Impact of metal mining on the water quality in the Tamar catchment

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Abstract

This study discusses the effects of past mining activities on sediment and water quality in streams and rivers in the Tamar catchment. High trace element concentrations, both in water and sediments, were observed in streams and rivers draining areas associated with abandoned mine sites. Maximum concentrations were observed in the Gunnislake/Calstock mining district, where intense metalliferous mining took place during the 19th century.

Mine waste from abandoned mine sites in this area contained up to 6.3% arsenopyrite, 5.8% pyrite, 0.3% chalcopyrite and 24% scorodite. As a result, high concentrations of trace elements of up to 180000 mg kg\(^{-1}\) As, 6500 mg kg\(^{-1}\) Cu were determined in these wastes. Sequential extraction of the mine waste revealed that in most cases, the oxidisable fraction accounted for large proportions of mobile species, followed by the reducible fraction. The exchangeable fraction was relatively low, except for Cu in samples from fine grained waste heaps, in which significant amounts of secondary minerals, such as Fe oxides/oxyhydroxides and Fe-As-O minerals were observed, suggesting trace elements had the tendency to be retained and recycled within the fine grained waste heaps. The Fe oxides/oxyhydroxides can contain up to 12% As and Fe-As-O minerals can contain up to 25% As and 6% Cu, indicating that the As and Cu associated with Fe oxide phases represent their reducible fraction. The coarse grained waste heaps, with higher permeability and low cohesion characteristics, had a higher potential to produce acid leachate and were more susceptible to erosion than the fine grained waste heaps.

Contaminants from abandoned mine sites entered aquatic systems within the catchment, as shown by the high concentrations of trace elements (up to 25000 mg kg\(^{-1}\) As, 28000 mg kg\(^{-1}\) Cu, 32000 mg kg\(^{-1}\) Mn, 9200 mg kg\(^{-1}\) Pb and 2700 mg kg\(^{-1}\) Zn) observed in sediments in water channels draining these mine sites. Some streams and adits draining abandoned mine sites carried acidic waters with pH values frequently below pH 4. Dissolved concentrations up to 560 µg L\(^{-1}\) As, 7600 µg L\(^{-1}\) Cu, 3800 µg L\(^{-1}\) Fe, 5700 µg L\(^{-1}\) Mn, 170 µg L\(^{-1}\) Pb and 2500 µg L\(^{-1}\) Zn, and particulate concentrations up to 1600 µg L\(^{-1}\) As, 7900 µg L\(^{-1}\) Fe, 290 µg L\(^{-1}\) Ni, 11 µg L\(^{-1}\) Pb and 91 µg L\(^{-1}\) Zn were observed in channels draining abandoned mine sites. In total, the annual flux of trace elements from 25 studied
streams and adits input ca. 13,000 kg Fe, 4300 kg Mn, 4200 kg Cu, 3600 kg Zn, 1400 kg As, 400 kg Ni, 350 kg Co, 43 kg Pb, and 6.6 kg Cd into the Tamar estuary. Seven important point sources of metals to the River Tamar were identified. The mass balance calculation revealed that over 50% of trace elements were not accounted for by the studied point sources, suggesting an importance of diffuse sources. The inputs of solid and dissolved contaminants from the intensive mining district affect the water and sediment quality of the Tamar estuary, an important ecosystem in southwest England. This work has provided important information on the relative importance of point and diffuse sources, which is essential in the formulation of effective catchment management strategies.
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In tribute to the teachers*

My head bows low in homage
To the teachers of bygone ages
Whose knowledge is my heritage

Also to the ones who instil
moral code, discipline and goodwill
To me at present, still

Before thee all I lay prostrate
Mindful of the great indebtedness
Boundless is my reverence to thee

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Chapter 1: Introduction

1.1 Importance of the Tamar catchment

The River Tamar, together with its tributaries the Rivers Tavy and Lynher, is the largest river that drains into Plymouth Sound (Langston, et al., 2003). The land use is characterised by agriculture throughout the catchment, with the legacy of past mining activities featuring in the middle and lower catchment (Langston, et al., 2003). The River Tamar becomes tidal at approximately 30 km inland and its freshwater is separated from the tidal reach by the Gunnislake Weir. The Tamar estuary can be classified as medium size and macrotidal (Uncles and Stephens, 2001).

The Tamar estuary is a complex of marine inlets, which provide wide mudflats and saltmarshes supporting nationally important birds (e.g. little egret *Egretta garzetta*), wildfowl and migratory birds (e.g. black-tailed godwit *Limosa limosa*) (Langston et al., 2003). Because of its ecological and historical value, much of catchment has been designated as Area of Outstanding Natural Beauty (AONB), Sites of Special Scientific Interest (SSSI), Special Protection Area (SPA) under the European Commission Directive on the Conservation of Wild Birds (79/409/EEC) and Special Area of Conservation (SAC).
Being classified as SSSI, SPA, SAC, the Tamar estuary is qualified as "a potential sensitive receptor" under the Contaminated Land Regulation (Part IIA) of Environmental Protection Act 1990, which came into force on 1st April 2000. The regulation requires the local authorities to identify any contaminated land in their areas and bring about its remediation. This process involves establishing a pollutant linkage between source and receptors, with attention to the likely exposure pathways, i.e. the way in which contaminants are exported from source to receptors.

In addition, a number of sections of the River Tamar and its tributaries including Rivers Lynher, Deer, Ottery, Carey, Inny, Lyd and Tavy are classified as Salmonid waters under the EC Freshwater Fish Directive (78/659/EEC).

1.2 Environmental status of the Tamar catchment

During the 19th century, the Tamar catchment had been subjected to intense metalliferous mining, during which mines in this region were the world's principal producers of Cu and As, and to lesser extent of Pb, Zn, Mn, Ag, Sn and W (Dines, 1956). Although the last mine in the region was closed by around 1950 (Rawlins, et al., 2003), mine working and processing has left the area with a legacy of waste piles and adits. Drainage from adits and leachate and erosion from waste heaps in the area still continues and is reflected by high concentrations of metals in water and sediments in many rivers, streams in the catchment and the Tamar estuary (Aston et al., 1975; Clifton and Hamilton, 1979; Langston et al., 2003; Mighanetara et al., 2008)

Elevated As concentrations in water and sediments in rivers and streams in the Tamar catchment, particularly in the intensive mining area, were reported by Aston et al. (1975). Concentrations up to 300 mg kg\(^{-1}\) in stream sediments and up to 250 µg L\(^{-1}\) in water were observed by the authors. Arsenic is toxic to most living organisms (Dopson et al., 2003) and is related to carcinogenesis in man (e.g. Langston et al., 2003). Although As concentrations in water were generally within the WHO guideline value (10 µg L\(^{-1}\)), high concentrations of up to 250 µg L\(^{-1}\) have been reported to occur occasionally in some locations by Aston et al. (1975) and up to 115 µg L\(^{-1}\) have been reported by Langston et al. (2003). This merits closer and continuous monitoring. In addition to As, elevated Cu
concentrations up to 4400 µg L$^{-1}$ in the run-off from Clitters Mine were reported by Langston et al. (2003).

In the estuary, As concentrations were generally below 10 µg L$^{-1}$, which is lower than the environmental quality standard (EQS) for dissolved As for the protection of saltwater life (25 µg L$^{-1}$, Cole et al., 1999). An increase in As concentrations in the River Tamar was observed as the river flows through the high mineralisation area and intense past mining activities in the Gunnislake/Calstock mining district. The highest As concentration being observed at the Weir, before a decrease in the low salinity region occurs, probably due to adsorption onto Fe-oxyhydroxides formed upon the mixing of freshwater and saltwater. Further seaward, an increase in As concentrations in the estuarine waters was observed in the mid-estuary (but typically still remaining below 10 µg L$^{-1}$ As) as a result of the combination of tidal mixing and enrichment of pore water with As as a result of dissolution of Fe and Mn hydroxides (Langston et al., 2003).

Removal of Cu from solution and remobilisation from the sediment in the estuary has a similar profile to that of As, but the position of the estuarine dissolved concentration maxima occur at different salinities (As: S = 12-15; Cu: S = 1-8) (Langston et al., 2003). Although the maximum concentration of Cu in the estuary is usually lower than the EQS values (5 µg L$^{-1}$), Cu concentrations upstream the Gunnislake Weir at times exceed the EQS (Langston et al., 2003). Copper is highly toxic to most aquatic organisms (USEPA, 2008) and elevated Cu in sediments in the Tamar estuary exceed the levels at which a range of organisms can be adversely affected (Probable Effect Level, PEL, 108 mg kg$^{-1}$) (Langston et al., 2003). Furthermore, pore waters in the estuary may contain up to 13-200 µg L$^{-1}$ Cu, which is 1-2 orders of magnitude higher than the overlying water (Watson, unpublished data in Ackroyd et al., 1986). Therefore, Cu can have possible toxicological significance for infauna.

The removal of Zn from the dissolved phase within the estuary was observed at salinities between 3 and 20, and dissolved concentrations of Zn in the estuary remain below the EQS (40 µg L$^{-1}$) (Langston et al., 2003). However, at times the previously observed values exceed the new Zn EQS for estuarine water (10 µg L$^{-1}$, Langston et al., 2003). Furthermore, Zn (as well as As, Pb, Hg) concentrations in sediments exceeded the PEL.
values (271 mg kg\(^{-1}\)Zn, 41.6 mg kg\(^{-1}\)As, 112 mg kg\(^{-1}\) Pb, 0.7 mg kg\(^{-1}\)Hg) in much of the estuary.

Evidence for ongoing contamination of estuarine sediment with trace metals, many decades after active mining has ceased in the Tamar catchment, has been revealed by a study of estuarine sediment conducted by Clifton and Hamilton (1979). The authors dated and analysed a sediment core from the lower Tamar estuary and found that the concentrations of Zn, Pb and Cu sediments increased sharply between the 1850s and 1870s, during the heyday of mining activity upstream. The accumulation of these metals in more recent sediment layers continued through to 1979, the year of study, seven decades after mining activity had been greatly reduced and nearly 30 years after the last mine closed. It is interesting that other than the metal concentrations in sediments and waters in the catchment (e.g. Aston et al., 1975; Langston, et al., 2003), there is no information about the ecological impact of metal contamination in riverine systems in the catchment.

1.3 EU Water Framework Directive (WFD)

The European Union’s Water Framework Directive (2000/60/EC), which is based on a risk-assessment approach, requires its member states to achieve good chemical and ecological status for all inland and coastal waters by 2015. The WFD aims to complement a number of existing legislative instruments, including the Bathing (76/160/EEC), Drinking (98/83/EC), Fish (78/659/EEC) and Shellfish (79/923/EEC) Water Directives, as well as those based on specific substances or sources of pollution (i.e. Dangerous Substances (76/464/EC), Groundwater (80/68/EEC), Nitrate (91/676/EEC) and Pesticide (91/414/EEC) Directives. Successful implementation of the WFD requires the establishment and use of existing and emerging and low-cost tools as part of monitoring programmes (Allan et al., 2006).

Because aquatic systems are complex, and the quality elements (physico-chemical, hydro-morphological, chemical and biological characteristics) of individual water body may vary, monitoring practices, which were scheduled to commence in December 2006, are required to cover three modes including surveillance, operational and investigative
monitoring (Allan et al., 2006). For a “good quality” water body, only surveillance monitoring is required to ensure that this status is maintained. However, for water bodies failing the environmental objectives of the WFD, operational monitoring is required to provide additional information, so that remediation strategies and following monitoring programmes can be effectively implemented. If a water body fails to meet the necessary standards and the cause of the problem is unknown or if the water body is subjected to accidental pollution events, investigative monitoring is required (Allan et al., 2006).

The Tamar river and estuary, due to its ecological and historical values discussed above, is of national importance. In addition to the influence of agricultural and urban/industrial activities in the catchment, contamination from abandoned mines continues to enter the water bodies in the catchment and potentially adversely affect the water quality and ecosystem functioning. Any catchment management plan targeted at achieving the environmental objectives of the WFD in the Tamar catchment will need to take into account the sources, pathways and fluxes of contaminants from the land associated with abandoned mines into the aquatic system.

1.4 Research aim and objectives

The overall aim of the study was to assess the impact of past mining activities on the aquatic environment in the Tamar catchment.

The objectives were:

1. To investigate the potential contamination pathways from abandoned mine sites to the wider environment.
2. To study solid materials (i.e. sediments and mining waste) with respect to their mineralogy and the mobility of metals associated with them.
3. To identify the major point sources of potentially toxic elements to the Tamar system.
4. To quantify the metal fluxes in dissolved and suspended solid phases in the Tamar catchment.
5. To assess the water and sediment quality in rivers and streams in the Tamar catchment and the impact of contamination on the aquatic environment.
In order to achieve these aim and objectives, this research utilises several approaches, including detailed investigation of mine waste materials and sediments and the seasonal study of water quality throughout the catchment. However, due to the constraints inevitably linked to research projects, this study did not investigate contaminant movement through the groundwater. Furthermore, in order to be able to assess the effects of mining activities within the catchment, the sampling strategy of this study covers a large area, but the numbers of samples taken at each site is limited. This applies, particularly to solid samples, whereby the reader should be aware of the underlying assumptions of relative temporal stability and spatial homogeneity.

1.5 Structure of thesis

This thesis consists of six chapters. The first chapter introduces the research background, including features of and threats to the study area, the rationale behind the research and its aim and objectives. In chapter 2, background information about the geography, hydrology, climate, land use, geology and mineralisation and some important abandoned mines in the Tamar catchment are reviewed. The findings of this chapter lead to the selection of mine sites and the sampling strategy for the research presented in the following three chapters. Chapter 3 assesses, through their physical and geotechnical characteristics, the potential pathways of contaminants from mining waste heaps into the wider environment. In chapter 4, the mineralogy of mine wastes and the mobility of metals and arsenic associated with solid materials are investigated, and the effects of the abandoned mine sites on stream sediment quality are discussed. Chapter 5 elucidates the effects of abandoned mine sites on water quality by investigating the concentration and fluxes of elements. Finally, Chapter 6 summarises the finding of this research and discusses unanswered questions for further research.

1.6 References

Chapter 1: Introduction


Chapter 2

Study area

2.1 Abstract

This chapter reviews the literature related to the background information of the study area. It commences with the geography, hydrology and climate of the Tamar catchment, followed by the geology and mineralisation in the region, which made the area became one of the worlds’ most important mining centres in the 19th century. The mining and ore dressing techniques, important abandoned mines in the area, and their potential as sources of arsenic and metal contamination to the River Tamar are discussed.

2.2 Geography, hydrology, climate and land use

The Tamar valley is located between Dartmoor and Bodmin Moor in southwest England (Figure 2.1). The River Tamar forms the border between Devon and Cornwall, originates in north Cornwall, about 6 km south east of Bude and the Atlantic Ocean, and flows south for some 80 km into the English Channel at Plymouth Sound. The catchment covers an area of approximately 1700 km$^2$ (Evan et al., 1993). The river has an annual average flow of 30 m$^3$ s$^{-1}$. Seasonal fluctuations range from 5 to 38 m$^3$ s$^{-1}$ but instantaneous peak flows sometimes exceed 100 m$^3$ s$^{-1}$ (Langston et al., 2003).

The long term annual average rainfall in the catchment from 1961 to 1990 was 1190 mm and 1450 mm for upper and lower catchments, respectively (Robinson, 1995&6). The
base flow index (BFI) varies depending on the bedrock. The BFI is the ratio of the volume of base flow to total flow. It gives an indication of the proportion of water transported by slow flow processes, which in many cases refers to groundwater discharge i.e., the higher the BFI, the more dominant the groundwater system. Impermeable bedrocks have small BFI values from 0.15 to 0.035 whilst permeable bedrocks have BFI values up to 0.9. In general, the rocks underlying the Tamar catchment have low permeability and porosity (i.e. small BFI), limiting groundwater flow and storage. At Gunnislake, approximately 30 km inland, the River Tamar has a BFI of 0.47 (Rawlins et al., 2003), which can be described as “fairly responsive” and indicates the tendency to spate flow following heavy rain events (Rawlins et al., 2003). Although extensive fractures and fissures caused by folding and faulting increase porosity and permeability, the overall groundwater storage in the Tamar catchment is low. Groundwater flows are restricted to shallow depths and are controlled by topography and local drainage pathways. Alluvial deposits along the valley floodplains provide additional groundwater resources (Robinson, 1996).

Figure 2.1 The Tamar catchment in southwest England, showing river systems and the location of granite bosses (patterned, DM: Dartmoor KH: Kit Hill, BM: Bodmin Moor; SA: St. Austell; CG: Carnmenellis Granite; LE: Land’s End). G: Tamar River freshwater endmember at Gunnislake.
Tributaries to the Tamar include the Rivers Deer, Carey, Ottery, Thrushel, Lyd and Inny in the river catchment, and the Tavy, Lynher and Tiddy in the estuary (Figure 2.2). On average, the Rivers Tavy and Lynher contribute about 30% and 20% respectively of the freshwater flow in the catchment (Langston et al., 2003).

The catchment is mainly rural (95% of land use) and the predominant land uses in the upper river catchment are agricultural (arable and pasture) and forestry. Intensive livestock farming has resulted in nutrient enrichment, and nutrient-associated water quality problems, such as chronically low levels of dissolved oxygen, have periodically occurred in the upper Tamar catchment (Langston, et al., 2003). Furthermore, intense agricultural practices can result in pesticide and herbicide accumulation in soils and/or enter into aquatic systems. According to Langston et al. (2003), DDT concentrations in the estuary are relatively high compared to its daughter products such as DDE and DDE, suggesting unknown sources of DDT in recent years, although the use of this pesticide has been banned in the UK for several decades.

The lower reaches of the river and the upper Tamar estuary are located within the former Gunnislake/Calstock mining district, and the Lynher and Tavy drain former copper and multi-metallic mining districts. As a consequence of the high mineralisation and its exploitation in the area, metal concentrations at alarming levels have been observed in both, water and sediments in the Tamar river and estuary (e.g. Aston et al, 1975; Langston et al., 2003). The effects of mining on the environment of the Tamar river and estuary and the environmental importance of the Tamar systems have been reviewed in the introduction chapter. Some important abandoned mines will be discussed in relation to their potential for metal contamination to the River Tamar later in this chapter.

The lower estuary is dominated by the city of Plymouth, which has ca. 230000 inhabitants, and from which industrial and sewage inputs originate, (Robinson, 1995 & 1996), and the Devonport dockyard, where heavy shipping traffic and boat building activities are believed to be the principal sources of toxic contaminants, such as tributyltin (TBT). Polycyclic aromatic hydrocarbons (PAHs), and radionuclides (Langston et al., 2003).
2.3 Geology and mineralisation

The River Tamar flows through various rock units. The upper part of the catchment is largely underlain by thickly bedded massive sandstones and argillaceous sedimentary rocks (mudstones and shales) of Carboniferous age, while further south, the bedrock consists mainly of Devonian slates and grits (Figure 2.3). The Devonian and Carboniferous rocks were metamorphosed by granite intrusions some 270-290 million year ago (Darbyshire and Shepherd, 1985), forming a series of granite bosses, namely, from east to west, Exmoor, Dartmoor, Bodmin Moor, Hensbarrow (St Austell), Carnmenellis, Land's End and the Isles of Scilly (Figure 2.1). This granite intrusion resulted in the formation of ore minerals within the metamorphic aureoles around the granite bosses. The extraction of tin and copper made southwest England a prosperous area since pre-historic times (Dines, 1956a; Atkinson et al., 1978).

In southwest England, tin and copper are generally found in lodes with an east-west orientation, and these were formed in the early stage of mineralisation. Later, this initial deposit was followed by north-south veins, mainly represented by lead, zinc and iron ores. The sequence of mineralisation is determined by the temperature and pressure of the cooling rock. Minerals, which crystallised out at high temperatures, for example cassiterite, wolfram and tourmaline, solidified nearest to the mass of the granite, while others occupied outward zones as the temperatures decreased to their crystallisation points. The order of deposition of principal metal ores from the granite mass is: tin, copper, zinc, lead and iron (Dines, 1956a). As an accessory mineral, arsenic is often found associated with tungsten, which occurs at the top of the tin zone. and it often extends upwards throughout the copper zone. After the deposition of these mineral zones, the overlying sedimentary rocks were subjected to erosion. This exposed the granite massifs and the metamorphic aureole of tin, copper, lead/zinc and iron ores as we see them today.
Chapter 2: Study area

<table>
<thead>
<tr>
<th>River</th>
<th>Area drained (km²)</th>
<th>Length of river (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lynher and Tiddy</td>
<td>245.3</td>
<td>34.8</td>
</tr>
<tr>
<td>Tavy</td>
<td>235.5</td>
<td>35.2</td>
</tr>
<tr>
<td>Inny</td>
<td>107.3</td>
<td>32.5</td>
</tr>
<tr>
<td>Lyde</td>
<td>105.0</td>
<td>25.2</td>
</tr>
<tr>
<td>Thrusel</td>
<td>116.5</td>
<td>21.4</td>
</tr>
<tr>
<td>Carey</td>
<td>68.0</td>
<td>21.5</td>
</tr>
<tr>
<td>Ottery</td>
<td>124.5</td>
<td>33.0</td>
</tr>
<tr>
<td>Deer</td>
<td>81.75</td>
<td>16.8</td>
</tr>
<tr>
<td>Tamar</td>
<td>Ca. 1700</td>
<td>Ca. 80</td>
</tr>
</tbody>
</table>

Figure 2.2 The Tamar and its tributaries, including the Rivers Tiddy, Lynher, Tavy, Inny, Lyd, Thrusel, Carey, Ottery and Deer. G: Tamar River freshwater end-member at Gunnislake. (Sub-catchment area and length of the river data: Robinson, 1995)

The most important mineral deposits in the Tamar Valley were formed within a belt of ca. 18 km x 6 km extending westward from the edge of the Dartmoor granite across the Gunnislake and Kit Hill granites. Most of the mineral lodes occur in Devonian rocks. The district is more prosperous in sulfide ores than in tin. Most of the copper lodes also yielded large amounts of pyrite and arsenopyrite (Dines, 1956b).
Figure 2.3 Geologic map of the study area (produced on the basis of data downloaded from Edina Digimap, 2007: Geological Map Data © NERC 2008).

Chalcopyrite (CuFeS$_2$) was the principle ore of copper in southwest England, while chalcocite (Cu$_2$S), a copper-rich secondary mineral, was mined in large quantities in some mines (Dines, 1956a). Arsenopyrite (FeAsS) was the only economic mineral ore of arsenic mined in this region. It was first regarded as waste material in the early 19th century, and often left in the stopes in copper lodes. Arsenic became valuable and was mined in the 1870s, when the demand for arsenic for the insecticide, paint and glass
industries increased (Dines, 1956a). Lead, found in north-south lodes, was extracted mostly from galena (PbS) that often carried silver (as argentiferous galena). Galena is often associated with ores of bismuth, cobalt, nickel and antimony in this area.

2.4 Mining and ore dressing techniques in the Tamar valley

Lead mining in the Bere Alston peninsular (in the southern parat of the catchment) dates back to the 13th century (Dines, 1956a; Stewart, 2003). Underground mining became a common engineering practice in the 16th century, when miners from Harz district in central Germany were brought to Cornwall (Earl, 1994). The principal mining technique consisted of driving levels from hill sides or shafts, depending on the depth and position of the lode, as well as the efficiency of the pumping system for dewatering of the mine. The flood water was drained either through adits discharging the water naturally through a portal side down the valley, or using a pumping system as in the case of deep shafts (see Figure 2.4) (Atkinson et al., 1978; Earl, 1994; Stanier, 1998).

![Figure 2.4](http://example.com/figure2.4) Schematic deep underground mining structures. The grey areas represent the areas where the ores have been extracted or stopped either by working upwards (overhand stope) or downwards (underhand stope) (adapted from Atkinson et al., 1978).
Chapter 2: Study area

In the 19th century, the ore was hand-picked, both at underground and surface levels. Once brought to the dressing floor, it was then broken by sledge hammers or mechanical stone breakers, separated manually from the waste material, before being fed to mechanical stamps for crushing. Metallic ores were finally separated from mining waste by a hydraulic process based on the difference in their specific gravities. The method for dressing copper was slightly different due to the friability of chalcopyrite (the main ore), which tends to break into a fine powder making it thus very difficult to treat. Accordingly, the copper ore was usually not finely crushed. The method consisted of hand sorting the copper ore in the dressing floor into prills (lumps of pure ore which do not require further separation process), drage (ore mixed with gangue minerals), and halvans (fragments of low ore concentrations) by successive processes known as spalling (broken of a large of ore into a smaller piece with a sledge hammer by a man), cobbling (broken of the size previously mentioned into yet a smaller piece with a special long-head hammer by a woman), picking (hand sorted), riddling (sized by being passed in succession through a couple of riddles of sieves) and jigging (separated by shaking either manually or mechanically). Both drage and halvans were crushed by stampers into a sandy state, before being separated by hydraulic processes (Earl, 1994; Stewart, 2003).

After dressing, arsenic can be sold either as arsenical pyrite, or can be further refined before being sold. After crushing and dressing, arsenical pyrite was calcined to produce arsenic oxide known as "crude arsenic" or "arsenic soot", which contains more than 80% of As$_2$O$_3$. As an example, the following section is a summary description of the production of refined arsenic at Devon Great Consols Mine, which had an output of over 70000 tons of crude arsenic in less than 40 years (1869-1906; Dines, 1956b).

The processed ore, brought to the arsenic works from various dressing floors, was roasted in a furnace at 538-593°C, the most efficient temperature for arsenic sublimation. At this stage, sulfur was eliminated and the arsenic oxide gases were passed to the condenser via brick-lined flue chambers (see Figure 2.5). Arsenic soot precipitated at the brick walls of the condenser (locally also called Labyrinth) when the temperature fell below 170°C. Workers scraped the crystals from the condenser walls into sacks during period when the furnaces were shut down. The crude arsenic, which contains ca. 10% impurities, was then recalcined in a flat bed reverberatory furnace. The crude arsenic after this stage had
a purity of over 99% As, and was milled and before being sold as “refined arsenic” (Pye and Dixon, 1989).

Figure 2.5 Arsenic works at Devon Great Consols Mine. (photo: Mighanetara, 2006)

2.5 Mining in the Tamar catchment

The most intensively mined area in the Tamar catchment followed the main mineral deposits described above (section 2.3). This area lies in the middle reach of the River Tamar and its upper estuary, known as Gunnislake/Calstock mining district (see Figure 2.6). The main metals mined in this zone were Cu, As and Pb and to lesser extent Zn. Manganese was mined mainly to the north of the Gunnislake/Calstock mining district, in the Thrushel sub-catchment and in the upstream sections of the River Inny (Figure 2.6), as well as in the sub-catchment of the river Kensey (a small river to the south of the Ottery, not shown on Figure 2.6). In addition to this region of intensive mining, Cu and As were mined at the upstream sections of the Rivers Lynher, Tiddy and in the Tavy sub-catchment, which drain into the Tamar estuary (Figure 2.6). Iron mines were scarce, and
there is no record of mining activity in the upper catchment (the Ottery, Carey, Deer and upstream Tamar) (Dines, 1956b; Rawlins et al., 2003; EA, 2008)

Figure 2.6 A: Outline of areas in the Tamar catchment mined for Zn, Pb, Mn, Cu and As, respectively (data source: Environmental Agency; Turner, 2008, Pers. Comms.). B: The area of most intensive mining activity in the Tamar Catchment selected as the study area is outlined in red. Areas of mining activity outside the study area affecting river water quality of tributaries to the Tamar are outlined in blue and brown, respectively.

2.6 Gunnislake and Calstock mining district: mines and contamination sources

From about 1860 to 1900, mines in the Gunnislake/Calstock mining district were the world’s main producers of copper and arsenic. Although the mining activities in this region ceased in around 1950 (Rawlins et al., 2003), the River Tamar continues to receive mine waters from numerous streams and adits draining abandoned mines sites, and erosion and run-off products from waste heaps in those sites. The locations of important abandoned mines and some of their associated drainage streams within the area of intensive mining around Gunnislake and Calstock are presented in Figure 2.7. Table 2.1 summarises the ores or metal yield during the operation of some of these mines, clearly showing the economic importance of Devon Great Consols, the largest copper mine in the
19th century. Table A-I (Appendix I) provides information on the minerals identified in these mines.

Figure 2.7 Important abandoned mines and main streams within the intensive mineralisation zone (Gunnislake/Calstock mining district) in the Tamar catchment.

The land associated with Devon Great Consols (DGC) mine covers 67.6 ha and the mine yielded over 740000 t Cu and some 71000 t refined As (1845-1906; Dines, 1956b). The main lode of this mine, the largest sulfide deposit in the west of England, is 2 ½ miles long, constituting of chalcopyrite(CuFeS$_2$), pyrite (FeS$_2$), quartz (SiO$_2$) in the centre of the lode, and arsenopyrite (AsFeS) on its walls (Dines, 1956). After the mine closure in 1903 (some small scale mining and reworking of extensive surface dumps was continued until about 1940 (Frederic Sherrell Limited, 2000)), the area was left with extensive waste piles containing various sizes of waste from different stages of ore dressing and
processing, slag and cinders as well as overburden and debris of demolished and ruined mine buildings (Figures 2.5&8). The remains of the arsenic works, such as calciners and flues, are highly contaminated with crystallised arsenic compounds (Klinck et al., 2005; Palumbo-Roe et al., 2007). Concentrations up to 205000 mg kg\(^{-1}\) As and 20900 mg kg\(^{-1}\) Cu in mine wastes at this site were reported by Palumbo-Roe et al. (2007).

The river Tamar receives mine waters, run-off and leachate from DGC via the river Cat and two draining channels: 1) the main drain collecting leachate and run-off in form of surface and groundwater from the main waste piles and mine waters from South Fanny adit, and 2) Blanchdown stream, which receives mine water from Blanchdown adit and run-off and leachate of waste piles on the mine site. Blanchdown adit is the main underground drainage of DGC and its drainage is slowed by a constructed terrace to encourage iron precipitation from these highly ochreous adit waters.

Luckett stream, before its confluence with the River Tamar, receives mine waters and run-off from New Great Consols Mine, in which over 15000 t Cu and 4000 t refined As were produced (Dines, 1956b). Upstream, the river collects mine waters from other Cu/Sn mines, such as Sheba (Cu), Downgate Consols (Sn/W) and Tom (Sn/Cu) mines (Dines, 1956b).
Table 2.1 The amount of metals or ores extracted from some mines in the study area (summarised from Dines, 1956b) Note: Cu = copper ore. Cu con. = concentrated copper; Sn = blank tin; Pb = lead ore; As = refined arsenic; W = wolfram/tungsten; Ag = silver.

<table>
<thead>
<tr>
<th>Mine</th>
<th>Time of operation</th>
<th>Main metals/ores mined</th>
</tr>
</thead>
<tbody>
<tr>
<td>Okeltor</td>
<td>1859-1874</td>
<td>13215 t Cu; 85 t Sn; 1.25 t Pb; 13371 t pyrite; 3550 t As</td>
</tr>
<tr>
<td>George and Charlotte</td>
<td>1852-1869</td>
<td>16595 t Cu; 110 t pyrite</td>
</tr>
<tr>
<td>Gawton</td>
<td>1853-1902</td>
<td>21876 t Cu; 22 t Sn; 1435 pyrite; 3850 t arsenopyrite; 15650 t As</td>
</tr>
<tr>
<td>Russel United</td>
<td>1852-1891</td>
<td>11 t Sn; 11400 t Cu; 10 t arsenopyrite</td>
</tr>
<tr>
<td>Dutchy Great Consols</td>
<td>1873-1876</td>
<td>486 t Cu; 240 t pyrite; 253 t As</td>
</tr>
<tr>
<td>Bedford United</td>
<td>1845-1889; 1906-1909; 1928</td>
<td>6590 t Cu; 25 t Sn; 501 t pyrite; 13497 arsenopyrite; 2111 t As; 25 t W; 72 t Cu con. 60 t fluor spar</td>
</tr>
<tr>
<td>Devon Great Consols</td>
<td>1845-1906</td>
<td>742427 t Cu; 21 t Sn; 9555 t pyrite; 540 t arsenopyrite; 70800 t As; 111 t ochre; 7 t Cu con.; 13 t As from the dump (in 1918)</td>
</tr>
<tr>
<td>Deer Park</td>
<td>1873</td>
<td>1.25 t Sn</td>
</tr>
<tr>
<td>Cotehele Consols</td>
<td>1880-1882</td>
<td>6 t Cu; 323 t arsenopyrite</td>
</tr>
<tr>
<td>New Great Consols</td>
<td>1863-1879; 1914-1918</td>
<td>15252 t Cu; 933 t Sn; 2479 t arsenopyrite; 4087 t As</td>
</tr>
<tr>
<td>Old Gunnislake</td>
<td>1913-1914</td>
<td>Failed / 11 cwt W</td>
</tr>
<tr>
<td>South Bedford and East Gunnislake</td>
<td>1855-1865; 1870-1871; 1873</td>
<td>4620 t Cu; 2 t Sn; 170 t pyrite</td>
</tr>
<tr>
<td>Gunnislake Clitters</td>
<td>1822-1827; 1860-1889; 1902-1904</td>
<td>33350 t Cu; 510 t Sn</td>
</tr>
<tr>
<td>Tamar River</td>
<td>1897-1898</td>
<td>234 t arsenopyrite</td>
</tr>
<tr>
<td>South Tamar</td>
<td>1849-1860</td>
<td>7140 t Pb; 350 t fluor spar; 262-470 oz Ag</td>
</tr>
<tr>
<td>Ding Dong</td>
<td>1811, 1819, 1915, 1942-1944</td>
<td>250 t Cu. 1000 t of Sn and W (the ratio was not provided)</td>
</tr>
<tr>
<td>Silver Valley</td>
<td>1852</td>
<td>9 t Pb</td>
</tr>
</tbody>
</table>
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Figure 2.8 A large volume of coarse grained material (mainly sand) mine waste from the main dressing floor (Lower Wheal Anna Maria) and ruins of arsenic works at Devon Great Consols Mine. (photo: Mighanetara, 2006).

Other streams within the area include: 1) Deer Park stream which collects mine water from Deer Park Mine, an unsuccessful mine, in which only 1.25 t Sn were raised, 2) Greenscoombe Wood stream which has no abandoned mine along its course, and therefore represents uncontaminated natural water of the area, 3) Danescoombe stream, which drains mine water from Cotehele Consols Mine, and 4) Cotehele stream collecting mine waters from the Silver Valley Mine upstream.

Streams associated with Gawton, Gunnislake Clitters and Okeltor Mines are of very low water flow, but these mine sites feature extensive waste piles that are located directly on the bank of the River Tamar, as illustrated for Gunnislake Clitters mine in Figure 2.9. These waste piles have a high potential as diffuse contamination sources, because run-off and erosion products enter the river without attenuation.
Figure 2.9 A large waste pile at Gunnislake Clitters Mine on the bank of the River Tamar. The run-off and erosion products from this waste pile can enter the river without attenuation. (photo: Mighanetara, 2006).

Most adits have low flow rates and a number of them, such as Ding Dong, Tamar River, Old Gunnislake Mines, display ochreous precipitates (Figure 2.10), while others (e.g. South Bedford East Gunnislake) show no visible signs of mine contamination. Some adits, for example from the former lead and silver mine South Tamar, drain directly into the Tamar estuary and display elevated conductivity as a result of tidal incursion.
2.7 Conclusions

The intense mining activities in the Tamar Catchment in the 19th century, particularly in the Gunnislake/Calstock mining district, have left the area with a legacy of waste piles and adits, which have the potential to affect the quality of water and sediments in the Tamar river and estuary.

Some of the extensive waste piles in the Devon Great Consols Mine, although are not located directly on the river bank, contain high concentrations of arsenic and copper. Therefore, they may have the potential to be the sources of metal contamination into the River Tamar via drainage channels which drain mine waters from adits and leachate from waste heaps within the mine site.

The waste heaps at Gunnislake Clitters, Okeltor, Gawton and New Great Consols Mines, although the information on the metal concentrations in these waste heaps is limited, are located directly on the river banks (e.g. the River Tamar and Lucket stream). As a result,
the run-off and erosion products from these waste heaps can enter the rivers without attenuation.

In the next chapter, the potential migration pathways of metal contamination from some selected waste heap into the River Tamar will be investigated.

2.8 References


Chapter 2: Study area


Chapter 3

Physical and geotechnical characteristics of selected mining waste heaps

3.1 Abstract

This chapter contains an overview of physical and geotechnical characteristics in relation to contaminant migration pathways. Grain size distribution, consistency limits, permeability and mathematical slope stability of four selected waste heaps were investigated. Due to their relatively high permeability, contaminants can be transported from coarse grained waste heaps via seepage and leachate, whereas this transportation pathway was not significant for fine grained waste heaps. Furthermore, due to coarse grained wastes are cohesionless materials and therefore more susceptible to erosion run-off than the fine grained wastes. Mathematical slope stability analysis suggested that, depending on soil strength parameters and slope geometry, one out of the four studied waste heaps had a potential to release large quantity of contaminants due to sudden slope failure.

3.2 Introduction

Metal contamination released from mining waste can be transported into aquatic systems through several mechanisms. For example, migration of contaminants can occur via acidic leachate containing high concentrations of dissolved metals resulting from oxidation of sulfide minerals, and run-off containing metal bearing particles discharged
directly from mine tailings and waste heaps, as illustrated in Figure 3.1, (Braungardt et al., 2003; Hudson-Edwards, 2003). In addition, slope failures can result in direct and/or indirect release of large volumes of metal contamination into nearby environmental or aquatic systems. Examples include slope failures of spoil tips at Aberfan coal mine, Wales in 1966, which generated ca. 110000 m$^3$ of debris and killed some 140 people (Bromhead, 1992), and at St Aidans opencast coal site, Leeds, England in 1988, at which a massive (600000 m$^3$) slope failure caused a breach of riverbanks and the flood protection levee of River Aire (Hughes and Clarke, 2001).

Geotechnical and physical characteristics of mine waste are key parameters controlling the migration pathways of contaminants. For instance, the flow rate of leachates within the waste material is related to permeability of the waste, and the stability of slopes of large volumes of mine waste is dependent on the solid material’s potential to develop its optimum frictional resistance between solid particles. Furthermore, both the shear strength and the permeability are affected by the state of waste heaps in terms of, not only their degree of plasticity, but also their degree of consolidation and their densities (Bolton, 1994; Powrie, 1997; Smith & Smith, 1998). Accordingly, geotechnical laboratory tests are required, once appropriate sites are selected, so as to assess the soil’s engineering properties essential to any stability, erodibility or leachate transport analyses.
Chapter 3: Physical and geotechnical characteristics of selected mining waste heaps

The aims of this chapter were to assess, at selected mine sites, the possibility of metal contamination spreading due to slope failure and erosion, and to determine the physical parameters (grain size distribution and permeability) of mine waste that influence sulfide oxidation and migration of leachate within and through the waste heaps. These aims were achieved by the following objectives:

1. Desk-top studies and preliminary field investigations were carried out to select the study area, determine dimensions of mine waste and visualise slope stability (e.g. vegetation and cementation).
2. Laboratory analysis of grain size distribution and permeability of mine waste materials.

3.3 Methods

3.3.1. Site selection

Two sites within the Gunnislake/Calstock mining area were selected for detailed investigation of geotechnical and engineering properties, namely Devon Great Consols and Gunnislake Clitter Mines (Figure 3.2).
Chapter 3: Physical and geotechnical characteristics of selected mining waste heaps

New Great Consols (Cu/As)

Important mine sites (mined metals)

Gunnislake Village

Devon Great Consols (Cu/As)

Gunnislake Clitters (Cu/Sn)

Okettor (As/Cu)

Gawton (Cu/As)

Figure 3.2 Location of large mine waste deposits near the river bank in the study area in the Tamar Valley.

Devon Great Consols Mine (DGC) was selected for this study, as it represents the most important, in terms of Cu and As ore production, mines in the Tamar Valley. The land associated with DGC mine covers approximately 67.6 ha, and the two waste heap sampled are located approximately 300 m from the eastern bank of the River Tamar. Ground levels of the entire site vary from approximately 130-150 m Above Ordnance Datum (AOD) on the high ground to the east, to somewhere between 0-20 m AOD in the Tamar valley to the west (Frederick Sherrell Limited, 2000). This site represents one of the most extensively studied abandoned mines in the Gunnislake/Calstock mining area as reflected in a number of reports on the concentrations (up to 205000 mg kg\(^{-1}\) As and 20900 mg kg\(^{-1}\) Cu, Palumbo-Roe et al., 2007) and geochemistry of contaminants at this site (e.g. Dybowska et al., 2005; Klinck et al., 2005; Palumbo-Roe et al., 2007). Most previous studies, however, focused mainly on quantifying chemical properties of waste materials. There is little information on how contaminants in this site might be...
Chapter 3: Physical and geotechnical characteristics of selected mining waste heaps

transported into nearby environmental systems. For this reason, three heaps constituted of different materials within this mine were selected, as per Figure 3.3, in order to assess the potential migration pathways of metal contamination.

![Diagram of waste heaps at Devon Great Consols mine](image)

**Figure 3.3** Main waste heaps at Devon Great Consols mine sampled for geotechnical analysis. Sampling points at each heap are marked x.

The characteristics of the selected waste heaps can be described as follows:

1. DGC1: Coarse grained waste material, consisting mainly of sand as shown in Figure 3.4, from Lower Wheal Anna Maria dressing floor of a volume of 160000-192000 m³.

2. DGC2: Finer grained waste material made of silt deposited in layers (see Figure 3.5), accumulated in the slime and tailings pond of Lower Wheal Anna Maria located at the foot of DGC1. This heap has a volume of 86500-110000 m³, which contains some portion of waste by volume generated from the re-worked coarse waste, which took place in 1902-1925 (Wardell Armstrong, 1992) to extract arsenic using more advanced processes.
3. DGC3: Slag and cinders of varying size, originating from ore processing and calcination of a volume of 15600-22800 m³.

Figure 3.4 Surface excavation at Lower Wheal Anna Maria dressing floor waste, Devon Great Consols Mine (the depth of the pit is 37 cm) (photo: Mighanetara, 2006).
Figure 3.5 Surface excavation at tailings and slimes heap, Devon Great Consols Mine. The spade blade is an indicator of scale (the visible edge of the spade is 22 cm) (photo: Mighanetara, 2006).

Devon Great Consols mine features three main water discharges into the River Tamar (Figure 3.6); these are:

- the main adit of the mine, known as Blanchdown adit,
- a stream draining Wheal Anna Maria spoil tip, which combines with the River Cat before entering the River Tamar, and
- the main drain which collects surface run-off, mine water from South Fanny adit, as well as shallow ground water from the area in which the two main heaps are located.

However, a direct link between water contamination and a specific source could not be established, since no flowing drain can be exclusively associated with any particular waste heap on this site.
At Gunnislake Clitters mine (sample GCM), the lower tailings waste heap was selected because its steep slopes, and its proximity to the west bank of the River Tamar, as illustrated in Figure 3.7. The heap constitutes a potential source for the long-term release of solid and dissolved contaminants through erosion, and can potentially increase the risk of contamination of the River Tamar through sudden slope failure. The waste deposit, locally known as ‘whitesands’, was generated from the ore processing waste associated with mining of copper, tin, wolfram and arsenic. The heap has a volume of 60000-87100 m³ and consists of a mixture of silt and clay, some of which have distinctive brown, purple and orange colours, layered in bands typical for tailings deposits as seen in Figure 3.8. Samples from 3 distinctive layers (brown, purple and orange) were taken randomly from each layer as different colour may indicate physical and chemical properties. Any such difference will be discussed in the result section.
Figure 3.7 Sampling location (marked x, see Figure 3.8) and an approximate size of Gunnislake Clitters waste heap.

Figure 3.8 Tailings deposit at Gunnislake Clitters Mine (Whitesands), showing layering of deposits, various slope angles and evidence of past slope failure and ongoing surface erosion. Three samples were collected at locations indicated “x”. (photo: Mighanetara, 2006).
Water emanating from a shaft/adit near the Whitesands waste heap drains into the River Tamar, but there is no permanently flowing drainage channel associated with the Whitesands heap. Because of its proximity to the river, any surface run-off from this heap or shallow groundwater would enter the river without attenuation. Given that the river bank is situated at the foot of the heap, which features slopes between 35° and 80°, gully erosion is likely to constitute an important contaminant pathway to the River Tamar.

3.3.2 Sampling

Mine waste samples were collected on 20/09/06 from a 1 m-deep trenches, dug into different slopes in waste heaps consisting of fine grained material (DGC2 and GCM) as shown diagrammatically in Figure 3.9. Five samples of the approximate size 11 cm x 11 cm x 15 cm were carefully extracted from the bottom of the excavation so as to keep sample disturbance to a minimum. Samples from waste heaps consisting of coarser material, namely DGC1 and DGC3, were taken at relatively shallow depth (ca. 30 cm), as disturbance of the sample could not be prevented due to the granular nature of the material extracted. All samples were transferred to plastic containers and sealed to prevent variation in their moisture content prior to analysis.

For each site, two replicate samples were analysed for particle size distribution, consistency limits, and permeability, except at GCM. At this waste heap, three samples were collected, and only one replicate of each sample was analysed for grain size distribution, as the grain size distribution of the samples from this heap were similar. As a result, these three samples will be treated as one in terms of the consistency limits analysis and permeability tests. The remaining samples were stored for further analysis.
3.3.3. Laboratory analysis

3.3.3.1 Particle size distribution

The particle size analysis was undertaken in triplicate using laser diffraction technique (Malvern Mastersizer Long-bed X with MS 17 autos-ampler), capable of measuring particle sizes ranging from 2 mm to 4 µm. Sample preparation consisted of removing organic matter using hydrogen peroxide digestion (H₂O₂, 30 ml, 6%) at room temperature for a duration of 24 hours. The samples were thereafter placed on a hot plate until effervescence ceased, then oven-dried (105°C) overnight. Samples were weighed and particles with a size larger than 2 mm were separated using wet sieving technique. The retained sample (>2 mm) was dried and weighed as before. Solids of less than 2 mm (equivalent) diameter were mixed with de-ionised water to form a homogenous paste, from which three separate aliquots were introduced to the instrument.

The results from wet sieving and laser diffraction techniques were then combined and the data was interpreted using Folk and Ward statistical method (Folk & Ward, 1957 in Azizi, 2008).
3.3.3.2. Liquid and Plastic limits

The consistency of the soil was determined by the liquid and plastic limits, which are only applicable to fine grained material (DGC2 and GCM). Tests were carried out in duplicate. The liquid limit was measured using a penetrometer fitted with a 35 mm long, 30° cone of stainless steel as shown in Figure 3.10. The cone and the sliding shaft had a mass of 80g. The soil sample was mixed with distilled water to form a thick paste, which was filled into a cylindrical cup (55 mm diameter, 40 mm deep) and levelled off to give a smooth surface. The cone was then lowered so that it just touched the surface of the soil, locked in its support then released for a period of five seconds, and its depth of penetration into the clay paste was recorded.

The cup was subsequently emptied and the paste was mixed with an additional small quantity of water, then the test was repeated. Depending on the penetration obtained from the previous test, additional water or relatively dried soil samples were added to ensure that the penetrations obtained from a total of five test cover the range of 15 to 25 mm. After each test, a sub-sample of the soil-water mixture was taken for analysis of the moisture content. The liquid limit $W_L$ is defined as the moisture content corresponding to a 20 mm rate of penetration (Azizi, 2007), and was calculated from the linear relationship obtained.

![Cone penetration test set](image_url)
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The plastic limit was determined by forming a thread of soil of 6 mm diameter and rolling it until it reaches 3 mm diameter. The same soil was used to form again a threat of 6 mm diameter and rolled to 3 mm. This process was repeated until a threat of 3 mm diameter started to crumble, thus reaching a state for which the corresponding moisture content is conventionally defined as the plastic limit $w_p$. The moisture content of the treated soil was determined by weighing and drying ($105^\circ$). The plasticity index, which is the difference between liquid and plastic limits, represents the range within which the soil in question is in a plastic state, and gives a good indication of the soil's degree of stickability.

3.3.3.3. Permeability

Two laboratory devices were used in conjunction with the measurement of permeability, depending on the soil type of the samples. Between three and seven tests were carried out for each sample, depending on the reproducibility obtained. The permeability of the coarse grained waste materials from Devon Great Consols site was measured using a constant head permeameter (see Figure 3.11a). The test is suited to granular soils, and is based on Darcy's law for laminar flow. It consists of measuring, in a given time $t$, the total quantity of flow $Q$ seeping steadily through a saturated sample of soil characterised by a cross sectional area $A$, and a flow path length $L$. Based on Darcy's law, the permeability of the soil $k$ is then calculated as follows:

$$k = \frac{QL}{hAt}$$

(3.1)

Where $h$ represents the head loss across the sample as illustrated in Figure 3.10a.

For fine grained soils (such as silts and clays), the quantity of discharge is relatively small, and the accuracy of the constant head test decreases appreciably (Cernica, 1995). Instead, a falling head permeameter (see Figure 3.11b) is more suitable for materials such as the ones extracted from DGC2 and GCM sites. The principle of the test consists of measuring, for any given time $t$, the drop in the hydraulic head from $h_1$ to $h_2$ inside a plastic tube of a cross sectional area $a$. The permeability $k$ is then calculated using the
following relationship, in which \( L \) and \( A \) represent the flow path length and the sample cross sections respectively:

\[
k = \frac{La}{At} \ln \frac{h_1}{h_2}
\]  

(3.2)

Figure 3.11 (a): Constant head permeameter, (b): falling head permeameter (after Azizi, 2007).

3.3.3.4. Slope stability analysis

The stability of mine waste slopes were analysed numerically using the software KUSlope (version 2.1). For each waste heap, a total of 44100 circular slip surfaces were assumed, for which the factor of safety (FoS) was calculated using equations 3.4 & 3.5, depending on the type of analysis (short term versus long term). The aim of these calculations was to locate the potentially critical slope failure surface, and to calculate the corresponding minimum factor of safety.
The stability of the slopes of four selected waste heaps (DGCI-3 and GC\1) were analysed using both, short term total stress and long term effective stress methods, depending on the state of each heap material. Coarse grained soils such as DGCI & 3 were characterised by a relatively high drainage potential, thus minimising any build-up of porewater pressure within the heap. Under such conditions, the soil can be assumed to develop its shear strength entirely from friction engendered between solid particles. Under such circumstances, an effective stress analysis is most appropriate, for which the stability is assessed using a 1 m-wide cross section of the heap as shown in Figure 3.12.

In its simplest form, the factor of safety against slope failure is defined as follows:

$$F = \frac{\tau_f}{\tau_{mob}}$$  \hspace{1cm} (3.3)

where $\tau_f$ corresponds to the shear strength of the soil (i.e. the entire maximum resistance inherent to the soil), and $\tau_{mob}$ is the shear stress mobilised along the potential failure surface, which corresponds to the fraction of the soil shear strength needed to balance the effect of any externally applied pressure including the self-weight of soil. In theory, slopes with FoS $\geq 1$ are safe; however, it is common practice to assume that only slopes with FoS $\geq 1.25$ should be considered safe.

Equation 3.3, however, is only a generic expression, and the factor of safety under effective stress conditions is derived by writing the equilibrium equations of horizontal forces and moments with respect to the centre of rotation of the soil mass illustrated in Figure 3.12 (Azizi, 2007):

$$\frac{1}{\sum w\sin \alpha} \sum \left[ c' + \frac{W}{u}(1 - \frac{W}{u})\tan \phi' \right] \left[ \frac{1}{\cos \alpha + \frac{\sin \alpha \tan \phi'}{F}} \right]$$  \hspace{1cm} (3.4)

Where $c'$ and $\phi'$ are the cohesion and angle of shearing resistance of the soil respectively. $u$ is porewater pressure, which is zero in this study as the heaps were not saturated, and all other parameters are as per figure 3.12.
Figure 3.12 Long term analysis of slope stability for selected circular slip surface for coarse grained waste heaps (DGC1&3). R is the radius of the slip surface. For the calculations, the slip surface was subdivided into vertical slices, where \( W_x \) is the weight of soil element of slice \( x \), \( b_x \) is the thickness of slice \( x \), and \( \alpha \) is the angle of the slip surface to the horizontal line.

The factor of safety \( F \) appears on either side of the equal sign in equation 3.4, and hence an iterative procedure is applied to solve the equation. This procedure can be summarized as follows:

1. Select a starting value for the \( F_1 \) (usually \( F_1=1 \)), then use equation 4 to calculate \( F_2 \);
2. Compare the selected value (\( F_1 \)) and the calculated value (\( F_2 \)), if they are similar then \( F= \) the selected value (and the calculated value), if they are different go to step 3;
3. Use the calculated value as a new selected value for \( F \), and calculate \( F_3 \) from equation 3.4;
4. If \( F_3 \) is different from \( F_2 \), repeat the calculations from step 3.

The calculations are assumed to have converged if the differences between selected and calculated values are within the precision required (0.01 in our study).

In contrast, fine grained soils (clay/silt) are liable to developing a head of water within the soil matrix. This increases the possibility of a slope failure occurring quickly (without warning). Accordingly, the appropriate method of analysis of slope failure is short term total stress analysis, in order to simulate a quick and unexpected slope failure. The short term slope stability analysis assumes that a soil section, with a unit width (i.e. 1 m wide),
and a total weight $W$ (kN m$^{-1}$), could potentially fail along a circular surface as illustrated in Figure 3.13.

![Diagram of slope stability](image)

**Figure 3.13** Short term analysis of slope stability for selected circular slip surface for fine grained waste heaps DGC2 & GCM. R: radius of the slip surface. W is the total weight of the sliding soil element, $d$ is the moment arm about the centre of the slip surface and $\alpha$ is the angle describing the arc AB of radius R (in radians).

The moment arm $d$ corresponds to the distance from the centre of gravity of the potentially failing surface to the vertical projection of the centre of the circle of radius R. Thus, with reference to Figure 3.13, it can be shown that in the short term, the factor of safety against slope failure is calculated by writing the equilibrium of moments with respect to the centre of rotation, leading to the following expression:

$$ F = \left( \frac{C_u R^2 \alpha}{W d} \right) $$

(3.5),

where $C_u$ represents the undrained shear strength of the soil, and $\alpha$ is the natural angle (in radians), as per Figure 3.13.

### 3.3.3.5. Erosion potential

Erosion pins (mild steel, 120 cm long, 12 cm in diameter) were positioned on the slopes at DGC1, 2 & 3 on 21/01/2005 by hammering ca. 110 cm of the pin into the spoil at right angles to the slope. At each heap, two vertical lines of four pins, approximately equally
Chapter 3: Physical and geotechnical characteristics of selected mining waste heaps

... spaced between the break of slope at the top and the foot of the heap were positioned. However, as the foot of DGCI was readily accessible by the public, leaving pins vulnerable to vandalism, no pin was positioned at the foot of the heap (Figure 3.14). The contact point between pin and the surface of the spoil was marked by a notch filed into the pin. The pins were surveyed on 11/09/2008, and any accretion or loss of material was measured.

Figure 3.14 Positioning of erosion pins on the slopes of DGCI heap in January 2005  (photo: Mighanetara, 2005).
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3.4. Results and Discussion

3.4.1. Particle size distribution

The results from the grain size analysis of samples are given in phi (\( \phi \)) intervals as:

\[ \phi = -\log_2 d \]  \hspace{1cm} (3.6)

where \( d \) is the grain diameter in millimeters.

The results are presented in Figure 3.15, and indicate that:

- **DGC1** was composed of 67-77% of coarse material, of which more than 50% is sand, the remainder being gravel. Silt constituted 21-29%, with traces of clay making up less than 2%.

- **DGC2** contained approximately 17% sand, 72% silt and 11% clay. The grain size analysis also suggested that in term of grain size distribution the materials from this waste heap were relatively homogeneous (see Figure 3.13)

- The cinder sample **DGC3** was composed of 32-47% gravel, 46-61% sand and ca. 7% silt

- The Gunnislake samples (**GCM 1-3**) consisted of 24-31% sand, 61-68% silt and 7-10% clay, and traces of gravel (<2%). At this waste heap, three main coloured layers were observed, which represent GCM 1-3. The grain size distribution of the three samples from this waste heap was similar. Furthermore, they were also similar to that of the samples from DGC 2 (Figure 3.15), suggesting the waste materials at DGC2 and GCM 1-3 are the product of similar ore processing methodology, and that the differently coloured layers in these slime and tailings ponds may indicate the deposition of waste from different ores being processed, or different environmental conditions (e.g. redox) during and/or after the deposition of the waste materials.
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Figure 3.15 Particle size distribution of the studied mine waste. The grain size of particle is given in phi ($\phi$) value.

Based on the Folk and Ward statistical method (Folk & Ward, 1957 in Azizi, 2008), the average grain size and the degree of sorting as defined by Equations 3.7 & 3.8 of each sample are summarized in Table 3.1.

Table 3.1 Soil description of mine waste materials based on the Folk and Ward statistical method. The average grain size was interpreted from the mean value (Equation 3.7), degree of sorting was interpreted from the standard deviation (Equation 3.8).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean</th>
<th>Soil type</th>
<th>Standard deviation</th>
<th>Degree of sorting</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGC 1-1</td>
<td>3.2</td>
<td>Very fine sand</td>
<td>2.80</td>
<td>Very poor</td>
</tr>
<tr>
<td>DGC 1-2</td>
<td>2.5</td>
<td>Fine sand</td>
<td>2.22</td>
<td>Very poor</td>
</tr>
<tr>
<td>DGC 2-1</td>
<td>5.9</td>
<td>Coarse silt</td>
<td>2.13</td>
<td>Very poor</td>
</tr>
<tr>
<td>DGC 2-2</td>
<td>6.0</td>
<td>Coarse silt</td>
<td>2.30</td>
<td>Very poor</td>
</tr>
<tr>
<td>DGC3-1</td>
<td>-0.4</td>
<td>Very coarse sand</td>
<td>2.51</td>
<td>Very poor</td>
</tr>
<tr>
<td>DGC 3-2</td>
<td>-0.4</td>
<td>Very coarse sand</td>
<td>2.37</td>
<td>Very poor</td>
</tr>
<tr>
<td>GCM 1</td>
<td>5.3</td>
<td>Coarse silt</td>
<td>2.36</td>
<td>Very poor</td>
</tr>
<tr>
<td>GCM 2</td>
<td>5.5</td>
<td>Coarse silt</td>
<td>2.56</td>
<td>Very poor</td>
</tr>
<tr>
<td>GCM 3</td>
<td>5.8</td>
<td>Coarse silt</td>
<td>2.66</td>
<td>Very poor</td>
</tr>
</tbody>
</table>
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- Mean grain size: \( M = \left( \frac{\phi_{16} + \phi_{50} + \phi_{84}}{3} \right) \) (3.7)

- Standard deviation: \( \sigma = \left( \frac{\phi_{84} - \phi_{16}}{4} + \frac{\phi_{95} - \phi_{50}}{6.6} \right) \) (3.8)

Where \( \phi_{5,16,50,84,95} \) represent % coarser than 5, 16, 50, 84 and 95 respectively.

3.4.2. Liquid and Plastic limits

The samples from Devon Great Consols Lower Wheal Maria slime & tailing pond were characterized by liquid limits \( w_L = 35-40\% \), plastic limits \( w_P = 28-31\% \), and a plasticity index of \( I_p = 7-9\% \). These results were in agreement with the laser grain size distribution tests, and implied that the material at this site can be accurately described as a sandy clayey silt (with approximately 70% silt, 17% sand and 11% clay). Gunnislake Clitters soil on the other hand showed \( w_L = 46-79\% \), \( w_P = 29-33\% \), and \( I_p = 16-17\% \), and can thus be termed as sandy silt (approximately 65% silt, 27% sand and 8% clay, with the remainder constituted gravel (Table 3.2).

Table 3.2 The grain size distribution and consistency limits of the mine wastes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain size distribution (%)</th>
<th>Consistency limits</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gravel</td>
<td>Sand</td>
</tr>
<tr>
<td>DGC 2</td>
<td>2- ca. 17</td>
<td>ca. 72</td>
</tr>
<tr>
<td>GCM</td>
<td>&lt;2</td>
<td>24-31</td>
</tr>
</tbody>
</table>

3.4.3. Permeability

The permeability test yielded similar results for the two tailings and slime heaps (DGC2 and GCM) of \( 1.9-2.3 \times 10^{-7} \) m s\(^{-1} \), typical of a clayey silt. The permeability of samples from the coarse grained DGC1 heap was \( 7.1-8.0 \times 10^{-5} \) m s\(^{-1} \), while the permeability of samples from the cinders (DGC3) ranged from \( 7 \times 10^{-5} \) m s\(^{-1} \) to \( 10^{-4} \) m s\(^{-1} \).

It must be emphasised, however, that a permeability value measured under laboratory conditions is very likely to be different from that \( \textit{in situ} \), due to the inevitable disturbance.
that occurs during sample extraction and preparation. Some authors report that the permeability determined in situ can be an order of magnitude lower than that measured in the laboratory (Powrie, 199; Azizi, 2007), and accordingly, the results obtained here should be interpreted with caution. Notwithstanding these limitations, the tests yielded some useful orders of magnitude that indicate whether the ingress or egress of water through any particular spoil heap is likely to play a major role in leaching or export of contaminants from a particular spoil heap.

Consequently, spoil heaps characterised by a relatively low permeability, such as DGC2 and GCM they are only partially saturated, and that the total quantity of seepage is bound to be low. The average quantity of flow seeping through the DGC2 and GCM heaps, based on the measured permeability and estimated from Darcy's law, is around 0.22 and 0.04 L s\(^{-1}\), respectively. Therefore, acid mine drainage (AMD) generation at these waste heaps is most likely to take place within the surface layer, where water is made available through infiltration after rainfall. Any acidic leachate generated within deeper layers of the waste heap over time is likely to be retained and recycled within the waste heap. Indeed, no seepage has been observed to emanate from these heaps during any survey.

In contrast, the coarse grained waste heaps (DGC1 & 3) are relatively permeable. Water infiltration in this case will enhance markedly the AMD generation, and acidic leachate is likely to seep out at the foot of the heap. The quantity of flow seeping through the DGC1 and 3 heaps, assuming a steady supply of water infiltration, was estimated at 70-100 L s\(^{-1}\) and 9-13 L s\(^{-1}\), respectively. This conclusion was supported by observations made after periods of prolonged rainfall (summers 2007 and 2008), where acidic (pH 3.1-3.8) containing up to 300 µg L\(^{-1}\) As and up to 36000 µg L\(^{-1}\) Cu seepage of a combined flow rate in the range of 4.6-12 L s\(^{-1}\) emanated from several points at the foot of the DGC1 heap (Turner, Pers. Comms.).
3.4.4 Slope Stability

3.4.4.1 Long term effective stress analysis

The slope stability of a soil is dependent on its shear strength parameters, drainage conditions, and slope geometry. Due to the level of disturbance and the nature of soil samples after extraction, the decision was made not to undertake triaxial tests which are usually used as a means to measure the soil’s shear strength. Instead, the shear strength parameters were estimated from literature (Das, 1994; Azizi, 2007) based on the determined consistency limits and grain size distribution for each sample. The values selected for each waste heap are summarised in Table 3.3.

Table 3.3 Soil parameters selected from literature for use in slope stability analysis (based on Das, 1994; Azizi, 2007). Cohesion values in brackets correspond to undrained shear strength (i.e. the soil resistance in the short term under total stress conditions).

<table>
<thead>
<tr>
<th>Waste heap</th>
<th>Soil type</th>
<th>Plasticity Index (PI)</th>
<th>Weight (γ) (kN m^3)</th>
<th>(Undrained) Cohesion (kN m^3)</th>
<th>Friction angle (ϕ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGC1</td>
<td>Silty sand</td>
<td>-</td>
<td>20</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td>DGC2</td>
<td>Clayey silt</td>
<td>7-9</td>
<td>19</td>
<td>(60)</td>
<td>-</td>
</tr>
<tr>
<td>DGC3</td>
<td>Gravelly sand</td>
<td>-</td>
<td>21</td>
<td>-</td>
<td>45</td>
</tr>
<tr>
<td>GCM</td>
<td>Clayey silt</td>
<td>16-17</td>
<td>19</td>
<td>(60)</td>
<td>-</td>
</tr>
</tbody>
</table>

The geometry of the heaps and slopes was determined from site surveys using a measuring tape and inclinometers, and checked against published survey data (Wardell Armstrong, 1992).

The waste heap DGC1 was assumed to be characterised by a high angle of shearing resistance, and a relatively low drained cohesion (10 kN m^3), due to the presence of some clay and silt within the soil mass.

The angle of slope measured on site was in the order of 45° (Figure 3.16). The use of effective stress analysis was justified by the fact that such a slope (made mainly of gravel and sand) is highly permeable, and hence any externally applied pressure was assumed not to generate any excess porewater pressure within the soil matrix. This results in the soil generating all its resistance through friction due to contact between solid particles.
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Figure 3.16 Slope geometry at DGC 1. Note the fans of eroded material at the bottom of the slope (photo: Mighanetara, 2006).

The result of the stability analyses (see Figure 3.17) of DGC 1 was a minimum Factor of Safety of $\text{FoS}_{\text{min}} = 1.36$, (calculated from equation 3.4). This indicates that the slope is safe given that in practice, the stability criterion is a FoS of 1.25 or more. The outcome of the numerical analysis was backed by site inspection, which showed no evidence of old or recent slope failures (see Figures 3.14 & 16). The stability is likely to have been enhanced by local cementation developed over the years.
Figure 3.17 Slope stability analysis result for DGC1. Calculation parameters: slope height = 25 m, slope angle = 45°, effective friction angle ($\phi'$) = 45°, drained cohesion ($c'$) = 10 kN m$^2$, unit weight ($\gamma$) = 20 kN m$^3$. $R_c$ refers to the radius of the critical failure surface.

Similar long term numerical analysis was undertaken on the heap DGC3, which is of similar grain size composition (ca. 60% sand) as DGC1. Given the high permeability of such material, effective stress analysis was carried out, for which zero cohesion was assumed, due to the lack of any cohesive material within the soil matrix. The numerical simulation resulted in a critical failure surface with a minimum factor of safety of $FoS_{min} = 1.65$ (Figure 3.18).
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Figure 3.18 Slope stability analysis result for DGC3. Calculation parameters: slope height = 15 m, slope angle = 30°, effective friction angle (ϕ') = 45°, cohesion (c') = 0 kN m² and unit weight (γ) = 21 kN m³. R<sub>cr</sub> refers to the radius of the critical failure surface.

3.4.4.2 Short term total stress analysis

The waste heap DGC2 is made of a more cohesive material (clayey silt), compared to DGC1 & 3, characterised by a relatively lower permeability (100 times lower than in the case of DGC1). Accordingly, any pressure applied to this heap was assumed to generate excess porewater pressure in the short term, due to a lack of drainage. Therefore, the resistance developed within the soil was based on the undrained shear strength of the soil, estimated at 60 kN m². The geometry of the slope was characterised by an angle of 35°, as illustrated in figure 3.19.
Figure 3.19 Left: Slope geometry at DGC2 and partial vegetation on the slope face, including bryophytes, grasses and heathers. The slope face at this site show no sign of instability which is consistent with the survey carried out Wardell Armstrong, 1992 (Right) (photo: Mighnetara, 2006).

Figure 3.20 shows the potential failure surface for DGC2, for which a factor of safety \( \text{FoS}_{\text{min}} = 1.44 \) was obtained. This indicates a high degree of safely for slope failure, an outcome reinforced by the slope conditions observed on site. The slopes of DGC2 were colonised by a succession of plants often found on mine sites, including bryophytes, grasses and heathers (figure 3.19), which are indicative of stable conditions and help to maintain the stability of this slope.
Figure 3.20 Slope stability analysis result for DGC2. Calculation parameters: slope height = 15 m, slope angle = 35°, undrained shear strength (Cu) = 60 kN m², unit weight (γ) = 19 kN m⁻³. Rcr refers to the radius of the critical failure surface.

At Gunnislake Clitters Mine the Whitesands heap (GCM, see Figure 3.21) consisted of clayey silt characterised by a very low permeability (1.9-2.3 x 10⁻⁷ m s⁻¹). An undrained shear strength of 60 kN m² was estimated, and the calculations were based on a slope angle of 50°, an intermediate value of slope angles determined on site (between 35° and 80°).
Figure 3.21 Gunnislake Clitters Mine. The left panel shows instability of the slope face at the Gunnislake Clitter heap (photo: Mighanetara, 2006), and the right panel shows the U-shaped slopes of this waste heap facing the River Tamar (based on Wardell Armstrong, 1992).

Under such conditions, the results obtained from the numerical analysis indicate that the critical failure surface (see Figure 3.22) is characterised by a minimum factor of safety of 0.81, which suggests that this waste heap is not stable in the short term.

It is worth noting that the low factor of safety is a conservative estimate, given that the slope of the site can be as high as $80^\circ$. In situ inspection of the site (refer to Figure 3.21) shows evidence of past slope failure in the form of two u-shaped ‘valleys’. Consequently, while the heap appeared to have been stable for the period of this research (2004-2008), the stability analysis indicates that a slope failure can potentially take place without any warning signs (short term quick failure).
3.4.5 Erosion potential

Of the 24 erosion pins placed in January 2005, eleven had been vandalised and rendered useless by September 2008, after 3.6 years (43.5 months). Two of the erosion pins (second and fourth from top) in the eastern row were recovered at DGCI. The second pin from the top in the original row (seen on the right margin of Figure 3.14) showed a loss of ca. 13 cm of material, and the bottom pin showed ca. 11 cm loss. This indicates an annual erosion loss of waste material from this slope of 4±0.47 cm. This result is consistent with the low cohesion of the material at DGCI and the observation of extensive fans of material at the bottom of this heap, which are, during events of high precipitation, periodically carried towards the rivers in drainage channels. Under the assumption of homogeneity, and based on the dimensions of the heap determined on site, this results can be extrapolated to an annual export of ca. 280-300 m³ of contaminated mine spoil from the three slopes (east, south and west) of DGCI, constituting <0.2% of its total volume (160000-192000 m³).
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At DGC2, one complete line of four pins at the centre of the heap was inspected, and no measurable sign of erosion or accretion of material was observed. This was confirmed by a fifth pin at the base of the slope (from the second row). This result is consistent with other observations of the slope condition, including the partial vegetation cover and grain size, which implies high cohesion of this material. Although bare surface material (not covered by vegetation) shows signs of pitting by heavy rainfall and is easily mobilised by footfall (animals, human), it appears that DGC2 has a relatively small potential for export of solid material through surface erosion.

At DGC3, the three lower pins of each row were recovered. In the western row, one of the pins placed on the slope showed ca. 1 cm loss of material. However, the resolution of the method does not allow firm conclusions to be drawn from this result, and the pin at the bottom of this row showed no measurable accretion. One of the pins in the eastern row at DGC3 happened to be located in the path of a gully that formed since the pins were placed (Figure 3.23). This pin showed ca. 19 cm loss of material in a channel between 5 and ca. 18 cm width, and the pin at the bottom of this row was located in the fan of material transported from the heap and buried to a depth of ca. 6 cm. Another pin on this slope was located to one side of this gully and showed no sign of material loss. This indicates the material at DGC3 is less prone to erosion of the slope surface than the material at DGC1. In comparison to DGC1, the material at DGC3 comprise of a sizable proportion of particles in the pebble/gravel class (Figure 3.15) made up from slag and cinders baked into coarse, angular and irregular shapes, which appear to interlock to form a relatively stable surface. Once this surface is broken, gully formation appears to be the dominant erosion process at this heap.
3.5 Conclusions

Physical and geotechnical characteristics and mathematical slope stability analysis of four selected waste heaps were investigated in order to determine migration pathways of contaminants. Coarse grained mine waste from the dressing floor (DGC1) and slag and cinder waste (DGC3) exhibited relatively high permeability, allowing water infiltrated through waste heaps, which contain some 176000-215000 m³ of contaminated materials. Water infiltration is likely to enhance the oxidation of sulfide, acid generation and mobilisation of contaminants within the heap, and their subsequent export from the waste heaps via acidic leachate. While mathematical analysis showed that the slopes of DGC1 and 3 are stable under present conditions, the erosion pin analysis indicated that substantial losses of coarse grained material occurs from these heaps, adding the export of contaminated solids to the dissolved load that enters the wider environment.

Waste from slime and tailing heaps at DGC2 and GCM consisted of fine grained material (mainly fine sand, silt and clay) and were characterised by a permeability 100-1000 times lower than the coarse grained materials studied. As a result, water infiltration into deeper layers of these waste heaps is likely to be insignificant, and the acidic leachate generated
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by sulfide oxidation was likely to be retained and recycled within the waste heaps. The physical characteristics of the slime and tailings heaps suggest high cohesion of the materials, and erosion pins results at DGC2 and partial vegetation of the slope of both heaps suggest resistance against erosion. However, the loosening of fine-grained surface materials by mechanical means (walking, rainfall, freezing, wind action) may enhance the susceptibility of the surface layer for leaching and erosion, at least in localised areas, and surface run-off may be an important mechanism for contaminant transport. The Whitesands heap at GCM, however, presents an additional contamination potential through sudden slope failure, which could export large quantities of contaminated material from the heap directly into the river Tamar. The proximity of this heap to the river commands that preventative action should be considered.

The results of this chapter suggested that contaminants in selected waste heaps can be exported into a wider environment via surface and erosion run-off, slope failure and leachate, depending on physical and geotechnical characteristics of the waste heaps. However, toxicity of contaminants depends largely on their chemical concentration and solubility. In the next chapter, chemical characteristics of mine waste will be investigated to better understand chemical behaviour and fate of contaminants both at sources (waste heaps) and disposition locations (streams).

3.6 References

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Chapter 4

Geochemistry of mine waste and stream sediments

4.1 Abstract

This chapter discusses the geochemistry and mineralogical compositions of mine wastes and stream sediments in relation to the degree of metal contamination and mobility, and examines the effects of these mine wastes on the sediments in streams receiving mine waters and erosion products of mine wastes.

The concentrations and potential mobility of the trace metals in the mine wastes studied were highly variable. The As and Cu concentrations in all samples studied, and Cd in a few samples, exceeded the Dutch intervention values, suggesting a high degree of contamination, whereas Pb and Zn concentrations in most samples were higher than the Dutch target values, indicating moderate contamination. All analysed elements, except Cd and Ni, which had mobile fraction concentrations lower than the LOD, had relatively high concentrations in the oxidisable phase, suggesting the mine wastes contained considerable amounts of sulfide minerals. The concentrations of the exchangeable fraction of most elements, except for Cu, were relatively low.

Trace metal concentrations in sediments in rivers in the peripheral mining areas and in streams and adits in the intensive mining area were elevated above the background values identified in the upper catchment, supporting the effects of mining area sources, such as mine waters and mine wastes, on the stream sediments. The stream sediments in the peripheral and intensive mining areas exhibited higher Pb and Mn concentrations than
those of the mine wastes. suggesting precipitation and/or adsorption onto stream sediments of these metals. The most potentially mobile elements in the stream sediments were Mn, Pb and Zn, followed by Cu>As= Fe. The mobility of As was associated with reducible iron, suggesting the adsorption of As onto Fe-oxyhydroxides. Furthermore, their patterns of mobility were similar to those in the mine wastes (oxidisable>reducible>exchangeable). The highest concentrations in the potentially mobile phases of Cu and Zn were in the the exchangeable fraction, which also accounted for large amounts of Pb and Mn mobility.

The mine wastes studied contained considerable amounts of sulfide minerals such as arsenopyrite, pyrite, chalcopyrite and secondary minerals such as scorodite and Fe-As-O minerals. This finding explained the presence of elements in the oxidisable fraction in the mine wastes. The results from the mineralogical analysis, together with the sequential extraction suggested that solubility of scorodite is relatively low. The results also suggested that Fe-oxyhydroxide contained considerable amounts of As and Cu, and may represent the reducible fraction of these elements.

4.2 Introduction

Following the works specified in the previous chapter, which involved the potential migration pathways of trace elements from abandoned mine sites into surface and groundwater systems, as well as physical factors influencing acid production and migration of leachate, such as grain size distribution and permeability of waste materials, this chapter will explore another characteristic of mine wastes in relation to their degree of contamination and the effects on sediments in rivers and streams draining the mining area.

The problem of sulfide oxidation associated with acidic leachate, known as acid mine/rock drainage (AMD/RMD), is well recognised and has been widely studied during the last decades. For example, Evangelou and Zhang (1995) made a detailed review of the mechanisms of oxidation of pyrite and acid mine drainage. Nordstrom and Southam (1995) emphasised the importance of microorganisms on pyrite oxidation and the formation of acid mine drainage; and in 1997 they proposed an oxidation model of iron by Acidithiobacillus ferrooxidans, which captures Fe$^{2+}$ and releases Fe$^{3+}$, to explain the
ability of microorganisms to oxidise ferrous (Fe$^{2+}$) to ferric iron (Fe$^{3+}$), which will be the oxidising agent in ferric path (Reactions 4.1-4.4) (see also Bigham et al., 1992; Solomons, 1995; Banks et al., 1997). Rimstidt et al. (1994) studied the oxidation rates of some sulfide minerals (galena, sphalerite, chalcopyrite, arsenopyrite) with ferric iron (Fe$^{3+}$) and pointed out that the reaction rates, the reaction orders and activation energies of studied minerals vary substantially. The authors concluded that the acid generating reaction mechanism of each sulfide mineral is different; hence pyrite, the most abundant gangue mineral, should not be used as a substitute for other sulfide minerals when investigating detailed studies of sulfide oxidation. Most of the research, however, has focused on the resulting water contamination and the remediation measures required. For example, Solomons (1995) reviewed the impact of metal contamination from mining activities. The author suggested that geochemical models can be used to predict metal concentrations in rivers affected by mine waters; therefore better prevention can be achieved. Treatment techniques, such as neutralisation of acidity with alkaline materials and constructed wetlands, are effectively implemented in many cases (Skousen et al., 1998; Gagliano et al., 2004; Sheoran and Sheoran, 2006).

Dold (2005) emphasised the need to investigate the mineralogy of the waste materials and physical and/or chemical reactions that take place within waste heaps. The mineral composition of mine waste has a significant influence on oxidation processes, yet it is, in many cases, poorly understood. Furthermore, the mobility, toxicity and bioavailability of the metals and metalloids depend on their phase and speciation; and the potential for waste materials to release metals or metalloids into the environment depends largely on mineralogy. Understanding the geochemistry of mining waste will provide a better prediction model for drainage quality and risk assessment, and is one of the key pieces of information for remediation measures.

The aim of this part of the study was to investigate the chemical and mineral composition of mine wastes and stream sediments from selected sites in relation to element mobility and concentrations of trace elements in river waters. The objectives of the study were:

1. To investigate the distribution and metal burdens in the waste heaps.
2. To investigate the effects of mine wastes on trace metal concentrations in stream sediments.
3. To determine the metal mobility of the stream bed sediments and the waste materials.

4. To investigate mineralogy of the stream bed sediments and the waste materials.

In order to achieve the above objectives, the following works were carried out:

1. Reviewing previous studies and preliminary field investigations in order to select the studied sites.

2. Sampling of 14 mine wastes from 5 abandoned mines in the Gunnilake/Calstock mining area, 15 main rivers in the Tamar catchment and 17 streams and adits in the intensive mining area.

3. Determining the physio-chemical properties such as grain size distribution, soil pH, total carbon and loss-on-ignition of the collected samples.

4. Analysing the total elements and operationally defined fractions of the mine wastes and stream sediments.

5. Investigating the mineralogical composition of mine wastes.

4.3 Mining waste and environmental concerns

4.3.1 Geochemistry of metal sulfide mine waste

As a product of sulfide ores, the mining waste in the study area has the potential to generate acid mine drainage. Common sulfide minerals in the study area include pyrite (FeS$_2$), chalcopyrite (CuFeS$_2$), arsenopyrite (FeAsS), chalcocite (Cu$_2$S), galena (PbS), sphalerite (ZnS) and stibnite (Sb$_2$S$_3$) (Dines, 1956a&b; Farago and Kavanagh, 1999). Upon exposure to atmospheric oxygen, sulfide minerals are oxidised, releasing acidity, metal ion and sulfate. The oxidation of pyrite, a common gangue mineral in sulfide ores, can be expressed as (Salmon, 2003):

\[
FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (4.1)
\]

\[
Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O \quad (4.2)
\]

\[
FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4.3)
\]

\[
Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad (4.4)
\]
Reaction 4.1 occurs abiotically and by direct bacterial oxidation. At pH > 4.5 with high sulfate, low iron concentrations and little or no acidity, reaction 4.2 occurs abiotically but the reaction rate decreases rapidly as pH decreases. At pH < 4.5, reaction 4.2 is predominantly determined by bacterial activity and ferric iron will become the primary oxidant of pyrite (Equation 4.3). The rate-determining step of the overall sequence is the formation of ferric ion (Equation 4.2), which at low pH (< 3) is accelerated by microorganisms such as *Acidithiobacillus ferrooxidans* (Dold, 2005; Murad and Rojik, 2003; Salomons, 1995). Singer and Stumm (1970, in Dold, 2005) reported that the presence of *Acidithiobacillus ferrooxidans* increases the oxidation rate of ferrous to ferric ion by five orders of magnitude. Providing that oxygen and water are available, the whole suite of AMD generating reactions is cyclic and self-propagating and will continue until either iron sulfide or ferric iron (Fe$^{3+}$) is depleted (Sahraei Parizi, H. et al., 2006). The availability of ferric ion for reaction 4.3 can be limited by relatively fast precipitation of ferric oxyhydroxide described in Equation 4.4. Otherwise, depending on pH-lith conditions, ferric ion may precipitate to ferrihydrite, schwertmannite, goethite or jarosite (Bigham et al., 1994 & 1996). The precipitation of ferric oxyhydroxides/oxyhydroxidesulfates can attenuate oxidation processes. This is because it removes ferric ion from the system, hence slows down the ferric path oxidation; and iron precipitates provide coatings or cemented layers, which prevent contact between sulfide minerals and oxidising agents (Perez-Lopez et al., 2005). Any metals released into solution through oxidation (Equation 4.5-4.12; sources: Dold, 2005; Rimstidt et al., 1994; Salmon, 2003) may co-precipitate with ferric oxyhydroxides or oxyhydroxide sulfates. reprecipitate (e.g. as efflorescent minerals), replace or enrich existing metals within mineral particles (such as the replacement of chalcopyrite by covellite; Dold, 2005), or are exported away from waste heaps. Secondary minerals play key roles in recycling, mobilisation and attenuation of metals and metalloids liberated by dissolution processes of mining waste (Dold, 2005; Hammarstrom et al., 2005).

Chalcopyrite oxidation (oxygen path)

\[ CuFeS_2 + 4O_2 \rightarrow Fe^{3+} + Cu^{2+} + 2SO_4^{2-} \]  (4.5)

Chalcopyrite oxidation (ferric iron path)

\[ CuFeS_2 + 16Fe^{3+} + 8H_2O \rightarrow 17Fe^{2+} + Cu^{2+} + 2SO_4^{2-} + 16H^+ \]  (4.6)

Arsenopyrite oxidation (oxygen path)

\[ FeAsS + 13O_2 + 6H_2O \rightarrow 4Fe^{3+} + 4SO_4^{2-} + 4H_2AsO_4^- + 4H^+ \]  (4.7)
Arpersonite oxidation (ferric iron path)

\[ \text{FeAsS} + 13 \text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 14\text{Fe}^{2+} + \text{H}_3\text{AsO}_4 + 13\text{H}^+ + \text{SO}_4^{2-} \]

(4.8)

Sphalerite oxidation (oxygen path)

\[ \text{ZnS} + 2\text{O}_2 \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-} \]

(4.9)

Sphalerite oxidation (ferric iron path)

\[ \text{ZnS} + 8\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-} + 8\text{Fe}^{2+} + 8\text{H}^+ \]

(4.10)

Galena oxidation (oxygen path)

\[ \text{PbS} + 2\text{O}_2 \rightarrow \text{Pb}^{2+} + \text{SO}_4^{2-} \]

(4.11)

Galena oxidation (ferric iron path)

\[ \text{PbS} + 8\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow \text{Pb}^{2+} + \text{SO}_4^{2-} + 8\text{Fe}^{2+} + 8\text{H}^+ \]

(4.12)

4.3.2 Trace element concentrations in mining waste and soils in southwest England

In southwest England, contamination of soils with Cu and As caused by past mining activities is well documented (Colbourne et al., 1975; Haswell, 1983; Thornton, 1994; Kavanagh et al., 1997; Farago and Kavanagh, 1999; Hamilton, 2000; Camm, et al., 2004; Lombi et al., 2004; Dybowska et al., 2005; Klinck, et al., 2005; Palumbo-Roe, et al., 2007). For example, Colbourne et al. (1975) reported that concentrations of 35-2000 mg/kg Cu and 90-900 mg/kg As were identified in alluvium deposits in the Tamar Valley, whereas 29-2000 mg kg\(^{-1}\) Cu and 60-2500 mg kg\(^{-1}\) As were observed in the vicinity of mining areas in southwest England. Haswell (1983) found that soils in the Tamar Valley contained 52-1400 mg/kg Cu and 14-880 mg/kg As. In mine waste and other contaminated areas associated with Devon Great Consols mine, concentrations between 170 and 52600 mg kg\(^{-1}\) As were reported by Farago and Kavanagh (1999) and Klinck et al. (2005). In other parts of the Tamar Valley 50-26500 mg/kg As were observed (Farago and Kavanagh, 1999). The previous studies on metal contaminations in southwest England and the Tamar Valley are summarised in Table 4.1

Metals in solid geological media deposit in different phases (e.g. exchangeable, reducible and oxidisable), as well as exist in different mineral species (e.g. carbonates, oxides, hydroxides, sulfates, silicates), at the same time may be present in different forms (e.g. amorphous, crystalline). Only the metal fraction that can be readily removed and mobilised from its solid state has high potential for causing harmful effects to organisms.
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and the environment. Therefore, quasi-total metal concentrations obtained by strong acid extractions (e.g. such as nitric acid, aqua regia or hydrofluoric acid) are not useful for environmental impact and risk assessments, as they only provide information on the degree of contamination but cannot be used to infer the mobility and bioavailability of metals. Such information can be better obtained by sequential extractions and mineralogical analysis of soils and sediments (Dybowska et al., 2005; Li and Thornton, 2001).


<table>
<thead>
<tr>
<th>Source</th>
<th>Location</th>
<th>Material studied</th>
<th>Cu</th>
<th>As</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colbourne et al., 1975</td>
<td>TV</td>
<td>Alv.</td>
<td>35-2000</td>
<td>90-900</td>
<td>60-1008</td>
<td>114-1020</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Soil</td>
<td>29-2000</td>
<td>60-2500</td>
<td>62-850</td>
<td>58-380</td>
</tr>
<tr>
<td>Hawsell, 1983</td>
<td>TV</td>
<td>Soil</td>
<td>52-1400</td>
<td>14-880</td>
<td>30-240</td>
<td>-</td>
</tr>
<tr>
<td>Thornton, 1994</td>
<td>CW</td>
<td>GS</td>
<td>-</td>
<td>144-892</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Kavanagh et al., 1997</td>
<td>GN</td>
<td>Soil</td>
<td>-</td>
<td>120-1695</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>DGC</td>
<td>MW</td>
<td>-</td>
<td>173-52600</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Cargreen</td>
<td>Soil</td>
<td>-</td>
<td>16-198</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hamilton, 2000</td>
<td>DGC</td>
<td>MW</td>
<td>960-8100</td>
<td>690-11300</td>
<td>47240</td>
<td>32-970</td>
</tr>
<tr>
<td>Camm., et al., 2004</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lombi et al., 2004</td>
<td>TV</td>
<td>Soil</td>
<td>1058</td>
<td>4772</td>
<td>140</td>
<td>125</td>
</tr>
<tr>
<td>Dybowska et al., 2005</td>
<td>DGC</td>
<td>MW</td>
<td>300-6144</td>
<td>5298-39715</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Klinck, et al., 2005</td>
<td>DGC</td>
<td>MW</td>
<td>-</td>
<td>249-68924</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>TV-U</td>
<td>Soil</td>
<td>-</td>
<td>17-172</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Palumbo-Roe, et al., 2007</td>
<td>DGC</td>
<td>MW-t</td>
<td>27-20900</td>
<td>1280-80000</td>
<td>42-922</td>
<td>20-535</td>
</tr>
<tr>
<td></td>
<td>MW-s</td>
<td></td>
<td>993-20900</td>
<td>12000-205000</td>
<td>386-994</td>
<td>920-3660</td>
</tr>
</tbody>
</table>

4.4 Methods

4.4.1 Reagents and materials

All aqueous solutions were prepared with Milli-Q (R ≥ 18 MΩ cm⁻¹, reverse osmosis followed by ion exchange). Standard solutions and reagents were prepared in class-100
laminar flow hood using trace metal clean techniques. Multi-element calibration standards were prepared from standard solutions listed in Table 4.2 by serial dilution and acidified with Q-HCl and Q-HNO₃ (Q for 'quality': acids purified by sub-boiling distillation in a PTFE unit).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration (μg L⁻¹)</th>
<th>Manufacture</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>10000</td>
<td>CPI Internatinoal</td>
</tr>
<tr>
<td>Cd</td>
<td>10000</td>
<td>Fisher</td>
</tr>
<tr>
<td>Co</td>
<td>10000</td>
<td>Fisher</td>
</tr>
<tr>
<td>Cu</td>
<td>10000</td>
<td>Fisher</td>
</tr>
<tr>
<td>Fe</td>
<td>10000</td>
<td>Fisher</td>
</tr>
<tr>
<td>Mn</td>
<td>10000</td>
<td>Fisher</td>
</tr>
<tr>
<td>Ni</td>
<td>10000</td>
<td>CPI Internatinoal</td>
</tr>
<tr>
<td>Pb</td>
<td>1000</td>
<td>Romil Pure Chemistry</td>
</tr>
<tr>
<td>Zn</td>
<td>10000</td>
<td>Fisher</td>
</tr>
</tbody>
</table>

Aristar grade acids were used for sample digestion and acid washing of materials, unless stated otherwise. High density polyethylene (HDPE, Nalgene, 250 ml) bottles for standard solution preparation and storage were rinsed with distilled water and soaked in detergent (Pyroneg, 2%) for one day and then rinsed thoroughly with distilled water. Subsequently, the bottles were immersed in HCl, 6 M for one week, followed by a rinse with MQ water and immersion in HNO₃, 2 M for one week. The bottles then were rinsed thoroughly with MQ water and stored in sealed plastic bags. Glass beakers and centrifuge tubes were rinsed with distilled water and soaked in detergent (Pyroneg, 2%) for one day, rinsed with distilled water, immersed in HCl (10% v/v) for one day and then rinsed thoroughly with distilled water followed by immersion in HNO₃ (10% v/v) for one day and a rinse with distilled water.
4.4.2 Sampling protocol and sample treatment

Mine waste samples were collected on 21/02/2006 from 5 mines that have extensive spoil heaps: Devon Great Consols, Gawton, New Great Consols, Gunnislake Clitters and Okeltor Mines (Figure 4.1). Where possible, 5 sub-samples were taken from the centre and each corner of a square metre grid at 2-5 centimetres depth using a trowel. At each waste heap, two to three replicate samples were collected, depending on the size of the waste heaps, except two waste heaps at Devon Great Consol Mine (DGC4&5), at which only one sample was taken. The number of samples collected for each waste heap is given in the results section (4.5.3).

![Diagram of sampling locations](image)

**Figure 4.1** The sampling locations of mining waste samples and stream bed sediment from streams and adits in the area of intensive mining (Zone C in Figure 4.2).

In order to assess the effects of intense past mining activities in the Gunnislake/Calstock mining district (Zone C, see Figure 4.2) on stream sediments, samples from stream beds
in streams and adits in the intensive mining area (Figure 4.1) and in tributaries of the River Tamar outside the mining area (Figure 4.3) were collected between 18/04/06 and 21/04/06. The Rivers Ottery, Carey, Deer and the upper stretches of the River Tamar represent an area of no mining activity (Zone A in Figure 4.2). The Rivers Thrushel, Lyd, Inny, Walkham, Tavy, Tiddy and Lynher flow through areas associated with past mining activity, although not as intense as in the Gunnislake/Calstock mining district, and they represent a peripheral mining area (Zone B, see Figure 4.2). The samples were stored in strengthened paper sample bags (Kraft).

Figure 4.2 A: Outline of areas in the Tamar catchment mined for Zn, Pb, Mn, Cu and As, respectively (data source: Environment Agency; Turner, 2008, Pers. Comms.). B: The area of most intensive mining activity in the Tamar Catchment selected as study area (Zone C, in red). ‘Peripheral mining areas’ upstream rivers and rivers draining estuarine tributaries (Zone B, in blue and brown). The upper catchment where there is no record of mining activity (Zone A, in green).

Once returned to the laboratory, the samples were dried at 30°C until constant weight was obtained. Each solid sample was gently disaggregated with a pestle and mortar and particles larger than 2 mm were removed. The <2 mm fraction was reduced to a 180 µm size (80-mesh) or smaller by a Tema Swing mill (30 seconds).
Figure 4.3 The sampling locations of stream bed sediments in tributaries of the River Tamar outside the intensive mining area (Zone A and B) for the catchment survey.

4.4.3 Instrumentation and analysis

4.4.3.1 Grain size distribution analysis

The particle size distribution of samples were analysed using the combination of mechanical sieve (≥ 2mm) and laser diffraction (< 2mm) techniques as described in chapter 3.
4.4.3.2 Soil pH

Four grams of each sample (<2 mm fraction) was made up into a soil suspension with 10 ml of de-ionised water in a 25 ml centrifuge tube. The samples were then shaken rigorously for ca. 1 minute. The pH of the samples was measured using Hanna a HI9024/5 pH meter (glass electrode, Merck for pH) after allowing the soil suspension to settle for 10 minutes. The pH meter was calibrated with pH 4 and 7 buffers (BDH Laboratory).

4.4.3.3 Carbon, Hydrogen and Nitrogen (CHN) analysis

The total carbon, hydrogen and nitrogen concentrations of samples were determined using a CHNS analyser (EA 1110, CE instruments). Approximately 8-10 mg of samples and certified reference material (CRM, PACS-1), and 1.8-2.2 mg of standard (analytical grade ethylene diamine tetra acetic acid, di-sodium salt (EDTA) were accurately weighed and placed in tin capsules before being introduced to the CHNS analyser. The percentage recovery for the CRM ranged from 97.8-98.9%.

4.4.3.4 Loss-on-ignition (LOI)

Approximately 2 g of each sample (oven dried at 105°C to constant weight) were placed into a pre-weighed crucible. The crucibles were then placed in a furnace at 440°C* overnight. The samples were cooled to room temperature in the desiccator and weighed again. The LOI was determined as the percentage of original weight lost.

4.4.3.5 Metal extraction and analysis

4.4.3.5.1 Total metal extraction

Each sample (0.1 g, < 180 µm) was digested with aqua regia (4 ml, 3:1 of concentrated HCl:HNO₃) in a glass beaker (50 ml) and heated at 120°C for 3 hours. Each beaker was covered with a watch glass to prevent evaporation.

* It should be noted that LOI carried out at temperatures above 440°C may cause weight losses from carbonate (such as CO₂) and from structural water within the crystal composition (Davies, 1974)
After cooling to ambient temperature, the digests were adjusted to 25 ml using a volumetric flask before being transferred into a universal container (polystyrene, 25 ml. Fisher) for storage. Particulate matter was allowed to settle under gravity for at least 4 hours before sample analysis by the inductively coupled plasma – optical emission spectrometer (ICP-OES, Varian 725-ES). The extraction method was verified against standard reference material (SRM) 2710 Montana Soil (National Institute of Standard & Technology). The wavelength used and the detection limit for each metal analysed are given in Table 4.2.

The percentage recovery of each metal was calculated from the ratio of the metal concentrations analysed in this study in the CRM to the certified value, which was achieved by the complete dissolution of the material. Three replicates of CRM were digested and the percentage recovery, together with the standard deviation and the wavelength used for each metal is summarised in Table 4.3.

**Table 4.3** Percentage recoveries of certified material SRM 2710 in aqua regia extraction. LODs are in mg kg\(^{-1}\) calculated from the analytical LOD (in mg L\(^{-1}\), 3 times standard deviation of bottom standard). *: based on a noncertified value.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Wavelength (nm)</th>
<th>Range of standard solutions (mg L(^{-1}))</th>
<th>LOD (mg kg(^{-1}))</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>188.98</td>
<td>0.1-1000</td>
<td>19</td>
<td>75±10</td>
</tr>
<tr>
<td>Cd</td>
<td>226.502</td>
<td>0.05-500</td>
<td>3.9</td>
<td>83±10</td>
</tr>
<tr>
<td>Co</td>
<td>238.892</td>
<td>0.05-500</td>
<td>8.7</td>
<td>8.9±4.1*</td>
</tr>
<tr>
<td>Cu</td>
<td>327.395</td>
<td>0.1-1000</td>
<td>14</td>
<td>75±11</td>
</tr>
<tr>
<td>Fe</td>
<td>259.940</td>
<td>0.1-1000</td>
<td>27</td>
<td>61±7.8</td>
</tr>
<tr>
<td>Mn</td>
<td>257.610</td>
<td>0.1-1000</td>
<td>7.2</td>
<td>62±8.2</td>
</tr>
<tr>
<td>Ni</td>
<td>230.299</td>
<td>0.05-500</td>
<td>13</td>
<td>92±19</td>
</tr>
<tr>
<td>Pb</td>
<td>220.353</td>
<td>0.05-500</td>
<td>15</td>
<td>109±3.5</td>
</tr>
<tr>
<td>Zn</td>
<td>213.857</td>
<td>0.05-500</td>
<td>4.2</td>
<td>68±8.0</td>
</tr>
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</table>
2.3.3.5.2 Sequential extraction

In this study, the sequential extraction scheme proposed by the Standards, Measurements and Testing programme of the European Union (SM&T – formerly BCR) was adopted. The BCR sequential extraction procedure consists of three main stages as follows:

1. Stage 1 - Exchangeable/acid extractable fraction (surface bound metals and carbonates)

An aliquot of each sample (0.5 g) was placed in a 50 ml polypropylene centrifuge tube (Sterilin). To each tube, 20 ml of acetic acid (0.11 M) was added and the containers were horizontally shaken (30 rpm, end to end shaker) for 16 h at room temperature. The extracts were centrifuged at 2500 rpm for 25 min. The supernatant was then carefully transferred into universal containers and stored at 4°C prior to analysis. The residue was centrifuged with 10 ml of Milli-Q water for 15 min and the washing was discarded.

2. Stage 2 - Reducible fraction (metals bound to Fe/Mn-oxides)

Hydroxylammonium chloride (20 ml, 0.1 M, adjusted to pH 2 with nitric acid) was added to each centrifuge tube and then shaken manually to break the cake that may develop during centrifugation in the previous step. The tubes were shaken at 30 rpm (in the same manner as for Stage 1) for 16 h at room temperature. The samples were then centrifuged, the supernatant was transferred into universal containers and the residue was washed by the same manner as for stage 1.

3. Stage 3 – Oxidisable fraction (metals bound to organic matter and sulfides)

To each tube, 5 ml of hydrogen peroxide (8.8 M) was added and gently shaken by hand to break the cake from the previous step. The samples were digested at room temperature for 1 h with occasional shaking. The digestion was then continued at 85°C using a hot water bath for 1 h before removing the cap of the centrifuge tubes and continued heating (at the same temperature) until the liquid was reduced to ca. 1 ml. A second aliquot of 5 ml of hydrogen peroxide was added to each sample and the tubes were then digested at the same temperature (at 85°C) with the cap on for 1 h before removing the cap until ca. 2 ml solution remained. Once the liquid reached the room temperature, 25 ml of ammonium acetate (1 M adjusted to pH 2 with nitric acid) was added to the centrifuge tubes. The samples were then shaken and centrifuged, the supernatant transferred and stored in the same way as for the previous stages.
The solutions were analysed for metal concentrations using ICP-OES and the extraction method was verified against Lake Sediment BCR 701 (Institute for Reference Materials and Measurements). The recovery values from 3 replicates are presented in Table 4.4.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Range of standard solutions (mg L⁻¹)</th>
<th>LOD (mg kg⁻¹)</th>
<th>% Recovery</th>
<th>LOD (mg kg⁻¹)</th>
<th>% Recovery</th>
<th>LOD (mg kg⁻¹)</th>
<th>% Recovery</th>
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<tbody>
<tr>
<td>As</td>
<td>0.1-100</td>
<td>2.4</td>
<td>N/C</td>
<td>4.0</td>
<td>N/C</td>
<td>3.9</td>
<td>N/C</td>
</tr>
<tr>
<td>Cd</td>
<td>0.05-10</td>
<td>0.26</td>
<td>81±1.2</td>
<td>0.46</td>
<td>92±1.2</td>
<td>0.60</td>
<td>98±29</td>
</tr>
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<td>Co</td>
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<td>1.4</td>
<td>N/C</td>
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<td>2.3</td>
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<td>Cu</td>
<td>0.1-100</td>
<td>0.90</td>
<td>124±3.0</td>
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</tr>
<tr>
<td>Fe</td>
<td>0.1-100</td>
<td>1.1</td>
<td>N/C</td>
<td>2.3</td>
<td>N/C</td>
<td>2.3</td>
<td>N/C</td>
</tr>
<tr>
<td>Mn</td>
<td>0.05-10</td>
<td>0.58</td>
<td>N/C</td>
<td>0.46</td>
<td>N/C</td>
<td>1.2</td>
<td>N/C</td>
</tr>
<tr>
<td>Ni</td>
<td>0.05-10</td>
<td>0.50</td>
<td>110±4.3</td>
<td>0.41</td>
<td>60±2.1</td>
<td>1.7</td>
<td>79±8.8</td>
</tr>
<tr>
<td>Pb</td>
<td>0.05-10</td>
<td>1.1</td>
<td>105±69</td>
<td>1.8</td>
<td>52±1.3</td>
<td>4.3</td>
<td>61±4.4</td>
</tr>
<tr>
<td>Zn</td>
<td>0.05-10</td>
<td>0.34</td>
<td>96±1.7</td>
<td>0.26</td>
<td>75±1.2</td>
<td>0.36</td>
<td>95±6.2</td>
</tr>
</tbody>
</table>

4.4.3.6 Mineralogical analysis

Mineralogy of samples was examined using low vacuum, backscattered scanning electron microscopy (SEM, JEOL 840 with Oxford Instruments Link AN10000 energy dispersive spectrometer) and automated SEM-base quantitative evaluation of minerals (QEMSCAN® 4300, EVO 50) and were carried out in collaboration with staff at Camborne School of Mine, Exeter University. Each appropriate sample (1 g, whole sample, gently broken with pestle and mortar) was mixed with graphite (1.5 g), and subsequently mixed with Epofix Resins and Epofix Hardener. The mixture was then poured into a mould of 30 mm diameter. The mould was then de-gassed for 30 minutes, followed by oven drying (50°C, at least 4 hr). Once set, the sample was polished and subsequently coated with carbon before being introduced to SEM/ QEMSCAN® (Rollinson, 2007, Pers. Comms).
4.5 Results and discussion

4.5.1 Grain size distribution, soil pH, total carbon and loss-on-ignition

The particle size distribution of mining waste samples is given in Table 4.5. At Devon Great Consols Mine, the waste materials were poorly sorted and the grain size distribution of the waste materials varied from heap to heap, mainly depending on the processes that generated the wastes. This mine was consolidated from several small mines in 1845. In its early stages, the main product of this mine was Cu and later, in the 1870s. As became one of the main products (Dines, 1956b; Wardell Armstrong, 2003). The particle size distribution of mine waste at Devon Great Consols Mine can be summarised as follows:

Table 4.5 Soil description based on Folk and Ward standard deviation (sorting) and an average particle size of mining waste sample (Folk and Ward 1957 in Azizi, 2008).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Soil description</th>
<th>Grain size distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Gravel</td>
</tr>
<tr>
<td>DGC 1</td>
<td>Poorly sorted gravelly sand</td>
<td>26</td>
</tr>
<tr>
<td>DGC 2</td>
<td>Very poorly sorted sandy silt</td>
<td>-</td>
</tr>
<tr>
<td>DGC 3</td>
<td>Very poorly sorted sandy gravel</td>
<td>53</td>
</tr>
<tr>
<td>DGC 4</td>
<td>Very poorly sorted silty sand</td>
<td>24</td>
</tr>
<tr>
<td>DGC 5</td>
<td>Not analysed (crystal sample)</td>
<td></td>
</tr>
<tr>
<td>NGC 1</td>
<td>Very poorly sorted silty sand</td>
<td>6</td>
</tr>
<tr>
<td>NGC 2</td>
<td>Very poorly sorted silty sand</td>
<td>-</td>
</tr>
<tr>
<td>GW 1</td>
<td>Very poorly sandy gravel</td>
<td>42</td>
</tr>
<tr>
<td>GW 2</td>
<td>Very poorly sandy gravel</td>
<td>53</td>
</tr>
<tr>
<td>GCM 1</td>
<td>Poorly sorted clayey silt</td>
<td>-</td>
</tr>
<tr>
<td>GCM 2</td>
<td>Very poorly sorted sandy silt</td>
<td>2</td>
</tr>
<tr>
<td>GCM 3</td>
<td>Very poorly sorted silty clay</td>
<td>1</td>
</tr>
<tr>
<td>OKT 1</td>
<td>Very poorly sorted silty sand</td>
<td>14</td>
</tr>
<tr>
<td>OKT 2</td>
<td>Very poorly sorted gravelly sand</td>
<td>10</td>
</tr>
</tbody>
</table>

- **DGC1**: poorly sorted gravelly sand. This waste originates from the Lower Wheal Anna Maria dressing floor, which was the main dressing floor of this mine (Wardell Armstrong, 2003 and chapter 2).
- **DGC2**: poorly sorted sandy silt. This waste is from a slime and tailing pond and contains waste from an ore processing technology that superseded the one that generated the waste of DGC1. Consequently, DGC2 is composed of finer grained...
material. This heap may also contain products from the re-working of the DGC 1 waste tip for As in the first half of the 20th century (Dines, 1956b; Doidge, 2007 Pers. Comms.; Wardell Armstrong, 1992).

- **DGC3**: poorly sorted sandy gravel. A slag and cinder waste heap containing the products from early ore processing and calcination of As ore (Gamble, 2007 Pers. Comms.).
- **DGC4**: poorly sorted silty sand. The waste heap of Wheal Anna Maria contains slightly cemented coarse grained material. This heap was one of the early waste heaps (during 1832-5, 1845) before the consolidation of Devon Great Consols Mine (Dines, 1956b; Wardell Armstrong, 2003).

The history of ore processing and the origin of waste at other mines is limited. The grain size distribution of mine waste at other mines is as follows:

- **Samples from New Great Consols Mine (NGC1 & 2)** were poorly sorted silty sand. This mine raised 15252 t Cu; 933 t Sn; 2479 t arsenopyrite and 4087 t As during 1863 to 1879 (Dines, 1956b).
- **Waste heaps at Gawton Mine (GW1 & 2)** consisted of poorly sorted sandy gravel. During 1853 to 1869, this mine produced 21876 t Cu; 22 t Sn; 1435 pyrite; 3850 t arsenopyrite; 15650 t As (Dines, 1956b).
- **Samples from a previous Cu and tin mine, Gunnislake Clitters, 2 & 3** consisted of poorly sorted clayey silt (GCM1), poorly sorted silty clay (GCM2) and poorly sorted silty sand (GCM3). This mine raised 33350 t Cu; 510 t Sn during 1822-7 and 1860 to 1989 (Dines, 1956b).
- **Mine waste from Okeltor Mine (OKTI & 2)** was made of poorly sorted silty sand and gravelly sand. This mine produced 13215 t Cu; 85 t Sn; 1.25 t Pb; 13371 t pyrite; 3550 t As during 1859-74 (Dines, 1956b).

The pH, total carbon and loss on ignition values of mine waste samples are given in Table 4.6. Apart from DGC5 (pH 7.0), which is the efflorescent precipitate on the calciner walls, all mine waste samples had acidic pH values, with the lowest identified at Gawton Mine (GW 2; pH 3.1) and the highest at Devon Great Consols Mine (DGC 3; pH 5.6). The range of soil pH was comparable with results reported by Dybowska et al (2005), who reported the pH of samples from this mine ranging from 3.2 to 6.8. The acidic soil pH is most likely to result from the oxidation of sulfide minerals within the waste heaps.
and lack of neutralising capacity within the waste piles. However, the average soil pH in the Tamar catchment is 4.9 (Rawlins et al. 2003), the result of the low carbonate content and mineralisation in the local bedrocks combined with the presence of organic acids and the natural acidity of the rainwater (pH 5.15-5.34, Coles 1999) in the southwest of England. The neutral pH at Devon Great Consols Mine (DGC 5; pH 7.0) may result from the dissolution of calcium arsenate, the efflorescence minerals identified at this site by Palumbo-Roe et al. (2007). Calcium arsenate was also identified as flue and calciner deposits in Wheal Busy, near Redruth, Cornwall (Potts et al. 2002).

Table 4.6 The pH, total carbon (from CHNS analysis), loss-on-ignition (LOI) of mine waste samples. 'NT': not analysed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Total Carbon (% wt.)</th>
<th>LOI (% wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGC 1</td>
<td>4.7</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>DGC 2</td>
<td>5.4</td>
<td>4.2</td>
<td>1</td>
</tr>
<tr>
<td>DGC 3</td>
<td>5.6</td>
<td>NT</td>
<td>0.3</td>
</tr>
<tr>
<td>DGC 4</td>
<td>3.4</td>
<td>0.1</td>
<td>1.1</td>
</tr>
<tr>
<td>DGC 5</td>
<td>7.0</td>
<td>NT</td>
<td>2</td>
</tr>
<tr>
<td>NGC 1</td>
<td>4.9</td>
<td>&lt;0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>NGC 2</td>
<td>3.8</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>GW 1</td>
<td>3.9</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>GW 2</td>
<td>3.1</td>
<td>&lt;0.1</td>
<td>1.4</td>
</tr>
<tr>
<td>GCM 1</td>
<td>5.1</td>
<td>&lt;0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>GCM 2</td>
<td>5.3</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>GCM 3</td>
<td>4.6</td>
<td>4.9</td>
<td>0.3</td>
</tr>
<tr>
<td>OKT 1</td>
<td>3.7</td>
<td>4.5</td>
<td>2.0</td>
</tr>
<tr>
<td>OKT 2</td>
<td>3.7</td>
<td>4.6</td>
<td>1.6</td>
</tr>
</tbody>
</table>

For CHNS analysis and loss-on-ignition (LOI), stream sediments were analysed in addition to mine waste. The results showed that stream bed sediments and the mine waste samples contained total carbon ranging from <0.1% to 7.4% w/w and organic matter between 0.1% to 2.3% w/w. The highest total carbon (7.4%) was detected in sample S16 (Blanchdown adit and its confluence). The sediments at this site contained 2.3% organic matter, measured by loss-on-ignition (LOI), suggesting a source of inorganic carbon from mineral composition. The organic contents of mine waste samples from Devon Great Consols Mine observed in this study (0.2% to 2%) were lower than the values reported by Dybowska et al. (2005, 2.6-12.3%) using the same method. However, in this study all
Chapter 4: Geochemistry of mine wastes and stream sediments

samples were mine waste while the values reported by Dybowska et al. (2005) were from mine waste and soils. Although the authors provided location and depth of samples, no other information was given, making it difficult to justify the difference between the two studies. Klinck, et al. (2005) reported that the mine waste in Devon Great Consols Mine had low organic matter contents, similar to this study. However, the authors did not report the data.

4.5.2 Metal concentrations in CRM

4.5.2.1 Aqua regia extractable metal concentrations in CRM

Various methods have been used to extract metals from soils or sediments. The choice of methods used, however, is dependent upon the nature of metals of interest. For example, hydrofluoric acid (HF), is required if metals of interest are bound within silicate lattices, while hydrochloric acid is appropriate for carbonate minerals (Dean, 2003). The CRM 2710 (Montana Soil) was collected from the top 10 cm of pasture land which is periodically flooded. It should be noted that the certified values of the CRM material were achieved from complete dissolution (e.g. HF digestion). In this study, "pseudo total" digestion using aqua regia (3:1 v/v of HCl : HNO₃) was adopted. The LODs were calculated from the analytical LOD, which was 3 time standard deviation of the bottom standard (99.7% confidence interval; Miller and Miller, 2000). The results suggested that percentage recoveries for As, Cd, Cu, Ni and Pb were greater than 70% and for Fe, Mn, and Zn were greater than 60% (Table 4.3). These values are considered adequate for this study because the aim of the analysis is to investigate the metal that can be released under normal environmental conditions with respect to pH, temperature and pressure. The recovery for Co was relatively low (8.9%). However, it should be noted that the value was based on a noncertified value. The low recovery of Co may be due to the association of cobalt with the silicate mineral matrix, which is not extractable by acid used in this study (aqua regia). As a result of low CRM recovery, cobalt will be excluded from the discussion.
4.5.2.2 BCR extractable metal concentrations in CRM

The BCR sequential extraction scheme was used to distinguish potentially mobile metals into three operationally-defined fractions, namely exchangeable/acid soluble, reducible and oxidisable fractions. The percentage recoveries of certified material BCR 701 (3 replicates) are summarised in Table 4.4. In general, the percentage recoveries of certified metals (Cd, Cu, Ni, Pb and Zn) for stage 1 and 3 were above 80%. The percentage recoveries of stage 2 were poor due to different reagent used. The BCR 701 is a reference material for a modified BCR sequential extraction. While the reagents for stage 1 and 3 used for certified material were similar to that of the ones specified in the standard BCR sequential extraction, reagent used for certified material for stage 2 was 0.5 M hydroxylammonium chloride while the reagent for the standard procedure of this stage was 0.1 M hydroxylammonium chloride. The standard deviations of all metals except Pb (stage 1) and Cd (stage 3) were within 10%. The reproducibility for Pb (stage 1) and Cd (stage 3) was poor with the standard deviations of 69% and 29% respectively. The reason for this is not clear.

It should be noted that, although re-adsorption of metals before they can be isolated for analysis and variability of reproducibility of BCR approach has been reported, in particular in Fe/Mn-oxides fraction (Mossop and Davidson, 2003), it is a simple, three-step operational defined sequential extraction and has been widely applied for metal fractionation in various matrices e.g. ash, soil, sediment and sludge (Filgueiras et al., 2002 in Poykio et al., 2006). In fact, according to Hudson-Edwards et al. (2004), there is no universally agreed standard for single or sequential extractions of As in soils and sediments. The authors strongly suggested that complementary techniques such as mineralogical and spectroscopic analysis and CRMs should be adopted to validate the results of sequential extraction.

4.5.3 Metal concentrations in mine waste

4.5.3.1 Aqua regia extractable metal concentrations in mine waste samples

The metal concentrations obtained by aqua regia extraction of 13 samples of mine waste from five mine sites are summarised in Table 4.7. In general, based on the typical
concentrations of these elements in shale, which is the country rock in this area, the mine waste samples contained moderate to high concentrations of As, Cu, Fe, Mn, Zn, and Pb. In most cases, Cd and Ni concentrations were lower than LOD.

Table 4.7 The pseudo total metals of mining waste samples. (n) represents number of sample, of which two replicates were extracted except GCM2, GCM3, OKT1 and OKT due to samples lost.

<table>
<thead>
<tr>
<th>Sample (n)</th>
<th>As (g kg⁻¹)</th>
<th>Cd (mg kg⁻¹)</th>
<th>Cu (g kg⁻¹)</th>
<th>Fe (g kg⁻¹)</th>
<th>Mn (g kg⁻¹)</th>
<th>Ni (mg kg⁻¹)</th>
<th>Pb (mg kg⁻¹)</th>
<th>Zn (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGC 1 (3)</td>
<td>24±3.8</td>
<td>&lt;LOD</td>
<td>2.6±0.6</td>
<td>110±54.7</td>
<td>0.6±0.2</td>
<td>23±1.2</td>
<td>34±6.7</td>
<td>0.1±0.06</td>
</tr>
<tr>
<td>DGC 2 (2)</td>
<td>25±3.3</td>
<td>&lt;LOD</td>
<td>3.0±0.4</td>
<td>180±43</td>
<td>0.8±0.1</td>
<td>52±13</td>
<td>155±20</td>
<td>0.6±0.08</td>
</tr>
<tr>
<td>DGC 3 (2)</td>
<td>34±6.5</td>
<td>&lt;LOD</td>
<td>6.0±0.8</td>
<td>160±37</td>
<td>1.8±0.3</td>
<td>49±5.9</td>
<td>91±7.6</td>
<td>0.5±0.08</td>
</tr>
<tr>
<td>DGC 4 (1)</td>
<td>55±3.3</td>
<td>&lt;LOD</td>
<td>0.9±0.05</td>
<td>99±6.3</td>
<td>&lt;0.1</td>
<td>&lt;LOD</td>
<td>35±3.3</td>
<td>0.03±0.003</td>
</tr>
<tr>
<td>DGC 5 (1)</td>
<td>140±31</td>
<td>&lt;LOD</td>
<td>0.6±0.3</td>
<td>130±8.2</td>
<td>&lt;0.1</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
</tr>
<tr>
<td>NGC 1 (1)</td>
<td>8.2±1.6</td>
<td>&lt;LOD</td>
<td>0.1±0.02</td>
<td>10±2.5</td>
<td>&lt;0.1</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
<td>0.02±0.004</td>
</tr>
<tr>
<td>NGC 2 (1)</td>
<td>180±4.2</td>
<td>&lt;LOD</td>
<td>1.0±0.07</td>
<td>150±3.8</td>
<td>&lt;0.1</td>
<td>&lt;LOD</td>
<td>360±16</td>
<td>0.09±0.003</td>
</tr>
<tr>
<td>GW 1 (1)</td>
<td>30±5.6</td>
<td>&lt;LOD</td>
<td>0.4±0.1</td>
<td>110±10</td>
<td>0.9±0.2</td>
<td>15±0.8</td>
<td>100±40</td>
<td>0.2±0.06</td>
</tr>
<tr>
<td>GW 2 (1)</td>
<td>59±11</td>
<td>&lt;LOD</td>
<td>1.1±0.8</td>
<td>130±28</td>
<td>0.4±0.01</td>
<td>&lt;LOD</td>
<td>85±3.5</td>
<td>0.3±0.2</td>
</tr>
<tr>
<td>GCM 1 (1)</td>
<td>3.4±0.7</td>
<td>&lt;LOD</td>
<td>1.7±0.3</td>
<td>42±11</td>
<td>0.5±0.2</td>
<td>&lt;LOD</td>
<td>91±15</td>
<td>0.1±0.03</td>
</tr>
<tr>
<td>GCM 2 (1)</td>
<td>8.5</td>
<td>5.6</td>
<td>2.3</td>
<td>71</td>
<td>0.6</td>
<td>21</td>
<td>430</td>
<td>1.3</td>
</tr>
<tr>
<td>GCM 3 (1)</td>
<td>1.7</td>
<td>&lt;LOD</td>
<td>1.0</td>
<td>41</td>
<td>0.7</td>
<td>&lt;LOD</td>
<td>52</td>
<td>0.09</td>
</tr>
<tr>
<td>OKT 1 (1)</td>
<td>76</td>
<td>31</td>
<td>3.3</td>
<td>290</td>
<td>2.0</td>
<td>37</td>
<td>230</td>
<td>2.9</td>
</tr>
<tr>
<td>OKT 2 (1)</td>
<td>140</td>
<td>40</td>
<td>4.6</td>
<td>170</td>
<td>0.8</td>
<td>38</td>
<td>620</td>
<td>1.8</td>
</tr>
</tbody>
</table>

It is clear from Table 4 that metal concentrations in mine waste samples varied markedly between each mine. The variation of metal contents in mine waste samples are dependent on metals mined, mineral ores presented, type of waste (e.g. from dressing floor, tailing pond or slag) and technology used (e.g. milling, dressing and separating of ore). For example, As contents at Gunnislake Clitters Mine were the lowest, as As was not mined at this site (Dines, 1956b). Furthermore, mine waste samples from dressing floor (e.g. DGC1 & 4 and samples from Okeltor Mine) had higher metal contents than the samples from the slime & tailings ponds at Gunnislake Clitters Mine. Unlike GCM, the slime & tailings pond samples from Devon Great Consols Mine (DGC2) contained high metal contents however. This may result from:

1. the different conditions (e.g. mineral ores and processing) present at these two mines, and
2. additional metals from other sources after the waste heap was deposited (e.g. dissolved metals from nearby sources which adsorbed onto the sediments at the top of the waste heap).

The results also suggested that mineral lodes at Okeltor Mine were richer in Mn, Pb and Zn than those at other mine sites.

Figure 4.4 shows average values for As, Cu, Mn, Pb and Zn in samples from each mine site as a summary of metal concentration of each mine. It is interesting that the mine waste samples from Okeltor Mine had the highest concentrations of all metals (except Cu, which was higher at Devon Great Consols Mine). This is probably because the mine waste at this site was less intensively worked. These high metal concentrations waste heaps, situated directly and nearby the bank of the River Tamar, therefore represent long term contamination sources for the river and estuary. The accumulation of metals in sediments in the Tamar estuary after the intensive mining activities had started was reported by Clifton and Hamilton (1979). Furthermore, a number of metals such as As, Cu, Pb and Zn in sediments in the Tamar river and estuary are within range where harmful effects are expected Langston et al. (2003).

The metal concentrations found in this study were highly variable not only from mine to mine but also within mine site. For example, As contents (as well as other metals) at Devon Great Consols Mine varied considerable depending on the processes that generated the waste as well as the degree of alteration of the waste product. For example, samples from a slag and cinder waste heap (DGC3) contained higher As, Cu, Fe and Mn contents (30400 to 37500 mg kg\(^{-1}\) As; 5400 to 6500 mg kg\(^{-1}\) Cu, 130000 to 182000 mg kg\(^{-1}\) Fe and 1600 to 2000 mg kg\(^{-1}\) Mn) than mine waste from dressing floor (DGC1: 21300 to 27200 mg kg\(^{-1}\) As; 2100 to 3300 mg kg\(^{-1}\) Cu, 73700 to 174000 mg kg\(^{-1}\) Fe and 420 to 840 mg kg\(^{-1}\) Mn). The former heap is the waste product from As calcination processes, which were not efficient in the 19\(^{th}\) century. Therefore some As which was not sublimed was left in the furnace ash. High concentrations in other metals in this heap suggest that the ore dressing and separating processes in the 19\(^{th}\) century were not efficient, and that the As ore (arsenopyrite) fed into the calciner contained minerals bearing other metals such as Cu and Mn. This is also the case for high metal contents in the dressing floor heap. The metal concentrations in slag and cinder samples were comparable to the results reported.
by Palumbo-Roe, et al. (2007; 12000 to 205000 mg kg\(^{-1}\) As; 993 to 20900 mg kg\(^{-1}\) Cu, 202000 to 304000 mg kg\(^{-1}\) Fe and 1600 to 1790 mg kg\(^{-1}\) Mn). The variation of metal concentrations in different waste product can be further highlighted with the sample from the walls of As calciner. This sample contained extremely high As contents (140000 mg kg\(^{-1}\)) whereas Cu, Mn, Pb and Zn contents in this sample were below the LOD. This is because this sample was resulted from precipitation of As left in the labyrinth and flue of As works.

![Diagram showing metal concentrations in various sites](image)

**Figure 4.4** Average As, Cu, Mn, Pb and Zn contents of samples from five waste heaps in abandoned mines in the Tamar Valley. Cadmium and Ni are excluded in this figure due to its low concentrations. Cobalt is not present due to its poor recovery. The results for Fe are not included in this figure due to its general abundance in the earth's crust, while the results for Ni and Cd are excluded due to their low concentrations. Note: the bars in the pictorial graphs are intended to show the relative differences of each element between the individual mine sites – the table at the bottom of the figure should be used to obtain approximate concentrations of elements at each mine site.
4.5.3.1.1 Degree of contamination of mine waste

In order to assess the degree of contamination, the Dutch soil guideline values (SGVs. Table 4.8) were used instead of the UK SGV for the following reasons:

1. The Dutch SGVs offer standards for more elements than the UK SGVs.
2. The UK SGVs are risk-based but in this study it is difficult to justify which category is appropriate. This is because some waste heaps are isolated from residential areas (e.g. Gawton Mine) and may be more appropriately classified as "industrial use", whereas other heaps (e.g. New Great Consols Mine) are located very close to the residential areas. Therefore, the Dutch SGV was used for the purpose of consistency.

The Dutch soil standards specify two guideline values namely the target value – an acceptable risk or natural concentration in the soil, and the intervention value – an unacceptable risk to man or the environment due to soil (Albering et al., 1999)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Target value</th>
<th>Intervention value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>20 (20)</td>
<td>29</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1,2,8* (30)</td>
<td>0.8</td>
</tr>
<tr>
<td>Cobalt</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>Copper</td>
<td>-</td>
<td>36</td>
</tr>
<tr>
<td>Chromium</td>
<td>130 (200)</td>
<td>-</td>
</tr>
<tr>
<td>Lead</td>
<td>450 (450)</td>
<td>85</td>
</tr>
<tr>
<td>Nickel</td>
<td>50 (75)</td>
<td>35</td>
</tr>
<tr>
<td>Zinc</td>
<td>-</td>
<td>140</td>
</tr>
</tbody>
</table>

Mine waste samples in all studied mines were rich in As. The lowest concentration (1700 mg kg\(^{-1}\)) was identified in a spoil heap at Gunnislake Clitters, a previous Cu and tin mine. The highest concentration (180000 mg kg\(^{-1}\)) was found in a sample from New Great Consols Mine, an abandoned Cu and As mine. In 1914 to 1918, spoil heaps in the latter mine were reworked for tin (180 t black Sn) and As (150 t refined As. Dines, 1956b).
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The concentration identified was markedly higher than the concentrations in tailing samples previously studied at the same mine (80000 mg kg\(^{-1}\); Palumbo-Roe, et al.. 2007) but comparable to As contents in slag samples (205000 mg kg\(^{-1}\)). Arsenic contents found in this study were 30-3200 higher than the Dutch intervention value (55 mg kg\(^{-1}\)). Although, the Dutch values were developed on the basis of human health and ecological receptors (RIVM, 2001) hence the values are relatively conservative for contaminated land. It is clear that mine waste at this mine (as well as others mine studied) is highly contaminated and therefore can be a potential source of environmental contamination.

Waste heaps at Gawton (30000-59000 mg kg\(^{-1}\) As) and Okeltor (76000-140000 mg kg\(^{-1}\) As) Mines are not only highly contaminated with As but are also located directly on the bank of the River Tamar. As a result, potential migration of metals through run-off and erosion from these heaps is significant and As may enter the River Tamar without attenuation.

Mine waste samples from Devon Great Consols Mine contained 24000-55000 mg kg\(^{-1}\) As in spoil heap samples and up to 140000 mg kg\(^{-1}\) As in a crystallised sample from the walls of As works. The results found in this study were comparable to the values reported by Kavanagh et al., 1997 (173 to 52600 mg kg\(^{-1}\)); Dybowska et al.. 2005 (5298 to 39715 mg kg\(^{-1}\)); Klinck, et al., 2005 (249 to 68924 mg kg\(^{-1}\)) and Palumbo-Roe, et al., 2007 (1280 to 205000 mg kg\(^{-1}\); see also Table 4.1). Although, this mine site is not located directly on the bank of the River Tamar like Gawton and Okeltor, the waste heaps at Devon Great Consols are clearly another source of potential environmental contamination in the area.

Similar to As, spoil heaps in Devon Great consols Mine were rich in Cu. The black furnace ash samples had the highest Cu contents amongst the mine waste studied, with the values ranging from 5400 to 6500 mg kg\(^{-1}\). The concentrations at the DGC1 (2100 to 3300 mg kg\(^{-1}\)) were relatively similar to those of DGC2 (2700 to 3200 mg kg\(^{-1}\)). The values observed at this mine exceeded the intervention value 11 to 34 times.

Most abandoned mines had Cd contents lower than LOD (29 mg kg\(^{-1}\)), except samples from Okeltor Mine (31 to 40 and mg kg\(^{-1}\)). The Cd concentrations found in the latter mine exceeded the guideline value (12 mg kg\(^{-1}\)). Cadmium bearing minerals were not
identified in this area, but Cd sulfide, greenockite (CdS) is often found associated with sphalerite (Zn, Fe)S (Mindat, 2007).

Zinc was found in all studied samples in moderate amounts (typically < 600 mg kg\(^{-1}\), n=17) except in a crystal sample on the walls of As works in Devon Great Consols Mine. The concentrations identified in most samples were, however, lower than the intervention value (720 mg kg\(^{-1}\)), except in that of Okeltor Mine samples (1800-29000 mg kg\(^{-1}\)). The elevated concentrations of Zn at Okeltor Mine may be connected to the source of Cd in this mine, as discussed above.

Similar to Zn, Pb was found in moderate amounts (30 to 430 mg kg\(^{-1}\)) but lower than the intervention value (530 mg kg\(^{-1}\)) except one sample from Okeltor mine (630 mg kg\(^{-1}\)). The results showed that cobalt and Ni concentrations of all mine waste studied (<30 and <52 mg kg\(^{-1}\) respectively) were lower than soil remediation intervention values suggested by the Dutch government.

4.5.3.1.2 Potential for transport of metals into the wider environment

The previous section demonstrated that As, and Cu in all samples studied and that Cd in mine wastes from Okeltor Mine were above the intervention values. This section will investigate the potential of these elements to be transported into the wider environment in term of the quantity of these elements. It should be noted that due to the waste heap geometry available (Refer to chapter 3), Gawton, New Great Consols and Okeltor Mines will be excluded from this discussion.

At Devon Great Consols Mine, the largest waste heap (DGC1) contained 21300 to 27200 mg kg\(^{-1}\) As and 2100-3300 mg kg\(^{-1}\) Cu. The heap was a product from Whcal Anna Maria dressing floor, the main dressing floor of this mine. It comprised of poorly sorted gravelly sand and yield high permeability of about ca. 8x10\(^{-5}\) m s\(^{-1}\) (chapter 3), suggesting that rain water can percolate through the waste heap immediately providing potential for As as well as other metals presented in the waste to be oxidised and transported away. This waste heap had an approximate volume of 183000 m\(^3\). By using a conservative dry density of loose sand, 1.5 g cm\(^{-3}\) (Das, 1994), this heap contains total As contents of 5900
to 7500 t As and 580-910 t Cu. This represents a long term source of As contamination to nearby residential areas and the River Tamar and its estuary.

Samples from DGC2 heap, a fine grained waste material situated at the bottom slope of the previous heap contained 23000 to 26900 mg kg\(^{-1}\) As and 2700-3200 mg kg\(^{-1}\) Cu. This waste heap was a product of slime and tailing pond of Wheal Anna Maria and despite having subjected to rework for As from 1903 to 1940 (chapter 2), this heap exhibit similar or slightly higher As concentrations to the DGC1. This may be due to enrichment, precipitation of leachate generated from the mine waste upslope (e.g. calciner, DGC1). This heap constitutes over 80% fine grain materials and yield low permeability (ca. 2.1 x 10\(^{-7}\) m s\(^{-1}\), see chapter 3), thus when subjected to rainfall and overflow from area of upper slope, the water is likely to be transported away via run-off and erosion and some retained in a shallow pond on the top of the heap. This pond is temporary and usually dries out rapidly during no incoming overflow and rain, enriching the top surface with metals from leachate of the upper slope. It is also possible that the enrichment of metals occurred during settling of slime and fine particle in the tailing pond when the mine was still in operation. Furthermore, the low permeability of this heap also suggests that this heap is only partially saturated and that the total quantity of seepage is bound to be low. The average quantity of flow seeping through the entire heap was estimated to be around 0.22 L s\(^{-1}\) (see chapter 3). Therefore, AMD generation at the waste heap is most likely to take place within the surface layer where water made available through infiltration after rainfall and the acidic leachate generated is likely to be retained and recycled within the waste heap. This waste heap had an approximate volume of 105000 m\(^3\). By applying a conservative dry density of clayey silt, 1.3 g cm\(^{-3}\) (Das, 1994), this waste heap is estimated to contain 3100 to 3700 t As and 370-440 t Cu.

Black furnace ash which taken from slag and cinder waste (DGC3) contained 30400 to 37500 mg kg\(^{-1}\) As and 5400-6500 mg kg\(^{-1}\) Cu. The waste materials at this heap were coarser and have slightly higher soil permeability than the DGC1. Therefore the contaminants in this heap will have similar migration pathways to that of the DGC1. Based on the metal contents and the estimated volume (21000 m\(^3\)), this waste heap is estimated to contain 960-1180 t As and 170-210 t Cu and is a potential source of these elements to the wider environment.
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The mine wastes at Gunnislake Clitters Mine exhibits grain size distribution and soil permeability similar to that of the DGC2. The waste materials from this heap contained 1700-8500 mg kg\(^{-1}\) As and 1000-2300 mg kg\(^{-1}\) Cu, and therefore contained an estimate of 160-774 t As and 60-210 t Cu.

It should be noted that the volumes of the contaminants presented above are calculated based on concentrations in a small number of samples which are not necessarily representative of those throughout each heap.

It is clear from the aqua regia extraction that spoil heaps in abandoned mines studied are potential sources of As and Cu and possibly for Pb and Zn contamination. However, environmental impact of these metals depends largely on their solid-phase partitioning and mobility, which can be identified by sequential extraction.

4.5.3.2 Mobility of metals in mine waste samples

In this study, the mobility of metal refers to the potential of metal being exported from sources via leaching. Therefore, it is defined in the following way: as the summation of exchangeable/acid soluble, reducible and oxidisable fractions from the BCR sequential extraction, expressed as percentages of pseudo total metal concentrations from aqua regia extraction. The residual fraction is assumed to be the difference between the pseudo total metal and the potentially mobile phases from the BCR sequential extraction. It is acknowledged that elements in these fractions are, in most cases, only potentially mobile, i.e. mobile under certain conditions and timeframes. It is widely accepted that metals in the exchangeable fraction are the most readily leached in the environment. However, leaching of metals in other operational defined fractions, e.g. oxidisation of sulphide minerals, can remove significant amounts of metals into wider environments.

4.5.3.2.1 Mobility of mine waste

Similar to aqua regia extraction, the results from BCR extraction were highly variable both from mine to mine and between individual waste heaps (Figure 4.5). For example, mine wastes from Okeltor (OKT, n=2) and Gunnislake Clitters (GCM, n=3) Mines, which are relatively homogeneous (in terms of grain size for example) throughout the mine site.
were less variable than Devon Great Consols (DGC, n=5), New Great Consols (NGC, n=2) and Gawton (GW, n=2) Mines where samples within the mine sites were relatively heterogeneous. As can be seen from Figure 4.5, As and Fe show similar pattern of mobility (oxidisable>reducible>exchangeable) in all mines studied.

Figure 4.5 The average percentages of exchangeable, reducible and oxidisable fractions of As, Cu, Fe, Mn, Pb and Zn to the total metals of mine waste samples for a) Devon Great Consols (DGC, n=4, sample DGC5 not included as this was not a mine waste as such but a precipitate on the calciner wall), b) New Great Consols (NGC, n=2), c) Gawton (GW, n=2), d) Gunnislake Clitters (GCM, n=3) and e) Okeltor (OKT, n=2). The error bar represents the mean value + standard deviation. Exchangeable Pb in all samples was lower than LOD except that of sample NGC2.
4.5.3.3.2 Mobility of individual elements

The average percentages for the exchangeable, reducible and oxidisable fractions of As, Cu, Fe, Mn, Ni, Pb and Zn in mining waste samples are presented in Figure 4.6.

Figure 4.6 The average percentages of exchangeable, reducible and oxidisable fractions of As, Cu, Fe, Mn, Pb and Zn to the total metals of mine waste samples. The error bar represents the standard deviation (n = 13; results from DGC 5 was excluded from this graph due to difference in origin). Exchangeable Pb in all samples was lower than LOD except that of sample NGC2, therefore it was not included in this graph.

Figure 4.6 shows that the average mobility of each metal in the mine waste samples varied markedly. The result from t-test analysis showed that except for As and Fe, there was no difference between each fraction (i.e. between exchangeable and reducible, exchangeable and oxidisable, and reducible and oxidisable) for Cu, Mn, Pb and Zn. High variation of Cu, Mn, Pb and Zn may suggest difference in mineralogy (both primary and secondary minerals) and environmental conditions after deposition of mine waste (e.g. groundwater level). For example, the high exchangeable/acid extractable fraction of Cu could possibly be as a result of the recycling of these metals occurred within waste heaps. It is interesting to note that significant oxidisable fractions were observed for As, Cu, Fe, Mn, Pb and Zn, suggesting that the ore dressing and separating at the time of operation of these mines were inefficient. As a result, considerable amounts of sulfide minerals such as arsenopyrite and chalcopryte were left in the mine waste.
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- **Mobility of As**

The statistical analysis (t-test) of all samples studied except DGC5 showed that oxidisable > reducible > exchangeable fractions ($p=0.006$ and 0.004 respectively). The potential mobility of As in mine waste samples from all mines studied is given in Figure 4.7. The results showed that As in mine waste at Gunnislake Clitters contained the most potentially mobile As (36%), followed by Devon Great Consols Mine (34%), Gawton Mine (28%), New Great Consols Mine (18%) and Okeltor Mine (17%). In general, the largest of the potentially mobile As fractions in the mine waste studied was the oxidisable fraction. This fraction is most likely to reflect the presence of sulfide minerals.

![Figure 4.7](image)

**Figure 4.7** The average percentage fractions of exchangeable, reducible and oxidisable fractions of As in mine waste samples from Devon Great Consols Mine (DGC, n=4, exclude DGC5 sample), New Great Consols Mine (NGC, n=2), Gawton Mine (GW, n=2), Gunnislake Clitters Mine (GCM, n=3) and Okeltor Mine (OKT, n=2). The error bar represents the standard deviation.

Mine waste at Gunnislake Clitters Mine contained the largest fraction of potentially mobile As. However, pseudo total As concentrations in this mine waste were low (ca. 4500 mg kg$^{-1}$) compared to other mines studied (ca. 70000 mg kg$^{-1}$). Furthermore, the volume of the heap is relatively small (60000-87100 m$^3$, see chapter 3) compared to DGC1 (ca.160000-192000 m$^3$) and DGC2 (ca.86500-110000 m$^3$). As a result, amongst the mines studied, this mine should have the least impact on the environment in terms of the quantity of As released (see Table 4.9). It should be noted that the figures presented
in Table 4.9 are based on As concentrations in a small number of samples which are not necessarily representative of those throughout each heap. The figures are also based on estimates (where calculated – i.e. for DGC1-3 and GCM) of waste heap volume (see chapter 3).

Table 4.9 The quantity of pseudo total, exchangeable/acid extractable, reducible, oxidisable and potentially mobile As. The calculation for pseudo total As was based on the minimum to maximum concentrations identified in each waste heap. Other As fractions were based on the mean value of the replicate sample for each waste heap. The waste volumes used were 160000-192000 m$^3$ (DGC1), 86500-110000 m$^3$ (DGC2), 15600-228000 m$^3$ (DGC3) and 60000-87100 m$^3$ (GCM). Information on the waste volume of other mines was not available.

<table>
<thead>
<tr>
<th>Waste heap</th>
<th>Pseudo total As (t)</th>
<th>Exchangeable/acid extractable As (t)</th>
<th>Reducible As (t)</th>
<th>Oxidisable As (t)</th>
<th>Potentially mobile As (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGC1</td>
<td>5900-7500</td>
<td>61-73</td>
<td>260-310</td>
<td>1440-1731</td>
<td>1770-2120</td>
</tr>
<tr>
<td>DGC2</td>
<td>3100-3700</td>
<td>82-110</td>
<td>450-580</td>
<td>540-690</td>
<td>1080-1370</td>
</tr>
<tr>
<td>DGC3</td>
<td>960-1180</td>
<td>37-54</td>
<td>150-220</td>
<td>220-330</td>
<td>410-600</td>
</tr>
<tr>
<td>GCM</td>
<td>160-774</td>
<td>0.8-1.2</td>
<td>60-87</td>
<td>69-100</td>
<td>130-190</td>
</tr>
</tbody>
</table>

Samples from Gawton and Okeltor Mines had high pseudo total As concentrations (29800 to 60300 and 75700 to 142500 mg kg$^{-1}$ respectively) and also relatively high potentially mobile As fractions (28% and 17% respectively). However, large amounts of As in these wastes were bound to sulfide minerals, which is likely to be released only from oxidation of these minerals. Furthermore, released As may be retained within the waste heaps due to precipitation or co-precipitation of secondary minerals when pH of the solution increases. The exchangeable/acid extractable fraction, which is the most readily available for leaching into surface and groundwater, was less than 1% of the pseudo total concentrations. However, this still represents a large amount of As, i.e. more than 180 t from DGC, based on the estimates shown in Table 4.9.

The highest pseudo total As content was identified in one of the samples at New Great Consols Mine (180000 mg kg$^{-1}$). However, the potentially mobile As of this sample was very low (< 1% for all fractions). Therefore, migration of As from this waste heap is more likely to be through runoff and erosion. Furthermore, material represented by this sample is less abundant compared to the other heap at this mine, which contained relatively mobile As fraction (36%), but had markedly lower pseudo total As contents (7400 to 8900 mg kg$^{-1}$).
Of four mine wastes studied, up to 34% of As in mine wastes at Devon Great Consols Mine is potentially mobile. This figure does not take into account the sample from the calciner walls, which contained 105000 µg kg⁻¹ in the exchangeable fraction. An additional mobility test for this sample, carried out with Milli-Q water (16 hr shaking), showed that As in this sample is very mobile, with ca. 27% wt. (37000±1200 mg kg⁻¹, n=2) available for dissolution by rain water. According to Palumbo-Roe et al. (2007), this material is likely to be calcium arsenate. Although, this mine waste has high mobility, it is the least abundant of the wastes studied, hence its impact on the environment may not be as significant as other heaps which have lower mobility and total metals content but are present in large quantities. Additionally, because it is present in limited amounts, it should be able to be confined readily.

Arsenic in a slag and cinder heap (DGC3) was the most potentially mobile, after the crystallised sample on the calciner walls. Approximately 50% of As in this heap was potentially mobile, with the largest potentially mobile fraction being the oxidisable (28%) and the smallest being in the exchangeable/acid extractable fraction (5%). For many years, slag has been considered relatively harmless because metals in slag are believed to be bound to the glass phases and silicate and oxide minerals that have low solubility in water (Wilson, 1994). However, relatively high mobility of As (and other metals discussed shortly) in slag and cinder samples in this study and the studies carried out by Lottermoser (2002) and Piatak et al. (2004) demonstrated that slag is not chemically inert as originally believed. The latter reported that up to 36 mg kg⁻¹ Cu, 9.4 mg kg⁻¹ Zn and 1 mg kg⁻¹ As were leached (using synthetic precipitation water) from slag produced by base metals smelting (total concentrations up to 13500 mg kg⁻¹ Cu, 10200 mg kg⁻¹ Zn and 555 mg kg⁻¹ As). Arsenic mobility in the slag samples in this study was markedly higher than the values reported by Piatak et al. (2004). This may be explained by slag and cinder waste at Devon Great Consol Mine being a product of As calcinations (Gamble. 2007 Pers. Comms). High variation in metal mobility in slag and cinder samples observed in this study and in other mines (e.g. in the study mentioned above) demonstrated that the composition of slags depends largely on the composition of the ore and the fluxes used. It should also be noted that chemicals used in this study were more aggressive (the weakest chemical was 0.11 M acetic acid, adjusted to pH 2) than those used in the previous study (H₂SO₄ + HNO₃ + DI water adjusted to pH 4.2).
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The results showed that about 31% of As in the DGCI heap, which is the largest waste heap at this mine, was mobile with the largest fraction being oxidisable (25%) and the smallest being exchangeable/acid extractable (1%). Mine waste from a slime and tailing pond (DGC2) was more mobile than the previous heap (38%). Additionally, the proportions of As in the exchangeable/acid extractable and reducible fractions in DGC2 (5 and 16% respectively) were higher than in DGCI (1 and 5% respectively), which contains a higher oxidisable fraction. This may be because the DGCI waste is coarser and exhibits higher permeability and because acidic leachate generated by sulfide oxidation can be transported away readily. In contrast to tailings from the dressing floor, because of its low permeability, leachate generated in the slime and tailings pond is likely to be retained and recycled within the heap.

Relatively high exchangeable/acid extractable As in the slag and cinder, and a slime and tailings pond heaps at Devon Great Consols suggest that As in these waste heaps can be easily mobilised, and may pose a significant risk to nearby environments and the organisms inhabiting them. Furthermore, considerable amounts of reducible As in these heaps can be released to the environment if redox conditions corresponding to soluble As species prevail. Because all the waste heaps studied have been exposed to atmospheric oxygen, sulfide oxidation at the surface of the heaps is inevitable. However, the rate and degree of oxidation within each heap may vary depending on oxygen availability which is controlled by, for example, grain size and sorting of waste materials, degree of compaction, permeability and groundwater level. For coarse grained waste, rainwater can infiltrate the heaps more easily than fine grained waste. Therefore mine waste at deeper levels of coarse grained waste such as waste from dressing floor (DGC1) and slag and cinder (DGC3) heaps is likely to be oxidised more than the fine grained waste such as in the slime and tailings pond heap.

Mobility of As in mine waste at Devon Great Consols was investigated previously by Kavanagh et al. (1997), Dybowska et al. (2005), Klinck et al. (2005), and Palumbo-Roe et al. (2007). However, because the extraction schemes used by the previous studies were different to this study and spatial variation of metals was high both within and between waste heaps, it is difficult to compare the results. For example, Dybowska et al. (2005) subdivided the Fe-Mn oxide fraction of the classic Tessier scheme into 3 steps as follows:

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1. Fe/Mn-oxides targeted by 0.4 M hydroxylammonium chloride (6 h).
2. Amorphous oxides (Fe, Al, Mn) targeted by 0.2 M NH$_4^+$-oxalate buffer (4 h) and.
3. Crystalline oxides (Fe, Al, Mn) targeted by 0.2 M NH$_4^+$-oxalate buffer in ascorbic acid (0.5 h).

The authors found that about 0.6% to 8.1% of As was bound to Fe/Mn-oxides, 53% to 99% was bound to amorphous oxides and 1.1% to 18% was bound to crystalline oxides. This study applied the BCR extraction scheme (0.1 M hydroxylammonium chloride, 16 h) for targeting metals bound to Fe/Mn-oxides or within the reducible fraction, and found that up to 23% of As was in the reducible fraction. The discrepancy of the results which may be affected by the use of different operationally defined extraction schemes can be further demonstrated by Kavanagh et al. (1997) who adopted sodium hydroxide (0.1 N, 18 h) and found that 30% to 60% of As was in Fe- and organic Fe-associated fractions. Furthermore, Palumbo-Roe et al. (2007) and Klinck et al. (2005) used aliquots of HNO$_3$ of increasing concentration (0.1 to 5 M for step 3 to 14) after leaching with DI water (step 1 and 2), followed by a complicated data processing technique, namely Chemometric Identification of Substrates and Element Distributions (CISED). The authors found that Fe was the main component in all samples analysed and over 80% of As in sandy tailings was in the Fe-As phase, whereas over 95% of As in black slag samples was in the Fe-As-(S) phase. As can be seen, the As results found in this study were markedly lower than these previous studies. Apart from the reasons discussed above, according to Van Herreweghe et al. (2003), it is also possible that reductive dissolution of amorphous Fe-oxides by hydroxylammonium chloride may be re-adsorbed to crystalline Fe-oxides such as goethite. Furthermore, the BCR procedure, like many other operationally defined sequential extraction schemes, is based on the scheme initially developed for sediments by Tessier et al. (1979), which was designed to extract cationic metals rather than anionic forms in which As occurs. Additionally, it was aimed at non-polluted or slightly polluted sediments and its application to industrial or mining polluted soils has not been widely used (Gleyzes et al., 2002 in Dybowska et al. 2005). This may explain the difference between this study and the previous studies.
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Mobility of Cu

The potential mobility of Cu (summation of BCR extractable fractions as a proportion of aqua regia extraction concentrations) in mine waste samples from all mines studied is shown in Figure 4.8. The results show that Cu in mine waste at New Great Consols Mine was lower than LOD in all 3 fractions (23 mg kg$^{-1}$) and exchangeable/acid extractable fraction in samples from Gawton and Okeltor Mine was low (<2.5%) compared to Devon Great Consols and Gunnislake Clitters (>13%). Mobility of Cu at Gunnislake Clitters and Devon Great Consols Mines was relatively high (ca. 80% and 70% respectively), with the largest fraction at Gunnislake Clitters Mine being exchangeable/acid extractable, and the smallest being oxidisable. The opposite pattern was observed at Devon Great Consols Mine. The mine waste at Gunnislake Clitters Mine was largely made of silt and clay (up to 93%) and exhibited low permeability, similar to the slime and tailings pond heap at Devon Great Consols Mine. It is apparent that fine grained waste with low permeability enhances element recycling within the heaps, leading to larger fractions of Cu present in exchangeable forms.

At Devon Great Consols Mine, similar to As, Cu in the slag and cinder waste heap was the most mobile (80%), followed by waste from the main dressing floor (78%) and the slime and tailings pond (54%). The largest mobile Cu fraction in the main dressing floor waste was the oxidisable fraction (ca. 58%), whereas the exchangeable/acid extractable and reducible fractions were relatively low (ca. 20%). In contrast, the slag and cinder waste and the slime and tailings pond waste contained higher exchangeable/acid extractable and reducible Cu (ca. 47% and ca. 36% respectively).

It should be noted that although Cu in the mine wastes at Gunnislake Clitter Mine were more mobile than those at Devon Great Consol, the total concentrations were considerably lower. Furthermore, the size of the waste heap at this mine was ca. 1.5-2 times smaller than that of the DGC1&2. The mine waste at Gunnislake therefore had the least potential for metals to be mobilised (e.g. eight times less than DGC; see Table 4.10).
Figure 4.8 The average percentage fractions of exchangeable, reducible and oxidisable fractions of Cu in mine waste samples from Devon Great Consols Mine (DGC, n=4, exclude DGC5 sample), New Great Consols Mine (NGC, n=2), Gawton Mine (GW, n=2), Gunnislake Clitters Mine (GCM, n=3) and Okeltor Mine (OKT, n=2). All Cu fractions in samples from New Great Consols Mine were lower than LOD (23 mg kg⁻¹). The error bar represents the standard deviation.

Table 4.10 The quantity of pseudo total, exchangeable/acid extractable, reducible, oxidisable and potentially mobile Cu. The calculation for pseudo total Cu was based on the minimum to maximum concentrations identified in each waste heap. Other Cu fractions were based on the mean value of the replicate samples for each waste heap. The waste volumes used were 160000-192000 m³ (DGC1), 86500-110000 m³ (DGC2), 15600-22800 m³ (DGC3) and 60000-87100 m³ (GCM). Information on the waste volume of other mines was not available.

<table>
<thead>
<tr>
<th>Waste heap</th>
<th>Pseudo total Cu (t)</th>
<th>Exchangeable/acid extractable Cu (t)</th>
<th>Reducible Cu (t)</th>
<th>Oxidisable Cu (t)</th>
<th>Potentially mobile Cu (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGC1</td>
<td>580-910</td>
<td>62-75</td>
<td>65-78</td>
<td>360-430</td>
<td>490-580</td>
</tr>
<tr>
<td>DGC2</td>
<td>370-440</td>
<td>56-71</td>
<td>65-83</td>
<td>62-79</td>
<td>180-230</td>
</tr>
<tr>
<td>DGC3</td>
<td>170-210</td>
<td>33-48</td>
<td>32-48</td>
<td>47-68</td>
<td>110-160</td>
</tr>
<tr>
<td>GCM</td>
<td>90-210</td>
<td>53-77</td>
<td>33-49</td>
<td>17-25</td>
<td>100-150</td>
</tr>
</tbody>
</table>

- Mobility of Fe

Iron is one of the most abundant metals found in this study (Table 4.7). However, Fe mobility was relatively low compared to other elements studied (Figures 4.5&6). Typically, the exchangeable/acid extractable Fe in mine wastes studied was lower than 0.5%, ranging from lower than LOD to 1.7% (DGC1). The pattern of potential mobility
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of Fe (oxidisable > reducible > exchangeable fractions, p=0.03 and <0.000 respectively) was similar to that of As. Similar to As and Cu, the oxidisable fraction of Fe may be accounted for by sulfide minerals (e.g. arsenopyrite, chalcopyrite and sphalerite).

- Mobility of other metals (Cd, Mn, Ni, Pb and Zn)

In general, the potential mobility of Mn in mine wastes was relatively low, with most of the exchangeable and reducible fraction being lower than LOD. Typically, mine waste samples showed large amounts of the oxidisable fraction with the value ranging from lower than LOD to up to 13% in a sample from DGC2. According to Dines (1956a & b), Mn minerals mined in this region were pyrolusite (MnO₂) and rhodonite (Mn, Fe, Mg, Ca)SiO₃. It is possible that the oxidisable fraction may be accounted for by alabandite (MnS), which so far has no record in this region. It is also possible that these data result from the operationally-defined nature of the sequential extraction - i.e. part of the oxidisable fraction could be accounted for by incomplete extraction of the reducible fraction, or by re-adsorption onto crystalline mineral phases, followed by subsequent extraction by the more aggressive reagent used for the oxidisable fraction (as discussed in mobility of As).

The mobility of Pb was highly variable. Eight out of the 14 samples studied, either had pseudo total concentrations or all mobile fractions lower than LOD. In four samples, Pb was only detected in the oxidisable mobile fraction. The highest pseudo total (360 mg kg⁻¹) and potentially mobile Pb (62%) was identified in the NGC2 sample.

In general, the mobility of Zn in the studied samples was relatively low (16±8.6%). Similar to other elements, the mine waste samples studied showed large proportions of oxidisable Zn, suggesting sulfide minerals as sources of Zn. For Cd and Ni, all mobile fractions were lower than LOD.

The results from the BCR sequential extraction demonstrated that, although highly variable, all elements analysed except Cd and Ni, which had mobile fractions lower than LOD, had relatively high oxidisable phases. The exchangeable fractions of most elements however were relatively low except those of Cu. It is interesting that some mine wastes exhibit high element pseudo total concentrations but their element mobility was relatively low (e.g. <1% of 18000 mg kg⁻¹ As is mobile in a sample from New Great
In the next section, this study will investigate the mineralogy of mine wastes in order to better understand their mobility.

**4.5.3.3 Mineralogy of mine waste**

QEMSCAN® is an automated mineral analysis system enabling rapid (ca. 10 ms per pixel) and accurate mineral analysis (Pirrie et al., 2004). However, in order to employ it effectively, it is necessary to have good background knowledge on the mineralogy of the samples. Furthermore, the quality of the data also depends on the pixel spacing. The more detailed the results, the more resources required. In consideration of this constraint, the QEMSCAN® analysis was carried out at 6 µm pixel spacing for particle mineral analysis (PMA) mode and 20 µm pixel spacing for field scan analysis. As a result, particles smaller than 20 µm may be underestimated in the field scan analysis, and 6 µm in PMA mode.

In contrast to QEMSCAN®, the SEM can identify particles as small as one micron (mass median diameter), depending on the quality of sample preparation. However, SEM analysis is more time consuming and does not allow automatic mineral interpretation. In this study, QEMSCAN® was applied to identify and quantify sulfide minerals (e.g. arsenopyrite, chalcopyrite, pyrite, sphalerite and galena) and the main component minerals (e.g. quartz and oxide minerals) in the mine waste. This is because sulfide minerals are potential sources for AMD. SEM was employed to investigate the alteration of primary sulfide minerals and identify secondary mineral phases to better understand the pathways and fate of As and metals released from sulfide oxidation. Additionally, the results from SEM were used to better interpret the results from QEMSCAN® analysis. The mineral composition of mine waste samples as determined by QEMSCAN® is summarised in Table 4.11.

The mineralogy of studied mine waste was composed predominantly of quartz and other silicate minerals (e.g. chlorite, clay) followed by arsenopyrite and its weathering products (e.g scorodite), pyrite, chalcopyrite and Fe-oxides or carbonates. In general, chalcopiyrite contents were much lower than arsenopyrite in most samples. This may be due to a number of waste heaps in this region being generated before As became a valuable commodity.
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Table 4.11 The mineral composition in percentages from QEMSCAN® analysis (field scan analysis; semi-quantitative) of mine waste samples. DGC = Devon Great Consols Mine, NGC = New Great Consols Mine, GW = Gawton Mine, GCM = Gunnislake Clitters Mine, OKT = Okeltor Mine.

<table>
<thead>
<tr>
<th>Sample</th>
<th>DGC1</th>
<th>DGC2</th>
<th>NGC1</th>
<th>NGC2</th>
<th>GW1</th>
<th>GW2</th>
<th>GCM 1</th>
<th>GCM 2</th>
<th>OKT1</th>
<th>OKT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>37.5</td>
<td>12.8</td>
<td>52.3</td>
<td>11.1</td>
<td>45.0</td>
<td>34.1</td>
<td>37.6</td>
<td>17.8</td>
<td>27.5</td>
<td>16.9</td>
</tr>
<tr>
<td>Other silicates than quartz</td>
<td>32.2</td>
<td>39.7</td>
<td>42.9</td>
<td>19.8</td>
<td>24.8</td>
<td>11.2</td>
<td>58.9</td>
<td>67.5</td>
<td>15.6</td>
<td>11.9</td>
</tr>
<tr>
<td>Pyrite</td>
<td>1.5</td>
<td>5.8</td>
<td>0.1</td>
<td>0.1</td>
<td>2.7</td>
<td>4.0</td>
<td>&lt;0.1</td>
<td>1.4</td>
<td>3.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>6.3</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>1.0</td>
<td>4.4</td>
<td>28.8</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>2.5</td>
<td>1.7</td>
</tr>
<tr>
<td>Scorodite</td>
<td>1.5</td>
<td>1.0</td>
<td>1.1</td>
<td>24.3</td>
<td>4.3</td>
<td>6.5</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>5.9</td>
<td>20.8</td>
</tr>
<tr>
<td>Other As Phases</td>
<td>0.5</td>
<td>0.2</td>
<td>1.7</td>
<td>0.6</td>
<td>0.5</td>
<td>0.5</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.7</td>
<td>4.0</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>0.3</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Other Cu Phases</td>
<td>0.3</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>0.7</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Galena</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Other Sulphides</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Fe-Oxides/CO3</td>
<td>11.6</td>
<td>36.6</td>
<td>1.9</td>
<td>40.7</td>
<td>15.2</td>
<td>12.5</td>
<td>2.5</td>
<td>10.8</td>
<td>41.8</td>
<td>40.7</td>
</tr>
<tr>
<td>Mn-Oxides/CO3</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Others</td>
<td>8.5</td>
<td>3.7</td>
<td>1.6</td>
<td>1.5</td>
<td>2.6</td>
<td>2.3</td>
<td>0.9</td>
<td>1.4</td>
<td>2.3</td>
<td>2.8</td>
</tr>
</tbody>
</table>

The highest amount of arsenopyrite shown in Table 4.11 is 29% but this figure is unlikely to be correct for reasons to be discussed later in this section. The next highest arsenopyrite content was identified in sample DGC1 (Lower Wheal Anna Maria dressing floor spoil tip, 6.3%), which also contained 0.3% chalcopyrite. Because it contained high arsenopyrite, this waste heap was reworked for As in 1918 and 13 tons of As were recovered (Dines, 1956b). However, according to Frederic Sherrell Limited (2000) and Doidge (2007, Pers. Comms.) some small scale mining and reworking of the extensive surface dump (represented by DGC1) was continued until about 1940 (no output record was available). The waste of this reworking, which was placed over the original slime and tailings pond waste (DGC2) contained markedly lower arsenopyrite (0.2%). The DGC2 heap, however, had As contents (23000 to 26900 mg kg⁻¹), as high as those in the DGC1 heap (21300 to 27200 mg kg⁻¹). This may be explained by the results from QEMSCAN® which showed that the DGC2 heap contained about 37% Fe-oxides or carbonates. Detailed examination under the SEM of particles identified by QEMSCAN® as Fe-oxides or carbonates showed that some of these particles contained As up to 12%. Because SEM cannot identify hydrogen, particles identified as Fe-oxides which have considerable amounts of As are likely to be Fe- oxyhydroxide or Fe- hydroxysulfate minerals. This is particularly true for the secondary minerals associated with sulfide oxidation.
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The secondary Fe oxyhydroxide or hydroxysulfate minerals in the acid mine drainage environment (see Equation 4.4) include goethite, ferrihydrite, schwertmannite and jarosite (Hammarstrom and Smith, 2002; Bigham et al., 1992). The ability of Fe-oxyhydroxides to absorb As and heavy metals due to their reactivity and large specific area is well documented. For example, Foley et al. (2002) reported As concentrations of up to 5000 g kg\(^{-1}\) in goethite and up to 40 g kg\(^{-1}\) in jarosite. The authors also reported that pyrite can contain up to 4% As by weight. Pierce and Moore (1982) observed that As is strongly sorbed by amorphous Fe-hydroxides. In his study as much as 92% of As was removed from solution and the adsorption was a function of pH. Fuller et al. (1993) pointed out that the co-precipitation process of As(V) with ferrihydrite is dependent upon diffusion processes and the adsorption decrease when ferrihydrite undergoing aging. These secondary Fe-As-oxides were also found to precipitate onto silica minerals such as quartz and chlorite (discussed shortly). The impregnation of silicate minerals (illite and chlorite) in mine waste samples at Devon Great Consols Mine was also reported by Palumbo-Roe et al. (2007).

Under manual SEM analysis, Fe-oxides or oxyhydroxides or hydroxysulfates in samples from the DGC2 heap occurred as a fibrous like feature (Figure 4.9a), which often showed silica and aluminium peaks. The latter two minerals are likely to be the results from quartz or silicate particles, which were enclosed during precipitation. This characteristic allowed for distinguishing between primary Fe-oxides, such as hematite, from the secondary ones. The Fe-oxide or oxyhydroxide minerals in this sample contained up to 12% As (Figure 4.9b).

The identification of considerable amounts of As associated with Fe-oxide or oxyhydroxide mineral phases explained high total As contents and large amounts of reducible fraction (metal bound to Fe/Mn-oxides) in samples from a slime and tailings pond waste heap (DGC2). Despite containing low arsenopyrite (0.2%) compared to waste from a dressing floor heap (DGC1. 6.3%), both heaps yielded similar As contents (ca. 25000 mg kg\(^{-1}\)). The results suggested that arsenopyrite is the main source of As in the dressing floor heap. This is in good agreement with the results from the BCR sequential extraction that the largest potentially mobile phase of As in this sample was in the oxidisable fraction (25%), followed by the reducible phase (5%). The reducible As is
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likely to be accounted for by Fe-oxides or carbonate minerals (12%) identified in this sample.

Mine waste in a slime and tailings pond heap (DGC2) consisted of 37% Fe-oxides or carbonates and its reducible As fraction was 16%. It is interesting that a similar proportion of As in this mine waste was found in the oxidisable fraction, although it contained only 0.2% arsenopyrite. This may be explained by the following:

1. Oxidisable As in this mine waste may be associated with pyrite. According to Foley et al. (2002), pyrite can contain up to 4% As by weight and this waste heap contained 5.8% pyrite.

2. It is possible that the reagent used (0.1 M hydroxylammonium chloride, 16 h) may not be able to extract As associated with stable Fe-oxyhydroxides or that As was re-adsorbed onto goethite at this stage of the sequential extraction. As discussed in the above section, As bound to Fe-oxides in this study (23%) was markedly lower than previous studies (ca. 50-99%). Arsenic which was not extracted or re-adsorbed during stage 2 (reducible) would be extracted by a more aggressive acid used in stage 3 (oxidisable), resulting in overestimation of As in the latter fraction.
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Figure 4.9 (a) Backscattered scanning electron microscopy image showing fibrous like texture of Fe hydroxide particle in sample DGC1 (slime and tailing pond spoil tip in Devon Great Consols mine). F-pyrite corresponds to frambiodal pyrite. (b) The semi-quantitative EDS spectrums showing As (5-12%) in Fe-oxide or oxyhydroxide minerals (images: Mighanetara, 2007).

Manual investigation showed that arsenopyrite particles were often enclosed by Fe-As-O mineral phases (Figure 4.10). The results from semi-quantitative energy dispersive spectrometer analysis (EDSA) showed that the Fe:As ratio of this Fe-As-O phase was ca. 1:1. A similar finding was reported by Flemming (2005), who studied the weathering products of arsenopyrite with SEM, electron probe micro-analysis (EPMA) and µXRD. The author concluded that Fe-As-O minerals associated with weathered arsenopyrite with a Fe:As ratio of 1:1 are scorodite (FeAsO₄·2H₂O), kankite (FeAsO₄·3.5H₂O) and amorphous Fe arsenate. Scorodite is a weathering product of arsenopyrite and...
precipitates under oxidising, acidic conditions (Dove and Rimstidt, 1985; Ahu and Merkel, 2001 cited from Flemming, 2005). Mok an Wai (1994) reviewed the mechanisms of As immobilisation and showed that scorodite is a co-precipitation mineral of As(V) and Fe(III) – oxyhydroxides which form according to the following reaction:

\[
Fe(OH)_3 + H_3AsO_4 \rightarrow FeAsO_4 \cdot 2H_2O + H_2O
\]  

(F.13)

Figure 4.10 Backscattered scanning electron microscopy image showing the alteration of arsenopyrite caused by the oxidation of sample DGC1 (Lower Wheal Anna Maria dressing floor spoil tip in Devon Great Consols mine). The Fe-As-O phase contained 44% O, 27% As and 25% Fe. Qtz = quartz (image: Mighanetara, 2007).

This Fe-As-O mineral phase was observed in sample DGC1, GW1, GW2, NGC1, OKT1 and OKT2. In a sample from Gawton Mine (GW2), the Fe-As-O phase was observed in particles having a fractured-like texture (Figures 4.11 a&b). They were found in abundant amounts (29%) in sample GW2. This mineral was identified as arsenopyrite by QEMSCAN®. However, the manual SEM results suggested that these particles contained ca.46% O, ca.28% Fe, ca.20% As and ca.6% S (Figure 4.12b), and are therefore unlikely to be arsenopyrite. Furthermore, the texture of these particles does not resemble arsenopyrite particles identified in all samples studied in this research (Figures 4.10& 11b) and the references herein (e.g. Flemming, 2005; Petrunic et al., 2006). It is not clear whether they were the complete oxidation of primary arsenopyrite particles or formed at later stages (i.e. precipitation). The fractured-like texture suggests that these Fe-As-O containing particles may have undergone a dehydration process, i.e. the
alteration from kankite (FeAsO$_4$ 3.5H$_2$O) to scorodite (FeAsO$_4$.2H$_2$O), which is more stable (Flemming, 2005). The presence of relatively high amounts of sulphur in these particles compared to the Fe-O-As material surrounding arsenopyrite (see Figures 4.12b&c) may be due to the substitution of (SO$_4$)$^{2-}$ for (AsO$_4$)$^{3-}$, which would also explain the relative deficiency of As in these particles (Fe:As slightly greater than 1, Figure 4.12b compared to most Fe-As-O minerals observed in this study which Fe≈As, Figure 4.12c). The substitution of (SO$_4$)$^{2-}$ for (AsO$_4$)$^{3-}$ in hydrated ferric arsenate was reported by Flemming (2005).

Figure 4.11 (a) Backscattered scanning electron microscopy image showing the distribution and abundance of the fractured Fe-As-O mineral particles (B) in sample GW2 (Gawton mine) (ca. 28%); (b) magnified backscattered scanning electron microscopy image showing arsenopyrite particle (A), the fractured Fe-As-O mineral particles (B) and other Fe-As-O mineral (C) (images: Mighanetara, 2007).
It is interesting to note that out of 10 samples studied, GW2 was the only one sample that appeared to have the discrepancy between the results form QEMSCAN® and the manual SEM. Although, quantifying the mineral composition by the manual SEM is difficult, this can be roughly estimated from the snapshot of the sample block. For example, as can be seen from the snapshot of NGC1 sample (Figure 4.13), this sample is composed virtually of quartz and chlorite minerals. This agrees with the results from QEMSCAN® which shows that this sample consists of 52.3% quartz and 42.9% other silicate minerals other than quartz.
A similar chemical composition to the Fe-As-O phase was also observed in a sample from New Great Consols (NGC2) but with a different texture. In this sample, the Fe-As-O phase occurred as a crystalline mineral precipitated onto nucleus particles such as chlorite, K-feldspar or clay particles (Figure 4.14). This sample contained as high as 24% of this Fe-As-O phase, making it is possible to analyse it with XRD and the results suggested the mineral analysed was scorodite. It should also be noted that, although this sample contained 180000 mg kg\(^{-1}\) As, but less than 1% of As in this sample was mobile. This is because the solubility of scorodite is considerably low making it is a desirable mineral for As attenuation (Flemming, 2005).
Chalcopryrite was found in much lower amounts than arsenopyrite and this was reflected in the pseudo total concentrations (As>>Cu). Most samples contained less than 0.1% chalcopryrite and the highest content (0.3%) was identified in mine waste from the main dressing floor of Devon Great Consols Mine (DGC1). In general, chalcopryrite particles were less weathered than arsenopyrite (Figure 4.15). This finding is consistent with previous studies (e.g. Rimstidt et al., 1994; Brock et al., 1984 in Jambor, 1994), which found that arsenopyrite is more reactive than chalcopryrite. Jambor (1994), however, reported that reactivity of sulfide minerals can vary markedly depending on the condition under which the oxidation occurs.

![Figure 4.15 Backscattered scanning electron microscopy image A: showing degree of weathering of chalcopryrite (Ch) and arsenopyrite (Ar); B: close up image of chalcopryrite particle; C: close up image of arsenopyrite particles and precipitates of Fe-oxides on quartz (Qtz) surface (images: Mighanetara, 2007).](image-url)
The results from by QEMSCAN® and manual SEM analysis revealed that all studied heaps, except one sample from Gunnislake Clitters Mine (GCM 1), contained higher amounts of As-bearing minerals than Cu-bearing minerals. This was in good agreement with the results from aqua regia extraction. Other Cu sulfide minerals identified with manual SEM and QEMSCAN® include tennantite and enargite. However, they were found in small amounts (typically <0.1%). Chalcopyrite and other Cu sulfides accounted for the oxidisable fraction, which was the largest potentially mobile phase (up to 58%) in most samples studied.

The manual SEM analysis also showed co-precipitation of Cu with Fe-As-O phases with Cu contents of up to 8% (Figure 4.16). This may provide a source of Cu in the reducible fraction (i.e. bound to Fe-oxides). Furthermore, other Cu minerals such as cornubite \( \text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4 \), cornwallite \( \text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4 \), brochantite \( \text{Cu}_4[(\text{OH})_6 \text{SO}_4] \) and azurite \( \text{Cu}_3 [\text{OH} \text{CO}_3]_2 \) have been identified previously at the studied mines (Mindat, 2007; see also chapter 2). Copper sulfates (e.g. brochantite) are relatively mobile in water (e.g. solubility of Cu (II) sulfate is 14.3 g (cold water) and 75.4 g (hot water) per 100 ml of water) (Weast et al., 1988). Additionally, Cu carbonates (e.g. azurite) are acid soluble. This may explain the relatively high exchangeable/acid extractable and reducible fractions of Cu in mine wastes particularly those from Devon Great Consols and Gunnislake Clitteres (Figures 4.5&6&8).

As can be seen from the metal contents (both pseudo total metals and sequential extractions) mine waste in most of the abandoned mines studied contained high As and Cu. The mineralogical analysis by QEMSCAN® and manual SEM revealed that mine waste commonly contained As and Cu-bearing minerals (e.g. arsenopyrite, scorodite and chalcopyrite). Additionally, Fe-oxides were shown to have considerable amounts of As and Cu. As for Pb, Zn and Cd, although galena and sphalerite were found in small amounts (<0.1%), their pseudo total contents were moderate (above target values but lower than intervention values). Taken together with the results from the wet chemistry, these mine wastes are potential sources for As and Cu contamination and to lesser extent Pb and Zn into the River Tamar and the nearby residential area. The next section will explore the contamination of these mine wastes on stream sediments in order to better understand the migration pathways of As and these metals and will investigate the
degree of contamination (if any) of streams receiving mine waters and run-off and erosion products from the studied waste heaps.

Figure 4.16 Backscattered scanning electron microscopy image showing co-precipitation of Cu with Fe-As-O minerals (images: Mighanetara, 2007).

4.5.4 Metal concentrations in stream sediments

Sediments play an important role in regulating water quality. They can serve as both sinks and sources of contamination. Generally, concentrations of trace metals in streambed sediments exceed their concentrations in the overlying water by between three and five orders of magnitude (Bryan and Langston, 1992). Prolonged accumulation of toxic metals in a streambed can have adverse effects on aquatic life, especially benthic organisms because they are in intimate contact with the sediments and pore water (Knezovich, 2007).

Sediment quality guidelines provide benchmarks for assessing the potential biological effects of sediments on aquatic systems using chemical measurements. At the present time, although several guidelines are available, there are no environmental standards for sediments applicable in the UK (Langston et al, 2003). The Centre for Environment, Fisheries and Aquaculture Science (CEFAS) has recommended the Canadian/US effects-
based approach (CCME, 1999; Long et al., 1995). This guideline contains two concentrations: the Interim Sediment Quality Guideline (ISQG, affecting the most sensitive species, lower guideline) and the Probable Effect Level (PEL, likely to affect a range of organisms, upper guideline), which is presented in Table 4.12.

Table 4.12 Interim Sediment Quality Guidelines (ISQGs) and Probable Effect Level (PELs) for studied metals (CCME, 1999).

<table>
<thead>
<tr>
<th>Metal</th>
<th>ISQG (mg kg⁻¹)</th>
<th>PEL (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>7.24</td>
<td>41.6</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.7</td>
<td>4.2</td>
</tr>
<tr>
<td>Copper</td>
<td>18.7</td>
<td>108</td>
</tr>
<tr>
<td>Lead</td>
<td>30.2</td>
<td>112</td>
</tr>
<tr>
<td>Zinc</td>
<td>124</td>
<td>271</td>
</tr>
</tbody>
</table>

It is clear from the previous section that waste materials present at the abandoned mines studied are highly contaminated with Cu and As, and to a lesser extent Pb, Zn and Cd. Because a number of the waste heaps are located directly on the banks of the River Tamar, mine waste can enter the river without attenuation. Furthermore, these mine wastes have the potential to generate acid mine drainage. Therefore leachate from these waste heaps may enter surface and groundwater systems within or under the mine sites and subsequently enter the River Tamar. Once they have entered the rivers, the contaminants in their dissolved form may, depending on the conditions of the system, sorb onto inorganic and organic colloids, which may be on the riverbed and/or in suspension, prior to subsequent settling on the riverbed.

The objectives of this section were:

1. To investigate the effects of mine waste on sediments in streams draining abandoned mine sites.
2. To assess whether or not contaminants are present in the streambed sediments at levels of concern.
4.5.4.1 Background As and metal concentrations in stream sediments (Zone A)

In order to assess whether or not trace metal concentrations in streambed sediments in the intensive mining area are elevated above background, metal concentrations in stream sediments from rivers upstream of the Gunnislake/Calstock mining area were determined (aqua regia extraction) and compared with those of the intensive mining area.

The results showed that the lowest As and metal concentrations in streambed sediments were observed in the upper catchment (Zone A: upper Tamar, Deer, Carey and Ottery rivers; Table 4.13; Figure 4.2). The metals concentrations in the upper Tamar catchment observed were in good agreement with those of Webb et al. (1978) and those of the BGS database (2003) also shown in Table 4.13. However, As concentrations in the upper catchment found in this study (20-80 mg kg\(^{-1}\)) were slightly higher than the results from these, and other, previous studies (e.g. 5-30 mg kg\(^{-1}\) by Webb et al., 1976; 4-16 mg kg\(^{-1}\) by Rawlins et al., 2003). The reason for this is not clear but may be explained by natural variation, particularly considering that the sample sites were not the same as those in the previous studies. It is interesting to note that As concentrations in the upper Tamar catchment (including the previous studies) are generally higher than those observed elsewhere in England and Wales (5-15 mg kg\(^{-1}\), Aston et al., 1975) and it is accepted that elevated levels of As in southwest England result from natural mineralisation in the region. This is discussed in detail in the following paragraphs. Therefore this zone may be seen as representative of the background concentrations of As and metals in the catchment.

Rivers in the upper catchment drain sandstones and argillaceous sedimentary rocks (mudstones and shales) of Carboniferous age (Rawlins et al., 2003). However, As and metal concentrations in streambed sediments in rivers draining the upper catchment were higher than the typical values for As and metals in shale (Krauskopf and Bird, 1995). For example, the background As concentrations (20-80 mg kg\(^{-1}\)) in stream sediments in the upper Tamar catchment exceed the typical values for shale (13 mg kg\(^{-1}\)) by a factor of 6. The As concentrations observed in this study are also higher than the value suggested by Aston et al. (1975). The authors investigated ranges of As concentrations in major geological divisions in this region and found that sediments in rivers draining Carboniferous rocks, which are the rock units underlain the upper catchment, contained
As up to 30 mg kg⁻¹. Furthermore, due to mineralisation in the region (Aston et al., 1975; Rawlins et al., 2003), the background concentrations for As observed in this study (up to 80 mg kg⁻¹) are already higher than the PEL values (likely to affect a range of organisms. 41.6 mg kg⁻¹ As) and the background concentrations for Cu (up to 80 mg kg⁻¹) and Zn (up to 200 mg kg⁻¹) are higher than the ISQG values (affecting the most sensitive species. 18.7 mg kg⁻¹ Cu, 124 mg kg⁻¹ Zn) of the sediment quality guidelines (Table 4.12). This however, does not simply mean that the sediments will cause adverse biological effects but further investigations (e.g. acid extractable concentrations, pore water metal concentrations, toxicity tests) should be undertaken (Simpson et al., 2005).

Abrahams and Thornton (1987) investigated the distribution of As, Cu, Pb and Zn contamination in Cornwall and proposed threshold values for high and moderate As, Cu, Pb and Zn contamination in stream sediments (100 to 500 mg kg⁻¹ for moderate and >500 mg kg⁻¹ for high As, Cu and Pb contaminations and 300-700 mg kg⁻¹ for moderate and >700 mg kg⁻¹ for high Zn contamination). Values as high as 14000 mg kg⁻¹ As and 8000 mg kg⁻¹ Cu, 3900 mg kg⁻¹ Zn and 1160 mg kg⁻¹ Pb were observed in streams in Cornwall by these authors. Based on the values proposed by Abrahams and Thornton (1987), the background concentrations adopted in the present study for As, Cu, Pb and Zn in the Tamar catchment were lower than the moderate contamination values.
Table 4.13. Ranges of metal concentrations (aqua regia extraction) in streambed sediments in the Tamar River catchment. Representative of Background (Zone A): upper Tamar, Deer, Carey, Ottery; Rivers receiving discharge from abandoned mines outside the main mining area (Zone B): Lynher, Tiddy, Inny, Lyd, Thrushel, Tavy, Walkham; Streams in the mining area (Zone C) including S2, 3, 5, 14b, 16, 17, 20, 21 and S25; Adits in the mining area (Zone C) including A1, 6, 12, 13, 14a, 15, 18 and A19. Ranges quoted as ‘<LOD’: all values were lower than the limit of detection (LOD); ‘<x’: some values were below the LOD. The values for zone A&B and the River Tamar at Greystone were obtained from one replicate per sample site; values for zone C were from two replicates per sample site. ‘nr’: not reported; *: from Krauskopf and Bird (1995); **: from Webb et al. (1978); ***: from Rawlins et al., 2003.

<table>
<thead>
<tr>
<th></th>
<th>As (mg kg⁻¹)</th>
<th>Cd (mg kg⁻¹)</th>
<th>Co (mg kg⁻¹)</th>
<th>Cu (mg kg⁻¹)</th>
<th>Fe (g kg⁻¹)</th>
<th>Mn (g kg⁻¹)</th>
<th>Ni (mg kg⁻¹)</th>
<th>Pb (mg kg⁻¹)</th>
<th>Zn (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average values for shale¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper Tamar catchment (Wolfson Atlas)²</td>
<td>13</td>
<td>0.3</td>
<td>19</td>
<td>45</td>
<td>47.2</td>
<td>0.85</td>
<td>68</td>
<td>20</td>
<td>95</td>
</tr>
<tr>
<td>Upper Tamar catchment (BGS database³)</td>
<td>5-30</td>
<td>≤2</td>
<td>4-45</td>
<td>15-74</td>
<td>34-48</td>
<td>0.41-1.4</td>
<td>21-60</td>
<td>13-32</td>
<td>64-196</td>
</tr>
<tr>
<td>Zone A (Upper Tamar, Deer, Carey, Ottery)</td>
<td>4-16</td>
<td>0.3-4</td>
<td>20-56</td>
<td>24-40</td>
<td>nr</td>
<td>nr</td>
<td>39-74</td>
<td>25-35</td>
<td>102-201</td>
</tr>
<tr>
<td>Tamar River, Greystone</td>
<td>20-80</td>
<td>&lt;LOD</td>
<td>17-22</td>
<td>40-80</td>
<td>40-76</td>
<td>1.5-4.1</td>
<td>32-72</td>
<td>&lt;LOD</td>
<td>100-200</td>
</tr>
<tr>
<td>Zone B (Lynher, Tiddy, Inny, Lyd, Thrushel, Tavy, Walkham)</td>
<td>50-7800</td>
<td>≤17</td>
<td>19-51</td>
<td>70-18000</td>
<td>38-190</td>
<td>0.9-7.9</td>
<td>38-110</td>
<td>30-320</td>
<td>100-1300</td>
</tr>
<tr>
<td>Tamar River, Gunnislake (BGS database³)</td>
<td>218</td>
<td>12</td>
<td>220</td>
<td>6700</td>
<td>nr</td>
<td>nr</td>
<td>300</td>
<td>90</td>
<td>1290</td>
</tr>
<tr>
<td>Intensive mining area / Zone C (Wolfson Atlas²)</td>
<td>70-430</td>
<td>3-4</td>
<td>9-45</td>
<td>74-440</td>
<td>42-65</td>
<td>0.87-5.7</td>
<td>60-99</td>
<td>104-274</td>
<td>450-1100</td>
</tr>
<tr>
<td>Zone C (Streams, mining area)</td>
<td>1300-25000</td>
<td>≤16</td>
<td>≤290</td>
<td>400-16000</td>
<td>56-260</td>
<td>0.7-8.2</td>
<td>33-120</td>
<td>35-260</td>
<td>200-1400</td>
</tr>
<tr>
<td>Zone C (Adits, mining area)</td>
<td>800-25000</td>
<td>≤38</td>
<td>≤550</td>
<td>900-28000</td>
<td>32-350</td>
<td>0.3-32</td>
<td>≤170</td>
<td>≤300</td>
<td>70-2700</td>
</tr>
<tr>
<td>Mine wastes</td>
<td>1700-180000</td>
<td>≤40</td>
<td>≤31</td>
<td>100-6000</td>
<td>10-290</td>
<td>0.1-2.0</td>
<td>≤52</td>
<td>≤623</td>
<td>20-2900</td>
</tr>
</tbody>
</table>
4.5.4.2 Arsenic and metal concentrations in stream sediments in the 'peripheral mining area' (Zone B)

The element concentrations in zone B varied considerably due to some rivers receiving waters and run-off from former Mn mines (e.g. Rivers Ottery, Thrushel and Lyd) and Cu, As, Pb and Zn mines (e.g. Tavy, Lynher and Tiddy; see Figure 4.2). As a result, the highest values observed in this zone were similar to the values observed in the intensive mining area (Zone C - see next section). For example, the 7800 mg kg\(^{-1}\) As observed in the River Tavy stream sediments was higher than some stream (e.g. 1300 mg kg\(^{-1}\)) and adit sediments (e.g. 800 mg kg\(^{-1}\)) in Zone C.

It also worth mentioning that geological units underlying this zone are also variable. For example, the River Tavy originates in and drains Dartmoor granite before flowing through Carboniferous and Devonian rocks in the south. The rivers draining Devonian rocks in this study were comparable to those of Aston et al. (1975). For example, in the River Tiddy which drains Devonian slates, 200 mg kg\(^{-1}\) As in stream sediments was observed (compared to up to 300 mg kg\(^{-1}\) for rivers draining mineralised Devonian rocks observed by Aston et al. 1975). The authors also reported a small hotspot of As around Tavistock which may be the source of high As in stream sediments in the River Tavy observed in this study (7800 mg kg\(^{-1}\)). These authors also state that As concentrations of >70 mg kg\(^{-1}\) in stream sediments in the Tamar catchment (Tamar/Tavy/Lynher) are widespread in the mineralised area and that values exceeding 5000 mg kg\(^{-1}\) are occasionally observed. Sediments in some rivers draining zone B (e.g. Rivers Tavy and Inny) had As, Cu and Zn concentrations which generally exceeded the high threshold values reported by Abrahams and Thornton (1987).

It is interesting that Mn concentrations in stream sediments in Zone B (900 to 79000 mg kg\(^{-1}\)) were markedly higher than in the mine wastes studied (< 100 to 2000 mg kg\(^{-1}\)). While, this may highlight the source of Mn from abandoned Mn mines, particularly in the Tavy and Lyd sub-catchments in this zone (Robinson, 1995). It is also worth mentioning that manganese is the third most abundant transition metal on the Earth's crust (Krauskopf and Bird, 1995) and its oxyhydroxides are present in most natural sediments and occur in a variety of solid forms (amorphous and crystalline) (e.g. Martin, 2005).
therefore, it is possible that high Mn concentrations may be observed in non AMD affected streams.

4.5.4.3 Arsenic and metal concentrations in stream sediments in the intensive mining area (Zone C)

4.5.4.3.1 Aqua regia extractable As and metal concentrations in Zone C

The results from aqua regia extractions showed that trace element concentrations in stream sediments in the intensive mining area (zone C; Table 4.13) were highly variable depending on geology (e.g. rock types and mineral ores) and characteristics of mine waste at each abandoned mine. For example, the lowest As concentration in zone C (800 mg kg\(^{-1}\)) was observed in adit sediments at a former Cu mine (George and Charlotte), whereas the highest value (25000 mg kg\(^{-1}\)) was observed in streams draining abandoned Cu/As mines (Devon Great Consols and Bedford United Mines).

The element concentrations observed in the intensive mining area (zone C) were significantly higher (t-test) than those of the upper Tamar catchment (zone A). T-test significance values were: \(p \leq 0.001\) for As, \(p \leq 0.001\) for Cu, \(p = 0.029\) for Fe, \(p = 0.049\) for Mn and \(p = 0.001\) for Zn. Because Pb concentrations in Zone A were lower than the LOD, the value of 24.8 mg kg\(^{-1}\) (the LOD) was used in statistical analysis. The t-test result based on this value showed that Pb concentrations in stream sediments in zone C were significantly higher than those in zone A \((p \leq 0.0003)\). This suggests the effects of the past mining activities (mine waste and adits) on streambed sediments in the Gunnislake/Calstock mining area.

According to the threshold values proposed by Abrahams and Thornton (1987), all studied streams and adits \((n = 16)\) were highly contaminated with As and Cu. seven watercourses were highly contaminated with Zn, and six of them were moderately contaminated with Pb. Furthermore, sediments in all streams and adits exceeded the PEL values for As and Cu, sediments in 13 watercourses exceeded the PEL value for Zn, and five watercourses exceeded the PEL values for Cd and Pb. It should also be noted that Cd concentrations in sediments in 11 watercourses were lower than the LOD in this study \((6.5\, \text{mg}\, \text{kg}^{-1}\, \text{Cd})\), which is already higher than the PEL level \((4.2\, \text{mg}\, \text{kg}^{-1})\).
The values observed in this study were within a wide range of concentrations in sediments affected by mining activities (Table 4.14). For example, the values in this study were relatively higher than those of the Rio Tinto mining district (e.g. Galan et al., 2003) but comparable to those of the Mount Bischoff system (Gault et al., 2005) and Camborne district, UK (Abrahams and Thornton, 1987).

Table 4.14 Arsenic and metal concentrations in stream sediments affected by acid mine drainage. 1: cited from Aslibekian and Moles, 2000.

<table>
<thead>
<tr>
<th>Source</th>
<th>Location</th>
<th>As (g kg⁻¹)</th>
<th>Cu (g kg⁻¹)</th>
<th>Fe (g kg⁻¹)</th>
<th>Pb (mg kg⁻¹)</th>
<th>Zn (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abrahams and Thornton, 1987</td>
<td>Cornwall, UK¹</td>
<td>≤14</td>
<td>&lt;8.0</td>
<td>-</td>
<td>≤1160</td>
<td>≤3900</td>
</tr>
<tr>
<td>Usero et al., 1999¹</td>
<td>Rio Tinto, Spain</td>
<td>2.37</td>
<td>1.22</td>
<td>420</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Galan et al., 2003</td>
<td>Rio Tinto, Spain</td>
<td>0.25-3.09</td>
<td>0.18-2.65</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ranville et al., 2004</td>
<td>California, USA</td>
<td>-</td>
<td>≤0.5</td>
<td>544-729</td>
<td>10-39</td>
<td>72-320</td>
</tr>
<tr>
<td>Gault et al., 2005</td>
<td>Tasmania, Australia</td>
<td>13.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>This study</td>
<td>Tamar catchment, UK</td>
<td>0.8-25</td>
<td>0.4-28</td>
<td>32-350</td>
<td>≤300</td>
<td>70-2700</td>
</tr>
</tbody>
</table>

The results from Pearson correlation analysis of As and metal concentrations in stream sediments in the 32 watercourses studied showed that As was significantly related with Cu (r = 0.67, p ≤ 0.0001), Fe (r = 0.52, p = 0.002) and Mn (r = 0.37, p = 0.04). Copper was found to be associated with Mn (r = 0.61, p ≤ 0.0001), Pb (r = 0.47, p = 0.03) and Zn (r = 0.40, p = 0.023). Nickel was related with Mn (r = 0.76, p ≤ 0.0001). Cadmium was found to be associated with Fe (r = 0.69, p = 0.04) and Mn (r = 0.83, p = 0.005).
These results suggest the association of As and other elements with the minerals bearing these metals in the Tamar catchment e.g. arsenopyrite, chalcopyrite, galena, Zn and Mn-oxides, all of which have been found in the Tamar catchment in previous studies (e.g. Dines, 1956a&b, Mindat, 2007, Klinck et al., 2005, Palumbo-Roe et al., 2007). Cadmium bearing minerals were not identified in this area but Cd sulfide, greenockite (CdS) is often found associated with sphalerite (Zn, Fe)S (Mindat, 2007).

It is clear from the pseudo total As and metal concentrations that stream sediments in the Gunnislake/Calstock mining area are elevated above the background levels observed in the upper catchment. All studied streams and adits in the intensive mining area were highly contaminated with As and Cu. A number of them were also highly contaminated with Zn, and some were moderately contaminated with Pb. The observed concentrations exceed the PEL values for As and Cu in all watercourses and are elevated above the PEL values for Zn, Pb, and Cd. In the next section, the potential mobility of As and metals in these stream sediments will be investigated in order to assess their environmental implications (e.g. potential effects on the water column above the sediments and the effects on organisms inhabiting them).

4.5.4.3.2 Mobility of As and metals in stream sediments in Zone C

The average percentages (of pseudo-total concentrations) of the three potentially mobile fractions for As, Cu, Fe, Mn, Ni, Pb and Zn in stream bed sediments in stream and adits in the mining area are presented in Figure 4.17. In general, the potentially mobility of metals in stream sediments (defined as the sum of the 3 BCR extractions) follows the sequence: Mn ≈ Pb ≈ Zn > Cu > As ≈ Fe. All metals presented in Figure 4.17, except As and Fe were relatively mobile, with the average potentially mobile phases being 85%, 84%, 82% and 78% for Mn, Pb, Zn and Cu respectively compared to As and Fe (38% for As and 31% for Fe). The potential mobility of Ni and Cd were low with most of the readings being lower than LOD.
Figure 4.17 The average percentage fractions of exchangeable, reducible and oxidisable of As, Cu, Fe, Mn, Pb and Zn to the total metals of stream bed sediments in streams and adits. The error bars represent the standard deviation (n= 16).

- Mobility of As and Fe

Due to its toxicity, As is one of the elements of most concern. It is discussed here together with Fe because the two elements are intrinsically linked in many cases. For example, in this study, As exhibited a similar pattern of mobility to Fe (Figures 4.5, 6 & 17) with the largest potentially mobile fraction being the oxidisable phrase and the smallest being exchangeable fraction. Also, in contrast to the other elements studied, the exchangeable fractions were often lower than LOD for both elements. Furthermore, the two elements are significantly correlated (see below).

For As, the average percentage values of the potentially mobile phases (as proportions of the pseudo total concentration) were 1.7% (up to 4%, concentrations of <LOD to 170 mg kg\(^{-1}\)) for the exchangeable fraction, 8.9% (up to 25%, or <LOD to 6200 mg kg\(^{-1}\)) for the reducible fraction and 27% (5.6 to 75%, or 270 to 7900 mg kg\(^{-1}\)) for the oxidisable fraction. For Fe, the exchangeable fractions to the pseudo total Fe were 0.2 to 0.5% (52 to 650 mg kg\(^{-1}\)), while the reducible fractions were 12 to 19% (1700 to 10600 mg kg\(^{-1}\)), and the oxidisable fractions were 14 to 23% (2600 to 18400 mg kg\(^{-1}\)).

The most mobile As was identified in stream S18 (an adit in Gunnislake Clitters Mine). The exchangeable, reducible and oxidisable fractions of this sample were <LOD, 16%
and 75% respectively (Figure 4.18). The summation of potentially mobile phases in this sample accounted for > 90% of the pseudo total As but the bulk As content (3600 mg kg\(^{-1}\)) was low compared to other streams and adits studied. On the contrary, the highest total As (25000 mg kg\(^{-1}\)) in sediments was observed in stream S20 (stream draining Wheal Anna Maria spoil tip at Devon Great Consols Mine), but only 6.2% of the As in this sample was mobile (Figure 4.19).

**Figure 4.18** Percentage fractions of exchangeable, reducible and oxidisable of As, Cu, Fe, Mn, Pb and Zn to the total metals of sample S18 (adit in Gunnislake Clitters Mine) The total metals were 3600 mg kg\(^{-1}\) As, 7400 mg kg\(^{-1}\) Cu, 45000 mg kg\(^{-1}\) Fe, 3700 mg kg\(^{-1}\) Mn, 82 mg kg\(^{-1}\) Pb and 400 mg kg\(^{-1}\) Zn.

**Figure 4.19** Percentage fractions of exchangeable, reducible and oxidisable of As, Cu, Fe, Mn, Pb and Zn to the total metals of sample S20 (stream drains Wheal Anna Maria spoil tip in Devon Great Consols Mine) The total metals were 25000 mg kg\(^{-1}\) As, 16000 mg kg\(^{-1}\) Cu, 75000 mg kg\(^{-1}\) Fe, 2900 mg kg\(^{-1}\) Mn, 170 mg kg\(^{-1}\) Pb and 1000 mg kg\(^{-1}\) Zn.
The Pearson correlation test showed that reducible As was significantly related to reducible Fe ($r = 0.68, p = 0.016$). This may be explained by co-precipitation of As with Fe-oxyhydroxides/ oxyhydroxysulfates. The attenuation of As and metals by Fe-oxyhydroxides/ oxyhydroxides has been studied by a number of researchers. For example, Gault et al. (2005) reported that $4900\pm1000$ mg kg$^{-1}$ As were associated with amorphous and poorly crystalline hydrous oxides of Fe and Al and $6800\pm1400$ mg kg$^{-1}$ As were retained in well crystallised hydrous oxides of Fe and As in streams receiving acid mine drainage from Mount Bischoff, Australia. Johnson and Thornton (1987) reported that up to 80% of As in waters affected by acid mine drainage in the Carnon River system, southwest England was found in the particulate phase, which contained a large quantity of amorphous Fe-oxides. Romero et al. (2003) investigated solid phase partitioning of As in stream sediments affected by mining activities in the Rio Loa Basin, Chile. The authors reported up to ca. 30% As in the carbonate and specifically adsorbed fractions (using NaOAc, 1M) and up to 40% As in the Fe/Mn-oxides fraction (using NH$_2$OH HCl, 0.04 M). The authors also concluded that As concentrations in stream sediments in the study area were significantly related to As concentrations in the water column. Chunguo and Zihui (1988) analysed waters, suspended solids and sediments in Xiangjiang River, China and concluded that aluminium arsenate, Fe arsenate and calcium arsenate were the main As species in sediments. The authors stated that As concentrations in suspended solids and sediments were 2000 times higher than those in river water, suggesting suspended solids and sediments are effective scavenging agents and sinks for As.

Mok and Wai (1994) stated that hydrous oxides of Fe, Mn and aluminium are important sinks of As in aquatic systems, which are readily mobilised under reducing environments. In anoxic environments and in the presence of sulfide, Fe sulfides will form. As will co-precipitate with Fe sulfides as arsenopyrite (FeAsS) or form As sulfides such as realgar (AsS) and orpiment (As$_2$S$_3$). These sulfide minerals are readily oxidised in the presence of oxygen (Forstner and Wittmann, 1981 in Mok and Wai, 1994), and therefore, under appropriate environments, release As into the water column.

A number of studies have highlighted the benefits of Fe-oxyhydroxides in regulating As and metals (see above). However, the precipitates can cause adverse effects to ecosystems. Letterman and Mitsch (1978) investigated relationships between physical
parameters and fish and benthic macroinvertebrate communities in a stream receiving acid mine drainage in Ben's Creek Watershed, Pennsylvania. They found that ochreous precipitates appear to be a major factor affecting the benthic community and fish population. This may be explained by Fe-oxyhydroxide precipitates limiting oxygen availability to the biota. They also reduce light penetration and hence interfere with photosynthesis and the vision of organisms (Kimmel, 1983).

- Mobility of Cu

The results in this study suggested that the most potentially mobile phase of Cu in stream sediments was mainly in the exchangeable (33%), followed by the oxidisable (28%) and the reducible (16%) fractions. Significant amounts of exchangeable Cu in stream sediments were identified in samples S5 (67%; 10700 mg kg$^{-1}$), S14a (53%; 740 mg kg$^{-1}$) and S18 (49%; 3600 mg kg$^{-1}$), in which pale green and bright blue coatings on rock or pebbles were observed at times during the visits for water sampling (July 2005 to June 2006) (Figure 4.20). At these sites, the exchangeable fractions of Cu were significantly higher ($p=0.01$) than in the rest of the samples ($n=13$) in streams and adits in the mining area (Figure 4.21). The pale green precipitates on the waterfalls in stream S14a were sampled and the sequential extraction results revealed that they contained 23% (9500 mg kg$^{-1}$) exchangeable, 29% (12000 mg kg$^{-1}$) reducible and 18% (7500 mg kg$^{-1}$) oxidisable Cu, as proportions of pseudo total Cu (42100 mg kg$^{-1}$). The potential mobility of Cu in the exchangeable fraction has been discussed in section 4.5.3.3)
Figure 4.20  a) The photograph showing bright blue coatings on rocks and pebbles in stream S5;  
b) the photograph showing pale green coatings on waterfalls in stream S14a (photos: Mighanetara, 2006).

Figure 4.21  Exchangeable Cu as proportions of pseudo-total Cu in: sample S5 (stream in Gawton mine; 10700 mg kg$^{-1}$, total Cu = 16000 mg kg$^{-1}$); S14a (stream in Bedford United Mine; 740 mg kg$^{-1}$, total Cu = 1400 mg kg$^{-1}$); S18 (stream in Gunnislake Clitters Mine; 3600 mg kg$^{-1}$; total Cu = 7400 mg kg$^{-1}$) and other stream and adit sediment samples (n= 13; 1600 mg kg$^{-1}$, total Cu = 6100 mg kg$^{-1}$).
Chapter 4: Geochemistry of mine wastes and stream sediments

- Mobility of other metals (Cd, Mn, Ni, Pb and Zn)

The main mobile phase of Mn was in the reducible fraction (ca. 54%) followed by the exchangeable phase (ca. 23%). Similar findings for Mn partitioning in stream bed sediments was reported by Gurrieri (1998). The author studied the distribution of metals in streams receiving acid mine drainage from MacLaren Mine, USA and reported up to 75% reducible Mn (ca. 980 mg kg\(^{-1}\)) as a proportion of total Mn (1300 mg kg\(^{-1}\) using HF-HClO\(_4\)). The formation of Mn-oxides depends largely on the redox potential and pH (e.g., Kelly, 1988) and microbial activity (Kennedy, et al., 2004). Abiotic oxidation of Mn\(^{2+}\) is extremely slow at pH<8 and is therefore predominantly controlled by microorganisms (Kennedy, et al., 2004; Villalobos et al., 2003). It is generally accepted that hydrous oxides of Mn play a key role in regulating trace elements in aquatic systems (Young and Harvey, 1992).

Large amounts of oxidisable (35%) and exchangeable (30%) fractions of Pb were observed. Given this condition, Pb is considered to be relatively mobile. Its reducible fraction was also significant (20%). In this study, the organic contents in stream sediments were low and therefore it can be inferred that the oxidisable Pb is mainly accounted for by Pb sulfide minerals. A similar finding was reported by Svete et al. (2001). The authors studied stream sediments affected by Pb and Zn mining and smelting in Mezica valley, Slovenia and concluded that the partitioning of Pb in stream sediments (using BCR extraction scheme) followed the sequence: oxidisable (ca. 45 to 60%) > exchangeable (ca. 15 to 33%) > reducible (typically <10%). However, the results observed in this study are different from those of Gurrieri (1998) and Bird et al. (2005). The authors found that Pb in sediments in streams receiving mine waters were mainly associated with Fe-oxides fraction. The reducible and exchangeable fractions of Pb observed in the present study and previous studies (e.g. Gurrieri, 1998; Bird et al., 2005) may be explained by adsorption of Pb onto the surface of carbonate and Fe-oxyhydroxide minerals, which are very reactive (Stipp and Hochella, 1991 in Al et al., 2000; Warren and Haack, 2001).

For Zn, the exchangeable fraction (46%) was the highest potentially mobile phase, while the reducible and oxidisable were somewhat similar to each other (ca. 19%). As with some of the other elements, given that exchangeable Zn is high, it is reasonable to expect...
that dissolved Zn may be present in considerable amounts in the water column. High levels of exchangeable Zn in streams affected by mining activities associated with Cu, Pb and Zn in western Romania were reported by Bird et al. (2005). The authors found that Zn was predominantly present in the exchangeable phase (using acetic acid), ranging from 6-65% of pseudo total Zn (using concentrate HNO₃). This exchangeable fraction is likely to result from adsorption of the Zn onto solid phases such as Fe-oxides/hydroxides. The adsorption of Zn (and Cu) onto Fe-hydroxides was observed by Johnson and Thornton (1987). The authors studied the transport and fate of Zn (as well as other elements e.g. Fe, Cu, and As) in the Carrion River and estuarine waters, Cornwall, UK and found that dissolved Zn (and Cu) was regulated by adsorption onto amorphous Fe-oxyhydroxides and the degree of adsorption depended on the pH and the amount of Fe-oxyhydroxides present in the system.

In this study all mobile fractions of Cd and Ni were constantly lower than the LOD.

In summary, the BCR extraction of stream sediments suggested that Cu, Mn, Pb and Zn were relatively mobile with the most potentially mobile fraction being the exchangeable phase for Cu and Zn. This can affect the metal concentrations in water column, particularly within pore water zone. On the other hand, the potential mobilities (defined as the sum of the three BCR fractions) of As and Fe were less than half those of the other elements. The most mobile As fraction in stream sediments was found to be associated with reducible Fe, which is believed to reduce As concentrations in the water column via co-precipitation. Furthermore, the pattern of the potential mobility of As and Fe in mine waste samples (Figures 4.5, 6 & 17) was similar to that of As and Fe in stream sediments. This may suggest that As and Fe in stream sediments were directly linked to As and Fe in mine wastes, i.e. the mine wastes were indeed the sources of As and Fe in stream sediments.

4.6 Conclusions

In total, 14 mine wastes from 5 abandoned mines in the Gunnislake/Calstock mining area, 15 samples from rivers in the Tamar catchment, 17 samples from adits and streams in the intensive mining area were sampled. The grain size distribution, soil pH, total carbon and loss-on-ignition, and pseudo total and the BCR extractable element concentrations were
determined in order to investigate the physiochemical and mineralogical composition of the mine wastes and the stream sediment and to study the effects of abandoned mine sites on the quality of stream sediments.

The grain size distribution of mine waste studied varied depending on the processes which generated the waste: e.g. fine grained materials from the slime and tailings pond waste and coarse grained materials from the dressing floor and slag and cinder wastes. A similar result was observed for the soil pH, with the value ranging from 3.1 to 7.0. The results from total carbon and loss-on-ignition analysis showed that the mine wastes and stream sediments studied had low organic carbon contents.

The pseudo As and metal concentrations in mine wastes, although highly variable, were elevated above the Dutch intervention values for As, Cu and Cd and exceeded the Dutch target values for Zn and Pb in most samples. The mobility of As and metals in mine wastes studied was also highly variable.

All elements except Cd and Ni had moderate to high oxidisable fractions, suggesting the mine wastes studied contain considerable amounts of sulfide minerals. The exchangeable fraction, which is readily leachable in the presence of rain and groundwater and therefore of most immediate concern, was relatively low compared to pseudo total concentrations for As, Fe, Mn and Zn. In contrast to most elements studied, Cu had relatively high exchangeable fractions, which may suggest the recycling (e.g. precipitation and adsorption) of these elements within the mine waste.

Investigation of the mineralogy of mine wastes suggested that the mine wastes contain considerable amounts of arsenopyrite, pyrite and chalcopyrite. This was in good agreement with the BCR sequential extraction which suggested substantial oxidisable fractions of all elements studied except Cd and Ni in most mine waste samples. The identification of scorodite explained low mobility of a sample which contained markedly high As. The manual SEM suggested that Fe oxyhydroxide minerals were significant sources of As and metals in the mine waste samples.

Pseudo total concentrations of As and metals in sediments from the upper catchment were slightly higher than some previous studies, but were used as background concentrations in
this study. The increase in As and metal concentrations in the peripheral and intensive mining areas compared to the upper catchment suggests contamination from past mining activity including the exportation of these elements from mine wastes into the rivers, streams and estuary. Furthermore, relatively high concentrations of Pb and Mn in stream sediments compared to the concentrations in mine waste samples suggest the attenuation (e.g. precipitation or adsorption) of these metals from water column.

The distribution pattern of the mobility of As and Fe in stream sediments was similar to that in mine wastes. While the mobility of As in stream sediments (as a percentage of pseudo-total As) was similar to those of mine wastes, the mobility of Fe in stream sediments was twice as high as those of the mine wastes. The relatively high exchangeable Cu, Mn, Pb and Zn in stream sediments suggest that sediments in rivers, streams and adits in the peripheral and intensive mining areas may be a source of these elements in the water column.

4.7 References


Chapter 4: Geochemistry of mine wastes and stream sediments


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5.1 Abstract

This chapter discusses the water chemistry of rivers, streams and adits in the Tamar catchment in relation to their geography, geology, mineral ores and mining history; and the effects of mine waters on the water quality of the River Tamar and its estuary.

Dissolved and particulate concentrations of trace elements (As, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn) and major ions in 11 rivers in the wider Tamar catchment and in 25 streams and adits within the main metalliferous mining area were examined. Trace elements and sulfate concentrations in the River Tamar, where it flows through the Gunnislake/Calstock mining area, were elevated above the catchment background concentrations established in this study.

The composition of mine waters was highly variable both locally and seasonally and the factors influencing this variability are discussed. A number of streams and adits draining abandoned mine sites, low pH waters in particular, carried high dissolved and particulate element concentrations (e.g. up to 7600 µg L⁻¹ dissolved Cu, up to 560 µg L⁻¹ dissolved As, up to 5700 µg L⁻¹ dissolved Mn, 2500 µg L⁻¹ dissolved Zn and up to 160 µg L⁻¹ dissolved Pb; up to 7900 particulate Fe). The metal speciation was investigated through thermodynamic speciation calculations in order to evaluate the potential risk to aquatic
organisms. The modelling results showed that metals (e.g. Cu, Cd, Ni and Zn) are likely to form strong complexation with dissolved organic matter and as a result, the resulting water usually contains free ionic ion concentrations lower than values reported to have adverse effects on green algae, diatoms and cyanobacteria.

The total annual flux of trace elements from the studied streams and adits was calculated by extrapolation from the instantaneous flux, and amounted to ca. 13,000 kg a\(^{-1}\) Fe, 4300 kg a\(^{-1}\) Mn, 4200 kg a\(^{-1}\) Cu, 3600 kg a\(^{-1}\) Zn, 1400 kg a\(^{-1}\) As, 400 kg a\(^{-1}\) Ni, 350 kg a\(^{-1}\) Co, 43 kg a\(^{-1}\) Pb, and 6.6 kg a\(^{-1}\) Cd. Seven important point sources of metals to the River Tamar were identified. The mass balance calculation revealed that over 50% of trace elements were not accounted for by the studied point sources, suggesting an importance of diffuse sources.

5.2 Introduction

The previous two chapters identified mining waste and associated contaminated land and sediment as sources of pollution to the wider environment, whereby the erosion and leaching of solids constitute major pathways. In addition, adits and other drainage channels are potential point sources for mining-related contamination to the aquatic environment. Freshwater and coastal ecosystems are vulnerable to such contamination, because of their important ecological function as recruitment zone for aquatic species, and the susceptibility of juvenile life stages to toxicants (Beiras and Albentosa, 2004; Calabrese et al., 1973; His et al., 1999). Furthermore, phytoplankton, the foundation of the aquatic food web, are sensitive to extremely low concentrations of certain metal species. For example, sub-lethal toxic effects on species such as green algae, dinoflagellates, diatoms and cyanobacteria have been reported the presence of free cupric ion concentrations ranging from 0.4 to 400 ng L\(^{-1}\) Cu\(^{2+}\) (Anderson and Morel, 1978; Sunda and Guillard, 1976; Brand et al., 1986).

As a member of the EU states, the UK is obliged to implement the EU Water Framework Directive (WFD) (2000/60/EC), which requires its member states to achieve good chemical and ecological status for all inland and coastal waters by 2015. In order to achieve this, watercourses must be characterised and monitored to provide the knowledge.
The River Tamar in southwest England flows through a historic mining area, in which, among other trace elements, Cu, As, Pb and silver were extracted during the 19th century. Although the last mine was closed by 1950 (BGS, 2003; see also Chapter 2), mining waste, adits, shafts and land contaminated by mineral processing remain sources of contamination to water courses, leaving the River Tamar at risk of failing the WFD targets (EA, 2004). A number of studies have demonstrated the impact of past mining activities on aquatic systems in this region. For example, Clifton and Hamilton (1979) reported the accumulation of Zn, Pb and Cu accumulating in sediment layers increased markedly approximately 25 years after the intense mining activities in the region started and the accumulation continued until the year of study, several decades after most mining activities ceased (see chapter 1). Furthermore, Interim Marine Sediment Quality Guideline (ISQG) values and the Probable Effect Levels (PEL), likely to adversely affect a range of organisms, have been reported to be exceeded in estuarine sediments for As, Cu, Pb and Zn. Concentrations of sediments in the estuary at such high levels can affect the quality of overlying water, because, as demonstrated by Watson (in Ackroyd et al., 1986), pore water in the Tamar estuary can contain up to 200 µg L⁻¹ Cu and 910 µg L⁻¹ Zn, which are one to two orders of magnitude higher than the overlying water. Consequently, elevated concentrations of trace metals have been reported in the Tamar River and estuary (e.g. 4400 µg L⁻¹ Cu in the run-off from Gunnislake Clitters mine and up to 115 µg L⁻¹ As in fresh water streams and adits in the Gunnislake area, Langston et al., 2003). Information about the metal fluxes discharged from specific abandoned mines into the River Tamar is a pre-requisite for setting catchment management priorities but currently little is known about such fluxes (Langston et al., 2003).

The aims of this chapter are:

1. To establish the effects of mine waters in the region of past intensive mining activity on the water quality of the Tamar River and estuary in terms of concentrations and fluxes of potentially toxic elements.
2. To identify the major sources (point and/or diffuse) and phases (dissolved and/or particulate) of potentially toxic elements.
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3. To investigate the geochemical behaviour of metals in the studied rivers, streams and adits draining mine waters.

These following work was carried out in order to achieve these aims:

1. Desk-top studies and preliminary field investigations were carried out to identify adits, drains and streams that carry mine waters directly into the Tamar River and estuary.
2. Twelve monthly surveys were carried out to measure stream flow and master variables, and sample water for analysis of metal and major ion concentrations in the identified adits, drains and streams.
3. Four quarterly catchment surveys of major tributary rivers in the Tamar catchment were carried out in order to establish the background metal and major ion concentrations.
4. Dissolved and particulate metal concentrations were determined, focussing on priority elements arising from the WFD and in addition those that are important components of the mineralogy in the Tamar mining area (As, Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn) and major ions (Ca, Na, Mg, Na and SO$_4^{2-}$).
5. Metal flux (dissolved and particulate) and mass balance calculations by means of simple extrapolations.
6. Thermodynamic equilibrium modelling of the inorganic metal speciation in selected water courses.

The geohydrology of streams and adits in the main area of abandoned mines is complex, and it was beyond the scope of this study to investigate all discrete and point sources separately. Therefore, an approach was taken that sought the direct inputs of mine waters into the Tamar River and estuary. This includes adits and drainage channels that discharge directly into the Tamar, as well as streams that drain sub-catchments of the Tamar, in which abandoned mines are located. The chemical composition of these streams arises from run-off and mine waters (surface drainage and underground leachate) as well as natural waters and agricultural or domestic run-off and in-stream mobilisation or attenuation of elements along its course. The streams therefore combine point and diffuse sources of contaminants. Both, point sources and streams were sampled just upstream of their confluence with the Tamar. Therefore, in this study, the terms "point
source” and “diffuse source” are not defined in their conventional sense but in relation to the bank of the River Tamar.

5.3 Acid mine drainage and the environment

Acid mine drainage (AMD) is a major environmental problem in the mining industry (Hulshof et al., 2006; Bigham, et al., 1992). Jarvis and Younger (2000) reported that in the UK, more than 700 km of watercourses are affected by abandoned coal mines. Kleinmann (1989) estimated that about 19300 km of rivers and streams in the US have been severely damaged by AMD. The AMD generating reactions are cyclic and self-propagating, and can continue for centuries after mine closure. For example, without remediation, AMD at Richmond Mine, Iron Mountain, California, will generate acidic leachate (pH<1) containing dissolved metals in the concentration range of grams per litre for some 3000 years (Nordstrom and Alpers, 1999). Similar figures have been reported by Kaline (2001), who estimated that a small Zn/Cu mine in Ontario, Canada may continue discharging AMD for 1000 to 35000 years. Current European Union legislation (e.g. Mining Waste Directive 2006/21/EC) requires mining companies to plan and provide for environmental management of mines after closure. However, the legislation does not apply retrospectively, and the cost of works carried out by the Environment Agencies in the UK to remedy or mitigate pollution in controlled waters arising from abandoned mines cannot be recovered from any person who caused or knowingly permitted the pollution before January 2000 (Johnston et al., 2008).

AMD is often acidic and contains high concentrations of sulphate, dissolved metals and metalloids such as Cd, Cu, Ni, Pb, Zn and As (Hulshof et al., 2006; Salomons, 1995; Oliveira et al., 2006). As a result, damage of habitats in and water quality of streams receiving untreated AMD has been widely reported. The degree of severity and damage is dependent on several factors including frequency, volume and chemistry of the drainage, and the size and buffering capacity of receiving streams (Kimmel, 1983). According to Biernacki (1978; in Nordstrom and Alpers, 1999), 10 million fish were reported killed in the United States during 1961-1975 from the effects of mining activities. The authors also emphasised that the number of fish killed reported was severely underestimated. Levings et al. (2004) found that acid drainage from Britannia Creek, British Columbia, Canada, has adverse effects on the estuarine food web.
water in the affected creek was highly acidic and contained high concentrations of dissolved Cu ($540\pm90$ µg L$^{-1}$), compared to the concentrations in unaffected nearby creek ($10\pm1$ µg L$^{-1}$ Cu). The authors described a decrease in abundance of food organisms for fish. Their laboratory toxicity test showed that sediments and water in the estuary were highly toxic to midge larva and marine amphipods. Short et al. (1990) reported the elimination of macroinvertebrates and fish fauna in a stream receiving low pH and high concentrations of dissolved metals.

According to Earle and Callaghan (1998) and Kimmel (1983), pH is the most crucial environmental variable, because most organisms have a well defined pH tolerance (e.g. 6-9 for fish; EU freshwater fish directive, 2006). If the pH decreases below the tolerance range, death will occur due to respiratory or osmoregulatory failure. Low pH disturbs the balance of sodium and chloride ions in the blood of aquatic animals (Morrise et al., 1989 in Earle and Callaghan, 1998). Furthermore, low pH enhances dissolution and mobility of metals (Banks, 2004) and results in a shift of metal speciation towards free ionic and other inorganic forms, which are thought to be readily biologically available (Paquin et al., 2002, and references therein). Trace metals, such as Zn, Cd and Cu are toxic at low concentrations and may act synergistically to suppress algal growth as well as affect fish and benthic organisms (Earle and Callaghan, 1998). Reynoldson (1987), however, stated that it is difficult to differentiate between adverse effects on the benthic community mediated by water and by sediments. This is because benthic invertebrates are constantly in contact with sediments (and pore sediment water) and therefore, it is difficult to assess the contribution of effect of sediment metals to overall toxicity.

Iron, Al and Mn are often found in associated mine waters. Of these, Al, which is released by the dissolution of silicate minerals, has the most severe adverse effects on aquatic life. The combined effect of pH $<5.5$ and Al concentrations higher than 0.5 mg L$^{-1}$ has been reported to eliminate all fish and most macroinvertebrates (Earle and Callaghan, 1998).

Because Fe can form precipitates at pH values as low as pH 3.5, it is difficult to distinguish between the toxic effects of Fe and of low pH (Earle and Callaghan, 1998). In acidic waters, the precipitation of Fe solids tends to be enhanced by Acidithiobacillus Acidithiobacillus, which are known for their ability to accelerate the formation of
ochreous precipitates and grow best in the environment with pH<4 (e.g. Dold, 2005; Bigham et al., 1992). Precipitation of Fe-oxides/oxyhydroxides also occurs at higher pH values. Because of their ubiquity and large surface area, Fe-oxides/oxyhydroxides are recognised as potential substances for regulating As and heavy metal concentrations in natural waters (e.g. Pierce and Moore, see also section 4.5). However, at the same time, Fe precipitates can decrease oxygen availability and have physiological effects, such as coating gills and body surface of aquatic organisms (Letterman and Mitsch, 1978; Earle and Callaghan, 1998). In addition to the physical degradation of habitat quality, Fe precipitates remove dissolved and particulate organic matter from the water column, hence decrease organic nutrients downstream. Furthermore, acidity and high concentration of metals can alter nutrient cycles in lotic systems by restricting decomposition processes of organic matter (Short et al., 1990).

Copper is highly toxic to most aquatic organisms (USEPA, 2008). According to Taylor et al. (2000), Cu concentrations at 20-60 µg L⁻¹ are acutely toxic to rainbow trout in moderately hard water. In general, toxicity is reduced with increasing water hardness and pH, and addition of humic substances (Handy, 2003) or other organic chelators. Copper toxicity is well recognised so that, in order to safeguard freshwater fish, under the EU Water Framework Directive, the new European Directive on Freshwater Fish (2006/44/EC) set the guideline values for Cu in salmonid and cyprinid waters to 5 µg L⁻¹ for soft waters (hardness ≤10 mg L⁻¹ CaCO₃) and 112 µg L⁻¹ for hard waters (hardness ≥300 mg L⁻¹ CaCO₃; EA, 2008). In comparison to aquatic life, Cu is relatively non-toxic to mammals (Flemming and Trevors, 1989), and their toxicological tolerance limits are 10-100 times higher than those of fish and crustaceans (Forstner and Wittmann, 1979 in Flemming and Trevors, 1989) and 1000 times higher than those of algae (Hodson et al., 1979 in Flemming and Trevors, 1989). This is reflected in the acceptable Cu concentrations in drinking water in many standards (e.g. 2 mg L⁻¹ for the EU guideline, Radojevic and Bashkin, 2006).

Like Cu, elevated Zn in aquatic systems can cause damage to fish gills (Skidmore and Tovell, 1972 in Taylor et al. 1996) and Zn toxicity is affected by similar factors to that of Cu. The pH and dissolved organic carbon (DOC) concentrations mainly determine the metal speciation, while ions related to water hardness compete with the free metal ions on gill membranes, thus alleviating toxicity (e.g. Heijerick et al., 2003; De Schamphelaere
and Janssen, 2004). These authors demonstrated that an increase in major cations concentrations (from 8 to 160 mg L\(^{-1}\) Ca, 1.2 to 73 mg L\(^{-1}\) Mg, 17 to 115 mg L\(^{-1}\) Na) and pH values (from 5.5 to 7.5) resulted in a reduction of chronic toxicity of Zn by the factor of 12, 3, >2 and 2, respectively. The EC freshwater fish guideline values for Zn are 30-500 µg L\(^{-1}\) (for water hardness of 10-500 mg L\(^{-1}\) CaCO\(_3\)) in salmonid waters and 300-2000 µg L\(^{-1}\) (for water hardness of 10-500 mg L\(^{-1}\) CaCO\(_3\)) in cyprinid waters (EA, 2008).

The toxicity of Ni on aquatic life is moderate compared to Cu and Zn (Nebeker et al., 1985). Concentrations of 7.8-10.9 mg L\(^{-1}\) Ni have been reported to cause acute toxicity to juvenile rainbow trout; and 3.1 mg L\(^{-1}\) Ni to fathead minnow (Eisler, 1998). The toxicity of Ni varies depending on pH, water hardness and DOC concentrations (Deleebeeck et al., 2007). According to Eisler (1998), to protect freshwater life, the author suggested that Ni should be regulated at total concentrations below 96 µg L\(^{-1}\). Under the EU Water Framework Directive (WFD), Ni is one of the metals regulated for standard drinking water (<20 µg L\(^{-1}\); Radojevic and Bashkin, 2006), and included in List II - dangerous substances (76/464/EEC), with an environmental quality standard (EQS) in fresh waters of 50-200 µg L\(^{-1}\) Ni for water hardness ranging from 0 to >250 mg L\(^{-1}\) CaCO\(_3\).

Cadmium has a similar chemistry to that of Zn and occurs in association with Zn ores. Cadmium is known to be toxic to most living organisms, including humans (e.g. Itai-Itai disease; Diez et al., 1997). The guideline value for the EU drinking water standard is 5 µg L\(^{-1}\) (Radojevic and Bashkin, 2006). The toxicity of Cd to aquatic organisms varies, largely depending on the target organisms and chemistry of waters. For example, acute toxicity to mysid shrimp was reported at total dissolved concentrations of 17 µg L\(^{-1}\) (Roberts et al., 1982); to fathead minnows at 1.05 mg L\(^{-1}\) (water hardness 20 mg L\(^{-1}\) as CaCO\(_3\)) and 72.6 mg L\(^{-1}\) (water hardness 360 mg L\(^{-1}\) as CaCO\(_3\); Pickering and Henderson, 1966); to rainbow trout at 1.3-2.6 mg L\(^{-1}\) (water hardness 61-65 mg L\(^{-1}\) as CaCO\(_3\)) and 5.7 mg L\(^{-1}\) (water hardness 283-317 mg L\(^{-1}\) as CaCO\(_3\); Pascoe et al., 1986). Cadmium is a List I dangerous substances (76/464/EEC) and its annual average EQS for fresh water is 5 µg L\(^{-1}\).

Like Cd, Pb is a non-essential and toxic element, whose known effects on biological systems are deleterious (Pattee and Pain, 2003). In aquatic systems, Pb is strongly absorbed onto sediments, hence reducing its availability to organisms. Its effect upon
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Aquatic organisms vary according to the organism and environmental factors, e.g. pH and water hardness (Pattee and Pain, 2003). Dissolved Pb concentrations in the range of 612-1912 µg L\(^{-1}\) have been reported to have chronic acute effects to *Daphnia magna* at a water hardness of 54-152 mg CaCO\(_3\) L\(^{-1}\) (USEPA, 1985 in Pattee and Pain, 2003). Lead is in List II dangerous substances (76/464/EEC) and has an EQS of 20-250 µg L\(^{-1}\) at a water hardness ranging from 0 to >250 mg L\(^{-1}\)CaCO\(_3\).

Arsenic is often found associated with AMD, due to the dissolution of As bearing minerals such as arsenopyrite (see chapter 4). The metalloid is non-essential and toxic to most living organisms (e.g. Dopson et al., 2003). Following the evidence of carcinogenic effects caused by elevated As in waters in Taiwan and India, the World Health Organisation (WHO) has recommended lowering the drinking water standard from 50 µg L\(^{-1}\) to 10 µg L\(^{-1}\) As in 1993 (Thornton, 1996). This health concern has drawn more attention on As contamination caused by mining activities (Thornton, 1996). Examples include Nordstrom and Alpers (1999), who reported up to 340000 µg L\(^{-1}\) As in acid drainage with negative pH in Richmond Mine, Iron Mountain, California. According to Plumlee et al. (1999), As concentrations in mine waters in the USA varied markedly, ranging from lower than 1 µg L\(^{-1}\) to 340000 µg L\(^{-1}\). Johnson and Thornton (1987) reported elevated As (140-550 µg L\(^{-1}\) as total As) in Carrion River, Cornwall, UK, in which 80% As in stream water was attributed to AMD. Klinck et al. (2005) reported elevated concentration of As in waters flowing within Devon Great Consols Mine, with concentrations as high as some 6600 µg L\(^{-1}\) in run-off at this mine site.

5.4 Geochemistry of mine waters

Acidic drainage rich in dissolved metals and metalloids is produced when sulfide minerals are exposed to oxygen and water. Oxidation processes of sulfide minerals, such as pyrite, chalcopyrite, arsenopyrite, sphalerite and galena (see chapter 4), occur in the study area. Oxidation facilitated by oxygen and ferric Fe, together with Fe (oxy)hydroxide precipitation and the role of bacteria on acid generation have been described in detail in chapter 4.

According to Solomons (1995), factors controlling the rate of acid generation include pH, temperature, oxygen concentrations in gas and water phases, chemical activity of ferric
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Fe, bacterial activity and surface area of the exposed sulfide minerals. Additionally, physical factors, in particular permeability and grain size of materials, are very important. Coarse grain materials typically have high permeability, which favours the diffusion and advection of oxygen, and consequently result in higher acid generation. The oxygen availability in bulk materials made up of fine grains, though characterised by a larger surface area, may be limited as a result of lower permeability. Other factors, which may affect the ultimate release of AMD include climate, hydrology and geological structures of mine sites and the terrain, mineralogy of waste materials, mining and ore processing techniques, materials used and discarded in mineral processing and vegetation cover (Nordstrom and Alpers, 1999).

Mine waters can be defined as ground or surface waters, which emanate from or flow over or through areas disturbed and contaminated by mining activities. Once acidic leachate caused by sulfide oxidation is generated, it can be altered by natural run-off, physically and chemically. Chemical changes include additions and dilution/attenuation of acidity, metal contents, sulphate, hardness and alkalinity, while major physical changes include addition and dilution of silt and sediment as well as temperature (Kimmel, 1983). As a result, mine waters may or may not have a low pH at the point of sampling. According to Skousen et al. (1998), mine waters can be classified into 6 groups as follows:

Type 1 mine drainage is characterised by its low pH (<4.5) or no alkalinity, and is therefore referred to as AMD. It contains high concentration of Fe, Al, Mn and other metals, acidity and oxygen. AMD also refers to water with pH less than 6.0, which contains a net acidity that is greater than its alkalinity.

Type 2 mine drainage exhibits a pH >6.0, and contains high total dissolved solids (including Fe\(^{2+}\) and Mn), with limited oxygen concentrations. Once oxygen and other factors that enhance sulfide oxidation become available, the pH can change rapidly and Type 2 mine drainage may develop into Type 1 AMD.

Type 3 mine drainage, also known as alkaline mine drainage, contains moderate to high total dissolved solids, low to moderate Fe\(^{2+}\) and Mn, and has no or low oxygen contents. It displays circum-neutral to alkaline pH (pH >6.0) and the alkalinity exceeds
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the acidity. This type of mine drainage occurs in areas where acid producing minerals are scarce or buffering materials are more abundant than sulfide minerals.

Type 4 mine drainage results from the neutralisation of AMD. It has pH values greater than 6.0 and high total suspended particulates, not yet completely settled. Over time, suspended particulates will settle and this type of drainage will develop into Type 5.

Type 5 mine drainage forms when suspended particulates and most metal hydroxides in Type 4 water have settled, leaving only major ions such as dissolved Ca and Mg and soluble oxyanions (e.g. bicarbonate, sulfate) in the water column. Its pH is greater than 6.0. This type of water cannot develop if alkalinity and oxygen is limited during neutralisation processes.

Type 6 mine drainage, known as inert or neutral water, occurs in mines where sulfide minerals are limited and contain low to moderate amounts of carbonate minerals. Typically, it is characterised by circum-neutral pH, low specific conductance (<100 µS/mm) and its acidity and alkalinity are nearly balanced.

Because the physical and chemical properties of mine waters vary significantly from mine to mine, as well as within the same mine (such as seasonal variation). Banks et al. (1997) emphasised that mine waters should not be perceived as problems in all cases. The authors demonstrated that some mine waters have been used for drinking water (e.g. Pb and fluoride mine, Derbyshire, while some are extremely problematic (e.g. Wheal Jane, Cornwall). Examples of water quality of various acid mine drainage affected waters are given in Table 5.1.

<table>
<thead>
<tr>
<th>Type</th>
<th>Rio Tinto, Rio Odiel¹</th>
<th>Zeexhan Field²</th>
<th>Lavant Mine³</th>
<th>Canon¹ (UK)</th>
<th>Flat Eyre¹ (Norway)</th>
<th>Ron (UK)</th>
<th>Avoca (Thailand)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.2-3.6</td>
<td>2.6-7.6</td>
<td>2.1-4.4</td>
<td>3.1-5.6</td>
<td>3.68</td>
<td>2.9-8.1</td>
<td>3.3-3.8</td>
</tr>
<tr>
<td>SO₄²⁻ (g L⁻¹)</td>
<td>530-2600</td>
<td>1.8-2420</td>
<td>595-11200</td>
<td>262-355</td>
<td>68</td>
<td>0.9-178</td>
<td>1240-1820</td>
</tr>
<tr>
<td>As (µg L⁻¹)</td>
<td>nr. up to 4640</td>
<td>up to 580*</td>
<td>nr.</td>
<td>nr.</td>
<td>nr.</td>
<td>4.8-583</td>
<td>5.25</td>
</tr>
<tr>
<td>Cd (µg L⁻¹)</td>
<td>33-670</td>
<td>up to 500</td>
<td>173-825</td>
<td>2-9</td>
<td>nr.</td>
<td>3.5-247</td>
<td>up to 500</td>
</tr>
<tr>
<td>Co (µg L⁻¹)</td>
<td>143-2290</td>
<td>up to 90</td>
<td>nr.</td>
<td>nr.</td>
<td>nr.</td>
<td>nr.</td>
<td>nr.</td>
</tr>
<tr>
<td>Cu (mg L⁻¹)</td>
<td>3.3-54</td>
<td>up to 7.6</td>
<td>nr.</td>
<td>0.5-0.8</td>
<td>0.8</td>
<td>1.5-73</td>
<td>1.0-10</td>
</tr>
<tr>
<td>Fe (mg L⁻¹)</td>
<td>2.2-1010</td>
<td>up to 200</td>
<td>nr.</td>
<td>2.0-11.4</td>
<td>nr.</td>
<td>0.004-4.2</td>
<td>85-240</td>
</tr>
<tr>
<td>Mn (mg L⁻¹)</td>
<td>2.6-43</td>
<td>up to 55</td>
<td>nr.</td>
<td>0.8-0.9</td>
<td>nr.</td>
<td>0.001-1.4</td>
<td>nr.</td>
</tr>
<tr>
<td>Ni (µg L⁻¹)</td>
<td>45-990</td>
<td>up to 170</td>
<td>nr.</td>
<td>nr.</td>
<td>2150</td>
<td>nr.</td>
<td>nr.</td>
</tr>
<tr>
<td>Pb (µg L⁻¹)</td>
<td>48-860</td>
<td>up to 3550</td>
<td>nr.</td>
<td>nr.</td>
<td>nr.</td>
<td>nr.</td>
<td>nr.</td>
</tr>
<tr>
<td>Zn (mg L⁻¹)</td>
<td>9.2-170</td>
<td>up to 50</td>
<td>nr.</td>
<td>3.2-10.1</td>
<td>0.2</td>
<td>0.007-4.2</td>
<td>25-403</td>
</tr>
</tbody>
</table>

Acidic drainage is neutralised during contact with natural carbonate-bearing rocks, or through treatment using alkaline materials, such as quicklime (CaO), hydrated lime (Ca(OH)₂), calcium carbonate (CaCO₃), caustic soda (NaOH) or soda ash (Na₂CO₃). The principle of acid neutralisation by lime is based on the following reactions (Kelly, 1988; Skousen et al. 1998 Nordstrom and Alpers, 1999):

1) Dissolution of alkaline materials is fast and provides products, which can neutralise acid such, OH⁻, HCO₃⁻ and CO₃²⁻ ions, for example:

\[ Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \]  \hspace{1cm} (5.1)

\[ CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \] \hspace{1cm} (5.2)

2) When the pH is raised to certain points, dissolved metals in solution will form insoluble metal hydroxides and precipitate (see Table 5.2). This is due to the fact that
most divalent and trivalent metals exhibit minimum solubility at circum-neutral pH values. In general, with increasing pH. and at metal concentrations greater than $10^{-6}$ moles per litre, metal hydroxides precipitate in the following sequence: Fe$^{3+}$ - Al - Pb - Cu - Zn - Ni - Fe$^{2+}$ - Cd - Mn$^{2+}$ (Table 5.2). It should be noted that adsorption or co-precipitation with Fe-(oxy)hydroxides limits the dissolved concentrations of trace metals present in the water column, hence may interfere with or limit the formation of trace metal hydroxides (Nordstrom and Alpers. 1999). Interactions among metals in AMD can influence the minimum pH at which metals precipitate. For example, precipitation of ferric hydroxide removes a large proportion of Mn from water column at pH 8 due to co-precipitation. However, this will take place only if the Fe concentration in AMD is about four times higher than that of Mn (Skousen et al. 1998).

Acid neutralisation by alkaline materials in AMD treatment schemes, produces large amounts of sludge (Kalin et al., 2006), which causes further environmental problems and additional cost. Furthermore, neutralisation by carbonates is relatively fast, hence only provides short term buffering capacity. In general, after completion of calcite dissolution, successive pH buffering at lower levels and slower rate will take place by dissolution of aluminosilicate minerals, such as chlorite, muscovite and plagioclase (Reactions 5.3-5.5). Because these minerals are often present in large quantities, they provide long term buffering capacity (Salmon, 2003).

Chlorite weathering

\[
\begin{align*}
&Mg_{4.5}Fe_{6.2}^{{II}}Fe_{0.2}^{{III}}Al_{3}Si_{3}O_{10}(OH)_{2} + 16H^{+} \rightarrow \\
&4.5Mg^{2+} + 0.2Fe^{2+} + 0.2Fe^{3+} + 2Al^{3+} + 3SiO_{2} + 12H_{2}O
\end{align*}
\]

(5.3)

Muscovite weathering

\[
\begin{align*}
&K_{0.8}Na_{0.2}(Fe_{0.8}Al_{1.9})AlSi_{3}O_{10}(OH)_{2} + 10H^{+} \rightarrow \\
&0.8K^{+} + 0.2Na^{+} + 0.1Fe^{3+} + 2.9Al^{3+} + 3SiO_{2} + 6H_{2}O
\end{align*}
\]

(5.4)

Plagioclase weathering

\[
\begin{align*}
&Na_{0.75}Ca_{0.25}Al_{1.25}Si_{2.75}O_{8} + 5H^{+} \rightarrow \\
&0.75Na^{+} + 0.25Ca^{2+} + 1.25Al^{3+} + 2.75SiO_{2} + 2.5H_{2}O
\end{align*}
\]

(5.5)
Table 5.2 Minimum pH for complete precipitation of metal ions as hydroxides for single and saturated solution. Sources - a: Kelly, 1988; b: Skousen et al., 1998; C: Nordstrom and Alpers, 1999.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Minimum pH for hydroxide precipitation</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe²⁺</td>
<td>4.3ᵃ (3.5)ᵇ</td>
<td>Fe³⁺ + 3OH⁻ → Fe(OH)₃</td>
</tr>
<tr>
<td>Al⁺</td>
<td>5.2ᵃ (4.5)ᵇ</td>
<td>Al³⁺ + 3OH⁻ → Al(OH)₃</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>6.3ᵃ</td>
<td>Pb²⁺ + 2OH⁻ → Pb(OH)₂</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>7.2ᵃ</td>
<td>Cu²⁺ + 2OH⁻ → Cu(OH)₂</td>
</tr>
<tr>
<td>Zn⁺</td>
<td>8.4ᵃ</td>
<td>Zn²⁺ + 2OH⁻ → Zn(OH)₂</td>
</tr>
<tr>
<td>Ni⁺</td>
<td>9.3ᵃ</td>
<td>Ni²⁺ + 2OH⁻ → Ni(OH)₂</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>9.5ᵃ (8.5)ᵇ</td>
<td>Fe³⁺ + 2OH⁻ → Fe(OH)₂</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>9.7ᵃ (10-11)ᶠ</td>
<td>Cd²⁺ + 2OH⁻ → Cd(OH)₂</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>10.6ᵃ (9.0-9.5)ᵇ</td>
<td>Mn²⁺ + 2OH⁻ → Mn(OH)₂</td>
</tr>
</tbody>
</table>

At any given pH, ferrous (Fe²⁺) hydroxide, known as “green rust” and rarely appearing in nature, is more soluble than Fe³⁺. It forms when solutions rich in Fe²⁺ mix with highly alkaline solutions and are allowed to oxidise slightly. It is not recognised as a mineral because it is unstable and poorly characterised (Nordstrom and Alpers, 1999). On the other hand, ferric (Fe³⁺) hydroxide forms a yellowish orange precipitates (known as yellow boy) at pH ≥ 3.5 (Skousen et al. 1998). According to Nordstrom and Alpers (1999), the first phase of ferric hydroxide when acidic waters are neutralised is ferrihydrite, a poorly crystalline metastable ferric hydroxide, which later will transform to a more stable forms, such as hematite and goethite. Acidithiobacillus ferrooxidans, which grow best in pH < 4.0, is believed to accelerate the formation of ochreous precipitates (e.g. Bigham et al., 1992). Transformation of ferrihydrite to more stable forms can result in a release of elements co-precipitated with Fe phases during their formation, and hence an increase in As and metal concentrations in the water column.

In mine waters, Ni tends to occur associated with Fe-oxyhydroxides, often forming alteration rims on pentlandite and nickeliferos pyrrhotite, or coprecipitate with goethite rather than as discrete Ni-hydroxides. Nickel remaining in solution may be exported from
the oxidation sites, and some may be taken up by vermiculite. Similar to Ni, Cu. once dissolved, is either transported in solution or immobilised in other secondary minerals such as sulfates, carbonates, silicates or co-precipitated with Fe-oxyhydroxides (Nordstrom and Alpers, 1999).

Manganese is one of the metals commonly found in mine waters. Its oxides and hydroxides are known to form associated with AMD, generally at considerable distance from the sources of sulfide oxidation or acid generation (Nordstrom and Alpers, 1999). Manganese is mobile over a broad pH range (~ 4.5-8; Bamforth et al., 2006) and therefore can be carried long distances from sources of AMD. Furthermore, according to Johnson and Younger (2005), Mn is difficult to remove from discharges due to the high activation energy required for Mn oxide precipitation. A number of documents reported that Mn-oxyhydroxides have higher ability to immobilise metals than Fe-oxyhydroxides, due to its greater electronegativity and higher adsorption bonding energy (Tamura et al., 1996; Trivedi and Axe, 2000; Lee et al., 2002). The formation of Mn-oxyhydroxides is predominantly controlled by microbial activity, as their abiotic precipitation is extremely slow at pH < 8 (Kennedy, et al., 2004). Lee et al. (2002) reported similar findings. The authors investigated the formation of Mn-oxides in AMD by neutralisation with NaOH and found that that Mn oxide does not form at pH < 7, hence should not play a significant role in scavenging metals in most acid mine waters. Skousen et al. (1998) reported that generally, Mn hydroxide precipitation occurs at pH values 9.0-9.5, but complete precipitation was not achieved even though the solution pH was increased to 10.5.

In contrast to most trace metals that occur as cations in solution (e.g Cu$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, Cd$^{2+}$, Zn$^{2+}$, Pb$^{2+}$) in aquatic environments, inorganic As is present in oxyanions, namely pentavalent arsenate (AsO$_4^{3-}$) and trivalent arsenite (AsO$_3^{3-}$). Arsenate is the dominant species under oxidising environments and adsorbs strongly onto surfaces of metal oxides, mainly Fe, Mn and Al. Under reducing conditions arsenate will transform to arsenite, a more soluble, mobile and toxic species. However, due to slow redox transformations, both species are found in either environment (Al-Abed et al, 2007).

The mobility of As in aquatic systems largely depends on adsorption/desorption and precipitation/dissolution reactions. At low pH, As mobility increases due to dissolution processes. On the other hand, alkaline pH can cause desorption of As from binding metal
oxides, resulting in high dissolved As concentrations. This can be explained by the influence of the zero point of charge (ZPC. ca. 7.7 for goethite, 8.0 for ferrihydrite) on element mobility: when the pH increases above the ZPC, the net surface charge of Fe oxides changes from positive to negative which will lead to the expulsion of negative charged ions such as arsenate (Hinkel and Polette, 1999). There is also a concern for an increase in dissolved As due to its release when meta-stable Fe-oxhydroxides, such as ferrihydrite, are transformed to more stable oxides such as goethite (e.g. Wayachunas et al., 1993). Furthermore, bacterial activity can enhance dissolution of As-rich Fe-oxides/oxhydroxides under reducing conditions (Mcreadie et al., 2000 in Casiot et al., 2003) or the reduction of adsorbed arsenate (Zobrist et al., 2000 in Casiot et al., 2003), both of which increase As mobility. Remobilisation of As can also be caused by anion exchange with phosphate (PO$_4^{3-}$). This is because arsenate and phosphate exhibit similar physiochemical properties. Phosphate, however, is smaller in size and higher in charge; hence can replace arsenate through competitive ion exchange, releasing As into solution (Dybowska et al., 2005). Bowell (1994) investigated the effects of pH and organic acids on As sorption and found that the sorption of As by goethite, hematite and lepidocrocite is dependent on pH, Eh and the presence of competing compounds such as fulvic acids. Highly acidic or reducing conditions enhance the dissolution of Fe-oxides/oxhydroxides, releasing associated As into the water column.

5.5 Methods

5.5.1 Reagents and materials

The quality, preparation of MQ water, Q-HCl and Q-HNO$_3$, bottles (both for sampling and standard preparation), cleaning processes, as well as multi-element standard preparation have been given in chapter 4.

5.5.2 Sampling protocol and sample treatment

In this study, the term point and diffuse sources is defined at their point of entrance into the River Tamar. The terms stream, adit and river are defined as:
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'Stream' represents water courses in Zone C (Figure 5.1B) that carry natural water mixed with adit outflow and/or leachate from contaminated land and mining waste piles into the River Tamar or its estuary.

'Adit' is a single-point source in Zone C that discharges mine water from underground drainage tunnels directly (i.e. not via a stream that allows attenuation or dilution) into the River Tamar or its estuary.

'River' corresponds to the River Tamar and its tributaries outside the Gunnislake/Calstock mining area (Zones A and B).

This work focused on 25 streams and adits within the Gunnislake/Calstock mining district, which was mined extensively during the 19th century. The surveyed water courses were potential carriers of dissolved and particulate metals into the River Tamar. The selection of sites was based on previous studies (e.g. Dines et al., 1956b; surveys of mine sites commissioned for the Tamar Valley Mining Heritage Project) and local knowledge (e.g. land owners, mine rescue service), combined with preliminary surveys and analysis. Hence, selected streams and adits should represent the main point sources within the Gunnislake/Calstock mining area (Zone C, Figure 5.1B), but do not include sources to the north of this area (mainly affected by Mn mines), or within the sub-catchment of the major tributaries (Zone B). Figure 5.1 A shows the outline of regions within the Tamar catchment in which certain elements (As, Cu, Mn, Pb and Zn) were mined, and Figure 5.1 B indicates in red Zone C, in which mine water samples for this survey were taken, as well as the peripheral mining areas (Zone B in blue and brown) and the catchment background (Zone A).
Water samples in Zone C were taken monthly from July 2005 to June 2006 at locations given in Figure 5.2, including a sample for the Tamar freshwater endmember upstream of Gunnislake weir, which separates freshwater from tidal water. In order to assess the effects of metal contamination caused by past mining activities in Gunnislake/Calstock mining district, additional water samples in Zones A and B at 15 locations given in Figure 5.3 were taken quarterly (July, October 2005 and January, April 2006). The sample sites include the River Tamar at various points upstream from Gunnislake and its major tributaries (Lynher, Tiddy, Inny, Ottery, Deer, Carey, Thrushel, Lyd, Tavy and Walkham) near their confluence with the River Tamar.
Figure 5.2 Location of sampling sites in Gunnislake/Calstock mining district (Zone C). Stream samples include sample site no. 2, 3, 4, 5, 6, 7, 9, 10, 14, 16, 17, 20, 21, 22, 23, 24 and 25. Adit samples include sample site no. 1, 8, 11, 12, 13, 15, 18 and 19.
Figure 5.3 The sampling locations of the catchment survey. The samples of the Tiddy, Lynher and Tavy Rivers were taken upstream of their respective tidal limits.
Stream pH and redox potential (Eh) were measured in situ using a portable instrument (Hanna, HI 9024/5). The pH electrode (glass electrode, Merck) was calibrated with pH 4 and 7 buffers (BDH Laboratory). The Eh electrode (Ag/AgCl electrode, Merck) was checked against Zobell standard solution (Nordstrom, 1977) and appropriate corrections were made, and the Eh was calculated from the summation of the corrected E_{measured} (emf) and E_{ref} (Nordstrom and Wilde, 2005). Conductivity was determined using a portable Hanna instrument, model HI 9635. Stream velocity was determined using a flow meter (Valeport Braystoke BFM002, small impeller). The measurement was taken at the centre of the stream at 0.6 x depth from the bottom of the streambed (all studied streams were less than 1.0 m deep), and where possible at a point of minimal turbulence. Streams wider than 0.5 m were divided into several (2-4) subsections and discrete measurement of each section was taken. Measured revolutions per time unit were converted into velocity using the calibration equation provided by the instrument manufacturer. Stream discharge was then calculated from flow velocity and stream cross-sectional area(s). For small drainages unsuitable for flow meter, the discharge was measured by channelling water into a vessel of known volume and timing the filling period with a stop watch.

Samples were vacuum filtered within hours of collection using cellulose nitrate membranes (0.2 µm, Whatman) fitted into a polycarbonate filtration unit (Nalgene). The filtrate was transferred to LDPE bottles and immediately acidified (2% sub-HNO₃). The filter membranes retaining the suspended particulate matter (SPM) were transferred to individual petri-dishes and stored frozen (-18 °C). Filter membranes were digested using concentrated HNO₃ (5 ml, 1 h at 120 °C under reflux) and centrifuged to obtain acid-extractable metals associated with the SPM.

5.5.3 Instrumentation and analysis

Inductive coupled plasma mass spectroscopy (ICP-MS) was used for analysing As, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn in filtered samples and acid extracts following internal ISO 9001:2000 accredited protocols. A series of five multi-element calibration standards was prepared from standard solutions as described in section 4.4.1. Two internal standards (In, Ir. each 100 µg L⁻¹, final concentration) were used for compensating instrumental drift during the time of analysis. The instrument model and operating conditions are given in Table 5.3.
Calcium, Fe and magnesium were analysed by Flame-AAS and ICP-OES (Varian 725-ES). The models and operating conditions for Flame-AAS are given in Table 5.4. Standard solutions for Flame-AAS and ICP-OES were prepared similar to that of ICP-MS, and the standard calibration range for each element is presented in Tables 5.4&5. The limit of detection (LOD) for each element was defined as 5 times the standard deviation (from 19 analyses) of the lowest standard. The accuracy of the analytical methods was verified against NWRI (National Water Research Institute) Certified Reference Material (CRM) for fortified freshwater (TM-DWS). For every individual analysis protocol, the CRM was tested until satisfied (typically <10% RSD, with a few exception for As, Ca and Ni) before analysing samples and the check standard was repeatedly introduced throughout each protocol. The limits of detection and the CRM recovery from ICP-MS and ICP-OES for each element are given in Table 5.5.

### Table 5.3 ICP-MS model and operating operations.

<table>
<thead>
<tr>
<th>Model</th>
<th>PlasmaQuad PQ2+Turbo (VG Element)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nebuliser</td>
<td>High Solid (Calan)</td>
</tr>
<tr>
<td>Spray Chamber</td>
<td>Double pass (Scott)</td>
</tr>
<tr>
<td>Forward power</td>
<td>1350 W</td>
</tr>
<tr>
<td>Gas flow rate (L min⁻¹)</td>
<td></td>
</tr>
<tr>
<td>- Nebuliser</td>
<td>0.85</td>
</tr>
<tr>
<td>- Auxiliary</td>
<td>1.0</td>
</tr>
<tr>
<td>- Coolant</td>
<td>16</td>
</tr>
</tbody>
</table>

### Table 5.4 Flame-AAS models and operating operations used for Ca, Fe and Mg analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>Model</th>
<th>Wavelength (nm)</th>
<th>Slit Width (nm)</th>
<th>Standard calibration range (mg L⁻¹)</th>
<th>Lamp current (mA)</th>
<th>LOD (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>Varian SpectrAA 50B</td>
<td>239.9</td>
<td>0.2</td>
<td>1-100</td>
<td>7</td>
<td>1.2</td>
</tr>
<tr>
<td>Fe</td>
<td>GBC 902</td>
<td>248.3</td>
<td>0.2</td>
<td>1-5</td>
<td>5</td>
<td>0.05</td>
</tr>
<tr>
<td>Mg</td>
<td>GBC 902</td>
<td>285.2</td>
<td>0.5</td>
<td>0.1-0.4</td>
<td>3</td>
<td>0.02</td>
</tr>
</tbody>
</table>
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Table 5.5 Percentage recovery of certified material and the limit of detection for each element. * from ICP-OES analysis Fe 238.204 nm. ** for samples containing low concentrations. As was re-analysed in a single-element protocol with a LOD of 0.95.

<table>
<thead>
<tr>
<th>Element</th>
<th>Certified Value (µg L⁻¹)</th>
<th>±2σ (%)</th>
<th>Recovery (%)</th>
<th>Limit of Detection (µg L⁻¹)</th>
<th>Standard calibration range (µg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>72.5±11.2</td>
<td>92.5±14.9</td>
<td>92.5±14.9</td>
<td>8.4**</td>
<td>8-5000</td>
</tr>
<tr>
<td>Cd</td>
<td>14.2±1.48</td>
<td>99.5±7.8</td>
<td>99.5±7.8</td>
<td>0.51</td>
<td>0.16-100</td>
</tr>
<tr>
<td>Co</td>
<td>65.2±6.25</td>
<td>104±5.7</td>
<td>104±5.7</td>
<td>0.40</td>
<td>1.6-1000</td>
</tr>
<tr>
<td>Cu</td>
<td>178±17.4</td>
<td>101±4.2</td>
<td>101±4.2</td>
<td>3.5</td>
<td>16-10000</td>
</tr>
<tr>
<td>Fe*</td>
<td>343±34.5</td>
<td>105±8.6</td>
<td>105±8.6</td>
<td>52.5</td>
<td>50-10000</td>
</tr>
<tr>
<td>Mn</td>
<td>86.2±9.19</td>
<td>109±8.0</td>
<td>109±8.0</td>
<td>1.3</td>
<td>16-10000</td>
</tr>
<tr>
<td>Ni</td>
<td>78.9±8.76</td>
<td>109±13.3</td>
<td>109±13.3</td>
<td>0.54</td>
<td>1.6-1000</td>
</tr>
<tr>
<td>Pb</td>
<td>34.2±3.44</td>
<td>95.3±5.2</td>
<td>95.3±5.2</td>
<td>0.40</td>
<td>1.6-1000</td>
</tr>
<tr>
<td>Zn</td>
<td>379±40.3</td>
<td>95.6±7.0</td>
<td>95.6±7.0</td>
<td>3.2</td>
<td>16-10000</td>
</tr>
</tbody>
</table>

Sulfate concentrations were determined by gravimetric method according to Radojčić and Bashkin (2006) and analysed with UV/Visible spectrophotometry at the wavelength of 420 nm (standard solutions range from 1-40 mg L⁻¹). Potassium was analysed by flame photometer (Corning 400). Typically, 5 mg L⁻¹ of standard solution was set to 10 reading units and a blank was set to zero reading, i.e. 1 reading unit per 0.5 mg L⁻¹. A check standard was repeatedly introduced throughout the analysis period.

5.6 Results and discussion

5.6.1 Master variables and major ions

All studied rivers in the catchment upstream of Gunnislake had circum-neutral pH (6.5 to 8.4), positive redox potential (310 to 700 mV) and low conductivity (13-84 µS; Table 5.6). In the River Tamar at Gunnislake, within the main mining area, the conductivity (35-170 µS) was elevated and the pH range somewhat lower (pH 6.1-8.2) compared to the upper catchment. Statistical analysis showed positive correlations (r = 0.69, p<0.0001) between the conductivity and summation of major cations (Table 5.7) in all sample categories (river, stream, adit).
In general, the cation composition of rivers in the Tamar catchment (Figure 5.4) was characterised by a combination of Ca (36-47%) and Na+K (23-44%, K<5% in all samples), with Mg in the range of 17 to 24%. The River Tiddy formed an exception with higher Ca (55%) than all other rivers. Relatively high Ca in the River Tiddy may result from inter-bedded limestones (Saltash Formation; Digimap. 2007: Geological Map Data © NERC 2008). The composition in the catchment differs from average freshwaters, which are dominated by Ca (Gibbs, 1970 in Chester, 2000). The cation composition in the Tamar at Gunnislake observed in this study agreed well with values obtained from the Environment Agency for the same period of time (Figure 5.4).

The rainwater cation concentrations in the region (1.6 mg L⁻¹ Ca and 5.6 mg L⁻¹ Na, Dartmoor station, Hayman et al., 2000) are considerably lower than most values observed in rivers, streams and adits in this study (3.9-79 mg L⁻¹ Ca and 6.9-23 mg L⁻¹ Na, Table 5.7), indicating that rocks and soils underlying the catchment are the dominant factors controlling water chemistry. Statistical analysis (t-test) revealed that major ions in rivers draining igneous rocks (Rivers Tavy and Lynher) were lower than those draining sedimentary rocks (Rivers Tamar upstream, Deer, Carey, Ottery, Thrusel, Lyd and Inny; p<0.0001 for sulfate, Ca, Mg and K; p=0.001 for Na; Table 5.8). This can be explained by sedimentary rocks releasing greater quantities of Ca, Mg, sulfate and bicarbonate than crystalline rocks (Maybeck, 1981; in Chester, 2000). The major ion concentrations in rivers in the Tamar catchment were higher than typical values for the World average river waters (Table 5.7).

Figure 5.5 shows the cation composition of rivers in the Tamar catchment and adits and streams in the Gunnislake/Calstock mining area from the May and June surveys. While most adits/streams were characterised by a composition similar to rivers, some exceptions can be noted, for example stream 4 (Na+K >66%) which is high in Na due to the influence of tidal water and therefore will be excluded from Tables 5.6-7. It is also interesting that although the major ions in streams and adits in the intensive mining area are highly variable, they drain the same bed rock (slate) and same soil unit (loamy soils) (Environmental Agency: Tunner, 2008, Pers. Comms.). As a result, the variation of the major ions is likely to result from the mineral ores and the processes by which the wastes were generated.
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Table 5.6 Ranges of pH, redox potential (Eh), Conductivity (Cond.), temperature (Temp.) and water discharge (Qi) measured in-situ between July 2005 to June 2006 in rivers of the Tamar catchment (four surveys), the River Tamar at Gunnislake and in streams and adits in the mining area (12 surveys). Greystone Bridge is located upstream of the main mining area. Streams and adits were sub-divided according to their metal concentrations and annual mean mean pH values (<5 and >5 respectively, cut-off in the region of local rain pH). The number of water course in each category is given. Adit 1 and stream 4 were excluded from this table as they were influenced by tidal water. ‘nd’ = not determined.

<table>
<thead>
<tr>
<th>No.</th>
<th>pH (mV)</th>
<th>Eh (µS)</th>
<th>Cond. (°C)</th>
<th>Qi (L s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rivers in upper catchment</td>
<td>6</td>
<td>7.0-8.4</td>
<td>310-700</td>
<td>39-84</td>
</tr>
<tr>
<td>Rivers in peripheral mining area</td>
<td>8</td>
<td>6.5-8.2</td>
<td>410-600</td>
<td>13-71</td>
</tr>
<tr>
<td>River Tamar at Greystone</td>
<td>1</td>
<td>7.3-7.8</td>
<td>410-570</td>
<td>24-57</td>
</tr>
<tr>
<td>River Tamar at Gunnislake</td>
<td>1</td>
<td>6.1-8.2</td>
<td>310-640</td>
<td>35-170</td>
</tr>
<tr>
<td>Streams similar to catchment background</td>
<td>4</td>
<td>6.4-7.7</td>
<td>400-690</td>
<td>16-220</td>
</tr>
<tr>
<td>Streams affected by mine waters (pH&gt;5)</td>
<td>11</td>
<td>6.2-7.9</td>
<td>300-690</td>
<td>13-160</td>
</tr>
<tr>
<td>Acidic streams (pH&lt;5)</td>
<td>2</td>
<td>2.9-6.4</td>
<td>440-700</td>
<td>44-460</td>
</tr>
<tr>
<td>Adits (pH&gt;5)</td>
<td>7</td>
<td>5.5-7.8</td>
<td>330-770</td>
<td>19-105</td>
</tr>
<tr>
<td>Acidic adits (pH&lt;5)</td>
<td>1</td>
<td>3.4-4.4</td>
<td>550-680</td>
<td>40-94</td>
</tr>
</tbody>
</table>
Table 5.7 Ranges of sulfate (SO\textsubscript{4}\textsuperscript{2-}), calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na) of rivers, streams and adits in the Tamar catchment (sampling). Adit 1 and stream 4 were excluded from this table as they were influenced by tidal water. All unit in mg L\textsuperscript{-1}. \textsuperscript{1} from Hayman et al. (2000); \textsuperscript{2} from Martin and Whitfield (1983) in Chester (2000).

<table>
<thead>
<tr>
<th></th>
<th>SO\textsubscript{4}\textsuperscript{2-}</th>
<th>Ca</th>
<th>Mg</th>
<th>K</th>
<th>Na</th>
<th>Σ major cations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical values for rainfall composition in SW England\textsuperscript{1}</td>
<td>6.5-9.2</td>
<td>0.9-1.6</td>
<td>1.1-2.8</td>
<td>up to 0.4</td>
<td>2.3-5.6</td>
<td>-</td>
</tr>
<tr>
<td>Typical values of World average river waters\textsuperscript{2}</td>
<td>8.7</td>
<td>13.3</td>
<td>3.1</td>
<td>1.5</td>
<td>5.3</td>
<td>-</td>
</tr>
<tr>
<td>Rivers in upper catchment</td>
<td>7.8-15</td>
<td>13-25</td>
<td>3.7-6.8</td>
<td>2.8-5.1</td>
<td>13-19</td>
<td>33-56</td>
</tr>
<tr>
<td>Rivers in peripheral mining area</td>
<td>5.2-16</td>
<td>5.1-33</td>
<td>1.6-6.4</td>
<td>0.7-2.8</td>
<td>6.9-24</td>
<td>14-66</td>
</tr>
<tr>
<td>River Tamar at Greystone</td>
<td>12-16</td>
<td>16-20</td>
<td>4.3-5.8</td>
<td>2.6-3.2</td>
<td>13-14</td>
<td>36-43</td>
</tr>
<tr>
<td>River Tamar at Gunnislake</td>
<td>13-26</td>
<td>15-20</td>
<td>4.1-6.3</td>
<td>1.9-6.7</td>
<td>12-23</td>
<td>46-81</td>
</tr>
<tr>
<td>Streams similar to catchment background</td>
<td>4.6-24</td>
<td>3.9-45</td>
<td>2.6-6.4</td>
<td>0.7-3.0</td>
<td>8.7-12</td>
<td>16-66</td>
</tr>
<tr>
<td>Streams affected by mine waters (pH&gt;5)</td>
<td>3.8-68</td>
<td>4.1-41</td>
<td>1.0-10</td>
<td>0.6-3.4</td>
<td>8.6-12</td>
<td>14-66</td>
</tr>
<tr>
<td>Acidic streams (pH&lt;5)</td>
<td>38-380</td>
<td>15-79</td>
<td>5.1-16</td>
<td>1.0-6.2</td>
<td>9.4-12</td>
<td>31-110</td>
</tr>
<tr>
<td>Adits (pH&gt;5)</td>
<td>10-89</td>
<td>5.7-23</td>
<td>3.0-8.9</td>
<td>0.9-3.9</td>
<td>8.4-17</td>
<td>18-53</td>
</tr>
<tr>
<td>Acidic adits (pH&lt;5)</td>
<td>26-73</td>
<td>7.1-17</td>
<td>5.5-11</td>
<td>1.5-2.9</td>
<td>13-14</td>
<td>28-45</td>
</tr>
</tbody>
</table>
Figure 5.4 Piper diagram of Ca, Mg and Na+K of the sum Ca+Mg+Na+K, based on milliequivalents in the Tamar River at Gunnislake determined in this study (red cross, this study), determined by the Environment Agency (purple cross, EA), and in the wider Tamar catchment (blue x).
Chapter 5: Geochemistry of mine waters and metal fluxes from abandoned mine sites

**Figure 5.5** Piper diagram of Ca, Mg and Na+K of the sum Ca+Mg+Na+K, based on milli-equivalents in the Tamar River and in adits and streams in the mining area.

**Table 5.8** Comparison of major ions between rivers draining igneous (Rivers Tavy and Lynher) and sedimentary (Rivers Tamar upstream, Deer, Carey, Ottery, Thrusel, Lyd and Inny). River Tiddy was excluded from the analysis due to its unusual high in calcium which may resulted from locally inter-bedded limestone (Saltash Formation; Digimap, 2007). Mean values are given in brackets. Units in mg L\(^{-1}\).

<table>
<thead>
<tr>
<th></th>
<th>(\text{SO}_4^{2-})</th>
<th>(\text{Ca})</th>
<th>(\text{Mg})</th>
<th>(\text{K})</th>
<th>(\text{Na})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rivers draining sedimentary rocks.</td>
<td>7.8-15 (11.3)</td>
<td>10-27 (17.2)</td>
<td>3.2-6.8 (4.9)</td>
<td>1.1-5.1 (3.2)</td>
<td>9.1-24 (15.4)</td>
</tr>
<tr>
<td>Rivers draining igneous rocks</td>
<td>5.2-10 (7.4)</td>
<td>5.1-14 (8.5)</td>
<td>1.6-5.9 (2.9)</td>
<td>0.7-2.4 (1.2)</td>
<td>6.9-11 (8.1)</td>
</tr>
<tr>
<td>(p) value</td>
<td>&lt;0.0001 &lt;0.0001 &lt;0.0001 &lt;0.0001</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Acidic water (pH<5; cut-off point determined by average rain water pH in the region) was observed at Streams 16 (pH 2.9-6.4) and 17 (pH 3.5-4.3) and Adit 13 (pH 3.4-4.4), whereas most streams and adits showed circum-neutral pH (5.5-7.9). The two acidic streams receive significant input of acidic mine waters from adits and run-off from waste piles within Devon Great Consols Mine, and also featured moderate to high sulfate...
concentrations (38-380 mg L\(^{-1}\)) compared to the circum-neutral streams and adits, in which sulfate concentrations below 100 mg L\(^{-1}\) were observed (Figure 5.6).

![Graph showing sulfate concentrations and pH in streams and adits in Zone C.](image)

**Figure 5.6** Range of sulfate concentrations and pH in streams and adits in Zone C.

Sulfate is a product of acid generating reactions (section 4.3.1), therefore considerable amount of sulfate is expected in acidic mine waters. However, Adit 13 showed low to moderate sulfate contents (26-73 mg L\(^{-1}\)) despite exhibiting acidic waters (pH 3.4-4.4), compared to the other two acidic streams (38-383 mg L\(^{-1}\) SO\(_4\)\(^{2-}\), pH 2.9-6.4). This may be due to the precipitation of sulfate generated by sulfide oxidation with Fe-hydroxides, forming Fe hydroxysulfate minerals such as jarosite (KFe\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\)) and schwertmannite (Fe\(_8\)O\(_8\)(OH)\(_6\)SO\(_4\)). The water composition also suggested that the loss of sulfate from the water column in Adit 13 should not be the result of sulfate reduction. This is because:

1. Organic compound concentrations, the substrate required for sulfate reduction, in the adit is expected to be low,
2. Secondary metal sulfide minerals (e.g. framboidal pyrite) were not identified in its streambed sediments (results from an additional SEM analysis for adit 13, not present here).
3. The alkalinity produced by sulfate reduction reactions (i.e. \( \text{HCO}_3^- \)) will neutralise the pH of the water resulting in an increase in the pH of the solution, whereas the pH of Adit 13 remained low (pH 3.4-4.4) throughout the sampling period (12 months).

Moderate sulfate concentrations (68 mg L\(^{-1}\)) in acidic mine waters (pH 3.7) have been reported by Arnesen and Iversen (1995 in Banks et al., 1997), and concentrations as low as 0.4 mg L\(^{-1}\) \( \text{SO}_4^{2-} \) in circum-neutral waters (pH 6.3) was reported by Williams et al. (1996). In general, sulfate concentrations in acidic streams and an adit observed in this study (73-380 mg L\(^{-1}\)) were comparable to those in the River Carnon (207-355 mg L\(^{-1}\)) that drains the St. Day mining district (Carnmenellis Granite, Figure 2.1) in the Fal catchment (Neal et al. 2005), but considerably lower than mine waters of the same pH ranges reported by Gray (1998), Bowell and Bruce (1995) and Braungardt et al. (2003) (Table 5.1).

Sulfate concentrations in the River Tamar at Gunnislake (12-26 mg L\(^{-1}\)) were slightly higher than those observed upstream of the main mining area (12-16 mg L\(^{-1}\)) and in the remainder of the catchment (5.2-16 mg L\(^{-1}\)) probably as a result of the mine waters input within Zone C.

Positive and relatively high redox potentials (Eh) were observed in all water courses, with the highest value recorded in Adit 18 (770 mV) and the lowest in Stream 4 (260 mV). The values observed were within the oxidising zone of the stability limits for water (+820 to -420 mV at pH 7; Radojevic and Bashkin, 2006).

The water flow at the time of measurement from the eight adits studied was low, with the maximum value of 33 L s\(^{-1}\) and the annual mean for individual adits ranging from 0.72 to 16.8 L s\(^{-1}\). The annual water flow from streams in the mining area varied from 0.1 to 350 L s\(^{-1}\). Out of 17 streams studied, the main contributions discharging into the River Tamar were Stream 2 (120-870 L s\(^{-1}\)), Stream 21 (20-600 L s\(^{-1}\)) and Stream 25 (74-1000 L s\(^{-1}\)). The water flow in the River Tamar at Gunnislake (2.8-43 m\(^3\) s\(^{-1}\)) was 13 times higher than the combined volume discharging from adits (up to 0.1 m\(^3\) s\(^{-1}\)) and streams (up to 3.1 m\(^3\) s\(^{-1}\)) within Zone C (Figure 5.7). Water flow in the River Tamar, streams and adits showed seasonal variation, with higher flow rate during autumn and winter than in spring and...
summer. The highest discharge in the Tamar was reported for November 2005 (ca. 43 m$^3$ s$^{-1}$), while the maximum instantaneous flow of the combined discharge of streams (3.1 m$^3$ s$^{-1}$) and adits (0.1 m$^3$ s$^{-1}$) occurred in January and December, respectively. The apparent difference in timing of the peak flow between adits/streams and the Tamar River is probably the result of the difference in measurement, the former are instantaneous values, the latter monthly averages calculated from daily observations. This difference may increase the uncertainty associated with mass balance calculations for metal fluxes (see section 5.6.4).

![Seasonal variation of combined instantaneous water discharge from streams and adits between July 2005 and June 2006](chart.png)

**Figure 5.7** Seasonal variation of combined instantaneous water discharge from streams and adits between July 2005 and June 2006. Monthly average discharge values for the River Tamar near Gunnislake (GN) and at Greystone Bridge (GS) were calculated from daily observations provided by the EA (SUM file).

### 5.6.2 Arsenic and metal concentrations

#### 5.6.2.1 Background concentrations

In order to establish the background concentrations in the catchment outside the mining area in Gunnislake/Calstock mining district, water samples from rivers in Zones A and B were collected in July, October 2005 and January and April 2006. The results showed that lowest dissolved and particulate As and trace metals were observed in upper catchment (Zone A: upper Tamar, Deer, Carey and Ottery) and in the River Tamar at Greystone Bridge (Table 5.9). The catchment of these rivers is characterised by
sandstones and shales, while rivers to their south (Zone B: Thrushel, Lyd, Inny, Tavy, Lynher and Tiddy) drain ore bearing rocks associated with metamorphic aureole of the granite intrusions as well as shales and slates. Statistical analysis (T-test) showed that dissolved As and Zn and particulate Fe concentrations in rivers in Zone A were significantly lower than in Zone B (p=0.001, 0.035 and 0.001, respectively), and occasionally dissolved Cu and Mn levels in rivers in Zone A were considerably lower (factor 1.5 and 3.3 respectively). As a result, As and metal concentrations in Zone A can be seen as representative of the catchment background. It is interesting that As background concentrations (as well as other metals) observed in this study are relatively higher than that of World average concentrations (e.g. World average dissolved and particulate As concentrations are 1.7 µg L⁻¹ and 5 µg L⁻¹ respectively, compared to up to 12 µg L⁻¹ dissolved As and 23 µg L⁻¹ particulate As observed in the present study). The average As concentrations in uncontaminated surface soils has been calculated by Berrow and Reaves (1984) as 10 µg g⁻¹ from nearly 2700 samples, while the BGS G-base survey reported values of 7.2-124 µg g⁻¹ As (ca. 200 samples, mean: 18.3 µg g⁻¹ As, Rawlins et al., 2003) for the upper Tamar catchment. This indicates somewhat elevated As concentrations in soils in a region of the catchment not mined for this element in the past, and suggests that the geology of the southwest region, with its igneous influence and high level metamorphism, has resulted higher levels of this element than uncontaminated soils in general.

5.6.2.2 Variation of As and metal concentrations in the River Tamar

Dissolved concentrations in the River Tamar at Gunnislake were higher than upstream at Greystone Bridge for sulfate (factor 1.5-1.7, p<0.0001), As (factor 1.6-10, p<0.0001), Cu (factor of 2.6-3.9, p=0.024), Ni (factor 2.9-4.3, p=0.01) and Zn (factor 1.7-5.4, p=0.02), and during some surveys higher for Co (factor 1.0-2.3) and Fe (factor 0.8-1.8). The elevation of sulfate, Cu, Zn, Ni and Co in the River Tamar at Gunnislake in comparison to Greystone was highest during the October survey, in spite of the increase in water flow in October at both locations compared to the previous months. For example, dissolved Cu concentrations at Greystone remained constant (ca. 12 µg L⁻¹ in July and October), whereas at Gunnislake the concentrations in July and October were 32 and 50 µg L⁻¹ Cu, respectively.
Table 5.9 Ranges of dissolved and particulate metal concentrations observed in the Tamar River catchment. Representative of Background: upper Tamar, Deer, Carey, Ottery; Rivers receiving discharge from abandoned mines outside the main mining area: Lynher, Tiddy, Inny, Lyd, Thrushel, Tavy, Walkham; Streams and adits in the mining area categorised as for table 1. All concentrations in μg L⁻¹. D: dissolved concentration, P: concentration associated with suspended particulate matter. Ranges quoted as ‘<x’ show that some values were below the limit of detection (LOD).

<table>
<thead>
<tr>
<th>Water course</th>
<th>Fe</th>
<th>Mn</th>
<th>As</th>
<th>Cd</th>
<th>Co</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Tamar, Deer, Carey, Ottery (Zone A)</td>
<td>D</td>
<td>60-390</td>
<td>2.1-120</td>
<td>≤2.3</td>
<td>4.1-5.9</td>
<td>7.6-17</td>
<td>1.2-5.3</td>
<td>0.6-0.7</td>
<td>≤6.4</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>230-970</td>
<td>8.0-180</td>
<td>≤0.6</td>
<td>0.11-2.0</td>
<td>0.35-10</td>
<td>0.23-4.2</td>
<td>0.05-6.4</td>
<td>1.1-14</td>
</tr>
<tr>
<td>Tamar River, Greystone (Zone B)</td>
<td>D</td>
<td>67-140</td>
<td>6.5-72</td>
<td>1.3-2.0*</td>
<td>≤LOD</td>
<td>≤5.2</td>
<td>12-13</td>
<td>1.7-4.9</td>
<td>≤LOD</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>170-530</td>
<td>12-39</td>
<td>≤4.3</td>
<td>≤0.17</td>
<td>0.1-1.1</td>
<td>1.0-1.1</td>
<td>0.32-1.7</td>
<td>≤0.81</td>
</tr>
<tr>
<td>Tamar River, Gunnislake (Zone C)</td>
<td>D</td>
<td>53-140</td>
<td>7.4-96</td>
<td>2.1-9.9</td>
<td>≤LOD</td>
<td>0.9-13</td>
<td>4.6-62</td>
<td>5.0-21</td>
<td>≤0.46</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>42-3600</td>
<td>0.15-390</td>
<td>1.9-10</td>
<td>≤0.1</td>
<td>0.03-1.7</td>
<td>1.0-67</td>
<td>0.16-9.7</td>
<td>0.53-1.8</td>
</tr>
<tr>
<td>Lynher, Tiddy, Inny, Lyd, Thrushel, Tavy, Walkham (Zone B)</td>
<td>D</td>
<td>53-320</td>
<td>5.7-390</td>
<td>8.6-21</td>
<td>≤0.78</td>
<td>3.4-12</td>
<td>3.7-25</td>
<td>1.1-13</td>
<td>0.50-1.6</td>
</tr>
<tr>
<td>Streams (mean pH &gt;5), mining area background (Zone C)</td>
<td>D</td>
<td>55-62</td>
<td>8.5-28</td>
<td>≤1.1</td>
<td>0.69-12</td>
<td>3.8-57</td>
<td>2.2-19</td>
<td>≤0.81</td>
<td>5.0-45</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>≤21</td>
<td>1.8-3.4</td>
<td>1.2-3.5</td>
<td>≤0.1</td>
<td>≤0.84</td>
<td>0.32-2.9</td>
<td>0.11-1.3</td>
<td>≤0.51</td>
</tr>
<tr>
<td>Streams (mean pH &gt;5), affected by mine waters (Zone C)</td>
<td>D</td>
<td>55-3000</td>
<td>3.6-1000</td>
<td>8.2-340</td>
<td>0.93-3.7</td>
<td>0.45-19</td>
<td>3.6-650</td>
<td>1.3-69</td>
<td>0.46-4.9</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>7.4-2400</td>
<td>0.13-110</td>
<td>1.2-180</td>
<td>0.09-5.3</td>
<td>0.06-16</td>
<td>0.36-280</td>
<td>0.11-8.9</td>
<td>0.11-8.1</td>
</tr>
<tr>
<td>Streams (mean pH &lt;5; Zone C)</td>
<td>D</td>
<td>230-3800</td>
<td>400-5700</td>
<td>9.8-560</td>
<td>1.0-4.6</td>
<td>12-270</td>
<td>60-7600</td>
<td>7.3-250</td>
<td>0.46-2.6</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>5.0-4300</td>
<td>1.9-20</td>
<td>2.5-1600</td>
<td>0.14-1.4</td>
<td>0.08-1.3</td>
<td>0.38-45</td>
<td>0.11-2.8</td>
<td>0.06-1.3</td>
</tr>
<tr>
<td>Adits (mean pH &gt;5; Zone C)</td>
<td>D</td>
<td>53-1700</td>
<td>3.5-770</td>
<td>8.7-280</td>
<td>7.0-11</td>
<td>0.51-33</td>
<td>5.6-1400</td>
<td>1.1-130</td>
<td>0.42-170</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>5.9-1000</td>
<td>0.27-44</td>
<td>1.0-120</td>
<td>0.09-0.39</td>
<td>0.12-1.6</td>
<td>0.57-210</td>
<td>0.13-15</td>
<td>0.12-11</td>
</tr>
<tr>
<td>Adits (mean pH &lt;5; Zone C)</td>
<td>D</td>
<td>1200-2600</td>
<td>430-2000</td>
<td>13-130</td>
<td>1.1-1.3</td>
<td>11-36</td>
<td>380-910</td>
<td>3.5-41</td>
<td>≤LOD</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>800-7900</td>
<td>0.85-64</td>
<td>38-240</td>
<td>≤LOD</td>
<td>0.31-2.5</td>
<td>2.8-32</td>
<td>0.13-2.8</td>
<td>≤0.52</td>
</tr>
</tbody>
</table>
Similar trends for particulate metals were observed, e.g. particulate Cu concentrations at Greystone were <LOD for both July and October surveys, whereas at Gunnislake the concentrations increased from 1.0 to 6.0 µg L⁻¹ (July and October, respectively). The increase in concentrations of these metals during the onset of the wet season is likely to be caused by the re-suspension of metal-rich particulates and fine sediments that accumulate in the riverbed during the low flow period. Furthermore, flushing during the start of wet season results in an increase in infiltration through the waste heaps, and this may facilitate the oxidation of ore minerals and dissolution of efflorescent salts. Rainfall also increases the quantity and rate of run-off, which can accelerate the erosion rate, thereby resulting in higher export of leachate and sediments from abandon mine sites. This indicates that river flow and intensity of rainfall are important factors in determining metal concentrations in and flux of some contaminants to rivers within the Gunnislake/Calstock mining area.

The highest enrichment of As, Mn and Fe at Gunnislake occurred in April, at the end of the wet season. For example, relatively constant dissolved As concentrations (ca. 0.5 µg L⁻¹) were observed at Greystone in January and April, whereas at Gunnislake, the concentrations increased from 2.4 to 5.7 µg L⁻¹ (January and April, respectively). This is likely to be the result of dilution from river flow, i.e. lower concentrations in January (higher flow, 22.2 m³ s⁻¹ at Gunnislake) in comparison to April survey (river flow 13.4 m³ s⁻¹). The particulate concentrations, however, showed the opposite trends, that is higher concentrations were observed in January (higher flow) in comparison to April. For example, particulate Fe concentrations at the Gunnislake decreased from 1174 µg L⁻¹ (January) to 215 µg L⁻¹ (April), indicating less re-suspension and lower rate of input of erosion materials during low flow.

At Gunnislake, maximum particulate concentrations of Fe, Mn, Cu, Zn and Ni were above the maximum catchment background (e.g. maximum particulate Mn 390 µg L⁻¹ at Gunnislake compared to the maximum value of 180 µg L⁻¹ in Zone A). Markedly high in particulate Fe levels (up to 3600 µg L⁻¹), value as high as those found in some ochreous streams and adits were observed in the River Tamar at Gunnislake.

Most rivers draining abandoned mines associated with the mineralisation in Zone B (Figures 5.1 & 5.3) carried dissolved and particulate concentration ranges similar to those
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in Zone A (Table 5.9). The exception was river Thrushel, in which dissolved Fe, Mn, As, Co, Cu, Ni, Pb and Zn were elevated above the catchment background, and particulate Fe concentrations up to 2200 µg L\(^{-1}\) were observed. This was probably the result of inputs from a cluster of abandoned Mn mines in close vicinity to the sampling point, indicating a highly mineralised location.

In general, the water quality in each stream and adit in the mining area was highly variable as a result of differences in underlying rocks and soils and mining waste materials. For example, some watercourses exhibited similar water chemistry to that of the catchment background concentrations (Stream 6, 7, 10 and 24). The rest, although varied considerably, their dissolved and particulate As and Cu concentrations were elevated above the maximum background values, i.e. affected by mine waters. The latter can be further classified according to their drainage types (stream or adit) and pH as: acidic and near-neutral streams, and acidic and near-neutral adits (Figure 5.8).

Relatively high metal concentrations (dissolved and particulate) in affected streams and adits were observed for Fe, Mn, Cu, As and Zn, which is consistent with the geological setting and the dominant mineral ores in this mining district. In comparison to most near-neutral streams and adits, high dissolved As and metal (Cd, Co, Cu, Ni, Pb and Zn) concentrations were observed in all acidic waters (Stream 16, 17 and Adit 13; Figure 5.8), indicating that these metals and metalloid were highly mobile at this pH range (2.9 to 6.4). This was consistent with the exchangeable metal fractions (BCR extraction) in streambed sediments in acidic streams (e.g. 1% As, 12% Cu, 37% Mn and 19% Zn), which were considerably lower than that of near-neutral streams and adits (4% As, 67% Cu, 63% Mn and 80% Zn), suggesting that large amounts of metals remained in the dissolved phase in acidic waters.

The highest levels of As (up to 560 µg L\(^{-1}\) dissolved and 1600 µg L\(^{-1}\) particulate), Cu (up to 7600 µg L\(^{-1}\) dissolved and 280 µg L\(^{-1}\) particulate) occurred in the acidic Streams 16 and 17, which also carried the highest dissolved Co (up to 270 µg L\(^{-1}\)), Ni (up to 250 µg L\(^{-1}\)), Zn (up to 1600 µg L\(^{-1}\)). Mn (up to 5700 µg L\(^{-1}\)) and moderate to high sulfate (38 to 383 mg L\(^{-1}\)) and highest conductivity (up to 460 µS compared to up to 160 µS for near-neutral streams and adits). Whereas, the highest particulate Fe concentrations (up to 7900
\( \mu g \text{ L}^{-1} \) occurred in the acidic, ochreous Adit 13 (Figure 5.9) which also had elevated dissolved Mn, As, Cu, Ni and Zn concentrations. Here, a deep layer of ochre (>1m) is retained by a dam at the adit portal, and ochreous material is suspended in the overflow, explaining the high particulate matter concentrations. Low sulfate contents in this acidic adit are believed to be associated with Fe-hydroxylsulfate minerals (discussed in section 5.6.1).

*Figure 5.8* Variations in pH and the sum of dissolved As and base metals (Cd, Co, Cu, Ni, Pb and Zn; modified from Ficklin et al., 1992) in streams and adits draining mining area in Gunnislake/Calstock area. Orange circle: acidic streams (S16 & 17); Pink circle: acidic adit (A13); Orange triangular: near-neutral stream (S5); Pink triangular: near-neutral adits (A1, 15&18); Black cross: other near-neutral streams and adits (n=20).

In contrast, Adits 1, 15 and 18, and Stream 5 exhibit circum-neutral pH (5.5-7.3), contain dissolved metals nearly as high as in acidic waters (Figure 5.8). The highest dissolved Pb concentrations (up to 170 \( \mu g \text{ L}^{-1} \)) were observed in Adit 1, a former Pb/Ag mine, while particulate Pb concentrations at this watercourse were low (up to 11 \( \mu g \text{ L}^{-1} \)) in comparison to its dissolved contents. These adits and stream also carried highest dissolved Cd (11 \( \mu g \text{ L}^{-1} \)), high As (230 \( \mu g \text{ L}^{-1} \)) and Cu (1380 \( \mu g \text{ L}^{-1} \)) and Zn (2500 \( \mu g \text{ L}^{-1} \)).
The formation of Fe-oxyhydroxides and hydroxysulfates plays an important role in regulating As and metal concentrations in the water column due to adsorption or coprecipitation of these metals and metalloid on to the surface secondary Fe minerals (e.g. Pierce and Moore, 1982; Johnson and Thornton, 1987; Bigham and Nordstrom, 2000). This can be seen from the relationships between particulate concentrations of Fe and As and of Fe and Cu. For example, significant relationships between particulate Fe and As (e.g. in Adit 13: \( r=0.78, p=0.002 \); Figure 5.10a) and between particulate Fe and Cu in (e.g. in Adit 13: \( r=0.61, p=0.03 \); Figure 5.10b) were observed.

Figure 5.9 Ochreous precipitates from overflow from Adit 13 (Ding Dong Mine). A deep layer of ochre (>1m) was observed at the adit outflow (photo: Mighanetara, 2005).

![Figure 5.9 Ochreous precipitates](image)

Figure 5.10 Relationship between particulate Fe and As (a) and particulate Fe and Cu (b) in Adit 13 (pH 3.4-4.4). \( r \): Pearson correlation; \( p \): p-value.
Out of 16 watercourses, for which particulate metal concentrations were determined (including the River Tamar), nine showed significant positive relationships between particulate Fe and As, whereas only six showed relationships between particulate Fe and Cu. This suggests that As adsorbs and co-precipitates with Fe-oxyhydroxides more readily than Cu. Similar observations have been reported for other systems (e.g. Bowell and Bruce, 1995). In the three acidic waters included in this survey particulate Cu and Fe showed a positive relationship only in Adit 13, while the relationship between particulate Fe and As was significant in all. Furthermore, as can be seen from Figure 5.10, in Adit 13, particulate Fe and As ($r=0.83$) shows stronger a relationship than that of particulate Fe and Cu ($r=0.61$). Adsorption of Cu onto particulate Fe was less pronounced in acidic, compared to circum-neutral waters, for example, the contribution of particulate Cu to the total Cu concentrations in the water column was small in all acidic streams (e.g. ca. 1% in Stream 17). In acidic waters, particulate As constituted up to 36% of the total As concentrations and was significantly correlated with particulate Fe (S16: $r=0.90$, $p<0.0001$; S17: $r=0.91$, $p=0.001$; A13: $r=0.78$, $p=0.002$). This can be explained by the positive charge that hydrous ferric oxides assume under acidic conditions through protonation, and therefore adsorption of oxyanions (e.g. As) is favoured over cations, such as Cu (e.g. Sheoran and Sheoran, 2006).

Proportions of dissolved and particulate concentrations for As and Fe varied between surveys and watercourses. For example, in ochreous streams and adits, particulate As and Fe, if not higher than their dissolved forms, contributed large amounts to their total concentrations (e.g. particulate As $>$ dissolved As in all surveys in adit 19). Whereas, in non-ochreous streams and adits, dissolved As exceeded the particulate forms (e.g. dissolved As $>$ particulate As in all surveys in stream 25), while dissolved Fe was highly variable (e.g. up to dissolved 60% Fe in stream 25 (pH 6.5-7.2) and <LOD in stream 20 (pH 6.2-7.2)).

Relationships between particulate Fe and Ni and Zn were not significant, suggesting less adsorption of these metals onto Fe-oxyhydroxides. Furthermore, dissolved concentrations of Mn and Zn in acidic waters were relatively high throughout the sampling period (up to 5700 mg L$^{-1}$ for Mn and up to 1610 mg L$^{-1}$ for Zn), suggesting high mobility of Mn and Zn at these pH values (2.9 to 6.4). The results also showed that in near-neutral streams and adits, dissolved Mn and Zn were higher than their particulate forms. It should be
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noted that, although the adsorption of As and Cu may reduce the concentrations of these elements from water column, a change in pH-Eh conditions can lead to a release of As and Cu from solid phases.

The comparison of particulate concentrations for some elements with their speciation in the sediment, as determined by sequential extraction (chapter 4) leads to the following suggestions:

1. Particulate As and Fe concentrations are strongly correlated in most water courses (see above). Whereas in sediments, reducible As and Fe are significantly correlated (see section 4.5.4.3.2). This suggests that particulate As is associated with particulate Fe, and they are most likely in reducible forms (e.g. adit 13).

2. Cu in stream sediments occurs mostly in the exchangeable and oxidisable forms. For streams that show a correlation between particulate Fe and Cu (e.g. stream 19), it can be inferred that Cu is largely associated with reducible Fe. For streams that exhibit low particulate Fe and high particulate Cu concentrations, particulate Cu will most likely be present in the exchangeable form (e.g. surface of particulate metals, colloidal, clay particles). An examples of sources featuring high particulate Cu concentration and low Fe levels include Stream 5 (16 to 284 µg L⁻¹ Cu, <LOD to 38 µg L⁻¹ Fe). In these waters blue and green precipitates (e.g. Cu carbonate and sulfate) were observed as surface coatings on the sediment pebbles and boulders (see section 4.5.4.2.2).

3. No significant correlations have been observed between particulate Fe and Zn and Pb. In the sediment, Pb and Zn were dominated by the exchangeable and oxidisable (Pb) form. Therefore, it is likely that Pb and Zn in the fine-grained suspended matter are present mostly in the exchangeable form.

As observed in this study, the contaminant concentrations in mine waters were highly variable between surveys, and this has also been found in other mining areas (e.g. Boul et al., 1994; Neal et al., 2005). The latter authors reported that over the period of an 18-month survey (daily monitoring), the pH ranged from 3.3-7.6; and dissolved concentrations of 20-1300 µg L⁻¹ Cu, 250-1500 µg L⁻¹ Mn and 120-23000 µg L⁻¹ Zn were observed in the River Carnon, Cornwall. The conditions determined in adits and streams in this study were within the wide range reported for mine drainage in other locations in
southwest England (e.g. Johnson, 1986; Bowell and Bruce, 1995; Neal et al., 2005) and elsewhere (Miller et al., 1996; Gray, 1998; Balistrieri et al., 1999; Dinelli et al., 2001; Braungardt et al., 2003 see also Table 5.1).

Except for Fe, which showed no distinct trend, dissolved metal, As, sulphate and major cation (e.g. Ca) concentrations in streams and adits were higher at the beginning of the survey (July–September), decreased through the winter to reach a low in January and February, and subsequently increased through the spring (e.g. stream 17: Fig. 5.11). Similar trends have been observed in other studies of mine waters and linked to seasonal cycles affecting element mobilisation (chemical, physical, biological) and precipitation, erosion and transport of solids, as well as dilution effects (McGinness and Johnson, 1993; Featherstone and O’Grady, 1997; Braungardt et al., 2003; Oliás et al., 2004).

![Variability of dissolved Cu, As, Mn, Co, Zn, sulphate and Ca concentrations in stream 17 throughout the sampling period. Stream 17 collects leachate and erosion products from mining waste and associated contaminated land as well as the outflow of several adits associated with Devon Great Consols mine. Note the logarithmic scale.](image)

Figure 5.11 Variability of dissolved Cu, As, Mn, Co, Zn, sulphate and Ca concentrations in stream 17 throughout the sampling period. Stream 17 collects leachate and erosion products from mining waste and associated contaminated land as well as the outflow of several adits associated with Devon Great Consols mine. Note the logarithmic scale.

Of the studied water courses, eight adits and 10 streams frequently carried total (dissolved + particulate) As concentrations above the EU drinking water guideline level of 10 µg L⁻¹
12 water courses exceeded the List II Water Quality Standard of the EC Dangerous Substances Directive (76/464/EEC) for As in fresh waters (50 µg L$^{-1}$). Most streams and adits exceeded the proposed water quality standards of the WFD (2000/60/EC) for ecological status for the annual average of total Zn (8–50 µg L$^{-1}$) and Cu (1–6 µg L$^{-1}$). Furthermore, dissolved Cu concentrations in the River Tamar at Gunnislake (5–61 µg L$^{-1}$) occasionally exceeded the EC Freshwater Fisheries Directive (78/659/EEC) for salmonid species (5–40 µg L$^{-1}$) within the water hardness category the Tamar at Gunnislake falls into (annual mean 100 mg L$^{-1}$, from EA data). Total Fe concentrations were consistently above the EA Environmental Quality Standard (EQS) of 1000 µg L$^{-1}$ (Mayes et al., 2005).

5.6.3 Arsenic and metal speciation

Metal speciation is important information in assessing the potential toxicity of particular trace metals. For example, ionic Cu (Cu$^{2+}$) and CuCl$_2$ are highly toxic, whereas CuCO$_3$ and Cu-EDTA have low toxicity (Zhu and Anderson, 2002). So far, this study has distinguished the dissolved form from the particulate one. However, metals in the dissolved phase may be present as free metal ions or bound to organic or inorganic ligands to form complexes.

Geochemical modelling was carried out to predict the concentrations of species that are present in the aqueous systems studied, in order to allow toxicity to be evaluated and risk assessments to be made. Furthermore, speciation modelling can provide an insight into the geochemical processes, which affect the fate and transport of the metals, e.g. hydrolysis and complexation reactions in the solution (Zhu and Anderson, 2002). The modelling was carried out using the PHREEQC computer code program (version 2), which is a thermodynamic equilibrium model, and hence does not take into account any kinetic factors. The program also included thermodynamic data of most metal species used in this study, except for As and some Cu species, which were added into the input file. The dissolved concentrations of As, Cd, Cu, Fe, Mn, Pb, Zn, Cl, SO$_4^{2-}$ and HCO$_3^-$ (in µg L$^{-1}$), together with the pH, pe (16.9 Eh), temperature and additional mass-action expressions with the solubility constants were defined in the input file. Because chloride and bicarbonate were not analysed, the value for Cl in streams and adits (11 mg L$^{-1}$) was chosen based on the major ions in World Average River Water (Martin and Whitfield,
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1983 and Riley and Chester, 1971 in Chester 2000) and HCO₃²⁻ concentration (25 mg L⁻¹) was selected based on the major ion in rivers draining plutonic and metamorphic rocks (Mayback, 1981 in Chester, 2000). These values were verified as realistic against constituents reported by the British Geological Survey in the GBASE database (Rawlins et al., 2003) for freshwater in the Tamar Catchment. Because HCO₃⁻ can vary considerably according to rock types (e.g. 100 mg L⁻¹ for sedimentary rock, higher value (50 mg L⁻¹) was applied to selected streams and adits to assess the change in speciation due to additional alkalinity. For acidic streams and adits, the HCO₃⁻ concentration (0.6 mg L⁻¹) was selected based on the equilibrium of CO₂ with the atmosphere at pH<4.5 (Stumm and Morgan, 1996, p. 154). For the values in the River Tamar, both parameters were chosen based on the EA data (22 and 50 mg L⁻¹ for Cl and HCO₃⁻ respectively). In this study, the Wateq4f thermodynamic database was used, except for CuCO₃ (log K=6.77) and Cu(OH)₂ (log K = -16.2) (Stumm and Morgan, 1996), and those of organic carbon of which the sources of the database will be given when discussed.

The modelling results in a system containing only inorganic species suggest that in acidic streams and adits, (S13, S16 and S17), over 70% of most cationic metals are present in their free ionic forms, which are believed to be readily bioavailable and therefore more toxic to biota than chelated and precipitated forms (Bitton et al., 2005). For example, in adit 13 (pH 3.4-4.4), the model suggests that over 90 % of Cd, Mn, Ni and Zn; >80% of Cu and >70% of Fe are in divalent free ionic forms. At low pH, depending on the availability of SO₄²⁻, these metals form sulfate complexes. This can be illustrated with Cu; at similar pH (adit 13: pH 3.4-4.4, stream 17: pH 3.5-4.3), the proportion of CuSO₄ was 2.4-6.1% of the total Cu concentration in adit 13, while in stream 17, at sulfate concentrations 5 to 6 times higher than adit 13, the proportion of CuSO₄ was 13-21%. Although the concentration of dissolved organic carbon (DOC) in these mine waters was not determined, it can be assumed that the DOC levels, and hence the complexing capacity of organic chelators in these acidic mine waters, was low. This assumption is supported by the low organic carbon content of the sediments in acidic streams and adits (1.0-2.3% C). Therefore, the assumption that the speciation of acidic mine waters was dominated by inorganic speciation should be valid. It follows, that a high proportion of the most toxic species of metals, the free hydrated ions, are released into the wider aquatic environment. For example, according to flux calculations, Stream 17 discharged ca. 1.1 t y⁻¹ of Cu²⁺ into the River Tamar (see also section 5.6.4).
Upon mixing with the River Tamar or streams containing higher carbonate contents, inorganic Cu forms strong CuCO₃ complexation. The calculations showed a gradual increase of CuCO₃ with increasing pH for streams containing 50 mg L⁻¹ HCO₃⁻. At pH ca. 6.9, CuCO₃ became the dominant specie for inorganic Cu (Figure 5.12). Increasing the HCO₃⁻ contents from 25 to 50 mg L⁻¹ resulted in the decrease of Cu²⁺ by a factor of 1.2 to 1.7, depending on the water chemistry of individual streams modelled. For example, Cu²⁺ in stream 25 decreased from 42.5% to 28.5% when HCO₃⁻ concentrations increased from 25 to 50 mg L⁻¹, whereas CuCO₃ and minor amounts of CuHCO₃ increased (e.g. CuCO₃ in the same example given for Cu²⁺ increased from 43.0% to 57.2% when HCO₃⁻ concentrations increased from 25 to 50 mg L⁻¹).

Figure 5.12 Distribution of inorganic Cu speciation in selected streams and adits (A1, S2, A13, S14, S16, S17, S25) and the River Tamar. The HCO₃⁻ concentrations used were 0.6 mg L⁻¹ for acidic streams and adit, 50 mg L⁻¹ for near-neutral streams and adit and the River Tamar.

The speciation calculation showed that Ni, Pb and Zn also form strong complexation with carbonate and follow similar trends to Cu with changing pH, but to different degrees. For example, at low pH (<5.5), Pb forms stronger complexation with SO₄²⁻ than Cu (log K PbSO₄ and CuSO₄ = 2.75 and 2.31 respectively), therefore ca. 57-89% of Pb²⁺ is present compared to 79-97% of Cu²⁺ in acidic streams and adits. In contrast, in streams and adits
with near-neutral pH, inorganic Pb is complexed by CO\textsubscript{3}, and PbCO\textsubscript{3} becomes the dominant specie at ca. pH >6.8 (e.g. up to 82%, Figure 5.13). The toxicity of the relatively high dissolved concentrations of Pb in adit 1 (up to 164 µg L\textsuperscript{-1}) may therefore be reduced by carbonate complexation (e.g. Sunda et al., 1990; Coale and Bruland, 1988). Conversely, up to 89% of total dissolved Pb is present as free ionic Pb in acidic streams and adits, but the toxicity in these water courses is limited by the relatively low (up to 2.6 µg L\textsuperscript{-1}) total dissolved Pb concentrations.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{distribution.png}
\caption{Distribution of inorganic Pb speciation in selected streams and adits (A1, S2, A13, S14, S17) and the River Tamar. The HCO\textsubscript{3}\textsuperscript{-} concentrations used were 0.6 mg L\textsuperscript{-1} for acidic streams and adit; 50 mg L\textsuperscript{-1} for near-neutral streams and adit and the River Tamar.}
\end{figure}

In contrast to Cu, Pb, Ni and Zn at near-neutral pH, Cd, Mn and Fe do not form strong complexation with carbonate. For example, the amounts of Cd\textsuperscript{2+} decrease from 90-94% to 89-93%; Mn\textsuperscript{2+} decrease from 91-96% to 86-93% when the HCO\textsubscript{3}\textsuperscript{-} increased from 25 to 50 mg L\textsuperscript{-1}. For Fe, at pH <5, Fe\textsuperscript{2+} is a dominant Fe specie, whereas at near-neutral pH, over 99% Fe is present in Fe(III), which occurs in two predominant species, Fe(OH)\textsubscript{3}, Fe(OH)\textsubscript{2}\textsuperscript{+} (Figure 5.14). At pH lower than ca. 7.2, Fe(OH)\textsubscript{2}\textsuperscript{+} is the dominant specie, whereas Fe(OH)\textsubscript{3} will become dominated at pH greater than this point.
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Figure 5.14 Distribution of inorganic Fe speciation in selected streams and adit (A13, S16, S17, S25) and the River Tamar, as calculated using PHREEQC and based on concentrations and Eh values (pH 2-8). Main graph: percentage of Fe(II) and Fe(III) of the total dissolved concentration. Inset: percentage of Fe hydroxide species of the total dissolved Fe concentration (pH 6-8). The HCO₃⁻ concentrations used were 0.6 mg L⁻¹ for acidic streams and adit; 50 mg L⁻¹ for near-neutral streams and adit and the River Tamar.

The model results also suggested that cupric ferrite (CuFe₂O₄), cuprous ferrite (CuFeO₂), Fe(OH)₂·7Cl₃, Fe(OH)₃, goethite (FeOOH), hematite (Fe₂O₃), maghemite (Fe₂O₃) and magnetite (Fe₃O₄) are supersaturated (Saturation Index, SI>0) in the near-neutral stream (S25) and the River Tamar; and cupric ferrite, cuprous ferrite, Fe(OH)₂·7Cl₃, goethite, hematite, maghemite and magnetite are supersaturated in the acidic stream and adit (S17 and A13). However, the thermodynamic speciation-solubility modelling is only capable to suggest which minerals can possibly precipitate from the solution (Saturation Indices (SI)>0). In actual systems, minerals with SI>0 may not be present because of kinetic processes and in situations where equilibrium is not be reached. Additionally, errors can arise from the lack of accuracy of thermodynamic data (Zhu and Anderson, 2002). Furthermore, the SI does not provide any information on the quantities of the minerals which may precipitate, e.g. the precipitates may occur as trace contents in other phases, making identification and observation difficult and costly. It should be noted that although considerable amounts of ochreous precipitates were observed during all surveys in adit 13 and stream 16, the model did not suggest the precipitation of Fe(OH)₃. This may indicate that the process of ochre formation may be enhanced by bacterial activity.
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(e.g. Acidithiobacillus; Dold, 2005; Bigham et al., 1992). Although the interpretation of model results in terms of which minerals actually precipitate may not be straightforward, speciation-solubility modelling provides useful information about metal complexation and precipitation, which are important mechanisms regulating metal mobility. Fe(III) complexation and precipitation, in particular, plays an important role, not only in the mobility of Fe but also that of As and other trace metals in a system. Additionally, oxidation mediated by Fe^{3+} is fast and determines the rate of sulfide mineral oxidation (Doulati, et al., 2005).

In acidic streams and adits, over 80% of the inorganic As is present as H_{2}AsO_{4}^{-} (Figure 5.15), with the remaining being H_{3}AsO_{4} (which increases with decreasing pH, i.e. increasing [H^{+}]). At pH >5, H_{2}AsO_{4}^{-} is gradually replaced by HAsO_{4}^{2-}, which progressively increases with increasing pH and becomes the dominant specie (>50%) at ca. pH >7. The model also suggested that, less than 33 pg L^{-1} of As(III), a more toxic and mobile specie, was found in stream 16, in which high concentrations (>200 µg L^{-1}) of dissolved As were constantly observed. The results were in agreement with Eh-pH diagram given by Smedly and Kinniburgh (2002).

![Figure 5.15](image)

**Figure 5.15** Distribution of inorganic As speciation in selected streams and adit (A1, S2, A13, S14, S16, S17, S25) and the River Tamar. The HCO_{3}^{-} concentrations used were 0.6 mg L^{-1} for acidic streams and adit; 50 mg L^{-1} for near-neutral streams and adit and the River Tamar.
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It should be noted that PHREEQC is based on ion-association and Debye-Hückel expressions to calculate ions activities, which is adequate for low ionic strengths solutions, but may break down at higher ionic strengths (in the range of seawater and above; Parkhurst and Appelo, 1999). Furthermore, the thermodynamic model refers to states of complete equilibrium, whereas, in natural systems, the true equilibrium is often not achieved, especially among redox couples in natural aquatic systems. Therefore, it can only be used to show which species may be present in certain environments (at equilibrium and abiotic), which may not reflect the actual metal speciation in the systems.

Natural organic matter (NOM) is ubiquitous in aquatic systems. Humic and fulvic acids in particular exhibit heterogeneous binding sites for metals, due to their complex structures and high molecular masses (500 to 2000 g mol\(^{-1}\) for FA, and 2000 to >5000 g mol\(^{-1}\) for HA). These binding sites form complex structures with a number of metals, especially those that are significantly complexed with CO\(_3^{2-}\) and OH\(^-\), such as Cu\(^{2+}\) and Pb\(^{2+}\) (Sigg and Behra, 2005; Stumm and Morgan, 1996). Sigg and Behra (2005) suggested that typical values for dissolved organic matter (DOC) in natural freshwater range from 1.2 to 12 mg L\(^{-1}\) C, and that the conditional stability constant between organic ligands and Cd, Cu, Ni and Zn were \(\log K_{\text{Cd}} = 10.4-12.5\), \(\log K_{\text{Cu}} = 13.5-16.0\), \(\log K_{\text{Ni}} = 13.0-14.5\) and \(\log K_{\text{Zn}} = 8.6-10.0\). To investigate the effect of organic ligands on aquatic metal speciation, 120 \(\mu\)g L\(^{-1}\) DOC (as C) with \(\log K_{\text{Cd}} = 10.4\), \(\log K_{\text{Cu}} = 13.5\); \(\log K_{\text{Zn}} = 7.8\) 13.5 and \(\log K_{\text{Ni}} = 12.0\) were applied to PHREEQC. The DOC concentration used in the calculations were based on the concentrations reported for the Tamar river and estuary (1300 to 5700 \(\mu\)g L\(^{-1}\) C; Miller, 1999), by choosing a conservative value of ca. 10% (i.e. 120 \(\mu\)g L\(^{-1}\) C) of the lowest concentration. The modelling results suggested that, in their natural conditions observed during samplings and with the presence of organic ligands at conservative levels (i.e.120 \(\mu\)g L\(^{-1}\) DOC as C), less than 1% of free ionic metals were present in the system (e.g. <0.00001% for Cu and Ni and 0.28% for Zn). An example of Cu speciation distribution in the River Tamar, in the presence of 120 \(\mu\)g L\(^{-1}\) DOC as C, is given in Figure 5.16. This was in good agreement with the Cu speciation in freshwater (lake water) studied by Xue and Sigg (1999), who reported 1.01\(\times\)10\(^{-14}\) g L\(^{-1}\) Cu\(^{2+}\) from 6.36\(\times\)10\(^{-7}\) g L\(^{-1}\) of total dissolved Cu (i.e. >>0.001%) in the presence of DOC (2.8 mg L\(^{-1}\)).
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Figure 5.16 Distribution of Cu speciation in the River Tamar in the presence of dissolved organic matter (Cu = 61.5 µg L⁻¹, DOC = 120 µg L⁻¹, As = 9.94 µg L⁻¹, Fe = 136 µg L⁻¹, Mn = 66.6 µg L⁻¹, Ni = 4.97 µg L⁻¹, Pb = 0.41 µg L⁻¹, Zn = 15.8 µg L⁻¹, HCO₃⁻ = 50 mg L⁻¹, SO₄²⁻ = 23.3 mg L⁻¹, Cl⁻ = 22 mg L⁻¹, Ca = 18.8 mg L⁻¹, Mg = 6.26 mg L⁻¹, K = 3.1 mg L⁻¹, Na = 22.39 mg L⁻¹, pH = 7.6, Eh = 488 mV.

When the River Tamar enters its estuary, its freshwater mixes with estuarine water, resulting in changes in metal speciation due to change in pH and inorganic ligands, such as the major ions Cl⁻, Na⁺, SO₄²⁻, K⁺, Ca²⁺, Mg²⁺, present in considerably higher concentrations than in freshwater. For the calculations the major ion concentrations were adjusted to represent a salinity of S = 11 (1/3 of the major ions for sea water (Chester, 2000), i.e. Na = 3600 mg L⁻¹, K = 130 mg L⁻¹, Ca = 140 mg L⁻¹; Mg = 430 mg L⁻¹, Cl⁻ = 6400 mg L⁻¹, SO₄²⁻ = 900 mg L⁻¹ and HCO₃⁻ = 100 mg L⁻¹) and pH 8.2. In general, for Cu, Ni, Pb and Zn, complexation with CO₃²⁻ forms dominant species (e.g. up to 78% CuCO₃), while minor proportions are complexed with Cl⁻ (up to 7.5%). In comparison, CdCl⁺ (up to 61%) was the dominant specie of Cd, with lesser amounts of CdCl₂ and Cd²⁺ (22% and 13% respectively). Mn was present mostly as Mn²⁺ with up to 16% of MnCl⁺.

Similar to the freshwater, the metal speciation in estuarine water depends largely on the presence of organic ligands. The model results (using the above parameters for estuarine water and DOC 120 µg L⁻¹) suggested that less than 0.00005% inorganic Cu (CuCO₃, Cu²⁺, CuOH⁺ and Cu(OH)₂), <0.05% inorganic Cd (CdCl⁺, CdCl₂, Cd²⁺ and CdOHCl), <0.002% inorganic Ni (NiCO₃, Ni²⁺, Ni(CO₃)₂²⁻ and NiCl⁺) and ca. 3% inorganic Zn
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(Zn\(^{2+}\), ZnCO\(_3\), ZnOHCl and Zn\((CO_3)^2^-\) were present in the system. This was in consistent with the results reported by Sunda and Hanson (1987), who used ligand competition technique and demonstrated that over 98% of Cu in estuarine water is associated with organic complexes with the remainder <2% being inorganic species (e.g. Cu\(^{2+}\), CuCO\(_3\), Cu(OH\(^+\), CuCl\(^+\)) in estuarine water.

The modelling also indicated that in the presence of 120 µg L\(^{-1}\) (as C) DOC, ca. 0.002 ng L\(^{-1}\) Cu\(^{2+}\), 0.025 ng L\(^{-1}\) Cd, 0.013 ng L\(^{-1}\) Ni\(^{2+}\) and 480 ng L\(^{-1}\) Zn\(^{2+}\) were present in the water column (using pH 8.2, Eh = 488 mV, DOC = 120 µg L\(^{-1}\) C, As = 9.94 µg L\(^{-1}\), Cd = 0.51 µg L\(^{-1}\), Cu = 61.5 µg L\(^{-1}\), Fe = 136 µg L\(^{-1}\), Mn = 66.6 µg L\(^{-1}\), Ni = 4.97 µg L\(^{-1}\), Pb = 0.41 µg L\(^{-1}\), Zn = 15.8 µg L\(^{-1}\), Na = 3600 mg L\(^{-1}\), K = 130 mg L\(^{-1}\), Ca = 140 mg L\(^{-1}\), Mg = 430 mg L\(^{-1}\), Cl = 6400 mg L\(^{-1}\), SO\(_4^{2-}\) = 900 mg L\(^{-1}\) and HCO\(_3^-\) = 100 mg L\(^{-1}\)).

It is interesting that the dissolved concentrations of some trace elements in the estuarine water reported by other researchers (e.g. Langston et al., 2003) were considerably higher than those observed in the River Tamar above the Gunnislake weir (i.e. freshwater) in this study. For example, up to 40 µg L\(^{-1}\) dissolved Zn and up to 1200 µg L\(^{-1}\) dissolved Fe were observed in the estuary compared to up to 28 µg L\(^{-1}\) dissolved Zn and up to 142 dissolved Fe observed in the River Tamar at Gunnislake. In contrast, dissolved concentrations of some trace elements were considerably lower in the estuary. For example, up to 6 µg L\(^{-1}\) dissolved Cu and up to 5.5 µg L\(^{-1}\) dissolved As were observed in the estuary compared to up to 61 µg L\(^{-1}\) dissolved Cu and up to 10 µg L\(^{-1}\) dissolved As observed in the River Tamar at Gunnislake in this study. On the contrary, dissolved metal concentrations of some trace elements in the estuary reported were markedly lower than the values observed in the River (e.g. up to 6 µg L\(^{-1}\) dissolved Cu in the estuary compared to up to 61 µg L\(^{-1}\) dissolved Cu in the River Tamar at Gunnislake). The above contradiction in river and estuarine waters is likely to be a result of:

1. adsorption onto particulates (e.g. Fe-oxyhydroxides formed upon the mixing of freshwater and saltwater), and
2. sediments re-suspension and/or metal complexation with natural organic and inorganic ligands.
Chapter 5: Geochemistry of mine waters and metal fluxes from abandoned mine sites

According to Money et al. (2008), in bioassays for acute toxicity testing, Pacific oyster larvae developed abnormalities at free ion concentrations of ca. 14.6 ng L\(^{-1}\) Cu\(^{2+}\), 9890 ng L\(^{-1}\) Cd\(^{2+}\), 8370 ng L\(^{-1}\) Zn\(^{2+}\) and 75000 ng L\(^{-1}\) Pb\(^{2+}\). Furthermore, synergistic effects induced by the simultaneous exposure of the bioassay to Cd, Zn or Pb in the presence of 14.6 ng L\(^{-1}\) Cu reduced the onset of toxicity to lower concentrations.

The modelling results in this study indicate that upon mixing with the estuarine water (at the water chemistry described above), free ionic Cu, Cd and Zn in the estuarine water were lower than the values reported to have acute effects on Pacific oyster larvae and microorganisms (e.g. 0.4 ng L\(^{-1}\) for green alga, dinoflagellates, diatoms and cyanobacteria: Anderson and Morel, 1978; Sunda and Guillard, 1976; Brand et al., 1986). The complexation of Pb with DOC was not included in the model due to the lack of thermodynamic data for Pb. However, it is known to form strong complexation with fulvic acid (e.g. Wu et al., 2003), therefore only small amount is likely to be present in free ionic form. The calculations did not account for the dilution effect for these trace metal concentrations arising from mixing with sea water in the estuary, or removal from solution due to metal-particle interactions often observed in estuaries. According to Langston et al. (2003), trace metal concentrations in the Tamar estuary were considerably lower than the River Tamar at Gunnislake (e.g. dissolved Cu up to 5.7 µg L\(^{-1}\) in Plymouth sound and its estuaries compared to dissolved Cu in the River Tamar in this survey of up to 61.5 µg L\(^{-1}\)). Therefore, it can be assumed that the concentration of each metal in isolation in estuarine waters should not adversely affect organisms, such as algae and bivalves. However, as suggested by Money et al. (2008), synergistic effects between metals and other toxins (e.g. agrochemicals) could threaten ecosystem functioning in the Tamar estuary. This threat is exacerbated by the large reservoir of metals associated with the sediment and interstitial waters in the Tamar estuary (Langston et al., 2003), both of which may act as secondary sources of metal contamination to the water column.

5.6.4 Arsenic and metal fluxes

Monthly and annual dissolved and particulate fluxes were calculated using the water flow and metal concentrations at the time of measurement of each survey and then extrapolated to monthly and annual figures. Because the flux calculation was made from a limited data set, it is based on the assumption that both values, i.e. the water flow and the
concentration, were constant throughout the month. Daily flow data for the River Tamar upstream and downstream of the main mining area (Greystone Bridge and Gunnislake gauging station respectively) was provided by the Environment Agency (EA). The daily flow was averaged to provide the monthly mean. In order to estimate the errors associated with the flux calculation, the relative standard deviation of the mean for each month is assumed to be the representative variability of stream flow measured in streams and adits studied; and the variability of the metal concentrations of each survey is assumed to be related to the metal concentrations throughout the sampling period (July 2005 to June 2006). The metal flux and the error propagation calculation are as follows:

\[ \text{Metal flux, } X = AB \]

\[ \text{Error of the metal flux, } \Delta X = X \sqrt{\left( \frac{\Delta A}{A} \right)^2 + \left( \frac{\Delta B}{B} \right)^2} \]

where

- \( A \) = stream flow,
- \( B \) = the metal concentration
- \( \Delta A \) = error of stream flow, \( A \),
- \( \Delta B \) = error of the metal concentration, \( B \)

\[ \text{Annual flux} = X_1 + X_2 + \cdots + X_{12} \]

\[ \text{Error of annual flux} = \sqrt{\Delta x_1^2 + \Delta x_2^2 + \cdots + \Delta x_{12}^2} \]

where

- \( X_1, X_2, \ldots, X_{12} \) are the metal flux in July 2005 to June 2006, respectively.
- \( \Delta x_1, \Delta x_2, \ldots, \Delta x_{12} \) are the error of metal flux in July 2005 to June 2006, respectively.

The annual total (dissolved+particulate) flux of elements from all adits and streams amounted to ca. 13,000 kg a\(^{-1}\) Fe, 4300 kg a\(^{-1}\) Mn, 4200 kg a\(^{-1}\) Cu, 3600 kg a\(^{-1}\) Zn, 1400 kg a\(^{-1}\) As, 400 kg a\(^{-1}\) Ni, 350 kg a\(^{-1}\) Co, 43 kg a\(^{-1}\) Pb, and 6.6 kg a\(^{-1}\) Cd (Table 5.10). Of this, ca. 50% of Fe, As and Pb was carried in the particulate phase, while overall, 83% of Co and ≥88% of the Mn, Cd, Cu, Ni and Zn flux was dissolved. Of the 25 sources surveyed, more than 65% of the total input of Fe, Mn, As, Co, Ni, Cu and Zn into the Tamar was carried by adits and streams into the fresh water zone upstream of Gunnislake. The remainder entered the estuary directly from sources 1–9 (see Figure 5.2).
As can be seen from Table 5.10, As and Zn flux (as well as other metals) of the Tamar at Gunnislake were markedly higher than the combination of those at Greystone and the flux from streams and adits upstream of the Gunnislake. This indicates the diffuse sources between the Tamar at Greystone and Gunnislake, i.e. effects from the mining activities, as important sources of metals into the River Tamar.

Seven specific sources, including streams 2, 14, 16, 17, 21 and 25 and adit 13 (Figure 5.17) accounted for more than 75% each of the total (dissolved + particulate) Fe, Mn, Cu, Zn, As, Ni, Co, Pb and Cd flux discharged annually from the Gunnislake/Calstock to the River Tamar and its estuary. The signal strength for each metal differed between these dominant sources, according to the source mineralogy and pathways involved. For example, the circum-neutral stream 2 collects drainage from several mine workings in an area of diverse mineralogy comprising ores of As, Cu, Zn, Fe, Mn, Pb, Sn, Ag and W, among others. Although the concentrations of contaminants were moderate (e.g. 12-90 µg L\(^{-1}\) dissolved Cu, 25-126 µg L\(^{-1}\) dissolved Zn, 49-800 µg L\(^{-1}\) particulate Fe), because of its high water discharge (120-870 L s\(^{-1}\)), stream 2 was an important contributor of dissolved Cu and Zn (ca. 470 kg a\(^{-1}\) Cu and 670 kg a\(^{-1}\) Zn) and particulate Fe (ca. 1980 kg a\(^{-1}\) ) to the Tamar.

The acidic ochreous adit 13 is connected to a Cu mine and a largely unsuccessful exploration mine for Cu and W (Dines et al., 1956a), and in spite of its low flow rate (3.2-30 L s\(^{-1}\)), was an important source of As, Fe and Cu (dissolved+particulate flux: ca. 66 kg a\(^{-1}\) As, 280 kg a\(^{-1}\) Cu, 1770 kg a\(^{-1}\) Fe). Streams 16, 17 and 21 are associated with Devon Great Consols (DGC) mine (Cu/As) and carry run-off, leachate and erosion products from different mine waste deposits, as well as adit outflow (County Councils). The acidic stream 16 combines leachate from a mine waste deposit and the main adit of DGC. This stream was identified as one of the major sources of As, Fe and other metals, accounting for high proportions of the sum of dissolved and particulate fluxes (e.g. 25% of dissolved and 47% of particulate As, 54% of dissolved and 21% of particulate Fe, 97% of dissolved and 19% of particulate Cd. Table 5.10) determined in the 25 streams and adits included in this study. Although its water flow rate was low (2.6-26 L s\(^{-1}\) ), the acidic stream 17 was the dominant point source of dissolved Cu (1430 kg a\(^{-1}\), or 39% of the total dissolved Cu flux from point sources) in the mining area.
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Table 5.10 Calculated annual dissolved and particulate flux of metals and As in kg a\(^{-1}\) extrapolated from monthly measurements of instantaneous flow and concentrations in the Tamar catchment and mining area. Water flow data at Greystone and Gunnislake was provided by EA. Flux upstream of Gunnislake includes adits and streams 14-25. Flux unaccounted for refers to the difference in metal/metalloid flux between Gunnislake and Greystone not accounted for by streams and adits surveyed upstream of Gunnislake. To calculate the flux not accounted for by monitoring the streams and adits in this survey, the flux in the Tamar at Greystone and the combined flux of adits/streams upstream of Gunnislake was subtracted from the flux at Gunnislake, and is given as percentage. na: not analysed.

<table>
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<th>As</th>
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<th>Co</th>
<th>Cu</th>
<th>Ni</th>
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<th>Zn</th>
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The circum-neutral stream 25 collects leachate from a series of multi-metallic mine workings (including W, Cu, Pb, Sn, As, Ag), cuts through major deposits of mining and fine grained ore processing waste and collects a deep adit outflow upstream of the sampling point near its confluence with the Tamar. High flow rates (74-1006 L⁻¹), combined with moderately high concentrations of contaminants make this stream an important source of As, Cu, Zn and Fe to the Tamar.

The flux calculations indicate that the adits and streams shown in Figure 5.17 (2, 13, 14, 16, 17, 21 and 25) should receive priority attention when considering remediation measures within a catchment management plan. It is in the nature of multi-metallic mining areas, such as the Gunnislake/Calstock region, to feature contamination sources characterised by a large diversity in chemical composition and source strengths. Each of the streams/adits identified as priority sources of mine drainage to the Tamar will have to be assessed in detail to establish the sources and pathways that lead to the contamination export from the site. As most of these are streams collating contaminants from a sub-catchment to the Tamar, a detailed investigation of the contribution of diffuse and point sources to the fluxes is necessary, before remediation strategies can be developed.

![Figure 5.17](image)

**Figure 5.17** Annual dissolved and particulate fluxes of As, Fe, Cu and Zn from selected adits and streams into the Tamar. The water flow is given as annual average of the instantaneous flow measured.
The flux of dissolved and particulate elements in the Tamar at Greystone was estimated by extrapolation to seasonal flux values (June-August, September-November, December-February, March-May) from the four catchment surveys and average monthly river flow data provided by the EA. Table 5.10 shows that the River Tamar at Greystone carried larger amounts of Fe (218000 kg a⁻¹), Mn (19100 kg a⁻¹), Co (1070 kg a⁻¹) and Ni (1210 kg a⁻¹) into the mining area than the streams and adits surveyed (9300 kg a⁻¹ Fe, 3410 kg a⁻¹ Mn, 262 kg a⁻¹ Co and 271 kg a⁻¹ Ni; all fluxes dissolved + particulate). The high flux of particulate Fe at Greystone is consistent with this metal's importance as a crustal and the elevated Fe concentrations in run-off from peat-rich upland areas (Mayes et al., 2008).

During times of low flow (July survey), the dissolved flux of Fe at Greystone was higher than at Gunnislake, indicating that attenuation within the river, for example through adsorption onto particles or precipitation, took place. Overall, this could have resulted in an under-estimation of the Fe flux in the mining area. Contributions to the metal flux at Gunnislake originating from the catchment at Greystone were similar to those from the streams and adits in the Calstock/Gunnislake area for As, Cu, Pb and Zn (Table 5.10). In addition to these elements, high Mn, Co and Ni fluxes were calculated for Greystone, indicating that important inputs of metals/metalloids occurred upstream. The likely sources of these are multi-metallic ore deposits and associated abandoned mines (e.g. Mn, Cu, Pb/Ag, Sn, Dines et al., 1956a; Robinson, 1995) in the catchments of tributaries to the Tamar upstream of the Gunnislake/Calstock mining area (see Figure 5.1 B, blue area).

The Rivers Tavy and Lynher contribute ca. 50% of freshwater into the Tamar estuary (Langston et al., 2003) and together they contributed (dissolved + particulate) ca. 75200 kg a⁻¹ Fe, 11800 kg a⁻¹ Mn, 21 kg a⁻¹ Cd, 2100 kg a⁻¹ Co, 4100 kg a⁻¹ Cu, 2000 kg a⁻¹ Ni, 500 kg a⁻¹ Pb and 8200 kg a⁻¹ Zn into the estuary. The trace element fluxes from the two rivers amount to 15-20% (for Fe, Mn), ca 30% (for Cu, Ni) and 50-60% (for Co, Zn) of fluxes calculated for the River Tamar, therefore adding markedly to the trace element fluxes into the estuary. The flux of Pb from the River Tavy and Lynher was higher than the flux of this metal in the River Tamar at Gunnislake. Although they drain sub-catchments outside the main Gunnislake/Calstock mining area, these rivers flow through area associated with past mining (e.g. some 20 Cu and 15 Pb mines in the Lynher sub-catchment, and some 32 Cu and 13 As mines in the Tavy sub-catchment. Turner, 2008.
Pers. Comms), and elevated trace elements in water in these two rivers have been reported (e.g. Aston et al., 1975). The analytical uncertainty for As analysis in the samples from the Lynher and Tavy were too high to merit flux calculations.

By applying a simple mass balance calculation for dissolved and particulate fluxes (subtraction of flux at Greystone from that at Gunnislake yields total flux between these points, from which fluxes calculated for adits/streams were subtracted), the flux not accounted for by the monthly surveys of streams and adits between Greystone and Gunnislake was calculated. The results show that for substantial proportions of dissolved and particulate contaminants (≥50%, Table 5.10), the sources remained unidentified in this work. Although the streams and adits included in this survey were not comprehensive, it is believed that all important point sources and streams draining sub-catchments were covered. Therefore it is likely that a large part of the missing flux originates from diffuse sources directly affecting the Tamar channel, such as contaminated groundwater injection in to the hyporheic zone, input of leachate and particles through erosion of mine waste, mobilisation/dissolution of bank sediment and efflorescent salts and in-stream mobilisation from metal-rich particles. Similar conclusions have been drawn from other studies evaluating the relative importance of diffuse and point sources of metals in abandoned mining areas (e.g. Mayes et al., 2005). Notwithstanding the uncertainty associated with the flux estimation, considering the magnitude of the flux not accounted for, it is important to investigate the nature of diffuse sources in river catchments affected by metal mining in order to provide the basis for developing effective remediation strategies.

The dissolved flux at Gunnislake was higher during the wet season (October–May) for all elements except Cd and Pb which concentrations often lower than LOD, and the same was true for the particulate flux. This can be partially attributed to the greater increase in river flow compared to the decline in element concentrations. For the Tamar, the ratio of average water discharge in wet to dry season was 6.4, while the concomitant decrease in element concentration was below 1.8 for all metals. Furthermore, a trend towards higher dissolved element fluxes during periods of higher flow was observed in most streams within the mining area, irrespective of their average flow rate (e.g. streams 17 and 25, Figure 5.18). The potential impact of increased winter rainfall, as observed in recent years in north Atlantic coastal regions (Klein Tank et al., 2002) and as is predicted in some
climate change scenarios (Wilby et al., 2006; Alcamo et al., 2007), on the element export from abandoned mine sites should be investigated.

![Graph](image)

**Figure 5.18** Monthly dissolved Cu and As fluxes versus water flow in two streams that contribute major element fluxes to the Tamar within the mining area.

The limitation of this method of flux estimation lies in the assumption that one monthly survey (or in the case of the catchment rivers, a quarterly survey) provides representative data for concentrations and water flow. For example, no flash flood events were monitored, as many of the sampling sites would be rendered inaccessible as a result of flooding. However, the erosion of metal-bearing particles from deep adits, mine or processing waste, and bank erosion during flood events may contribute appreciably to the contamination load in this area, as several mine waste deposits are located on or near the banks of the Tamar and its tributaries (e.g. at Gunnislake Clitters, Okeltor and New Consols), and streams 14, 16, 17 and 25 run through mine waste piles. At stream 25,
Chapter 5: Geochemistry of mine waters and metal fluxes from abandoned mine sites

Sediment prone to bank erosion contained up to 180000 mg kg\(^{-1}\) As, 2000 mg kg\(^{-1}\) Cu and 148000 mg kg\(^{-1}\) Fe. Although, the potential mobility of As, Cu and Fe of this waste material were low (<1% to pseudo total concentrations of all trace elements mentioned here), the waste materials can be exported into the River Tamar via erosion. Visits to sampling locations following heavy rain events revealed loss of sediments (grained sediments, precipitates and ochre) from adits and streams, as well as evidence of erosion (e.g. deepening of gullies) and export of solids from the surface of mine spoil heaps (e.g. fan of material at foot of heap). Evidence of erosion as diffuse source of mine contamination has been provided for similar river systems in Cornwall (e.g. Fal estuary. Pirrie et al., 2003). Here, small grains of the dominant ore materials (e.g. arsenopyrite, chalcopyrite), representing mine tailings too fine to be recovered during mineral processing at the time, as well as altered (e.g. by oxidation, precipitation) minerals have been documented as important sediment fraction. Furthermore, the authors showed that metal concentrations in Cornish river sediments are akin to concentrations commonly found in mine tailings around the world (e.g. Rio Tinto mines), indicating the importance of sediments as sources of secondary, diffuse contamination to the water column. In addition, occasional collapses (e.g. River Cat, winter 2006, personal observation) within abandoned mines can result in the discharge of substantial volumes of acid mine drainage carrying suspended ochreous material. High concentrations of metals/metalloids have been observed in ochreous sediments associated with some adits (e.g. 13, 16, 19) in the studied mining area (e.g. up to 28000 mg kg\(^{-1}\) As and 4500mg kg\(^{-1}\) Cu and 370000 mg kg\(^{-1}\) Fe), but the metal input due to such events remains difficult to estimate.

5.6.5 Impact of mine contamination on the estuarine environment

Coastal systems are important ecosystems because of their high biodiversity, productivity and their function as a recruitment zone for many marine species. This function makes them vulnerable to anthropogenic contaminants, especially as juveniles of many species are more susceptible to toxicants than their adult counterparts (e.g. bivalve molluscs: Beiras and Albentosa, 2004; Calabrese et al., 1973; His et al., 1999). Estuaries are highly dynamic systems in which rapidly changing chemical, biological and physical process interact to control the geochemical cycling and transport of constituent elements (Millward, 1995; Millward and Liu, 2003). In the Tamar (Ackroyd et al., 1986; Morris, 1986) and other estuaries (Achterberg et al., 2003; Parkman et al., 1996; Pirrie et al.,
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2003), particles and sediments have been found to form important sinks for contaminants released through mining activities, such trace metals. On the other hand, the re-mobilisation of metals and metalloids from (re-)suspended sediments and pore waters has been observed in the mid-Tamar estuary (Knox et al., 1984) and elsewhere (e.g. Braungardt et al., 2003), leading to a localised addition of contaminants to the dissolved phase. According to this study, the estuary received approximately 440 t Fe, 81 t Mn, 16 t Cu, 14 t Zn, 6.3 t Ni, 5.6 t As, 4.2 t Co and 260 kg Pb in dissolved and suspended form from its catchment during the study period (July 2005-June 2006). This continued input in combination with the re-working of the fine-grained sediment (Grabemann et al., 1997) results in high levels of contaminants in sediments throughout the estuary. For example, concentrations of 0.7–3 mg kg\(^{-1}\) Cd, 270–580 mg kg\(^{-1}\) Cu and 190–500 mg kg\(^{-1}\) Pb have been reported for the sediments near the Tamar road bridge (lower value) and in the upper estuary (upper value), respectively (Langston et al., 2003). These values exceed the Interim Marine Sediment Quality Guidelines (IMSQ) for Cd, Cu and Pb and Probable Effect Levels (PEL) (on biota and/or ecosystem) for Cu and Pb. The IMSQ and PEL for As, Hg and Zn are also exceeded in the Tamar estuary (Langston et al., 2003). The continued impact of the mining legacy on estuarine ecosystem quality was indicated by Clifton and Hamilton (1979), who reported that concentrations of Cu, Pb and Zn in a dated sediment core from the lower Tamar estuary had not decreased (in contrast to the mining-related Si signal) by the late 1970s, a century after the peak of Cu mining and several decades after the last large-scale mining activities in the catchment ceased. Studies of metal levels in Nereis diversicolor, a relatively tolerant polychaete, and in Fucus vesiculosus, a marine macroalga, have shown accumulation of some metals (e.g. Cu, Zn, Cd and/or Pb) within the Tamar estuary system above background concentrations (Langston et al., 2003). Of particular concern regarding its toxic effects on marine biota is Cu (Brand et al., 1986; Sharp and Stearns, 1997; Grout and Levings, 2001). The dissolved Cu levels in the estuary only occasionally exceed the Environmental Quality Standard (5 \(\mu g\) L\(^{-1}\)) for the protection of saltwater life. However, a recent study (Money et al., 2008) of the ecotoxicological impact of water quality using a biological assay based on the embryo of the Pacific Oyster, Crassostrea gigas, found a 100% toxic response in the middle reaches of the Tamar estuary, while the bioassay response was lower at the mouth of the Tamar. Although the toxic response in this study was induced by the complex mixture of compounds present in the water column, including agrochemicals and other
organics, the concentrations of Cu, Pb and Cd in estuarine waters were inferred to have played a contributing role.

5.7 Conclusions

The water chemistry of 11 rivers in the Tamar catchment, including four points in the River Tamar, as well as 25 streams and adits in the Gunnislake/Calstock mining area were studied in order to investigate the effects of abandoned mines on river water quality and ecosystem functioning. Comparison of trace metals and sulfate concentrations in the River Tamar upstream and within the Gunnislake/Calstock mining area confirmed that the input from abandoned mine sites has resulted in elevated concentrations of dissolved ions and some trace elements (e.g. Cu and As) in the River Tamar. Furthermore, trace elements, such as Cu, As, Fe, Ni, Pb and Zn exceeded environmental quality standards and/or guideline levels for fresh and estuarine water and/or freshwater fish directive in a number of streams and adit flows, and at times in the River Tamar.

The investigation showed that the studied abandoned mines represent a long-term input of metal mining-related contaminants into the River Tamar and estuarine system, which is an important aquatic ecosystem in southwest England. As a result, some stretches of the River Tamar, its estuary and some of its tributaries are at risk to fail the water quality objectives of the Water Framework Directive.

In general, the metal concentrations in the estuary are considerable lower than the values observed in the River Tamar at Gunnislake (i.e. freshwater). This is likely to result from adsorption onto particulates (e.g. Fe-oxyhydroxides formed upon the mixing of freshwater and saltwater). The modelling results showed that free ionic metal (Cu, Cd and Zn) concentrations in the estuarine water were lower than the value reported to have acute effects on organisms such as Pacific oyster larvae, green alga, diatoms and cyanobacteria. However, the trace metals adsorbed on Fe-oxyhydroxides or sediments can be released into water column if the conditions (e.g. pH, redox and ligands) of releasing are prevailed as seen in dissolved Cu and Zn concentrations in pore water in the Tamar estuary were 1-2 orders of magnitude higher than in the overlying water (Watson, unpublished data in Ackroyd et al., 1986). This may have adverse effects on organisms living on or scavenging see beds.
Seven specific sources (streams 2, 14, 16, 17, 21 and 25 and adit 13) carried more than 75% of total annual flux (dissolved and particulate) of the elements Fe, Mn, Cu, Zn, As, Ni, Co, Pb and Cd determined within the Gunnislake/Calstock mining area into the River Tamar and its estuary. These sources should receive priority attention when considering remediation measures within a catchment management plan. Six of these sources are indeed streams transporting water and solid materials from several contamination sources (point and diffuse) within their sub-catchment.

The mass balance between the River Tamar at Greystone Bridge and at Gunnislake suggested that the studied streams and adits were not the dominant sources of main drainage to the River Tamar. Rather, the contribution of metals and As from diffuse sources was implied to be of high importance. Therefore, a detailed investigation of diffuse sources within this mining area is imperative in order to provide the basis for developing effective remediation strategies and this should be addressed in future work.

5.8 References


Chapter 5: Geochemistry of mine waters and metal fluxes from abandoned mine sites


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Chapter 6

Conclusions and future work

6.1 Conclusions

This research applied several approaches such as grain size analysis, permeability test, mathematical slope stability analysis, metal extraction of solids (pseudo and sequential) and water analysis (dissolve and particulate) to investigate the effects of past mining activities on the quality of aquatic systems in the Tamar catchment.

The catchment-wide investigation of metal concentrations in waters and sediments revealed that the levels of As in the upper catchment, where no mining activities have been recorded, are generally higher than the values observed elsewhere in England and Wales. These elevated concentrations are the result of the general geological setting, which features widespread igneous influence, metamorphism and mineralisation. Detailed studies focussed on the Calstock/Gunnislake mining district, an area in the centre of the Tamar catchment that saw intensive ore exploration in the 19th and early 20th century. Within this district, the dissolved, particulate and sediment metal concentrations in streams and rivers were higher than those observed in the upper catchment. The elevated metal and arsenic concentrations in these streams were the result of inputs from abandoned mines in form of acid mine drainage and erosion of particles from contaminated land, such as mining waste piles. Furthermore, elevated metal and As concentrations have been detected in the middle reaches of the River Tamar and its upper
Chapter 6: Conclusions and future work.

These findings highlight the adverse effects of intense past mining activities on the water and sediment quality in the Tamar river and estuary, with two potential consequences: (i) failing of the water quality criteria stipulated in the Water Framework Directive, and (ii) impairment of the ecosystem functioning within regions classified as Area of Outstanding Nature Beauty (AONB), Sites of Special Scientific Interest (SSSI) and Special Protection Area (SPA) under the EC Birds Directive and Special Area of Conservation (SAC).

Investigations of potential contamination pathways suggest that the mechanism of contaminant export from abandoned mine sites is highly dependent on the physical and geotechnical characteristics of individual waste heaps and their history. In the study area, the remains of different ore processing techniques have generated coarse-grained, highly permeable material (from gravitational separation, as well as slags and cinders), and fine-grained slimes and tailings (from hydraulic separation of fine material). The number of waste heaps investigated was limited. However, results indicate that surface erosion and/or gullying and infiltration followed by leaching of acid mine drainage are dominant contamination export pathways from coarse mine waste. This is the result of the low cohesion within these materials and is exacerbated by the presence of steep slopes. In contrast, fine-grained tailings are by nature high-cohesion materials and proved to be more favourable for colonisation and stabilisation by plants. Under equal conditions (e.g. amounts of rain fall, slope angle), fine-grained waste heaps are less susceptible to run-off erosion compared to the cohesionless materials. Furthermore, infiltration is largely limited to the weathered surface layer of these heaps, and hence contaminant export is likely to occur mainly through run-off of contaminated water and sudden slope failure. The likelihood for the latter to occur increases with the slope angle.

The studied mining waste materials contain sulfide minerals, such as arsenopyrite, pyrite and chalcopyrite, as well as secondary minerals such as Fe-oxyhydroxides. Some waste materials contain extremely high metal concentrations of some metals, for example up to 6500 mg kg\(^{-1}\) Cu, 620 mg kg\(^{-1}\) Pb, 2900 mg kg\(^{-1}\) Zn, 52 mg kg\(^{-1}\) Ni, 40 mg kg\(^{-1}\) Cd, 1800 mg kg\(^{-1}\) Mn and 290000 mg kg\(^{-1}\) Fe. Arsenic concentrations up to 180000 mg kg\(^{-1}\) As were determined in mine waste heaps. The highest As, Cu and Cd concentrations in mine wastes exceed the Dutch intervention levels, suggesting these mine wastes can
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cause unacceptable risks to man or the environment; and Zn and Pb concentrations are elevated above the acceptable risk levels for the Dutch standards.

The high permeability observed at coarse grained waste heaps is likely to make water and oxygen available at depth, hence enhances the potential for sulfide oxidation to take place, as well as facilitates good drainage for acidic leachate generated within the waste heaps. This assumption was evident at Devon Great Consols main dressing floor waste heap, where low pH (<3.8) seepage containing up to 300 µg L⁻¹ As and 36000 µg L⁻¹ Cu was observed at the base of the waste heap after periods of prolonged rainfall. The mineralogy of this heap and the operationally defined speciation obtained from the BCR extraction of mine waste indicate that sulfide minerals are the major source of the acidic (pH<5), metal-rich (particularly As, Cu, Fe, Mn and Zn) waters observed in the main drain at Devon Great Consols Mine. Sulfide oxidation may also be an important process in contributing to the high metal concentrations determined in the acid drainage at Blanchdown and Ding Dong adits, as well as in near-neutral waters within the mining region, such as South Tamar and Gunnislake Clitters adits. Furthermore, acidic waters generated by sulfide oxidation can also enhance the dissolution of As and metals that are present in other phases, for example the exchangeable fraction. Therefore, although a high proportion of the mine wastes studied showed a low concentration of potentially exchangeable As and metals (Fe, Zn and Mn), the general mobility of these elements may increase in the presence of acidic waters.

In addition to sulfide minerals, the fine grained waste materials contain considerable amounts of secondary minerals such as Fe-oxyhydroxides, which can contain up to 12% As. These Fe-oxyhydroxides are likely to be the major phases of As and other metals in the reducible fraction, which constitutes a larger proportion in the fine grained, than the coarse grained wastes. However, in spite of the high As and metal concentrations observed in some of the fine grained waste heaps, and the relatively high exchangeable and reducible fractions of some trace elements compared to those observed in the the coarse grained waste materials, the fine grained waste heaps have a lower potential to be the sources of metal contamination to the wider environment, unless their slopes are are unstable. This is because the low permeability of the fine grained materials limits water infiltration and the availability of oxygen at depth, and therefore limits the potential for acid leachate generation within the fine-grained waste heaps. Furthermore, the high
proportion of Fe-oxyhydroxide minerals observed in the fine grained wastes and other secondary minerals, such as scorodite, resulted in the low fraction of exchangeable metals observed in these wastes, limiting their potential to be dissolved by rainwater.

Once exported from the waste heaps into aquatic systems, either in dissolved or solid forms, the contaminants may be removed from solution, deposited and remobilised depending on the physiochemical conditions in rivers and streams. For example, statistical analysis of aquatic solids indicated a relationship between total As and Fe concentrations in suspended particles and between reducible As and Fe in stream sediments of most water courses within the mining area. This suggests that As concentrations in the aquatic systems are strongly controlled by adsorption onto and coprecipitation with Fe-oxyhydroxides. The attenuation of metals in aquatic environments is evident from the relatively high total concentrations of Pb and Mn. and high exchangeable Pb, Mn, Cu and Zn in stream sediments compared to their concentrations in waste materials. Furthermore, precipitates (e.g. Cu carbonate) were observed as surface coatings on the sediment pebbles and boulders in some water courses. The mobilisation of metals from stream sediments was indicated by an increase in dissolved and particulate trace metal concentrations in the River Tamar during the onset of wet season. This illustrates that the fate of mining-related contaminants in surface waters is complex and dependent on a multitude of physical and chemical parameters, as well as biological factors, the study of which was beyond the scope of this work.

The dissolved and particulate concentrations of trace elements in the water courses within area of intensive mining were highly variable, spatially and temporally. Acidic waters, for example adit outflow and leachate emanating from contaminated land, carried high concentrations of As and metals (e.g. up to 560 µg L⁻¹ As and up to 7600 µg L⁻¹ Cu were observed in streams draining Devon Great Consols Mine). In contrast, the concentrations of these metals in some near-neutral waters were similar to those in rivers of the catchment background (e.g. up to 13 µg L⁻¹ As in Deer Park stream compared to the background values of up to 12 µg L⁻¹ As), while other near-neutral waters carried high concentrations. The Cu, As, Fe, Ni, Pb and Zn concentrations observed in a number of streams and adits within the mining area, and at times in the River Tamar exceed environmental quality standards and/or guideline levels for fresh and estuarine water and/or the freshwater fish directive.
In total, the studied streams and adits in the mining area input ca. 13,000 kg Fe, 4300 kg Mn, 4200 kg Cu, 3600 kg Zn, 1400 kg As, 400 kg Ni, 350 kg Co, 43 kg Pb, and 6.6 kg Cd to the Tamar estuary during the year of our survey. Approximately 50% of Fe, As and Pb were carried in the particulate phase, while about 83% of Co and over 88% of Mn, Cd, Cu, Ni and Zn were carried in the dissolved phase. Seven water courses, including Cotehele stream, Ding Dong adit, the stream collecting run-off and adit waters in Bedford United Mine, Blanchdown adit, the main drain at Devon Great Consols Mine, the River Cat and Lucket stream, account for over 75% of the total (dissolved and particulate) Fe, Mn, Cu, Zn, As, Ni, Co, Pb and Cd flux discharged annually from the Gunnislake/Calstock mining area to the River Tamar and its estuary, and can be seen as important point sources. Of the total flux, over 50% of trace elements were not accounted for by the studied point sources, suggesting an importance of diffuse sources.

6.2 Future work

This study highlights the effects of the past mining activities on water and sediment quality in the Tamar catchment. The information obtained is useful for catchment management and decision making for water resource management and remediation approaches. Through this study, it is also recognised that future investigation on the following aspects are needed in order to develop effective remediation strategies:

1. Further work on migration pathways, particularly the rates of erosion, at other abandoned mines in close proximity to river banks, including Gawton, New Great Consols and Okeltor Mines.
2. A detailed investigation of diffuse sources within this mining area.
3. A detailed investigation of contaminant transport through soils and shallow ground water, and associated attenuation of contaminants.
4. Bioaccumulation of trace elements from water and stream sediments, and their environmental implication on organisms.
5. Further research on sediment transportation in relation to stream and river velocity. It is clear from this study that suspended particulates are a dominant migration pathway for some trace element. However, a better understanding on particle size that can be transport by the River Tamar has not been addressed.
Appendix I

List of minerals found in the studied area
<table>
<thead>
<tr>
<th>Mine</th>
<th>Mineral found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Devon Great Consols Mine</td>
<td>Arsenolite $\text{As}_2\text{O}_3$</td>
</tr>
<tr>
<td></td>
<td>Arsenopyrite $\text{FeAsS}$</td>
</tr>
<tr>
<td></td>
<td>Carbonate-fluorapatite var: Francolite $\text{Ca}_5 [{(\text{F, O}</td>
</tr>
<tr>
<td></td>
<td>Cassiterite $\text{SnO}_2$</td>
</tr>
<tr>
<td></td>
<td>Chalcopyrite $\text{CuFeS}_2$</td>
</tr>
<tr>
<td></td>
<td>Chlorite Group $\text{(Mg, Fe)}_3(\text{Si, Al})<em>4\text{O}</em>{10}(\text{OH})_2(\text{Mg, Fe})_3(\text{OH})_6$.</td>
</tr>
<tr>
<td></td>
<td>Cornubite $\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4$.</td>
</tr>
<tr>
<td></td>
<td>Cornwallite $\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4$.</td>
</tr>
<tr>
<td></td>
<td>Fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$</td>
</tr>
<tr>
<td></td>
<td>Fluorite (also fluorspar) $\text{CaF}_2$</td>
</tr>
<tr>
<td></td>
<td>Hematite $\text{Fe}_2\text{O}_3$</td>
</tr>
<tr>
<td></td>
<td>Pyrite $\text{FeS}_2$</td>
</tr>
<tr>
<td></td>
<td>Siderite $\text{FeCO}_3$</td>
</tr>
<tr>
<td></td>
<td>Wolframite $(\text{Fe, Mn})\text{WO}_4$</td>
</tr>
<tr>
<td>Okeltor Mine</td>
<td>Childrenite $(\text{Fe}^{2+}, \text{Mn}^{2+})\text{Al} [(\text{OH}_2 \text{[PO}_4 \text{]} \cdot \text{H}_2 \text{O} \text{CaF}_2)$</td>
</tr>
<tr>
<td>Cotehele Consols Mine</td>
<td>Chlorite $\text{(Mg, Fe)}_3(\text{Si, Al})<em>4\text{O}</em>{10}(\text{OH})_2(\text{Mg, Fe})_3(\text{OH})_6$.</td>
</tr>
<tr>
<td>Mine</td>
<td>Mineral found</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---------------------------------------------------</td>
</tr>
<tr>
<td>Gunnislake Clitter Mine</td>
<td>Aragonite $\text{CaCO}_3$</td>
</tr>
<tr>
<td></td>
<td>Azurite $\text{Cu}_3[\text{OH}]_2[\text{CO}_3]_2$</td>
</tr>
<tr>
<td></td>
<td>Bismuthinite $\text{Bi}_2\text{S}_3$</td>
</tr>
<tr>
<td></td>
<td>Bornite $\text{Cu}_2\text{FeS}_4$</td>
</tr>
<tr>
<td></td>
<td>Brochantite $\text{Cu}_4[(\text{OH})_6</td>
</tr>
<tr>
<td></td>
<td>Carbonate-fluorapatite $\text{Ca}_5\left[(\text{F}, \text{O}</td>
</tr>
<tr>
<td></td>
<td>Cassiterite $\text{SnO}_2$</td>
</tr>
<tr>
<td></td>
<td>Chalcedony $\text{SiO}_2$</td>
</tr>
<tr>
<td></td>
<td>Chalcocite $\text{Cu}_2\text{S}$</td>
</tr>
<tr>
<td></td>
<td>Chalcopryite $\text{CuFeS}_2$</td>
</tr>
<tr>
<td></td>
<td>Chalcosiderite $\text{Cu}(\text{Fe}^{3+}, \text{Al})_6[(\text{OH})_4(\text{PO}_4)_2] \cdot 4\text{H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Chlorite Group</td>
</tr>
<tr>
<td></td>
<td>$\text{(Mg, Fe)}_3(\text{Si, Al})<em>4\text{O}</em>{10}(\text{OH})_2 \cdot (\text{Mg, Fe})_3(\text{OH})_6$.</td>
</tr>
<tr>
<td></td>
<td>Connellite $\text{Cu}<em>{19}[(\text{OH})</em>{32}\text{SO}<em>4\text{Cl}</em>{14}] \cdot 3\text{H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Copper $\text{Cu}$</td>
</tr>
<tr>
<td></td>
<td>Covellite $\text{CuS}$</td>
</tr>
<tr>
<td></td>
<td>Cuprite $\text{Cu}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Ferberite $\text{FeWO}_4$</td>
</tr>
<tr>
<td></td>
<td>Fluorite $\text{CaF}_2$</td>
</tr>
<tr>
<td></td>
<td>Galena $\text{PbS}$</td>
</tr>
<tr>
<td></td>
<td>Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$</td>
</tr>
<tr>
<td></td>
<td>Langite $\text{Cu}_4(\text{SO}_4)(\text{OH})_6\cdot 2(\text{H}_2\text{O})$</td>
</tr>
<tr>
<td></td>
<td>Malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$</td>
</tr>
<tr>
<td></td>
<td>Orthoclase var: Adularia $\text{KAlSi}_3\text{O}_8$</td>
</tr>
<tr>
<td></td>
<td>Pyrite $\text{FeS}_2$</td>
</tr>
<tr>
<td></td>
<td>Quartz $\text{SiO}_2$</td>
</tr>
<tr>
<td></td>
<td>Roscherite $\text{Ca}(\text{Mn}^{2+}, \text{Fe}^{2+})_3\text{Be}_4(\text{PO}_4)<em>6(\text{OH})</em>{16}(\text{H}_2\text{O})$</td>
</tr>
<tr>
<td></td>
<td>Siderite $\text{FeCO}_3$</td>
</tr>
<tr>
<td></td>
<td>Tetrahedrite $(\text{Cu, Fe})_{12}\text{Sb}_3\text{S}_3$</td>
</tr>
<tr>
<td></td>
<td>Torbernite (radioactive) $\text{Cu(UO}_2)_2(\text{PO}_4)_2 \cdot 8 \cdot 12(\text{H}_2\text{O})$</td>
</tr>
<tr>
<td></td>
<td>Varlamoffite $(\text{Sn, Fe})(\text{O, OH})_2$</td>
</tr>
<tr>
<td></td>
<td>Wolframite $(\text{Fe, Mn})\text{WO}_4$</td>
</tr>
</tbody>
</table>
### Luckett Mine

<table>
<thead>
<tr>
<th>Mineral found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenopyrite $\text{FeAsS}$</td>
</tr>
<tr>
<td>Beryl $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$</td>
</tr>
<tr>
<td>Chalcopyrite $\text{CuFeS}_2$</td>
</tr>
<tr>
<td>Løllingite $\text{FeAs}_2$</td>
</tr>
<tr>
<td>Pyrite $\text{FeS}_2$</td>
</tr>
<tr>
<td>Quartz $\text{SiO}_2$</td>
</tr>
<tr>
<td>Sphalerite $\text{ZnS}$, iron impurity often found such as marmatite $(\text{Zn},\text{Fe})\text{S}$</td>
</tr>
</tbody>
</table>

### Bedford United Mine

<table>
<thead>
<tr>
<th>Mineral found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase $\text{TiO}_2$</td>
</tr>
<tr>
<td>Arsenopyrite $\text{FeAsS}$</td>
</tr>
<tr>
<td>Azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$</td>
</tr>
<tr>
<td>Brochantite $\text{Cu}_4[(\text{OH})_6</td>
</tr>
<tr>
<td>Chalcopyrite $\text{CuFeS}_2$</td>
</tr>
<tr>
<td>Chalcosiderite $\text{Cu}(\text{Fe}^{3+},\text{Al})_6[(\text{OH})_4</td>
</tr>
<tr>
<td>Clinoclase $\text{Cu}_3(\text{AsO}_4)(\text{OH})_3$</td>
</tr>
<tr>
<td>Copper $\text{Cu}$</td>
</tr>
<tr>
<td>Cornubite $\text{Cu}_3(\text{AsO}_4)_2(\text{OH})_4$</td>
</tr>
<tr>
<td>Cornwallite $\text{Cu}_2(\text{AsO}_4)_2(\text{OH})_4$</td>
</tr>
<tr>
<td>Cuprite $\text{Cu}_2\text{O}$</td>
</tr>
<tr>
<td>Langite $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2(\text{H}_2\text{O})$</td>
</tr>
<tr>
<td>Libethenite $\text{Cu}_2(\text{PO}_4)(\text{OH})$</td>
</tr>
<tr>
<td>Olivenite $\text{Cu}_2(\text{AsO}_4)(\text{OH})$</td>
</tr>
<tr>
<td>Scheelite $\text{Ca}(\text{WO}_4)$</td>
</tr>
<tr>
<td>Scorodite $\text{Fe}^{3+}(\text{AsO}_4)_2 \cdot 2(\text{H}_2\text{O})$</td>
</tr>
</tbody>
</table>
## Appendix I

<table>
<thead>
<tr>
<th>Mine</th>
<th>Mineral found</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Tamar Mine</td>
<td>Fluorite CaF₂</td>
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<tr>
<td>Gawton Mine</td>
<td>Anatase TiO₂</td>
</tr>
<tr>
<td></td>
<td>Arsenolite As₂O₃</td>
</tr>
<tr>
<td></td>
<td>Arsenopyrite FeAsS</td>
</tr>
<tr>
<td></td>
<td>Chalcopyrite CuFeS₂</td>
</tr>
<tr>
<td></td>
<td>Hemimorphite Zn₄Si₂O₇(OH)₂·H₂O</td>
</tr>
<tr>
<td></td>
<td>Limonite Fe(OH)₆·H₂O</td>
</tr>
<tr>
<td></td>
<td>Pyrite FeS₂</td>
</tr>
<tr>
<td></td>
<td>Siderite FeCO₃</td>
</tr>
<tr>
<td>Russel United Mine</td>
<td>Carbonate-fluorapatite Ca₅[(F,O)][(PO₄,CO₃)₃]</td>
</tr>
<tr>
<td></td>
<td>Chlorite (Mg,Fe)₃(Si,Al)₄O₁₀(OH)₂·(Mg,Fe)₃(OH)₆</td>
</tr>
<tr>
<td></td>
<td>Chalcopyrite CuFeS₂</td>
</tr>
<tr>
<td></td>
<td>Arsenopyrite FeAsS</td>
</tr>
<tr>
<td>Mine</td>
<td>Mineral found</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------------------------------------------</td>
</tr>
<tr>
<td>Ding Ding Mine</td>
<td>Carbonate-fluorapatite $\text{Ca}_5 [(\text{F,O})(\text{PO}_4,\text{CO}_3)]_3$</td>
</tr>
<tr>
<td></td>
<td>Wolframite $(\text{Fe,Mn})\text{WO}_4$</td>
</tr>
<tr>
<td></td>
<td>cassiterite $\text{SnO}_2$</td>
</tr>
<tr>
<td></td>
<td>mispickel (german for arsenopyrite) $\text{FeAsS}$</td>
</tr>
<tr>
<td></td>
<td>quartz $\text{SiO}_2$</td>
</tr>
<tr>
<td></td>
<td>chlorite $(\text{Mg,Fe})_3(\text{Si,Al})<em>4\text{O}</em>{10}(\text{OH})_2(\text{Mg,Fe})_3(\text{OH})_6$</td>
</tr>
<tr>
<td></td>
<td>Chalcopyrite $\text{CuFeS}_2$</td>
</tr>
<tr>
<td></td>
<td>Fluorite (also fluorspar) $\text{CaF}_2$</td>
</tr>
<tr>
<td>Mine</td>
<td>Mineral found</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>----------------------------------------------------------------</td>
</tr>
<tr>
<td>Old Gunnislake Mine</td>
<td>Antlerite Cu$_3$SO$_4$(OH)$_4$</td>
</tr>
<tr>
<td></td>
<td>Autunite (radioactive) Ca(UO$_2$)$_2$(PO$_4$)$_2$·10H$_2$O</td>
</tr>
<tr>
<td></td>
<td>Azurite Cu$_3$(CO$_3$)$_2$(OH)$_2$</td>
</tr>
<tr>
<td></td>
<td>Carbonate-fluorapatite Ca$_5$(PO$_4$,CO$_3$)$_3$F</td>
</tr>
<tr>
<td></td>
<td>Cassiterite SnO$_2$</td>
</tr>
<tr>
<td></td>
<td>Chalcopyllite Cu$_{18}$Al$_2$(AsO$_4$)$_3$(SO$_4$)$_3$(OH)$_7$·3·H$_2$O</td>
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<tr>
<td></td>
<td>Chenevixite Cu$_2$Fe$^{3+}$(AsO$_4$)$_2$(OH)$_4$·(H$_2$O)</td>
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<tr>
<td></td>
<td>Chrysocolla CuSiO$_3$·nH$_2$O</td>
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<td></td>
<td>Connellite Cu$_{10}$SO$_4$Cl$<em>4$(OH)$</em>{32}$·3H$_2$O</td>
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<tr>
<td></td>
<td>Cuprite var: Chalcotrichite Cu$_2$O</td>
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<tr>
<td></td>
<td>Cuprotungstite Cu$_3$(WO$_4$)$_2$(OH)$_2$</td>
</tr>
<tr>
<td></td>
<td>Erythrite Co$_3$(AsO$_4$)$_2$·8(H$_2$O)</td>
</tr>
<tr>
<td></td>
<td>Fluorapatite Ca$_5$(PO$_4$)$_3$F</td>
</tr>
<tr>
<td></td>
<td>Libethenite Cu$_2$(PO$_4$)(OH)</td>
</tr>
<tr>
<td></td>
<td>Malachite Cu$_2$CO$_3$(OH)$_2$</td>
</tr>
<tr>
<td></td>
<td>Metatorbernite Cu(UO$_2$)$_2$(PO$_4$)$_2$·8(H$_2$O)</td>
</tr>
<tr>
<td></td>
<td>Mixite BiCu$_6$(AsO$_4$)$_3$(OH)$_6$·3(H$_2$O)</td>
</tr>
<tr>
<td></td>
<td>Olivenite Cu$_2$(AsO$_4$)(OH)</td>
</tr>
<tr>
<td></td>
<td>Pharmacosiderite KFe$^{3+}$$_4$(AsO$_4$)$_3$(OH)$_4$·7(H$_2$O)</td>
</tr>
<tr>
<td></td>
<td>Pseudomalachite Cu$_5$(PO$_4$)$_2$(OH)$_4$</td>
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<tr>
<td></td>
<td>Reichenbachite Cu$_5$(PO$_4$)$_2$(OH)$_4$</td>
</tr>
<tr>
<td></td>
<td>Scheelite Ca(WO$_4$)</td>
</tr>
<tr>
<td></td>
<td>Scorodite Fe$^{3+}$(AsO$_4$)$_2$·2(H$_2$O)</td>
</tr>
<tr>
<td></td>
<td>Tenorite CuO</td>
</tr>
<tr>
<td></td>
<td>Torbernite (radioactive) Cu(UO$_2$)$_2$(PO$_4$)$_2$·11(H$_2$O)</td>
</tr>
<tr>
<td></td>
<td>Tyrolite CaCu$_5$(AsO$_4$)$_3$(CO$_3$)(OH)$_4$·6(H$_2$O)</td>
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<tr>
<td></td>
<td>Uraninite UO$_2$</td>
</tr>
<tr>
<td></td>
<td>Wolframite (Fe,Mn)WO$_4$</td>
</tr>
<tr>
<td></td>
<td>Zippeite K$_4$(UO$_2$)$_6$(SO$_4$)$<em>3$(OH)$</em>{10}$·4(H$_2$O)</td>
</tr>
</tbody>
</table>
Appendix II

Published paper
Contaminant fluxes from point and diffuse sources from abandoned mines in the River Tamar catchment, UK

Krongkaew Mighanetara a, Charlotte B. Braungardt b,*, John S. Rieuwerts b, Fethi Azizi a

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ABSTRACT

Acid mine waters have the potential to seriously impair the environmental quality of aquatic systems long after mining activities have ceased. This detailed study of dissolved and particulate metal fluxes from adits, drains and streams in the River Tamar catchment, southwest England, showed that seven specific sources of the 25 adits and streams surveyed, accounted for more than 75% each of the 13 t a⁻¹ Fe, 4.3 t a⁻¹ Mn, 4.2 t a⁻¹ Cu, 3.6 t a⁻¹ Zn and 1.4 t a⁻¹ As that we estimated to be discharged annually from the abandoned metalliferous mining area centred around Calstock and Gunnislake. Upstream of this study area, widespread metalliferous mineralisation contributed to the flux of Fe, Mn, As, Co, Cu and Zn within the River Tamar. Simple mass balance calculations indicated that a large proportion (≥50% for most dissolved and particulate metals) of the metal flux in the River Tamar was unaccounted for by our survey, and therefore is likely to have an important diffuse component, which is subject to ongoing investigations. Potential impacts of mine contamination on the estuarine environment are discussed. The study provided information necessary to prioritise monitoring and remediation efforts in the context of sustainable catchment management.

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1. Introduction

In southwest England (Fig. 1), metal ores occur within the metamorphic aureoles around a string of granite bosses of Carboniferous age, which include the upland areas of Dartmoor, Kit Hill and Bodmin Moor in the wider Tamar catchment, as well as further outcrops extending west towards the River Fal and beyond (Dines et al., 1956b). Mined since pre-Roman times, the area experienced its heyday of mineral extraction in the latter part of the 19th century, with lower levels of activity (including the re-working of tailings with more efficient methods) continuing into the 1990s. The principal commercial minerals were Cu/As, Cu/Fe and Fe/As ores, such as arsenopyrite (FeAsS), chalcopyrite (CuFeS₂) and cornwallite (Cu₃ (OH)₆As₄O₁₄), cassoiterite (SnO₂), as well as ores of lead, zinc, silver, uranium and tungsten (Dines et al., 1956b; Joylon, 2007).

Drainage entering rivers and estuaries from abandoned metal mines poses a particular challenge to the Environment Agency of England and Wales (EA) in the implementation of the EU Water Framework Directive (WFD, 2000/60/EC). The main objective of the WFD is to reach good chemical and ecological water quality status by 2015, and in order to achieve this, contamination sources to water-courses must be characterised in order to provide the information on which management strategies are based. Although metal mining has ceased in southwest England, mining waste, adits, shafts and land contaminated by mineral processing remain sources of contamination to water courses, leaving some rivers, such as the Tamar and the Fal, at risk of failing WFD targets (EA, 2004). In addition, the Tamar estuary is a vulnerable ecosystem designated a Special Protection Area under the EU Directive on the Conservation of Wild Birds (79/409/EEC) and Special Area of Conservation under the EU Habitats Directive (92/43/EEC).

In this paper we present data from a study in the former mining area of Gunnislake and Calstock in the River Tamar catchment. The study aimed to quantify the flux of mining-related contaminants (As, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn) from point sources into the river and estuary, to identify contamination hot spots and to estimate the importance of diffuse sources of metals to the river.

2. Study area

The River Tamar forms the boundary between Devon and Cornwall (Fig. 1), is about 78 km long and its catchment covers an area of ca. 1700 km² (Evans et al., 1993). The bedrock consists largely of hard mudstones, shales, slates and siltstones, with some hard sandstone present in the upper catchment, and granite on its margins. Overall,
the River Tamar is classed as 'fairly responsive' with a Base Flow Index of 0.47 (Robinson, 1995). The mean annual flow of the Tamar is 30 m³ m⁻² s⁻¹ (range: 5–58 m³ s⁻¹), with occasional instantaneous flash flows in excess of 100 m³ s⁻¹. The estuary is 31 km long, of medium size and macrotidal (Uncles and Stephens, 2001). While land use in the catchment is predominantly agricultural (95%; arable, pasture), the lower reaches of the river and the upper estuary are located within the former Gunnislake/Calstock mining district and tributaries of the estuary (Lynher, Tavy) drain abandoned mines associated with the mineralisations of Bodmin Moor and Dartmoor. The city of Plymouth, from which industrial and sewage inputs originate, borders the lower estuary.

During the mid- to late 19th century much of the world's Cu and As originated from the Gunnislake/Calstock district (BGS, 2003), largely produced by Devon Great Consols Mine (economic ores: chalcopyrite, arsenopyrite), which has been the focus of a number of studies (Kavanagh et al., 1997; Hamilton, 2000; Dybowska et al., 2005; Klink et al., 2005; Palumbo-Roe et al., 2007). This and other mining sites in the area feature remains of engine houses, mills and/or smelters, shafts, as well as mining waste heaps containing slag and cinders, coarse-grained and fine-grained wastes from different stages of ore processing, tailings ponds, as well as overburden and gangue. Remains of calcarious are highly contaminated with crystallised As compounds. Adits or drainage channels that carry run-off and leachate directly into the Tamar are associated with most abandoned mines. Solid mine waste at some mine locations is situated directly on the bank of the river. These waste piles have the greatest potential impact as diffuse contamination source, because run-off, leachate and erosion products enter the river without attenuation. While the Tamar estuary receives inputs that at times exceed the freshwater Environmental Quality Standard values for metals, such as Cd and Cu, the large reservoir of sediment-associated metals in the estuary is also of concern. For example, sediment concentrations up to 545 µg g⁻¹ Cu and 239 µg g⁻¹ Pb (dry weights) have been reported for the Tamar estuary, and the Interim Marine Sediment Guidelines and Probable Effect Levels are exceeded for As, Cu, Pb, Hg and Zn (Langston et al., 2003).

3. Experimental

3.1. Reagents and equipment

The preparation and handling of reagents and samples was carried out in a Class-100 laminar flow hood using trace metal clean techniques. High purity water (MQ water) was obtained from a Milli-Q system (Millipore, 18 MΩ cm⁻¹, reverse osmosis followed by ion exchange) and was used to prepare all aqueous solutions. Unless stated otherwise, reagents were of analytical reagent grade. Nitric acid and hydrochloric acid were cleaned by distillation at sub-boiling temperatures (sub-HNO₃, sub-HCl). Multi-element calibration standards were prepared from standard solutions (1.0 or 10 g L⁻¹, Fisher, Romil Pure Chemistry or CPI International) by serial dilution, acidified using sub-HNO₃, and matrix-matched where necessary.

Low density polyethylene (LDPE, Nalgene) bottles were cleaned by immersion in a series of solutions (Decon 90, 2% v/v, > 24 h; HCL, 6 mol L⁻¹, ≥ 7 days, HNO₃, 2 mol L⁻¹, ≥ 7 days), and rinsed with deionised water after the first step and with MQ water after all subsequent steps. The bottles were dried in a Class-100 laminar flow hood, or, if designated for sampling, were filled with acidified MQ water (sub-HNO₃, pH 2). All bottles were stored in two plastic bags. Sampling bottles were rinsed three times with the sample before final sample collection. Filtration units (polycarbonate, Nalgene) were cleaned with Decon 90 and immersion in HCl (2 mol L⁻¹, > 2 days), rinsed, dried and stored as described above. Filter membranes (cellulose nitrate, 0.2 µm pore size, Whatmann) were cleaned by immersion in sub-HCl (1.2 mol L⁻¹, 24 h) and soaking in MQ water.

3.2. Sampling, sample treatment and analysis

In the following, streams within the mining area will be distinguished from adits. The former represent water courses that carry natural waters mixed with adit outflow and/or leachate from contaminated land and waste piles, hence combine contamination from a number of point and diffuse sources. The latter are single-
point-source discharges from mine drainage tunnels directly into the River Tamar. The term 'river' is used for the Tamar and any of its tributaries outside of the Gunnislake/Calstock mining area.

This work focused on 25 adits and streams within the Gunnislake/Calstock mining area that were potential carriers of dissolved and particulate metals directly into the River Tamar. The streams included by several abandoned mine sites within it. As the main objective of this study seen as 'point sources' to the Tamar. The selection of sites was based on records drawn from a variety of sources (e.g. surveys of mine sites commissioned for the Tamar Valley Mining Heritage Project; Dines et al., 1956b) and local knowledge (e.g. land owners, mine rescue service), combined with wide-ranging preliminary surveys and sample analysis. Therefore, the authors regard the selection as representative of the main streams and point sources of mining-related contamination within the Calstock/Gunnislake mining district.

Water samples were taken and physical parameters measured in situ monthly between July 2005 and June 2006 at locations given in Fig. 2. Monthly samples were also taken in the Tamar freshwater end-member (upstream of the weir separating the tidal from the freshwater reaches) at Gunnislake. In addition, fresh water samples were taken quarterly (July and October 2005, January and April 2006) at 15 locations throughout the wider catchment, including the Tamar at various points and its major tributaries (Lynher, Tiddy, Inny, Ottery, Deer, Carey, Thrushel, Lyd, Tavy and Walkham) near their confluence with the Tamar. Conductivity, pH and redox potential ( Eh) were measured in situ using calibrated portable instruments (Hanna HI9024/5, Hanna HI9635). The velocity in water courses was measured using a Valeport Braystoke BFM002 with a small impeller in the centre of the stream at a point of minimal turbulence. All streams had a depth of less than 1.0 m, so that the measurement was undertaken at 0.6× depth from the bottom. Measured revolutions per time unit were converted into velocity by means of the calibration equation and multiplied by the area of the cross-section. Streams wider than 0.5 m were divided into several sub-sections of ca. 0.25 m length, and measurements undertaken in each. In small discharges unsuitable for impeller measurements the flow was measured by channeling the water into a vessel of fixed volume and timing the filling with a stop watch.

Samples were vacuum filtered in the laboratory within hours of collection. The filtrate was transferred to LDPE bottles and acidified (25% sub-HNO3). The filter membranes retaining the suspended particulate matter (SPM) were transferred to individual petri-dishes and stored frozen (-18°C). Filter membranes were digested using hot concentrated nitric acid (1 h, 120 °C under reflux) and centrifuged to obtain acid-extractable metals associated with the SPM. Dried sediment and spoil were subjected to hot aqua regia (4 h, 120 °C) digestion after being dried, disaggregated, sieved, (2 mm), milled (180 µm). Both filtered samples and acid extracts were analysed using ICP-MS for As, Cd, Co, Cu, Mn, Ni, Pb and Zn, following internal ISO 9001:2000 accredited protocols and using In and Ir as internal standards. Iron was analysed by Flame-AAS or ICP-OES. The limits of detection (LOD, 5σ of lowest standard, n≥5) for elements were 0.51 µg L-1 Cd, 0.40 µg L-1 Co, 3.4 µg L-1 Cu, 1.3 µg L-1 Mn, 0.54 µg L-1 Ni, 0.4 µg L-1 Pb, 2.7 µg L-1 Zn. The LOD for As in multi-elemental analysis using ICP-MS was 7.7 µg L-1; samples containing low concentrations of As were re-analysed in a single-element mode with a LOD of 0.95 µg L-1. The accuracy of the analytical methods was verified for each instrument run against NWRI (National Water Research Institute) Certified Reference Material (TM-DWS, fortified fresh water). Typical values of recovery for the certified elements in TM-DWS were 92.5% As, 99.5% Cd, 104% Co, 101% Cu, 105% Fe (ICP-OES), 109% Mn, 95.3% Pb and 95.6% Zn.

![Fig. 2. Sampling locations of adits (1, 8, 11 - 13, 15, 18, 19) and streams surveyed as point sources of mine water contamination to the River Tamar. The location of important mine waste deposits associated with the named mines are indicated (Δ). The weir separating the freshwater from the tidal reaches of the river is located upstream of sample site 9.](image-url)

The water flow in the Tamar at Gunnislake (monthly average: 2.8-3.4 m³ s⁻¹) and streams (up to 3.1 m³ s⁻¹) within the mining area (Fig. 3). Water flow changed seasonally, with higher flow rates in the Tamar, streams and adits during autumn and winter than in spring and summer.

4.2. Metal and arsenic concentrations

The lowest dissolved and particulate metal concentrations were generally observed in the upper catchment (upper Tamar, Deer, Carey, Ottery) and in the Tamar at Greystone Bridge (Table 2). The catchment of these rivers is characterised by sandstones and shales, while rivers to their south (Inny, Tiddy, Lynher, Thrushel, Lyd, Tavy) drain the ore-bearing rocks associated with the metamorphic aureole of the granite intrusions. It follows that, with respect to the main Gunnislake/Caustock mining area, dissolved concentrations of, for example, <12 µg L⁻¹ As, <17 µg L⁻¹ Cu and <9.3 µg L⁻¹ Zn and particulate concentrations of <970 µg L⁻¹ Fe, <180 µg L⁻¹ Mn and <14 µg L⁻¹ Zn can be seen as representative of the catchment background. Dissolved concentrations in the Tamar at Gunnislake were higher than at Greystone Bridge for sulphate (factor 1.5-1.7), As (1.6-10), Cu (2.6-3.9) and Zn (1.7-5.4), and during some surveys higher for Ni (0.31-4.36), Co (1-2.34), Mn (1.1-23) and Fe (0.8-18). The enrichment of SO₄²⁻, Cu, Zn, Ni and Co at Gunnislake, compared to Greystone Bridge, was highest during the October survey, at the onset of the wet season (Fig. 3), although their dissolved concentration in the Tamar at both locations and in the streams and adits decreased, probably as a result of dilution effects (e.g. stream 17: Fig. 4). This indicates that mobilisation mechanisms linked to flow and precipitation were important in determining the flux of some contaminants to the river within the Gunnislake/Caustock mining area. Increased water volume and velocity underground and at surface may cause re-suspension of precipitates, facilitate the oxidation of ore minerals and dissolution of efflorescent salts, and increase infiltration and erosion of mining waste, thereby adding to higher export of leachate and solids from abandoned mine sites. The highest enrichment of As, Mn and Fe at Gunnislake occurred in April, at the end of the wet season. Maximum particulate concentrations of Fe, Mn, Cu, Zn and Ni at Gunnislake were above the maximum catchment background, whereby the Fe levels (up to 3600 µg L⁻¹) were as high as those found in some streams and adits. Most rivers draining abandoned mines associated with the mineralisation on the periphery of the catchment and abandoned Mn mines north of the main Gunnislake/ Caustock mining area (Lynher, Tiddy, Inny, Lyd, Tavy and Walkham) carried dissolved and particulate concentration ranges similar to those in rivers representing the catchment background (upper Tamar, Deer, Carey and Ottery). The exception was river Thrushel, in which dissolved Fe, Mn, As, Co, Cu, Ni, Pb and Zn were elevated above the background. Dissolved concentrations in the Tamar at Gunnislake exceed the maximum catchment background, whereby the Fe levels (up to 3600 µg L⁻¹) were as high as those found in some streams and adits. Most rivers draining abandoned mines associated with the mineralisation on the periphery of the catchment and abandoned Mn mines north of the main Gunnislake/ Caustock mining area (Lynher, Tiddy, Inny, Lyd, Tavy and Walkham) carried dissolved and particulate concentration ranges similar to those in rivers representing the catchment background (upper Tamar, Deer, Carey and Ottery). The exception was river Thrushel, in which dissolved Fe, Mn, As, Co, Cu, Ni, Pb and Zn were elevated above the background. Dissolved concentrations in the Tamar at Gunnislake exceed the maximum catchment background, whereby the Fe levels (up to 3600 µg L⁻¹) were as high as those found in some streams and adits. Most rivers draining abandoned mines associated with the mineralisation on the periphery of the catchment and abandoned Mn mines north of the main Gunnislake/ Caustock mining area (Lynher, Tiddy, Inny, Lyd, Tavy and Walkham) carried dissolved and particulate concentration ranges similar to those in rivers representing the catchment background (upper Tamar, Deer, Carey and Ottery). The exception was river Thrushel, in which dissolved Fe, Mn, As, Co, Cu, Ni, Pb and Zn were elevated above the
catchment background, and particulate Fe concentrations up to 2200 µg L⁻¹ were observed. This was probably the result of inputs from a cluster of abandoned Mn mines in close vicinity to the sampling point, indicating a highly mineralised location.

In most adits and streams within the mining area (except 6, 7, 10, 24) the dissolved and particulate As and Cu concentration ranges were elevated above the maximum background values (Table 2). The highest levels of As (up to 560 µg L⁻¹ dissolved and 1600 µg L⁻¹ particulate) and Cu (up to 7600 µg L⁻¹ dissolved and 280 µg L⁻¹ particulate) occurred in the acidic streams 16 and 17, which also carried the highest dissolved Co (up to 270 µg L⁻¹), Ni (up to 250 µg L⁻¹), Zn (up to 1600 µg L⁻¹) and Mn (up to 5700 µg L⁻¹) concentrations observed in streams. Lead concentrations in the mining area were similar to the catchment background, with the exception of adit 1 (up to 170 µg L⁻¹ dissolved Pb), the only adit of a former Pb/Ag mine included in the survey. The highest particulate Fe concentrations (up to 7900 µg L⁻¹) occurred in the acidic streams 16 and 17, which also had increased Mn, As, Cu, Ni and Zn concentrations. A deep layer of ochreous material is suspended in the overflow, explaining the high particulate matter concentrations.

The highest metal concentrations in streams and adits were observed for Fe, Mn, Cu, As and Zn, which is consistent with the geological setting and the dominant mineral ores in this mining district. Furthermore, the highest dissolved metal concentrations occurred in waters with lowest pH values and highest conductivity and sulphate concentrations. The conditions observed in adits and streams in this study were within the wide range reported for mine drainage in other locations in southwest England (e.g. Johnson, 1986; Bowell and Bruce, 1995; Neal et al., 2005) and elsewhere (Millar et al., 1996; Gray, 1998; Baltisieri et al., 1999; Dinelli et al., 2001; Braungardt et al., 2003). As observed in other mining areas, the contaminant concentrations in mine waters were highly variable between surveys (e.g. Boul et al., 1994; Neal et al., 2005). Except for Fe, which showed no distinct trend, dissolved metal, As, sulphate and major cation (e.g. Ca) concentrations in streams and adits were higher at the beginning of the survey (July–September), decreased through the winter to reach a low in January and February, and subsequently increased through the spring (e.g. stream 17: Fig. 4). This trend has been observed in other studies of mine waters and linked to seasonal cycles affecting element mobilisation (chemical, physical, biological) and precipitation, erosion and transport of solids, as well as dilution effects

### Table 2

Ranges of dissolved and particulate metal concentrations observed in the Tamar River catchment

<table>
<thead>
<tr>
<th>Water course</th>
<th>Fe</th>
<th>Mn</th>
<th>As</th>
<th>Cd</th>
<th>Co</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper catchment</td>
<td>D 60-390</td>
<td>2.1-120</td>
<td>±12</td>
<td>±2.3</td>
<td>4.1-5.9</td>
<td>7.6-17</td>
<td>1.2-5.3</td>
<td>0.6-0.7</td>
<td>±6.4</td>
</tr>
<tr>
<td>P 230-970</td>
<td>8.0-180</td>
<td>0.44-23</td>
<td>±0.6</td>
<td>0.11-2.0</td>
<td>4.9-5.2</td>
<td>12-13</td>
<td>1.7-4.9</td>
<td>±100</td>
<td>4.2-9.3</td>
</tr>
<tr>
<td>River Tamar at Greystone</td>
<td>D 67-140</td>
<td>6.5-72</td>
<td>±4.3</td>
<td>±0.17</td>
<td>0.1-1.1</td>
<td>1.0-1.1</td>
<td>0.32-1.8</td>
<td>±0.81</td>
<td>2.5-5.6</td>
</tr>
<tr>
<td>P 170-530</td>
<td>12-39</td>
<td>±2.3</td>
<td>±0.17</td>
<td>0.1-1.1</td>
<td>1.0-1.1</td>
<td>0.32-1.8</td>
<td>±0.81</td>
<td>2.5-5.6</td>
<td></td>
</tr>
<tr>
<td>River Tamar at Gunnislake</td>
<td>D 53-140</td>
<td>7.4-96</td>
<td>2.1-9.9</td>
<td>±100</td>
<td>0.9-13</td>
<td>4.6-6.2</td>
<td>5.0-21</td>
<td>±0.46</td>
<td>3.1-28</td>
</tr>
<tr>
<td>P 42-3600</td>
<td>0.15-390</td>
<td>1.9-10</td>
<td>±0.1</td>
<td>0.03-1.7</td>
<td>1.0-6.7</td>
<td>0.16-9.7</td>
<td>0.53-1.8</td>
<td>±4.2-9.3</td>
<td></td>
</tr>
<tr>
<td>Sub-catchments in peripheral mining area</td>
<td>D 53-320</td>
<td>5.7-390</td>
<td>8.6-21</td>
<td>±0.78</td>
<td>3.4-12</td>
<td>3.7-25</td>
<td>1.1-13</td>
<td>±0.50-0.16</td>
<td>±4.6</td>
</tr>
<tr>
<td>P 44-2200</td>
<td>0.2-170</td>
<td>0.82-64</td>
<td>±0.21</td>
<td>0.05-1.38</td>
<td>0.33-3.7</td>
<td>±0.12-14</td>
<td>±0.54-0.40</td>
<td>±4.4-10</td>
<td></td>
</tr>
<tr>
<td>Streams similar to catchment background</td>
<td>D 55-62</td>
<td>±21</td>
<td>8.6-28</td>
<td>±1.1</td>
<td>0.69-12</td>
<td>3.8-57</td>
<td>2.2-19</td>
<td>±0.081</td>
<td>5.0-45</td>
</tr>
<tr>
<td>P ±21</td>
<td>1.8-3.4</td>
<td>1.2-3.5</td>
<td>±0.5</td>
<td>0.08-4.2</td>
<td>0.32-29</td>
<td>1.1-13</td>
<td>±0.51</td>
<td>0.76-2.2</td>
<td></td>
</tr>
<tr>
<td>Streams (mean pH&lt;5), affected by mine waters</td>
<td>D 55-3000</td>
<td>3.5-1000</td>
<td>8.2-340</td>
<td>±0.3-3.7</td>
<td>0.45-10</td>
<td>3.6-650</td>
<td>1.3-69</td>
<td>0.46-4.9</td>
<td>±3.8-320</td>
</tr>
<tr>
<td>P 7.4-2400</td>
<td>0.13-110</td>
<td>1.2-180</td>
<td>±0.09-5.3</td>
<td>0.05-16</td>
<td>0.26-280</td>
<td>0.1-8.9</td>
<td>0.11-8.1</td>
<td>±0.48-91</td>
<td></td>
</tr>
<tr>
<td>Streams (mean pH&gt;5)</td>
<td>D 230-3800</td>
<td>400-5700</td>
<td>9.8-560</td>
<td>10-4.6</td>
<td>12-270</td>
<td>60-7600</td>
<td>7.3-250</td>
<td>±0.46-26</td>
<td>±84-1600</td>
</tr>
<tr>
<td>P 5.0-4300</td>
<td>1.9-20</td>
<td>2.5-1600</td>
<td>±0.14-1.4</td>
<td>0.08-13</td>
<td>0.38-45</td>
<td>0.11-28</td>
<td>±0.06-13</td>
<td>±0.08-12</td>
<td></td>
</tr>
<tr>
<td>Adits (mean pH&lt;5)</td>
<td>D 53-1700</td>
<td>3.5-770</td>
<td>8.7-280</td>
<td>±10-11</td>
<td>0.51-33</td>
<td>5.6-1400</td>
<td>1.1-130</td>
<td>0.42-170</td>
<td>±3.9-2500</td>
</tr>
<tr>
<td>P 5.0-1000</td>
<td>0.27-44</td>
<td>1.0-120</td>
<td>±0.09-0.39</td>
<td>0.12-16</td>
<td>0.57-210</td>
<td>±0.13-15</td>
<td>0.12-12</td>
<td>±0.51-46</td>
<td></td>
</tr>
<tr>
<td>Adits (mean pH&gt;5)</td>
<td>D 1200-2600</td>
<td>430-2000</td>
<td>13-130</td>
<td>1-13</td>
<td>31-380</td>
<td>390-910</td>
<td>3.45-1</td>
<td>±0.51-400</td>
<td></td>
</tr>
<tr>
<td>P 800-7900</td>
<td>0.85-64</td>
<td>38-240</td>
<td>±LOD</td>
<td>±1.2-2.8</td>
<td>32-12</td>
<td>±0.13-2.8</td>
<td>±0.52</td>
<td>0.57-88</td>
<td></td>
</tr>
</tbody>
</table>

Representative of catchment background: upper Tamar, Deer, Carey, Ottery. Rivers receiving discharge from abandoned mines outside the main mining area (peripheral sub-catchments): Lynher, "fiddy, Inny, Lyd, Thrushel, Tavy, Walkham: streams and adits in the mining area categorised as for Table 1. All concentrations in µg L⁻¹. D: dissolved concentration, P: concentration associated with suspended particulate matter. Ranges quoted as ±sd show that some values were below the limit of detection (LOD). ±LOD denotes that all values were below LOD.
Table 3: Calculated annual dissolved (D) and particulate (P) flux of metals and arsenic (in kg a⁻¹) extrapolated from monthly measurements of instantaneous flow and concentrations observed in the Tamar catchment and mining area.

<table>
<thead>
<tr>
<th>Metal</th>
<th>D</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>44,000</td>
<td>1700</td>
</tr>
<tr>
<td>Mn</td>
<td>12,100</td>
<td>610</td>
</tr>
<tr>
<td>As</td>
<td>450</td>
<td>&lt; LOD</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; LOD</td>
<td>210</td>
</tr>
<tr>
<td>Co</td>
<td>810</td>
<td>280</td>
</tr>
<tr>
<td>Cu</td>
<td>2100</td>
<td>240</td>
</tr>
<tr>
<td>Ni</td>
<td>960</td>
<td>320</td>
</tr>
<tr>
<td>Pb</td>
<td>1300</td>
<td>280</td>
</tr>
<tr>
<td>Zn</td>
<td>3500</td>
<td>240</td>
</tr>
</tbody>
</table>

Water flow data at Greystone and Gunnislake provided by EA. Flux unaccounted for refers to the difference in metal/metalloid flux between Gunnislake and Greystone that was not accounted for by streams and adits surveyed upstream of Gunnislake, and is given in percent of the difference. Fluxes denoted as 'LOD' signify that all measured concentrations were below the limit of detection.

4.3. Metal and arsenic fluxes

The annual total (dissolved + particulate) flux of elements from all surveyed adits and streams amounted to ca. 13,000 kg a⁻¹ Fe, 4300 kg a⁻¹ Mn, 4200 kg a⁻¹ Cu, 3600 kg a⁻¹ Zn, 1400 kg a⁻¹ As, 400 kg a⁻¹ Ni, 350 kg a⁻¹ Co, 43 kg a⁻¹ Pb, and 6.6 kg a⁻¹ Cd (Table 3). Of this, ca. 50% of Fe, As and Pb was carried in the particulate phase, while overall, 83% of Co and ≥88% of the Mn, Cd, Cu, Ni and Zn flux was dissolved. Of the 25 sources surveyed, more than 65% of the total input of Fe, Mn, As, Co, Ni, Cu and Zn into the Tamar was carried by adits and streams into the fresh water zone upstream of Gunnislake, the remainder entered the estuary directly from sources 1-9 (Fig. 2).

Seven specific sources (Fig. 5) accounted for more than 75% each of the total (dissolved + particulate) annual Fe, Mn, Cu, Zn, As, Ni, Co, Pb and Cd flux determined in the 25 adits and streams. The signal strength for each metal differed between these dominant sources, according to the source mineralogy and pathways involved. For example, the circum-neutral stream 2 collects drainage from several mine workings in an area of diverse mineralogy comprising ores of As, Cu, Zn, Fe, Mn, Pb, Sn, Ag and W, among others. Although the concentrations of contaminants were moderate, because of its high water discharge, stream 2 was an important contributor of dissolved Cu and Zn and particulate Fe to the Tamar. The acidic ochreous adit 13 is connected to a Cu mine and a largely unsuccessful exploration mine for Cu and W (Dines et al., 1956a), and despite of its low flow rate, was an important source of As, Fe and Cu. Streams 16, 17 and 21 are associated with Devon Great Consols (DGC) mine (Cu/As) and carry run-off, leachate and erosion products from different mine waste
deposits, as well as adit outflow (County Councils). The acidic stream 16 combines leachate from a mine waste deposit and the main adit of DGC and was one of the major source of As, Fe and dissolved Zn measured. Despite its low flow rate (2.6-26 L s⁻¹), the acidic stream 17 is the dominant point source of dissolved Cu in the mining area. The stream flows directly into the mine and was sampled near its confluence with the Tamar. High flow rates, combined with moderately high concentrations of contaminants make this stream an important source of Cu, Zn, Zn and Cu to the Tamar. The adits and streams shown in Fig. 5 should receive priority attention when considering remediation measures within a catchment management plan, whereby the nature of diffuse and point sources contributing to the fluxes in streams will have to be researched in detail.

The flux of dissolved and particulate elements in the Tamar at Greystone was estimated by extrapolation to seasonal flux values (June-August, September-November, December-February, March-May) from the four catchment surveys and average monthly river flow data provided by the EA. Table 3 shows that the River Tamar at Greystone carried larger amounts of Fe, Mn, Co and Ni into the mining area than the streams and adits surveyed. High flow rates of particulate Cu is consistent with this metal's importance as a crustal element and the elevated Fe concentrations in run-off from peat-rich upland areas (Mays et al., 2008). During times of low flow (July survey), the dissolved flux of Fe at Greystone was higher than at Gunnislake, indicating that attenuation within the river, for example through adsorption onto particles or precipitation, took place, which overall could have resulted in an under-estimation of the Fe flux in the mining area. Contributions to the metal flux at Gunnislake originating from the catchment at Greystone were similar to those from the streams and adits in the Calstock/Gunnislake area for As, Cu, Pb and Zn indicating that important inputs of metals/metalloids occurred upstream. The likely sources of these are multi-metallic ore deposits and associated abandoned mines (e.g. Mn, Cu, Pb/Ag, Sn, Dines et al., 1996a: Robinson, 1995) in the catchments of tributaries to the Tamar upstream of Greystone (e.g. Thrushel, Lyd), which merit further investigation.

By applying a simple mass balance calculation for dissolved and particulate fluxes (subtraction of flux at Greystone from that at Gunnislake yields total flux between these points, from which fluxes calculated for adits/streams were subtracted), the flux not accounted for by the monthly surveys of streams and adits between Greystone and Gunnislake was calculated. The results show that for substantial proportions of dissolved and particulate contaminants (25%), the sources remained unidentified in this work. Although the streams and adits included in this survey were not comprehensive, the authors believe that all important point sources and streams draining sub-catchments were covered. Therefore it is likely that a large part of the missing flux originates from diffuse sources directly affecting the Tamar channel, such as contaminated groundwater injection in to the hyporheic zone, input of leachate and particles through erosion of mine waste, mobilisation/dissolution of bank sediment and effluent salts and in-stream mobilisation from metal-rich particles. Similar conclusions have been drawn from other studies evaluating the relative importance of diffuse and point sources of metals in abandoned mining areas (e.g. Mays et al., 2005). Notwithstanding the uncertainty associated with the flux estimation, considering the magnitude of the flux not accounted for, it is important to investigate the nature of diffuse sources in river catchments affected by metal mining in order to provide the basis for developing effective remediation strategies.

The dissolved flux at Gunnislake was higher during the wet season (October-May) for all elements except As, and for Fe, As, Cu and Co the same was true for the particulate flux. This can be partially attributed to the greater increase in river flow compared to the decline in element concentrations. For the Tamar, the ratio of average water discharge in wet to dry season was 6.4, while the concomitant decrease in element concentration was below 1.8 for all metals. Furthermore, a trend towards higher dissolved element fluxes during periods of higher flow was observed in most streams within the mining area, irrespective of their average flow rate (e.g. streams 17 and 25, Fig. 6). The potential impact of increased winter rainfall, as observed in recent years in north Atlantic coastal regions (Klein Tank et al., 2002) and as is predicted in some climate change scenarios (Wilby et al., 2006: Alcamo et al., 2007), on the element export from abandoned mine sites should be investigated.

The limitation of this method of flux estimation lies in the assumption that one monthly survey (or in the case of the catchment rivers, a quarterly survey) provides representative data for concentrations and water flow. For example, the first flash flood events monitored, as many of the sampling sites would be rendered inaccessible as a result of flooding. However, the erosion of metal-bearing particles from deep adits, mine or processing waste, and bank erosion during flood events may contribute appreciably to the contamination load in this area, as several mine waste deposits are located on or near the banks of the Tamar and its tributaries (e.g. at Gunnislake Clitters, Okeotor and New Consols). and streams 14, 16, 17 and 25 run through mine waste piles. At stream 25, sediment prone to bank erosion contained up to 186,000 mg kg⁻¹ As, 2000 mg kg⁻¹ Cu and 148,000 mg kg⁻¹ Fe. Visits to sampling locations following heavy rain events revealed loss of sediments (grained sediments, precipitates and ochre) from adits and streams, as well as evidence of erosion (e.g. deepening of gullies) and export of solids from the surface of mine spoil heaps (e.g. fan of material at foot of heap). Evidence of erosion as diffuse source of mine contamination has been provided for similar river systems in Cornwall (e.g. Fal estuary, Pirrie et al., 2003). Here, small grains of the dominant ore materials (e.g. arsenopyrite, chalcopyrite), representing mine tailings too fine to be recovered during mineral processing at the time, as well as altered material (e.g. by oxidation, precipitation) minerals have been documented as important sediment fraction. Furthermore, the authors showed that metal concentrations in Cornish river sediments are akin to concentrations observed in recent years in north Atlantic coastal regions (Klein Tank et al., 2002) and as is predicted in some climate change scenarios (Wilby et al., 2006: Alcamo et al., 2007), on the element export from abandoned mine sites should be investigated.
commonly found in mine tailings around the world (e.g. Rio Tinto mines), indicating the importance of sediments as sources of secondary, diffuse contamination to the water column. In addition, occasional collapses (e.g. River Cat, winter 2006) within abandoned mines can result in the discharge of substantial volumes of acid mine drainage carrying suspended ochreous material. High concentrations of metals/metalloids have been observed in ochreous sediments associated with the adits in the studied mining area (e.g. up to 28,000 mg kg\(^{-1}\) As and 4500 mg kg\(^{-1}\) Cu and 370,000 mg kg\(^{-1}\) Fe), but the metal input due to such events remains difficult to estimate.

4.4. Impact on the estuarine environment

Coastal systems are important ecosystems because of their high biodiversity, productivity and their function as a recruitment zone for many marine species. This function makes them vulnerable to anthropogenic contaminants, especially as juveniles of many species are more susceptible to toxins than their adult counterparts (e.g. bivalve molluscs: Beiras and Albentosa, 2004; Calabrese et al., 1973; His et al., 1999). Estuaries are highly dynamic systems in which rapidly changing chemical, biological and physical process interact to control the concentration and transport of constituent elements (Millward, 1995; Millward and Liu, 2003). In the Tamar (Ackroyd et al., 1986; Morris, 1986) and other estuaries (Achterberg et al., 2003; Parkman et al., 1996; Pirrie et al., 2003), particles and sediments have been found to form important sinks for contaminants released through mining activities, such trace metals. On the other hand, the re-mobilisation of metals and metalloids from (re-)suspended sediment and pore waters has been observed in the mid-Tamar estuary (Knox et al., 1984) and elsewhere (e.g. Braungardt et al., 2003), leading to a localised addition of contaminants to the dissolved phase. According to this study, the estuary received approximately 440 t Fe, 81 t Mn, 16 t Cu, 14 t Zn, 6.3 t Ni, 5.6 t As, 4.2 t Co and 260 kg Pb in dissolved and suspended form from its catchment during the study period. This contributed to the contamination and re-mobilisation with the re-working of the fine-grained sediment (Grabemann et al., 1997) results in high levels of contaminants in sediments throughout the estuary. For example, concentrations of 0.7–3 mg kg\(^{-1}\) Cd, 270–580 mg kg\(^{-1}\) Cu and 190–500 mg kg\(^{-1}\) Pb have been reported for the sediments near the Tamar road bridge (lower value, Fig. 1) and in the upper estuary (upper value), respectively (Langston et al., 2003). These values exceed the Interim Marine Sediment Quality Guidelines (IMSQ) for Cd, Cu and Pb and Probable Effect Levels (PEL) on biota and/or ecosystem for Cu and Pb. The IMSQ and PEL for As, Hg and Zn are also exceeded in the Tamar estuary (Langston et al., 2003). The continued impact of the mining legacy on estuarine ecosystem quality was indicated by Clifton and Hamilton (1979), who reported that concentrations of Cu, Pb and Zn in a dated sediment core from the lower Tamar estuary had not decreased (in contrast to the mining-related Si signal) by the late 1970s, a century after the peak of Cu mining and several decades after the last large-scale mining activities in the catchment ceased. Studies of metal levels in Nereis diversicolor, a relatively tolerant polychaete, and in Fucus vesiculosus, a marine macroalga, have shown accumulation of some metals (e.g. Cu, Zn, Cd and/or Pb) within the Tamar estuary system above background concentrations (Langston et al., 2003). Of particular concern regarding its toxic effects on marine biota is Cu (Brand et al., 1986; Sharp and Stearns, 1997; Grout and Levington, 2001). The dissolved Cu levels in the estuary only occasionally exceed the Environmental Quality Standard (5 µg L\(^{-1}\)) for the protection of saltwater life. However, a recent study (Money et al., submitted for publication) of the ecotoxicological impact of water quality using a biological assay looking at the toxicity of the embryo of the Pacific Oyster, Crassostrea gigas, found a 100% toxic response in the middle reaches of the Tamar estuary, while the bioassay response was lower at the mouth of the Tamar. Although the toxic response in this study was induced by the complex mixture of compounds present in the water column, including agrochemicals and other organic compounds, the toxic concentrations of Cu, Pb and Cd in estuarine waters were inferred to have played a contributing role.

5. Conclusions

The long-term input of metal mining-related contaminants into the River Tamar and estuarine system has resulted in concentrations of elements, such as Cu, As and Zn, that locally exceed environmental quality standards and/or guideline levels for water and/or sediments. Environmental metal concentrations alone pose a threat to ecosystem functioning and are likely to cause failure of this system to meet the environmental objectives of the Water Framework Directive. This study has highlighted seven priority sources of mining-related contamination that should be the focus for a catchment management strategy. Six of these sources are indeed streams transporting water and solid materials from several contamination sources (point and diffuse) within their sub-catchment. This supports another outcome of this study, namely the importance of diffuse sources in contributing to the metal flux within this catchment. As it is highly likely that similar observations can be made in other mining areas in the Southwest, the investigation of the nature of diffuse pollution sources in the Tamar system is of great importance and indeed is addressed in a current project.

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County Council. Surveys of the hydrology of mines within this area are available from the Devon and Cornwall County Councils, respectively.

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