2016-06

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Beane, SJ

http://hdl.handle.net/10026.1/4663

10.1016/j.chemosphere.2016.03.022
Chemosphere
Elsevier BV

Abandoned metal mines and their impact on receiving waters: A case study from Southwest England

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Key words: metals, contamination, mines, hotspots, assessment, speciation

Abstract: Historic mine sites are a major source of contamination to terrestrial and river environments. To demonstrate the importance of determining the significance of point and diffuse metal contamination and the related bioavailability of the metals present from abandoned mines a case study has been carried out. The study provides a quantitative assessment of a historic mine site, Wheal Betsy, southwest England, and its contribution to non-compliance with Water Framework Directive (WFD) Environmental Quality Standards (EQS) for Cd, Cu, Pb and Zn. Surface water and sediment samples showed significant negative environmental impacts even taking account of the bioavailability of the metal present, with lead concentration in the stream sediment up to 76 times higher than the Canadian sediment guidelines 'Probable Effect Level'. Benthic invertebrates showed a decline in species richness adjacent to the mine site with lead and cadmium the main cause. The main mine drainage adit was the single most significant source of metal (typically 50% of metal load from the area, but 88% for Ni) but the mine spoil tips north and south of the adit input added together discharged roughly an equivalent loading of metal with the exception of Ni. The bioavailability of metal in the spoil tips exhibited differing spatial patterns owing to varying ambient soil physico-chemistry. The data collected is essential to provide a clear understanding of the contamination present as well as its mobility and bioavailability, in order to direct the decision making process regarding remediation options and their likely effectiveness.

Key words: metals; mines; pollution; bioavailability; risk; sources

1. Introduction

Historic mining for metals in Europe dates back to pre-Roman times, but with notable exceptions most have ceased operations. These abandoned sites are an important source of environmental contamination with elevated levels of toxic elements often recorded in soils and adjacent river systems (e.g. Pirrie et al., 2003; Rieuwerts et al., 2014; Hudson-Edwards et al., 1996). For example, in many areas of the UK, such as southwest England and other parts of Europe, evidence of uncontrolled historic mining activities has shown to have a large and lasting impact (Galan et al., 2003; Nieto et al., 2006; Rieuwerts et al., 2009). Discharge of metal rich water from abandoned mines to surface and groundwater, and contamination of soils and sediments through associated industrial activity are among the highest recorded in the UK. For example, sediments in the regions Camel, Erme, Fal, Fowey, Gannel and Tamar estuaries are amongst the most contaminated in the UK for cadmium (Cd), lead (Pb), zinc (Zn) and copper (Cu) (Environment Agency, 2008a).

As a consequence, the legacy of historic mining in Europe poses a significant management issue and a potential barrier to achieving new Environmental Quality Standards (EQS) set under the EU Water Framework Directive (WFD - 2000/60/EC) for metals such as Cu, Cd, Cr, Hg, Ni and Pb. For example, 72% of failures to achieve the Cd quality standard in UK freshwaters are found in mined areas (Environment Agency, 2008b) and for the Specific Pollutants (UKTAG, 2008) with EQS set by the UK (Cu, Zn, manganese (Mn), iron (Fe) and chromium (Cr)) mine impacted catchments contribute an estimated 9% of rivers at risk in England and Wales and 2% in Scotland (Environment Agency, 2008b).

Dissolved metals and metalloids may enter the surface waters from point sources such as mine adits and from diffuse sources; mainly rainwater which has percolated through spoil heaps and leached metals and metalloids therein (Galan et al., 2003; Nieto et al., 2006; Rieuwerts et al., 2009). Metals in runoff from spoil heaps may enter receiving waters as dissolved minerals or adsorbed to particulates, which are transported downstream and deposited by river processes (Jarvis et al., 2006). Over time, suspended sediments will settle in the river or estuary, leading to a gradual accumulation of metals in sediments. Metals within river systems are subject to varying physico-chemical conditions, transferring between the dissolved and solid phases of the aquatic environment, and depending on conditions, may move from a relatively refractory phase into phases with greater mobility and bioavailability, thus impacting on the ecology present (Klerks and Levinton, 1989).

Sediments acting as reservoirs for contaminants in the aquatic environment have been widely documented (e.g. Hartl, 2002; Pirrie et al., 2003; Sasaki et al., 2005 and Rainbow et al., 2011) and can as a result cause negative impacts to benthic ecology. Subsequently, macroinvertebrate biological indices have become a fundamental component of ecological monitoring in the UK and Europe (Metcalfe 1989; Hering & Sandin, 2004). To meet the UK's obligations under the WFD, the UK has developed the River Invertebrate Classification Tool (RICT) which runs the RIVPACS IV software (Wright et al., 2000; SEPA, 2015).

A cost-effective strategy to deal with the pollution from abandoned metal mines cannot be developed until the extent of the contamination is understood. The UK has prioritised 226 waterbodies in England and Wales where pollution from mines is the main cause of EQS failures under the WFD (Environment Agency, 2012; Defra, 2012). However, in few cases is there a clear quantitative understanding regarding the significance of the point and diffuse sources of mine inputs to receiving waters and their relative bioavailability (Banks & Palumbo-Roe, 2010; Mighanetara et al., 2009; Mayes et al., 2008). Speciation-based methods are available to characterise the form of metals within soils and sediment based on sequential extraction to determine which fractions including exchangeable, carbonate, reducible, oxidisable and residual phases the metals are associated with (Konradi et al., 2005; Passos et al., 2011; Zhong et al., 2011 and Rieuwerts et al., 2014). Weakly bound metal, in particular, will be more mobile and potentially bioavailable (and therefore toxic) and so determination of this fraction allows a more detailed site assessment to identify hotspots and risks to the terrestrial and aquatic ecology of the area. Furthermore, models are available which provide site specific predicted no effect concentrations for terrestrial organism exposed to potentially toxic elements including lead, nickel, copper and zinc in soils based on ambient conditions of cation exchange capacity, pH, clay content and organic carbon fraction (Arche, 2014).

Until recently, surface water EQS have been derived from hardness-based corrections as a surrogate for metal bioavailability. Metals related research has significantly added to the understanding of physico-chemical influences on metal speciation (e.g. Pettersson et al. 1993; Vink 2002) and the development of biotic ligand models (e.g. Dixon. 1980; Meyer et al., 1999: Santore et al., 2002). These models enable the prediction of bioavailable concentrations based on a combination of the physico-chemical properties of water and ecotoxicological data (Comber et al., 2008). By accounting for bioavailability, it is possible to provide the most environmentally and ecologically relevant metric for metal risk. This approach has led to new aquatic EQS being derived at an EU levels for Pb and Ni and in the UK for Cu, Mn and Zn (Table A1 of supplementary data). Proposed Predicted No Effect Concentrations for soils have been developed taking account of a combination of pH, organic carbon, % clay and cation exchange capacity for Pb, Cu, Zn and Ni (Arche, 2014).

It is therefore now possible to estimate the chemical availability, and hence potential bioavailability, of metals in all relevant environmental media at a contaminated site. This potential has been tested here in combination for the first time using a contaminated mine site as a case study to demonstrate the benefits of using such an approach to identify hotspots of bioavailable metal most likely to cause negative impacts to biological receptors. Although not comprehensive from a temporal point of view, sufficient samples were taken over a 6 month period to provide excellent spatial distribution and to demonstrate the benefits of the approach when considering contaminated land remediation.

The main objective of the research was to identify and propose a risk assessment framework utilising available methods (chemical fractionation and modelling) capable of estimating the potential bioavailability of metals in soil, spoil, sediment and water at a contaminated site and demonstrate its benefits via a case study. The case study was based at Wheal Betsy an abandoned silver-lead mine which has been shown to be contaminating Cholwell Brook, a tributary of the Tavy (Figure 1). Specific objectives to achieve these aims were to:(1) Utilise chemical and model-based methods to determine the mobility and potential bioavailability of key metals in soil, spoil, sediment and water (2) identify the major sources and pathways of heavy metal contamination into surface waters using spot samples and apportioning loads where possible; (3) demonstrate how impacts on receptors may be measured by using benthic-macroinvertebrates as biological indices..

2. Materials and Methods

2.1 Study area

The study was conducted at Wheal Betsy, a former Pb-Ag mine on a north-south lode of the Culm Measures (shales and thin sandstones) located on the north-west edge of Dartmoor, Devon, UK (Ordnance Survey grid reference SX 51012 81385). Records indicate that over its operation lifetime (1806 to 1877), 400 t of Pb and 113 kg of Ag were mined and processed on site (Booker, 1967). Mineralogy can be divided into three areas covering 59,300 m^3 Turner (2011); (1) the northern slopes dominated by steeply sloping spoil tips, comprising of coarse gravels, pebbles and cobbles; (2) the southern slopes which are a collection of finely grained spoil tips, varied in colour (yellow clays, orange sands and grey slates) and typical of mineral processing and; (3) the stream valley bottom. Cholwell Brook flows south down a steep valley through the highly contaminated areas of mine waste, and then into the River Tavy 3 km downstream, a main tributary of the River Tamar which flows into the English Channel at Plymouth. The mine's main adit and spoil tips at Wheal Betsy are an important source of Cd, Cu, Pb and Zn.

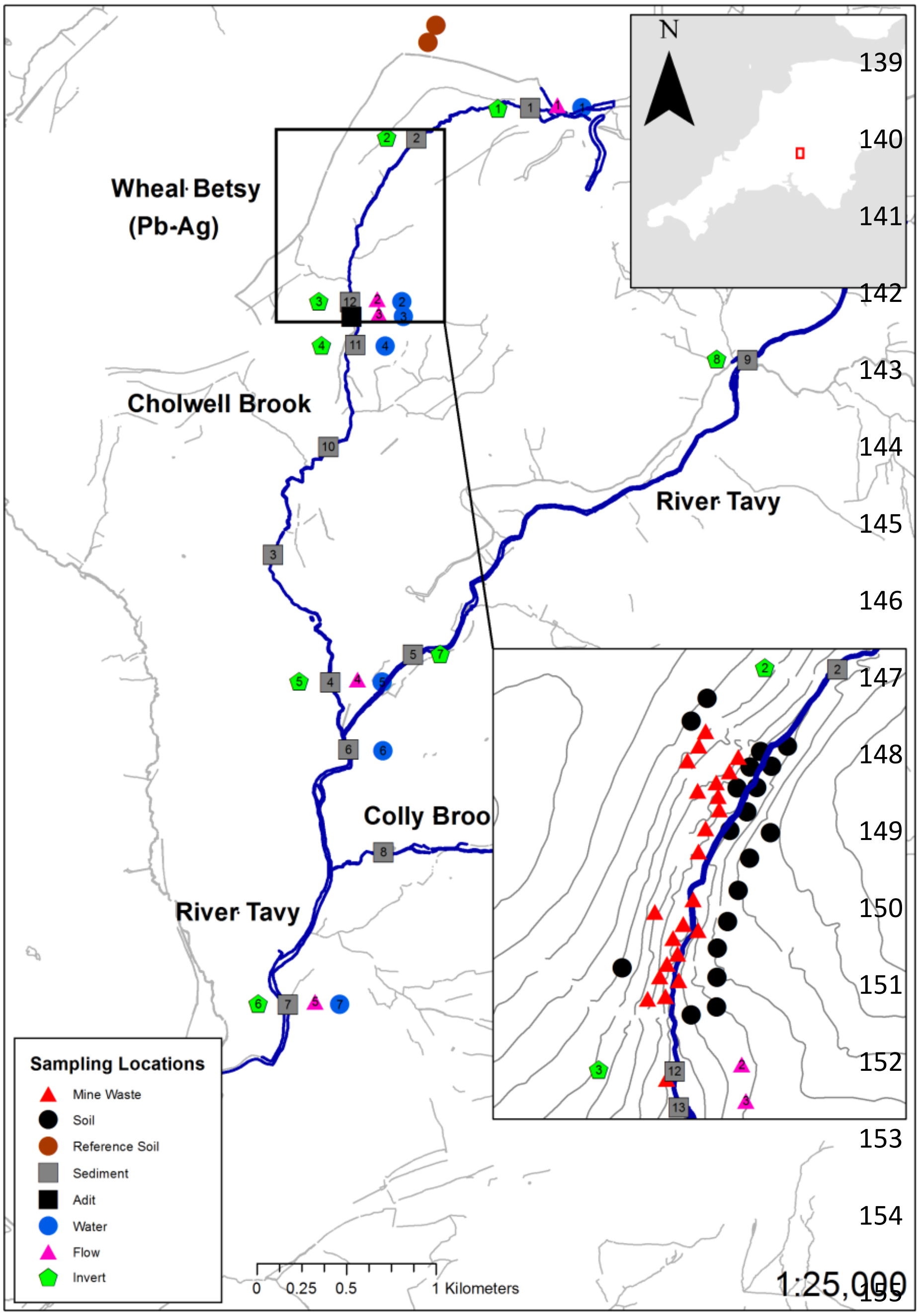

Figure 1 Sampling locations from Wheal Betsy mine site and the Cholwell Brook, Colly Brook and River Tavy. Location of point discharge from adit indicated by ■. Numbers on markers correspond to sample no. and locations.

2.2 Sampling protocol and sample treatment

2.2.1 Soil, mine waste and stream sediment sampling

Twenty-five mine waste samples were collected from spoil heaps and waste material and twenty soil samples of topsoil in and around the area (Figure 1, and Table A2 of supplementary material). In addition, two soil samples were collected from Dartmoor away from any recorded mining activity and used as a control for background concentrations. At each sampling site, five sub-samples were taken from the centre and each corner of a square metre grid to 15 cm depth using a stainless steel trowel. Nine sediment samples were collected at locations indicated by squares in Figure 1 along the Cholwell Brook from its headwaters on Dartmoor, through the mine waste to its confluence with the River Tavy. An additional three sediment samples were taken from the Colly Brook and River Tavy, and a single sample from Wheal Betsy adit for comparative purposes (Table A3 supplementary Material). All samples were stored in strengthened paper (“Kraft”) sample bags.

2.2.2 Sample treatment and measurement of physico-chemical properties

Once returned to the laboratory, all samples were dried at 50°C for one week until constant weight was obtained. Standard methods were used for determination of soil properties. For pH, cation exchange capacity (CEC), loss-on-ignition (LOI) and total carbon content, dried samples were gently disaggregated with a pestle and mortar and passed through a 2 mm stainless steel sieve (particles >2 mm were removed). For pH analysis, 4 g of each sample (<2 mm fraction) were shaken in 10 ml of de-ionised water in a 25ml centrifuge tube and left over night, the pH of the supernatant was measured using an Oakton Acorn series pH 6 meter (glass electrode), calibrated at pH 4.0 and 7.0. LOI and total carbon content analysis followed the method developed by Heiri et al (2001). CEC was measured using US Environmental Protection Agency method 9081 (United States Environmental Protection Agency, 2000) employing a methane flame photometer Corning 400. For sequential extraction analysis, a sub-sample of particles <2 mm were reduced sieved to 180 µm and 125 µm size respectively and stored separately.

2.2.3 Water sampling, physico-chemical properties and flow measurement

Sampling sites (Table A3 supplementary material) were coordinated in partnership with the Environment Agency (EA) as part of their routine environmental monitoring and assessment for mine impacted catchments. Seven samples of stream water were collected along the Cholwell Brook from its headwaters on Dartmoor to its confluence with the River Tavy, 3 km downstream, on two separate occasions: April and June 2014 (Figure 1). Data for September and October 2013 were supplied by the EA. Water samples were collected in two 250 ml polyethylene bottles (of which one sample was filtered through a 0.45µm cellulose acetate membrane) and sent to the Environment Agency's UKAS accredited ISO/IEC 17025:2005 National Laboratory Service for chemical analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Optical Emission Spectrometry (ICP-OES). Duplicate samples and blanks were included at each sampling event for quality control. Conductivity, pH and dissolved oxygen (DO) were measured in situ using a calibrated multi-parameter meter (Hanna HI9024/5). For suspended solids, an additional water sample was collected in a 1 litre acid-washed bottle following the methodology outlined by Environment Canada (1979). The velocity of water was determined using a Valeport Braystroke BFM002 flow meter with a small impeller at the centre of the stream and at a depth approximately one third from the bottom of the streambed and at a point of minimal turbulence. Combining velocity measurements with the stream cross-sectional area allowed conversion to m^3 s^{-1} which was then used to calculate metal loads within the catchment. The contaminant load distribution along the study stream helped to identify sources of pollution. Metal bioavailability was predicted using Biotic Ligand Model (BLM) based screening tools (Bio-Met, 2014) to derive site specific EQS for Pb, Zn, Mn and Ni.

2.2.4 Macro-invertebrate sampling and analysis

Sampling sites (Figure 1) were chosen in accordance with EA protocol for the routine monitoring of benthic invertebrates as part of the WFD. Six invertebrate samples were collected using BS EN 27828:1994, ISO 7828 – 1985 from shallow-flowing waters by disturbing the substratum with the feet ('kick sampling') and upstream of a hand net (with a mesh size 1 mm) held vertically on the riverbed and preserved in industrial methylated spirits. Identification of benthic invertebrates was assessed to species level by an experienced EA freshwater biologist. The RICT predictive model was then used to generate an 'expected' fauna from measured environmental variables including altitude, slope, flow, velocity, distance from source, width, depth, alkalinity and bed sediment typre (boulder, pebble, sand and silt fractions) (see SEPA, 2015 for further details). A set of unique biotic indices were then calculated for the 'expected' and 'observed' fauna and compared using the Ecological Quality Ratio (EQR) to determine the ecological status. (Table A4 supplementary material). Macroinvertebrate data was analysed using De-trended Correspondence Analysis (DCA) using R Version 3.1.1 software and used to produce a 2-dimensional 'Decorana' graph using community assemblage at each site versus total metal concentrations in water and sediment to assess, by comparison, the impact from heavy metal contamination on benthic invertebrate communities.

2.3 Sequential extraction and analysis

2.3.1 Reagents and materials

Analytical grade reagents (Aristar/PrimarPlus Trace) and high purity (MQ water) obtained from a Milli-Q system (Millipore, 18.2 MΩ cm^{-1} at 25ºC) were used to prepare all aqueous solutions. All plastic and glassware were pre-washed in hydrochloric acid (10% v/v) for 24 hours and then rinsed thoroughly with Milli-Q water. The sampling and analytical procedures incorporated a strict quality control programme using reagent blanks, triplicate samples (10 %) and certified reference materials (including CRM 701 for sediment from SM&T). Check standards were used at regular intervals to ensure analytical accuracy.

2.3.2 Instrumentation

Analysis was of water and extracted particulate samples at mg L^{-1} levels was achieved using a Thermo Scientific™ iCAP™ 7400 ICP-OES with a mass-flow controlled nebuliser gas flow for long-term signal stability, across a wavelength range of 166 – 847 nm. For samples requiring lower limits of detection (µg L^{-1} range) a Thermo Scientific XSeries 2, ICP-MS was used with a collision cell to reduce interferences. The limits of detection (LOD) for multi-elemental analysis using ICP-OES were 30 µg L^{-1} Fe, 10 µg L^{-1}, Mn and 1 µg L^{-1} Ca. The LOD for elements using ICP-MS were 1 µg L^{-1} Cu, 2.0 µg L^{-1} Pb, 0.5 µg L^{-1} Cr, 0.1 µg L^{-1} Cd, 1 µg L^{-1} Ni, 5.0 µg L^{-1} Zn, 10 µg L^{-1} Al. An MSE Centaur 2, was used for all centrifugation at 4000 rpm, and a Stuart SSL2, 25- 250 rpm, linear reciprocating end-over shaker was used.

2.3.3 Sequential extraction

The modified sequential extraction scheme proposed by Rauret et al. (2001) for the Standards, Measurements and Testing programme of the European Union (SM&T – formerly BCR) and detailed in Rauret et al. (1999) was used for all solid samples. The exchangeable / acid soluble fraction (F1) is indicative of metals that are most readily leached and therefore, present the greatest risk to the environment. The reducible fraction (F2) represents the content of metals bound to Fe and Mn oxides that could be released under reducing conditions. The oxidisable fraction (F3) reflects the amount of metal bound to sulfides and organic matter, which would be released into the environment under oxidising conditions. The residual fraction (R) contains metals with a strong association to the crystalline structure of minerals and is considered to be inert in the environment. According to Rubio et al.

(2010), metals with anthropogenic sources are mainly found in the first three fractions, while metals with lithogenic origins are found in the residual fraction.

Soil, mine waste and sediment samples (1 g, <180 µm) were sequentially extracted for four operationally-defined fractions in 50 ml centrifuge tubes and subjected to the following extraction regime:

(F1) exchangeable/acid fraction (surface bound metals to carbonates) – soil sample extracted with 40 ml of acetic acid, 0.11 M, shaken end to end at 30 rpm for 16 h, room temperature;

(F2) reducible fraction (bound to Fe/Mn oxides, oxyhydroxides) – residue from step one extracted with 40 ml hydroxylammonium chloride, 0.1 M, pH adjusted to 1.5 with 25 ml nitric acid, shaken end to end at 30 rpm for 16 h, room temperature;

(F3) oxidisable fraction (bound to organic matter and sulphides) – residue from step 2 digested in 10 ml hydrogen peroxide, 8.8 M (30%) at room temperature for 1 hr with occasional manual shaking. Mixture heated to 85 ºC for 1 h or longer (water bath) until volume reduced to 3ml. Double extraction was repeated twice, followed by an addition of 50 ml ammonium acetate, 1.0 M, adjusted to pH 2 with nitric acid, shaken end to end for 16 h, room temperature; and

(R) residual fraction (crystal lattice of original mineral, identified as 'inactive' fraction) – the residue from step 3 was used to provide a pseudo-total concentration and digested in 10 ml *aqua regia* (3:1 v/v HCl: HNO_3, 120ºC, 1.5 h) in a 50 ml glass beaker covered with a watch glass, and is assumed to be the difference between total concentration and the secondary-phase fraction (SPF), the sum of F1, F2, and F3. The SPF is often referred to in the results and discussion as the potentially-mobile fractions, and is considered potentially hazardous to organisms in the aquatic environment. After each extraction, separation was done by centrifugation at 3000 rpm for 20 minutes and the supernatant carefully transferred to universal acid-washed bottles, and stored at 4 ºC before analysis by ICP-OES. Procedural blanks were below the LOD.

Analysis of CRMs (Table A5 supplementary material) revealed a general trend for a negative bias (i.e. lower values than the certified value) in step 1 and step 3; however statistical analysis using the two sample t-test observed that the values of certified and measured fractions of CRM 701 do not differ at the 99.9% ($p<0.001$) level of confidence, except in the first step for Cr, Cu and Pb and the third step for Cd, Ni, Pb and Zn. The sum of metals extracted from step 4 were added to F1, F2 and F3 to provide a pseudo-total concentration with >92% recovery recorded for all metals except Ni, with a recovery of 88%. The extractable mass fractions recorded were similar to those in Horváth et al. (2010), with negative bias in step 1 for Cr, and step 3 for Ni and Zn (Table A5 supplementary material). Fernández et al. (2004) also reported discrepancies and reliability issues when using the BCR modified method with irregular recoveries for Cr, Cu, Ni and Zn, similar to those experienced in this study.

2.4 Environmental Quality Standards

2.4.1 Water Quality Standards

The Biotic Ligand Model principle was applied to the water data using the BioMet tool to determine site specific EQS for Cu, Ni Zn, Mn which required inputs of dissolved Ca, dissolved organic carbon (DOC) and pH (BioMet, 2014). An EQS correction for the Pb EQS was achieved using the BLM screening tool (Arche, 2014).

2.4.2 Soil Quality Standards

Soil quality standards are established for human health as part of contaminated land reclamation requirements, but recently a model for predicting no effect concentrations has been produced for terrestrial ecology under REACH (Smolders et al., 2009) and is available for downloading for free (http://www.arche-consulting.be/). The spreadsheet model required inputs for pH, organic carbon content, clay content, effective cation exchange capacity and derives site specific PNECs for Zn (added to background), Cu, Co, Mo, Ni and Pb. A generic value of 1.1 mg kg^{-1} is used for Cd.

2.4.3 Sediment Quality Standards

There are no standardised EU sediment quality standards. Consequently the established values derived by Environment Canada were used for assessing sediment impacts for the metals. The lower value, referred to as the threshold effect level (TEL), represents the concentration below which adverse biological effects are not expected to occur. The probable effect level (PEL), defines the level above which adverse effects are expected to occur frequently (CCME, 2001). Risk Characterisation Ratios (RCR) have been calculated based on observed concentrations expressed as a fraction of the PEL for either exchangeable metals, to represent bioavailable fractions or total metal to show a comparable risk if bioavailability is not taken into account (data to total RCRs show in supplementary data).

3. Results & Discussion

To demonstrate the advantages of taking account of metal bioavailability in environmental risk assessments, two datasets are shown in the following sections, one utilising total metal concentrations and the other bioavailable metal based on readily available measurements or modelling outputs. Consequently, all concentrations are normalised to the risk characterisation ratio (RCR), in other words, the measured metal concentration (total or bioavailable) divided by the quality standard. Any values greater than 1, suggest a negative impact occurring within the matrix, decreasing RCRs suggest diminishing risk.

3.1 Physico-chemical characteristics of soil, mine waste and stream sediments

The general physico-chemical properties of the soil, mine waste and sediments are critical in controlling the speciation and fate of the metal present. Without this data, it would not be possible to predict the bioavailability of the metal within the spoil and soil or plan effective remediation. Table 1 shows that reference soils used as a controls for background concentrations in this study were naturally acidic (pH 4.3 – 4.4), characteristic of the acidic permeable upland soils of Dartmoor, with high organic matter content (LOI) and CEC. Soil samples collected from around the mine site exhibited similar characteristics with high LOI (19.3%) and CEC (27.6 mEq 100 g^{-1}) and pH in the range 4.50 to 6.56. CEC was significantly correlated (<0.001) with LOI, illustrating the importance of organic matter as an ion exchanger. Due to the heterogeneity of mine waste samples and varying composition of the western and southern slopes and limited vegetation cover, typically low values were reported for CEC and LOI. Mean pH values (pH 4.49) for mine waste samples were low, characteristic of low OC content, oxidation of sulphide minerals within the spoil heaps and/or lack of neutralising capacity. Stream sediments were found to have the lowest LOI (3.37%) and CEC (8.42 mEq 100 g^{-1}), with a mean pH of 6.0. In contrast, a single sample of sediment, taken from Wheal Betsy adit recorded the highest CEC and high LOI, which is attributed to the a build-up of organic matter from surrounding woodland.

Table 1. Summary of physico-chemical characteristics of soil, mine waste and sediments.

Sample	Statistical Analysis	pH	LOI (%)	CEC (mEq 100 g^{-1})
Soil (*n* – 20)	Mean	5.93	16.1	27.6
	Standard Deviation	0.58	5.1	8.0
	Min	4.50	6.0	11.4
	Max	6.56	28.6	47.2
	Coefficient of variation (%)	10	32	29
Mine Spoil (*n* – 25)	Mean	4.49	5.9	12.2
	Standard Deviation	1.31	2.7	5.0
	Min	3.09	1.7	4.9
	Max	7.29	12.6	22.3
	Coefficient of variation (%)	29	45	41
Sediment (*n* – 9)	Mean	6.00	3.4	8.4
	Standard Deviation	0.54	4.2	2.1
	Min	5.39	1.5	4.4
	Max	6.00	4.6	10.9
	Coefficient of variation (%)	9	32	25
Adit (*n* – 1)	Mean	6.02	17.3	41.7
Reference Soil (*n* – 2)	Mean	4.44	19.3	36.7
	Standard Deviation	0.15	4.6	10.4
	Min	4.33	16.0	29.3
	Max	4.54	22.5	44.0
	Coefficient of variation (%)	3	24	28

3.2 Water concentration

The starting point for any aquatic compliance assessment under the WFD is the concentration of the metal present in the water. Individual survey data are provided in Figures A1 and A2 supplementary material. Mean concentrations for each site sampled for the four surveys were calculated then plotted as a ratio of the relevant standards, all of which take some account of bioavailability. For Cd, hardness is used as a surrogate for metal toxicity, whereas for Mn and Pb a DOC concentration correction is applied to take account of complexation reducing bioavailability and hence toxicity. For Cu, Ni and Zn, a combination of DOC, pH and Ca concentrations are used to amend a generic EQS to take account of the physico-chemical ambient water quality's impact on metal bioavailability (Comber et al., 2008; WFD-UKTAG, 2008, 2013). In all cases, the assumptions are conservative to ensure protection of the aquatic organism present and to all for possible mixture effects. Assumptions and limitations of the models are described in detail elsewhere (Environment Agency, 2009). Figure 2 shows a consistent pattern; upstream of Wheal Betsy all metals measured are EQS compliant. Downstream of the mine site, including the adit drain (Site 3) the EQS for all metals are exceeded. The exceedances however, are variable in their magnitude. The Pb EQS is exceeded by over 50 times downstream of the adit, whereas for Ni, there is only marginal non compliance; with the other metals lying between these extremes, typically in the 10 to 20 times the EQS range. This pattern is not unexpected given the mineralogy being associated with Pb, which generally leads to Zn and Cd being associated with the ore body, unlike Ni. The Cu EQS is relatively low, and so only minor contamination leads to exceedances. For the rest of the Cholwell Brook down to its confluence with the Tavy, the EQS is also exceeded, although concentrations do decrease through dilution. The other mines in the area do not appear to contribute significantly to the observed contamination, which reflects the fact that Wheal Betsy is the largest mine in the vicinity with the most extensive spoil tips and the most significant flow from the adit. From a mitigation standpoint, this data immediately identifies the Wheal Betsy site as the target for any further action.

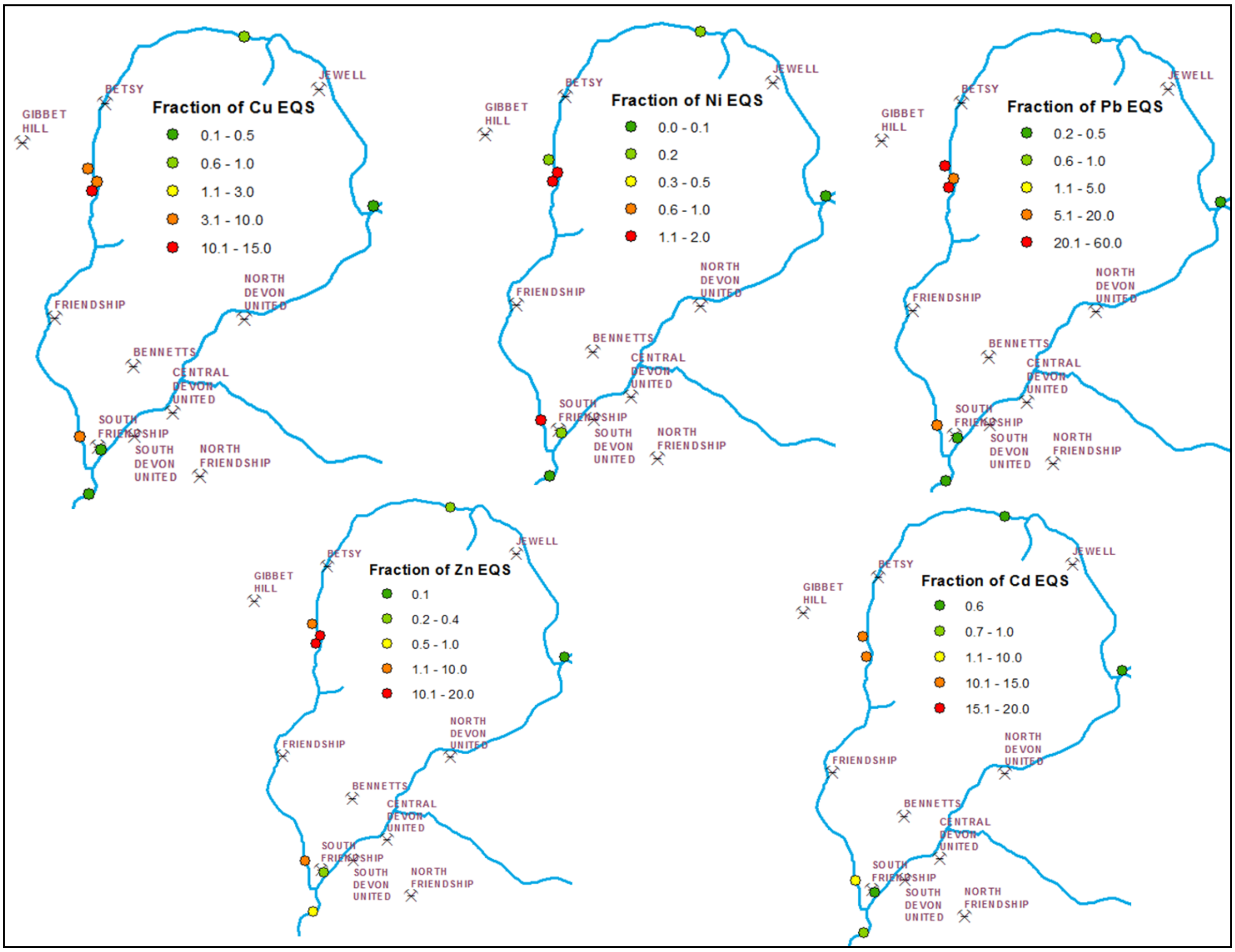

Figure 2 Fraction of water EQS for the Wheal Betsy mining area

3.3 Sediment concentrations

The WFD sets expectations regarding ecological health of a waterbody which includes diatoms, invertebrates, macroalgae and fish. Although water quality will largely impact on diatoms and fish; sediment quality will influence invertebrate (and to a certain extent macroalgae) ecology to a greater degree. Although there are no metal sediment quality standards available as yet for Europe, the Canadian values for threshold and probable effect levels are widely used for comparative purposes (CCME, 2014).

Total metal concentrations measured in the sediment samples (Table A6 supplementary material) were comparable with previous research by Rieuwerts et al. (2009), who reported mean concentrations of Pb and Zn equal to 2,909 mg kg^{-1} and 564 mg kg^{-1} respectively. The exchangeable fraction (and therefore potentially available to aquatic life) in the stream sediments amounted to approximately 15% for Cu, Cd, Pb, Zn and Mn of the total metal present (Figure A3 and Table A6 supplementary material). This was lower than soil values which may represent the loss of some more labile metal through partitioning with overlying water from Cholwell Brook. However, the sediment exchangeable fraction (and to a large degree the reducible and oxidisable fractions) was higher than the corresponding spoil for all metals examined with the exception of Cr. This suggests that the oxygenated, acidic waters have advanced the oxidation process of the minerals to a greater extent than the spoil heaps exposed to the atmosphere and therefore generated more exchangeable metal. As previously reported (e.g. Tuzen, 2003; Purushothaman & Chakrapani, 2007) a significant proportion of Pb (average sediment value of 42%) and Mn (61%) was found in the reducible fraction reflecting the insoluble nature of oxidised species of these elements. The oxidisable fraction (F3) was low for all metals excluding Cu (36%) and Zn (25%), which are well known to form strong complexes with organic matter.

Owing to the exchangeable fraction being the most significant phase regarding metal bioavailability this phase is compared with total concentrations in the discussion below (Table A7 supplementary material). Exchangeable metal concentrations in the sediments of Cholwell Brook and Tavy expressed as RCRs where observed concentrations divided by the quality standard, in this case the Canadian Probable Effect Level (PEL) and are shown in Figure 3 below. The data reflect both the inputs of metals from Wheal Betsy and the physico-chemical characteristics of the individual metals. None of the sampling points show an exceedance of the exchangeable concentration of Ni, Cu and Zn sediment threshold standard, with only a marginal exceedance for Cd downstream of Wheal Betsy.. Pb conversely shows an exceedance downstream by a factor of almost 15 directly downstream of the adit, reflecting its stronger association with sediment, the source from Wheal Betsy and the high concentrations in the dissolved phase. Previous research by Palumbo-Roe et al. (2011) at Rookhope Burn, a historic Pb mine in the Northern Pennines, also reported elevated Pb levels in sediments and water, highlighting the impacts from Pb rich sediments on dissolved Pb levels in the water column.

Cu, Zn and Cd show higher RCR's for exchangeable metal:PEL fractions downstream (Figure 3), which may be explained by the moderate mobility of these metals (USEPA, 2005) leading to slow migration downstream of contaminated sediment. The fact that relative concentrations are not high directly downstream of Wheal Betsy suggests either the particulate metals enter the stream more strongly bound, or that the magnitude of contamination has decreased over time. Total metal RCRs calculated as a fraction of the PEL are obviously be much higher (Table A8 supplementary material), with the Pb RCR of 190 at the adit discharge, and the RCR for the other metals ranging up to between 3 (Ni) and 7 (Cd). The significantly lower RCRs for the exchangeable metal concentrations compared with the total values do illustrate that the contamination of the sediment is potentially less serious than otherwise concluded.

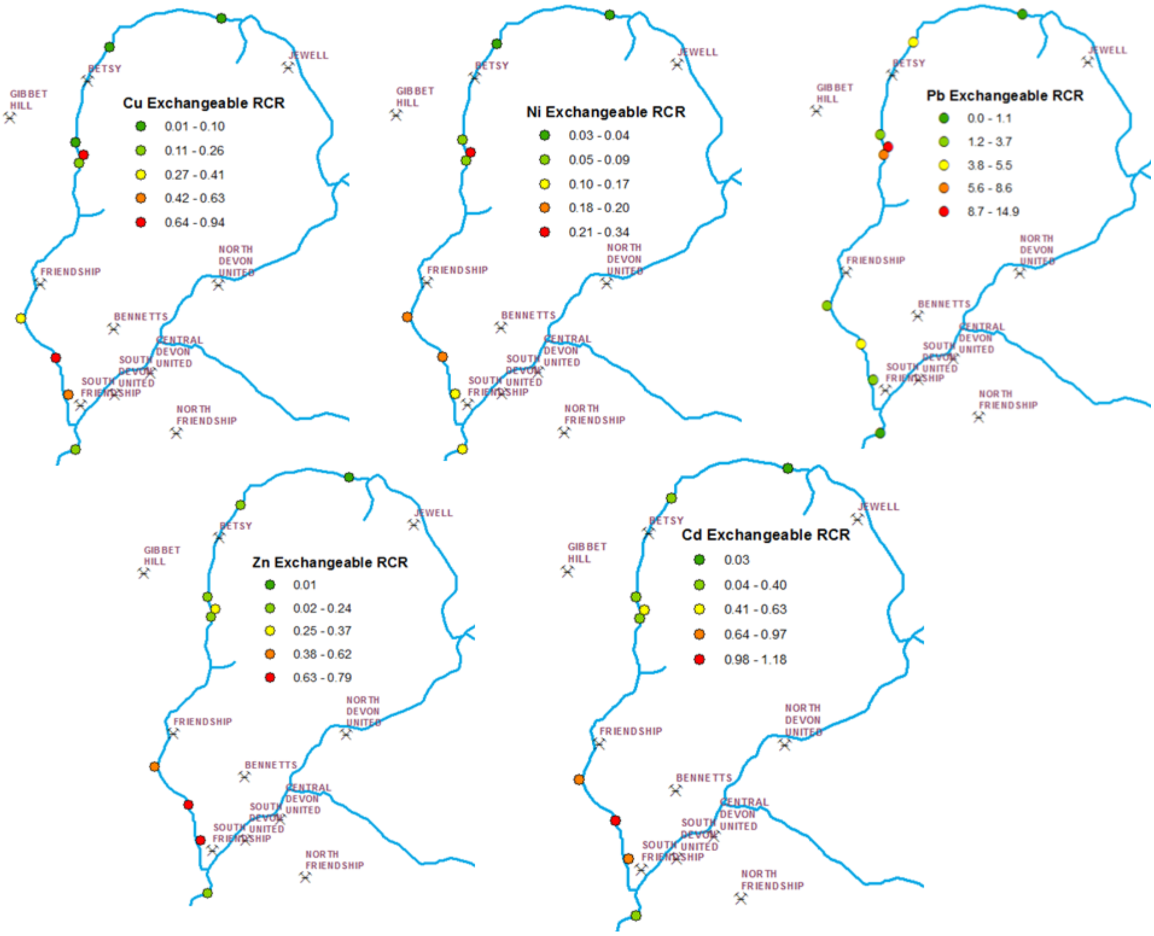

Figure 3 **Exchangeable metal concentrations expressed as a ratio to the sediment quality standard (PEL)**

When considering remediation options, with the exception of Pb, the exchangeable metal, considered to be the bioavailable fraction, is not a major concern. Only Pb exceeds the Probable Effect Level (PEL) downstream of Wheal Betsy. The strong affinity of lead for sediment and its presence in the residual and oxidisable phases suggests levels will remain high in the foreseeable future, even if input of metal to the catchment is reduced through remediation. Physical transport of polluted sediment away from the site is likely to be the main process by which lead levels in sediment within the vicinity of the mine reduce.

3.4 Spoil metal concentration spatial distribution

Although decontaminating sediment would be a significant undertaking, the potential for removing or stabilising contaminated spoil at the site is more feasible and would be a requirement to ensure long term reductions in the loads of metals entering the stream from the site. As part of any remediation processes, the extent of the spoil contamination needs to be assessed for (i) potential to leach dissolved, bioavailable metals into the stream; (ii) potential for loss of total metal via washout of particulate material into the stream and (iii) the toxicity of the metals present from the point of view of phytostabilisation of the tips via seeding with metal-tolerant plants. Again, sequential extractions were undertaken to determine the most likely bioavailable and mobile fractions of metal present and how they may be impacting on the local ecology. Figure 4 shows RCR values for the site specific soil quality standards for both the total metal present and the exchangeable fraction.

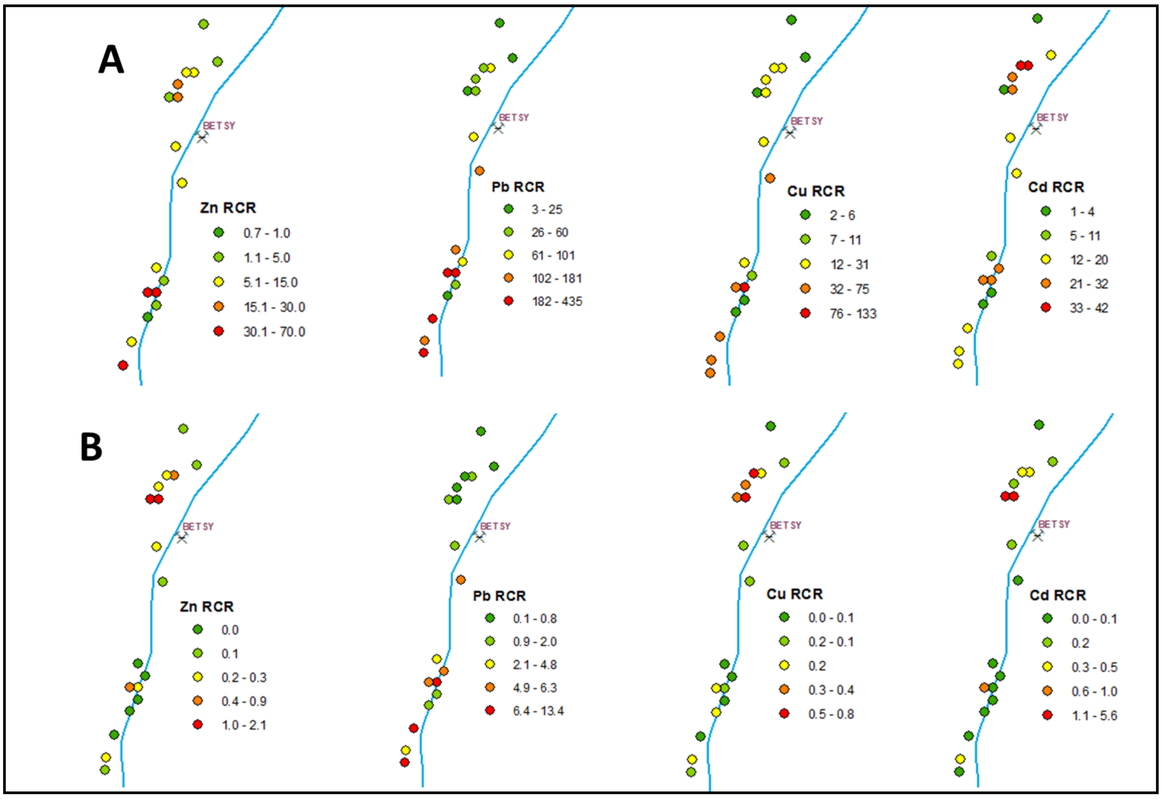

Figure 4 **RCR for spoil based on (A) total metal concentrations and (B) exchangeable metal levels)**

For RCRs based on total Ni in spoil, there were no values greater than 1 for exchangeable Ni in spoil and for total measured Ni, only 2 sites exceed a value of 1, with a maximum RCR of 2.0, consequently the data is not shown here (Tables A9 and A10 supplementary material).

For the other metals, the data show a considerable difference between total concentrations and exchangeable values, with RCRs up to 100 times higher for Cu for example. Based on total concentrations, almost all samples are exceeding the RCR for all metals. Taking account of the bioavailable fraction as determined by the exchangeable metal present, however, Zn, Cu and Cd RCRs are largely less than 1, with only Pb ranging to over 10 at three sites (a maximum RCR of 13.4), reflecting the mineralogy present. From a soil toxicity point of view, the data suggest that metal concentrations in the northern tips are unlikely to be un-vegetated owing to metals concentrations, but potentially more likely a result of low OC, poor nutrient levels and low water holding capacity. The southern tips by comparison may be impacted by lead toxicity.

The spatial distribution of the contamination is interesting, for Pb highest concentrations and RCRs for both total and exchangeable Pb are found in the southern most spoil heaps, which is in agreement with previous studies on total Pb concentrations (Turner, 2011). For Zn contamination total RCR data show the contamination to be more diffuse across the site. Copper data, however, show a very different pattern with higher RCR for total metal in the southern spoil tips compared with higher RCR in the northern tips for exchangeable metal. The spoil in the southern tips is characterised by slightly higher organic carbon (OC) contents and cation exchange coefficients, potentially related to generally finer particle sized material being present. This leads to the PNECs being slightly higher owing to a combination of binding of Cu to OC and the increased availability of inorganic anionic sites available for exchange of Cu on the soil particulates. Total metal concentrations are in several cases significantly higher in the southern tips (Table A10 supplementary material), but the complexation of the Cu to particulate OC and inorganic phases renders exchangeable concentrations lower and so also reduces the RCR significantly. The reason why Zn and Cd do not show the same effect is likely to the lower affinity they exhibits towards particulates and organic carbon compared with Cu (Harter, 1983; de Matos et al., 2001). These results show the importance of considering the speciation of the metal present in contaminated environments as it significantly impacts on the decision making process and focus for any potential remediation work to be carried out.

Taking account of the exchangeable concentrations and the RCRs, the data presented here, therefore would lead to the conclusion that the southern spoil tips would be the highest priority for further investigation and potential mitigation measures. Correlation analysis of the first three sequential extraction fractions (F1+F2+F3) as well as the summed total concentrations including the *aqua regia* digests, exhibit significant inter-correlation between Cu, Pb and Zn indicating a common source and mineralogy (data not shown). Differences in observed concentrations and physico-chemical characteristics of the spoil within the mine site area is likely to reflect changing practices at the mine including dumping of different grade ores with differing particle sizes, reprocessing of older waste material leading to size fractionation and metal concentration, and also on site hydrology and weathering processes.

3.5 Soil metal concentration spatial distribution

Fifteen samples were collected from vegetated areas across the site and the data for all metals shows are reasonable degree of agreement (Figure 5). Total and exchangeable concentrations were typically an order of magnitude lower than their equivalent spoil levels, although there is still an enrichment compared with non-mineralised areas, local and further afield (Kabata-Pendias, 2011; Rawlins et al., 2003). Although there are RCR values for total metals greater than 1; for exchangeable metal concentrations RCR values for total metals are generally below 1, with the exception of 1 sample for Cd.

There was no obvious trends in concentrations across the area sampled, which is unsurprising as the samples of background soils should not have been unduly influenced by mining activity, but reflect the general mineralogy of the area. The higher OC, pH and CEC also results in a significantly higher PNEC concentration (typically double the spoil samples) which also influences the RCR in favour of lower values. The natural heathland vegetation present also reflected adequate water holding capacity, nutrient supply and metals concentrations below threshold toxicity values.

This assessment was useful in that it demonstrated that the contamination and potential remediation requirements are restricted to the obvious mine working area and that the surrounding area should not exhibit significant ecological impacts.

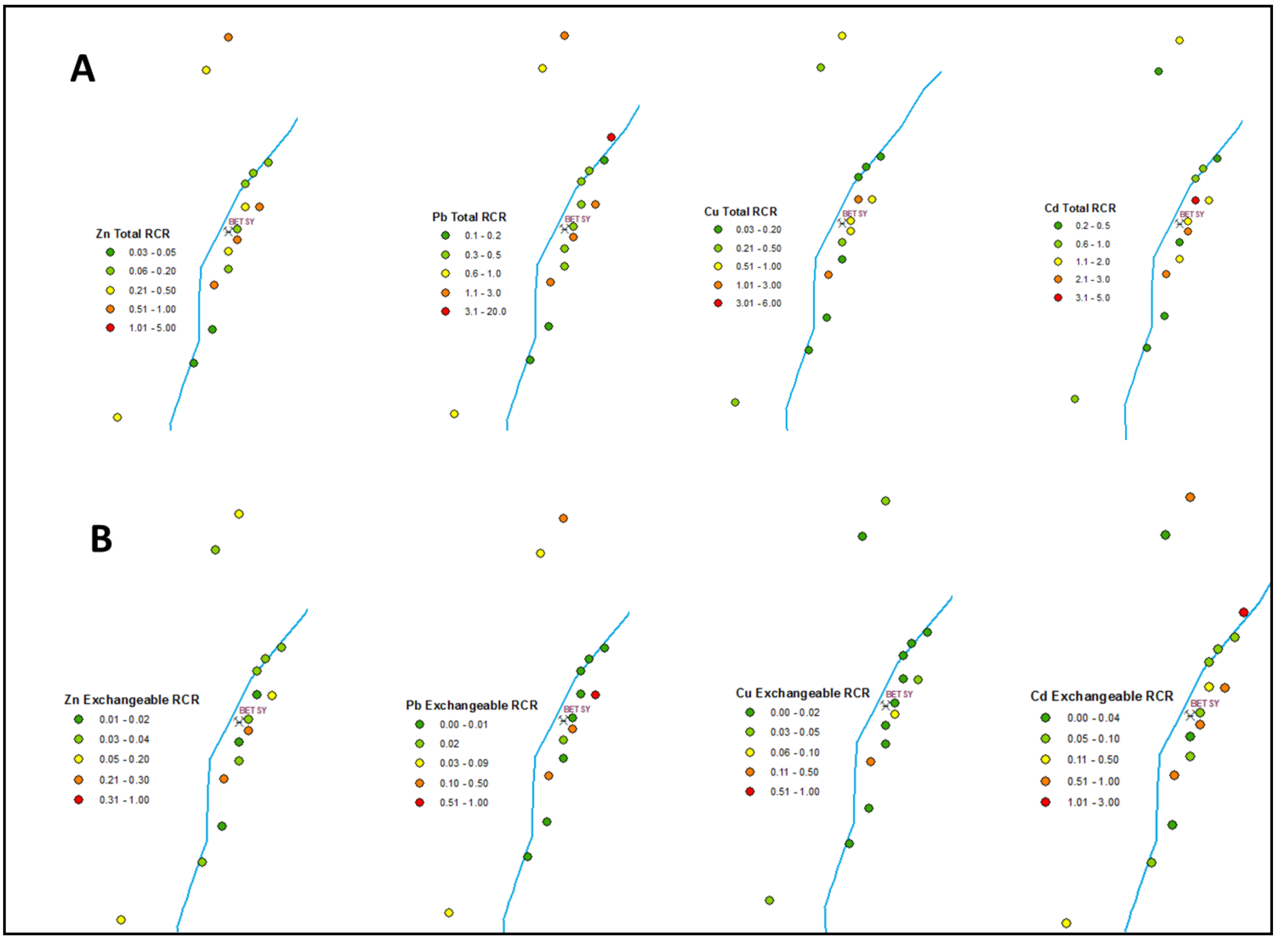

Figure 5 **RCR for soil based on (A) total metal concentrations and (B) exchangeable metal levels)**

3.6 Source apportionment

Metals can enter the aquatic environment via two main pathways, direct discharge of adit drainage and/or a combination of diffuse inputs from particulates washed from mine sites or leaching from the same sources via the dissolved phase. Diffuse inputs from mine sites in the SW of England have been previously shown to contribute significant loadings of metals to receiving waters (Turner, 2011). Before planning remediation options, it is essential to determine the relative proportions of these sources to the contamination observed within the receiving water so that effective measures are identified.

Sampling site 3, the Wheal Betsy adit drainage exhibits the impact from point source mine water inputs, with a sharp elevation and the highest recorded concentration of each metal. However, Pb and Cd concentrations in the river are elevated in the vicinity of the mine spoil heaps prior to the adit input, confirming the main spoil heaps as a significant source of these metals. A similar, though less pronounced pattern is seen for Cu and Zn, albeit still sufficient to exceed site specific BLM derived EQS prior to the adit input.

For the two sampling occasions where flow and concentration data were collected, load data is presented for key metals in Figure 6 and Table A11 supplementary material. Unsurprisingly, metal loads were lower during dry conditions compared with after periods of rainfall. The majority of the metal being discharged to the stream is in the dissolved phase for Cu, Cd and Zn. For Pb and Mn the proportion in the dissolved phase reduces to around 50% in the adit water and downstream. Comparing the mine site samples with those upstream and downstream it was possible to estimate loads from the northern spoil tips, the adit and the southern tips. Comparing the adit loads with the difference between downstream and upstream sites showed good agreement for metals which exhibit a more conservative behaviour expected from simple mixing of adit water with upstream loads (e.g. Zn, Cu, Cd). For Mn and Fe and to a lesser extent Pb, the difference between the downstream and upstream sites compared with the adit drain itself were generally more marked with loads downstream being less than the sum of the upstream and adit loads. This is not unexpected owing to the instability of these metals in solution leading to them oxidising and precipitating rapidly upon mixing with receiving waters. Expressed as a percentage of the total mine site contributions were relatively consistent for the wet and dry sampling days, suggesting a common source (Table 2).

Table 2. Metal and suspended solids loads from spoil heaps and adit

	Load contribution					
	Northern spoil u/s of adit		**Adit**		**Southern spoil d/s of adit**	
Dissolved	**24/4/15 (wet)**	**11/6/14 (dry)**	**24/4/15 (wet)**	**11/6/14 (dry)**	**24/4/15 (wet)**	**11/6/14 (dry)**
Cu (g d^{-1}; %)	54 (32%)	19 (25%)	77 (45%)	41 (53%)	38 (22%)	16 (21%)
Cd (g d^{-1}; %)	6.5 (36%)	2.2 (28%)	5.3 (30%)	2.9 (38%)	6.1 (34%)	2.7 (34%)
Zn (g d^{-1}; %)	814 (32%)	275 (22%)	1036 (41%)	606 (49%)	705 (28%)	350 (28%)
Ni (g d^{-1}; %)	10 (12%)	0.6 (1%)	73 (88%)	47 (87%)	0.3 (0.4%)	6.4 (12%)
Pb (g d^{-1}; %)	393 (42%)	140 (31%)	278 (30%)	209 (46%)	266 (28%)	102 (23%)
Susp' solids (kg d^{-1}; %)	22 (28%)	7 (18%)	47 (60%)	21 (53%)	10 (12%)	11 (29%)

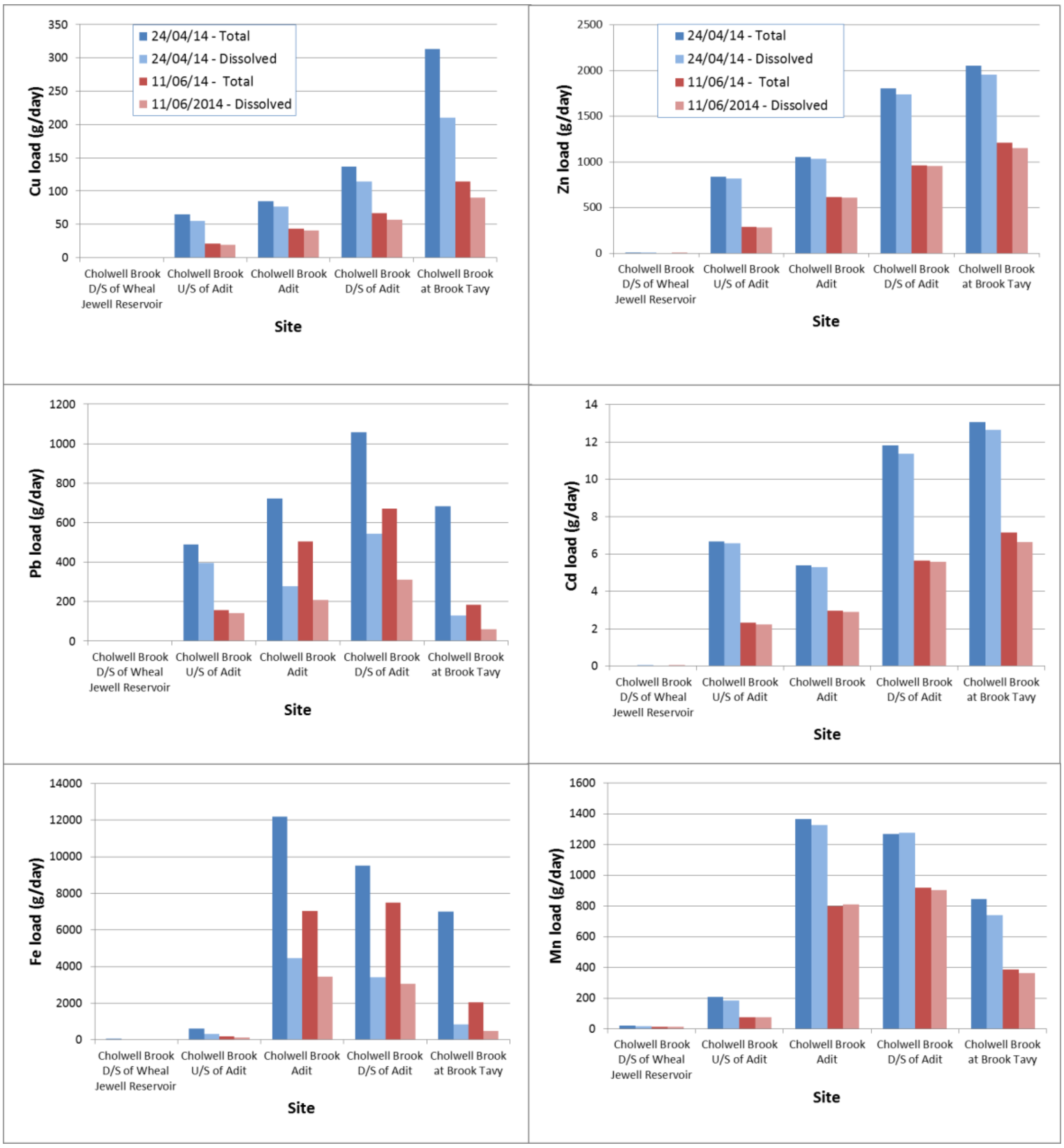

Figure 6. Loads of total and dissolved metal for Cholwell Brook

The adit contribution relative to the upstream and downstream spoil tips is relatively consistent, typically 50% for all metals with the exception of Ni, where the adit dominates the load to the river at ~88%, reflecting the soluble nature of the element. The proportions of Fe and Mn were not calculated owing to their instability in the water column.

Total suspended sediments also show the mine site to be a major contributor to the stream loadings, with contributions of loads from the site split roughly evenly between the adit and the two spoil tips, highlighting the importance of the transport and deposition of highly contaminated material to water bodies (Table 2). The results show the cumulative transfer of metals as the Cholwell Brook moves through the areas of mine waste and the influx of metals from the adit.

Based on these estimates and comparing them with the observed concentrations of metals upstream and downstream of the adit discharge, and assuming a correlation between the load of metal entering the stream and the observed concentrations, then even if treatment of the adit water took place to prevent all the metal from this source entering the water, then the EQS for Cd, Pb and Zn would still be exceeded. For Ni, Cu and Mn, compliance would be potentially achievable, however, giving the WFD uses the 'one out all out' principle, all of the chemical and biological standard are required to be of 'good status' prior to achieving the Directive's objectives. This highlights the importance of undertaking such a risk assessment procedure in order to identify the most cost effective measures that may be employed to best improve the aquatic environment.

3.7 Impacts on benthic-macroinvertebrates communities

Table 3 shows the results from the River Invertebrate Classification Toll (RICT) statistical model (SEPA, 2015) from the 5 sampling locations identified in Figure 1. WFD EQR values are summarised in Table A12.

Table 3. RICT results from the macroinvertebrate data collected from Cholwell Brook

	ASPT				**NTAXA**			
Site	**Observed**	**Predicted**	**EQR**	**Grade**[1]	**Observed**	**Predicted**	**EQR**	**Grade**[1]
1.Cholwell Brook d/s of Wheal Jewell reservoir	6.4	6.2	0.98	H/G	20	21.9	0.95	H/G
2. Cholwell Brook u/s Wheal Betsy adit	6.6	6.3	1.00	H/G	18	23.7	0.79	G/M
3. Cholwell Brook, Wheal Betsy adit	6.5	6.4	0.95	H/G	13	26.0	0.54	M/P
4. Cholwell Brook d/s Wheal Betsy adit	6.9	6.4	1.00	H/G	11	26.0	0.47	P/B
5. Cholwell Brook at Brook Tavy	5.8	6.4	0.87	H/G	14	26.0	0.58	M/P

ASPT = Average Score per Taxa; NTAXA = Number of TAXA; EQR = Ecological Quality Ratio

[1] H/G = High/Good; G/M = Good/Moderate; M/P = Moderate/Poor and P/B = Poor/Bad

The results from RICT show a sharp decline of N-taxa found in the Cholwell Brook as the stream waters move through the mine waste, displaying a reduction in the richness and abundance of macroinvertebrates as metal concentrations increase, with the EQR value reducing from H/G to P/B. This appears to be a localised impact with species diversity increasing further downstream to M/P, indicating a degree of recovery. Conversely, the ASPT classification remains ‘High’ throughout Cholwell Brook and is in some cases considered a more precise index than N-taxa. This is because the ASPT is an average, whereas N-taxa are more susceptible to sampling and temporal variation. This variation is not uncommon for highly mineralised sites where although the overall number of taxa are diminished, high ranking species such as stoneflies, mayflies and caddisflies are present, therefore maintaining the ASPT classification, potentially through adaption over many generations to cope with elevated metal concentrations (Comber 2008). From a WFD compliance point of view, however, this is an interesting issue as to be classified as ‘good ecological status’ conditions are required to be near reference condition, thus requiring the biodiversity (NTAXA) to also be good as well as the ASPT. Figure 7 shows the DCA 2-dimensional plot of macroinvertebrates from each sample location, plotted against the dissolved total metal (µg L^{-1}) concentrations in stream water. Macroinvertebrate data supplied by the EA for the River Tavy has been included for comparison and as a set of control sites (See Figure 1).

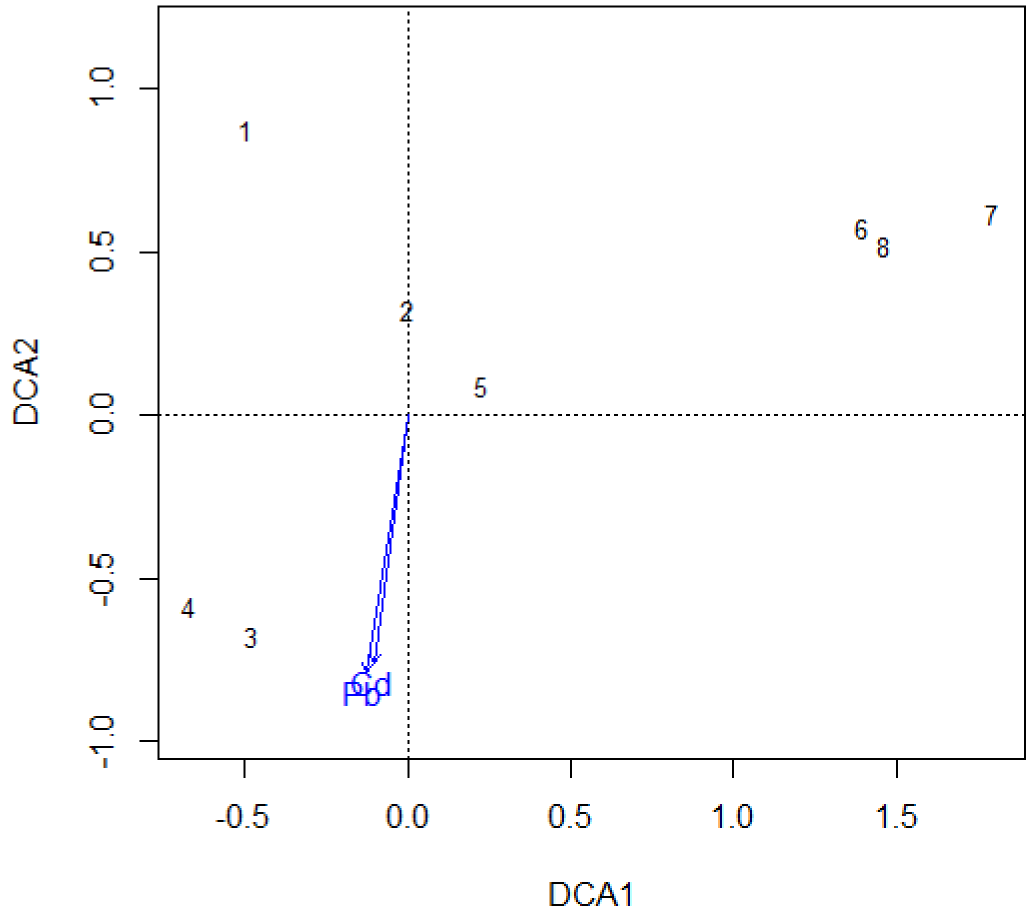

Figure 7. Ordination 2-dimensional graph showing macroinvertebrate communities by site number with the concentrations of dissolved metals (μg L^{-1}) in stream water as an environmental variable (moving in a downstream direction from site 1). Vector lines show the direction of gradient and the length of the arrow is proportional to the correlation between the macroinvertebrates and the dissolved metals.

The ordination 2-dimensional graph using DCA shows the correlation between the macroinvertebrate communities and the dissolved metal concentrations in stream water at Cholwell Brook, with Cd and Pb influencing the aquatic biota. Distinct community assemblages can be seen moving downstream from the fringes of Dartmoor, through the mine waste. The site at the adit discharge and the site immediately downstream are most impacted. These results correlate with the chemical speciation and more labile fractions of Cd and Pb that are found in soils, mine waste and sediments in large quantities. In addition, Cd and Pb are ‘priority’ and ‘priority hazardous’ substances respectively under the WFD and known to exert toxicological effects on aquatic biota. A recovery of species diversity can be observed further downstream as heavy metals undergo dilution and geochemical transformations moving them into the solid phase. Sample sites 6, 7 and 8 are taken from the River Tavy upstream from the Cholwell Brook and display their own unique community assemblage of benthic invertebrates. No correlations were observed between heavy metal concentrations (mg kg^{-1}) in sediments and macroinvertebrates. The results show the clustering of unique community assemblages of benthic invertebrates that adapt to anthropogenic stressors. Results of the present study indicate that previous exposure of contaminants could be attributed to the ‘community conditioning hypothesis’, as reported by Clements, (2000), where exposure to contaminants over long periods of time directly influences the community structure, with heavy metal tolerance retained in ecological communities.

5. Conclusion

The intensive sampling programme described here was undertaken within a period of 6 months which limited the temporal analysis which could be performed, however the main objective of research was to demonstrate the benefits of taking account of bioavailability of metals when assessing a contaminated site, thereby allowing effective remediation to be focussed on soil, spoil, water and sediment which is likely to offer the greatest threat to the local ecology. The legacy of historic mining has left a long and lasting impact at Wheal Betsy, 140 years after operations ceased, with significant sources of environmental contamination contributing to the Cholwell Brook’s non-compliance with WFD EQS for Cd, Cu, Pb and Zn (and to a lesser extent Mn and Fe). The study employed a rigorous environmental monitoring programme using sequential extraction and speciation modelling to identify the main sources of contamination from total and bioavailable metal. Water quality data showed significant exceedances, even taking account of bioavailability, of aquatic environmental quality standards associated with the adit discharge as well as the spoil tips adjacent to the stream, to the north and south of the adit input. Discharge of contaminated mine water from Wheal Betsy adit was the largest single contributor of all metals, but the spoil tips to the north and the south of the adit, were shown to contribute an almost equal loading of all metals with the exception of Ni. There were subtle differences in the distribution of metals in the exchangeable phases of the spoil sampled with the northern heaps exhibiting greater concentrations of labile Cd and Cu, and the southern tips relatively higher exchangeable Pb concentrations.

The erosion products of soils and mine waste particles have been transported in large quantities to the Cholwell Brook, which has resulted in highly contaminated sediments, with total and extractable Pb concentrations 190 and 15 times higher than the Canadian Probable Effect Levels respectively, impacting on species richness, if not overall average score per taxa. The ecological impacts, however, were found to be localised within the Cholwell Brook upstream of the confluence with the Tavy. The impact on macroinvertebrates has been assessed using RICT, and although sampling was limited to a single survey and repeat sampling is required to confirm the observed data, the available data suggest a decline in species richness and abundance, although the ASPT remains Healthy/Good. Further analysis using ordination has identified Cd and Pb as the main elements impacting invertebrate biodiversity and the presence of unique community assemblages of benthic invertebrates, suggesting there is strong evidence of the ‘community conditioning hypothesis’, whereby exposure to contaminants over long periods of time directly influences the community structure, with heavy metal tolerance retained in ecological communities.

The data presented here demonstrates that measures employed to address the adit discharge alone, will not lead to WFD compliance, and that the spoil heaps north and south of the adit discharge would also need to be stabilised with respect to loss of suspended solids and leaching of metals into the river. For the first time, the bioavailability of key metals in all media (soil, spoil, water and sediment) has been evaluated and reported for an abandoned mine site to evaluate potential contamination hotspots impacting local ecological receptors and thereby inform future targeted remediation.

Acknowledgments

The authors would like to thank the Environment Agency for providing support in sampling and site background data, in particular Karolina Krupska and Tim Geatches. The authors would also like to thank the laboratory technicians at Plymouth University for their support, namely, Andy Arnold and Andy Fisher.

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Abandoned metal mines and their impact on receiving waters: A case study from Southwest England

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A1 Sequential Extraction methodology

(F1) exchangeable/acid fraction (surface bound metals to carbonates) – soil sample extracted with 40 ml of acetic acid, 0.11 M, shaken end to end at 30 rpm for 16 h, room temperature;

(F2) reducible fraction (bound to Fe/Mn oxides, oxyhydroxides) – residue from step one extracted with 40 ml hydroxylammonium chloride, 0.1 M, pH adjusted to 1.5 with 25 ml nitric acid, shaken end to end at 30 rpm for 16 h, room temperature;

(F3) oxidisable fraction (bound to organic matter and sulphides) – residue from step 2 digested in 10 ml hydrogen peroxide, 8.8 M (30%) at room temperature for 1 hr with occasional manual shaking. Mixture heated to 85 ºC for 1 h or longer (water bath) until volume reduced to 3ml. Double extraction was repeated twice, followed by an addition of 50 ml ammonium acetate, 1.0 M, adjusted to pH 2 with nitric acid, shaken end to end for 16 h, room temperature; and

(R) residual fraction (crystal lattice of original mineral, identified as 'inactive' fraction) – the residue from step 3 was used to provide a pseudo-total concentration and digested in 10 ml *aqua regia* (3:1 v/v HCl: HNO_3, 120ºC, 1.5 h) in a 50 ml glass beaker covered with a watch glass, and is assumed to be the difference between total concentration and the secondary-phase fraction (SPF), the sum of F1, F2, and F3. The SPF is often referred to in the results and discussion as the potentially-mobile fractions, and is considered potentially hazardous to organisms in the aquatic environment. After each extraction, separation was done by centrifugation at 3000 rpm for 20 minutes and the supernatant carefully transferred to universal acid-washed bottles, and stored at 4 ºC before analysis by ICP-OES. Procedural blanks were below the LOD.

Table A1. Table displaying the current hardness based Environmental Quality Standards (EQS) and the new proposed European and UK river water EQS for dissolved metals using the BLM. All concentrations as µg l^{-1} as dissolved metal

Element	Old EQS	New WFD EQS	
Cadmium (Cd)	UK standard: 5.0 (annual mean total Cadmium)	EU Standard (dissolved annual mean): ≤0.08 = <40mg $CaCO_3$/l 0.08 = 40 to <50 0.09 = 50 50 <100 0.15 =100 to <200 0.25 = ≥ 200	a
Copper (Cu)	0-50 mgl^{-1} $CaCO_3$ = 1 (dissolved) 50-110 mgl^{-1} $CaCO_3$ = 6 (dissolved) 100-250 mgl^{-1} $CaCO_3$ = 10 (dissolved) >250 mgl^{-1} CaCO3 = 28 (dissolved)	1.0 (bioavailable)	b, c
Iron (Fe)	1000 dissolved	730 (total)	d, e
Manganese (Mn)	30 (dissolved annual average)	123 (bioavailable)	f, b
Nickel (Ni)	0-50 mgl^{-1} $CaCO_3$ = 50 (dissolved) 50-100 mgl^{-1} $CaCO_3$ = 100 (dissolved) 100-250 mgl^{-1} $CaCO_3$ = 150 (dissolved) >250 mgl^{-1} $CaCO_3$ = 2001 (dissolved)	4.0 (bioavailable)	c, g
Lead (Pb)	4-250 (inorganic - dissolved varies with hardness)	1.2 (bioavailable)	c, g
Zinc (Zn)	0-50 mgl^{-1} $CaCO_3$ = 8 (total metal) 50-100 mgl^{-1} CaCO3 = 50 (total metal) 100-250 mgl^{-1} CaCO3 = 75 >250 mgl^{-1} CaCO3 = 125	10.9 (bioavailable)	c, g

Sources: (a) Environment Agency (2011) Chemical Standards Report – Cadmium. [online] Available at: http://evidence.environment-agency.gov.uk/ChemicalStandards/report.aspx?cid=29. (Accessed: 06 August 2014). (b) WFD-UKTAG, 2013. Updated Recommendations on Environmental Standards - River Basin Management (2015-21). WFD-UKTAG: Edinburgh. Available at: http://www.wfduk.org/sites/default/files/Media/Environmental%20standards/Specific%20pollutants%20proposals_Final_010608.pdf. (Accessed: 02 August 2014). (c) Environment Agency (2013) Significant Water Management Issues - Draft risk assessments for review and comment. Environment Agency: Bristol. (d) WFD-UKTAG (2013). Updated Recommendations on Environmental Standards - River Basin Management (2015-21). WFD-UKTAG. (e) Environment Agency, (2011) Chemical Standards Report – Iron. [online] Available at: http://evidence.environment-agency.gov.uk/ChemicalStandards/ (e) Environment Agency, (2011) (f) Environment Agency, 2011c. Chemical Standards Report – Manganese. [online] Available at: http://evidence.environment-agency.gov.uk/ChemicalStandards/report.aspx?cid=91. (Accessed: 07 August 2014).(g) Peters, A., Merrington, G. and Crane, M., (2012) Estimation of background reference concentrations for metals in UK freshwaters. WFD-UKTAG: Edinburgh

Table A2. Soil, mine waste and sediment locations

Sample No.	Longitude	Latitude (D, M)	Sample No.	Longitude Latitude (D, M)	Sample No.
Spoil 1	50°36.78'N	004°06.30'W	Soil 1	50°36.60'N	004°06.35'W
Spoil 2	50°36.76'N	004°06.31'W	Soil 2	50°36.57'N	004°06.34'W
Spoil 3	50°36.75'N	004°06.31'W	Soil 3	50°36.53'N	004°06.34'W
Spoil 4	50°36.74'N	004°06.34'W	Soil 4	50°36.50'N	004°06.32'W
Spoil 5	50°36.74'N	004°06.35'W	Soil 5	50°36.45'N	004°06.35'W
Spoil 6	50°36.78'N	004°06.33'W	Soil 6	50°36.06'N	004°06.30'W
Spoil 7	50°36.73'N	004°06.36'W	Soil 7	50°36.68'N	004°06.24'W
Spoil 8	50°36.72'N	004°06.36'W	Soil 8	50°36.64'N	004°06.23'W
Spoil 9	50°36.72'N	004°06.37'W	Soil 9	50°36.69'N	004°06.31'W
Spoil 10	50°36.68'N	004°06.36'W	Soil 10	50°36.71'N	004°06.30'W
Spoil 11	50°36.65'N	004°06.35'W	Soil 11	50°36.73'N	004°06.30'W
Spoil 12	50°36.56'N	004°06.39'W	Soil 12	50°36.74'N	004°06.29'W
Spoil 13	50°36.55'N	004°06.38'W	Soil 13	50°36.75'N	004°06.27'W
Spoil 14	50°36.57'N	004°06.37'W	Soil 14	50°36.77'N	004°06.26'W
Spoil 15	50°36.58'N	004°06.38'W	Soil 15	50°36.71'N	004°06.28'W
Spoil 16	50°36.56'N	004°06.38'W	Soil 16	50°36.68'N	004°06.31'W
Spoil 17	50°36.56'N	004°06.39'W	Soil 17	50°36.64'N	004°06.34'W
Spoil 18	50°36.52'N	004°06.41'W	Soil 18	50°36.52'N	004°06.47'W
Spoil 19	50°36.49'N	004°06.42'W	Soil 19	50°36.83'N	004°06.36'W
Spoil 20	50°36.50'N	004°06.42'W	Soil 20	50°36.86'N	004°06.33'W
Spoil 21	50°36.54'N	004°06.39'W			
Spoil 22	50°36.23'N	004°06.25'W			
Spoil 23	50°36.48'N	004°06.47'W			
Spoil 24	50°36.35'N	004°06.32'W			
Spoil 25	50°36.59'N	004°06.41'W			
Reference Soil 1	50°37.17'N	004°06.09'W			
Reference Soil 1	50°37.14'N	004°06.15'W			

Table A3. Sediment, water, flow and macroinvertebrate sampling locations. Sediment, macro invertebrate, water chemistry and flow measurements locations (F = Flow; W = Water; I = Invertebrate sample; *n* = corresponds to site number).

Location Name	Ordnance Survey Grid Reference	Sediment	Water	Flow	Invertebrate
CHOLWELL BROOK D/S OF WHEAL JEWELL RESERVOIR	SX 52155 81720	1	1	1	1
CHOLWELL BROOK U/S OF MAIN SPOIL HEAPS	SX 51214 81478	2			2
CHOLWELL BROOK U/S WHEAL BETSY ADIT	SX 50927 80683	12	2	2	3
CHOLWELL BROOK, WHEAL BETSY ADIT	SX 50996 80574	13	3	3	
CHOLWELL BROOK D/S WHEAL BETSY ADIT	SX 50956 80505	11	4		4
U/S MARY TAVY SPOIL HEAPS	SX 50470 79205	10			
CHOLWELL BROOK AT MARY TAVY	SX 50758 78872	3			
CHOLWELL BROOK U/S OF SEWAGE TREATMENT WORKS	SX 50863 78565	4	5	4	5
RIVER TAVY D/S CHOLWELL BROOK	SX 50928 78106	6	6		
RIVER TAVY AT HARFORD BRIDGE	SX 50574 76748	7	7	5	6
RIVER TAVY U/S CHOLWELL BROOK	SX 50102878460	5			7
RIVER TAVY HILL BRIDGE	SX 53177 80388	9			8
COLLY BROOK AT PETER TAVY	SX 51400 77630	8			

Table A4. Class boundaries for the WFD EQR

Boundary	ASPT EQR Value	NTAXA EQR Value
H/G	0.97	0.85
G/M	0.86	0.71
M/P	0.75	0.57
P/B	0.63	0.47

ASPT = Average Score Per Tax; NTAXA = Number of Taxa present

Table A5. Certified and measured extractable mass fraction based on dry mass in CRM 701. Horvath et al., (2010) observations included for comparison. (*n* = repeated number of extractions. 1) Mean value of the number of repeated extractions from each data set . 2) Half-width of the 95% confidence interval of the mean defined in 1)).

Extractable mass fraction based on dry mass (mg kg^{-1})

Step	**Element**	**Certified (*n* = 14)**			**Horvath et al., (2010) (*n* = 3)**			**Measured (*n* = 6)**			**Difference on 99.9%** [a]	**Recovery (%)**
		1)		2)	1)		2)	1)		2)		
1	Cd	7.3	±	0.4	6.78	±	0.04	6.8	±	0.27	-	93
	Cr	2.26	±	0.16	1.12	±	0.02	1.8	±	0.27	+	80
	Cu	49.3	±	1.7	46.5	±	0.25	37.2	±	3.2	+	76
	Ni	15.4	±	0.9	14.4	±	0.12	13.5	±	0.74	-	88
	Pb	3.18	±	0.21	6.78	±	0.01	2.46	±	0.24	+	77
	Zn	205	±	6	183	±	1.07	188.4	±	6.75	-	92
2	Cd	3.77	±	0.28	3.28	±	0.01	4.02	±	0.27	-	108
	Cr	45.7	±	2.0	47.3	±	0.004	49.6	±	2.4	-	108
	Cu	124	±	3	109	±	0.04	131.6	±	5	-	107
	Ni	26.6	±	1.3	25.3	±	0.01	30	±	1.27	-	113
	Pb	126	±	3	109	±	0.06	121.7	±	2.1	-	97
	Zn	114	±	5	106	±	0.17	123.2	±	6.3	-	109
3	Cd	0.27	±	0.06	0.32	±	0	0.17	±	0.01	+	62
	Cr	143	±	7	104	±	0.15	137.6	±	6.57	-	96
	Cu	55	±	4	40.3	±	0.1	50	±	1.01	-	91
	Ni	15.3	±	0.9	10.4	±	0.03	12.9	±	0.67	+	83
	Pb	9.3	±	2.0	11.6	±	0.11	7	±	0.91	+	74
	Zn	46	±	4	27.2	±	0.12	38.2	±	2.29	+	83

Notes: [a] Indicative value.

Significant (+); not significant (-)

Table A6. Fraction concentrations of heavy metals in soil, mine waste, sediment, reference soil. The SPF fraction (ΣF1+F2+F3) is expressed as a percentage total and the fractions that are considered to be potentially mobile in the environment

Sample	Fraction	Cd	Cu	Fe	Mn	Ni	Pb	Zn
		Mean ± standard deviation (mg kg^{-1})						
Soil	Exchangeable (F1)	0.8 ± 1.1	21.0 ± 38.3	90.9 ± 73.9	71.3 ± 0.1	0.8 ± 0.1	178.1 ± 0.5	57.8 ± 94.1
(*n* – 20)	Reducible (F2)	0.3 ± 0.4	11.8 ± 35.3	3383.7 ± 1509.2	146.5 ± 0.0	0.5 ± 0.1	441.9 ± 8.3	27.8 ± 49.5
	Oxidisable (F3)	0.2 ± 0.1	59.0 ± 54.8	1894.4 ± 825.9	11.9 ± 0.2	1.5 ± 0.1	156.4 ± 3.2	20.0 ± 26.7
	Residual (F4)	1.0 ± 1.1	67.9 ± 88.4	15699.9 ± 9077.1	88.1 ± 0.5	9.7 ± 0.2	256.8 ± 3.3	78.2 ± 90.4
	Sum of all Fractions	2.3 ± 2.5	159.7 ± 188.8	21068.9 ± 9543.5	317.7 ± 0.6	12.5 ± 0.4	1033.2 ± 8.5	183.8 ± 253.6
	Secondary Phase (ΣF1+F2+F3)	1.3 ± 0.1	91.8 ± 2.8	5369.0 ± 301.8	229.6 ± 0.3	2.8 ± 0.2	776.4 ± 12.1	105.6 ± 3.2
	% of Total	**55.1%**	**57.5%**	**25.5%**	**72.3%**	**22.7%**	**75.1%**	**57.5%**
Mine waste	Exchangeable (F1)	3.1 ± 7.8	52.4 ± 128.4	41.7 ± 50.3	68.8 ± 123.0	0.8 ± 1.9	882.2 ± 752.9	179.0 ± 405.6
(*n* – 25)	Reducible (F2)	2.6 ± 5.8	92.4 ± 187.2	7951.3 ± 5608.9	406.5 ± 918.9	1.1 ± 3.5	4477.5 ± 6192.0	204.7 ± 509.7
	Oxidisable (F3)	1.0 ± 1.6	123.3 ± 242.7	1156.5 ± 1009.7	33.7 ± 67.4	1.7 ± 3.0	2047.1 ± 3917.5	143.8 ± 313.3
	Residual (F4)	20.4 ± 14.4	2074.4 ± 1814.1	91596.8 ± 45659.9	301.0 ± 337.7	15.4 ± 26.9	17779.3 ± 14412.5	1229.1 ± 1227.2
	Sum of all Fractions	27.2 ± 18.0	2342.6 ± 1752.0	100746.3 ± 49914.6	810.0 ± 1294.3	18.9 ± 34.8	25186.0 ± 21286.8	1756.6 ± 1716.6
	Secondary Phase (ΣF1+F2+F3)	6.8 ± 14.9	268.2 ± 432.2	9149.5 ± 6307.0	509.0 ± 1103.0	3.6 ± 8.1	7406.7 ± 9923.9	527.5 ± 1216.8

Sample	Fraction	Cd	Cu	Fe	Mn	Ni	Pb	Zn
		Mean ± standard deviation (mg kg^{-1})						
	% of Total	**24.8%**	**11.4%**	**9.1%**	**62.8%**	**18.9%**	**29.4%**	**30.0%**
Sediment	Exchangeable (F1)	2.2 ± 1.4	78.7 ± 58.9	20.7 ± 10.0	300.7 ± 103.0	4.8 ± 2.2	312.3 ± 219.6	132.5 ± 92.0
(*n* – 9)	Reducible (F2)	1.3 ± 1.0	69.4 ± 54.5	6046.4 ± 1972.1	1237.6 ± 718.4	7.2 ± 5.3	1110.6 ± 580.0	73.1 ± 53.7
	Oxidisable (F3)	1.7 ± 1.4	184.2 ± 138.9	1231.1 ± 513.0	57.7 ± 28.8	6.9 ± 4.1	115.5 ± 69.6	196.7 ± 148.9
	Residual (F4)	6.8 ± 6.2	178.9 ± 98.2	47507.4 ± 14221.8	432.9 ± 264.8	40.2 ± 29.3	1129.4 ± 859.6	389.4 ± 244.7
	Sum of all Fractions	12.0 ± 9.6	511.1 ± 320.4	54805.5 ± 15570.4	2028.8 ± 1073.8	59.1 ± 38.3	2667.7 ± 1618.3	791.7 ± 519.4
	Secondary Phase (ΣF1+F2+F3)	5.2 ± 3.7	332.2 ± 235.8	7298.1 ± 2192.4	1596.0 ± 833.6	18.9 ± 11.0	1538.4 ± 802.8	402.3 ± 285.9
	% of Total	**43.1%**	**65.0%**	**13.3%**	**78.7%**	**32.0%**	**57.7%**	**50.8%**
Adit	Exchangeable (F1)	2.2 ± 0.0	185.2 ± 3.6	184.8 ± 7.5	844.6 ± 24.7	12.1 ± 0.2	1362.9 ± 5.2	115.3 ± 3.0
(*n* – 3)	Reducible (F2)	1.3 ± 0.1	102.0 ± 1.6	55811.0 ± 1406.4	11203.7 ± 14.2	15.5 ± 0.1	3375.2 ± 76.2	100.6 ± 0.7
	Oxidisable (F3)	0.0 ± 0.0	212.5 ± 37.9	30519.0 ± 4141.0	80.5 ± 11.6	2.0 ± 0.5	7214.6 ± 1127.2	44.4 ± 1.5
	Residual (F4)	10.6 ± 1.5	140.3 ± 22.1	130199.4 ± 11361.7	213.5 ± 30.2	5.1 ± 0.5	5427.3 ± 874.0	120.7 ± 14.3
	Sum of all Fractions	14.3 ± 1.6	640.1 ± 27.6	216714.1 ± 13512.1	12342.4 ± 68.3	34.8 ± 0.6	17379.9 ± 941.9	381.0 ± 17.6
	Secondary Phase (ΣF1+F2+F3)	3.6 ± 0.1	499.8 ± 5.8	86514.7 ± 2820.0	12128.9 ± 47.9	29.7 ± 0.2	11952.7 ± 150.2	260.3 ± 4.4
	% of Total	**25.3%**	**78.1%**	**39.9%**	**98.3%**	**85.3%**	**68.8%**	**68.3%**

Sample	Fraction	Cd	Cu	Fe	Mn	Ni	Pb	Zn
		Mean ± standard deviation (mg kg^{-1})						
Reference Soil	Exchangeable (F1)	0.1 0.0	0.3 ± 0.1	21.3 ± 2.4	2.3 ± 0.1	0.6 ± 0.1	1.0 ± 0.5	7.2 ± 2.3
(*n* – 2)	Reducible (F2)	0.2 ± 0.0	0.0 ± 0.0	875.6 ± 219.2	0.0 ± 0.0	0.7 ± 0.1	31.5 ± 8.3	3.7 ± 0.9
	Oxidisable (F3)	0.0 ± 0.0	5.8 ± 2.7	243.7 ± 90.0	0.6 ± 0.2	0.5 ± 0.1	12.5 ± 3.2	0.6 ± 0.3
	Residual (F4)	0.0 ± 0.0	2.1 ± 0.9	185.0 ± 31.2	2.3 ± 0.5	0.5 ± 0.2	3.4 ± 3.3	0.8 ± 0.3
	Sum of all Fractions	0.3 ± 0.1	8.2 ± 2.0	1325.6 ± 300.2	5.2 ± 0.6	2.2 ± 0.4	48.4 ± 8.5	12.3 ± 3.0
	Secondary Phase (ΣF1+F2+F3)	0.3 ± 0.1	6.1 ± 2.8	1140.6 ± 301.8	2.9 ± 0.3	1.7 ± 0.2	45.0 ± 11.6	11.5 ± 3.2
	% of Total	**90.2%**	**74.3%**	**86.0%**	**55.6%**	**79.4%**	**93.0%**	**93.5%**
PEL		3.5	197	-	-	35.9	91.3	315
TEL		0.596	36.7	-	-		35	123

[†] PEL: Probable effect level; draft freshwater sediment quality guidelines. (CCME, 2014). TEL; Threshold effect level; draft freshwater sediment quality guidelines (CCME, 2014).

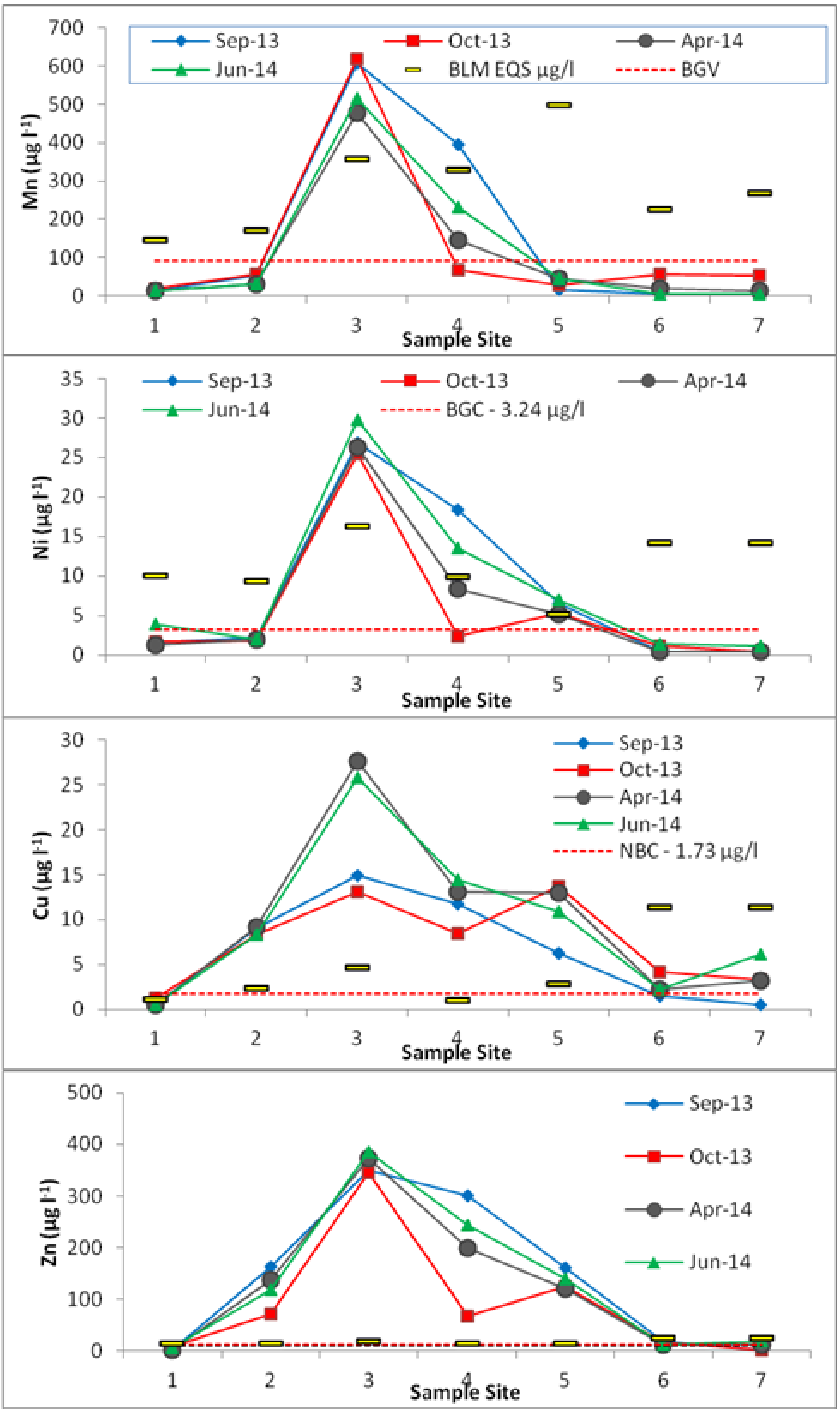

Figure A1. Mn, Ni, Cu, Zn concentrations in Cholwell Brook; along a 3 km transect. Natural background concentrations from the Tamar Valley (red dotted line) and EQS (black dotted line) have been added for comparative purposes. Site specific EQS (Yellow bar) have been calculated using the BLM.

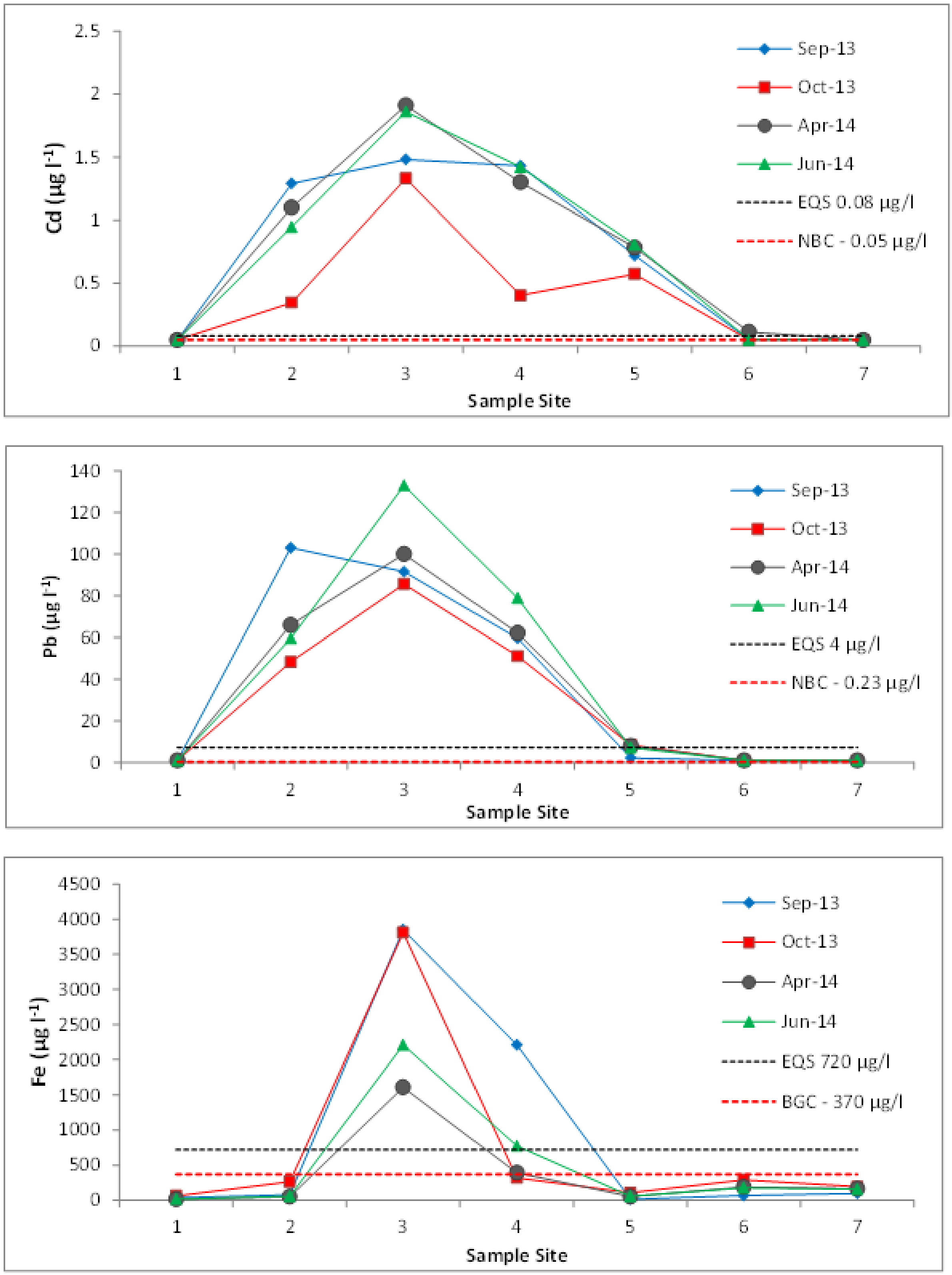

Figure A2. Cd, Pb and Fe concentrations in Cholwell Brook; along a 3 km transect from headwaters to confluence with Tavy. Natural background concentrations from the Tamar Valley (red dotted line) and EQS (black dotted line) have been added for comparative purposes.

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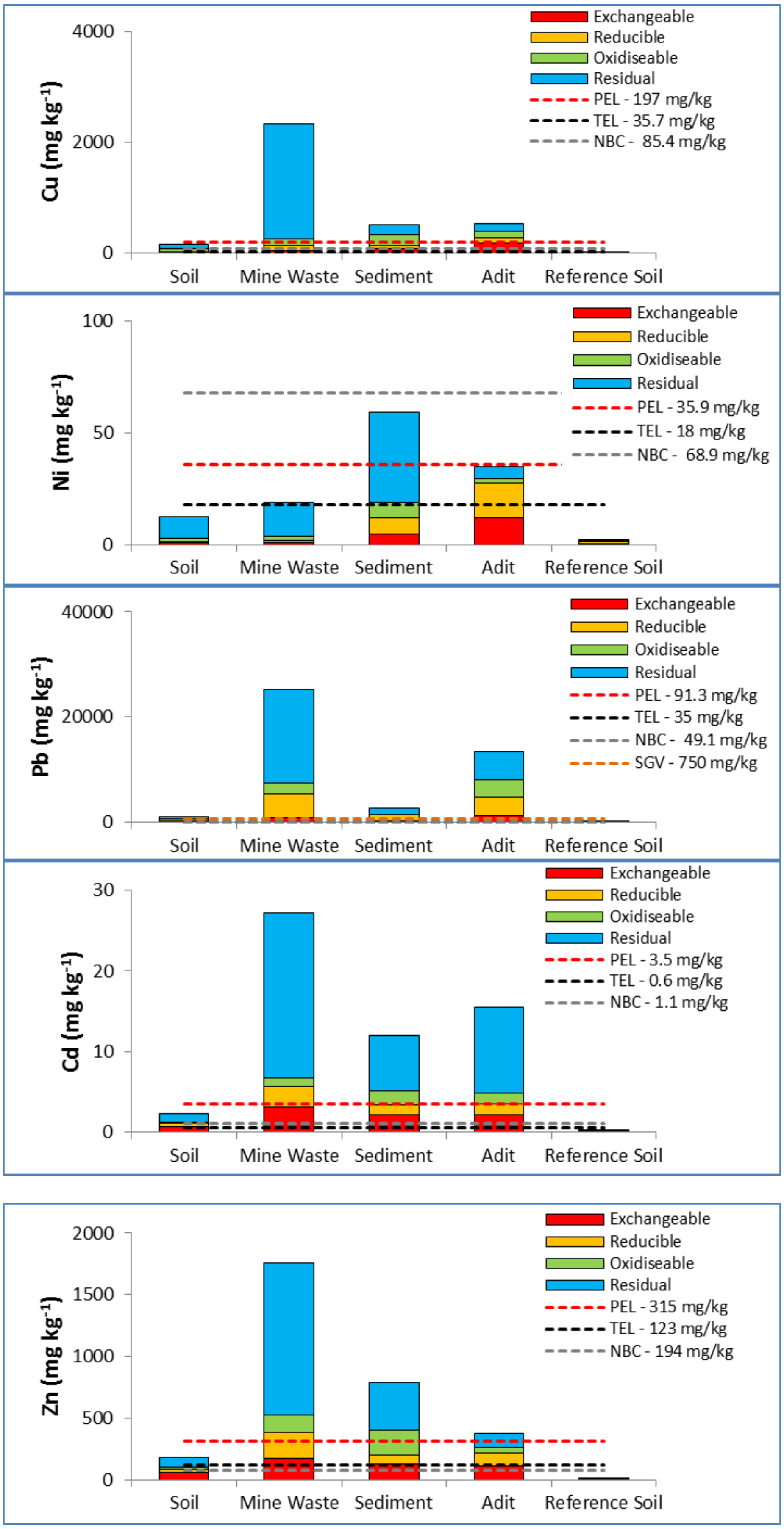

Figure A3. Mean fraction distributions for particulate samples.

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Table A7 Exchangeable concentrations and RCR for sediment

	Exchangeable sediment concentration (mg kg^{-1})					RCR				
	Cd	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**
PEL	**3.53**	**197**	**35.9**	**91.3**	**315**					
Sediment 1	0.11	1.79	0.99	409.81	4.54	0.03	0.01	0.03	0.03	0.01
Sediment 2	0.78	10.47	1.54	503.86	43.66	0.22	0.05	0.04	4.49	0.14
Sediment 3	4.16	179.92	7.01	300.12	247.81	1.18	0.91	0.20	5.52	0.79
Sediment 4	3.41	124.04	6.08	61.61	227.39	0.97	0.63	0.17	3.29	0.72
Sediment 6	1.42	33.90	5.33	97.26	74.36	0.40	0.17	0.15	0.67	0.24
Sediment 7	2.17	115.44	6.63	328.88	86.52	0.61	0.59	0.18	1.07	0.27
Sediment 10	2.96	80.96	6.73	789.61	196.37	0.84	0.41	0.19	3.60	0.62
Sediment 11	0.84	50.73	3.06	340.85	57.89	0.24	0.26	0.09	8.65	0.18
Sediment 12	1.00	19.99	3.22	0.35	63.84	0.28	0.10	0.09	3.73	0.20
Sediment 13	2.23	185.24	12.12	1363	115.32	0.63	0.94	0.34	14.93	0.37

Table A8 Total concentrations and RCR for sediment

	Total sediment concentration (mg kg^{-1})					RCR				
	Cd	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**
PEL	**3.53**	**197**	**35.9**	**91.3**	**315**					
Sediment 1	0.2	31.1	8.3	49.1	33.0	0.1	0.2	0.2	0.5	0.1
Sediment 2	1.8	96.6	12.3	1590	189	0.5	0.5	0.3	17.4	0.6
Sediment 3	18.7	837.3	109.1	4146	1278	5.3	4.3	3.0	45.4	4.1
Sediment 4	24.8	843.1	97.0	3299	1424	7.0	4.3	2.7	36.1	4.5
Sediment 6	7.6	424.9	50.7	864	347	2.2	2.2	1.4	9.5	1.1
Sediment 7	7.0	732.6	32.6	1001	504	2.0	3.7	0.9	11.0	1.6
Sediment 10	8.8	433.2	73.4	3270	764	2.5	2.2	2.0	35.8	2.4
Sediment 11	8.3	323.0	17.2	5532	721	2.3	1.6	0.5	60.6	2.3
Sediment 12	4.8	214.4	55.5	2996	602	1.4	1.1	1.5	32.8	1.9
Sediment 13	14.3	640.1	34.8	17380	381	4.0	3.2	1.0	190.4	1.2

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Table A9 Exchangeable concentrations, PNEC and RCR for metals in soil and spoil (highlighted cells show RCR values greater than 1).

	Concentration of exchangeable metal (mg kg^{-1})					Arche PNEC (mg kg^{-1})					RCR				
Sample	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**
Soil 6	0.01	1.6	0.7	7	2.3	1.1	155	73	427	239	0.01	0.010	0.010	0.086	0.010
Soil 7	0.04	1.1	0.7	2	2.3	1.1	120	46	341	180	0.04	0.009	0.015	0.021	0.013
Soil 8	0.05	0.4	0.5	3	6.2	1.1	170	92	466	281	0.05	0.002	0.005	0.005	0.022
Soil 9	0.07	1.8	0.7	4	6.1	1.1	145	68	415	251	0.07	0.012	0.011	0.007	0.024
Soil 10	0.12	3.4	1.1	2	5.2	1.1	163	82	448	265	0.11	0.021	0.014	0.008	0.020
Soil 11	0.07	0.4	0.6	1	5.8	1.1	157	78	438	260	0.07	0.003	0.008	0.005	0.022
Soil 12	0.06	0.2	0.4	1	6.5	1.1	169	87	457	268	0.06	0.001	0.005	0.002	0.024
Soil 13	0.09	0.2	0.2	831	10.6	1.1	173	91	463	270	0.08	0.001	0.003	0.002	0.039
Soil 14	3.18	112	1.1	246	269	1.1	86	27	238	145	2.9	1.3	0.042	3.5	1.9
Soil 15	0.88	7.7	1.4	123	46	1.1	171	86	455	244	0.80	0.045	0.016	0.542	0.19
Soil 16	1.09	13.0	1.1	178	68.8	1.1	145	65	406	231	0.99	0.090	0.017	0.302	0.30
Soil 17	0.92	54.8	0.7	30	52.2	1.1	157	74	431	242	0.83	0.35	0.009	0.414	0.22
Soil 18	0.38	6.6	1.0	41	30.7	1.1	168	86	455	264	0.34	0.040	0.012	0.067	0.12
Soil 19	0.005	1.4	0.9	107	7.6	1.1	165	81	445	235	0.01	0.008	0.011	0.093	0.032
Soil 20	0.58	4.8	1.0	371	45.5	1.1	151	73	427	256	0.53	0.032	0.014	0.25	0.18
Soil 21	2.42	4.6	1.3	20	143	1.1	218	132	513	285	2.2	0.021	0.010	0.72	0.50
Soil 22	0.14	0.7	0.7	226	8.9	1.1	147	70	419	251	0.13	0.004	0.011	0.047	0.035
Soil 23	0.06	19.9	0.7	21	2.5	1.1	145	69	419	193	0.06	0.14	0.010	0.54	0.013
Soil 24	0.13	3.8	0.6	3	9.5	1.1	88	28	248	153	0.12	0.043	0.019	0.086	0.062
Soil 25	0.08	0.4	0.6	92	3.8	1.1	120	49	355	166	0.07	0.003	0.013	0.009	0.023
Spoil 1	0.43	22.1	0.4	105	23.9	1.1	85	35	290	115	0.39	0.26	0.012	0.32	0.208
Spoil 2	0.39	16.4	0.4	19	15.0	1.1	74	27	237	91	0.36	0.22	0.013	0.44	0.164
Spoil 3	0.16	8.1	0.4	469	8.6	1.1	111	54	371	149	0.15	0.073	0.008	0.052	0.058
Spoil 4	0.6	12.8	0.3	278	64.3	1.1	81	34	282	103	0.54	0.16	0.007	1.7	0.623

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	Concentration of exchangeable metal (mg kg^{-1})					Arche PNEC (mg kg^{-1})					RCR				
Sample	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**
Spoil 5	0.56	73.3	0.3	39	48.0	1.1	98	46	340	140	0.51	0.75	0.007	0.82	0.344
Spoil 6	0.02	3.1	0.3	76	2.3	1.1	51	13	127	59	0.02	0.061	0.027	0.31	0.039
Spoil 7	0.22	17.2	0.3	196	16.2	1.1	49	15	151	57	0.20	0.35	0.021	0.50	0.29
Spoil 8	6.13	95.3	0.3	135	348	1.1	116	49	353	184	5.6	0.82	0.006	0.55	1.9
Spoil 9	1.26	17.0	0.4	392	171	1.1	44	10	102	81	1.1	0.39	0.035	1.3	2.1
Spoil 10	0.18	6.8	0.2	1432	15.8	1.1	69	28	247	84	0.17	0.099	0.007	1.6	0.189
Spoil 11	0.03	5.2	0.2	471	5.1	1.1	73	27	237	90	0.03	0.071	0.009	6.1	0.057
Spoil 12	0.01	2.8	0.2	495	1.2	1.1	53	14	139	62	0.01	0.053	0.014	3.4	0.018
Spoil 13	0.01	5.2	0.4	2018	1.6	1.1	94	34	282	127	0.01	0.055	0.012	1.8	0.013
Spoil 14	0.04	5.8	0.1	752	2.2	1.1	101	41	320	132	0.04	0.058	0.002	6.3	0.016
Spoil 15	0.02	2.9	0.2	1503	1.8	1.1	57	17	163	67	0.02	0.051	0.014	4.6	0.026
Spoil 16	0.08	2.9	0.2	1218	9.7	1.1	42	13	127	45	0.07	0.071	0.014	11.8	0.216
Spoil 17	1.07	9.4	0.2	2298	60.9	1.1	60	22	207	70	0.97	0.16	0.010	5.9	0.864
Spoil 18	0.01	3.0	0.2	2613	1.3	1.1	65	21	197	80	0.01	0.046	0.009	11.7	0.016
Spoil 19	0.09	6.5	0.9	1388	4.2	1.1	65	21	196	79	0.08	0.10	0.043	13.4	0.053
Spoil 20	0.43	14.1	0.4	524	21.6	1.1	87	35	290	114	0.39	0.16	0.012	4.8	0.19
Spoil 21	0.01	13.4	0.3	<0.1	0.6	1.1	88	30	257	119	0.01	0.15	0.010	2.0	0.005

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Table A10 **Total concentrations, PNEC and RCR for metals in soil and spoil (highlighted cells show RCR values greater than 1).**

	Concentration of total metal (mg kg^{-1})					Arche PNEC (mg kg^{-1})					RCR				
Sample	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**
Soil 6	0.6	57	10.6	439	37	1.1	155	73	427	239	0.5	0.4	0.1	1	0.2
Soil 7	0.5	41	15.1	109	67	1.1	120	46	341	180	0.5	0.3	0.3	0.3	0.4
Soil 8	1.2	32	5.2	186	31	1.1	170	92	466	281	1.1	0.2	0.1	0.4	0.1
Soil 9	1.6	89	8.8	138	33	1.1	145	68	415	251	1.4	0.6	0.1	0.3	0.1
Soil 10	3.4	220	32.1	204	99	1.1	163	82	448	265	3.1	1.4	0.4	0.5	0.4
Soil 11	0.6	27	5.2	118	25	1.1	157	78	438	260	0.6	0.2	0.1	0.3	0.1
Soil 12	0.6	14	4.9	121	25	1.1	169	87	457	268	0.5	0.1	0.1	0.3	0.1
Soil 13	0.5	12	2.1	79	24	1.1	173	91	463	270	0.4	0.1	0	0.2	0.1
Soil 14	7.5	587	19.6	3995	760	1.1	86	27	238	145	6.9	6.8	0.7	17	5.3
Soil 15	1.9	113	21.0	924	149	1.1	171	86	455	244	1.7	0.7	0.2	2.0	0.6
Soil 16	2.5	116	15.4	742	203	1.1	145	65	406	231	2.3	0.8	0.2	1.8	0.9
Soil 17	2.2	321	14.5	1008	150	1.1	157	74	431	242	2	2	0.2	2.3	0.6
Soil 18	0.9	78	14.0	295	92	1.1	168	86	455	264	0.8	0.5	0.2	0.6	0.3
Soil 19	0.4	49	21.5	319	60	1.1	165	81	445	235	0.3	0.3	0.3	0.7	0.3
Soil 20	1.6	93	12.4	1107	209	1.1	151	73	427	256	1.5	0.62	0.17	2.6	0.815
Soil 21	5.1	182	10.3	2967	447	1.1	218	132	513	285	4.7	0.8	0.1	5.8	1.6
Soil 22	0.7	34	7.4	389	57	1.1	147	70	419	251	0.6	0.2	0.1	0.9	0.2
Soil 23	3.6	235	8.8	1423	25	1.1	145	69	419	193	3.3	1.6	0.1	3.4	0.1
Soil 24	0.6	31	5.3	129	24	1.1	88	28	248	153	0.6	0.4	0.2	0.5	0.2

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	Concentration of total metal (mg kg^{-1})					Arche PNEC (mg kg^{-1})					RCR				
Sample	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**
Soil 25	0.3	10	1.7	50	9	1.1	120	49	355	166	0.3	0.1	0	0.1	0.1
Spoil 1	38.7	2964	12.0	25609	1323	1.1	85	35	290	115	35.2	34.9	0.3	88	12
Spoil 2	40.5	3054	12.3	26522	1340	1.1	74	27	237	91	36.8	41.5	0.5	112	15
Spoil 3	19	584	13.4	9143	498	1.1	111	54	371	149	17.3	5.3	0.2	25	3.3
Spoil 4	46	1495	7.6	24021	1178	1.1	81	34	282	103	41.9	18.5	0.2	85	11
Spoil 5	46.5	2586	6.5	13584	1656	1.1	98	46	340	140	42.3	26.3	0.1	40	12
Spoil 6	1.4	89	16.4	899	142	1.1	51	13	127	59	1.2	1.8	1.3	7.1	2.4
Spoil 7	35.7	931	10.9	8610	978	1.1	49	15	151	57	32.5	19.1	0.7	57	17
Spoil 8	25.2	3627	4.9	12986	2798	1.1	116	49	353	184	22.9	31.3	0.1	37	15
Spoil 9	2.1	84	20.0	349	304	1.1	44	10	102	81	1.9	1.9	2	3.4	3.8
Spoil 10	17.5	1229	14.2	24916	1148	1.1	69	28	247	84	15.9	17.9	0.5	101	14
Spoil 11	21.3	3179	9.7	42729	863	1.1	73	27	237	90	19.4	43.8	0.4	181	9.6
Spoil 12	2.8	603	4.0	8299	45	1.1	53	14	139	62	2.6	11.4	0.3	60	0.7
Spoil 13	4.6	538	13.5	10143	234	1.1	94	34	282	127	4.2	5.7	0.4	36	1.8
Spoil 14	25.1	904	12.6	30677	549	1.1	101	41	320	132	22.8	9	0.3	96	4.2
Spoil 15	12.3	1205	8.7	21329	395	1.1	57	17	163	67	11.2	21.2	0.5	131	5.9
Spoil 16	32.9	5530	3.5	55284	2382	1.1	42	13	127	45	29.9	133	0.3	435	53
Spoil 17	26	3908	6.3	72871	3684	1.1	60	22	207	70	23.7	65.3	0.3	352	52
Spoil 18	17.8	3056	6.7	70134	896	1.1	65	21	197	80	16.2	47	0.3	357	11
Spoil 19	22	4895	11.7	55685	5741	1.1	65	21	196	79	20	75.2	0.6	285	72
Spoil 20	17.1	3818	6.7	39435	3994	1.1	87	35	290	114	15.6	44.1	0.2	136	35
Spoil 21	1.5	174	14.0	2704	92	1.1	88	30	257	119	1.4	2	0.5	11	0.8

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Table A11. Load data

24/04/14 - Total Concentrations (After rainfall)

Site Location	**Discharge ($m^{3/}S$)**	**Cu (µg/l)**	**Load (g/day)**	**Zn (µg/l)**	**Load (g/day)**	**Pb (µg/l)**	**Load (g/day)**	**Cd (µg/**
Cholwell Brook D/S of Wheal Jewell Reservoir	0.017	0	0	5.1	8	0	0.0	0
Cholwell Brook U/S of Adit	0.069	10.9	65	140	836	81.8	488	1.12
Cholwell Brook Adit	**0.032**	**30.4**	**84**	**379**	**1053**	**260**	**722**	**1.94**
Cholwell Brook D/S of Adit	0.101	15.6	136	206	1802	121	1059	1.35
Cholwell Brook at Brook Tavy	0.187	19.4	313	127	2052	42.2	682	0.809
Diff' betw'n d/stream & upstream of adit (g/day)			71		966		570	
% Adit of d/stream – u'stream load (g/day)			118%		109%		127%	
% Contribution of Adit load to d/s Adit sample			62%		58%		68%	
% Contribution of Adit at Brook Tavy			27%		51%		106%	

11/06/14 - Total Concentrations (Dry conditions)

Site Location	**Discharge ($m^{3/}S$)**	**Cu (µg/l)**	**Load (g/day)**	**Zn (µg/l)**	**Load (g/day)**	**Pb (µg/l)**	**Load (g/day)**	**Cd (µg/**
Cholwell Brook D/S of Wheal Jewell Reservoir	0.012	<1	0	0	0	<2	-	<0.1
Cholwell Brook U/S of Adit	0.027	8.9	21	121	286	66.3	157	0.98
Cholwell Brook Adit	**0.018**	**27.8**	**44**	**391**	**613**	**322**	**505**	**1.9**
Cholwell Brook D/S of Adit	0.046	17.1	67	245	964	170	669	1.44
Cholwell Brook at Brook Tavy	0.095	13.9	115	147	1211	22.2	183	0.86
Diff' betw'n d/stream & upstream of adit (g/day)			46		678		512	
% Adit of d/stream – u'stream load (g/day)			94%		91%		99%	
% Contribution of Adit load to d/s Adit sample			65%		64%		76%	
% Contribution of Adit at Brook Tavy			38%		51%		276%	

24/04/14 - Dissolved loads

Site Location	**Discharge (m^3)**	**Cu (µg/l)**	**Load (g/day)**	**Zn (µg/ l)**	**Load (g/day)**	**Pb (µg/l)**	**Load (g/day)**	**(**
Cholwell Brook D/S of Wheal Jewell Reservoir	0.017	0.5	0.7	2.5	3.7	1	1.5	0
Cholwell Brook U/S of Adit	0.069	9.24	55.2	137	818	66	394	
Cholwell Brook Adit	**0.032**	**27.6**	**76.7**	**373**	**1036**	**100**	**278**	**1**
Cholwell Brook D/S of Adit	0.101	13.1	114.6	199	1741	62.2	544	
Cholwell Brook at Brook Tavy	0.187	13	210.0	121	1955	7.95	128	0
11/06/2014								
Diff' betw'n d/stream & upstream of adit (g/day)			59.44		923		150	
% Adit of d/stream – u'stream load (g/day)			129%		112%		185%	
% Contribution of Adit load to d/s Adit sample			67%		60%		51%	
% Contribution of Adit at Brook Tavy			37%		53%		216%	

Site Location	**Discharge (m^3)**	**Cu (µg/l)**	**Load (g/day)**	**Zn (µg/ l)**	**Load (g/day)**	**Pb (µg/l)**	**Load (g/day)**	**(**
Cholwell Brook D/S of Wheal Jewell Reservoir	0.012	0.50	0.5	6.06	6.2	1	-	0
Cholwell Brook U/S of Adit	0.027	8.31	19.7	119	281.5	59.6	141.0	0
Cholwell Brook Adit	**0.018**	**25.80**	**40.5**	**386**	**605.5**	**133**	**208.6**	**1**

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Cholwell Brook D/S of Adit	0.046	14.40	56.6	243	955.9	78.9	310.4
Cholwell Brook at Brook Tavy	0.095	10.90	89.8	140	1153.7	7.16	59.0
Diff' betw'n d/stream & upstream of adit (g/day)			37.0		674		169
% Adit of d/stream – u'stream load (g/day)			109%		90%		123%
% Contribution of Adit load to d/s Adit sample			71%		63%		67%
% Contribution of Adit at Brook Tavy			45%		52%		354%

Table A12. Macroinvertebrate raw data collected from the Cholwell Brook and River Tavy.

Water Body	**CHOLWELL BROOK**	**CHOLWELL BROOK**	**CHOLWELL BROOK**	**CHOLWELL BR**
Site/Station Name	**DOWNSTREAM WHEAL JEWELL RESERVOIR**	**UPSTREAM WHEAL BETSY SPOIL**	**UPSTREAM CHOLWELL ADIT**	**DOWNSTREA CHOLWELL A**
Site/Station ID	171217	171218	171219	171220
Site/Station Location	SX 52155 81720	SX-51214-81478	SX 50927 80683	SX 50956 805
Sample Date	04-Apr-14	04-Apr-14	04-Apr-14	04-Apr-14
TAXA	NUMBER ESTIMATED	NUMBER ESTIMATED	NUMBER ESTIMATED	NUMBER ESTIMA
Polycelis felina	3		4	
Potamopyrgus antipodarum				
Pisidium		1		
Oligochaeta	1	10		
Erpobdella octoculata				
Hydracarina		1		
Gammarus pulex				
Alainites muticus				
Baetis rhodani				
Baetis vernus	3	40		
Rhithrogena semicolorata				
Ecdyonurus				
Electrogena lateralis	70	3		
Serratella ignita				
Caenis rivulorum				

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Water Body	CHOLWELL BROOK	CHOLWELL BROOK	CHOLWELL BROOK	CHOLWELL BRO
Site/Station Name	DOWNSTREAM WHEAL JEWELL RESERVOIR	UPSTREAM WHEAL BETSY SPOIL	UPSTREAM CHOLWELL ADIT	DOWNSTREA CHOLWELL A
Brachyptera risi	3	1	3	
Protonemura meyeri	3		50	6
Amphinemura sulcicollis	3			
Nemurella picteti				3
Leuctra hippopus	100	90	400	400
Leuctra inermis	60	300	500	200
Leuctra nigra		2		1
Isoperla grammatica	20	2		
Chloroperla torrentium	10	10	4	1
Cordulegaster boltonii			1	
Velia caprai	4			1
Gerris najas				
Oreodytes sanmarkii				
Agabus				1
Agabus guttatus	2			
Orectochilus villosus				
Hydraena gracilis				
Elodes	2		1	
Elmis aenea	1	1		
Limnius volckmari		3	2	
Rhyacophila		2		
Rhyacophila dorsalis	2	2		
Agapetus				
Philopotamus montanus				
Wormaldia	4			

Water Body	**CHOLWELL BROOK**	**CHOLWELL BROOK**	**CHOLWELL BROOK**	**CHOLWELL BR**
Site/Station Name	**DOWNSTREAM WHEAL JEWELL RESERVOIR**	**UPSTREAM WHEAL BETSY SPOIL**	**UPSTREAM CHOLWELL ADIT**	**DOWNSTREA CHOLWELL A**
Tinodes		1		
Polycentropodidae	2			
Plectrocnemia	8	1		1
Plectrocnemia conspersa	8	3	2	
Plectrocnemia geniculata	2			
Polycentropus			1	
Polycentropus flavomaculatus				
Polycentropus kingi				
Hydropsyche siltalai	1	7	20	5
Lepidostomatidae				
Crunoecia irrorata				
Lepidostoma hirtum				
Limnephilidae	5	1		
Drusus annulatus		4		
Halesus radiatus	1			
Potamophylax cingulatus		3		
Silo pallipes		3		
Beraea maurus				1
Sericostoma personatum				
Odontocerum albicorne				1
Adicella reducta				
Oecetis testacea				
Limoniidae			1	
Pedicia	1		1	1
Dicranota		20	1	2

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Water Body	**CHOLWELL BROOK**	**CHOLWELL BROOK**	**CHOLWELL BROOK**	**CHOLWELL BR**
Site/Station Name	**DOWNSTREAM WHEAL JEWELL RESERVOIR**	**UPSTREAM WHEAL BETSY SPOIL**	**UPSTREAM CHOLWELL ADIT**	**DOWNSTREA CHOLWELL AD**
Simulium	60	90	40	10
Simulium tuberosum				
Simulium variegatum				
Chironomidae	3	400	9	5
Empididae		20		1
Ibisia marginata				
Neolimnomyia		1		
BMWP	128	119	84	76
ASPT	6.40	6.61	6.46	6.91
N-TAXA	20	18	13	11