The spatial distribution and source of arsenic, copper, tin and zinc within the surface sediments of the Fal Estuary, Cornwall, UK

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ABSTRACT

Estuarine sediments commonly form major sinks for contaminants released during industrial activity. Many industrial processes lead to the release of metals initially in solution, which can then be adsorbed on to, for example, Fe hydroxides or clay minerals. However, in the mining industry, there are two major contaminant waste streams: (1) metals discharged in solution via mine drainage; and (2) particulate grains of the ore-forming or related minerals released after ore processing. The release of particulate waste can have a major long-term impact on environmental geochemistry. In this study, we have mapped the distribution of arsenic, copper, tin and zinc within the surficial sediments of the Fal Estuary, Cornwall, UK, an area that drains a historically important polymetallic mining district. There are clear spatial variations in the contaminants, with the highest levels (> 2800 p.p.m. As, >5000 p.p.m. Cu, > 3000 p.p.m. Sn and >6000 p.p.m. Zn) within Restronguet Creek on the western side of the estuary. Mineralogical studies show that small (< 20 μm) grains of detrital arsenopyrite, chalcopyrite, cassiterite and sphalerite are very abundant within the surface sediments. Most of the sulphide grains are fractured, but mineralogically unaltered, although some grains show alteration rims caused by oxidation of the sulphides. The geochemistry and mineralogy are indicative of sediment supply from the discharge of particulate waste into the estuary during historical mining activity. Subsequently, this particulate waste has been largely physically and biologically reworked within the surface sediments. Although considerable effort has been made to minimize contaminants released via mine drainage into the estuary, the potential flux of contaminants present within the intertidal and subtidal sediments has not been addressed. Benthic invertebrates living within the area have adapted to be metal tolerant, and it is likely that the dominant source of bioavailable metals is a result of alteration of the particulate mine waste present within the intertidal and subtidal sediments.

Keywords Arsenic, contamination, copper, Cornwall, UK, estuaries, tin, zinc.

INTRODUCTION

Estuarine sediments commonly form major sinks for contaminants released during both past and present industrial activity. In particular, during mining activity, contaminants may be released into adjacent fluvial catchments either in solution as a result of acid-mine drainage or in particulate form, predominantly as fine-grained waste products from mineral processing. Both these

processes can have a major impact upon sedimentation and regional environmental geochemistry. Commonly, heavy metals released in solution from industrial activity are adsorbed on to other mineral surfaces (e.g. Rubio *et al.*, 2001) but, in mining districts, a significant component of the metal loading to the sediment is in the form of discrete grains of the ore minerals themselves.

The Fal Estuary in Cornwall, UK (Fig. 1), is an important marine habitat, but has also received long-term contamination as a result of large-scale polymetallic mining activity in the catchment area.
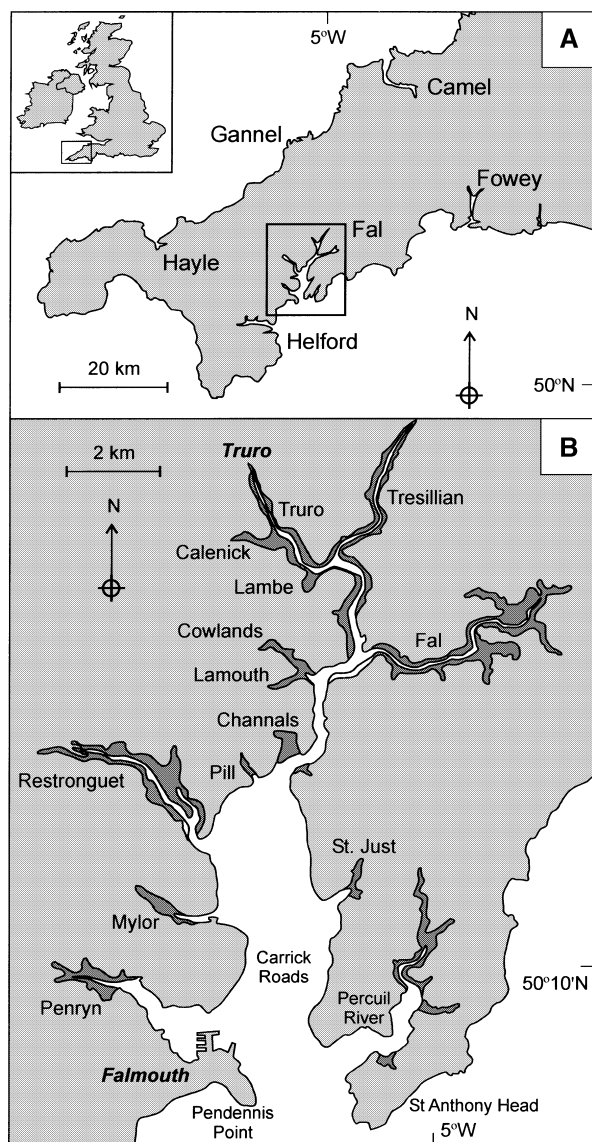

Fig. 1. Maps showing (A) the major estuaries of Cornwall, UK, all of which have received sediment as a result of mining activity and (B) the major components in the Fal Estuary; dark grey shaded areas are intertidal mudflats and minor saltmarsh areas, whereas the clear areas are subtidal.

The impact of mining on the area was highlighted in 1992, when a major pollution event (the Wheal Jane incident) occurred with the sudden discharge of 50 million litres of acidic, heavy metal-contaminated mine water (Banks *et al.*, 1997; Younger, 2002). Biological studies both before and after this discharge indicated that the estuary has a distinctive benthic invertebrate community, which has adapted to be heavy metal tolerant (e.g. Bryan & Gibbs, 1983; Bryan *et al.*, 1987; Somerfield *et al.*, 1994a,b; Austen & Somerfield, 1997; Millward & Grant, 2000). These studies have assumed that the only source of metal contaminants in the area is via acid-mine drainage, whereby metals in solution in the river discharge are adsorbed on to clays and Fe or Mn oxides/hydroxides within the tidal mixing zone and are subsequently deposited within the estuary. However, the intertidal sediments throughout the estuary also contain a very large volume of sulphidic mine waste tailings released during past mining and mineral processing activity (Pirrie *et al.*, 1997).

This study aims to: (1) present geochemical maps allowing the visualisation of the distribution of arsenic, copper, tin, zinc and lead in the surface sediments throughout the estuary; (2) quantify the sediment mineralogy, to allow (3) the relative contributions of particulate waste vs. metals associated with mine drainage to be assessed. This study has clear implications for the longevity of coastal contamination as a result of the discharge of particulate mine waste.

REGIONAL SETTING

Geomorphology

The Fal Estuary is a ria system on the south coast of Cornwall, UK (Fig. 1), which developed in response to Holocene sea-level rise (Bird, 1998). The estuary extends 18 km inland from its mouth to the northern tidal limit at Tresillian and has a total shoreline length of 127 km. Broadly speaking, it can be divided into two regions: the inner tidal tributaries and the outer tidal basin, termed Carrick Roads. The estuary is macrotidal with a maximum spring tide of 5·3 m at Falmouth, but mesotidal at Truro with a spring tide of 3·5 m. The estuary covers 2482 ha with 1736 ha covered by the subtidal area, 653 ha of intertidal mudflats and 93 ha of saltmarsh (Stapleton & Pethick, 1996). Historical records show that there has been extensive siltation in the main tidal tributaries (Restronguet Creek, River Fal, Tresillian

River, Truro River, Calenick Creek) largely as a result of the release of particulate mine waste from (a) placer mining (tin streaming); (b) polymetallic metal mining; and (c) china clay mining (Pirrie & Camm, 1999). For example, the tidal limit on the River Fal has migrated some 4·5–5·5 km seaward since 1500 (Pirrie *et al.*, 1996; Stapleton & Pethick, 1996; Pirrie & Camm, 1999). Early accounts of the estuary included estimates for the rate of sediment accumulation, which ranged from 1·3 cm year^{-1} to 9·7 cm year^{-1} in both the River Fal and Restronguet Creek (Whitley, 1881). Sedimentation rates of >3 cm year^{-1} were also reported in the Carnon Valley, which drains into Restronguet Creek, in the period 1815–1870 (Henwood, 1870).

Regional geology

The regional geology around the Fal Estuary comprises Devonian metasediments into which were intruded the Carnmenellis Granite to the west and the St Austell Granite to the east (Leveridge *et al.*, 1990) (Fig. 2). The Devonian metasediments comprise the Mylor Slate Formation, which crops out throughout the western side of the estuary, and the Portscatho Formation that crops out on the northern and western side of the estuary. The catchment area also drains the Devonian Porthtowan and Bovisand formations. Devonian basaltic sheets, locally referred to as greenstones, are common within the Mylor Slate Formation (Leveridge *et al.*, 1990). Granitic magmatism occurred between 290 and 270 Ma with the emplacement of the Carnmenellis Granite and the St Austell Granite as part of the larger Cornubian batholith (Manning, 1998).

The Devonian metasediments and the granites host very significant polymetallic mineralization. The dominant economic mineralization is hydrothermal in origin and occurs in main-stage NE–SW orientated lodes (veins). These main-stage veins are dominated by an early assemblage of cassiterite, wolframite and arsenopyrite followed by a later assemblage dominated by Cu-Zn-Fe-As-Pb sulphides (Scrivener & Shepherd, 1998). These main-stage lodes are cross-cut by younger N–S trending Pb-Ag-Zn dominated veins, referred to locally as cross-courses, which are commonly developed along extensional faults (Scrivener & Shepherd, 1998). Subsequently, weathering of the vein-hosted mineralization in possibly the late Mesozoic and early Tertiary led to the formation of extensive fluvial cassiterite placer deposits throughout much of south-west England (Camm & Hosking, 1985; Camm, 1999). In addition, hydrothermal alteration and subsequent chemical weathering led to extensive kaolinization in the western part of the St Austell Granite (Manning *et al.*, 1996; Bristow, 1998).

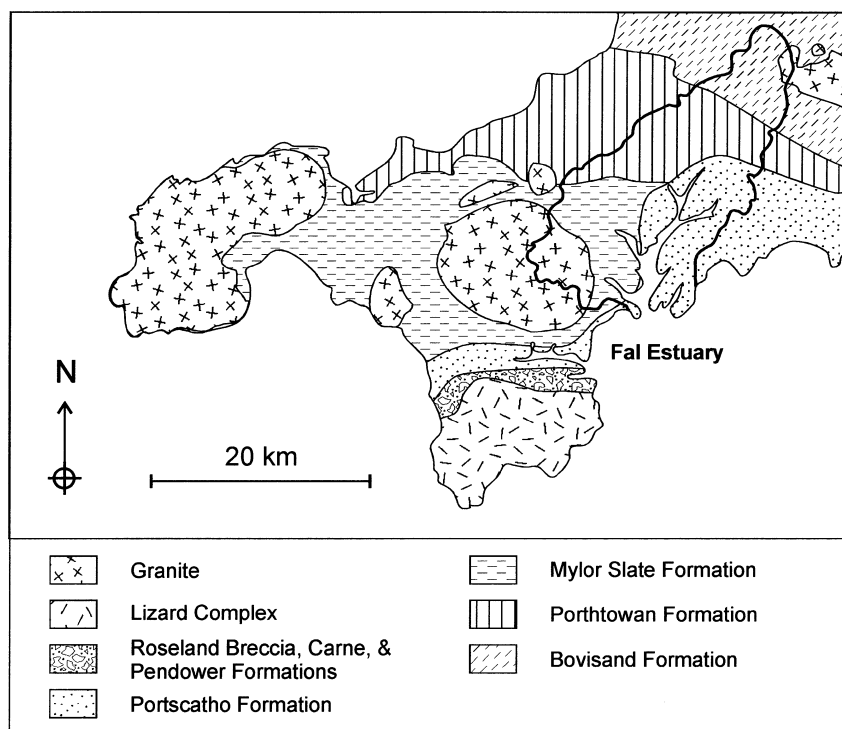The valley systems draining the present-day land mass of SW England can be mapped offshore

Fig. 2. Simplified geological map of the area around the Fal Estuary; solid line indicates the catchment area of the estuary. The granite on the western side of the catchment is the Carnmenellis Granite, whereas that to the east is the St Austell Granite.

Legend:
- Granite
- Lizard Complex
- Roseland Breccia, Carne, & Pendower Formations
- Portscatho Formation
- Mylor Slate Formation
- Porthtowan Formation
- Bovisand Formation

and were established during sea-level lowstand in the Devensian (Camm & Dominy, 1998; Camm, 1999). During the Devensian, periglacial conditions were present in Cornwall with the deposition of head deposits as a result of slope processes within the coastal valley systems. These head deposits unconformably overlie the Devonian metasediments throughout the area (Leveridge *et al.*, 1990) and underlie the Holocene sedimentary record preserved throughout the estuary.

Mining history

Mining in Cornwall dates back to the early Bronze Age (Gerrard, 2000), as indicated by the discovery of Bronze age artefacts from the tin-bearing sediments during later episodes of mining (Penhallurick, 1986). The earliest mining activity involved the working of fluvial placer tin deposits, a mining method referred to as tin streaming (Gerrard, 2000). Hard rock mining commenced in about the thirteenth century (Gerrard, 2000), initially for tin, but then for copper and a range of other metals. Copper and tin production peaked in the 1860s and 1890s, respectively, and then declined rapidly. In addition to tin and copper, there was significant production of arsenic, lead, zinc, tungsten, silver and uranium (Burt, 1998). From the late nineteenth century onwards, the local minerals industry largely shifted from metal mining to the extraction of china clay, particularly from the western side of the St Austell Granite, with ≈ 150 million tonnes of recorded china clay production from southwest England (Bristow, 1998). The last tin mine in Cornwall ceased production in 1998.

The metal and china clay mining industry has had a major impact on the regional environmental geochemistry with an estimated 4888 ha of contaminated land (Edwards *et al.*, 1998). Numerous studies have examined the soil geochemistry in the region (e.g. Abrahams & Thornton, 1987) and, more recently, have been focusing on the potential uptake of contaminants such as arsenic by the local population and its potential impact on human health (Kavanagh *et al.*, 1998; Peach & Lane, 1998).

PREVIOUS WORK

The geochemical impact of mining on the Fal Estuary is widely documented, with work focusing on: (a) the discharge of polluted mine water into the estuary; and (b) the adaptation of benthic invertebrate assemblages within the area. Contaminated mine water has been discharged into the estuary for hundreds of years (Younger, 2002). However, in January 1992, the Wheal Jane incident led to a very visual mine water pollution event when 50 million litres of acidic (pH 3·1; Somerfield *et al.*, 1994a), metal-laden water, carrying abundant suspended Fe hydroxides, was discharged into the estuary (Banks *et al.*, 1997; Younger, 2002). Although very visual, there was limited mixing of this contaminated water with the denser estuarine waters, and the plume was largely dispersed seawards, causing no significant biological impact (Somerfield *et al.*, 1994a). Despite this fact, subsequent upstream remediation measures involving the construction of initially a passive, and then an active, water treatment system have been carried out at a cost to date in excess of £20 million (Younger, 2002).

Although the Wheal Jane incident had no discernible long-term biological effects, the overall invertebrate community structure and individual species within the Fal Estuary are adapted to be heavy metal tolerant and differ significantly from the communities present in other estuaries in SW England (Somerfield *et al.*, 1994a; Warwick, 2001). In addition, there is also a clear spatial variation in the invertebrate community within the estuary, with a distinctive nematode and copepod assemblage present in Restronguet Creek (Somerfield *et al.*, 1994a); this is interpreted to result from long-term pollution in this area. Other studies have shown that the soft tissues of polychaetes (e.g. Williams *et al.*, 1998) and crustaceans (Pedersen & Lundebye, 1996) show elevated Cu concentrations.

Although the biological studies indicate that some of the contaminants present within the estuary must be bioavailable, there has been an assumption that all the metals were originally introduced in solution either as a result of discharge of polluted mine water or from run-off of metal-laden water from spoil heaps. However, previous sedimentological studies have shown that both the surface sediments (Hosking & Obial, 1966; Pirrie & Camm, 1999) and the sediment profile within the intertidal areas of the estuary (Pirrie *et al.*, 1997; Hughes, 1999) have very high levels of particulate metal contamination. Thus, an alternative potential source of bioavailable metals is through the alteration of particulate sulphide waste present within the intertidal and subtidal sediments.

METHODS

Sampling

In total, 405 surface sediment samples collected throughout the estuary have been included in this study. They comprise: (1) samples collected from the intertidal sediments throughout the tidal tributaries of the estuary between 1995 and 2002; (2) sediment samples collected using a drop corer in the subtidal, deeper water areas in the estuary in March 2002, with a sample spacing of 100–200 m; and (3) drop core samples collected as part of a regional geochemical exploration project in 1980. In the intertidal areas of the estuary, samples of the uppermost 5 cm of the sediment profile were collected at low tide. In the subtidal areas, sea-floor sediment samples were collected using a drop corer with the uppermost 5 cm of the sediment profile analysed. Core recovery using the drop corer was achieved in water depths of up to 30 m. In both the recent sampling programmes, the sample location was fixed using a hand-held GPS with an accuracy of ± 5 m. The samples collected in 1980 were also collected by drop coring, and sample location was fixed by theodolite.

Sediment geochemistry and mineralogy

Samples were dried and then representative 50 g subsamples were ground to a fine powder in a chrome steel tema mill and prepared as pressed powder pellets using a boric acid jacket and elvacite binder. The samples were then analysed using a Phillips PW1400 X-ray fluorescence spectrometer (XRF) fitted with a Mo-Sc X-ray tube. All samples were analysed for Sn, Cu, Zn, Pb and As. Results are expressed as p.p.m. with an analytical error of ± 10 p.p.m. The National Research Centre for Certified Reference Materials (NRCCRM) standards GBW07405 and GBW08303 were used routinely. The complete geochemical data set is available on request from the authors (see also *Supplementary material*). A summary of the geochemical data is given in Table 1.

The mineralogy of representative samples has been examined by both X-ray diffraction (XRD) using a Siemens D5000 diffractometer and CuKα radiation and the analysis of polished grain mounts using a Jeol 840 scanning electron microscope (SEM) with an Oxford Instruments Link AN10000 energy dispersive spectrometer. Nine samples were also examined using an automated SEM-based mineral characterization system (QemSCAN) at CSIRO Minerals. QemSCAN is based upon a LEO 438VP SEM fitted with an array of three Gresham energy-dispersive spectrometers. The $< 20~\mu$m grain-size fraction was separated and prepared as polished blocks before QemSCAN analysis. The system is based upon the rapid acquisition of energy-dispersive spectra (EDS) measured at a predefined pixel spacing (in this case 1 μm). The generated EDS are then compared against a database of known spectra, and a mineral name is assigned to each pixel spectrum. In this study, particle mineral analysis was carried out. This method systematically maps the composition of each discrete particle, or a predefined number of particles, within the polished block. This provides quantitative data on mineralogy along with particle grain size and shape. Effectively, QemSCAN provides rapid automated quantitative modal data. In this study, between 4000 and 6000 grains were measured in each sample.

Data analysis

Geochemical maps for the surface sediments were prepared using industry standard VisiDATA INTERDEX software. VisiDATA INTERDEX creates

Table 1. Summary of geochemical data for the surface (uppermost 5 cm) sediment samples in each of the major creeks in the Fal Estuary.

	No.	Cu Min.	Cu Max.	Sn Min.	Sn Max.	As Min.	As Max.	Pb Min.	Pb Max.	Zn Min.	Zn Max.
Restronguet	33	1172	**5073**	752	**3400**	983	**2803**	217	570	950	**6600**
Calenick	49	217	1266	186	3190	60	834	121	**902**	130	2733
Truro (to Fal)	37	130	495	56	2028	27	244	40	218	268	1181
Tresillian	31	154	346	330	657	39	124	90	161	325	905
Fal (to Turnaware)	83	21	558	71	442	13	185	16	298	97	685
Carrick Roads	136	90	2330	10	1800	17	1260	20	134	145	2800

Note that maximum concentrations of Cu, As, Sn and Zn (highlighted in bold) occur within Restronguet Creek, with maximum concentrations of Pb in Calenick Creek. All values in p.p.m.

images using an inverse distance-squared gridding method. This method involves dividing the area to be imaged into a regular grid of squares (pixels) and calculating a value for each pixel in the grid. The calculation of each pixel uses a moving weighted average, comprising all data values within a defined search radius of the centre of the pixel. The contribution to the final pixel value of each data value is inversely proportional to the square of the distance of the data value from the centre of the pixel. The data had been given a bias location of isotropic and linear weighting. Two sets of geochemical maps were prepared: linear maps based upon the actual measured elemental concentrations and log-transformed data maps. The log-transformed data maps (referred to as the logarithmic maps) enable smaller scale variations in the data set to be visualized, which are masked on the linear maps by the extreme variation in the contaminants present. Geochemical maps were prepared for the whole estuary and also for the northern tributaries, western tributaries and eastern tributaries/ Carrick Roads.

RESULTS

Sediment characteristics

Throughout the estuary, the surface sediment samples are composed of light to dark grey to brown clays and silts with a very minor (< 5%) very fine to fine sand component. Samples collected from the eastern tributaries (principally the Fal River) are light grey in colour, indicative of the increased abundance of kaolinite in this area relative to the western tributaries of the estuary (Hughes, 2000). Samples from the deeper water subtidal areas contained a higher proportion of coarse-grained (mm scale) carbonate shell debris, which was screened out of the samples before geochemical analysis. All the recovered sediments show moderate to intense bioturbation.

Geochemical maps

Linear and logarithmic geochemical maps of the whole of the Fal Estuary for arsenic, copper, tin and zinc are shown in Fig. 3, and the geochemical data are summarized in Table 1. As can be seen in Table 1, there are very marked variations in the surface sediment geochemistry throughout the estuary, with the western side showing the highest levels of contamination. Maximum concentra-

tions of Cu (5073 p.p.m.), As (2803 p.p.m.), Sn (3400 p.p.m.) and Zn (6600 p.p.m.) occur in Restronguet Creek and maximum concentrations of Pb (902 p.p.m.) in Calenick Creek. In contrast, the rivers and creeks draining the eastern side of the estuary have the lowest levels of contamination. In all the geochemical maps, the dominant contaminated area is Restronguet Creek, with a significant plume of contamination entering the western side of Carrick Roads and extending towards the south. The upper reaches of the River Fal show the lowest levels of contamination. The extreme concentrations in Restronguet Creek mask more subtle variations elsewhere in the estuary, but these can be visualized more clearly in the logarithmic geochemical maps presented in Fig. 3. The As geochemical map shows significant contamination in Restronguet Creek with a uniform As distribution through the main body of the estuary, and the lowest levels of contamination in Lamouth, Cowlands and St Just creeks as well as the River Fal. The Cu geochemical map reveals a similar pattern with a major plume extending southwards along the western side of the estuary from Restronguet Creek. Sn concentrations are highest in Restronguet Creek but are also significantly elevated in the Truro River, Calenick Creek and the Tresillian River. Lowest Sn concentrations are at the head of the River Fal. Zn is again significantly enriched in the upper parts of Restronguet Creek and as a plume flowing south towards Mylor Creek; intermediate Zn values occur throughout the majority of the rest of the estuary with low levels in the River Fal.

In addition to the geochemical maps of the whole estuary, enlarged maps for individual areas are also presented (Fig. 4) allowing the recognition of smaller scale variation in the sediment geochemistry. For example, the distribution of zinc in the Truro/Tresillian area reveals locally increased levels of Zn in the middle part of the Truro River with uniform Zn concentrations elsewhere (Fig. 4A). The Pb distribution in this area is given in Fig. 4B, which shows that Calenick Creek has the highest levels of Pb contamination, followed by the Truro River; the Tresillian River has lower Pb concentrations and, to the south of the confluence of the Tresillian and Truro rivers, there are low levels of Pb contamination. The geochemical map for As in the Fal and Cowlands part of the estuary illustrates how locally variable the As distribution is (Fig. 4C). Very low levels of As occur at the head of the River Fal and increase towards the west, to the south of Cowlands Creek; this
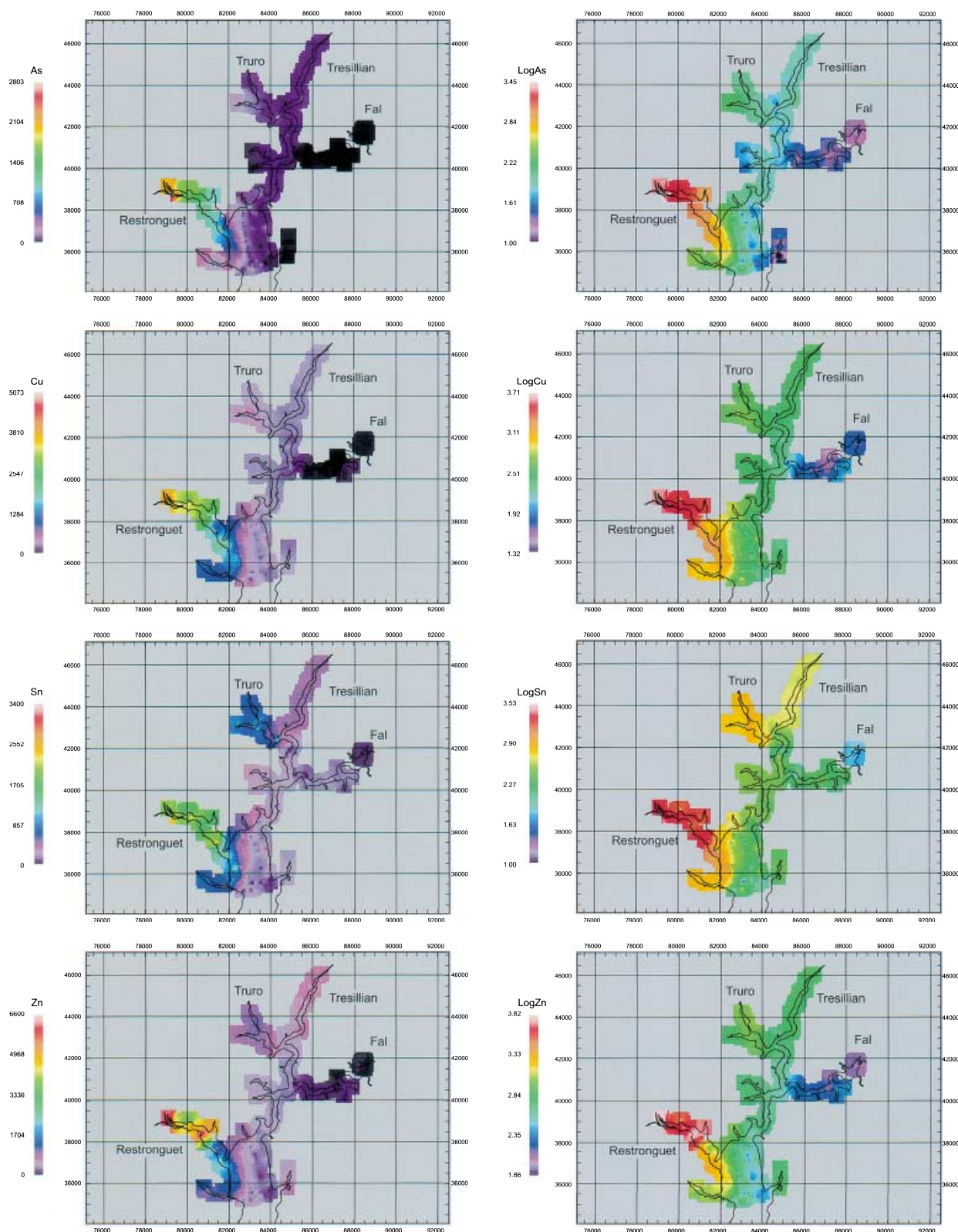
Fig. 3. Contoured geochemical maps for As, Cu, Sn and Zn concentrations in the surficial sediments (top 5 cm) throughout the Fal Estuary. Maps are presented as both linear geochemical maps (left column) based on the absolute measured concentrations in p.p.m. and logarithmic geochemical maps (right column), which allow smaller scale variation in the sediment geochemistry to be recognized. The colour shading is extended beyond the outline of the estuary for ease of visualization.
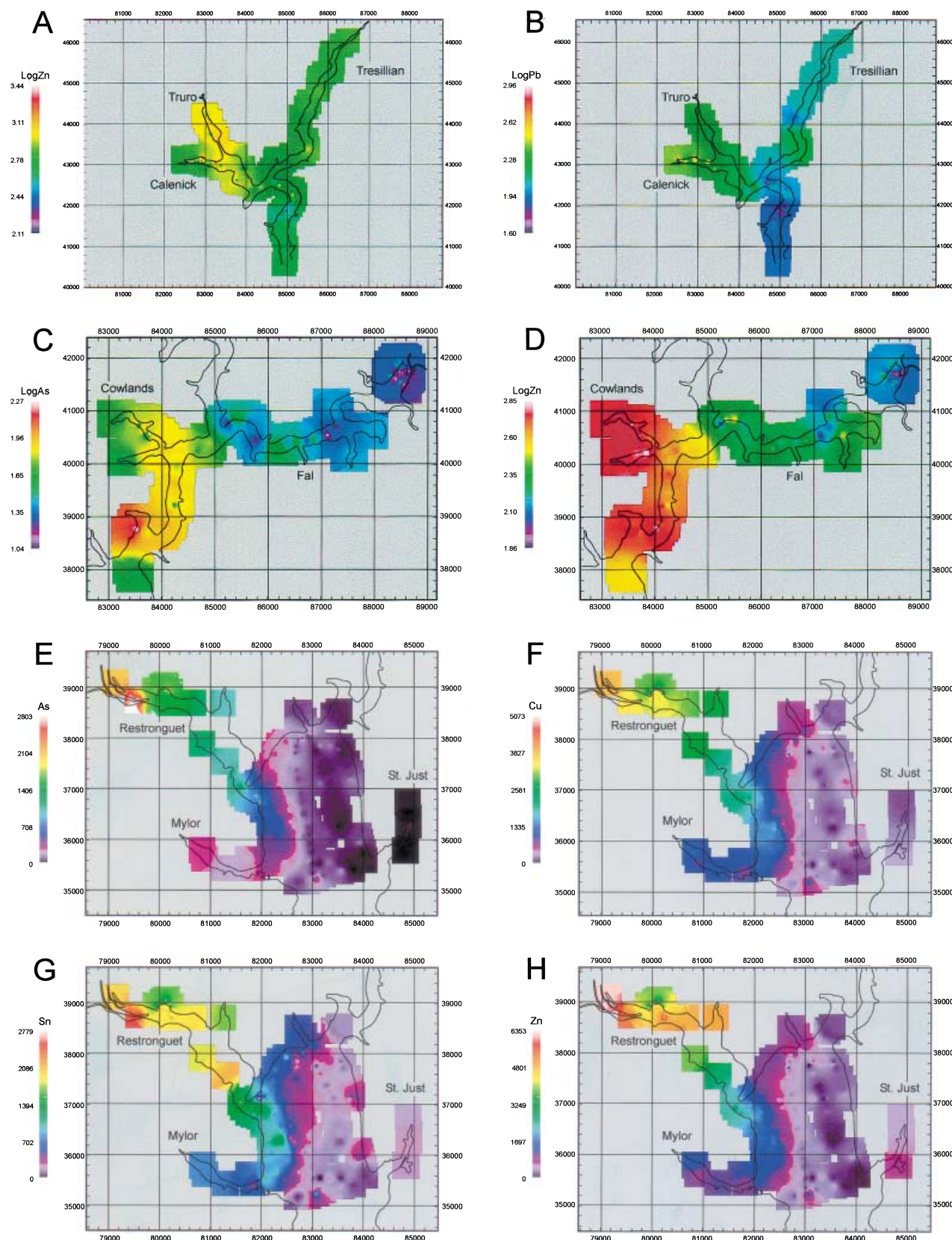
Fig. 4. Detailed logarithmic and linear geochemical maps for specific areas within the Fal Estuary. (A) Logarithmic Zn distribution in the Truro and Tresillian areas; note the higher levels of Zn contamination in the middle reaches of the Truro River. (B) Pb logarithmic distribution for the Truro and Tresillian area. Pb concentrations are highest in Calenick Creek. (C) Logarithmic As distribution in the River Fal and Cowlands Creek area showing an increase in concentration of As towards the southern part of this area. (D) Logarithmic Zn distribution in the area around the River Fal and Cowlands Creek, again showing a marked increase in Zn concentration towards Cowlands Creek and towards the south. Diagrams E, F, G and H show the linear geochemical maps for As, Cu, Sn and Zn, respectively, for Restronguet Creek and Carrick Roads. Note that, in all these diagrams, highest levels of contamination are in the upper reaches of Restronguet Creek with an apparent plume of contamination extending from Restronguet Creek and dominantly extending towards the south, although higher levels of contamination for Sn and Cu also extend northwards along the western side of the estuary. Note that the unshaded areas in Restronguet Creek result from a lack of samples in this area for field safety considerations.

appears to be the northward continuation of the plume of contamination entering the estuary from Restronguet Creek. The distribution of Zn in this area is slightly different, with again the lowest levels of contamination at the head of the River Fal decreasing westwards, but with the highest levels of Zn contamination in an area between Lamouth and Cowlands creeks and extending south along the main river channel (Fig. 4D). The spatial distribution of As, Cu, Sn and Zn in Restronguet Creek and out into the subtidal deep-water part of the estuary, Carrick Roads, is shown in Fig. 4E–H. All four maps show a very similar spatial pattern with the highest levels of contamination at the head of Restronguet Creek and an apparent plume of contamination extending southwards from Restronguet Creek along the western side of Carrick Roads as far south as Mylor Creek. The eastern side of Carrick Roads and St Just Creek have low levels of contamination, and there appears to be little transfer of contaminants from the western side of the estuary towards the east.

Mineralogy

Fifteen sediment grain mounts were examined manually under SEM. Heavy mineral abundance was estimated at between 0·5% and 1·5%. The heavy mineral suite is dominated by chalcopyrite,

sphalerite, arsenopyrite, pyrite and cassiterite along with minor ilmenite, wolframite, monazite and zircon (Fig. 5). The heavy mineral grains are typically angular in shape, predominantly < 20 μm in size and occur as both liberated (i.e. they are not enclosed within another mineral phase; Fig. 5A) and locked grains (Fig. 5B). Many of the sulphide grains including arsenopyrite and chalcopyrite (Fig. 5C and D) are fresh and unaltered. However, some grains have alteration rims around the grain margin. For example, chalcopyrite grains have an Fe-rich, Cu-poor rim (Fig. 5E), and some sphalerite grains have an Fe-rich alteration zone surrounding a sphalerite core (Fig. 5F). Pyrite is present as both detrital angular grains and diagenetic framboidal pyrite (Fig. 5G). Man-made slag products occur rarely (Fig. 5H).

Nine samples were selected for quantitative mineral analysis using QemSCAN. Analysis focused on the < 20 μm grain-size fraction, as preliminary SEM analysis had identified that the majority of the heavy minerals were in this size fraction. Modal data are presented in Table 2. The dominant detrital heavy minerals identified were cassiterite, chalcopyrite, sphalerite and arsenopyrite, along with minor rutile, ilmenite, zircon, xenotime, monazite, chromite, bornite and galena. Pyrite was also very abundant, but detrital vs. diagenetic grains were not distinguished. Although the modal data show that the heavy minerals are very abundant, the QemSCAN data indicated that their mean particle size (in the sub 20 μm grain-size fraction) was < 6 μm. Bulk XRD analyses of the surface sediment samples show that the dominant phases present are quartz, kaolinite, chlorite, muscovite, calcite and pyrite.

DISCUSSION

Source of the contaminants

The geochemical maps presented here show a clear spatial variation in As, Cu, Zn and Sn throughout the surface sediments in the Fal Estuary. The source of these contaminants is a result of historical industrial activity around the estuary (Ratcliffe, 1997). Shipping is a significant industry, but only in the port of Falmouth to the south of the study area, although Truro also has a small loading quay (Ratcliffe, 1997). Other potential sources of contaminants are small landfill sites around the estuary. However, based upon previous studies in the estuary (e.g. Pirrie *et al.*,
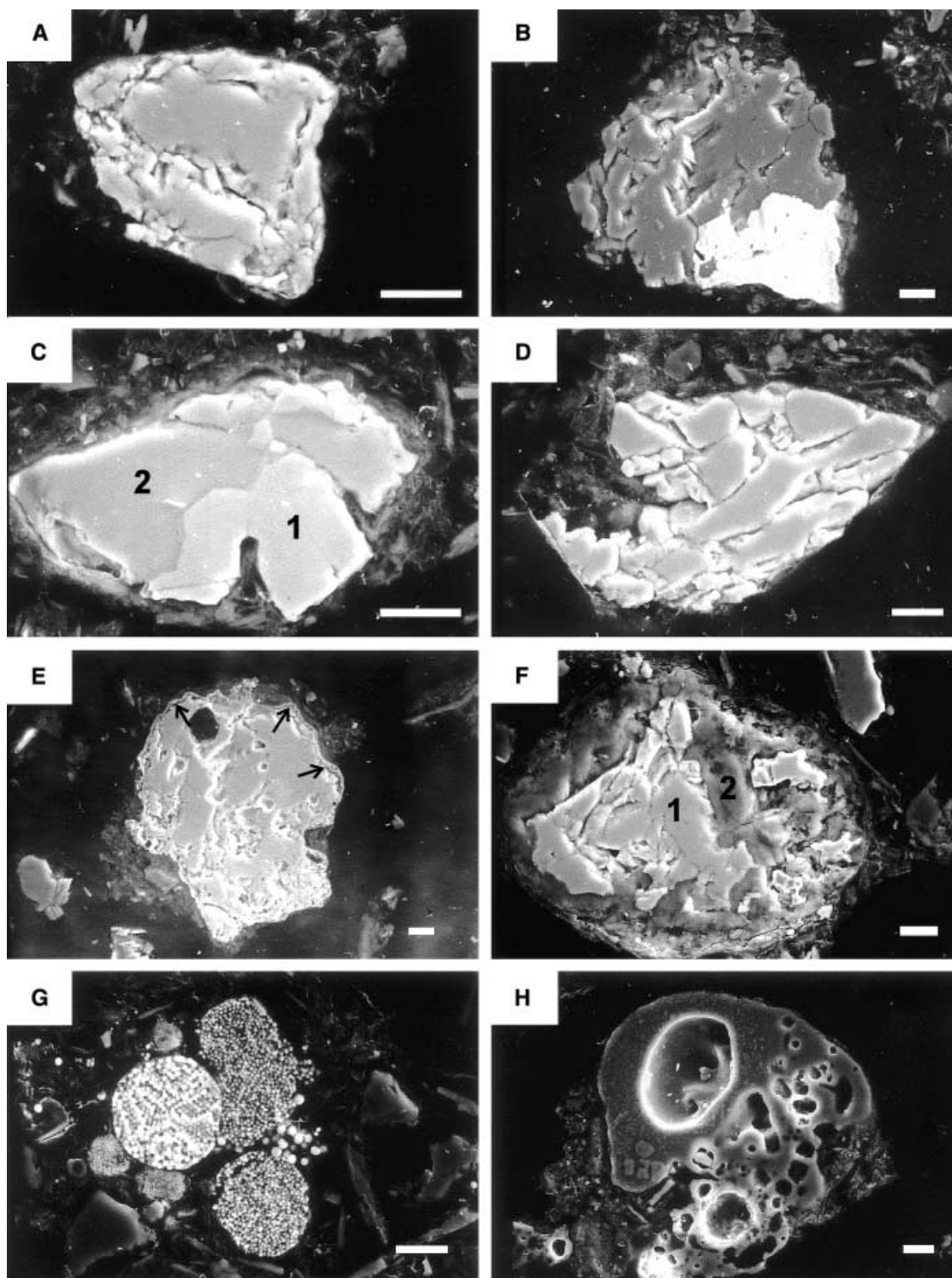
Fig. 5. Scanning electron microscope images of polished grain mounts of samples from the Fal Estuary. (A) Liberated grain of chalcopyrite. (B) Cassiterite grain (bright phase) locked within feldspar. (C) Composite sulphide grain composed of arsenopyrite (1) and chalcopyrite (2). (D) Liberated grain of arsenopyrite. (E) Chalcopyrite grain with an alteration rim (arrowed) enriched in Fe and depleted in Cu. (F) Altered grain with a sphalerite core (1) and an Fe-rich envelope (2). (G) Diagenetic framboidal pyrite. (H) Man-made slag grain with a Si-Al groundmass and blebs of Al-Mg-Fe. All scale bars are 10 μm.

Table 2. Summary of the QemSCAN modal data.

Mineral	(A)									(B)								
	RA1	RA2	RA4	RA5	RC3	RC4	RD1	RD2	RD3	RA1	RA2	RA4	RA5	RC3	RC4	RD1	RD2	RD3
Rutile	116	68	98	77	91	41	82	39	91	3	1	2	1	2	1	1	1	1
Ilmenite	34	12	17	16	30	12	23	12	27	1	0	0	0	1	0	0	0	0
Ti-magnetite	24	3	12	9	23	5	11	10	13	1	0	0	0	0	0	0	0	0
Zircon/xenotime	50	66	33	37	44	52	53	51	44	1	1	1	1	1	1	1	1	1
Monazite	104	90	82	68	78	49	68	48	75	2	2	1	1	1	1	1	1	1
Chromite	53	85	106	47	98	46	77	39	56	1	1	2	1	2	1	1	1	1
Cassiterite	526	696	380	584	554	427	532	389	605	12	12	6	10	9	10	9	10	10
Chalcopyrite	187	468	528	725	520	429	565	351	696	4	8	9	12	9	10	9	9	11
Bornite	34	18	9	37	18	12	13	14	29	1	0	0	1	0	0	0	0	0
Cu other	41	73	82	94	85	93	167	96	96	1	1	1	2	1	2	3	2	2
Galena	21	12	17	22	11	11	12	12	16	0	0	0	0	0	0	0	0	0
Sphalerite	29	218	264	204	199	210	273	138	177	1	4	4	3	3	5	4	4	3
Zn other	19	36	47	14	31	17	30	16	29	0	1	1	0	1	0	0	0	0
Arsenopyrite	23	164	105	158	115	120	53	45	65	1	3	2	3	2	3	1	1	1
As other	19	36	47	14	31	17	30	16	29	0	1	1	0	1	0	0	0	0
Pyrrhotite	63	42	55	64	55	48	84	39	53	1	1	1	1	1	1	1	1	1
Pyrite	620	966	1330	1205	1099	822	1195	711	1144	14	16	22	20	18	19	19	18	19
Quartz	214	262	252	206	254	129	215	128	254	5	4	4	3	4	3	3	3	4
Other silicates	1537	1701	1772	1676	1668	1108	1601	1002	1715	36	29	29	27	28	25	26	26	28
Other	584	872	877	877	971	704	1073	704	909	14	15	14	14	16	16	17	18	15
Total	4298	5888	6113	6134	5975	4352	6157	3860	6123	100	100	100	100	100	100	100	100	100

(A) Primary QemSCAN data showing the number of mineral grains assigned to each mineral phase or grouping in the $< 20\ \mu$m grain-size fraction. Note that between 3860 and 6157 individual grains were quantified based on the interpretation of their EDS analysis.
(B) Recalculated percentages. 'Cu other' includes phases identified as cubanite, CuS (covellite and chalcocite) and Cu-silicate minerals. 'Zn other' includes Zn metal and Zn-silicate boundary phases. 'As other' includes As sulphides (other than arsenopyrite) and other unidentified As species. 'Other' is dominated by carbonates. Note that the pyrite mineral grouping includes both detrital and diagenetic pyrite.

1997) and the absence of other large-scale industry in the area, we interpret the main source of these contaminants to be from historical mining activity. Downcore variations in the sediment geochemistry in the intertidal areas of the estuary typically show a clear covariance in Sn, Zn, As, Cu and Pb (Pirrie *et al.*, 1997; Hughes, 1999, 2000), which is consistent with the source of these contaminants being derived from polymetallic mining operations (Fig. 6). It is also important to note that, within the downcore geochemical profile, the peak concentrations of potentially more mobile elements such as Cu and As correspond with the peak concentrations of Sn, which, based on the mineralogical studies, is predominantly present as the geochemically stable oxide cassiterite. The mineralogical data suggest that Sn, Cu, As and Zn are largely present as discrete, very small (typically $< 6\ \mu$m) liberated grains of the dominant ore minerals from the area (cassiterite, chalcopyrite, arsenopyrite and sphalerite) or, less commonly, larger grains of the ore

minerals enclosed within rock fragments. These small liberated ore mineral grains represent fine-grained mine tailings in which the grains were too small for successful concentration during mineral processing. Thomas (1913) suggested that, in 1913, some 30% of the mined cassiterite ore was not recovered during mineral processing. This fine silt-sized tailings waste was discharged into the adjacent fluvial systems and led to extensive siltation within the upper reaches of the estuary (e.g. Whitley, 1881).

As shown on the geochemical maps, there is a clear spatial variation in contaminant concentrations throughout the estuary. Contamination levels are lowest in the Fal River; this area received kaolinitic mining waste up until the introduction of environmental legislation in 1968. This china clay waste has low levels of metal and As contamination. In contrast, the highest levels of contamination are in Restronguet Creek. The catchment area for Restronguet Creek covers an area of ≈ 96 km^2 and drains an area that
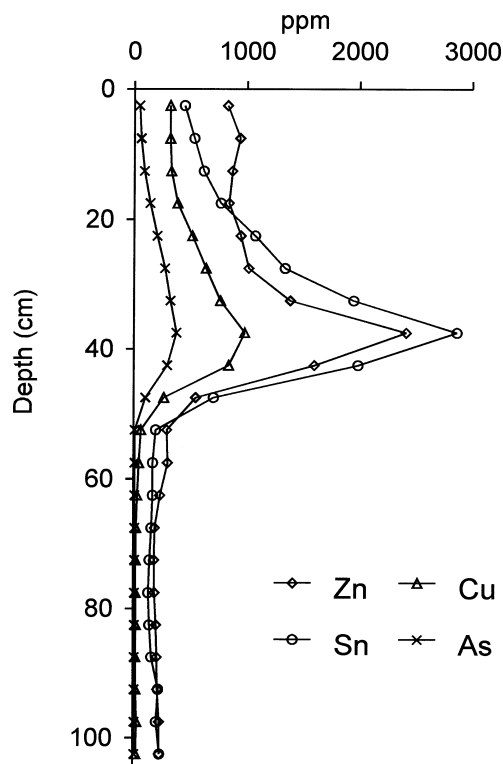
Fig. 6. Representative downcore sediment geochemical profile for a core recovered from the Truro River. The abrupt increase in metal concentrations at 40 cm is interpreted to reflect the sudden discharge of mine waste tailings into the estuary. Note that the surface sediment geochemistry has significantly higher concentrations of Zn, Cu, Sn and As than that observed at the base of the core. Data from Hughes (2000).

historically was intensely mined (Fig. 7). Mining activity in this catchment area peaked in the 1890s and continued sporadically up until the closure of Wheal Jane mine in 1991. The recorded output from hard rock mines in this catchment area before 1950 was 1.8×10^6 tons of Cu ore at 7·6% Cu, 22 500 tons of cassiterite, 28 800 tons of arsenopyrite, 3700 tons of galena, 2500 tons of sphalerite and 71 900 tons of pyrite (Dines, 1956). The deliberate discharge of mine waste tailings into Restronguet Creek had ceased by 1950 and, even by that time, was minimal in comparison with historical levels of mine waste discharge. The accidental acid-mine drainage discharge from Wheal Jane in early 1992 carried metals in solution or adsorbed on to Fe and Mn hydroxides, which were dispersed from Restronguet Creek out into Carrick Roads (Younger, 2002). No changes in the sediment geochemistry were recognized as a result of this mine water discharge (Somerfield *et al.*, 1994a). Therefore, the very high levels of contamination within Restronguet Creek and the

plume issuing from Restronguet Creek and out into Carrick Roads is interpreted to result from the deposition and subsequent reworking of historically released particulate mine waste. Once particulate waste has been deposited within the estuarine sediments, it can be reworked by natural physical processes such as tidal currents or lateral channel migration, as a result of bioturbation by both the invertebrate benthos and feeding wading birds and as a result of human activity in the estuary, such as minor engineering works and bait digging. The plume of elevated levels of contaminants discharging into the estuary from Restronguet Creek closely mirrors the dominant tidal flow directions (Fig. 8) and is interpreted to be caused by the reworking of the particulate waste by tidal currents.

Elsewhere in the estuary, the levels of contaminants can also be interpreted as a result of the reworking of historical mining and mineral processing waste streams. For example, the elevated levels of tin in the Truro River and Calenick Creek may be related to the local presence of a number of important smelters in this area (Fig. 7). However, the geochemical maps also reveal areas where a direct mining-related origin for the levels of contamination is less immediately apparent. For example, there is a localized increase in Zn in the middle part of the Truro River (Fig. 4A). This is interpreted as resulting from the accidental release of Zn ore concentrate into the river from a loading quay present in this area during shipping activity.

Although the Fal Estuary is an internationally recognized marine habitat, when compared with other estuarine systems, it is clear that it is very heavily contaminated. Table 3 summarizes the sediment geochemistry of a number of estuaries. As can be seen, all the estuaries in Cornwall are extremely contaminated compared with other areas affected by contamination from other industrial process routes. In fact, the maximum levels of contamination seen in the Cornish estuaries are more directly comparable with geochemical data for sulphidic mine waste tailings. For example, in 1998, sulphidic tailings were accidentally discharged from the Aznalcollar mine in the Iberian pyrite belt of SW Spain. The tailings contained up to 21 200 p.p.m. Zn, 2120 p.p.m. Cu, 8500 p.p.m. Pb and 6100 p.p.m. As and caused significant downstream environmental impact (Leblanc *et al.*, 2000). Recorded maximum concentrations of Cu, Sn and Pb are all higher in the estuaries of Cornwall than in this catastrophic tailings spill.
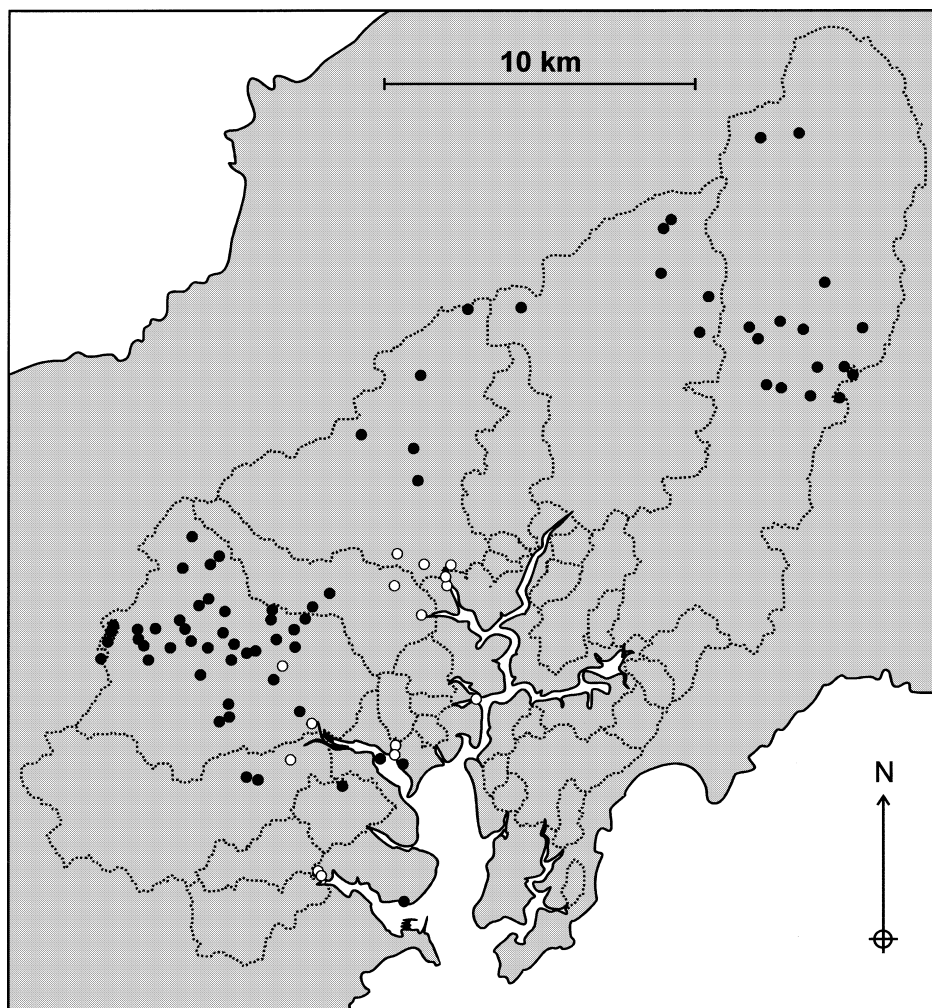
Fig. 7. Map showing each of the discrete fluvial catchments (dotted lines) that discharge into the Fal Estuary along with the distribution of the major hard rock mines (filled circles) and smelters (open circles) within the catchment area of the Fal Estuary. Note that the largest concentration of mines is within the catchment area for Restronguet Creek.

Mineralogical stability and bioavailability of the contaminants

The mineralogical studies show that many of the sulphide grains are fresh and unaltered. However, some of the sulphide grains clearly show alteration rims, which appear to show the successive loss of Cu, As and Zn from the original sulphide grains (cf. Hudson-Edwards *et al.*, 1998). What cannot be proven is whether this alteration under oxidizing conditions occurred within the adjacent fluvial system before deposition within the estuary or subsequently after deposition. However, diagenetic mobility of contaminants within the estuarine sediments in Restronguet Creek is clearly indicated by the presence of diagenetic copper minerals (Thorne, 1983a,b; Beer, 1992). In other estuaries in Cornwall, a wide range of other

diagenetic Zn, Cu, Pb and As minerals have been documented (e.g. Pirrie *et al.*, 2000a,b). Previous studies on the downcore geochemistry of cores from the northern part of the Fal Estuary (Pirrie *et al.*, 1997; Hughes, 1999) showed that, from about 50 cm below the present-day sediment surface, low levels of contamination by Sn, As, Zn, Pb and Cu suddenly increase rapidly to peak concentrations and then decrease in concentration towards the sediment surface, but the levels of the contaminants always remain significantly higher at the present-day sediment surface than the concentrations at the base of the cores (Fig. 6). This was interpreted to represent a pulse in mine waste contamination, which, although still identifiable as a discrete event, has been mixed vertically as a result of bioturbation and physical reworking. Thus, this vertical 'smearing' of
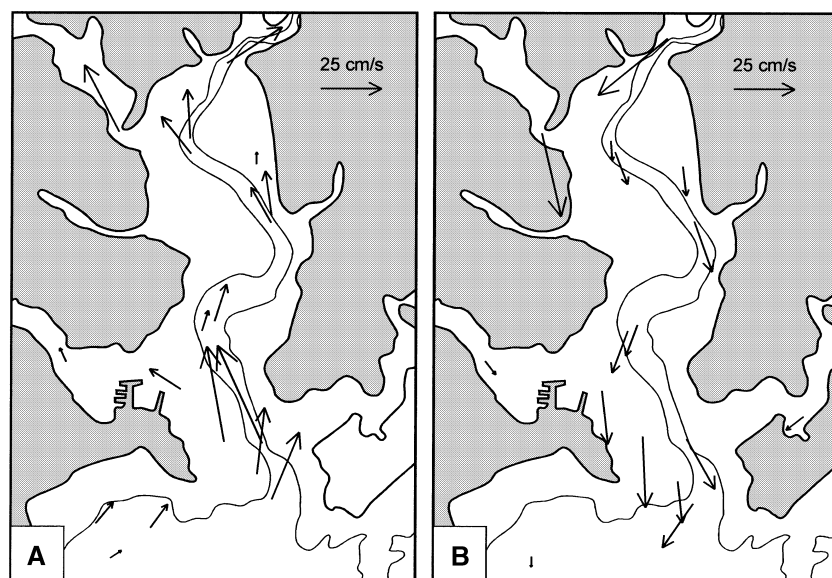
Fig. 8. Map showing the dominant tidal flow directions in the Fal Estuary (from Stapleton & Pethick, 1996) for (A) 3 h before high water and (B) 3 h after high water. Note that the observed plume in contamination entering Carrick Roads from Restronguet Creek mirrors the dominant southerly tidal flow directions.

Table 3. Comparison of the maximum levels of contamination by Sn, Cu, As, Pb and Zn in the surface sediments in the Fal Estuary compared with both other estuaries in south-west England and other contaminated sites.

Location	Sn (p.p.m.)	Cu (p.p.m.)	As (p.p.m.)	Pb (p.p.m.)	Zn (p.p.m.)	Reference
Fal Estuary, Cornwall, UK	3400	5073	2803	902	6600	This study
Fowey Estuary, Cornwall, UK	1210	527	144	131	420	Pirrie *et al.* (2002)
Gannel Estuary, Cornwall, UK	262	315	526	8530	1620	Pirrie *et al.* (2000a)
Camel Estuary, Cornwall, UK	842	282	283	71	245	Pirrie *et al.* (2000a)
Medway Estuary, UK	5	42	14	67	138	Spencer (2002)
Humber Estuary, UK	ND	70	103	127	319	Grant & Middleton (1990)
Wellington Harbour, NZ	ND	73	40	104	221	Dickinson *et al.* (1996)
Halifax Harbour, Canada	ND	230	ND	340	640	Buckley *et al.* (1995)
Jordan Cove, Connecticut	ND	77	ND	167	231	Benoit *et al.* (1999)
Rio Tinto tailings	ND	1300	2900	31 000	1300	Hudson-Edwards *et al.* (1999)
Aznalcollar tailings	22	2120	6100	8500	21 200	Leblanc *et al.* (2000)

ND, not determined.

discrete historical pulses of mine waste discharge within the sediment profile is probably largely the result of physical/biological reworking of particulate grains rather than large-scale diagenetic remobilization. However, if the sulphidic mineral grains are reworked and redeposited within the surface sediments, then it is likely that oxidation of the sulphides will occur providing a flux of biologically available contaminants (Salomons, 1995).

Biological studies on the Fal Estuary have recognized that the invertebrate fauna within Restronguet Creek differs in overall composition from other creeks in the estuary and also from other south-west estuaries (e.g. Somerfield *et al.*, 1994a; Williams *et al.*, 1998; Warwick, 2001). This is interpreted as resulting from the contam-

ination gradient within the estuary. The source of the metals for uptake has been assumed to be related to the discharge of acid-mine drainage, with the metal ions adsorbed on to clays and Fe/ Mn oxy/hydroxides. In addition, the analytical procedures used in many of the previous studies assessing metal bioavailability have involved digesting the sample in concentrated HNO_3 before analysis by flame atomic absorption spectrophotometry (e.g. Somerfield *et al.*, 1994a; Williams *et al.*, 1998). As HNO_3 is an oxidizing agent as well as an acid, this technique will also digest (either wholly or partially) sulphide minerals (e.g. Beckett, 1989). Thus, the reported metal concentrations will also have a significant component derived from the dissolution of the abundant sulphidic mine waste within the estuary

sediments. An alternative interpretation for the source of the bioavailable metals is that, since the discharge of the sulphide-rich mine waste into the estuary sediments occurred, there has been a continued metal flux within the sediment profile as a result of the *in situ* oxidation of the sulphide mine waste. Furthermore, *in situ* oxidation of sulphide minerals will lead to the release of metals in solution that can also be adsorbed on to clays and Fe/Mn oxides within the sediment. Clearly, it would be impossible to distinguish between adsorbed metals sourced via mine drainage vs. those sourced internally within the sediment column from sulphide oxidation. However, this study does show that a substantial component of the total metal budget is present as the primary ore minerals.

CONCLUSIONS

1 Surficial sediments from the Fal Estuary, Cornwall, UK, contain very high levels of As and metal contamination with maximum values of 5073 p.p.m. Cu, 3400 p.p.m. Sn, 2803 p.p.m. As, 6600 p.p.m. Zn and 902 p.p.m. Pb.

2 There is a clear spatial distribution of the contaminants within the estuary with maximum levels on the western side (Restronguet Creek) and to the north (Calenick Creek and the Tresillian River) with the lowest concentrations to the east. The geochemical data reveal a clear plume of contamination entering the estuary from Restronguet Creek and then following the dominant tidal flow directions to both north and south.

3 Heavy mineral suites in the samples are dominated by cassiterite, chalcopyrite, sphalerite and arsenopyrite, along with minor rutile, ilmenite, zircon, xenotime, monazite, chromite, bornite and galena. Detrital and diagenetic pyrite is also abundant. There is a clear correlation between the sediment geochemistry and the mineralogy, suggesting that the contaminants are largely present as discrete particulate grains.

4 Together, the mineralogy and geochemistry are consistent with sediment supply from historical mining and mineral processing activity. This mining activity largely ceased ≈ 100 years ago, but subsequent physical processes and bioturbation have reworked this mine waste within the present-day surficial sediments.

5 Previous biological studies have recognized that the invertebrate communities in the estuary are adapted to be heavy metal tolerant. It has been assumed that the bioavailable metals were largely sourced from acid-mine drainage, yet it is very likely that there is a long-term release of contaminants as a result of the oxidation of reworked sulphide minerals within the estuarine sediments.

6 Previous studies assessing total bioavailable metals using a methodology involving digesting the sample in concentrated HNO_3 before analysis by flame atomic absorption spectrophotometry have probably over-reported bioavailable metals, as sulphidic minerals within the sediment would also have reacted with the HNO_3 reagent.

7 The release of particulate mine waste into estuarine systems results in the long-term storage and localized potential remobilization of contaminants long after the initial dispersal. Management strategies for contaminated coastal areas need to consider carefully particulate contaminants as well as contaminants released in solution.

SUPPLEMENTARY MATERIAL

The following material is available from http://www.blackwellpublishing.com/products/journals/suppmat/sed/sed566/sed566sm.htm

Table S1. The complete geochemical data set.

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