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MINE WATERS IN ESTUARINE ENVIRONMENTS

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Abstract

Acid mine waters have the potential to seriously impair the environmental quality of aquatic systems long after mining activities have ceased. This detailed study of dissolved and particulate metal fluxes from adits, drains and streams in the Tamar river catchment, southwest England, showed that four specific sources accounted for most of the estimated 12 t of non-iron metals and metalloids annually discharged from an abandoned metalliferous mining area. Speciation studies revealed that the fraction of biologically available Cu in estuarine waters reaches concentrations (0.095 µg L^{-1} Cu) that can be toxic to some estuarine species. The study provided information necessary to prioritise remediation efforts in the context of sustainable catchment management.

Introduction

In England's Southwest, magma intrusions occurred during the Carboniferous into the country rock (killas) of Devonian age and formed granite rocks during cooling (Fig. 1). Metal ores bodies formed within the metamorphic aureoles around the granite bosses, which today form a string of five granite upland areas, including Dartmoor and Kit Hill in the Tamar catchment. Mined since pre-Roman times, the Tamar mining area experienced its heyday of mineral extraction in the latter part of the 19th century, with lower levels of activity (including the re-working of tailings with more efficient methods) continuing into the 1950s. The principal commercial minerals were Cu-As, Cu-Fe and Fe-As ores, such as arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$), and cornwallite ($Cu_5[(OH)_2|AsO_4]_2$), as well as ores of lead, zinc, silver, tin, uranium and tungsten (Dines et.al., 1956; Joylon, 2007).

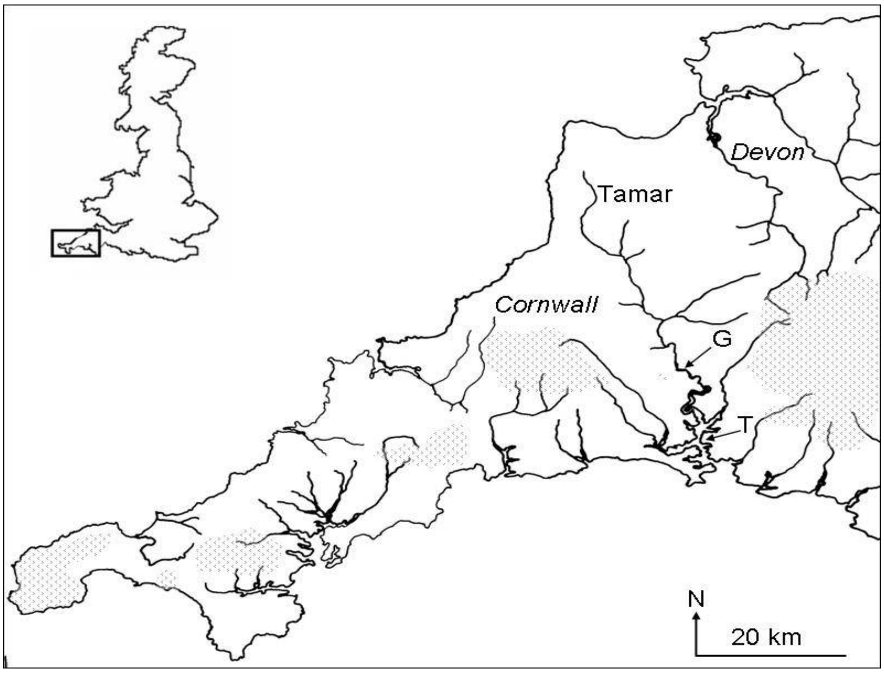

Figure 1. Map of England's Southwest, showing river systems and the location of granite bosses (patterned). 'G': Tamar river freshwater end-member at Gunnislake. 'T': site of tidal cycle study in the mid-estuary. Dartmoor is the large patterned area to the East of the Tamar and Kit Hill is the very small granite upland to the West of the Tamar.

Drainage entering rivers and estuaries from abandoned metal mines poses a particular challenge to the Environment Agency of England and Wales (EA) in the implementation of the EU Water Framework Directive (WFD). The main objective of the WFD is to reach good chemical and biological water quality status, whereby the biological availability of metals is taken into account. Diffuse and point sources of mine drainage include surface run-off and leachate from large numbers of mine waste heaps entering the groundwater and the hyporheic zone, as well as outflow from adits and shafts. It is the vulnerable coastal environment receiving mine effluent where the most severe impact on ecosystem functioning occurs. In this paper we present preliminary data from a study in the former mining area in the Tamar river catchment (southwest England) (Fig. 1). The study aimed at quantifying the flux of metals into river and estuarine systems and assessing their fate in and impact on the coastal environment.

Methods

Monthly surveys of 24 adits, drains and tributaries (ADTs) of the Tamar river were carried out between July 2005 and June 2006 (preliminary results for the period between July and December 2005 are presented here). Stream flow and physico-chemical parameters (pH, conductivity, temperature) were measured *in-situ*. Total dissolved concentrations of As, Cd, Co, Cr, Cs, Cu, Mn, Ni, Pb, Sn, W and Zn were analysed using established spectrophotometric methods (ICP-MS and Flame-OES) after filtration (0.2 µm pore size) and acidification (1 ml HNO_3 conc. per L sample). Acid-extractable particulate element concentrations were determined by subjecting filter papers to hot acid digestion (aqua regia, 4 h) and subsequent analysis of the extracts by spectrophotometric methods. Sulfate concentrations were estimated gravimetrically. Monthly and annual dissolved and particulate metal fluxes were estimated by calculating the instantaneous flux for each survey and factoring in the numbers of days of the month. The river water flow for the freshwater end-member (river upstream of the limit of tidal incursion) was obtained from the Environment Agency for England and Wales (EA) from the continuous river gauging station at Gunnislake. The biological availability of Cu, Pb and Cd in the Fal and Tamar estuaries was approximated by deploying an *in-situ* analytical tool into surface waters over periods of a full tidal cycle. The Voltammetric i*n-situ* Probe (VIP) measures an operationally defined fraction (named 'dynamic', mainly free hydrated ions, inorganic molecules, and small organic molecules) of metals in the water column, that excludes all compounds that are larger than 4 nm in size. Full details of the VIP can be found in Idronaut (2007) and Howell et. al. (2003) and references therein. Total estuarine dissolved metal concentrations were measured using the VIP in laboratory mode after filtration, acidification and destruction of interfering organic compounds by UV-photolysis.

Results and Discussion

Dissolved metal concentrations in the 24 ADTs varied with location and between surveys. The highest dissolved concentrations were observed for Cu (7600 µg L^{-1}), Mn (5700 µg L^{-1}), Zn (2500 µg L^{-1}) and As (560 µg L^{-1}) (Table 1), which is consistent with the geological setting and the dominant mineral ores in this mining district. The observed pH values (pH 2.87-7.83), conductivity (13-335 µS cm^{-1}) and sulphate concentrations (10-430 mg L^{-1} SO_4) were most extreme (low pH, high conductivity and SO_4) in ADT waters with high metal concentrations. The conditions observed in this study are within the wide range of conditions reported for mine drainage in other locations in southwest England (e.g. Bowell and Bruce, 1995; Johnson, 1986;) and elsewhere (Balistrieri et al., 1999; Braungardt et al., 2003; Dinelli et al., 1995, 2001; Gray, 1998; Miller et al., 1996).

The total combined dissolved flux of dissolved non-iron metals and arsenic from the 24 ADTs was 6460 kg/six months. This dissolved input to the Tamar river consisted mainly of Mn (1950 kg), Cu (1770 kg) and Zn (1670 kg), with important amounts of other toxic elements, such as As (310 kg) and Cr (180 kg) making up the remainder (Table 1). Dissolved metal fluxes from most sources were higher during October, November and December, compared to the period between July and September. For the July, August and September surveys (preliminary results) the element concentrations in suspended particulate matter reached up to 120 µg L^{-1} As, 9.6 µg L^{-1} Cu, 38 µg L^{-1} Mn and 31 µg L^{-1} Zn. The suspended particulate matter (SPM) concentrations in ADTs during these months of low rainfall were generally low (<20 mg L^{-1}), and as a consequence, the contribution of metals/metalloids associated with particles to the total metal flux into the River Tamar was limited (Table 1).

The limitation of this method of flux estimation lies in the assumption that one monthly survey provides representative data for concentrations and water flow. For example, no flash flood events were monitored, as many of the sampling sites are rendered inaccessible as a result of flooding from the river Tamar. Visits to sampling locations following heavy rain events revealed loss of sediments (grained sediments, precipitates and ochre) from ADTs, as well as evidence of erosion and export of solids from the surface of mine spoil heaps. For example, at stream L, sediment prone to bank erosion contained up to 12.3 g kg^{-1} As and 0.8 g kg^{-1} Cu. In addition, occasional collapses within abandoned mines can result in the discharge of substantial volumes of acid mine drainage carrying suspended ochreous material. High concentrations of metals/metalloids have been observed in ochreous sediments associated with the adits in the studied mining area (e.g. up to 15 g kg^{-1} As and 3.3 g kg^{-1} Cu at 230 g kg^{-1} Fe), but the metal input due to such events remains difficult to estimate.

From these preliminary results, priority point sources of metal pollution to the river were identified, whereby 75% of the dissolved metal flux originated from six point sources on three mine sites. Two of these were streams collecting the drainage of a series of abandoned mining sites (spoil, adits, runoff) into the Tamar. Although the dissolved concentrations within these two streams were relatively low, the high river water flow (80-720 L s^{-1} for stream L and 120-660 L s^{-1} for stream C) resulted in a substantial contribution of Cr, Co, Ni, Zn, As, Ag, Cd and Cs to the total flux (Table 1). The streams each contribute 17% to the total dissolved metal flux into the River Tamar. The flux from mine D combines the output of one adit with a stream draining a number of mine tailings and a drainage channel that intercepts leachate and ground water flow from a large mine site comprising of mine tailings, waste from ore processing and several adits, one of which has ochreous outflow. Much higher element concentrations were observed in these three sources, which all had lower flow rates (1-85 L s^{-1}), compared to the streams L and C. Mine D also differed in the composition of the drainage, which was dominated by Mn, Co, Ni, Cu, Zn and As (Table 1), and accounts for 42% of the total non-Fe metal flux into the River Tamar. The particulate element flux was highest in streams of high water discharge and velocity and in ochreous adit effluent. More than 80% of the particulate metal/metalloid flux originated from stream L, mine D and the ochreous adit DM. In addition, stream L was a contributor of particulate tin and tungsten (0.35 kg/3 months Sn, 0.7 kg/3 months W), whereas the dissolved concentrations of these metals were below the detection limit. The identification of main point sources is an important step towards the development of remediation strategies.

The dissolved element concentrations measured in the River Tamar freshwater end-member (Table 1) are the combined result of background values (including natural and anthropogenic contributions upstream) and point and diffuse inputs of metals within the mining area. With the exceptions of Zn and Cd, dissolved element concentrations exceed several-fold those in the world average river water (GESAMP, 1987).

The dissolved metal flux of the River Tamar, i.e. the output into the estuary, was estimated from the instantaneous concentrations (As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) in the freshwater end-member and river flow data for the sampling days measured by the Environment Agency (EA) at Gunnislake New Bridge (2.86-42.8 m^3 s^{-1} for July-December). Combined, the Tamar discharge of dissolved elements was between 1.2 and 25.2 t month^{-1}, with lower element fluxes during periods of low water flow (Jul-Sep) and higher fluxes during the wetter months (Oct-Dec). During low flow condition, up to 47% of the element flux originated from the ADT, compared to 6-11% at higher water flow. This indicates that processes in the catchment upstream of the mining area, as well as diffuse sources of ADT are important in determining the water quality, and this is subject of further investigations.

Table1. Results from dissolved (July-December 2005) and particulate (July-September) metal analysis in samples collected during monthly surveys in 24 adits, drains and tributaries (ADT) discharging directly into the River Tamar. Concentration ranges of dissolved elements (min and max) are given for all ADT combined and for the River Tamar at the freshwater end-member. Dissolved element flux estimated from the results and river flow measurements. The contributing proportions of the total dissolved flux are given for the main sources, i.e. collective for mine site D (1 adit, 2 drains) and for two streams L and C that are tributaries to the Tamar. The combined contribution to the total particulate metal flux from mine site D, stream L and mine adit DM to the Tamar is also given. Average concentrations in global river waters from GESAMP (1997).

	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Pb
Concentration range, ADT : min	6.3	9.3	3.9	2.9	4.30	0.56	4.3	0.13	0.40
(µg L^{-1}) max	180	5700	270	250	7600	2500	560	11	160
Concentration range, Tamar: min	7.6	20	6.1	5.0	13	5.3	7.0		0.41
(µg L^{-1}) max	18	96	13	21	61	28	18	<LOD	0.46
Average concentration in global river water (µg L^{-1})	1.0	8.2	0.2	0.5	1.5	30	1.7	0.02	0.01
Dissolved element flux from ADTs for six months (kg/6 months)	180	2000	210	230	1800	1700	300	3.50	8.30
Mine D proportion of dissolved flux (%)	15	56	30	27	49	28	25	15	6
Stream L proportion of dissolved flux (%)	30	10	22	21	9	27	36	15	0
Stream C proportion of dissolved flux (%)	30	10	25	27	16	23	15	25	3
Particulate element flux from ADTs for three months (kg/3 months)	2.5	25	0.72	0.28	7.6	27	50	<LOD	0
Mine D, mine DM and stream L proportion of particulate flux (%)	81	93	98	95	87	88	94	0	0

In order to assess the impact of acid mine drainage in the Tamar estuary, dissolved concentrations of Cu, Cd and Pb were measured, as these are of main concern with regards to their effects on marine biota (Brand et al., 1986; Grout and Levings, 2001; He et al., 1998; Williams et al., 1998). A research vessel was moored under the Tamar road bridge ('T', Fig. 1) in the mid-estuary and samples were taken and *in-situ* measurements were made at regular intervals over the time of several tidal cycles. The ranges of salinity (11.8-33.5) and pH (8.39-8.5) encountered were representative for the mid-reaches of this macrotidal estuary. Total dissolved concentrations observed during three surveys (March, April 2003 and May 2006) spanned the ranges of 1.45-3.14 μg L^{-1} Cu, 25.7-170 ng L^{-1} Cd and 43.5-506 ng L^{-1} Pb. These concentrations were up to 42 times lower for Cu and than those registered in the freshwater end-member. However, maximum concentrations for Pb in the estuary were similar to, and those of Cd higher, than those observed in the river. This is probably the result of the long-term accumulation of Pb and Cd within estuarine sediments and sediment/water exchange. The Tamar features a well-studied turbidity maximum zone (TMZ) that predominantly results from tidal resuspension of estuarine sediment and upstream transport of suspended particles. The estuarine processes arising from the mixing of saltwater of high ionic strength with freshwater and the physical forces that cause the mobilisation of estuarine sediment result in a redistribution of elements between the dissolved and particulate phases. Elements are trapped within the TMZ and cycled between the dissolved and particulate phases, with some transport into the lower reaches and into coastal zones (Millward, 1995; Morris et al., 1986).

The Tamar estuary has been subjected to mining related contamination since at least the mid-19th century, and as a result, the sediment has become a rich source for secondary contamination. For example, concentrations of 0.7-3 mg kg^{-1} Cd, 270-580 mg kg^{-1} Cu and 190-500 mg kg^{-1} Pb have been reported for the sediments near the Tamar road bridge (first value) and in the upper estuary (second value), respectively (Langston et al., 2003). These values exceed the Interim Marine Sediment Quality Guidelines (IMSQ) for Cd, Cu and Pb and Probable Effect Levels (PEL) (on biota and/or ecosystem) for Cu and Pb. The IMSQ and PEL for As, Hg and Zn are also exceeded in the Tamar Estuary.

Metal measurements in the water that determine Cu, Cd and Pb species that are an approximation of the biologically available metal fraction, spanned the ranges of 0.21-1.15 μg L^{-1} Cu, 14.7-97.9 ng L^{-1} Cd and 2.69-92.6 ng L^{-1} Pb. These concentrations are biologically relevant for Cu, as indicates by ecotoxicological tests on the larvae of the Pacific Oyster, *Crassostrea gigas*, which showed 50% abnormal development during the early life stage (24 hours) at concentrations around 0.095 μg L^{-1} Cu (C. Money, pers. comm., 2007).

Conclusions

The long-term input of metal mining related contaminants into the Tamar river and estuarine system has resulted in environmental concentrations of elements, such as Cu, As and Zn that are likely to pose a threat to ecosystem functioning. Combined non-iron metal/metalloid fluxes from ADTs into the Tamar river amount to an estimated 30-35 kg per day, from four dominant sources. This study represents the first step towards reducing the metal input to this river system by locating priority pollution sources. Current projects address the development and testing of suitable remediation options.

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