

## THE DISTRIBUTION OF TRACE METAL POLLUTANTS WITHIN INTERTIDAL SEDIMENTS OF THE TAMAR ESTUARY, SW ENGLAND

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The Tamar Estuary is a partially mixed, flood dominant estuary, the middle and lower parts of which are flanked by extensive intertidal flats and saltmarsh deposits. The southern part of the Tamar valley is highly mineralised with tin, copper and arsenic production during the 19<sup>th</sup> century. Consequently, the mining history is likely to have had a huge effect on the local environmental geochemistry. In this study the concentration of selected trace elements (As, Cu, Pb and Zn) from intertidal sediments from the Tamar Estuary have been measured in order to examine the downstream distribution pattern in relation to historical sources of pollution. The results show highest concentrations in the middle parts of the estuary and notably a distinct absence of elevated concentrations immediately adjacent to mine sites. This pattern is consistent with the dominance of down estuary transport of sediment during winter. A decrease in concentration of metals seawards from the head of the estuary is thought to be a response to physical transport processes and the input of sediments derived from offshore.

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### INTRODUCTION

Concentrations of trace metal pollutants are frequently reported from intertidal sediments (e.g. Bryan and Langston, 1992; French, 1993; Lindsay and Bell, 1997; Pirrie *et al.*, 1997, 2000) and as these areas are often sites of intense human and animal activity, the level of contaminants are of particular interest with respect to environmental health (Rae, 1997; Clark, 1997). When trace metals are released into the water column they can be transferred rapidly to the sediment phase either by adsorption onto suspended particulate matter followed by sedimentation (Turner *et al.*, 1993; Lindsay and Bell, 1997) or directly incorporated within the sediment as particles. Contaminants may subsequently be concentrated in specific areas, remote from their point of introduction (McLaren and Little, 1987), as a result of sediment transport and the mixing capabilities of the waters within the estuary. Studies of the distribution of sediment borne pollutants can therefore be used as an indication of the mixing ability of the system and in the identification of sources of pollutant input (French, 1993).

This study carried out in the Tamar Estuary of SW England, aims to describe the downstream dispersal and possible controls upon the distribution of selected trace metal pollutants within the intertidal sediments of the estuary.

The mineralized district of SW England was one of the world's greatest mining areas, renowned for tin, copper and arsenic production and hence the mining history is likely to have had a huge effect on the local environmental geochemistry. Previous studies relating to the distribution of metals within the intertidal sediments of the Tamar Estuary (e.g. Bryan and Langston, 1992; Lindsay and Bell, 1997) have shown that certain metals such as As, Cu, Pb and Zn are enriched within the sediments. A number of more detailed analyses regarding trace metal distribution within the Tamar estuary have been undertaken by Knox *et al.* (1981), Morris *et al.* (1982; 1986) and Ackroyd *et al.* (1986, 1987), particularly focussing upon dissolved and suspended particulate material. The studies of Morris *et al.* (1986) and Ackroyd *et al.* (1987) also examined the trace metal concentrations (including Fe, Cu, Cd and Zn) of surficial sediments from the middle and upper parts of the Tamar Estuary. They suggested that there was substantial internal metal recycling within the estuary and the distribution of metals was also

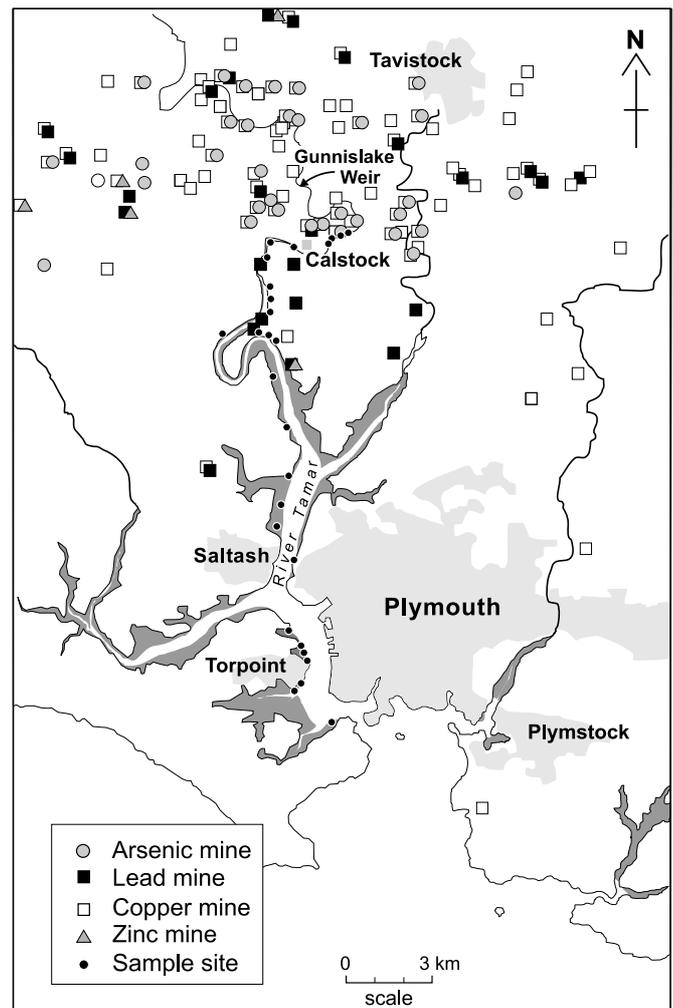


Figure 1. Map showing the location of sampling sites and mining activity with the Tamar Estuary. (Mine data derived from Dines, 1969 and Burt *et al.*, 1984).

dependent on the input of new particulate material associated with seasonal variations in river flow.

**STUDY AREA AND METHODOLOGY**

The Tamar Estuary is a partially mixed, flood dominant estuary and has a tidal range of ~2.1 m at neap and ~4.7 m at spring tides (Dyer, 1997). The head of the estuary is located at Gunnislake Weir (Figure 1), which is the tidal limit. The middle and lower parts of the estuary are flanked by extensive intertidal flats and saltmarsh deposits. The estuary exhibits strong turbidity maxima in its low-salinity reaches (Uncles *et al.*, 1994; Grabemann *et al.*, 1997) whereby suspended sediment concentrations generally reach maximum values between 5 and 15 km below the head of the estuary (Ackroyd *et al.*, 1986; Dyer, 1997).

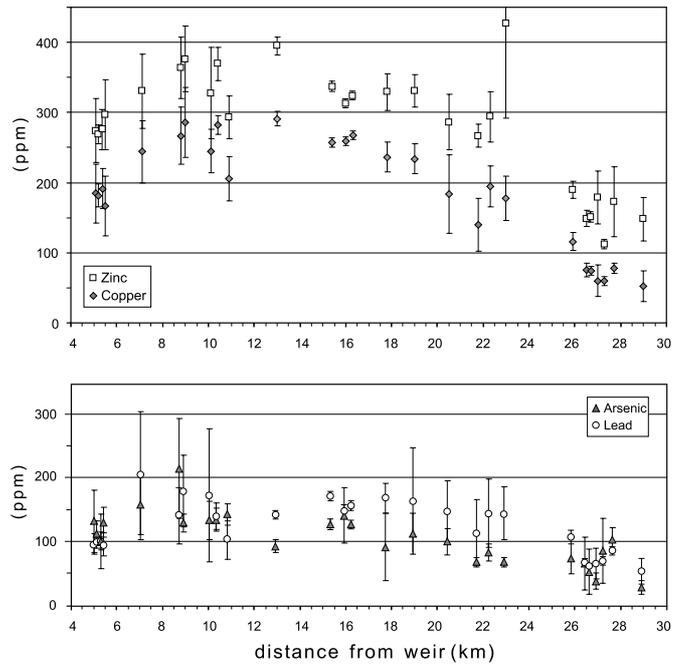
The mines of the highly mineralised southern part of the Tamar valley were the world's principal producers of copper and arsenic during the middle of the 19th century. For example the estimated total production of copper metal from Devon Great Consols, the largest mine in the Tamar valley from 1848 to 1883 is estimated to be over 40000 tonnes (Burt *et al.*, 1984). Silver, lead, zinc and tungsten have also been mined in quantity (Dines, 1969). Over 100 mines have been in operation in the Tamar valley (Figure 1), most of which had ceased functioning by the end of the 19th century. The legacy of such extensive operations includes the abandoned and derelict mine buildings, kilns, smelters (Booker, 1967), unvegetated spoil tips and soils highly contaminated with a range of metals (Kavanagh *et al.*, 1997).

Samples were collected from 27 sites from the topmost 2 cm of recently deposited intertidal sediment along the estuary (Figure 1) between the months of December and February (2000/2001). Between 6 and 14 samples were collected from each site. During sampling care was taken to avoid reworked material and strandline debris. After collection all samples were dried at 40°C to constant weight. The <125 µm size fraction was analysed, in order to reduce any grain-size effects. Concentrated nitric acid was added in stages to each weighed sample, allowing for any effusive reaction to take place. All samples were then placed on a hot plate (set to 40 °C) for 24 hours and the solution evaporated to incipient dryness. To this residue dilute (2%) nitric acid was added. Elemental concentrations were determined using a Perkin Elmer 3100 Atomic Absorption Spectrometer. Reproducibility, based upon replicate analysis was estimated generally to be less than ±5% of the measured concentration of each element.

The hot HNO<sub>3</sub> technique digests organic-rich particle surface layers, sulphides and results in partial aluminosilicate lattice dissolution (e.g. Krumgalz and Fainshtein, 1989). The nitric acid digestion technique also provides continuity with other studies where nitric acid digestion has been used (e.g. Langston 1986, Bryan and Langston, 1992). The HNO<sub>3</sub> digestion method was further assessed by analysis of the certified reference material MESS-2, obtained from the National Research Council of Canada. The elemental concentrations obtained through HNO<sub>3</sub> digestion compared with certified values, that represent complete digestion of the standard, are shown in Table 1. The concentrations obtained in this study are slightly lower, reflecting the partial digestion of the sample (c.f. Krumgalz and Fainstein, 1989). Hence recovery using this extraction method ranged between 78-97%.

	Copper (ppm)	Lead (ppm)	Zinc (ppm)	Arsenic (ppm)
Certified MESS-2 concentrations	39.3	21.9	172.0	20.7
MESS-2 concentrations derived using HNO <sub>3</sub> (this study)	38.0 (sd = 2.7)	17.8 (sd = 2.2)	134.1 (sd = 4.3)	17.9 (sd = 0.2)

**Table 1.** The trace metal analyses of the certified reference material MESS-2, obtained using hot HNO<sub>3</sub> acid technique.



**Figure 2.** Distribution of As, Cu, Zn and Pb within the superficial sediments of the Tamar Estuary.

**RESULTS**

The variation in trace metal concentration is shown in Figure 2 and Table 2. The mean and one standard deviation at each sample location are shown plotted against distance (in km) down estuary from Gunnislake Weir. At most sample sites Zn is highest in concentration, followed by, in decreasing order, Cu, Pb and As. The highest concentrations (325-400 ppm for Zn; 210-290 ppm Cu) are typically observed in the upper 7 – 10 km of the estuary. The distribution of Pb and As shows a similar, but less distinct trend, whereby within the middle parts of the estuary relatively high concentrations are recorded from the estuarine sediments. These metal concentrations are considerably lower than concentrations observed in other estuaries affected by mining and associated industrial activity within southwest England. For example, 1740 ppm As and 2821 ppm Zn has been recorded in Restronguet Creek (Bryan and Langston, 1992) and 8500 ppm Pb and 1600 Zn have been recorded from sediments of the Gannel Estuary (Pirrie *et al.*, 2000). A considerably greater range of values of As (120-52600 ppm) has been recorded from spoil tips and highly contaminated soils within the Devon Great Consols Mine site (Kavanagh *et al.*, 1997).

It is apparent from Figure 2, that there also appear to be a number of areas showing anomalously high levels of trace metals within the lower part of the estuary. Three samples derived from the site located opposite Saltash (see Figure 1) contain between 405-750 ppm Zn. Such concentrations are considerably greater than any recorded in this study from the Tamar Estuary.

**DISCUSSION**

The Tamar Estuary exhibits a number of physical characteristics that may, in part, account for the distribution of trace elements seen in Figure 2. Within the summer months, with low river flows and low energy resuspension, a relatively quiescent sedimentary environment prevails and sediment accumulation occurs in mid estuary (Morris *et al.*, 1986; Ackroyd *et al.*, 1987). During high river flows prevalent in winter, high-energy resuspension and thorough mixing of inputs and surficial estuarine sediment occurs (Morris *et al.*, 1986). Hence Ackroyd *et al.* (1987) suggested that up estuary mass transport of sediment was occurring in summer and down estuary in winter. This degree of seasonal mixing is considered to account for the absence of elevated concentrations close to mine sites in the

Sample Location	Grid Reference	Zinc (ppm)	Copper (ppm)	Arsenic (ppm)	Lead (ppm)
Harewood Farm1	SX 448688	274	184	131	96
Harewood Farm2	SX 447688	269	182	112	97
Harewood Farm3	SX 445689	292	214	99	108
Harewood Farm4	SX 444689	296	167	130	95
Ferry Farm	SX 435684	330	244	157	203
Cotehele Wood	SX 426683	364	267	215	140
Cotehele Quay	SX 425681	376	286	129	178
South Ward Farm	SX 427675	328	245	133	172
Braunder Wood	SX 428671	369	282	134	140
Braunder Farm	SX 428667	293	206	142	102
Halton Quay	SX 417655	395	291	92	142
South Hooe	SX 423654	337	257	127	172
Hewton	SX 427655	313	260	141	147
Hole's Hole	SX 429654	323	266	127	156
Salter Mill	SX 432638	329	236	91	168
Penyoke	SX 436615	331	234	112	165
Neal Point	SX 432612	286	183	99	146
Tamar Park	SX 431600	267	140	68	112
Saltmill Creek	SX 431596	294	195	83	144
Riverside	SX 434587	427	178	67	144
Looking Glass	SX 436565	190	116	72	106
North Thackes Lake	SX 438558	149	76	65	66
Thackes Lake	SX 438555	150	75	52	66
Torpoint	SX 441553	179	60	37	65
Marine Drive1	SX 440547	112	60	85	68
Marine Drive2	SX 438545	173	78	102	85
Cremyll	SX 454534	148	52	27	52

**Table 2.** A summary table of results giving average concentrations of elements analysed from the Tamar Estuary.

uppermost parts of the estuary. Given that the sampling took place during the winter months it is conceivable that higher river flows, resuspension and mixing of inputs and surficial sediments concentrated metals within sediments downstream in the upper 7 – 10 km of the estuary. A similar trend has also been recorded by Morris *et al.* (1986) and Ackroyd *et al.* (1987).

Notably in the studies of Morris *et al.* (1986) and Ackroyd *et al.* (1987) and as seen in Figure 2 and Table 2, zinc is consistently present in the greatest concentrations, compared with the other elements analysed in this study. Zinc ore (principally sphalerite) although widespread in the Tamar valley, has not been commonly found in workable quantities (Dines, 1969; Burt *et al.*, 1984). As a consequence, sphalerite was frequently discarded as a waste product. Hence the abundance of zinc may partially reflect the abundance of sphalerite on spoil heaps. Sphalerite is often found in association with copper lodes which may explain the clear covariance between Zn and Cu (Figure 2).

The more uniform distribution of Pb and As may reflect a difference in possible land based sources of these pollutants. A number of Pb mines and smelters are located in the middle parts of the estuary (Figure 1) which may have provided a more localised source of pollutants. Furthermore, arsenic can enter estuaries in dissolved inorganic form permitting a relatively wide dispersal of this metal. During mixing of fresh and salt water a large proportion of As entering the estuary can adsorb onto precipitating amorphous iron oxyhydroxides and particulate matter (Bryan and Langston, 1992). Detrital arsenopyrite has been recorded as a common constituent of all the contaminated estuaries in Cornwall (e.g. Pirrie *et al.*, 1999a, 1999b, 2000). An electron microscope examination of the sediments from the Tamar Estuary, adjacent to Calstock (Figure 1), did reveal a limited amount of detrital Cu (As) sulphides. In tidally energetic estuaries, such as the Tamar, the remobilisation of As from the sediments, and porewaters, is frequently observed (Bryan and Langston, 1992) and hence may in part account for the more uniform distribution of As seen in Figure 2.

The lower reaches of the Tamar are characterised by modern industrial activity including the Royal Navy dockyards that provide a further possible source of contaminants. The dockyard is known to be a source of contaminants (Harris *et al.*, 1991), for example antifouling paint can contain up to 500 g/L of copper (Clark, 1997). Zinc is also used in shipbuilding as a protective coating on galvanised iron and steel. Such industrial activities could account for the anomalously high levels of zinc recorded

in the lower part of the estuary (at Saltash). Surprisingly, however, low concentrations of all metals examined are recorded within the sediments closest to the Royal Navy dockyards, adjacent to Torpoint. It is possible therefore that in this lower part of the estuary the influence of sediment derived from offshore may be more dominant within the sediment budget.

## CONCLUSIONS

The trace metals from the superficial sediments within the Tamar Estuary clearly record concentrations consistent with contamination from past mining activity and weathering of spoil tips. The highest concentrations are seen in the middle parts of estuary. It is considered that the distinct absence of elevated concentrations immediately adjacent to mine sites in the uppermost parts of the estuary relates to the dominance of down estuary transport of sediment during winter. Lower concentrations in the lowermost parts of the estuary are thought to be a result of a dilution of sediment originating from offshore. Although remobilisation of such sediments and therefore pollutant metals can occur as a result of channel migration and particularly dredging operations, it is within the lower reaches of the Tamar, characterised by modern industrial activity and dredging, that elemental concentrations are lowest.

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