. Despite the wide range of pH values found in the studied area, the two largest rivers in Westland, the Buller and the Grey River, have circum-neutral pH when discharging into the sea.

The two rock parameters that influence water pH, namely ANC and MPA, are compared in Fig. 3. If the overall ability of the rock to produce acidity (MPA) is greater than the ability of the rock to neutralize (ANC) the rock analysis will plot above the 1:1 line and waters draining these rocks can be expected to be acidic. If the rock analysis plots below the 1:1 line waters in contact with the rock are neutralised or remain above neutral. The diagram (Fig. 3) confirms the findings of the pH distribution described above. Rocks from coal mining related areas (hollow squares) plot mostly above the 1:1 line, which correlates with the low pH found in those areas. Rocks from the mineralized Greenland Group (crosses) plot mostly below the 1:1 line, which is in accordance with the typical circum-neutral pH associated with the gold fields.

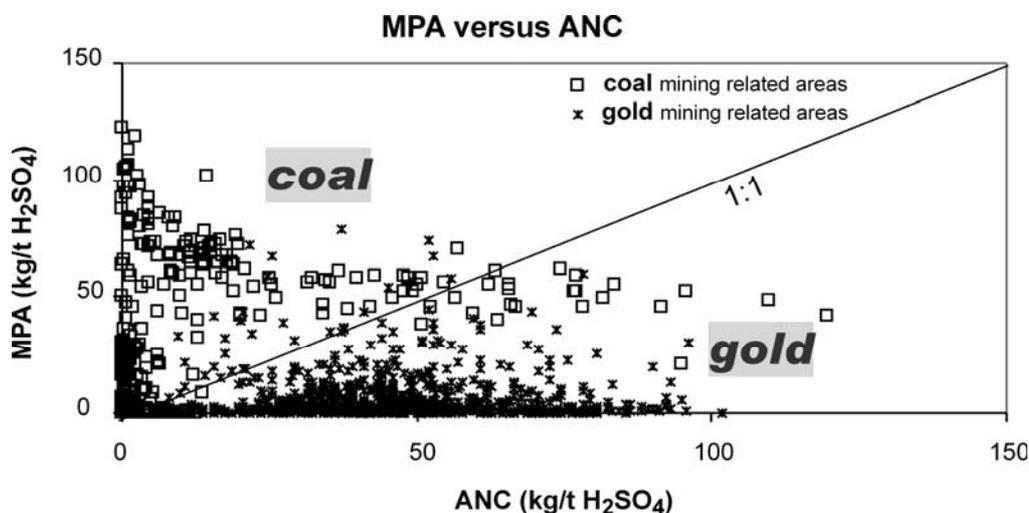


Figure 3. MPA versus ANC in gold and coal mining related areas.

Arsenic distribution and attenuation at historic gold mines

The majority of the As analyses from the Westland area fall below the WHO drinking water threshold concentration (0.01 mg/L, WHO, 1996), (Fig. 4a). The widest range of As concentrations were found associated with gold mineralized areas. In the Reefton gold field As concentrations range from 78 mg/L around the Prohibition Mill site (Blackwater Mine, Fig. 4c) and 59 mg/L in the region of the Globe Progress Mine (Fig. 4b) to below WHO drinking water thresholds (WHO 1996). In contrast, the Buller coal field and the Greymouth coalfield surface waters stay below 0.01 mg/L, apart from one location in the Greymouth coal field with elevated As concentrations (0.01 to 1 mg/L).

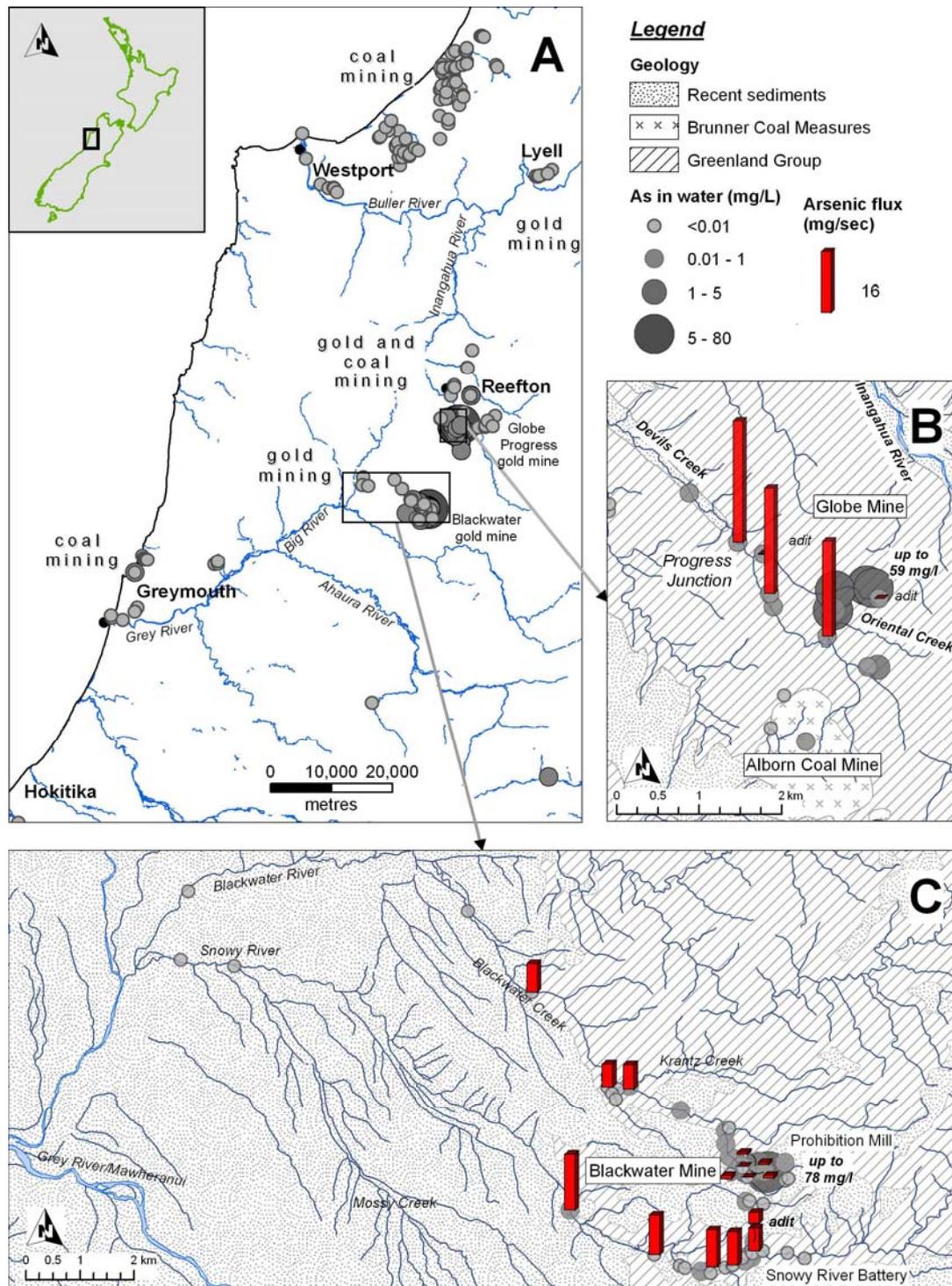


Figure 4. (A) Arsenic concentrations in West Coast surface waters, (B) geology, As concentrations and flux in the Globe Progress Mine area, (C) and the Blackwater Mine area.

The attenuation of the anomalously high As concentrations derived from the Prohibition Mill site and the Globe Progress Mine has been studied by specific sampling campaigns and the results are depicted in Fig. 5a, b. In case of the Prohibition Mill site drainage, high As site waters (52 mg/L) are attenuated by over an order of magnitude in the small creek draining the site (2.4 mg/L) (Fig. 5a). Arsenic concentrations continuously decrease further downstream, which is especially pronounced when tributaries join the drainage pathway. At approximately 4 km downstream of the Prohibition Mill site, As concentrations fall below the WHO drinking water guidelines (WHO, 1996) (Fig. 5a).

It should be noted that the sampling campaigns in the Globe Progress area cover a smaller distance (~1.5 km) compared to the sampling of the Prohibition Mill site drainage (~15 km). Hence, only local attenuation of As was observed in the former site. Similar to the Prohibition Mill site, waters discharging from the Globe Progress Mine adits are effectively attenuated immediately downstream of the adits (Fig. 5b). Adit drainage waters discharge into the Oriental Creek which experiences elevated As concentrations in the vicinity of the Globe Progress Mine (0.01 to 1 mg/L, see Methodology) and are over an order of magnitude higher than the concentrations found upstream of the mine area (< 0.01 mg/L). At Progress Junction the Oriental Creek joins the Devils Creek and As concentrations drop to 0.1 mg/L.

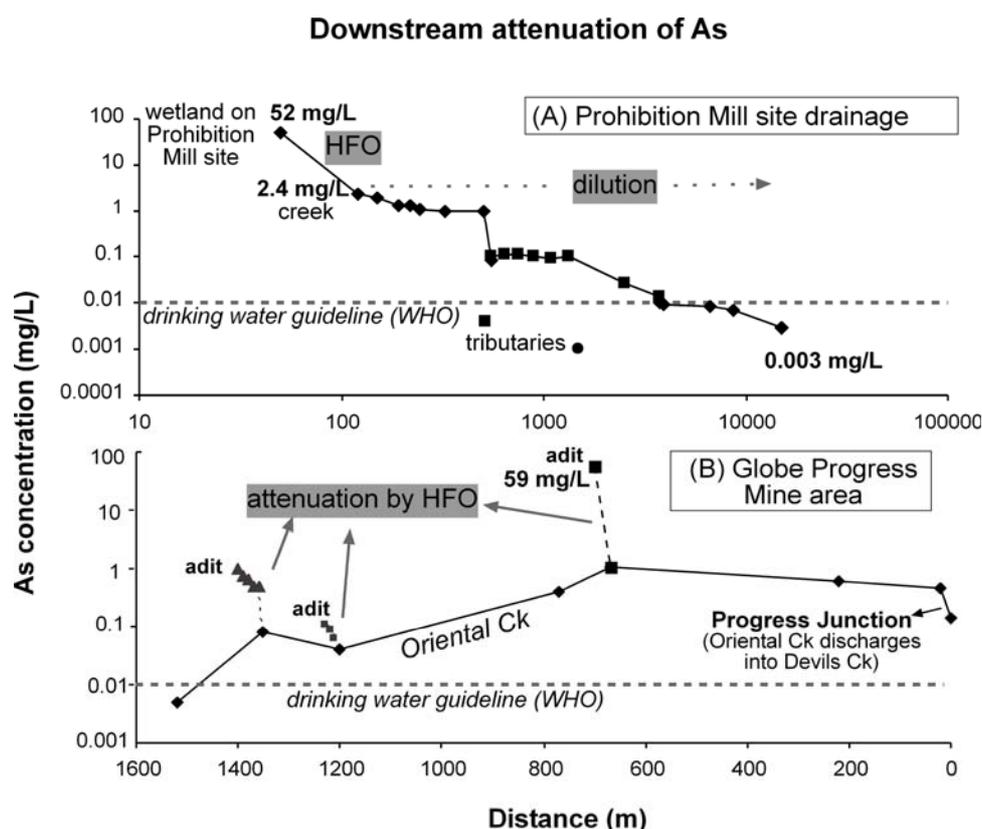
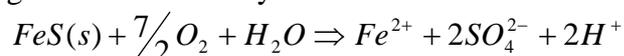


Figure 5. Downstream attenuation of arsenic (A) at the Prohibition Mill site (Blackwater Mine) and (B) in the Progress Mine area.

Discussion and conclusion

Greenland Group Geochemistry

Arsenic occurs naturally in the mesothermal deposits of the Greenland Group which consist mainly of quartz with variable amounts of pyrite, arsenopyrite, and stibnite (Christie and Brathwaite, 2003). Samples collected for a study of the Reefton Gold field contained as much as 5% disseminated arsenopyrite (Christie and Brathwaite, 2003). The oxidation of exposed sulphide bearing rocks gradually releases As into the environment (e.g. Bowell, 1992; Ashley and Lottermoser, 1999; Clark and Raven, 2004). This process is accompanied by the generation of acidity which is shown for the oxidation of pyrite in the following equation:



Mining practices can accelerate the natural rate of As mobilisation and acidification by increasing the area of exposed sulphide minerals in waste rock and tailings (Williams, 2001; Leblanc et al., 1996; Roussel et al., 1998; Langmuir et al., 1999; Shuvaeva et al., 2000).

However, the consequent elevated acid rock drainage (ARD) will be a problem only if oxidation of sulphide minerals produces more acidity than the parent carbonates can neutralise; i.e., when $MPA > ANC$ for a given body of rock. The Greenland Group metasediments contain calcite as a metamorphic mineral (typically 2-5%, Wilson, 2003), which is a very efficient pH buffer and counteracts acidification. In addition, the mineralised rocks of the Greenland Group also contain other carbonate minerals, such as ankerite (Christie and Brathwaite, 2003). These minerals, and others, contribute to high acid neutralising capacity (ANC) of the Greenland Group (Sherlock et al., 1995; Craw, 2001), (Fig. 3). In comparison, the MPA of these rocks is relatively low, as illustrated in Fig. 3, which shows that the waters draining these sites are effectively carbonate buffered resulting in circum-neutral pH. This is in accordance with the findings in Fig. 1, which shows that the typical pH of waters draining Greenland Group rocks possess alkaline pH values. In contrast, coal mining related areas consist of rocks possessing higher MPA than ANC (Fig. 3). For example, Brunner coal measures contain up to 5 wt% sulphur (Suggate, 1957) but the ANC for a set of Brunner Coal Measures samples from the Reefton area ranges as low as 0.0 - 0.1 wt% $CaCO_3$ (equivalent), (Hewlett et al., 2005) Thus waters draining coal fields fall generally into the acidic regime. Acid rock drainage in the West Coast region has been identified to be an issue for water quality and aquatic ecology, particularly downstream in catchments where Brunner Coal Measures are located (James, 2003). Mining can further lower the already naturally lowered pH and enhance the chemical signal of the underlying geology in the drainage waters.

Arsenic mobilisation

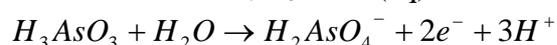
Mine sites commonly generate elevated high As concentrations and act as a point source of As. The extent of As mobilisation depends on the As minerals present and the oxidation-pH regime. The primary As source, arsenopyrite, is relatively stable under water-saturated near surface conditions (dissolved As $< 10^{-5}$ ppm, Craw et al., 2003). In oxidising conditions, however, arsenopyrite decomposes. Thermodynamic calculations predict that small (< 100 mV) redox rise yields up to thousands of ppm of dissolved As, neglecting kinetic effects and the development of a protective oxide coating on arsenopyrite surfaces (Craw et al., 2003). The dissolved As forms oxyanions, either arsenite ($H_xAsO_3^{3-x}$) or arsenate ($H_xAsO_4^{3-x}$) depending on redox conditions. Thus, at $pH < 9$ (Vink, 1996) arsenic decomposition can be described as follows:



This process can lead to very high As concentrations, which range up to 59 mg/L in the Globe Progress gold mining area (Fig. 4). If the mining operations involved the roasting of the ore, the presence of arsenic trioxide, As_2O_3 , either in the form of arsenolite or claudetite, can be expected (La Brooy et al., 1994; Clark and Raven, 2004) and ample arsenic trioxide was found at the Prohibition Mill site and the Snowy River Battery site, both part of the Blackwater gold mine. Arsenic trioxide is very soluble ($10^{-0.8} m$, ~12 g/L As; Vink, 1996). Hence, when rainwater interacts with the exposed arsenic trioxide it dissolves according to the following equation:



The product of reaction (X) is again the reduced arsenic species arsenite, $H_3AsO_3(aq)$. In the surficial environment (oxidizing conditions) $H_3AsO_3(aq)$ is unstable and will eventually oxidize to arsenate, $H_3AsO_4(aq)$. The following reaction may occur between pH 2.2 and 6.7:



In the presence of Arsenic trioxide very high As concentrations were encountered. For example, site waters of the Prohibition Mill site contained up to 78 mg/L. This means that according to Abernathy (1993), who suggested a lethal dose of 70 mg As, an intake of one litre of this water could be fatal. It should be noted that the significance of these issues to the

downstream environment is also in part related to the climate of the mining area, in particular rainfall. The sites examined are located in a wet climate, with As being mobilized on a daily or weekly basis.

Controls on arsenic mobility

The expanse and diversity of the samples included in the DAME database provide an insight into the hydrochemistry of As under widely differing pH regimes. The relationship between pH and aqueous As concentration is plotted in Fig. 6. 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 ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). In oxidising conditions and in the absence of goethite, scorodite is predicted to precipitate as a metastable phase in acidic solutions (pH < 5) with $a_{\text{As}} = 10^{-6}$. If dissolved As concentrations exceed $a_{\text{As}} > 10^{-4}$ scorodite can precipitate even under near-neutral conditions. The solubility curve of scorodite is added to Fig. 6. Different approaches and thermodynamic data causes some discrepancy in the final position of the curve. However, the overall trend remains the same matching the trend for dissolved As concentrations. Thermodynamic equilibrium is seldom reached in natural systems and it is therefore not surprising that the samples have lower As concentrations than the predicted scorodite solubility. These findings are confirmed by samples collected from the Blackwater mines where scorodite has been identified on the mine sites. The strong control of scorodite on the dissolved As output concentration under oxidizing conditions has also been noted in other cases (Krause and Ettel, 1988; Vink, 1996; Deutsch, 1997; Ashley and Lottermoser, 1999; Craw *et al.*, 2000; Williams, 2001; Smedley and Kinniburgh, 2002; Garcia-Sanchez and Alvarez-Ayuso, 2003; Borba *et al.*, 2003).

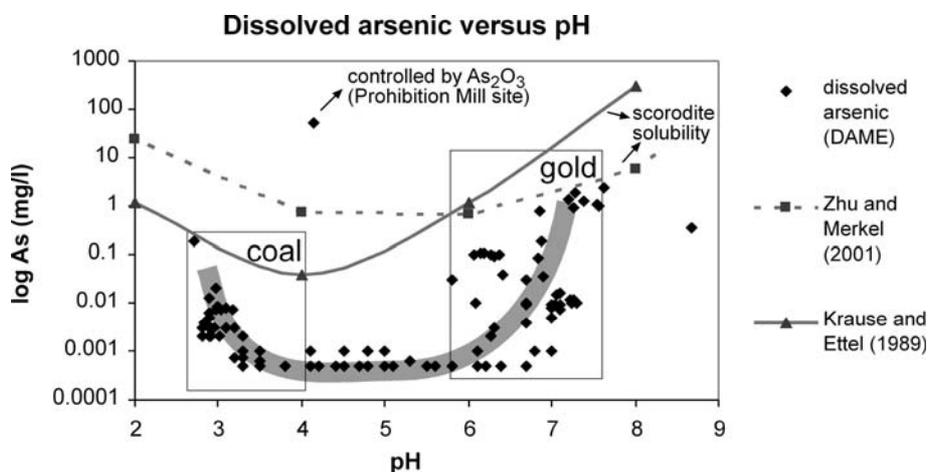


Figure 6. Dissolved As versus pH, including the scorodite solubility curve after Krause and Ettel (1989) and Zhu and Merkel (2001).

Arsenic attenuation

Once As rich mine waters enter the catchment, attenuation of As typically occurs via dilution and/or adsorption to iron oxyhydroxide (HFO) (Bowell 1994; Roddick-Lanzilotta *et al.* 2002; Swedlund and Webster 1999). The process of attenuation depends largely on the specific geology of the area. HFO is formed when acidic Fe-rich waters are mixed with circum-neutral waters. For example, the mineralised zone of the Globe Progress area is dominated by disseminated pyrite (Christie and Brathwaite 2003; Maw 2000) providing an abundant source of dissolved Fe. Thus, at the Globe Progress mine adsorption of As onto HFO is an important

attenuation mechanism in and adjacent to many mine sites (Hewlett et al. 2005; Wilson 2003; Craw et al. *in press*) and water discharging from the adits in the Globe Progress mine area experiences a decrease in As concentrations by approximately an order of magnitude before discharging into the Oriental Creek (Fig. 5b).

Around the Blackwater Mine mineralization occurs in well-defined quartz veins and compared to the Globe Progress area pyrite and resulting HFO are relatively rare (Christie and Brathwaite, 2003; Maw, 2000). Nevertheless, some localised HFO can form from the oxidation of ankerite in the host rock. This is the case at the Prohibition Mill site (Blackwater mine) where the oxidation of ankerite and subsequent precipitation of HFO reduces As concentration by over an order of magnitude from 52 mg/L in the wetland on site to 2.4 mg/L in the site discharge (Fig. 5a). Farther downstream, however, attenuation occurs exclusively via dilution which is the dominant attenuation process in this part of the gold field where pyrite is rare. The attenuation via dilution is less effective compared to the removal of As from the water phase by HFO and thereby allows elevated As signals to persist further downstream.

Arsenic flux

Arsenic concentrations in surface waters yield important information on the potential impact on the biosphere. However, they are not useful when defining the sources of As contributing to the overall river load. In order to compare the contributions of As rich mine water to the natural regional input, the As flux is calculated for the Blackwater and Globe Progress mines where possible. The results are displayed in Fig. 4b, c. The Blackwater Mine is drained by two major rivers, the Blackwater River and the Snowy River. The As flux in the Snowy River ranges from ~6 mg/sec upstream to ~10 mg/sec downstream of the Snowy River Battery site. The difference between the upstream and downstream value corresponds roughly to the contribution from the Snowy River Battery site, i.e. ~4 mg/sec, of which ~3 mg/sec originate from an adit discharging into the Snowy River just upstream of the battery site. The Prohibition Mill site possesses site waters with over two orders of magnitudes higher As concentrations compared to the Snowy River Mine site but this mine site contributes less than 10 % to the overall As river load of the Blackwater river (~7 mg/sec). These findings correlate with the data from the Globe Progress area where the As flux from adits discharging into the Oriental Creek (>0.3 mg/sec) is insignificant compared to the As flux of the receiving Devils Creek (up to 25 mg/sec). It can be summarised that even though some historic gold mine sites in the West Coast possess high As concentrations, they only contribute a small fraction (~25 g/day) to the regional catchment load of As. Consequently, the majority of the As is derived from natural background input (>5000 g/day).

Acknowledgements

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