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The hydrochemistry of Frongoch mine, mid Wales

Minerals and Waste Programme

Open Report OR/10/006



BRITISH GEOLOGICAL SURVEY

MINERALS AND WASTE PROGRAMME

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The hydrochemistry of Frongoch mine, mid Wales

J Bearcock, B Palumbo-Roe, V Banks, and B Klinck

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Photo taken from 272200, 274200 looking ESE over tailings and surface runoff at the Frongoch mine site, towards uncontaminated farmland

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British Geological Survey offices

BGS Central Enquiries Desk

☎ 0115 936 3143 Fax 0115 936 3276
email enquires@bgs.ac.uk

Kingsley Dunham Centre, Keyworth, Nottingham NG12 5GG

☎ 0115 936 3241 Fax 0115 936 3488
email sales@bgs.ac.uk

Murchison House, West Mains Road, Edinburgh EH9 3LA

☎ 0131 667 1000 Fax 0131 668 2683
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☎ 01392 445271 Fax 01392 445371

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☎ 01491 838800 Fax 01491 692345

Geological Survey of Northern Ireland, Colby House, Stranmillis Court, Belfast BT9 5BF

☎ 028 9038 8462 Fax 028 9038 8461
www.bgs.ac.uk/gsni/

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon SN2 1EU

☎ 01793 411500 Fax 01793 411501
www.nerc.ac.uk

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Summary

This report describes the hydrochemistry of the Frongoch mine site, mid Wales. The study characterises the spatial and temporal variations of groundwater and surface waters, and assesses dominant controlling processes.

The Frongoch mine site [SN 72 74] is situated in mid Wales. It was once mined for Pb, and to a lesser extent, Zn. The mine was abandoned in the early 20th century, leaving potentially reactive spoil and tailings which have a detrimental effect on the local groundwater and surface water.

Previous work has described the location and stratigraphy of the tailings area at Frongoch. The tailings layer is approximately 1 metre thick deposit discontinuously underlain by peat. The peat layer, of variable thickness, is underlain by glacial till and occupied the valley prior to the tailings deposition.

Groundwater was samples from three trial pits excavated to depths ranging from 1.65 to 3.35 metres below ground level and from three boreholes installed in the waste heaps to a depth ranging from 2 to 4 metres below ground level. The groundwater pH varied between 4.8 and 6.5. All waters were clearly dominated by SO₄ and characterised by very low alkalinity. This dominance is caused by the oxidative weathering, and subsequent dissolution of sulphide minerals. The scarcity of pyrite accounts for the pH values closer to neutrality. Zinc is the main contaminant of concern, with concentrations reaching 1735 mg/L in the groundwater. Other potentially harmful elements including Fe, Al, Ni, Pb, Co, Cu, Cr, and Cd, were highly concentrated.

The highest concentration of contaminants was generally found in the groundwater intercepting the tailings and underlying peat. Water collected from the clayey till underlying the tailings and peat units, although relatively less enriched in Zn, SO₄, Pb and Cd, has similar chemistry. This suggests that the contaminant plume extends down the underlying tailings through the peat layers to the glacial till.

Groundwater redox measurements reflect the redox potential dominated by the Fe (II/III) redox couple in the system. These measurements ranged from 210 to 470 mV.

Anglesite (PbSO₄) is at equilibrium or close to equilibrium at all the sites, except the adit and the mill pond, and it is likely to be the main mineral phase controlling the Pb concentration in solution. Modelled saturation indices for Zn minerals suggest that no obvious mineral exerts solubility control for Zn concentrations in solution.

The impact of the discharge of the tailings groundwater and surface runoff to the receiving Frongoch stream is indicated by very high concentrations of Zn (up to 97 mg/L), Fe, Al, Ni, Pb, Co, Cu, Cr, and Cd, which are present in waters discharging from the site in concentrations that could cause failure of water quality standards.

Water chemistry seasonal variations were indistinct in many element distributions (e.g. Cu, Cr, Pb, Ba, Sr), although Co, Ni, Zn and SO₄ had a strong seasonal relationship, with concentrations being higher in summer months.

1 Introduction

This study concerns the chemical quality of the surface water and groundwater at the abandoned Pb-Zn Frongoch mine in mid Wales. The mine was locally very important to the economy when it was operational, but now only mine spoils and an abandoned tailings lagoon exist. Frongoch mine site was included in the Environment Agency's (EA) Metal Mine Strategy for Wales, which highlighted the 50 abandoned mine sites within Wales that were known to have the greatest environmental impact.

This report characterises the groundwater and surface water of this site, outlining both temporal and spatial variability and assesses the likely controls on the hydrochemistry.

2 Geographical and geological setting

The Frongoch mine is located in mid Wales (Figure 2.1). It is situated in the catchment of the Afon Ystwyth, which drains westwards into the Irish Sea at Aberystwyth. The site is surrounded by pasture land. The site remains in industrial use, it is now occupied by a saw mill (Palumbo-Roe et al., 2009). The closest town is Aberystwyth, approximately 14 km to the west of the mine site.

Mineralisation at the Frongoch mine site is hosted in the Silurian, Llandovery, Devil's Bridge Formation (Figure 2.1). This is largely composed of thin turbiditic sandstone and mudstone couplets. The mudstones (up to 30 cm thick) are generally thicker than the sandstones and commonly comprise >60% of the sequence (Davies et al., 1997).

Mid Wales has a long history of metal mining. Early mining, principally for Cu, is attributed to the Bronze Age and is thought to have occurred at a number of sites in the mid Wales ore

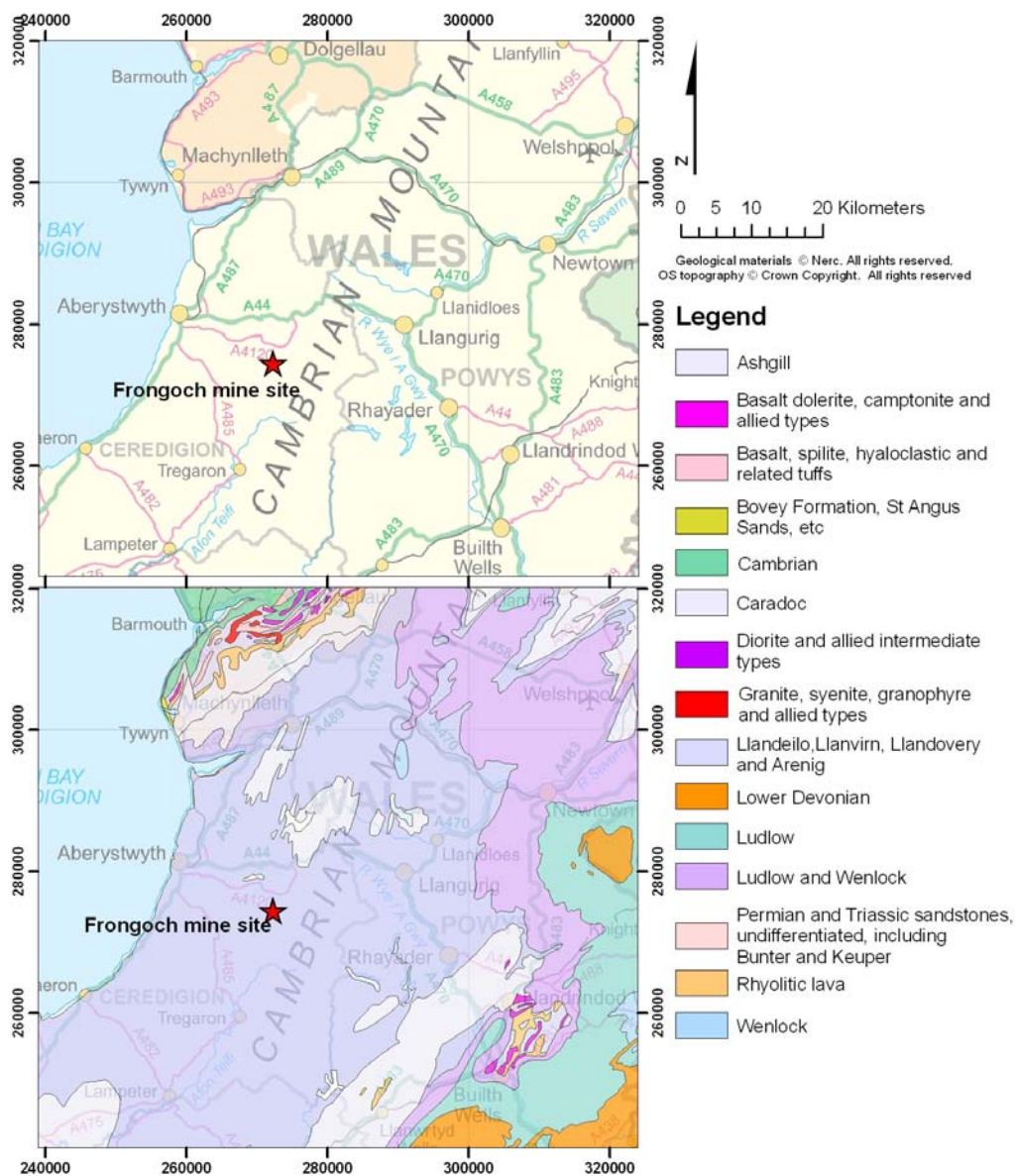


Figure 2.1 Location of Frongoch mine site within Wales and geology of the area

field, including Copa Hill near Cwm Ystwyth. It is thought that mining was temporarily abandoned in this area around 1400 BC because of drainage problems exacerbated by increased rainfall. The expense of installing and maintaining drainage is a factor that can make many modern mines uneconomical (Timberlake, 2003). It is thought that Romans were attracted to Britain because of its metal mining potential (EA, 2002) and there is evidence of Roman Pb, Au and Cu mining in mid Wales. After the Romans left, and the Anglo-Saxons and Danes invaded, metal mining was mostly neglected by the Britons and there is little archaeological evidence of metal mining during this time (Richardson, 1974). Subsequent to the Norman Conquest, mining regained importance; Pb was mined extensively in Wales during the 13th and 14th centuries and Pb was one of the principal exports during the Middle Ages. However, after the Black Death in 1348, the industry declined dramatically (Richardson, 1974; EA, 2002). A revival of metal mining in Great Britain occurred a few centuries later, especially when, in 1717 smelting began in the lower Swansea Valley using local coal as fuel. The use of metals boomed during the industrial revolution (1750-1900). The decline of metal mining in Great Britain began in 1850 and most of the mining had ceased entirely by the early 1920s (Richardson, 1974).

The mid Wales ore field is characterised by lodes: steeply dipping wall-like ore bodies. These were generally worked by shafts sunk through adjacent strata (Rees, 1969). Most of the mineralised veins in the mid Wales ore field are developed in steeply-dipping east-north-east-trending normal faults and joints. Where there is displacement across the veins it is very small. Many of these faults can be traced for several kilometres, but only small sections contain economic mineralisation (Davies et al., 1997). The most important economic minerals were galena, sphalerite, and to a lesser extent chalcopyrite. Lead was the main metal produced, with silver as a by-product. Zinc production varied locally from mine to mine and did not correlate in any way to the quantity of lead produced. During the main period of production, the price of Zn was low; hence this may have been left unworked in favour of the more economically viable Pb. Besides the economic minerals, quartz was the main gangue mineral, being ubiquitous throughout the ore field (Davies et al., 1997).

The Frongoch mine is typical of the mid Wales ore field and is one of seven mines exploiting the east-north-east-trending Frongoch Fault. The most productive section of this fault, which was about 450 m long, 260 m deep, and 11 m wide, was mined at the Frongoch site. Here the vein comprised two galena-rich lodes, and a sphalerite-rich lode (Davies et al., 1997).

The lease on Frongoch was taken up in 1759 (Lewis, 1967 cited in Palumbo-Roe et al., 2009) and continuously exploited for Pb until 1903, while in the early days of production Zn was only produced as a by-product when sphalerite was mixed with the galena. Owing to its low economical value a large amount of sphalerite would have been dumped on the tips. After 1879, when the mine operations transferred to new management, sphalerite became the dominant economic mineral and it was removed from the walls of the lode. The mine ceased operation in 1903 (Jones, 1922), and remained abandoned until a company was set up in the 1920s to exploit the sphalerite remaining on the tips. This continued until 1930, when mining activity at Frongoch ceased (Bick, 1996).

In 2002 the Environment Agency Wales produced a document designed to highlight the 50 metal mine sites in Wales with the biggest environmental impact. The Metal Mine Strategy for Wales aimed to bring together the site-specific opinions of various stakeholders to enable an assessment of all the problems at each site for use in future site management strategies. Stakeholders include local authorities, mining companies, archaeological and heritage groups, environmental groups and recreational groups, all of whom have different priorities relating to the sites. The longer term objectives were to review remedial action with relevant

stakeholders and to identify and secure funding for collaborative projects. The metal mine strategy summarises the key findings of the reports and provides detailed mine information on each of the 50 mine sites. Frongoch is included as one of the top 50 Welsh mines that impact the environment. This inclusion was on account of the abandoned tailings pond and tips which still contain abundant sulphidic material. The discharge from the mine causes “significant failure” of water quality in the Nant Cwmnewydion and Nant Cell (EA, 2002; Palumbo-Roe et al., 2009).

3 Hydrological setting

The low permeability of the strata that underlie the area has given rise to a high density of surface water courses. There are two westerly flowing rivers that capture the surface water of the area; these are the Afon Rheidol to the north and the Afon Ystwyth to the south. The mine tailings at Frongoch fall within the catchment of the Afon Ystwyth. Upstream of Frongoch in the Ystwyth catchment, the average annual rainfall is almost 2000 mm per year (1961-1990 average) (NRFA, 2009).

Figure 3.1 shows the locations of the hydrological features discussed in the text, below. Water enters the site by two main routes: overland flow from heavy rainfall, and from the Llyn Frongoch. Water from Llyn Frongoch, which is fed in part by an area of peat to the north of the site, discharges southward to an old mill pond at Blaenpenentre and continues in a southerly direction to a smaller mill pond [SN 7241 7453] on the mine site (Figure 3.2) and waterfall that enters the mine workings [Frongoch Stope; SN 7243 7456] (Figure 3.3). Water draining from Llyn Frongoch is clean, uncontaminated water, as it does not contact the tailings or spoil. Upon entry to the mine the surface water mixes with ground water, including a minewater contribution from the adjacent Wemyss Mine, which primarily discharges via the main adit [SN 713 742] (Figure 3.4) to the Nant Cwmnewydion, before entering the Afon Ystwyth at Abermagwr [SN 659 740].

Surface water falling on the site drains either directly (Figure 3.5), or via a culvert [SN 723 741] (Figure 3.6) on the eastern side of the tailings lagoon into a small stream (Figure 3.7),



Figure 3.1 The hydrological setting of the Frongoch mine (see text)

which flows along the eastern boundary of the site to discharge into the Nant Cell, before entering the Afon Ystwyth at Pont-rhyd-y-groes [SN 739 726]. The culvert is understood to strike approximately east, or southeast beneath the tailings lagoon, where it collects leachate from the tailings before discharging to the surface stream. The surface stream also collects field drainage from the agricultural land to the east of the site with further contributions (during wet conditions) from the sedge covered areas to the south of the site.



Figure 3.2 The mill pond at Frongoch mine site [SN 7241 7453]



Figure 3.3 Frongoch stope [SN 7243 7456]



Figure 3.4 Frongoch adit [SN 713 742]



Figure 3.5 Surface runoff



Figure 3.6 The culvert [SN 723 741]



Figure 3.7 Frongoch stream immediately downstream the culvert

4 Methodology

4.1 SITE INVESTIGATION

At the time of the investigation the Frongoch site was occupied by: a saw mill; old mine building; significant volumes of mine waste, and a former tailings lagoon, which occupied an area of approximately 170 m x 70 m, as indicated on historical (1887) maps (Figure 4.1). The lateral and vertical variability of the tailings were investigated with exploratory trial trenches (Palumbo-Roe et al., 2009), an electrical resistivity survey and a less extensive ground radar survey (Kuras et al., 2008). The investigation revealed the extent of the tailings deposits (up to 1 m bgl) as well as the nature of underlying strata, including peat (approximately 0.5 m) and glacial till (thickness not proven). A key observation was that low resistivities, matching those of the tailings, were found to extend to significant depths (up to 14 m bgl), suggesting downward leaching of solute from the tailings. Subsequently, a programme of core drilling and piezometer installation was implemented in order to verify the geophysical survey, to ascertain the groundwater level, quality and site stratigraphy and to provide some tailings core material for a PhD study on the microbiology of the tailings.

The findings of the ongoing study were used to produce a conceptual model of the tailings lagoon (Figure 4.2). The former tailings lagoon sits on a dark brown peat layer of variable

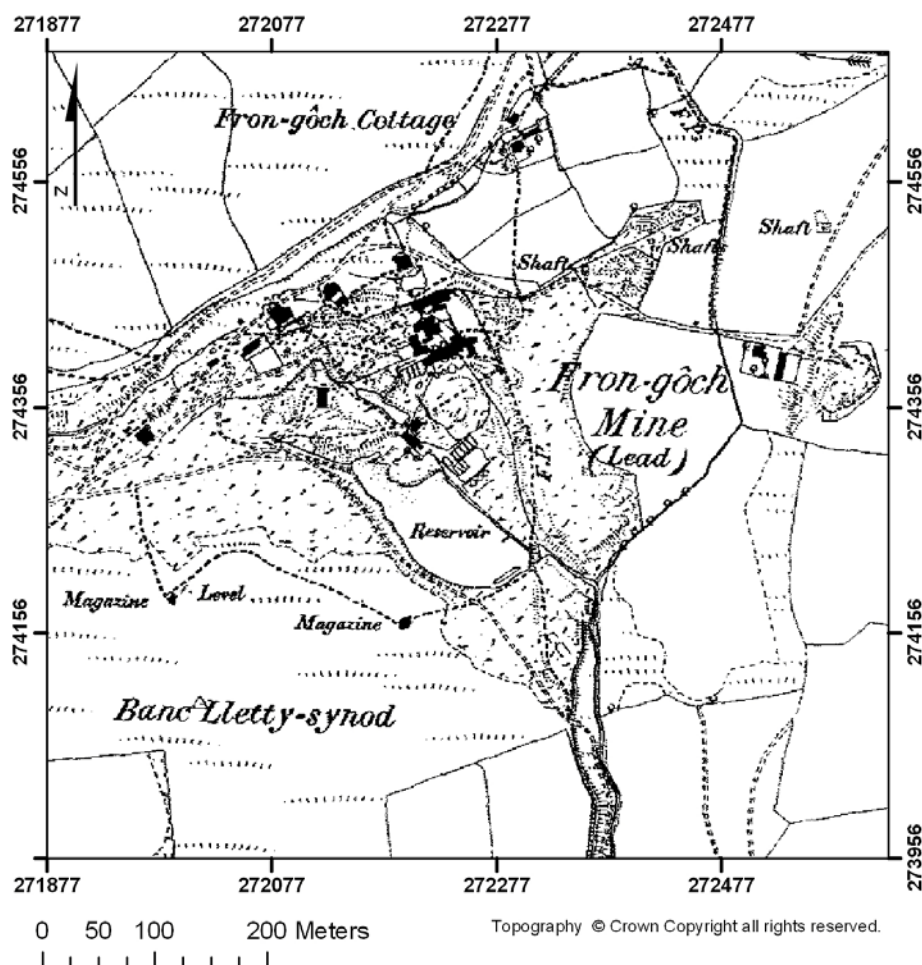


Figure 4.1 1887 map of the Frongoch mine site, showing tailings reservoir

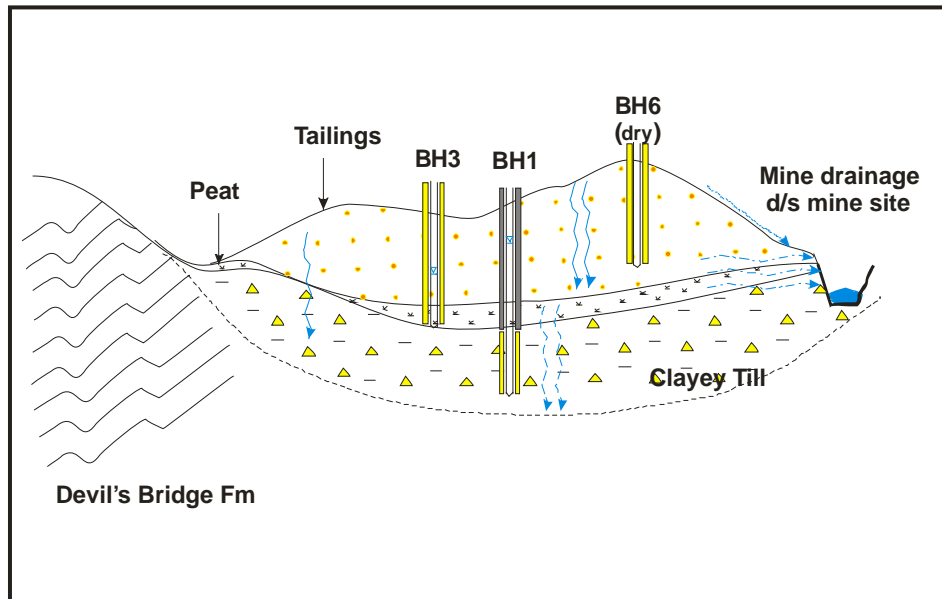


Figure 4.2 Conceptual model of Frongoch tailings lagoon and piezometer setting

thickness, underlain by clayey till (possibly head). The peat occupies a natural hollow in the bedrock. Historically, many tailings impoundments were placed directly on peat bogs to take advantage of their low permeability liner and potential to absorb ions. The peat layer is not, however, continuous throughout the base of the Frongoch tailings and contaminated seepage may infiltrate down to the clayey till. In addition to its hydraulic properties, the peat layer also provides an abundant source of organic carbon which may facilitate microbial sulphate reduction.

Figure 4.2 also shows the three boreholes and piezometers that were installed to monitor the groundwater quality of: the clayey till (BH1); the tailings and peat layers (BH3), and the coarser tailings stockpiled on the perimeter of the historical lagoon (BH6). The water that enters the mine waste heaps and tailings lagoon is thought to discharge via the culvert south of the tailings lagoon [SN 723 741] to the Frongoch stream. Site visits also revealed the significance of rainfall events in mobilising suspended solids, via runoff, from the tailings lagoon area.

4.2 TRIAL PITS

Prior to borehole drilling, three trial pits were excavated (Figure 4.3) in order to establish: the lateral and vertical variability of the tailings; the approximate groundwater level, and to provide an initial indication of groundwater quality. The pits were excavated on 8/8/06 using a JCB excavator, operated by the site owner, Mr John Bray. Trial pit 1 was excavated to a depth of 1.65 m below ground level; Trial pit 2 to 2.7 m below ground level and Trial pit 3 to 3.35 m below ground level. Groundwater seepages were encountered at the boundary between the tailings and the underlying peat, 0.72 m and 1.20 m below ground level in Trial pits 1 and 2 respectively. Two groundwater strikes were encountered in Trial pit 3; the first occurrence of groundwater was at 1.10 m below ground level at the tailings/peat boundary (Sample Trial Pit 3A), then the second groundwater strike was at 3.35 m below ground level (Sample Trial Pit 3B) in the mudstone (till). In addition to water samples, disturbed samples of sediment

were taken from the trench at each visible change in lithology. These sediment samples are discussed in Palumbo-Roe et al. (2009).

4.3 BOREHOLE DRILLING

During the 29-30th July 2008, eight boreholes (numbered BH 1-8, Figure 4.3) were drilled to depths of between 1 and 4 metres using the BGS Dando Terrier 2002 drilling rig. The rig was used in percussion mode with a 117 mm diameter casing. The exception to this was BH 8, for which a 102 mm diameter casing was used. The cores from boreholes 2, 4, 5, 7, and 8 were logged and returned to the BGS for sampling, and the holes were allowed to collapse. Piezometers were installed in boreholes 1, 3, and 6 (Figure 4.2). The piezometer in BH 1 was installed to the base of the drilled borehole. The borehole was back-filled with bentonite clay from 2.94 m below ground level to the surface, in order to intercept the groundwater flow in

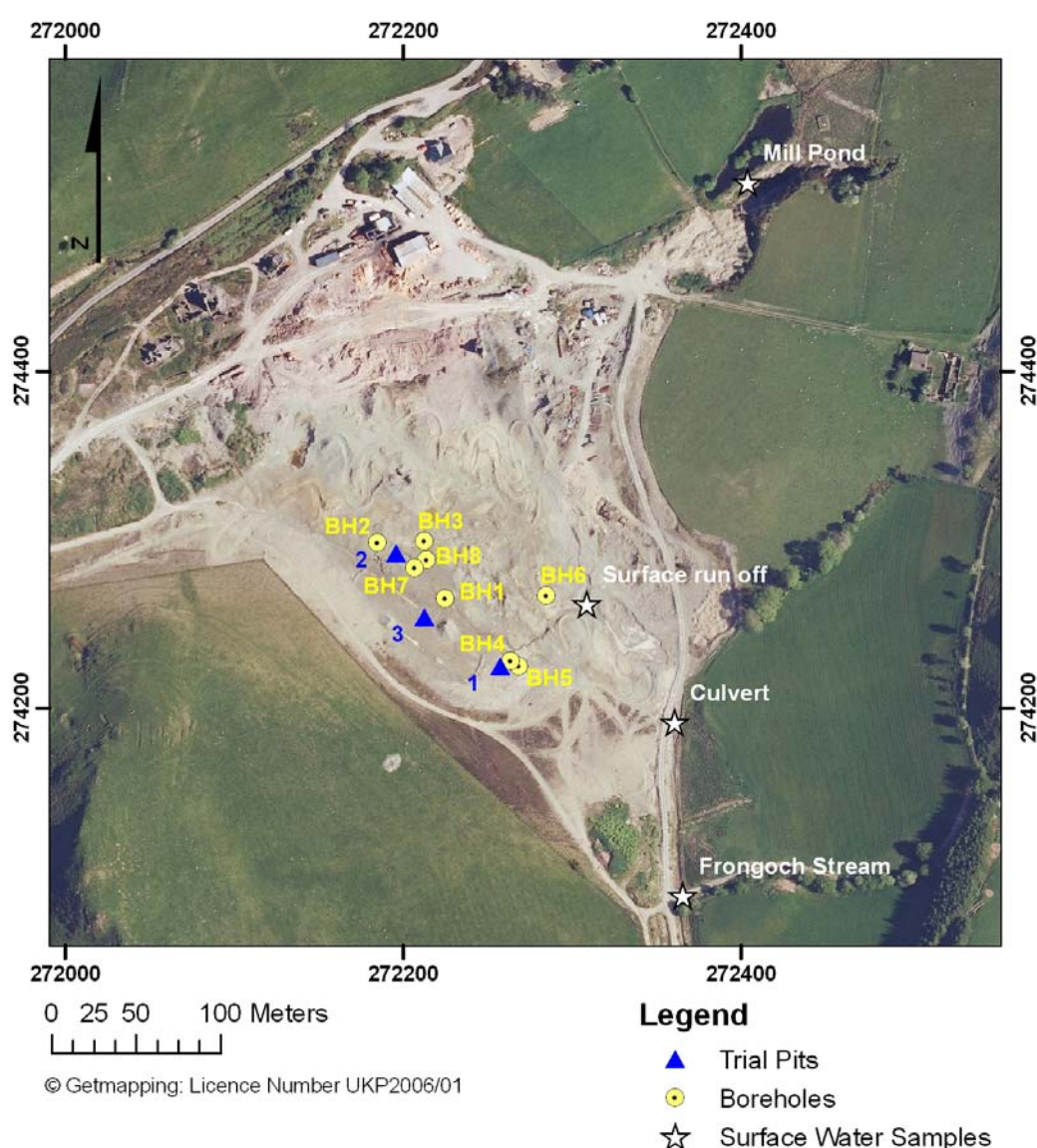


Figure 4.3 Location of trial pits, boreholes and surface water sampling points within the Frongoch mine site

the clayey till only. The piezometer in BH 3 was installed at the base of the drilled borehole at 2 m below ground level and intercepted the groundwater flow in the peat and overlying tailings. Borehole 6 was originally drilled to 4 m, but was back-filled with bentonite clay to allow the piezometer to be installed at 2.5 m below ground level, and to intercept groundwater in the tailings.

4.4 SAMPLING AND ANALYSIS

Samples of groundwater and surface water were taken at the Frongoch mine site between 2006 and 2009 in order to establish spatial and temporal hydrochemical variations. The samples were taken at different times of the year in order that any seasonal variability may be assessed, because seasonality of the hydrological regime may play an important role in controlling the concentrations of trace elements in solution.

All sampling sites and borehole locations are marked on Figure 4.3 and Figure 4.4. Sample site names and corresponding location information is given in Table 4.1. This table also shows which samples were taken on each visit to the mine site. Details of sampling procedures are given below.

4.4.1 Surface water sampling

Surface water sampling was undertaken where the water could be accessed safely at: the mill pond and waterfall upstream of the site; the culvert, the adit and “surface runoff” to determine the potential impact of the site on surface water quality, and Frongoch stream. The “surface runoff” refers to the transient runoff that flows over the tailings surface after rainfall; it was sampled to quantify the release of elements from the spoil during a short-term rainfall event. The mill pond was sampled to provide local background concentrations of the determinands, as this water does not contact mine spoil or tailings. Although some of the water that was sampled may originate from underground, i.e. the culvert and adit, they are accessed at the surface, so the surface water sampling methodology is used.

At surface water sampling sites, *in situ* measurements were made of: temperature, specific electrical conductance (SEC), pH, and redox potential (see Table A1). The water was filtered immediately using a syringe and a Millex sealed filter pre-loaded with a 0.45 µm cellulose membrane. For colorimetric Fe (II) analysis, 15 mL of the filtrate was added to 1.5 mL of a pre-made reagent containing the colour-forming agent 2,2' dipyridyl. The filtrate was also collected in two new sample-rinsed 30 mL Nalgene™ high density polyethylene bottles. One of these samples was allocated for cation analysis and was acidified to 1% (v/v) HNO₃ to prevent metal precipitation and minimise sorption on the container walls. The other sample was left un-acidified for anion analysis. An unfiltered sample was collected in a 30 mL Nalgene™ high density polyethylene bottle, and preserved with a pellet of NaOH for sulphide analysis. On the 2009 sampling trips filtered water was also collected for S isotope analysis, the volume required depended upon SO₄ concentration, which was estimated from the results of previous samples. In addition, a fresh sample of unfiltered water was used to determine dissolved O₂ (DO) using a Hach DR/850 colorimeter. The method uses a DO sensitive reagent vacuum sealed in a high range DO AccuVac® Ampule. When this Ampule is broken in the presence of DO a purple colour forms, which is proportional to the concentration of DO. Alkalinity was determined by titrating 25 mL filtered water against H₂SO₄, using a bromocresol green indicator solution.

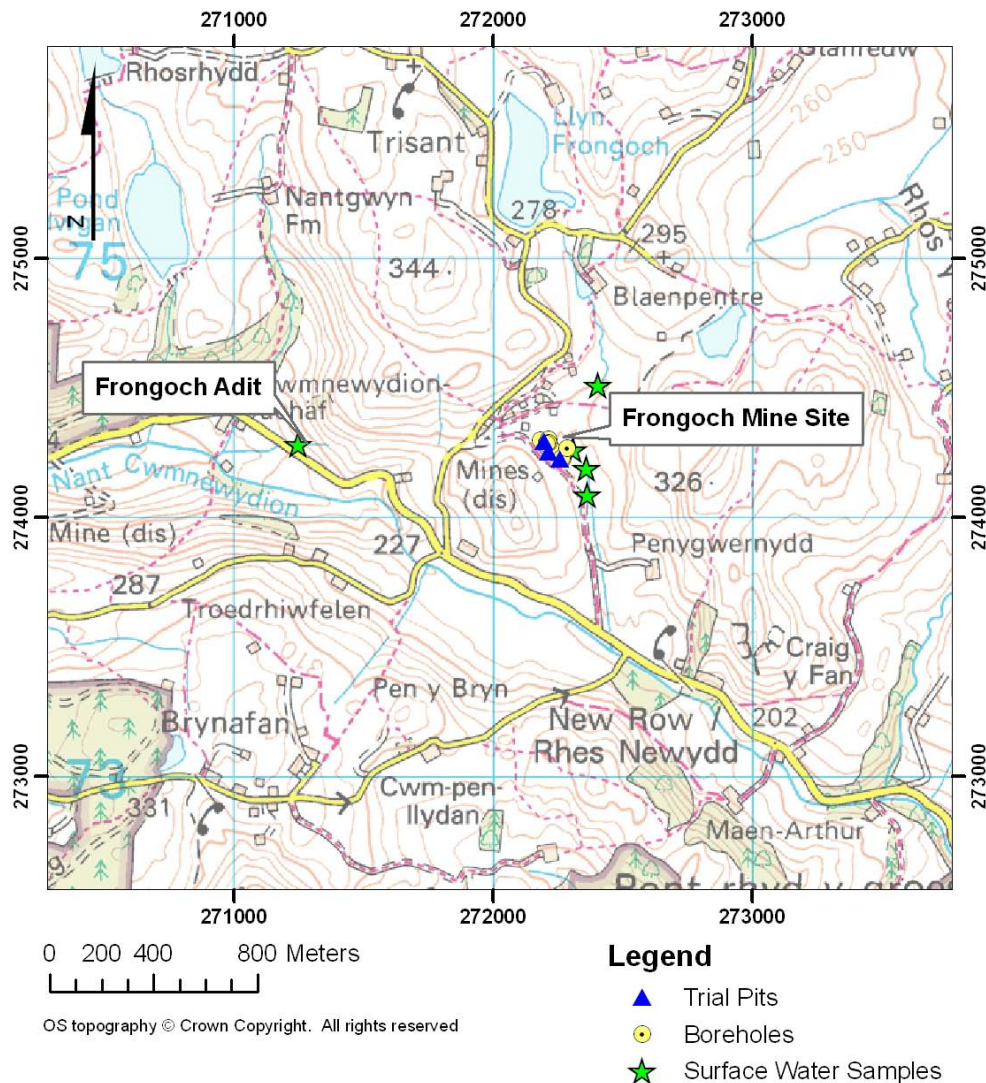


Figure 4.4 Location of Frongoch Adit in relation to the mine site

4.4.2 Groundwater sampling

Groundwater samples were pumped from each of the boreholes using an inertia pump. This process disturbs the water, and may introduce oxygen. Approximately 1 L of the groundwater was collected into a plastic jug, from which samples were taken and the physico-chemical parameters (Table A1) were measured. The subsequent procedure for sampling the pumped groundwater closely followed the surface water procedure (Section 4.4.1). The exceptions to this were: a high capacity groundwater filter was used, and DO could not be determined colorimetrically owing to high suspended sediment masking the colour-forming agent.

During the visit on 03/03/2009 approximately 1L of groundwater was pumped from each borehole and subsequently sampled using the methodology described above. Approximately an hour later a duplicate sample was taken. On 30/07/2009 BH 3 was sampled following this methodology, and BH 1 was sampled five times at intervals of approximately 20 minutes. This was to examine the effect that time and quantity of purged water would have on the results. Each time a sample was taken, about 1 L was pumped from the borehole.

Borehole 7 was allowed to collapse on the day of drilling, and BH6 had been dry on return sampling trips, so only the trial pits give an exclusive measurement of groundwater from within the tailings. It should be noted that BH3 intercepts groundwater present in both the tailings and the peat.

4.4.3 Analytical methods and data quality

Samples were stored in a cool box until they could be returned to the laboratory, where they were stored in a fridge (c.4°C) pending analysis. Analyses were carried out at the BGS Analytical Geochemistry laboratories in Keyworth. Analysis of major cations and total SO₄ were carried out by inductively-coupled plasma optical emission spectrometry (ICP-OES), Cl, SO₄, NO₃, NO₂, Br and F were determined by ion chromatography (IC) and a range of trace elements were analysed by inductively-coupled plasma mass spectrometry (ICP-MS).

The 2,2' dipyridyl-preserved water samples were analysed for Fe(II) using colorimetric analysis. During the analysis it was noted that reduced iron data for Zn-rich samples are subject to an unquantified interference from zinc that has not been corrected for and may be

Table 4.4-1 Samples and duplicates (*) taken on each visit to Frongoch

Site	Unique Lab ID	Easting	Northing	Sampled
Trial Pit 1	11475-0001	272258	274225	08/08/2006
Trial Pit 2	11475-0002	272196	274292	08/08/2006
Trial Pit 3A	11475-0003	272213	274254	08/08/2006
Trial Pit 3B	11475-0004	272213	274254	08/08/2006
Stream	11944-0001	272366	274089	30/07/2008
Culvert	11944-0002	272361	274192	30/07/2008
BH1	11944-0003	272225	274265	30/07/2008
BH3	11944-0004	272213	274299	30/07/2008
BH7	11944-0005	272214	274288	30/07/2008
Culvert	12093-0005	272354	274173	03/03/2009
Surface Runoff	12093-0006	272309	274262	03/03/2009
Mill Pond	12093-0007	272404	274512	03/03/2009
Adit	12093-0008	271251	274282	03/03/2009
BH1	12093-0001	272224	274263	03/03/2009
BH1 *	12093-0003	272224	274263	03/03/2009
BH3	12093-0002	272215	274295	03/03/2009
BH3 *	12093-0004	272215	274295	03/03/2009
Culvert	12188-0002	272354	274173	29/07/2009
Culvert*	12188-0003	272354	274173	29/07/2009
Surface Runoff	12188-0013	272289	274257	30/07/2009
Surface Runoff*	12188-0014	272289	274257	30/07/2009
Mill Pond	12188-0001	272404	274512	29/07/2009
Adit	12188-0004	271251	274282	29/07/2009
Adit*	12188-0005	271251	274282	29/07/2009
BH1	12188-0008	272224	274263	30/07/2009
BH1 * ¹	12188-0009	272224	274263	30/07/2009
BH1 * ²	12188-0010	272224	274263	30/07/2009
BH1 * ³	12188-0011	272224	274263	30/07/2009
BH1 * ⁴	12188-0012	272224	274263	30/07/2009
BH3	12188-0006	272215	274295	30/07/2009
BH3 *	12188-0007	272215	274295	30/07/2009

subject to a positive bias. As a result, the Fe(II) data marked with # in table A2 are exceeding the total Fe and the values are reported for information only.

Concentrations of major and trace elements determined in procedural blanks were negligible when compared with the reported data, less than 0.1%. Repeatability (i.e. the closeness of the agreement between the results of successive measurements carried out under the same conditions of measurement) estimated from field duplicates obtained from the adit and culvert samples was better than 2% for all elements under investigation (except for Fe and NPOC with a repeatability value of 5.2 % and 8.9%, respectively).

4.5 DATA ANALYSIS

The chemical data collected between 2006 and 2009 are presented in Section 5 and Tables A1, A2 and A3). The major-ion data are presented on a Piper diagram, which is used to describe the water type based on dominance of major solutes. All elements are discussed with regards to their concentration, seasonality, and the effects of borehole purging.

Saturation indices (SIs) were calculated for a selection of minerals (see Table A4 in Appendix 1) using PHREEQC (Parkhurst and Appelo, 1999) and the WATEQ4F.dat database (Ball and Nordstrom, 1991). Saturation indices were calculated twice using alternatively the Fe(II)/(III) redox couple and the Pt electrode-measured Eh value to derive the solution redox state, and the results of the methods were compared. Saturation indices are further discussed in Section 5. The SI is calculated from the equation: $SI = \text{Log}(IAP/K_{ss})$, where IAP is the ionic activity product of the specific reaction and K_{ss} the equilibrium constant. A SI of zero indicates that the solution is in equilibrium with a particular mineral. A $SI < 0$ indicates that the solution is undersaturated with respect to a particular mineral and a $SI > 0$ indicates oversaturation.

5 Hydrochemistry of Frongoch

Results presented here describe the hydrochemistry of the Frongoch mine site. There are three factors to consider: the concentrations and any general observations, seasonal variation, and the effect of borehole purging on the concentration in solution. The chemical concentrations and measured physico-chemical parameters are tabulated in Appendix 1.

5.1 PHYSICO-CHEMICAL PARAMETERS

5.1.1 General observations

The temperature of the *in-situ* samples varied between 6 and 20°C, but were broadly similar on each sampling trip.

The groundwater pH varied between 4.8 and 6.5. The surface water pH was highly variable with the adit and mill pond circum neutral, while the surface runoff and the culvert had values as low as 4.4 and 4.9, respectively.

The waters are generally oxidised. Where dissolved O₂ measurements are available, they indicate fully oxidised surface water. However, these measurements are not available for the groundwater, as this contained too much suspended sediment, which masked the colour forming agent in the colorimetric field method. This sediment could not be filtered or allowed to settle as these processes would introduce oxygen, and invalidate the result. The measured Eh values (Pt electrode-corrected values of 219-574 mV) also indicate that the waters are generally oxidised. The highest Eh values were found in the fastest flowing waters of the adit, culvert and drainage from the mill pond. The groundwaters had lower measured Eh values, but still represent waters which will have a tendency to oxidise.

The specific electrical conductance (SEC) varied greatly between sample. Specific electrical conductance can be seen as a proxy for total dissolved ions. The mill pond had the lowest SEC, at 69 µS/cm. Such a value is typical of waters with low concentrations of dissolved ions, and where rocks are resistant to attack (after Hem, 1992). In contrast, the adit has an SEC of ~120 µS/cm, the surface runoff and culvert ~300-380 µS/cm, the groundwater sampled from BH1 ~700 µS/cm and the groundwater sampled from BH3 had an SEC of up to 2200 µS/cm.

5.1.2 Seasonal variation

Whilst the lowest temperatures were recorded during winter sampling, and the highest temperatures during summer sampling, the groundwaters were generally cooler than the surface waters in winter and warmer than the surface waters in summer. Surface waters are more affected by ambient conditions, whereas groundwaters better reflect the long-term average temperature. As these groundwaters are most likely quite young this difference is slight and the groundwaters had a very similar temperature to the surface water on each sampling trip.

The measured Eh showed no particular seasonality, while the average pH value was slightly higher in summer (~pH 6) than winter (~pH 5.6). This is not a particularly large difference, but these values could reflect a different rainfall/ drainage regime over the different seasons.

The seasonality of SEC values was generally not significant. Any seasonal trends are limited for most of the sites, such that the measurements taken in the summer cannot be distinguished from those taken in winter months for the adit, surface runoff, culvert and ground water sampled from BH1. In contrast ground water sampled from BH3 varied significantly as the winter conductivity was 500 µS/cm, whereas the summer conductivity for this sample was

1800-2200 $\mu\text{S}/\text{cm}$. Borehole 7 was only sampled once, in the summer, and the SEC of the groundwater sample was comparable to that of BH3 at 1314 $\mu\text{S}/\text{cm}$.

5.1.3 Effect of borehole purging

Borehole 1 was sampled 5 times, extracting 1 L each time. This was to establish if there were any changes in concentration which could be attributed to volume of water purged prior to taking a sample. The difference between the minimum and maximum values was less than 5% for the temperature and pH, and the difference was less than 10% for the Eh and SEC. Temperature and Eh values fell with increased sample pumping, while conductivity increased. The pH values decreased slightly from 5.88 to 5.7, but increased again in the last sample collected (pH 5.88). This overall trend is indicative of a fresher groundwater sample being taken after more purging. Stagnant water within the borehole will gradually adjust to air temperature and equilibrate with air.

5.2 MAJOR ELEMENTS

General observations

Figure 5.1 presents a summary of the major-ion content of the water samples taken from the Frongoch mine site. It presents all the samples, including duplicates and sites visited multiple times, which were taken between 2008 and 2009. The trial pit data are not included. The cation data show a cluster of data points with no obvious dominance by Ca, Mg or Na+K. The original Na data reported (Table A3 in Appendix 1) are largely below detection. This is caused by dilutions, necessary because of the large Zn concentrations and analytical interference with Zn. Manipulated data were used to create Figure 5.1.

The anions are clearly divided into groups: those which are dominated by SO_4 and those which are not. All of the boreholes, the surface runoff on top of the tailings, and samples from the culvert which drains the tailings are clearly dominated by SO_4 . This dominance is caused by the oxidative weathering, and subsequent dissolution of sulphide minerals. The main sulphide minerals present in the mine waste heaps are sphalerite and minor galena, with only traces of pyrite (Palumbo et al., 2009). The scarcity of pyrite in the sulphide mineral assemblage may account for the observed absence of very low pH values typical of acid mine drainage. Excepted from the SO_4 domination are the mill pond, the adit, and a sample downstream of the culvert in Frongoch Stream. The mill pond represents clean water; this does not contact the tailings and is derived from the Llyn Frongoch (Figure 4.4). In the adit the relatively low SO_4 concentration may be attributable to mixing with unpolluted groundwater. The sample point downstream of the culvert was situated downstream of the zone of mixing of the culvert and the Frongoch Stream.

5.2.1 Seasonal variation

The concentrations of SO_4 , in particular, display some seasonal variations. For example in BH3 the concentrations of SO_4 were much higher in summer than winter. The SO_4 concentration in the samples taken during the winter was around 200 mg/L, in the samples taken in summer 2008 the concentration was almost 880 mg/L, and in the samples taken in the summer of 2009 the average concentration was around 2000 mg/L. Despite these large variations the water type does not change. Sulphate remains the dominant major ion for all of the mine site waters.

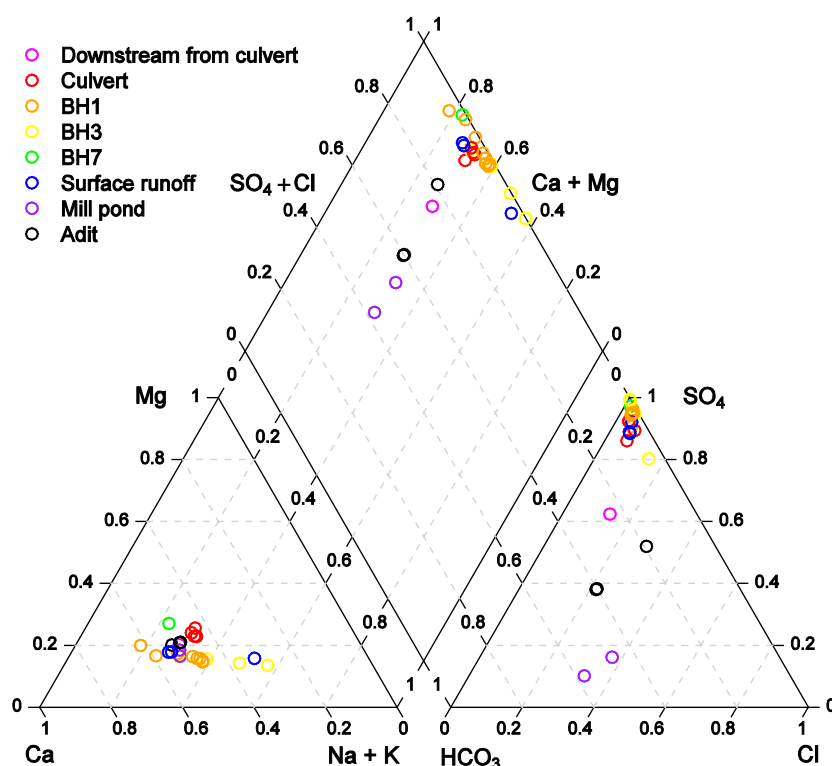


Figure 5.1 Piper diagram of samples taken from Frongoch site

5.2.2 Effect of borehole purging

On 3/3/09 BH 1 was sampled successively 5 times, extracting 1 L on each occasion, in order to establish if there were any changes in concentration that could be attributed to volume of water purged prior to taking a sample. The difference between the minimum and maximum values was less 10% for Cl, and SO₄, 10-25% for Ca, Mg and K, and 45% for HCO₃. The concentrations of Ca, Mg, K, HCO₃, and SO₄ showed a general trend of increasing concentrations within successive samples, consistent with increases in conductivity (section 5.1.3). While in some cases these increases may be small, it is evident that increased borehole purging gives rise to higher concentrations of these solutes.

Only the concentrations of K and SO₄ reached a plateau, after an initial rapid increase in concentration in the first few samples. As the remaining determinands did not plateau over time it appears that the water sample taken was not entirely representative of the *in situ* groundwater. These results indicate that in order to obtain a sample which better represents the groundwater these boreholes need in excess of 5 L of water purged prior to sampling.

5.3 POTENTIALLY HARMFUL AND MINOR ELEMENTS

These data (Table A2) are more variable than the major-ion data and are described below. Some of the potentially harmful elements are also discussed with reference to the relevant environmental quality standards (EQS), where applicable. These standards were established in order to provide a benchmark in order that the cleanliness of water courses could be assessed with a view to their improvement, as required by Article 16 of the Water Framework

Directive (2000/60/EC). The main aim of this Directive is that waters achieve “good” ecological status by 2015, which is assessed with respect to criteria set for various aspects of water quality (Wilby et al., 2006; EA, unknown date).

5.3.1 General observations

The dissolved organic carbon (DOC) concentration is very variable, both spatially and temporally. The concentration in the culvert varies between 0.5 and 2.3 mg/L, and this variation is typical of the surface waters; the mill pond ranges from 1.8 to 4.4 mg/L, and the surface runoff ranges from 0.6 to 4 mg/L.

The concentration of DOC in the groundwater varies between 1 and almost 10 mg/L. The highest concentration was recorded in a sample taken from BH 7 (tailings) on the day of drilling. Other than this maximum value, the samples taken from BH 3 generally have the most DOC on each sampling visit. The peat layer contained in BH3 is likely to be the source of the elevated concentrations. In addition examination of the cores revealed remains of timber buried in the tailings, which may provide an additional source of DOC.

The mill pond and the adit had the lowest concentrations of Mn (4-37 µg/L). The water samples were at the upper end of this concentration range when sampled during summer. The concentrations in the culvert were similar to those in the groundwater (250-550 µg/L) and the Mn present in the surface runoff was approximately half the concentration of the groundwaters.

Total Fe concentrations were very low in the surface samples (<0.5 mg/L). In contrast, the groundwater contains up to 31.1 mg/L. The Fe is present in the groundwater as almost entirely Fe (II) in thermodynamic equilibrium with the measured pH and redox conditions (Figure 5.2). Iron concentrations were lowest in the groundwater in the clayey till (head) (BH1), up to twice as concentrated in the groundwater intercepting the peat and tailings (BH3), and twice as concentrated in the groundwater in the tailings (BH7). The tailings surface runoff contains very little dissolved Fe.

Analyses of Fe (II/III) redox species and speciation with the WATEQ4F code (Ball and Nordstrom, 1991) were used to calculate Eh values of the studied waters. Comparison of calculated Eh and platinum electrode measured Eh (reading adjusted to a potential relative to that of the standard hydrogen electrode) shows a good correlation for most samples (Figure 5.3). Largest agreement is found for those samples with dissolved Fe concentrations above 10^{-5} mole/L (Figure 5.4).

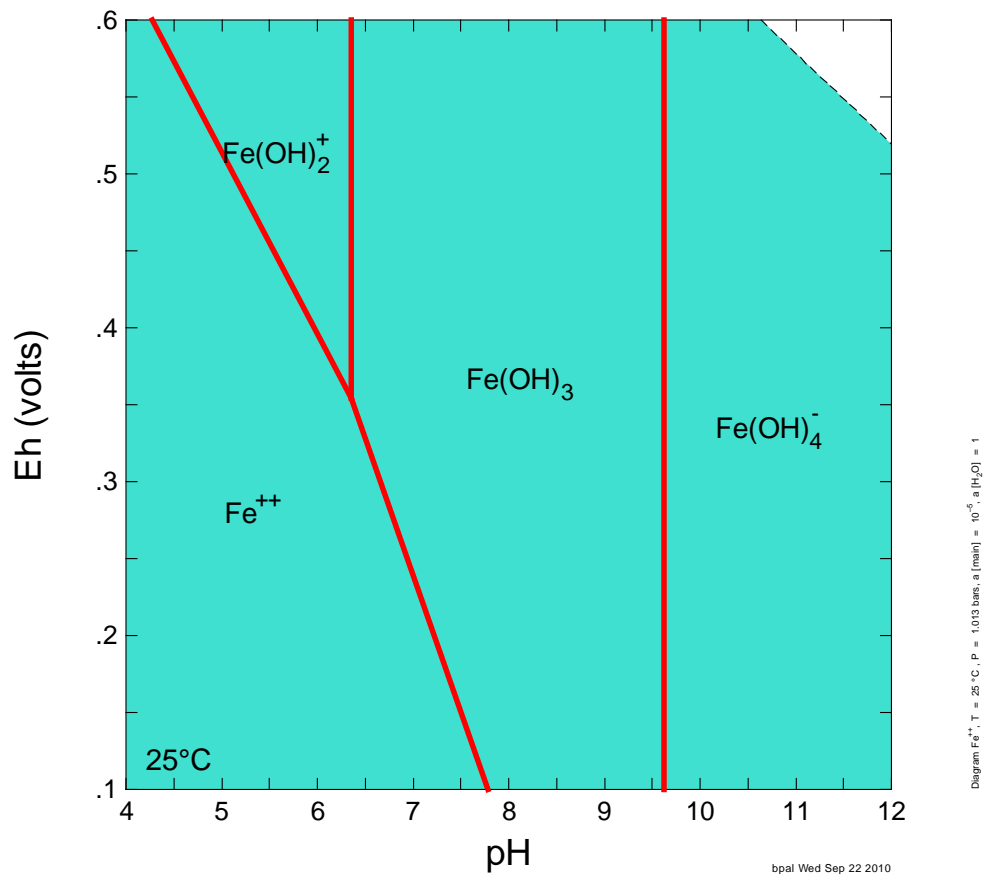


Figure 5.2 Eh-pH diagram showing aqueous Fe speciation at 25°C and Fe tot 1⁻⁵ mol/L derived from Geochemist's Workbench. Water samples fall in the aqueous Fe(II) stability field on the basis of the field Eh and pH measurements.

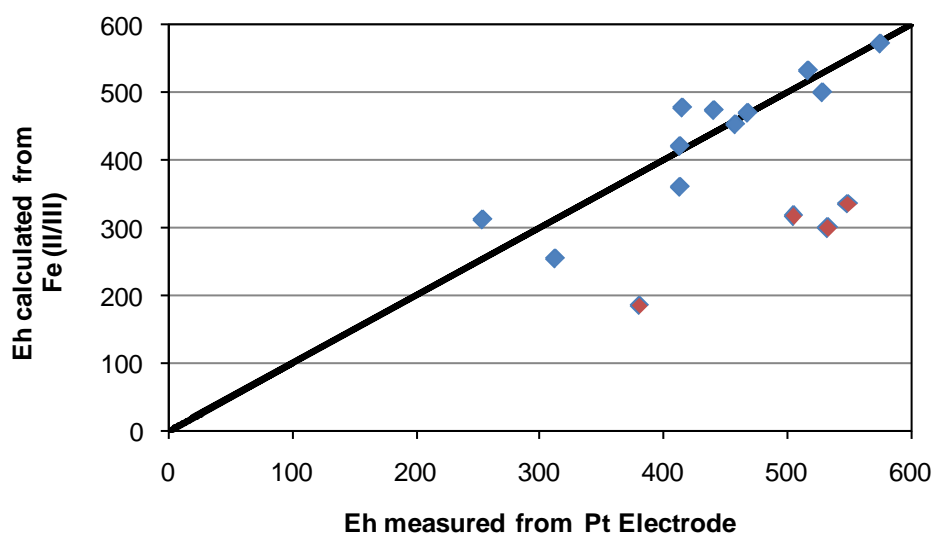


Figure 5.3 Calculated Eh (in mV) from Fe(II/III) redox species versus measured Eh in Frongoch water samples. Waters with the greatest deviations are highlighted with red diamond symbols.

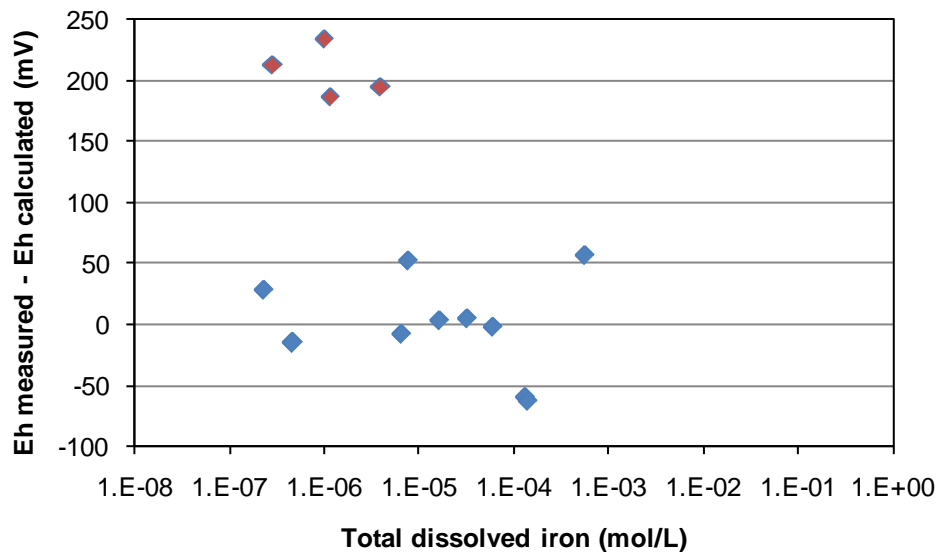


Figure 5.4 Difference between calculated and measured Eh plotted as function of total dissolved Fe concentrations. Symbols as in Figure 5.3.

The highest concentrations of Al are found in the groundwater and culvert samples. The maximum concentration was from groundwater taken from BH3 at 3.48 mg/L. The lowest concentrations were found in the mill pond and adit where the Al is below the detection limit (10 µg/L). The groundwater draining into the culvert contributes measurable Al, whereas Al in the adit was below detection. Aluminium is found in solution in waters of low or high pH (Stumm and Morgan, 1996). Unless there are complexing ions present, Al is only found at very low concentrations in circum neutral waters (at up to 100 µg/L) (Hem, 1992). This pH dependence is reflected in the data presented here; where the pH is above 5.5 the concentration of Al in solution is a maximum of 104 µg/L; below pH 5.5 the concentrations of Al in solution vary from 160 µg/L to 3.48 mg/L (Figure 5.5). The Al concentrations were generally higher in BH3 than BH1, indicating that, like the Fe, Al has probably originated in the tailings and percolated through to lower units.

Cobalt and Ni show very similar trends to Al. Both were below detection limits (3 and 5 µg/L, respectively) in the mill pond, and were very close to the detection limits in the adit. The highest concentrations were all found in the groundwater and the maximum concentrations of 163 µg/L Co and 169 µg/L Ni were found in the groundwater pumped from BH3. The concentrations in groundwater pumped from BH1 were generally lower. Cobalt and Ni have similar geochemical characteristics (Hem, 1992), they may substitute for Fe in certain minerals and tend to co-precipitate with Fe and Mn oxides. Hem (1992) identified a number of studies where Ni was shown to have a tendency to occur in waters where there were elevated concentrations of Co. The pH values of hydrolysis of Ni and Co in dilute solutions are 6.7 and 6.8 (Levinson, 1974). In the four instances where waters exceeded this pH the concentrations of Co and Ni are either below, or very close to, the detection limits defined above.

The national EQS for Ni is dependent upon water hardness. Increasing water hardness has a beneficial effect by reducing toxicity of certain elements, including Ni. The Frongoch samples were all soft water ($\text{HCO}_3^- < 25 \text{ mg/L}$), thus the maximum allowable annual average of Ni is $50 \text{ } \mu\text{g/L}$ (EA, unknown date). While the dilutional effects in the adit (section 5.2) mean that the Ni concentrations in the adit do not present problematic Ni concentrations, the drainage emerging from the culvert poses a risk of failure of this EQS. Cobalt concentrations are not covered by the statutory EQS, but the Environment Agency has included Co in their list of non-statutory EQS. The annual average of Co must be below $3 \text{ } \mu\text{g/L}$, with a maximum allowable concentration of $100 \text{ } \mu\text{g/L}$ (EA, unknown date). Despite dilution of the groundwater the drainage emanating from the adit and the culvert pose a serious risk of failure to meet this EQS, even after mixing farther downstream.

The copper concentrations were generally very low – most are below the detection limits ($5 \text{ } \mu\text{g/L}$). The only measurable concentrations were found in the surface runoff and the culvert; there was no detectable Cu in the groundwater. The highest concentrations were in the culvert at $154 \text{ } \mu\text{g/L}$. Copper is only stable in solutions with acidic pH values, and the culvert has some of the lowest pH values. Indeed the pH of hydrolysis of Cu^{2+} in dilute solutions is 5.3 (Levinson, 1974), and all the sites where Cu was below detection have a pH close to or above this.

Copper is another element where the toxicity and hence EQS is affected by water hardness. The annual average of dissolved Cu allowable is $1 \text{ } \mu\text{g/L}$ (EA, unknown date). The detection limit of the Frongoch data is $5 \text{ } \mu\text{g/L}$ meaning in many samples it is unclear if the drainage exceeds the EQS. The water draining from the culvert contains up to $154 \text{ } \mu\text{g/L}$, presenting a serious potential to breach the EQS, even after further mixing downstream.

Zinc is the most significant contaminant of concern at the Frongoch site. As sphalerite was often discarded as a waste material, the tips in particular contain much reactive Zn ore. Zn is stable in solution at circum-neutral to acidic pH values, which covers the entire range of sites

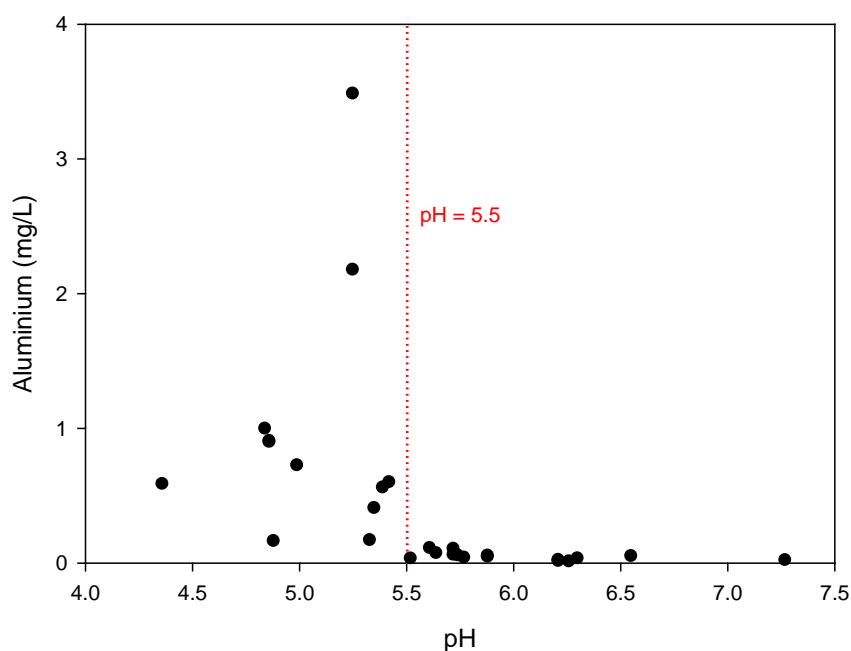


Figure 5.5 Effect of pH on Al concentration

in this study. The lowest concentrations were found in the mill pond. Both analyses of the mill pond (31 and 9 µg/L) are at the lower range of baseline groundwater concentrations for the area (after Shand et al., 2005). All the remaining samples contained significantly elevated concentrations of Zn. Groundwater from BH1 contained up to 250 mg/L Zn, but the highest concentrations were found in groundwater from BH3 (up to 1700 mg/L). This elevated Zn concentration correlates with the elevated SO₄ concentration and SEC measured in this sample. The surface runoff, which has contact with the surface of the tailings contained up to 85 mg/L Zn, indicating the extent of reactive surfaces. The culvert contained up to 97 mg/L Zn and the adit almost 6 mg/L.

These elevated Zn concentrations significantly exceed the WFD EQS (<http://www.defra.gov.uk/environment/quality/water/wfd/classification.htm>), which states that to protect aquatic life the total Zn must not exceed an annual average of 8 µg/L for waters with low alkalinity (hardness range 0-50 mg/L as CaCO₃). The dissolved Zn exceeds both of these values in the culvert and the adit.

The Cr concentration is close to, or below, detection limit (2 µg/L) in both the mill pond and adit. It is at concentrations of 4-5 µg/L in the culvert and surface runoff. Chromium is at its highest concentrations in the groundwater, between 6 and 22 µg/L. Higher concentrations are generally found in the water from the tailings and peat (BH3) rather than in the head (BH1), indicating that this element originates in the tailings and has percolated down to the underlying units. For the protection of sensitive fish life the dissolved Cr must not exceed an annual average of 5 µg/L. For the protection of other aquatic life the annual average dissolved Cr must not exceed 150 µg/L (EA, unknown date). The concentration of Cr in the culvert poses a potential problem to salmonid fish.

Arsenic measured in the Frongoch samples was rarely above the detection limit (15 µg/L). It was only measurable in the groundwater, where it is also generally close to the detection limit. The maximum concentration was 30 µg/L, which was measured in the BH1 water after 5 L had been pumped. The annual average of dissolved As must not exceed 50 µg/L (EA, unknown date). It is unlikely that discharges from the site will exceed this. Arsenic can sorb to Fe (III) oxyhydroxides (Hem, 1992), which, if colloidal/ suspended can contribute to the total As concentration.

Cadmium was below detection in the clean mill pond water (2 µg/L). There were relatively low concentrations in the adit (<10 µg/L). The surface runoff ranged from 150 to 260 µg/L and the culvert contained 110-200 µg/L. The groundwater contained the most Cd with around 300 µg/L measured in samples from BH1 and 300 µg/L to 1.7 mg/L in BH3. The annual average of total Cd must not exceed 5 µg/L (EA, unknown date). The concentrations of dissolved Cd in the culvert far exceeded this, indicating a potential environmental problem downstream of the site.

Lead was the main metal mined at this site, and while it occurs associated with Zn it was the galena which was exploited and therefore removed from tip and tailings material as thoroughly as possible. While there is no detectable Pb in the unpolluted mill pond, all the remaining samples contained appreciable quantities of dissolved Pb. The adit contained up to 414 µg/L Pb, BH1 contained up to 1 mg/L Pb, while the surface runoff and culvert contained up to 4.62 and 5.88 mg/L Pb, respectively. These were comparable with concentrations of Pb in BH3, which were up to 5.27 mg/L. In addition, groundwater in the trial pits contained 9.54 mg/L Pb. At low hardness values, such as at Frongoch, the annual average of Pb in salmonid waters must not exceed 4 µg/L, and in non salmonid waters it must not exceed 50 µg/L (EA, unknown date). The effluent discharged from the adit and the culvert significantly

exceed these concentrations, suggesting that, even after downstream mixing, the Pb concentrations may still exceed the EQS.

Sulphate is the main S species. The mill pond had the lowest SO_4 concentration (<5 mg/L), and the groundwater taken from BH3 during the summer months had significantly elevated concentrations of SO_4 (up to 2600 mg/L). In most cases reduced S accounts for $<1\%$ of the total S.

The range of SiO_2 concentrations in natural waters is generally 1–30 mg/L (Hem, 1992). The range of concentrations of SiO_2 recorded from the Frongoch site during this study was 1.5–25 mg/L. The lowest concentrations were found in samples of water from the adit and the mill pond; the highest concentrations in groundwater samples. While the maximum concentration is not particularly high it is possible that percolation through the tailings, with its large surface area, is responsible for relatively elevated concentrations of this solute. It is thus likely that the main control on SiO_2 concentration is a physical one.

Barium was generally found at very low concentrations in the Frongoch water samples. With the exception of the trial pits and the samples from BH7, the concentrations ranged from below detection (2 $\mu\text{g/L}$) to 24 $\mu\text{g/L}$. There is little to differentiate the groundwater from the surface water. High concentrations of SO_4 keep the concentrations of Ba low through the solubility limit of barite (Hem, 1992).

Strontium concentrations varied between 9 and 85 $\mu\text{g/L}$. The mill pond had some of the lowest concentrations (11–12 $\mu\text{g/L}$), and the adit and the culvert had Sr concentrations of 17–18 $\mu\text{g/L}$. Samples taken from the boreholes generally contained around 25 $\mu\text{g/L}$. An anomalously high concentration of 450 $\mu\text{g/L}$ was found in a sample from BH3 only in the 08/08/2006 sampling.

Molybdenum, Se, and V were below detection limits (15, 25, and 10 $\mu\text{g/L}$ respectively) or very close to them. Lithium and B (both 25 $\mu\text{g/L}$) were generally below detection except in July 2008 when they can be detected in all the groundwaters and July 2009 when they are detected in groundwaters sampled from BH3.

5.3.2 Seasonal variation

Samples were taken following a cold wet winter (in March 2009) and following two drier, warmer summer periods (30/7/2008 and 29–30/7/2009). Most of the samples were thus taken three times: twice during the summer and once during the winter (Table 4.1). Results were compared according to which season they were sampled in.

Cobalt, Ni and Zn have a strong relationship to the season in which sampling took place. Concentrations of these are generally higher in samples taken during summer months. This is especially true for samples taken from BH3, which contained 20 $\mu\text{g/L}$ Co in March 2009, but 78 and 163 $\mu\text{g/L}$ Co in the summers of 2008 and 2009, respectively. Likewise there was 70 $\mu\text{g/L}$ Ni in March 2009, but 230 $\mu\text{g/L}$ in the summer of 2008 and 169 $\mu\text{g/L}$ in the summer of 2009. Additionally, in groundwaters sampled from BH3, Zn was present at up to 143 mg/L when sampled in March, and at concentrations of 480 and 1700 mg/L when sampled in the summers of 2008 and 2009.

In general, Mn was found to be more concentrated during the summer months than in the samples taken during winter. For example, when sampled during the winter the Mn was present at about 140 $\mu\text{g/L}$ in the groundwater sampled from BH3. In the summers of 2008 and 2009 the concentrations were 1.55 mg/L and 550 $\mu\text{g/L}$, respectively.

Concentrations of Al were highest during the summer of 2009, especially in groundwater taken from BH3. This does not correspond to elevated concentrations in the groundwater taken from BH3 during the summer of 2008. The Al was more concentrated in winter than summer in groundwater sampled from BH1. This apparent lack of consistency in the Al data can be explained by the strong dependence on pH.

There are many constituents that do not appear to demonstrate a strong seasonality; these are: Cu, Cr, Cd, Pb, DOC, SiO₂, Ba, and Sr. There appears to be no clear seasonal variation in Cu, which seems to be purely controlled by pH (section 5.3.1 above). The pH is a little higher in summer than winter (section 5.1.2), but these differences are not sufficient to cause any Cu seasonality. It is difficult to define the seasonal variation of Cr as the concentrations are fairly low and constant. However, in general the concentrations of Cr are highest in summer, with the exception of samples taken from BH 1 where the samples taken in the winter contain more Cr. Cadmium also has little obvious seasonal variation. Concentrations of Cd in the culvert have increased with each successive visit, while concentrations in BH1 have decreased. In contrast the Cd in BH3 is present in low concentrations when sampled in March 2009, and higher concentrations when sampled in summer months. Lead appears to show little seasonality. There are fluctuations in concentrations, but these do not relate to the different times of year. There is no apparent DOC seasonality, which may be controlled by the variable distribution of organic matter within the surface environment and tailings. Variations in SiO₂ and Ba concentration between sampling trips do not appear to be seasonal. There is no clear pattern and it is likely that variation of SiO₂ is not controlled by temperature or rainfall. The Sr measured in solution is generally similar between sampling trips. The exceptions to this are the groundwater samples taken in July 2008, which are the highest three Sr measurements and bear no resemblance to the subsequent summer samples.

5.3.3 Effect of borehole purging

On 3/3/09 BH 1 was sampled successively five times, extracting 1 L each time. This was to establish if there were any changes in concentration which could be attributed to volume of water purged prior to taking a sample.

Manganese, Co, Sr, Ni, and Zn concentrations increased in each subsequent 1L sample. The concentration change may not be very large, but the increasing trends suggest that a representative sample had not yet been taken. Specifically the concentration of Mn in the repeat samples of BH1 increased by 16 µg/L between the first and last purging sample, whilst the Co concentrations changed by only 3 µg/L over the 5 successive samples. Similarly, Sr increased by 1 µg/L with each sample, from 22-26 µg/L. The concentration of Zn in solution increased steadily from 185 to 217 mg/L. The progressive increase in concentration implies that more purging is needed to obtain a concentration representative of the *in situ* groundwater.

Cadmium, Pb, and SiO₂ appeared to show a stabilisation of concentration in the purged samples. Concentrations of Cd in the first four samples increased from 278 µg/L to 330 µg/L. The 5th sample has a concentration of 320 µg/L. The Pb follows the same pattern, the first four samples show a successive increase from 665 µg/L to 1 mg/L, while the 5th sample has a concentration of 826 µg/L. Silica concentrations increased gradually between 11.9 and 12.6 mg/L in the first 4 samples, the final sample gave a reading of 12.4 mg/L. These data may represent a stabilisation of Cd, Pb, and SiO₂ concentrations, but the latter reading could be an anomaly. Further sampling would be needed to assess sample representation.

Aluminium, Cr (8 to 9 $\mu\text{g/L}$) and DOC did not show any trend with increased purging. In contrast the Al concentration varied from 39-104 $\mu\text{g/L}$; and DOC from 1.69-3.35 mg/L ; it is unclear if increased purging would give a more stable result.

Barium concentrations varied between 11 and 14 $\mu\text{g/L}$, and showed a general downward trend, stabilising after the 3rd reading. The range of concentrations is so small that this may not represent any hydrochemical change with increased purging.

Iron is the only element where both redox-sensitive species have been accounted for. The Fe(II) is measured and the Fe(III) is calculated by subtraction from total Fe. The time-series data from waters sampled from BH 1 demonstrate how the total Fe concentration was controlled by the oxidation of Fe(II) and subsequent precipitation of Fe(III) oxide. In all cases the Fe in solution was present as reduced Fe (II). The first sample, which would have been exposed to air in the borehole contained <4 mg/L total Fe. The concentration increased sharply in the following 2 samples to ~7 mg/L , and reached a plateau in the final 2 samples. The fresher samples contained more Fe as the sample stabilised immediately with HNO_3 , so that the Fe did not oxidise and precipitate.

5.4 MINERAL SATURATION INDICES

Mineral saturation indices (SIs) in Table A3 indicate the thermodynamic tendency of the analysed waters to precipitate or to dissolve certain minerals. The SIs were calculated using the Fe(II)/(III) redox couple whenever available to derive the solution redox state.

Calcite and dolomite are undersaturated in the Frongoch waters. This is typical of carbonate-poor siliclastic rocks. Calcite and dolomite are amongst the most reactive minerals meaning that their dissolution products are disproportionately abundant in natural waters. When calcium carbonate minerals are present in rocks and soils at a level of 1% or more they will tend to dominate the aqueous chemistry (Langmuir, 1997). The undersaturation of these minerals in the Frongoch waters indicates their scarcity in the host rocks.

Quartz ranges from undersaturated to supersaturated, yet the more soluble amorphous SiO_2 is universally undersaturated. In comparison quartz is very insoluble so saturation can be obtained after limited quartz dissolution. Quartz is undersaturated in the waters which may be young or mixed with young waters (the mill pond and adit), which have had less time to equilibrate.

Despite the low solubility of barite (Hem, 1992), the scarcity of it in the mid-Wales orefield means that it generally does not obtain saturation in the Frongoch waters. The degree of undersaturation is greatest in the young water of the mill pond and the diluted water of the adit. In most other cases the barite is close to equilibrium. If it was more abundant the low solubility would mean that barite saturation was attained.

Fluorite and gypsum are all undersaturated. Fluorite is a common gangue mineral with low solubility, so it may be expected to be saturated in the Frongoch waters; this is not the case however. Fluoride concentrations in stream waters are low <30 $\mu\text{g/L}$ over much of mid-Wales as a result of the underlying geology (British Geological Survey, 1999). It is therefore likely that the availability of fluoride is limited at the Frongoch site. Gypsum is a very soluble mineral, which is reflected in its SI as it is under saturated. As sulphate dominates the waters, the Ca concentration will be the controlling factor. The decomposition rate of anorthite is slow (Hem, 1992), which is reflected in the understauration in all the waters at the Frongoch site, which are relatively young.

All the samples are supersaturated in goethite and most samples (except for the mill pond) are saturated with respect to poorly crystalline ferric hydroxide. Because goethite is less soluble

than metastable hydrous ferric oxides, it will always be supersaturated in a solution that is saturated with respect to ferrihydrite and amorphous ferric hydroxides (Nordstrom and Alpers, 1999). The waters sampled from the culvert, mill pond, and adit are all undersaturated with respect to jarosite. These are the sample sites with the lowest SO_4 and K concentrations, which are constituents of this mineral. Surface runoff from the tailings and some of the groundwaters with a pH ranging from 4.36 to 5.74 (except for one sample with pH 6.21) show supersaturation in jarosite. Plumbojarosite is identified by mineralogical analysis on the top layers of the tailings, so it is possible that this mineral is also controlling the solution composition. Melanterite, the Fe(II) sulphate salt is undersaturated in all waters.

The sulphates of Zn and Cd, zincosite (ZnSO_4) and CdSO_4 , are mostly undersaturated in the Frongoch waters as a result of their relatively higher solubility in comparison to the carbonates of these elements (after Faure, 1998). The SIs for the carbonates of Zn, and Cd (smithsonite, and otavite) are generally closer to equilibrium, however, without reaching equilibrium, with the exception of Zn supersaturated with respect to smithsonite in one water sample (BH3 on 30/07/2008).

Anglesite (PbSO_4) is at equilibrium or close to equilibrium at all the sites, except the adit and the mill pond. It is likely to be the main mineral phase controlling the Pb concentration in the SO_4 anion-dominated solutions. Anglesite is also identified by mineralogical analysis in the tailings. Cerussite (PbCO_3) is near saturation in the adit and in the Frongoch stream downstream the culvert; the greater stability of cerussite rather than anglesite in these waters corresponds to a decrease in sulphate in solution.

6 Conclusions

6.1 LEVEL OF CONTAMINATION

The Frongoch mine site features in the EA's metal mine strategy for Wales as one of the 50 most polluting sites in Wales. Groundwater and surface water runoff from the site provide potentially harmful solutes to local watercourses, and many trace elements (Fe, Al, Ni, Zn, Pb, Co, Cu, Cr, and Cd) are present in concentrations that can cause failure of environmental quality standards. Potentially harmful elements (PHEs) including Fe, Al, Ni, Zn, and Pb are concentrated in groundwater and surface waters at concentrations reported in mg/L. The points from which contaminated water can issue are numerous, which is typical of many abandoned mine sites. This makes devising a suitable remediation strategy complex.

In terms of solute concentration, the most polluting output from the site is derived from the culvert, although after mixing with the Frongoch stream the PHE concentration is generally comparable with the adit. The exceptions to this are Zn, which is around 3.5 times more concentrated in the Frongoch stream than the adit, Pb which is 4.5 times more concentrated in the stream than the adit, and Cd which is around 3.5 times more concentrated in the stream than the adit. This assessment does not take the flow and therefore total metal loading into account. Flow data are needed to evaluate the total potentially harmful element input into the Ystwyth catchment.

6.2 SEASONAL VARIATION

Palumbo-Roe et al. (2009) noted that the solute transport in the tailings is governed by unsaturated flow, and is controlled by seasonal precipitation-evapotranspiration cycles. If this is the case the concentrations should be higher in summer months, which are generally drier and therefore any rainfall event will mobilise freshly precipitated soluble salts. In general, where any seasonality is displayed, elemental concentrations are higher in the summer months, and this is especially true of the groundwater sampled from BH3.

6.3 EFFECTS OF BOREHOLE PURGING

Assessment of successive sampling of five litre samples of water has indicated that more borehole flushing is required to obtain a stable sample. Stagnant water within the borehole, and adjacent flow is unlikely to reflect the nature of the groundwater. The water resting within and around the borehole must be removed before a representative sample may be obtained.

Appendix 1

Appendix 1 presents the tabulated hydrochemical data recorded from each sampling visit to Frongoch, as described in Section 4.4. Table A1 records the major-ion data, Table A2 records the minor constituents and potentially harmful elements, and Table A3 records the saturation indices data. These data are discussed in Section 5.

Table A4 - Physico-chemical parameters and major ion chemistry of Frongoch mine site. Results are in mg/L, except pH (unitless), temperature (°C), Eh (corrected mV), and SEC (at 25°C) (µS/cm). nd indicates not determined, and x indicates the analysis could not be performed because the sample was too cloudy. * indicates duplicate. Note that many Na analyses are below detection, caused by dilutions needed for Zn and analytical interferences with Zn

Site	Lab ID	Temp	Eh	pH	HCO ₃ ⁻	SEC	DO ₂	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
Trial Pit 1	11475-0001	18.5	365	5.52	nd	580	nd	nd	6.13	2.50	10.69	1.20	7.61	313	0.893
Trial Pit 2	11475-0002	18.6	422	5.33	nd	686	nd	nd	16.0	2.07	3.80	2.94	6.08	353	0.040
Trial Pit 3A	11475-0003	21.3	402	4.84	nd	702	nd	nd	10.5	3.11	12.72	2.38	5.17	393	0.083
Trial Pit 3B	11475-0004	13.6	393	4.88	nd	653	nd	nd	18.0	4.50	10.90	1.41	6.92	373	0.086
Stream	11944-0001	13.9	337	6.30	24	172	10	58	9.77	2.36	<17.5	0.660	7.77	49.3	5.75
Culvert	11944-0002	10.7	440	5.35	14	268	11	134	7.86	2.79	<17.5	0.577	6.66	124	3.20
BH1	11944-0003	17.1	253	6.26	25	792	14	396	23.9	4.68	<17.5	3.60	18.5	429	0.412
BH3	11944-0004	20.1	219	6.55	63	1816	8	1816	91.7	17.5	55.74	9.32	123	878	0.706
BH7	11944-0005	17.2	312	5.64	12	1314	7	657	16.2	5.31	<17.5	4.06	10.3	818	0.338
Culvert	12093-0005	7.3	528	5.39	6	305	nd	103	8.62	2.76	<17.5	1.07	5.96	106	2.25
Surface Runoff	12093-0006	5.6	574	4.36	6	297	nd	120	3.92	1.17	<17.5	2.28	4.74	128	<0.600
Mill Pond	12093-0007	6.2	533	6.75	17	91	nd	53	8.97	1.71	6.09	<0.500	7.63	4.50	3.02
Adit	12093-0008	7.7	549	6.81	9	125	nd	nd	10.8	2.48	5.96	0.549	7.61	18.6	3.50
BH1	12093-0001	6.6	457	5.61	5	720	nd	385	15.6	2.66	<17.5	2.26	8.34	378	0.671
BH1*	12093-0003	6.4	415	5.74	5	659	nd	325	11.1	2.23	<17.5	2.10	7.42	325	<0.600
BH3	12093-0002	6.6	466	4.99	3	500	nd	205	10.1	2.11	<17.5	6.82	6.13	203	<0.600
BH3*	12093-0004	6.6	467	5.42	nd	500	nd	211	11.4	2.21	<17.5	7.98	6.84	205	0.680
Culvert	12188-0002	11.9	516	4.86	9	378	9	nd	7.70	2.37	<35	1.37	4.81	167	3.17
Culvert*	12188-0003	11.9	516	4.86	9	378	9	nd	7.56	2.35	<35	1.33	4.83	167	3.15
Surface Runoff	12188-0013	20.3	413	6.21	9	357	15	nd	10.2	2.00	<35	2.07	5.07	110	3.27
Surface Runoff*	12188-0014	20.3	413	6.21	9	357	15	nd	9.87	1.98	<35	2.11	5.32	108	3.28
Mill Pond	12188-0001	15	380	7.27	21	69	12	nd	7.49	1.62	4.99	<0.500	6.83	2.92	0.972
Adit	12188-0004	11.5	505	6.86	25	120	11	nd	9.46	2.41	5.93	0.586	8.05	19.1	1.93
Adit*	12188-0005	11.5	505	6.86	25	120	11	nd	9.65	2.42	5.97	0.598	7.91	18.8	1.93
BH1	12188-0008	13.2	372	5.88	5	693	x	nd	10.8	2.03	<35	2.45	7.61	272	<0.500
BH1* ¹	12188-0009	13.2	379	5.77	6	733	x	nd	11.0	2.20	<35	2.92	7.50	290	<0.500
BH1* ²	12188-0010	13	368	5.72	6	728	x	nd	11.3	2.28	<35	3.16	7.71	291	<0.500
BH1* ³	12188-0011	13.2	375	5.72	10	733	x	nd	11.7	2.38	<35	3.13	7.47	294	<0.500
BH1* ⁴	12188-0012	12.6	356	5.88	8	743	x	nd	12.5	2.41	<35	3.24	7.34	290	<0.500
BH3	12188-0006	12.4	460	5.25	6	2202	x	nd	15.7	3.67	<70	6.35	8.29	1459	1.59
BH3*	12188-0007	12.4	460	5.25	6	2202	x	nd	14.7	4.11	<70	6.78	8.09	2616	1.12

Table A5 - Minor constituent and potentially harmful element chemistry of Frongoch mine site. Results are in mg/L. nd indicates not determined. * indicates duplicate. Note that Fe(II) values marked by # are subject to an unquantified interference from zinc that has not been corrected for and are subject to a positive bias; their values are reported for information only (continued overleaf)

Site	Lab ID	DOC	Mn	Fe(t)	Fe(II)	Al	Co	Ni	Cu	Zn	Cr	As	Cd	Pb
Trial Pit 1	11475-0001	2.73	0.386	7.29	7.62 [#]	0.032	0.046	0.102	<0.002	170	0.007	0.020	0.197	1.14
Trial Pit 2	11475-0002	2.40	0.108	1.87	1.97 [#]	0.168	0.031	0.098	<0.002	189	0.006	<0.015	0.532	6.50
Trial Pit 3A	11475-0003	1.49	0.270	6.58	6.41	0.996	0.045	0.103	<0.002	221	0.007	<0.015	0.707	9.54
Trial Pit 3B	11475-0004	4.60	0.811	17.3	15.4	0.161	0.060	0.107	<0.002	174	0.008	0.066	0.031	0.546
Stream	11944-0001	1.71	0.105	0.033	0.099 [#]	0.033	0.005	0.013	0.033	20.9	<0.002	<0.015	0.037	1.88
Culvert	11944-0002	2.33	0.273	<0.010	<0.050	0.407	0.015	0.037	0.101	70.4	0.004	<0.015	0.114	2.51
BH1	11944-0003	4.27	0.620	7.29	7.05	0.010	0.058	0.130	<0.005	252	0.011	0.016	0.416	0.144
BH3	11944-0004	8.90	1.55	6.95	8.62 [#]	0.050	0.078	0.230	<0.005	483	0.016	<0.015	0.431	0.885
BH7	11944-0005	9.73	0.793	31.0	31.0	0.072	0.165	0.436	<0.005	464	0.022	0.024	0.298	1.48
Culvert	12093-0005	0.539	0.253	0.013	<0.050	0.560	0.015	0.039	0.121	63.0	0.005	<0.015	0.137	3.70
Surface Runoff	12093-0006	0.683	0.119	0.915	0.831	0.585	0.019	0.042	0.064	85.9	0.005	<0.015	0.260	4.62
Mill Pond	12093-0007	1.81	0.004	0.056	0.052	<0.010	<0.002	<0.005	<0.005	0.031	<0.002	<0.015	<0.002	<0.010
Adit	12093-0008	1.11	0.008	0.016	<0.050	<0.010	<0.002	0.005	<0.005	4.94	<0.002	<0.015	0.008	0.315
BH1	12093-0001	1.61	0.542	1.79	1.55	0.110	0.058	0.117	<0.005	235	0.012	<0.015	0.363	0.945
BH1*	12093-0003	1.02	0.458	7.80	4.33	0.056	0.050	0.103	<0.005	214	0.013	0.018	0.320	0.661
BH3	12093-0002	1.63	0.138	2.22	2.34 [#]	0.724	0.019	0.067	<0.005	127	0.006	<0.015	0.284	4.28
BH3*	12093-0004	1.81	0.145	3.34	2.91	0.599	0.020	0.070	<0.005	143	0.009	<0.015	0.304	4.82
Culvert	12188-0002	0.758	0.419	0.027	0.36 [#]	0.905	0.027	0.053	0.154	96.6	0.005	<0.015	0.203	5.88
Culvert*	12188-0003	0.693	0.402	0.026	<0.20	0.897	0.026	0.052	0.153	95.8	0.005	<0.015	0.200	5.77
Surface Runoff	12188-0013	3.97	0.246	0.429	0.32	0.022	0.015	0.028	0.006	71.8	0.004	<0.015	0.167	3.73
Surface Runoff*	12188-0014	3.72	0.253	0.365	<0.20	0.013	0.015	0.027	<0.005	70.1	0.004	<0.015	0.155	3.72
Mill Pond	12188-0001	4.44	0.037	0.222	0.21	0.020	<0.002	<0.005	<0.005	0.009	<0.002	<0.015	<0.002	<0.010
Adit	12188-0004	1.77	0.014	0.064	<0.20	<0.010	0.003	0.005	<0.005	5.75	0.002	<0.015	0.010	0.413
Adit*	12188-0005	1.80	0.015	0.065	n/a	<0.010	0.003	0.006	<0.005	5.82	<0.002	<0.015	0.010	0.414
BH1	12188-0008	3.35	0.437	3.82	4.18 [#]	0.054	0.045	0.085	<0.005	185	0.008	<0.015	0.278	0.665
BH1* ¹	12188-0009	1.69	0.451	6.04	6.66 [#]	0.039	0.046	0.087	<0.005	191	0.009	0.019	0.305	0.673
BH1* ²	12188-0010	1.84	0.448	7.12	9.78 [#]	0.059	0.046	0.086	<0.005	197	0.009	0.026	0.310	0.787
BH1* ³	12188-0011	2.00	0.452	7.31	10.8 [#]	0.104	0.047	0.089	<0.005	191	0.008	0.026	0.330	1.02
BH1* ⁴	12188-0012	3.15	0.453	7.37	9.85 [#]	0.045	0.048	0.089	<0.005	217	0.009	0.030	0.320	0.826
BH3	12188-0006	6.07	0.388	7.24	9.98 [#]	2.18	0.105	0.140	<0.005	1001	0.015	<0.015	1.30	5.27
BH3*	12188-0007	4.00	0.551	13.6	14.4 [#]	3.48	0.163	0.169	<0.005	1735	0.019	<0.015	1.69	4.54

Table A2 continued -Minor constituent and potentially harmful element chemistry of Frongoch mine site. Results are in mg/L. nd indicates not determined. * indicates duplicate

Site	Lab ID	Mo	Se	Total S	Reduced S	Si	SiO ₂	Ba	Sr	V	Li	B
Trial Pit 1	11475-0001	<0.015	<0.015	98.8	0.94	5.64	12.1	0.024	0.015	<0.010	<0.025	<0.025
Trial Pit 2	11475-0002	<0.015	<0.015	113	0.12	4.42	9.46	<0.002	0.029	<0.010	<0.025	<0.025
Trial Pit 3A	11475-0003	<0.015	<0.015	130	0.04	7.55	16.1	0.002	0.022	<0.010	0.032	<0.025
Trial Pit 3B	11475-0004	<0.015	<0.015	122	0.38	8.37	17.9	0.063	0.049	<0.010	0.031	0.026
Stream	11944-0001	<0.015	<0.025	17.1	0.01	2.90	6.21	0.006	0.016	<0.010	<0.025	<0.025
Culvert	11944-0002	<0.015	<0.025	42.9	0.01	4.84	10.4	0.007	0.017	0.015	<0.025	<0.025
BH1	11944-0003	<0.015	<0.025	152	0.01	6.13	13.1	0.024	0.085	<0.010	0.032	0.035
BH3	11944-0004	<0.015	<0.025	331	0.01	5.75	12.3	0.023	0.410	<0.010	0.107	0.135
BH7	11944-0005	<0.015	<0.025	284	0.01	11.7	25.1	0.049	0.049	<0.010	0.053	0.052
Culvert	12093-0005	<0.015	<0.025	46.0	nd	4.80	10.3	0.010	0.018	<0.010	<0.025	<0.025
Surface Runoff	12093-0006	<0.015	<0.025	52.8	nd	2.06	4.41	<0.002	0.009	<0.010	<0.025	<0.025
Mill Pond	12093-0007	<0.015	<0.025	2.02	nd	0.689	1.47	<0.002	0.012	<0.010	<0.025	<0.025
Adit	12093-0008	<0.015	<0.025	7.32	nd	1.78	3.81	0.006	0.018	<0.010	<0.025	<0.025
BH1	12093-0001	<0.015	<0.025	134	nd	6.20	13.3	0.012	0.029	<0.010	<0.025	<0.025
BH1*	12093-0003	<0.015	<0.025	120	nd	5.60	12.0	0.010	0.020	<0.010	<0.025	0.033
BH3	12093-0002	<0.015	<0.025	82.9	nd	5.39	11.5	0.003	0.023	<0.010	<0.025	0.025
BH3*	12093-0004	<0.015	<0.025	92.2	nd	5.43	11.6	0.003	0.026	<0.010	<0.025	0.027
Culvert	12188-0002	<0.015	<0.025	56.2	0.01	4.42	9.46	0.008	0.017	<0.010	<0.025	<0.025
Culvert*	12188-0003	<0.015	<0.025	55.7	0.01	4.35	9.30	0.008	0.018	<0.010	<0.025	<0.025
Surface Runoff	12188-0013	<0.015	<0.025	44.7	0.03	3.54	7.56	0.016	0.023	<0.010	<0.025	<0.025
Surface Runoff*	12188-0014	<0.015	<0.025	42.5	0.04	3.46	7.41	0.017	0.021	<0.010	<0.025	<0.025
Mill Pond	12188-0001	<0.015	<0.025	1.26	0.03	1.22	2.61	<0.002	0.011	<0.010	<0.025	<0.025
Adit	12188-0004	<0.015	<0.025	6.30	<0.01	1.83	3.92	0.007	0.017	<0.010	<0.025	<0.025
Adit*	12188-0005	<0.015	<0.025	6.32	0.01	1.84	3.93	0.007	0.017	<0.010	<0.025	<0.025
BH1	12188-0008	<0.015	<0.025	98.3	1.6	5.55	11.9	0.014	0.022	<0.010	<0.025	<0.025
BH1* ¹	12188-0009	<0.015	<0.025	107	2.1	5.71	12.2	0.014	0.023	<0.010	<0.025	<0.025
BH1* ²	12188-0010	<0.015	<0.025	110	2.8	5.73	12.3	0.011	0.024	<0.010	<0.025	<0.025
BH1* ³	12188-0011	<0.015	<0.025	108	nd	5.87	12.6	0.011	0.025	<0.010	<0.025	<0.025
BH1* ⁴	12188-0012	<0.015	<0.025	125	nd	5.81	12.4	0.012	0.026	<0.010	<0.025	<0.025
BH3	12188-0006	<0.015	<0.025	487	0.54	6.33	13.5	0.002	0.029	<0.010	0.028	<0.025
BH3*	12188-0007	<0.015	<0.025	809	nd	7.63	16.3	<0.002	0.025	<0.010	0.033	0.028

Table A 6 - Saturation indices calculated using PHREEQCi (redox values calculated using Fe(II) and Fe(III) concentrations, where available).

	Calcite	Dolomite	Quartz	Barite	Fluorite	Gypsum	Goethite	Ferric hydroxide	Jarosite(ss)
	CaCO ₃	CaMgCO ₃	SiO ₂	BaSO ₄	CaF ₂	CaSO ₄	FeO(OH)	Fe(OH)3(a)	KFe ₃ (SO ₄) ₂ (OH) ₆
Trial Pit 1	-4.61	-9.34	0.05	0.19	-3.29	-2.25	6.30	0.65	-0.34
Trial Pit 2	-4.39	-9.41	-0.05	-1.18	-4.58	-1.81	6.12	0.46	0.06
Trial Pit 3A	-5.01	-10.25	0.14	-0.90	-6.53	-1.98	1.70	-4.05	-11.93
Trial Pit 3B	-4.82	-10.05	0.30	0.73	-2.72	-1.74	5.44	-0.03	-0.15
Stream	-2.81	-6.05	-0.17	-0.75	-4.78	-2.57	5.70	0.22	-5.64
Culvert	-4.22	-8.75	0.11	-0.42	-7.03	-2.37	3.71	-1.64	-7.56
BH1	-2.69	-5.85	0.11	0.25	-3.37	-1.61	7.51	1.91	1.58
BH3	-1.55	-3.55	0.04	0.24	-2.33	-0.94	6.80	1.08	-1.11
BH7	-3.91	-8.06	0.39	0.64	-5.28	-1.66	5.23	-0.38	-2.85
Culvert	-4.56	-9.54	0.16	-0.22	-6.77	-2.37	5.30	0.08	-2.43
Surface Runoff	-5.83	-12.14	-0.18	-1.11	-7.28	-2.65	5.16	0.00	1.03
Mill Pond	-2.61	-5.88	-0.66	-2.29	-4.60	-3.53	6.32	1.14	-6.60
Adit	-2.75	-6.06	-0.28	-0.96	-4.62	-2.87	6.91	1.67	-3.77
BH1	-4.35	-9.40	0.28	0.15	-4.59	-1.79	6.98	1.78	3.08
BH1*	-4.35	-9.34	0.24	0.06	-4.20	-1.97	8.27	3.08	6.43
BH3	-5.16	-10.94	0.22	-0.53	-6.92	-2.12	7.37	2.19	3.75
BH3*	-4.58	-9.82	0.23	-0.62	-6.58	-2.08	7.04	1.85	3.88
Culvert	-5.76	-11.88	0.05	-0.26	-8.02	-2.30	4.32	-1.09	-3.83
Culvert*	-5.78	-11.90	0.04	-0.27	-8.02	-2.31	5.20	-0.20	-1.18
Surface Runoff	-4.30	-9.02	-0.18	-0.25	-3.66	-2.32	7.10	1.38	-0.91
Surface Runoff*	-4.31	-9.03	-0.19	-0.24	-3.62	-2.34	7.63	1.91	0.65
Mill Pond	-2.55	-5.55	-0.56	-2.64	-5.00	-3.79	6.91	1.39	-7.89
Adit	-4.31	-9.06	-0.33	-1.00	-4.57	-2.92	7.49	2.10	-2.57
Adit*	-4.28	-9.02	-0.33	-1.01	-4.58	-2.92	7.43	2.04	-2.77
BH1	-4.70	-9.94	0.13	0.00	-3.98	-2.05	7.02	1.56	1.35
BH1* ¹	-4.72	-9.96	0.14	0.02	-3.87	-2.02	7.01	1.55	1.78
BH1* ²	-4.73	-9.98	0.15	-0.06	-4.04	-2.02	6.74	1.29	1.17
BH1* ³	-4.72	-9.95	0.15	-0.08	-4.41	-1.99	6.87	1.42	1.57
BH1* ⁴	-4.55	-9.64	0.16	-0.06	-3.85	-1.99	7.01	1.58	1.50
BH3	-5.13	-10.72	0.20	-0.54	-6.44	-1.60	5.92	0.50	1.43
BH3*	-5.29	-10.96	0.29	-0.87	-6.77	-1.56	6.12	0.69	2.31

Table A3 continued - Saturation indices calculated using PHREEQCi (redox values calculated using Fe(II) and Fe(III) concentrations, where available).

	Melanterite	Zincosite	Smithsonite	Zincite(c)	Cadmium sulphate	Otavite	Anglesite	Cerrusite
	Fe(SO ₄)*7H ₂ O	ZnSO ₄	ZnCO ₃	ZnO	CdSO ₄	CdCO ₃	PbSO ₄	PbCO ₃
Trial Pit 1	-4.61	-8.95	-1.92	-3.33	-8.96	-2.94	-0.61	-1.44
Trial Pit 2	-5.19	-8.88	-2.07	-3.67	-8.51	-2.71	0.17	-0.90
Trial Pit 3A	-4.62	-8.67	-2.42	-4.45	-8.27	-3.04	0.33	-1.21
Trial Pit 3B	-4.12	-9.15	-2.63	-4.90	-9.91	-4.40	-0.87	-2.37
Stream	-7.48	-10.62	-1.27	-2.80	-10.37	-2.03	-1.00	0.34
Culvert	-7.92	-9.96	-2.07	-4.41	-9.72	-2.85	-0.44	-0.67
BH1	-4.56	-8.81	-0.44	-1.80	-8.66	-1.30	-1.56	-1.10
BH3	-4.53	-8.31	0.39	-0.89	-8.49	-0.80	-0.85	0.03
BH7	-3.79	-8.43	-1.23	-2.86	-8.69	-2.51	-0.38	-1.10
Culvert	-7.91	-10.22	-2.53	-4.56	-9.82	-3.14	-0.26	-0.80
Surface Runoff	-5.59	-10.13	-3.34	-6.61	-9.56	-3.78	-0.11	-1.61
Mill Pond	-8.06	-14.78	-3.91	-5.13	-13.17	-3.32	-4.52	-1.93
Adit	-11.64	-11.91	-1.91	-2.73	-11.60	-2.62	-2.07	-0.29
BH1	-5.06	-9.38	-2.02	-3.72	-9.13	-2.78	-0.60	-1.49
BH1*	-4.65	-9.47	-1.92	-3.49	-9.23	-2.69	-0.78	-1.49
BH3	-4.42	-9.79	-2.90	-5.16	-9.37	-3.50	-0.04	-1.41
BH3*	-4.95	-9.74	-2.32	-4.25	-9.35	-2.94	0.00	-0.84
Culvert	-7.15	-9.67	-3.46	-5.20	-9.34	-4.14	0.03	-1.83
Culvert*	-7.53	-9.68	-3.47	-5.20	-9.35	-4.15	0.03	-1.84
Surface Runoff	-6.27	-9.51	-2.18	-2.12	-9.23	-2.92	-0.33	-0.81
Surface Runoff*	-7.79	-9.53	-2.18	-2.13	-9.27	-2.94	-0.33	-0.80
Mill Pond	-7.74	-15.03	-4.24	-4.10	-12.98	-3.21	-4.80	-1.99
Adit	-8.24	-11.62	-3.31	-2.32	-11.36	-4.07	-1.80	-1.58
Adit*	-8.25	-11.62	-3.29	-2.32	-11.36	-4.04	-1.80	-1.56
BH1	-4.88	-9.22	-2.25	-2.85	-9.06	-3.10	-0.84	-1.91
BH1* ¹	-4.66	-9.19	-2.27	-3.07	-9.01	-3.10	-0.82	-1.94
BH1* ²	-4.58	-9.19	-2.28	-3.16	-9.01	-3.11	-0.76	-1.89
BH1* ³	-4.57	-9.19	-2.30	-3.17	-8.97	-3.09	-0.64	-1.78
BH1* ⁴	-4.57	-9.19	-2.10	-2.83	-9.02	-2.95	-0.75	-1.72
BH3	-4.28	-8.27	-2.15	-3.65	-8.18	-3.07	0.25	-1.69
BH3*	-3.94	-7.98	-2.05	-3.51	-8.03	-3.11	0.22	-1.92

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