

DYNAMIC UP-FLOW PERCOLATION TESTS - A MODEL FOR MINING WASTE LEACHATE GENERATION

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ABSTRACT

Column experiments, based on the European standard up-flow percolation test (TS 14405), were applied to waste rock from an abandoned Pb/Zn mine in southwest England. The aim was to investigate the range and magnitude of pollutants transported from mine waste tips to surface watercourses. The dynamic leaching test was chosen to mimic the transport of rainwater through mine spoil, thereby providing a laboratory proxy for field conditions. A range of metals (Cd, Cu, Mn, Pb, Zn) and major ions were determined in the column leachate, covering solid:liquid ratios of 0-10 L kg⁻¹. The highest concentrations of Zn (200 µmol L⁻¹), Cu (17.4 µmol L⁻¹) and Cd (0.70 µmol L⁻¹) in the leachate were observed at low L/S ratios. Leachate concentrations decreased exponentially for most elements, except Pb, which maintained high concentrations (up to 80 µmol L⁻¹) throughout the experiment. Batch extractions with L/S ratios of 2, 5 and 10 L kg⁻¹ were applied to the same material. Concentrations in the supernatant were generally comparable to results from column experiments, but some differences at high L/S were attributed to the dynamic mode of leaching and the resulting higher adsorptive capacity of the solid phase in the column. Concentrations of Zn and Cd determined in shallow groundwater collected at the former mine site were of the same order of magnitude as concentrations obtained from the column experiments at high L/S ratios, showing that the column experiments provide a good approximation of field conditions. However, Pb and Cu concentrations, which showed close agreement between batch and column experiments, were much lower in the field (max. 3.0 µmol L⁻¹ and 1.9 µmol L⁻¹, respectively), probably due to the prevailing higher pH and/or a higher L/S ratio. This discrepancy highlights the limitations of using laboratory experiments to predict pollutant sources at abandoned mine sites.

1. INTRODUCTION

In southwest England, the legacy of metal mines, abandoned before remediative action was required by law, affects the environmental quality of surrounding landscapes. In particular, the concentrations of metals (e.g. Cd, Cu, Pb, Zn) in some rivers and coastal waters and their sediments exceed limits set by the Environment Agency for England and Wales to meet the requirements of the European Water Framework Directive (WFD, 2000/60/EC; EA, 2008) and Probable Effect Levels in sediments (Langston *et al.*, 2003). Nine percent of rivers in southwest England have been categorised as 'at risk' or 'probably at risk' due to abandoned metal mine pollution (Jarvis *et al.*, 2008). Leachate and run-off from mining waste, collected in surface streams and outflows, have been reported to carry high concentrations of contaminants to watercourses of southwest England (e.g. Howell and Bruce, 1995; Neal *et al.*, 2005; Mighanetara *et al.*, 2009) and elsewhere. However, metal fluxes from diffuse sources are difficult to determine accurately and expensive to investigate and hence remain largely unknown. The subtraction of point source fluxes from the total metal flux in a water course can provide a useful first estimate of diffuse inputs (Mayes *et al.*, 2008; Mighanetara *et al.*, 2008). However, this general approach does not provide detailed information on the dominant sources of contamination in a water course, as is required for river catchment assessment and management in the context of the WFD.

The aim of this study was to investigate diffuse metal fluxes emanating from a selection of mining-related sources in southwest England. In order to achieve this aim, controlled laboratory experiments were combined with field studies of run-off from mine spoil and shallow groundwater flow into surface water courses.

2. METHODS

Reagents and Apparatus

All aqueous solutions were prepared with MQ water (Millipore, R ≥18.2 MΩ cm⁻¹, reverse osmosis/ion exchange). Standard solutions and reagents were prepared in a Class 5 (BS EN 150 14644) laminar flow hood using trace metal clean techniques. Multi-element calibration standards were prepared as serial dilutions from standard solutions (1000 or

10000 $\mu\text{g L}^{-1}$, Romil Pure Chemistry, Fisher and BDH) and acidified to $<\text{pH } 2$ with Q-HNO_3 (purification by sub-boiling distillation, Romil SPA). All equipment was immersed in detergent (Decon 90, 2% v/v, >24 h) and rinsed with MQ water before cleaning with analytical reagent grade acids. Polyethylene centrifuge tubes (50 mL) and high density polyethylene bottles (HDPE, Nalgene) used for sample collection and standard preparation were cleaned by immersion in a series of acids (HCl , 6 mol L^{-1} , ≥ 7 days, HNO_3 , 2 mol L^{-1} , ≥ 7 days). Perspex™ columns used in leach experiments were immersed in HNO_3 ($\text{pH } 2$, ≥ 7 days). Filtration units (polycarbonate, Nalgene) and other apparatus were immersed in HCl (2 mol L^{-1} , ≥ 3 days). All items were rinsed with MQ water after each of the cleaning steps, dried in a laminar flow hood and stored in plastic zip-lock bags.

Site Description

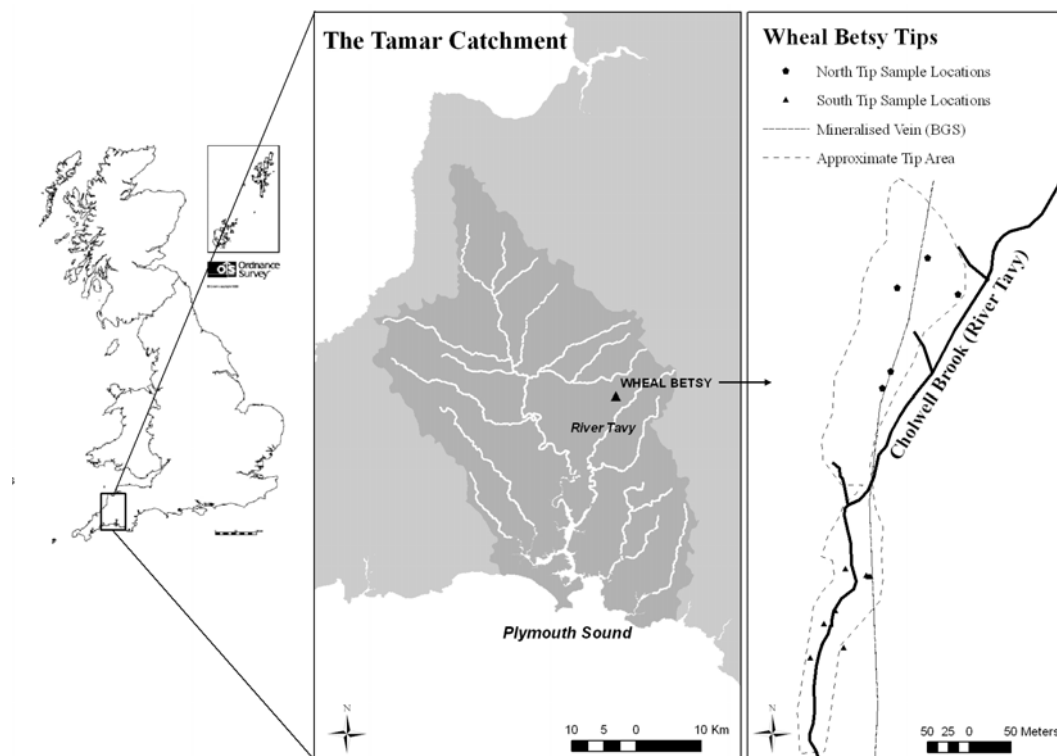


Figure 1. Location of Wheal Betsy within the Tamar catchment, southwest England, showing major river courses (centre). Site plan (right) of tips in relation to Cholwell Brook (solid black line), showing sample locations of mine waste material (north tip: ●, south tip: ▲). © Crown Copyright/database right 2009. An Ordnance Survey/EDINA supplied service.

The metalliferous deposits of southwest England host two major types of economic mineralisation: Sn oxide (cassiterite), Cu, As and Zn sulphide mineralisation, largely in E-W trending lodes and N or NW trending lodes, known as crosscourses, comprising Pb, Ag and Zn veins. The abandoned Wheal Betsy, which is the subject of the current study, was worked for Pb, Ag and Zn between 1740 and 1877 (Dines, 1956). The bedrock consists of slates and thin beds of limestones and grits of the Carboniferous Culm Measures. The veins are dominated by quartz, siderite, galena and sphalerite, with minor presence of pyrite, arsenopyrite, some Cu and Ag ores and traces of cadmium bearing ores (Dines, 1956; Page, 2008). Underground workings followed the N-S trending lode from a depth of 65 to ca. 270 m and were serviced by several shafts, engines and adits. The underground workings were drained to ca 70 m by means of a connecting adit to Wheal Friendship, located to the south of the site (Richardson, 1995; Hamilton Jenkin, 2005; Dines, 1956). Today, the site features the remains of engine houses, adits and a number of waste heaps of diverse materials along the banks of Cholwell Brook, a small tributary of the River Tavy (Figure 1). The waste tips at the north of the site mainly consist of poorly sorted coarse to medium sand (60-80%), with some larger pebbles and cobbles of quartz and slate and with iron hardpan horizons. Material in the south tips is similar in composition, but more heterogeneous, containing more clay and fine sands ($< 0.25 \text{ mm}$, 24% WBS and 14% WBN).

Sampling Protocol and Sample Treatment

Five composite samples of ca. 1.5 kg were taken from both, the northern and southern tip areas using a stainless steel trowel (Figure 1, north tip: 10-50 cm depth, south tip: 10-40 cm depth) Surface crusts, root layers and large pebbles ($>16 \text{ mm}$, Wentworth Scale) were omitted by hand sorting. The material was collected into zip lock bags and stored at 4°C . The individual mine waste samples were sieved (4 mm) and combined to form two composite samples representative of the north and south tip areas, respectively. The composite samples ($<4 \text{ mm}$) in the columns constituted 39% and 53% by weight of the sample material for WBN and WBS, respectively. The composite samples were

homogenized by cone and quartering and recombining (5 repetitions), placed in an airtight HDPE container and stored at 4°C. To sample shallow groundwaters flowing through the northern mine spoil (WBN) and towards Cholwell Brook, five piezometers (50 mm diameter) were installed. A schematic of the installation is provided in Figure 2.

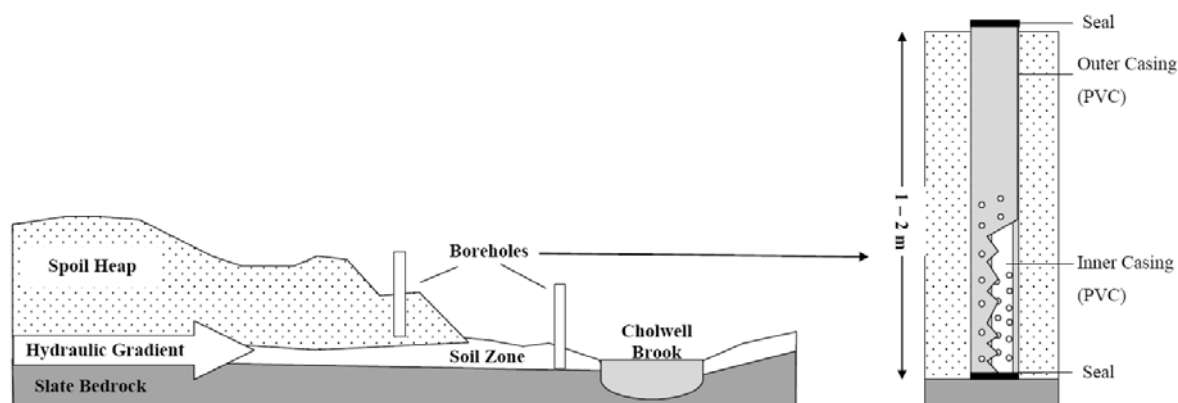


Figure 2. Cross-section schematic of borehole installation at Wheal Betsy (northern tips). On the right, the double-layer construction of the installed tubes is shown.

Double-layer tubes were installed into five boreholes (50 mm diameter) in order to intercept shallow groundwaters flowing from the northern mine spoil (WBN) towards Cholwell Brook (Figure 2). Boreholes were sampled via a Wattera™ bailer and purged to at least three borehole volumes prior to sample collection. Water samples were transferred to HDPE bottles after three rinses with sample water, and stored cool. Conductivity, pH and redox potential (Eh) were determined in situ using portable instruments (Hanna HI9635, MeterLab PHM201 and Hanna H9025 respectively). The pH meter was calibrated using standard solutions (pH 4 and 7, BDH), and the Eh measurements were made against ZoBell's solution (Nordstrom, 1977). In the laboratory, water samples were vacuum filtered (0.2 µm pore size, Whatmann Nuclepore). Samples for anion determination were stored cool (<3 days). Samples for metal determination were acidified (Q-HNO₃, pH 2).

Dynamic Up-Flow Column Experiments

Composite samples of mine spoil from the Wheal Betsy north (WBN) and south (WBS) tip areas were subjected in triplicate to up-flow column extraction procedures (standard European method (CEN/TS 14405, 2004). The leaching solution (aerated MQ water) was transported by a peristaltic pump at a constant flow rate (2.0 mL min⁻¹) into the bottom of the column. The out flowing solution (leachate) was filtered in-line (filter holder 47 mm diameter, Swinnex) in two stages (0.45 µm and 0.2 µm, Whatman Nuclepore). The leachate was either directed through a flow chamber for in-line determination of Eh and pH, or was collected for chemical analysis (Figure 3).

The complete column flow circuit, including filter holders, was cleaned in-line by circulating Q-HNO₃ followed by MQ water. The sample material was introduced to the column in 5cm layers, each reproducibly compacted with a 125g weight, dropped 50 times from a height of 20cm. The sample weight and the percent effective porosity of the column were determined gravimetrically. The columns were saturated with leaching solution (MQ water) and equilibrated at room temperature for 72 h. Subsequently, the MQ water was pumped continuously through the columns and leachate was sampled (ca. 30 mL) at L/S ratios from 0 to 10. Three aliquots (2 mL) of each sample were stored in glass HPLC vials and refrigerated pending quantification of anions. The remaining sample was stored in HDPE bottles and acidified (Q-HNO₃, pH 2) for metal analysis. The leachate pH (Hanna HI9025, VWR electrode) and Eh (Hanna HI9025, redox-ORP electrode, VWR) were recorded at time intervals throughout the experiment. The cumulative leachate volume for all columns was >10 L kg⁻¹.

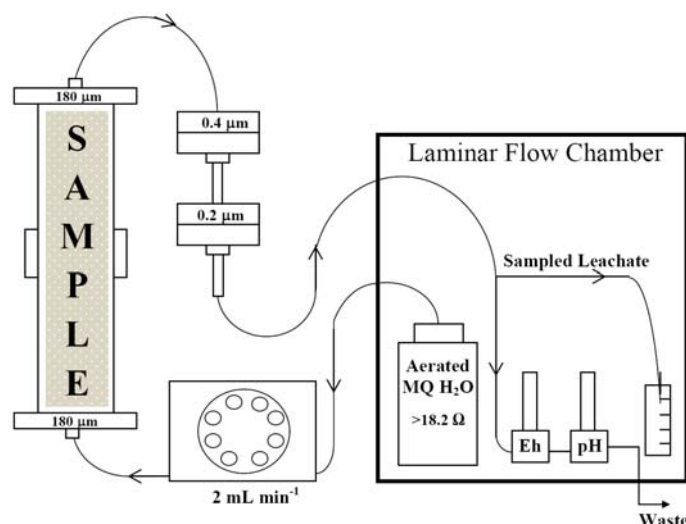


Figure 3. Schematic diagram of dynamic column experiment showing the complete flow circuit comprising leaching solution (aerated MQ water) supply, peristaltic pump, column packed with mine waste, double filtration and sample collection.

Batch Extractions

Composite Wheal Betsy north (WBN) and south (WBS) tip material was dried (40°C, 72 h). Sub-samples of homogenized material (4, 8 and 10 g) were accurately weighed into 50 mL centrifuge tubes. MQ water was added at L/S ratio's of 10, 5 and 2 respectively (in triplicate). Samples were laid horizontally and shaken for 16 h (orbital shaker), then immediately centrifuged (3000 rpm, 15 min). The supernatant was carefully removed via auto-pipette and acidified (Q-HNO₃, pH 2) for metal analysis.

Instrumentation and Analysis

Moisture content was determined in triplicate gravimetrically after drying (105°C) of sieved and homogenized samples (10 g). The organic matter content was determined gravimetrically as loss on ignition (450°C, 4h). Metal analysis in water samples and column leachate was carried out by ICP-OES (Varian 725-ES Inductively Coupled Plasma Optical Emission Spectrometer) and ICP-MS (VG Plasma Quad PQ2+ Turbo Inductively Coupled Plasma Mass Spectrometer) in an ISO9001:2000 accredited analytical research facility. Yttrium and indium (100 µg L⁻¹) were used as internal standards. Dissolved anions were determined by ion chromatography (Dionex DX-500 system, Dionex Ionpac AS9-HC column). Na and K analysis was performed by flame photometer (Corning 400). Analyses were verified against a certified reference material for trace elements (TMDA-64, National Water Research Institute, Canada) and the recovery was within 96 and 115% for all certified elements.

3. RESULTS AND DISCUSSION

Test Conditions

Up-flow percolation experiments were carried out at ambient temperatures of 18.2-23°C, and the initial moisture content of the samples was 13.2-14.7%. The organic matter content (LOI) was 7.5% and 4.7% at WBN and WBS, respectively. Test conditions showed good reproducibility between the triplicate columns of the same waste material (Table 1). The minor variations in the dry mass (ca. 0.84 kg), saturated pore volume (ca. 0.084 L), linear velocity (32 cm h⁻¹) and flow rate (1.5 ± 0.2 ml min⁻¹) of the leachate arose from small differences in the packing of the columns. WBN and WBS material produced leachate of similar pH values (1.9-2.6), whereby a gradual decline in pH by ca.0.6 units was observed during the experiment. The redox potential in the leachate remained positive (715-800 mV) throughout the experiment, indicating that the columns were not oxygen limited.

Table 1. up-flow percolation test characteristics for each column: flow rate, moisture content, temperature, dry mass, saturated pore volume, linear velocity, initial l/s ratio, median ph and ph and eh ranges.

Tip Material:	Wheal Betsy North (WBN)			Wheal Betsy South (WBS)		
Column No.	1	2	3	4	5	6
Mean flow rate (mL min ⁻¹)	1.44	1.39	1.61	1.45	1.31	1.69
Dry mass of solid sample (kg)	0.866	0.833	0.810	0.848	0.842	0.850
Saturated pore volume (L) ¹	0.085	0.086	0.094	0.079	0.081	0.079
Linear Velocity (cm h ⁻¹) ²	30.5	29.1	30.8	33.0	29.1	38.5
Initial L/S ratio (L kg ⁻¹) ³	0.10	0.10	0.12	0.09	0.10	0.09
pH range	1.9-2.6	1.8-2.5	1.9-2.6	2.0-2.5	2.3-2.6	2.3-2.6
Median pH ⁴	2.3			2.4		

¹ Water volume in saturated column, determined gravimetrically

² Determined from saturated pore volume per unit length of column (cm mL⁻¹) and the average flow rate (mL h⁻¹)

³ Initial L/S ratio calculated from saturated pore volume and dry sample mass

⁴ Median pH determined from all three replicates at L/S ratio >0.2 L kg⁻¹.

Reproducibility of Dynamic Up-Flow Column Experiments

In Figures 4 and 5, the elemental concentrations in column leachate, normalised for dry mass, were plotted against the L/S ratio. The resulting release curves were highly reproducible for triplicate columns for all elements, as illustrated in Figure 4 for Zn leached from WBN tip material. In the following sections, triplicate column results were combined to produce a single data set for each sample.

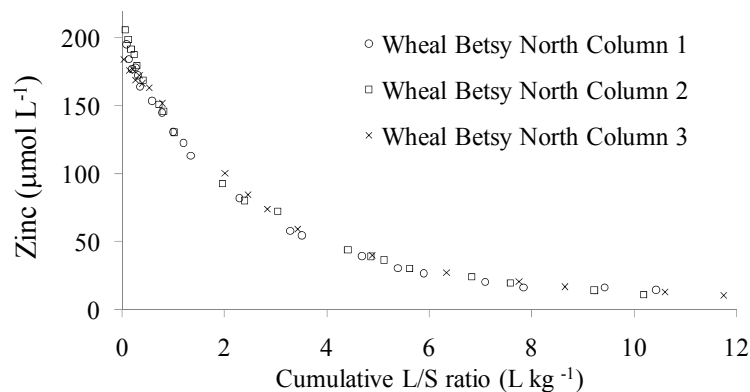


Figure 4. Concentration of dissolved Zn in leachate from replicate columns of WBN tip material versus cumulative liquid to solid (L/S) ratio. Concentrations were corrected for dry mass in the column. LOD_{Zn} = 0.025 µmol L⁻¹.

Elemental Release Curves

The chloride release curve (Figure 5A) demonstrates the leaching behaviour of a highly soluble ion with low affinity for the column material. The shape of release curves reflects the release rate of an element under conditions of changing L/S ratios and is influenced by the solubility of the source mineral phase and the adsorption or complexation strength with the column matrix. The steep gradient of the Cl release curve at low L/S ratios can be seen as representative for the behaviour of the most mobile elements, which are rapidly removed from the tip material. Elemental concentration in leachate generated towards the end of the experiment (L/S ≤ 10) tended towards a steady state, termed here the *dynamic equilibrium* concentration. The dynamic equilibrium condition is reached when the rate of an element's release into pore waters is in equilibrium with the rate of its removal from the column by fluid transport. It represents the concentration of an element found in solution after the 'first flush' of the solid material with eluent.

In comparison to Cl, the release of Zn, Cd and Cu from the column (Figure 5A, B, D, E) occurred at a slower rate and exhibited exponential decrease with increasing L/S ratio. The shape of these curves indicates a release mechanism influenced by surface sorption/desorption processes for elements of lower mobility, relative to that of chloride. The maximum leachate concentrations recorded at low L/S (WBN: 200 µmol L⁻¹ Zn, 0.7 µmol L⁻¹ Cd, 17.4 µmol L⁻¹ Cu; WBS: 13.8 µmol L⁻¹ Zn, 0.17 µmol L⁻¹ Cd, 0.71 µmol L⁻¹ Cu) were an order of magnitude higher than the dynamic equilibrium concentrations, and provide an estimate of the peak release from the waste tip material after a cycle of drying and wetting. The Pb concentrations in the column leachate exhibited a small decrease (<15% of initial concentration) at low L/S ratios, before recovering to previous levels and remaining stable for the remainder of the experiment. This indicates that Pb release from the column is in dynamic equilibrium over the full range of L/S ratios

applied. As a result, Pb ($35.3\text{--}77.9\ \mu\text{mol L}^{-1}$), along with SO_4^{2-} ($285\text{--}403\ \mu\text{mol L}^{-1}$), represent the dominant dissolved ions in the leachate at dynamic equilibrium.

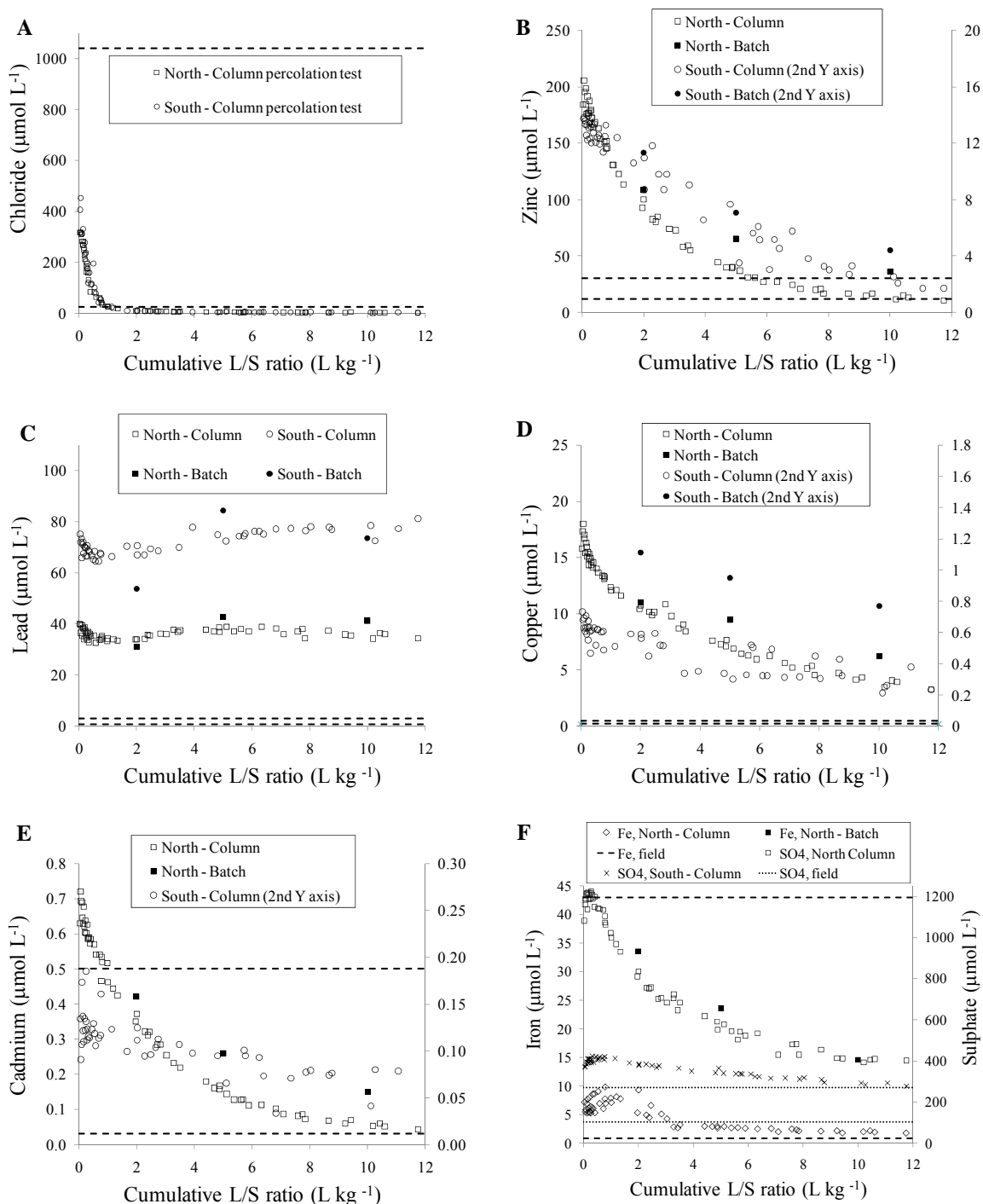


Figure 5. Dissolved concentrations of metals and chloride in column leachate and batch extractions with respect to L/S ratio (LOD, $\mu\text{mol L}^{-1}$): Zn (0.025), Cu (0.0036), Cd (0.003), Pb (0.003), Fe (0.32), Mn (0.05) SO_4^{2-} (3.34) and Cl^- (1.39). Dashed lines represent the range of concentrations determined in borehole samples at Wheal Betsy North (scale on left axis).

The iron release curve from Wheal Betsy north tips was characterised by an initial concentration increase (L/S < 2) from $6.1\ \mu\text{mol L}^{-1}$ Fe to a maximum of $9.2\ \mu\text{mol L}^{-1}$ Fe (Figure 5F). After reaching the maximum, concentrations initially decreased steeply, then less so, reaching a dynamic equilibrium around $2\ \mu\text{mol L}^{-1}$ Fe. The release curves for sulfate at WBN and WBS followed a similar trend. This behaviour indicates the interplay between mobilisation from the solid phase (dissolution of primary and secondary minerals and desorption) and loss from the dissolved phase due to the precipitation of secondary phases, such as amorphous iron hydroxides and iron hydroxysulphates, under changing conditions. It is likely that during the initial equilibration stage of the column, iron was mobilised into the pore water and reached a balance between the solid and dissolved phases. As the dynamic stage of the experiment commenced,

readily mobile Fe phases leached from the column at a rate that increased with the L/S ratio up to the point (at L/S >2) where the release curve followed an exponential decrease, as observed for Zn, Cd and Cu. Iron concentrations were below or very close to the LOD (0.32 $\mu\text{mol L}^{-1}$) in Wheal Betsy South leachate.

Based on the maximum observed concentrations in column leachate and assuming conservative transport, a dilution factor of 1000 would be required to reduce maximum Pb concentrations (WBS: 90 $\mu\text{mol L}^{-1}$, WBN: 39.7 $\mu\text{mol L}^{-1}$) below the current fresh water Environmental Quality Standard (EQS) (low alkalinity). Similarly, a dilution factor of 1000 (WBN) or 100 (WBS) would be necessary to reduce peak Zn concentrations (200 $\mu\text{mol L}^{-1}$ and 13.8 $\mu\text{mol L}^{-1}$, resp.) and a dilution factor of 100 (WBN, WBS) would be necessary to reduce Cd concentrations (up to 0.7 $\mu\text{mol L}^{-1}$) in order to meet with EQS, and therefore WFD, requirements. Based on recent stream sampling and previous studies (Austin, 2005) Cholwell Brook enters the mine site with low background concentrations of contaminant metals but exceeds current freshwater EQSs for Zn, Cd, Pb and Cd upon leaving it. Given the size of the tips and their close proximity to Cholwell Brook, the tip drainage represents a significant source of contamination to the watercourse. The severity and downstream extent of the contamination depends on the magnitude of dilution and the mobility of individual metals. Therefore, accurate prediction of the impact of spoil heap drainage is limited by the availability of accurate hydrological data and knowledge of in-stream processes (i.e. dilution, element-specific sorption, complexation and precipitation).

Cumulative Element Loads

Cumulative contaminant loads ($\mu\text{mol kg}^{-1}$ of dry mass) released during the experiment (Figure) were calculated by summing the product of the concentration of collected column fractions and the L/S ratio (up to L/S 10). Wheal Betsy south material leached predominantly Pb and Zn (730 $\mu\text{mol kg}^{-1}$ and 59 $\mu\text{mol kg}^{-1}$ respectively), while north tip material was characterised by a wider range of contaminants (including Zn at 518 $\mu\text{mol kg}^{-1}$) and a higher sulphate load (6.1 mmol kg^{-1}).

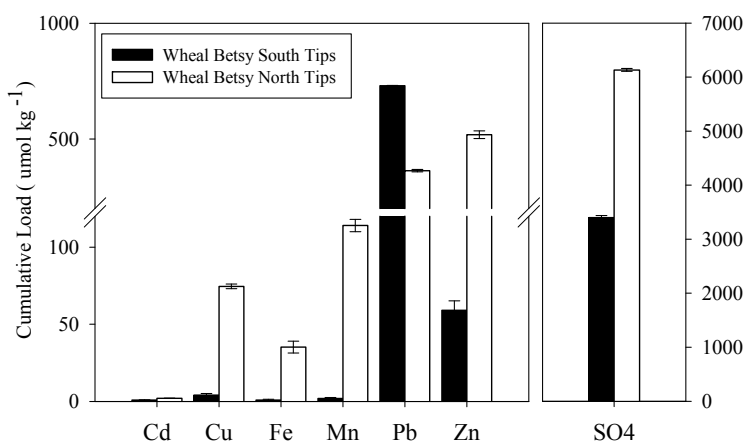


Figure 6. Cumulative metal and sulphate loads ($\mu\text{mol kg}^{-1}$) leached from Wheal Betsy north and south tip material during up-flow percolation tests. Error bars represent ± 1 s.d. (n=3).

The cumulative contaminant loads from the column experiments on WBN material are compared with results from batch extractions, performed on the same homogenised material at L/S ratios of 2, 5 and 10, in Figure 7. Batch and column tests showed closest agreement at L/S = 2, after which the column release curves diverged from the batch experimental results. Iron release was much lower in column experiments than in batch extractions (Figure 7E). This suggests that percolation as mode of leaching encourages the precipitation of iron oxides within the column matrix and as a consequence, through co-precipitation and/or adsorption, the mobility of other metals is also reduced. The ability of Fe and Mn hydroxides to adsorb metals has been shown to be particularly strong for Pb(II) and Cu(II), compared with Zn(II) and Cd(II) (Elliott *et al.*, 1986; Han *et al.*, 2006; Covelo *et al.*, 2007; Dong *et al.*, 2007). This may explain the lower release of Pb in the column experiment, compared with the batch experiments (Figure 7B). At high dissolved concentrations this adsorption effect can be masked, as was the case for Cu at WBN (Figure 7C), but becomes apparent at the lower concentrations released from WBS material (Figure 7F). Cadmium, released at lower concentrations than Cu at WBN (Figure 7D), did not exhibit the same behaviour, due to a lower affinity for Fe/Mn hydroxide binding sites.

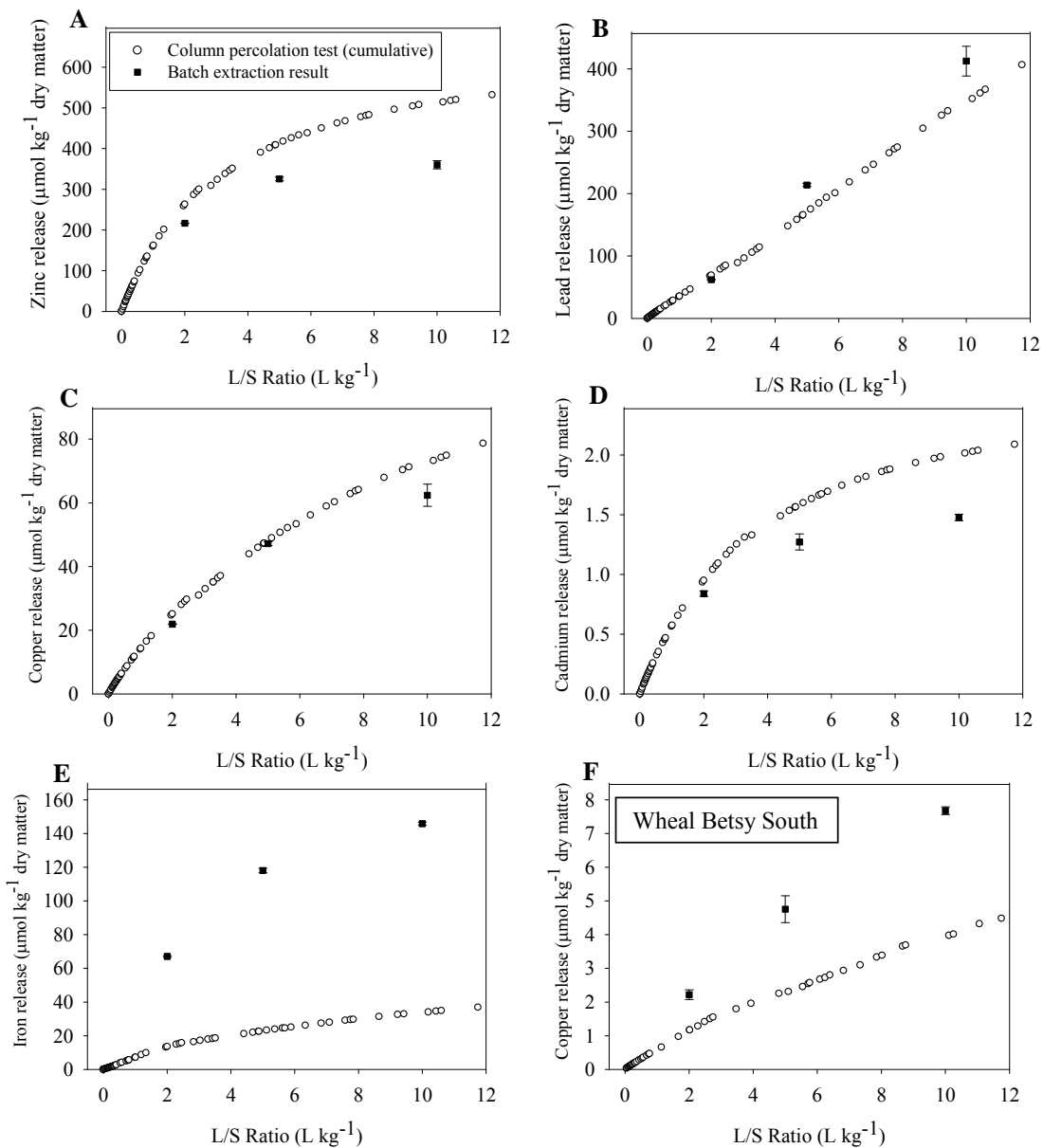


Figure 7. Metal, sulphate and chloride release from batch and column percolation tests for Wheal Betsy North material ($\mu\text{mol kg}^{-1}$) and Cu release from batch experiment for Wheal Betsy South material. Error bars for batch extraction represent ± 1 s.d (n=3).

It has been shown that preferential adsorption can cause metals with the lowest affinity for the column matrix to largely remain in solution (Covelo *et al.*, 2007). This can also account for the number of moles of Zn, Cd and Cu released from the column being progressively higher with increasing L/S ratio than the metal release in the batch experiments. In the presence of high dissolved concentrations of metals with higher affinity for Fe/Mn hydroxide binding sites, Zn and Cd are more likely to remain in solution than Pb and Cu. Overall, the dynamic experiment appeared to encourage greater desorption than the static batch experiment, and this is consistent with previous studies. Several explanations have been given for this discrepancy, including the kinetics of adsorption (Allen *et al.*, 2002) and the effects of preferential flow within columns (Porro *et al.*, 2000). The dynamic leaching experiment creates a dissolved element concentration gradient within the column, with pristine leaching solution constantly supplied to one end. Therefore, it is unlikely that equilibrium conditions between the solid and the dissolved phases become established during a dynamic column experiment. However, in batch extractions metal mobilisation is constrained by this equilibrium (Plassard *et al.*, 2000).

Comparison with Natural Waters

The concentration ranges of Zn (12-30.4 $\mu\text{mol L}^{-1}$) and Cd (0.03-0.5 $\mu\text{mol L}^{-1}$) observed in the boreholes installed at Wheal Betsy were of the same order of magnitude as the respective dynamic equilibrium concentrations obtained in the column leach experiments (Figure 5). For these metals, the column leaching was a good proxy for the conditions of dynamic flow prevailing in mine spoil and below the water table, even though the composite samples used in the laboratory experiments cannot be fully representative of the waste tip material present in the field. Dissolved

concentrations of Pb (0.7-3.0 $\mu\text{mol L}^{-1}$) and Cu (0.2-1.9 $\mu\text{mol L}^{-1}$) in borehole samples were lower than in column leachate, but still exceeded freshwater EQSs by one order of magnitude. This discrepancy may be related to the higher pH values (pH 3.8-5.1) observed in the boreholes, compared with the column experiments (pH 1.8-2.6), influencing ion exchange and sorption of Pb and Cu onto Fe/Mn hydroxide phases. Ion exchange processes are pH dependant. According to results reported by Tan *et al.*, (2008) and Oh *et al.*, (2009), a shift from the pH range observed in column leachate to those determined in boreholes is likely to result in a markedly higher Pb sorption onto mineral surfaces. The redox potential (455-650 mV) varied between boreholes and surveys and was somewhat lower than values recorded during the column experiment (715-800 mV). The redox and pH sensitivity of Fe influences its distribution between the solid and dissolved phases, as well as that of associated metals, and can contribute to differences between field and laboratory data.

The L/S ratio of 10:1 in the column test was designed to elute all the easily mobilised metals from the spoil material. However, in the case of Pb and Cu, it appeared that the dynamic equilibrium position was not attained by the end of the column test and did not satisfactorily predict Pb and Cu mobility in the field. In shallow groundwater the L/S ratio is unknown, but over time is likely to be $\gg 10$. Therefore, it is plausible that the borehole concentrations represent the true dynamic equilibrium position for Pb and Cu, which was not approximated by the column test. However, not all spoil material in the field exists below the water table and is subject to cyclic wet and dry conditions. The column experiments at low L/S ratio provide an important indicator of the maximum concentrations that could emanate from mine spoil following a heavy rainfall event.

A more detailed analysis of the field surveys is presented in the accompanying poster presentation: ‘Braungardt *et al.*, Acid mine waters at Wheal Betsy, an abandoned Pb/Zn mine in southwest England’.

4. CONCLUSIONS

In cases where extensive field investigations are not viable, the up-flow percolation experiment provides a means of mimicking the conditions of dynamic flow through mine spoil. Results from column experiments and sampled boreholes were similar for some metals (Zn and Cd) and may provide a useful tool for prediction of leachate composition. The highest concentrations of Zn (200 $\mu\text{mol L}^{-1}$), Cu (17.4 $\mu\text{mol L}^{-1}$) and Cd (0.70 $\mu\text{mol L}^{-1}$) in the leachate were observed at low L/S ratios. Concentrations at dynamic equilibrium were one order of magnitude below the maxima, with the exception of Pb which remained high. Lowest observed leachate concentrations in the field and laboratory remained elevated by one order of magnitude, with respect to the EQSs. For all elements, the dynamic equilibrium concentration from column experiments was more closely matched to field conditions than results obtained from the batch extractions. The discrepancies between column and batch experiments was small enough to suggest that batch experiments could be useful for developing management strategies where it is necessary to survey large areas for contaminant mobility. The largest difference between laboratory and field experiments was observed for Pb and Cu concentrations, where mobility was much reduced in the borehole samples in comparison with the high loads recorded for both batch and column experiments. An explanation for this may be the higher pH measured in the borehole waters (pH 3.8-5.1) compared with the more acidic leachates derived in the laboratory. Alternatively, the borehole may represent the true dynamic equilibrium position for Pb at a higher L/S ratio. The differences observed between laboratory and field based assessment approaches, demonstrates the limitations of applying laboratory data to the field scale. It also highlights the necessity to consider the effect of different physico-chemical and hydrological situations on the contamination potential of mine spoil.

5. REFERENCES

- Allen, H. E., Chen, Y.-T., Li, Y., Huang, C. P. and Sanders, P. F. (2002) “Soil Partition Coefficients for Cd by Column Desorption and Comparison to Batch Adsorption Measurements”. *Environmental Science & Technology*, **29** (8), 1887-1891.
- Austin, S. (2005) “Analysis of potentially toxic elements in the vicinity of Wheal Betsy, a former lead-silver mine.” MSc Thesis. University of Plymouth.
- Bowell, R. J. and Bruce, I. (1995) “Geochemistry of Iron Ochres and Mine Waters from Levant Mine, Cornwall.” *Applied Geochemistry*, **10** (2), 237-250.
- Covelo, E. F., Vega, F. A. and Andrade, M. L. (2007) “Competitive Sorption and Desorption of Heavy Metals by Individual Soil Components.” *Journal of Hazardous Materials*, **140** (1-2), 308-315.
- DD CEN/TS 14405:2004, Characterisation of Waste - Leaching Behaviour Test - up-Flow Percolation Test (under specified conditions). British Standards Institute.
- Dines, H. G. (1956). *The Metalliferous Mining Region of South-West England*. British Geological Survey, HMSO, London.
- Dong, D., Liu, L., Hua, X. and Lu, Y. (2007) “Comparison of Lead, Cadmium, Copper and Cobalt Adsorption onto Metal Oxides and Organic Materials in Natural Surface Coatings.” *Microchemical Journal*, **85** (2) 270-275.
- Elliott, H. A., Liberati, M. R. and Huang, C. P. (1986). “Effect of Iron Oxide Removal on Heavy Metal Sorption by Acid Subsoils.” *Water, Air, & Soil Pollution*, **27** (3) 379-389.
- Hamilton Jenkin, A. K. (2005). *Mines of Devon*. Cromwell Press, Trowbridge.

- Han, R., Zou, W., Zhang, Z., Shi, J. and Yang, J. (2006) "Removal of Copper(II) and Lead(II) from Aqueous Solution by Manganese Oxide Coated Sand: I. Characterization and Kinetic Study". *Journal of Hazardous Materials*, **137** (1), 384-395.
- Jarvis, A. P., Johnston, D., Mayes, W. H. and Potter, H. A. B. (2008) "Application of a New Methodology for Assessing the Priorities for Abandoned Mine Water Pollution Remediation at a National Scale: Results and Implications from a Study across England and Wales". Rapantova, N. and Hrkel, Z. (eds) *Conference Proceedings of the 10th International Mine Water Association Congress Karlovy Vary, Czech Republic*. 2-5 June 2008.
- Langston, W. J., Chesman, B. S., Burt, G. R., Hawkins, S. J., Readman, J. and Worsfold, P. (2003) "Characterisation of the South West European Marine Sites: Plymouth Sound and Estuaries CSAC, SPA." *Journal of the Marine Biological Association of the United Kingdom, Occasional Publication No. 9*.
- Mayes, W. M., Gozzard, E., Potter, H. A. B. and Jarvis, A. P. (2008). "Quantifying the Importance of Diffuse Minewater Pollution in a Historically Heavily Coal Mined Catchment". *Environmental Pollution*, **151** (1), 165-175.
- Mighanetara, K., Braungardt, C. B., Rieuwert, J. S. and Azizi, F. (2008) "Contaminant Fluxes from Point and Diffuse Sources from Abandoned Mines in the River Tamar Catchment, UK". *Journal of Geochemical Exploration*, **100**, 116-124.
- Neal, C., Whitehead, P. G., Jeffery, H. and Neal, M. (2005). "The Water Quality of the River Carnon, West Cornwall, November 1992 to March 1994: The Impacts of Wheal Jane Discharges". *Science of The Total Environment*, **338** (1-2), 23-39.
- Nordstrom, D. K. (1977). "Thermochemical Redox Equilibria of Zobell's Solution". *Geochimica et Cosmochimica Acta*, **41**, 1835-1841.
- Oh, S., Kwak, M. Y. and Shin, W. S. (2009). "Competitive Sorption of Lead and Cadmium onto Sediments." *Chemical Engineering Journal*, **152** (2-3), 376-388.
- Page, K. (2008). "County Geological Sites in West Devon and their Contribution to the Cornwall and West Devon Mining Landscape's World Heritage Site.", *Notes from the Devonshire Association Excursion*. University of Plymouth.
- Plassard, F., Winiarski, T. and Petit-Ramel, M. (2000) "Retention and Distribution of Three Heavy Metals in a Carbonated Soil: Comparison between Batch and Unsaturated Column Studies." *Journal of Contaminant Hydrology*, **42** (2-4), 99-111.
- Porro, I., Newman, M. E. and Dunnivant, F. M. (2000) "Comparison of Batch and Column Methods for Determining Strontium Distribution Coefficients for Unsaturated Transport in Basalt." *Environmental Science & Technology*, **34** (9), 1679-1686.
- Richardson, P. H. G. (1995). *Mines of Dartmoor and the Tamar Valley after 1913*. Devon Books, Torquay.
- Tan, X. L., Chang, P. P., Fan, Q. H., Zhou, X., Yu, S. M., Wu, W. S. and Wang, X. K. (2008). "Sorption of Pb(II) on Na-Rectonite: Effects of Ph, Ionic Strength, Temperature, Soil Humic Acid and Fulvic Acid." *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **328** (1-3), 8-14.