Inventory of aquatic contaminant flux arising from historical metal mining in England and Wales

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Abstract

The impact of discharges from abandoned metal and ironstone mines has been much-studied form of aquatic pollution in recent decades. Few attempts however, have been made to accurately determine the overall contaminant mass flux arising from abandoned mine sites at scales above catchment level. Such assessments are critical to determine the significance of former mining to national, regional and ultimately global trace metal flux. This paper presents the most comprehensive national survey to date across England and Wales of the total pollution burden discharged at source from abandoned non-coal mine sites. 338 discharges have been identified (from 4923 known abandoned mines) and while concurrent flow and contaminant concentration records are only available for around 30% of these, significant quantities of metals (and As) have been quantified to be discharged. A minimum of 193 tonnes of Zn, 18.5 tonnes of Pb, 0.64 tonnes Cd, 19.1 tonnes of Cu, 551 tonnes Fe, 72 tonnes Mn

and 5.1 tonnes As are released in water discharges from abandoned non-coal mines to the surface water environment of England and Wales each year. Precautionary extrapolation of mass fluxes based on the frequency distribution of measured concentration and flow data, for discharges with absent data, suggests the actual total mass flux for these contaminants could be up to 41% higher. The mass flux of Pb released from mines exceeds that of all currently permitted discharges (e.g. active industrial sites and wastewater treatment works) to surface waters across England and Wales, while those of As, Cd and Zn are of a similar magnitude. This data puts into context the enduring legacy of historic mining on the water environment, highlighting its significance relative to more highly regulated polluting sites. Comparison of the figures with estimates of global trace metal flux suggests that the national total identified here is significant on a global scale.

1. Introduction

Anthropogenic perturbation to global trace metal cycles has long been identified since the pioneering atmospheric trace metal inventories of Nriagu (1978) and Lantzy and Mackenzie (1979). For the water environment, assessments of global trace metal flux and associated human impacts have been developed since the study of Martin and Meybeck (1979), which provided the first comprehensive overview of river particulate composition and associated global river fluxes. Over the past three decades the average elemental composition (both particulate and dissolved

components) of many important global rivers has become better characterised and efforts to develop and update global databases (e.g. Poulton and Raiswell, 2000; Carey et al., 2002, Galliardet et al., 2003; Viers et al., 2009) have consistently alluded to the major human perturbation to the mass flux of trace metals in river systems. The mining and associated processing of metalliferous ores have long been documented to cause acute and persistent damage to the water quality of receiving water courses over scales from individual streams (e.g. Kimball et al., 2005; Nuttall & Younger, 1999), to entire river basins (e.g. Sarmiento et al., 2009), up to national level (e.g. Mayes et al., 2009). In their benchmark inventory of global trace metal cycles, Nriagu and Pacyna (1988) made the first and most comprehensive estimate to date of the total mass flux arising from the base metal mining and refining sector for a suite of metals and metalloids. Few attempts have been made since then to provide a detailed regional or global flux estimate for the mining sector on emissions to the water environment due to (a) the lack of suitably comprehensive datasets of source discharge flow and quality on which to base such assessments and (b) the short half lives of trace metal contaminants in the aqueous phase as they rapidly transfer from water column to fluvial sediments (Nriagu and Pacyna, 1988). The latter point renders assessments of metal discharge flux at source from ambient water quality monitoring stations problematic since they usually lie some distance downstream from polluting sources. The resultant contamination of sediments that arises due to instream attenuation processes of aqueous contaminants has been well characterised in many mining-impacted streams (Macklin et al., 2006) and the longevity of the sediment-borne metal pollution equally well-described (e.g. Coulthard and Macklin, 2003). However, assessments of trace contaminant release at source are essential for fully appreciating the ongoing pollution inputs from abandoned mines into the

surface water environment which ultimately contribute to the secondary sources of contaminated sediments in mining-affected river systems.

Regional studies of one major mining region and comparison with global trace metal flux recently undertaken by Sarmiento et al. (2009), have suggested that the notorious mining-impacted Odiel river basin, which drains the Iberian Pyrite Belt in Spain contributes up to 15% of the global dissolved Zn flux to the oceans as quantified by Gaillardet et al. (2003). Similar perturbations to global sulphur cycles have also recently been suggested to occur due to coal mining activity (Raymond & Oh, 2009). While acknowledging the large uncertainty surrounding extrapolations from two long-term datasets from two large catchments in Pennsylvania, Raymond and Oh (2009) suggest that sulphur released through the generation of acidic coal mine drainage could account for between 28-40% of the global riverine sulphate flux produced through pyrite oxidation.

These studies certainly suggest the stark impact that historic mining activity can have on global scale pollutant fluxes. However, given that such sizeable contributions are determined from localised, albeit acutely polluted systems, and mining derived water pollution has been well-documented in every continent of the world except Antarctica (e.g.; Kuma & Younger, 2004; Lottermoser et al., 1998; Kimball et al., 1999; Van Damme et al., 2008; He et al., 1997; Younger et al., 2002), it is likely that the mining-derived contribution of riverine metal fluxes is globally significant.

This paper presents results from a national assessment of polluting abandoned metal and ironstone mines in England and Wales. Related previous work has summarised

the methodology for collating mine data and objectively assessing the impacts of abandoned non coal mine sites on the aquatic environment nationally (Mayes et al., 2009). The data presented here provide an inventory of the mass loading of common contaminant metals (and As) discharged at source by base metal and ironstone mines into the surface waters of England and Wales. As such, it provides a case study for one region of globally important historic mining, which is used to highlight, (1) the significance of pollution from a relic industrial sector (the peak of base metal mining in the UK was between 100-200 years ago) compared to contemporary sources of aquatic pollution nationally and (2) consider the significance of the mining-derived mass fluxes in terms of global trace metal cycles.

2. Methods

As part of a national assessment of pollution arising from abandoned metal mines in England and Wales (see Mayes et al., 2009, for detail), specialists from the Environment Agency (the government environmental regulator for England and Wales) were asked to populate a database with details of known polluting discharges from abandoned mines. Such discharges comprise drainage adits, shafts and runoff from spoil heaps or other metal rich wastes. A range of information was requested from the EA respondents (who encompassed specialist environmental scientists, hydrogeologists, chemists and biologists) including the location and nature (e.g. point or diffuse discharge) of any discharges and their impacts on downstream ecology and water resources (see Mayes et al., 2009). Crucial to the assessment undertaken here however, were data detailing mean flow rates and mean metal (and As)

concentrations for identified discharges. Total (unfiltered) concentration data were requested. Such information is collected during both ambient and campaign water quality monitoring undertaken by the Environment Agency and analysed in accredited laboratories in accordance with statutory water quality monitoring protocols. Concentration data were requested for As, Cd, Cu, Fe, Mn, Ni, Pb and Zn, which represent the most common (and most commonly measured) pollutants discharged from abandoned metal mines in England and Wales (Mayes et al., 2009). These concentration and flow data were used to compute an annual mass flux (in tonnes/year) for each contaminant at each site. Flow data for mine sites is sparse in many cases. Where flow data is available, it ranges between base-flow spot measurements usually undertaken during sampling campaigns for informing remediation feasibility assessments, to continuous flow measurement (e.g. calibrated weirs with stage loggers) at some of the larger discharges. In addition to the data return from the Environment Agency, a thorough review of published and grey literature (e.g. student theses, contract reports by environmental consultants) has been undertaken to collate currently available information detailing flow and / or chemical composition of metal mine discharges in England and Wales. Furthermore, manual collection of mine discharge flow and water quality data was undertaken at several sites known to the authors where data was absent in the return from the EA. Where manual data collation was undertaken (for 25 mine discharges), flow rates were measured using the velocity-area method (Shaw, 1994) and a Valeport 301 velocity meter with a flat electromagnetic sensor during base-flow conditions (July-August 2009). This device was particularly suited to measuring velocity in mine drainage adits given the typically shallow depth of water (generally <0.1m) with smooth, almost laminar flow. Total metal (and As) concentrations in acidified (with 5 drops

of concentrated trace element grade HNO_3) samples collected in accordance with standard water quality sampling procedures (APHA, 2005) were analysed using a Varian Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Reliability of sample analyses was tested by comparison with certified reference materials.

3. Results and Discussion

3.1 Contaminant flux at point of discharge

Figure 1 illustrates the geographic distribution and relative magnitude of the contaminant flux from abandoned base metal and ironstone mines, while Table 1 provides the summary flux totals of the 338 mines. Sample data for some of the most polluting sites are given in Table 2. In terms of total elemental flux, that of iron exceeds the individual mass fluxes of any other monitored contaminants. A significant portion of this Fe release arises from ironstone mine discharges in the Cleveland Ironstone Field of north east England (see Younger, 2000a), accounting for 25% of the total Fe release. Two other single discharges, the Dyffryn Adda Adit draining the Parys Mountain copper mine complex on the Isle of Anglesey, North Wales and the County Adit, which underdrains a large portion of the Cornwall tin mining district account for 34% and 26% respectively of the total Fe release nationally. Fe concentration in the discharges shows a bi-modal distribution with 57% of the data clustering below total Fe concentrations of 0.5mg/L and a second peak in Fe concentration in between 20-40mg/L in which 12% of the data fall. This reflects the fact that relatively few base metal mines have significant quantities of

pyrite, marcasite (FeS_2) and / or siderite ($FeCO_3$) associated with the extracted ores. Areas where there is appreciable Fe in base metal discharges include parts of the Western Wales orefield in Ceredigion, many of the discharges from the Sn-Cu mining district of Cornwall and some discharges in the North Pennines which, along with ironstone mines, account for the secondary, higher peak in Fe concentration.

Manganese is often associated with Fe in the mine discharges (correlation of concentrations of the two elements produces an r^2 of 0.71) and as such, the major inputs of Mn from abandoned metal mines largely mirrors that of Fe. The largest single contributor of Mn is the Saltburn Gill discharge in the Cleveand Ironstone Field (23.7 tonnes/year), with significant releases also reported at the Rispey Siderite mine (North Pennines: 12.7 tonnes/year), the County Adit (11.0 tonnes/year) and Dolcoath Adit (southwest England: 10.7 tonnes/year).

Given the mobility of Zn in the aquatic environment (Stumm & Morgan, 1996) it is no surprise that it is the most common contaminant reported from abandoned metal mines in England and Wales (Mayes et al., 2009). The total flux of Zn release exceeds 193 tonnes/year for those discharges where both flow and concentration are known. As with many of the parameters, a few single large discharges account for a sizeable portion of the Zn release. Some of the major single contributors are outlined in Table 2 which highlights the County Adit and Dyffryn Adda Adit releasing significant mass of Zn along with a series of discharges in central Wales in the Afon Ystwyth and adjacent Afon Rheidol catchments (see Fuge et al., 1991 for detail). In many cases the single large discharges represent major shallow-gradient drainage levels that were commonly used to dewater significant portions of (and in some cases

entire) base metal orefields in England and Wales (and is a practice common to many orefields elsewhere, e.g. Younger et al., 2002). Examples of such discharges in the database include ten high-yielding drainage levels (locally called 'soughs') across the lead mining catchments of the Derwent, Lathkill and Wye (Derbyshire in the Humber RBD); the County Adit which is over 60km in length and underdrains much of the Sn-Cu orefield of western Cornwall; two multi-kilometre levels in the North Pennines (Blackett Level, Nent Force Level, Northumbria RBD) and the largest single mining drainage feature in England and Wales: the Milwr Tunnel, which underdrains much of the Halkyn Mountain orefield in North Wales and discharges a mean of 1347 L/s of mine water and associated groundwater into the Dee Estuary in North Wales (Figure 1).

Release of Pb is centred in the orefields of Western and North Wales, the Pennine orefields and the few discharges so far characterised in the Lake District of north-west England. Exceptionally high Pb flux occurs in central Wales in the sub-catchments of the Afon Ystwyth where high flow rates are combined with elevated Pb concentrations. The Frongoch Adit releases up to 11.8 tonnes Pb/year, while nearby discharges, Frongoch Stream and the Kingside Adit (Cwmystwyth mine site), release 1.8 and 0.4 tonnes Pb/year respectively. Other major sources of Pb include two major drainage levels: the Meerbrook Sough in Derbyshire (0.4 tonnes Pb/year: see Shepley, 2007) and the Milwr Tunnel in North Wales (1.3 tonnes Pb/year). The large flux at these two sites is driven primarily by the very high flow rates (mean of 0.74 and 1.3m^3/s respectively) with concentrations of Pb (and other contaminants) so low that the discharges are used for potable and industrial water abstractions respectively.

Cadmium is classed as a 'Priority Hazardous Substance' under the European Union's Water Framework Directive (2000/60/EC) due to its toxicity, bioaccumulation and persistence in the environment and as such is one of the mining-related contaminants of particular regulatory concern. While absolute flux of Cd is far less than for Pb it does correlate well with Pb (r^2 of 0.66) and Zn (r^2 of 0.52) flux. As such, the major contributors to Cd release to surface waters of England and Wales are similar to that of Pb and Zn (Figure 1, Table 2). The single biggest Cd release occurs from the Frongoch Stream (Cwmystwyth Mine) at 145kg/yr. Other major drainage levels such as the Milwr Tunnel, County Adit, Meerbrook and Yatestoop Soughs and the Dyffryn Adit each contribute over 40kg/year of Cd to the surface water environment.

Data for Cu, As and Ni release are sparse for many of the mine sites. In areas where these contaminants pose particular concerns, reasonable datasets are available, for example in the south west of England where arsenic pollution is relatively common. Indeed the bulk of the identified As flux arises from the County and Dolcoath Adits (67% of the national As flux), with a further 27% arising from discharges within the River Tamar catchment (Mighanetera et al., 2009). Other small As contributions arise from the Owlercoombe mine complex in the River Lemon catchment (South West England) and from mines in north-west England where As is associated with the mined galena (PbS_2) and barite ($BaSO_4$) ores (e.g. Force Crag and Carrock Fell Mine). The quantified Cu mass flux is focussed around two main loci of former Cu mining: the Parys Mountain complex in North Wales (71% of Cu released) and the South West Sn-Cu mining district. Within the latter, discharges in the Tamar catchment account for 22% of the national total, with the County Adit and Wheal

Maid Tailings Dam (Carnon River) accounting for a further 5% of the flux. A large number of other mine sites across the Pennine regions and Western Wales have low Cu concentrations that contribute only slightly to the overall Cu flux. The datasets are most incomplete for Ni flux, which primarily reflects a lack of monitoring data. Again, the key locus for Ni release is in south west England where the County Adit and discharges in the heavily-mined River Tamar account for 72% of the total Ni release.

Although data detailing the partitioning of particulate and dissolved phases has not been collected for all discharges, where such data has been collated it typically illustrates very high proportions of dissolved contaminants at source (e.g. Merrington and Alloway, 1994; Nuttall and Younger, 1999; Mighanetera et al., 2009), prior to the transformation of metals into particulate form through instream and hyporheic biogeochemical processes.

It is essential to highlight that the data collated on the flux of metals discharged at source are likely to underestimate the total pollution burden for several reasons:

- There are thought to be many more than the 338 discharges so far identified nationally. Only a few areas of England and Wales have been subject to intense surveys of abandoned mine features (e.g. Environment Agency Wales, 2002). As such, mining archives are not comprehensive and certain geographic areas appear under-represented in the flux estimates. Examples include the lead mining region of the Yorkshire Pennines, the West Shropshire orefield and the Mendip orefield (Figure 1) which have not been subject to such intense water quality monitoring efforts as in many other former mining regions. Widespread

sediment contamination in the Swale and wider Ouse basin which drains much of the Yorkshire Pennine orefield has however been well documented (e.g. Hudson-Edwards et al., 1999; Coulthard & Macklin, 2003) and numerous discharges are reported suggesting there are significant fluxes of contaminants discharged from these mines, but flow and / or concentration data are not currently available.

- As Table 1 highlights, data are not available for each parameter used to determine flux.

- data requested from Environment Agency respondents were mean data (where possible), but in many cases represent results of specific campaigns undertaken during base-flow (i.e. summer) which are likely to underestimate the total annual flux. Discharges from abandoned metal mines, particularly in the Pennine areas are characterised by permeable, Carboniferous limestone host strata with distinct summer and winter flow regimes (e.g. Shepley, 2007). In addition, many abandoned metal mines are susceptible to rapid ingress of waters during intense rainfall events which can lead to distinct, but short-term contaminant flushing episodes (e.g. Nordstrom, 2009).

- The data return consisted only of mine sites with discrete discharges from abandoned mines (e.g. discharges from mine adits, drainage levels or distinct channels draining waste rock heaps) as information on more diffuse sources of contaminants are not widely available. Where studies on the significance of diffuse mining-related pollution (e.g. through larger scale erosion and entrainment of metal rich waste rock, or direct groundwater-surface water transfer) have been undertaken they have always found a significant non-point contribution to instream contamination (e.g. Gozzard, 2008; Mayes et al., 2006; 2008).

3.2 Extrapolation scenarios for absent data

Clearly the sites where data is sparse or completely absent for all parameters limit the effectiveness of total metal flux estimates from abandoned metal mines. However, given the large dataset collated it is possible to use the distribution of the existing data to make reasoned, yet precautionary estimates for the absent data (i.e. by extrapolating to all 338 known discharges). Figure 2 displays the frequency distribution of recorded flow, Cd, Cu, Fe, Pb and Zn concentrations. Given the strongly bi-modal distribution of Fe and Mn concentration (a feature of the ironstone mine data and base metal sites where extracted veins were enriched in pyrite, marcasite or siderite) and the small sample size for As and Ni (n = 17 and 43 respectively) it was not prudent to extrapolate flux estimates using such curves for these contaminants.

Figure 2 shows the concentration and flow data to be strongly right-skewed, with a small number of either high flow rate or high concentration discharges. This skew is highlighted by the discrepancy between mean values and the much lower median (P_{50}) values (Figure 2). Therefore using mean data nationally (or even regionally) to infill for missing data will likely lead to significant over-estimation of the actual flux. Centile data are shown in Figure 2 up to median values, while extrapolated total national flux for Cd, Cu, Pb and Zn using the respective centiles are provided in Table 1. In any inventory of pollution sources, data are more likely to be available for the most acutely polluting sites. Such discharges will have merited the attention and resources of environmental managers and researchers and as such will likely be over-represented in databases. Given this, a generalisation to the effect that sites with

absent data (and sites for which not even a location is known) are likely to be less polluting than sites for which data are available does not seem unreasonable. Hence it is likely that extrapolations using sub-50th percentile data may represent the most realistic estimate of the total pollution burden currently arising from abandoned metal mines in England and Wales given there may be numerous more discharges than the 338 currently identified.

The different extrapolations for the various centiles below median values show modest incremental increases in the total flux of the various contaminants. The Cu data show only a modest increase of 3.9% from the measured flux to the 50th percentile estimate which is likely a feature of the very strongly skewed Cu concentration data. The bulk (88%) of the Cu concentration data fall below 0.01mg/L with a small number of high Cu concentration discharges (peak recorded concentration is 43mg/L at the Dyffryn Adda Adit at Parys Mountain, Wales) skewing the concentration distribution. Thus the incremental centile extrapolations are contained within the bulk of the low concentration data. The other contaminants are less markedly skewed and show more appreciably increased total flux values with the various centile extrapolations. The P_{50} extrapolations for Zn, Pb and Cd exceed the measured flux values by 27%, 35% and 41% respectively and may provide a better estimate of the overall flux burden given the known limitations in data availability discussed above.

3.3 National context relative to other discharges

The UK Government (Environment Agency and Department for Environment, Food and Rural Affairs: DEFRA) have recently published databases detailing the mass flux

of a suite of pollutants from all permitted active industrial / domestic wastewater treatment sectors to all environmental compartments (Defra, 2009). The Defra (2009) data uses chemical quality data, derived from standard analyses in accredited laboratories, and flow data which is either measured directly (e.g. calibrated weir) or worked out through mass balance estimates to compute annual loadings. This annual total mass flux for each discharge is typically computed from 12 monthly samples of water quality and flow. Table 1 displays the total releases of As, Cd, Cu, Ni, Pb and Zn reported to be released to water alongside the flux estimates of metal (and As) release from abandoned metal mines collated here. The data show that the measured release of Pb from mines exceeds that of all permitted discharges, while As, Zn and Cd release from mines are of a similar magnitude to the regulated discharges. When the centile extrapolations for the metal mine pollutant burden are compared it suggests that the Zn and Cd release from mines is also likely to significantly exceed that from industrial sectors. Cu and Ni release from metal mines are substantially less than permitted industrial releases, while As mass flux is only marginally less than the permitted contemporary discharges. The data highlight the continuing role of (un-controlled) mining-related pollution on the water environment relative to contemporary sources that are subject to intense regulatory monitoring and control.

It is important to highlight that the mass fluxes recorded currently from abandoned metal mines are likely to be dwarfed by historical contaminant release. In the few cases where recently abandoned metal mine sites have been routinely monitored, the decline from high 'first flush' concentrations – termed vestigial acidity by Younger (1997) - to longer term asymptotic contaminant concentrations (juvenile acidity) can be well described by non-linear exponential decay models as shown by Younger

(1997) for the discharge from the Wheal Jane tin mine in Cornwall in the mid-1990s. Even in cases for orefields abandoned much longer ago, long-term decline in contaminant concentrations appear to be fairly clear. Such an example is the Afon Ystwyth in mid-Wales, which drains one of the most productive parts of the central Wales orefield, and has been the subject of numerous studies since 1928 when the few remaining mines in the catchment were in decline. While acknowledging the uncertainties associated with comparing spot water quality measurements using different analytical techniques, data from the catchment illustrates the long term decline in downstream Pb concentrations (see Table 3). Similar patterns are visible elsewhere across the UK, such as in the Rookhope Burn catchment in the Northumbrian River Basin District. Here long term water quality data show a noisy, albeit gradual exponential decline in ambient Zn concentrations since the bulk of mine closures in the catchment between 1900 and 1941, punctuated by a sudden rise and subsequent exponential decline to pre-perturbation levels following the abandonment of the most recent active mine in the catchment (Frazer's Grove in 1999 – see Younger, 2000b for details). Such trends put into context how the contemporary pollution burden is likely to represent only a fraction of the historic contaminant release from metal mining to the water environment in the UK.

3.4 International context

The most comprehensive estimates of the contribution of global base metal mining to freshwater pollution were made by Nriagu and Pacyna (1988). Their data incorporated review of concentration data ranges (emission factors) of various industrial discharges and computing the mass fluxes to different environmental

compartments (atmosphere, soil and water) based on estimates of discharge volumes

for active industrial and domestic discharges in 1983. For the metal mining / dressing

sector figures, the water demand per tonne of material mined and dressed was used

by Nriagu and Pacyna (1988) to derive cumulative flux estimates based on

contemporaneous base metal production statistics. It is therefore crucial to note that

pollution from abandoned mine sites is not explicitly addressed in the assessment by

Nriagu and Pacyna (1988). Comparison with the data collected here does however

serve as a useful exercise to highlight (a) how relic sources of pollution from

abandoned sites compare with that from active mines and (b) how the mass flux from

one small, albeit historically significant centre of global mining compares with the

best available estimates of global metal release.

Table 1 shows the range of mass flux estimated by Nriagu and Pacyna (1988) relative

to the data collected in this study. It is clear that for some of the global estimates, the

flux from England and Wales represents a sizeable contribution, as in the case of Zn

(P_{50} extrapolated flux equals 4.4 - 1300% of the global estimate), Pb (1.1-11.4%), Cu

(2.2-199%) and Cd (>3.6%). Certainly the lower bounds of the global estimates

appear to represent significant underestimations for all elements with the possible

exception of Mn. Both the actual concentrations (emission factors) of base metal

wastewaters and volumes of water released quoted by Nriagu and Pacyna (1988)

appear to be low compared to the data collated in this study. Where flow rates are

available for UK discharges, the sum total of these discharges is 1.8×10^8 m^3/year,

which equates to 37% of the global total, while peak emission factor ranges of 5 and

12 ng/L for Pb and Zn respectively (Nriagu and Pacyna, 1988) appear modest

compared to Figure 2. The former discrepancy can be explained in part by the fact

that water draining from post-closure mines is likely to be far greater in volume than during active mining given dewatering operations (Younger et al., 2002). The concentration data similarly may reflect the lesser importance of accelerated weathering processes in dewatered active mining operations than post-closure phases, and that active sites are likely to have some treatment prior to discharge.

The comparisons put into perspective the enduring environmental costs associated with historic metal mining and processing and highlight the requirement for flux estimates from abandoned mine sites to be included in regional and global assessments of trace metal flux. Although the scale of the problem in the UK has diminished in the decades to centuries since mine abandonment (see Section 3.3), the residual impact is now more apparent in some respects as efforts to clean up and regulate the other major sources of riverine metal pollution (e.g. active industries, sewage works) have led to significant improvements over the past three decades as they have in much of western Europe, North America and Japan (Meybeck, 2003). Data such as that collected here can assist in informing where to direct limited remedial funds when considered in combination with national impact assessment programmes (e.g. Mayes et al., 2009) and catchment scale mass flux assessments (e.g. Mayes et al., 2008).

4. Conclusions

Data have been collated from national environmental archives, published and grey literature and manually collected from abandoned metal mines to detail the mass flux

of a suite of trace elements from polluting mine sites into the water environment of England and Wales. A minimum of 193 tonnes/yr of Zn, 18.5 tonnes/yr of Pb, 0.64 tonnes/yr Cd, 19.1 tonnes/yr of Cu, 551 tonnes/yr Fe, 72 tonnes/yr Mn and 5.1 tonnes/yr As are released into the surface waters of England and Wales from polluting mine water discharges. A significant portion of this flux is concentrated in a relatively small number of discharges where future management efforts should be targeted. For example, 67% of the Zn flux reported arises from the ten most polluting discharges. Extrapolation of these data using a series of sub-median centile data derived from frequency distributions of some of the most commonly monitored metals (Cd, Pb and Zn) and flow suggest their total fluxes could be in the region of 27-41% higher when datasets for flow and water quality become more complete. The total flux of Pb from abandoned metal mines exceeds that released by all formally permitted discharges to the surface waters of England and Wales, while As, Cd and Zn fluxes are of a similar scale. This provides a stark indication of the scale of the enduring pollution from abandoned metal mines nationally. The flux data reported here appear significant on an international scale when compared with estimates of trace element flux from active base metal mining globally. Whether this is an accurate depiction of the situation or an artefact of underestimation of global totals requires further study. The data presented here represent just one locus of former metal mining activity and there are likely to be similarly considerable fluxes in other former mining regions and indeed there is much monitoring and research to suggest such is the case. Future research efforts should aim to collate flux estimates of contaminant release at point of discharge from major active and historic global mining fields to better characterise the role of mining in driving changes in regional and global trace metal cycles in the aquatic environment.

Acknowledgements

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Table 1 – Total mass flux in tonnes/year of 7 metals (and arsenic) released into the water environment from abandoned metal mine sites in England and Wales compared with 2008 mass flux of metal release to surface waters from all permitted discharges in England and Wales and global estimates of trace element flux from base metal mining (tonnes/year). $n_{(conc)}$ = number of mine sites where concentration data are available for selected element (from total of 338 identified discharges); $n_{(flux)}$ = number of mines where coincident flow and concentration data are available to formulate flux estimates. Extrapolated flux, n = 338: see section 3.2 for explanation.

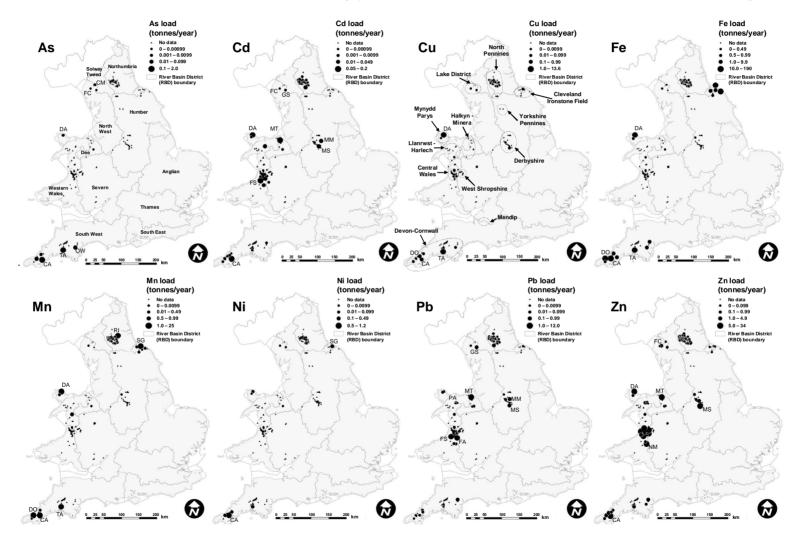|	As	Cd	Cu	Fe	Mn	Ni	Pb	Zn
$n_{(conc)}$	17	112	84	95	87	52	125	149
$n_{(flux)}$	13	65	52	67	58	22	85	100
Measured flux	5.10	0.64	19.1	550	72.4	2.14	18.5	193
Extrapolated flux P_{10}	-	0.70	19.1	-	-	-	19.7	199
Extrapolated flux P_{20}	-	0.76	19.3	-	-	-	21.1	207
Extrapolated flux P_{30}	-	0.83	19.4	-	-	-	22.5	215
Extrapolated flux P_{40}	-	0.92	19.6	-	-	-	24.8	230
Extrapolated flux P_{50}	-	1.09	19.9	-	-	-	28.5	266
Permitted discharges n	130	177	140	-	-	276	194	161
Permitted discharges flux	6.01	1.04	78.1	-	-	46.7	18.3	198
Nriagu & Pacyna (1988) global base metal mining flux to water estimate	0 – 750	0-30	10-900	-	800-1200	10-500	250-2500	20-6000

Table 2. Selected total trace element loadings (tonnes/year) and mean flow rates (L/s) for the top 20 mine water discharges ranked by Zn flux. ('-' = no data)

Discharge name	Location RBD	Flow	Total load						
			As	Cd	Cu	Fe	Mn	Pb	Zn
County Adit	South West	454	2.7	0.06	0.9	140.8	11.0	0.07	34.0
Dyffryn Adda adit (Joint Level)	Western Wales	10	0.08	0.05	13.6	189.0	6.1	0.012	22.5
Frongoch Stream	Western Wales	125	-	0.14	0.02	-	-	1.8	14.9
Frongoch Adit	Western Wales	60	-	-	-	-	-	11.8	10.5
Nant y Mwyn Lower Boat Adit	Western Wales	30	-	0.03	-	-	-	0.09	10.0
Pughs Adit	Western Wales	13	-	0.01	0.003	0.4	-	0.24	9.2
Milwr Tunnel	Dee	1347	-	0.05	-	-	-	1.28	8.6
Meerbrook Sough	Humber	740	-	0.05	0.02	-	-	0.40	8.4
Cwm Rheidol Adit 9	Western Wales	3	-	0.009	-	-	-	0.002	6.6
Caplecleugh	Northumbria	23	-	0.007	0.003	0.3	0.1	0.04	6.2
Kingside adit	Western Wales	18	-	0.02	0.003	-	-	0.4	5.2
Cwm Rheidol Adit 6	Western Wales	11	-	0.01	-	-	-	0.26	4.8
Rispey Breakout	Northumbria	60	-	0.004	-	8.8	12.7	-	4.5
Bridford mine adit	South West	5	-	0.006	-	3.0	-	0.32	4.4
Wheal Maid Tailings Dam	South West	5	0.008	0.008	0.11	4.7	-	0.002	4.4
Dolcoath Adit	South West	31	0.7	0.009	0.0005	37.9	10.6	0.009	4.3
Yatestoop Sough	Humber	20	-	0.04	-	-	-	0.11	3.9
Nent Force Level	Northumbria	19	-	0.006	0.003	0.11	-	0.02	2.6
Barney Craig	Northumbria	20	-	0.003	-	-	-	0.002	2.5
Gills Lower adit	Western Wales	19	-	0.006	0.004	-	-	0.21	2.5

Table 3. Total Pb concentrations in the lower reaches of the Afon Ystwyth, Mid Wales from several studies

Year of sample	Pb (μg/L)	Reference
1919	400-500	Carpenter (1924)
1922	<100	Carpenter (1924)
1939	<50	Jones (1940)
1953	<100	Jones (1958)
1975-1977	2-100	Craig Goch Field Surveys Group (1976)
1990	58	Fuge et al., (1991)
2003-2005	13	Current mean from Environment Agency datasets used in Mayes et al.(2009)

Figure 1. Proportional symbols highlighting the distribution of major metal (and As) releases from metal mine discharges in England and Wales. River Basin Districts (RBD) are labelled in the As plot, major orefields are labelled in the Cu plot. Codes for discharges referred to in text: CA: County Adit, CM: Carrock Mine, DA: Dyffryn Adda Adit, DO: Dolcoath Adit, FC: Force Crag, FA: Frongoch Adit, FS: Frongoch Stream, GS: Greenside mine, MM: Magpie Mine, MS: Meerbrook Sough, MT: Milwr Tunnel, NM: Nant-y-Mwyn Boat Level, OW: Owlercoombe Mine, PA: Parc Mine, RI: Rispey Mine, SG: Saltburn Gill, TA: combined flux from River Tamar discharges.
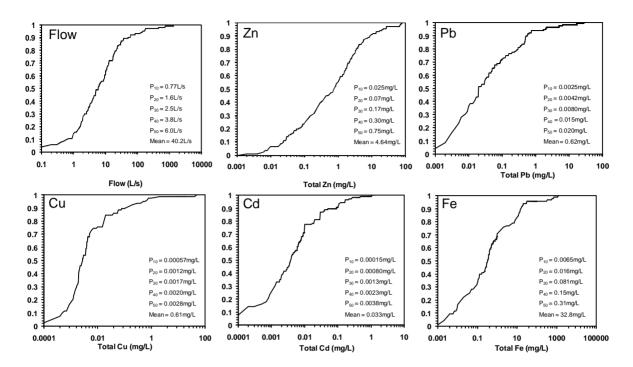
Figure 2. Frequency distribution of contaminant concentration and flow data collated during this study.

Flow

$P_{10} = 0.77L/s$
$P_{20} = 1.6L/s$
$P_{30} = 2.5L/s$
$P_{40} = 3.8L/s$
$P_{50} = 6.0L/s$
Mean = 40.2L/s

Flow (L/s)

Zn

$P_{10} = 0.025mg/L$
$P_{20} = 0.07mg/L$
$P_{30} = 0.17mg/L$
$P_{40} = 0.30mg/L$
$P_{50} = 0.75mg/L$
Mean = 4.64mg/L

Total Zn (mg/L)

Pb

$P_{10} = 0.0025mg/L$
$P_{20} = 0.0042mg/L$
$P_{30} = 0.0080mg/L$
$P_{40} = 0.015mg/L$
$P_{50} = 0.020mg/L$
Mean = 0.62mg/L

Total Pb (mg/L)

Cu

$P_{10} = 0.00057mg/L$
$P_{20} = 0.0012mg/L$
$P_{30} = 0.0017mg/L$
$P_{40} = 0.0020mg/L$
$P_{50} = 0.0028mg/L$
Mean = 0.61mg/L

Total Cu (mg/L)

Cd

$P_{10} = 0.00015mg/L$
$P_{20} = 0.00080mg/L$
$P_{30} = 0.0013mg/L$
$P_{40} = 0.0023mg/L$
$P_{50} = 0.0038mg/L$
Mean = 0.033mg/L

Total Cd (mg/L)

Fe

$P_{10} = 0.0065mg/L$
$P_{20} = 0.016mg/L$
$P_{30} = 0.081mg/L$
$P_{40} = 0.15mg/L$
$P_{50} = 0.31mg/L$
Mean = 32.8mg/L

Total Fe (mg/L)

Figure 3. Long-term decline in instream total zinc concentration in the Rookhope Burn (Northumbria River Basin District) at Eastgate, County Durham, UK. Inset highlights the effects of closure of the Frazer's Grove fluorite/Pb mine on instream Zn concentrations and resultant decline to pre-closure concentrations.