GEOCHEMICAL AND MINERALOGICAL RECORD OF HISTORICAL MINING, HAYLE ESTUARY, CORNWALL, UK

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The release of particulate waste as a result of major historical mining activity within the polymetallic Cornubian orefield, Cornwall UK, has locally caused significant contamination of estuarine sediments. In this study the impact of historical mining on the southwest Hayle Estuary, Cornwall, UK, was evaluated by examining the sediment geochemistry and mineralogy of nine shallow (<1 m) cores along with surface sediment sampling throughout the intertidal areas of the estuary. The sediment geochemistry of all of the cores shows very elevated levels of tin and copper (maximum Sn value of 7041 ppm and Cu 29,869 ppm). Surface (uppermost 5 cm) sediment samples are also contaminated, with up to 4520 ppm Cu, 5455 ppm Sn, 2292 ppm As, 522 ppm Pb and 1777 ppm Zn. Core dating indicates that the sediments currently exposed at the surface were deposited prior to 1880. The detrital heavy mineral assemblage is dominated by cassiterite, chalcopyrite, arsenopyrite, sphalerite and pyrite along with minor galena, monazite, zircon, stannite, wolframite, plumbogummite, covellite, bornite and ilmenite. In addition, man made slag and smelt products are common. Diagenetic pyrite, chalcopyrite and atacamite are also present. The sediment geochemistry and mineralogy are interpreted to represent (a) the input of historic mine waste tailings and smelt waste into the estuary probably prior to 1880, and (b) the subsequent exposure of these contaminated sediments as a result of recent erosion.

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INTRODUCTION

Modern sedimentary systems commonly retain a geochemical and mineralogical record of the impact of industrial activity on the environment (e.g. Cundy *et al.*, 2003). Mining has had a major impact on the global environment, with the discharge of contaminants either initially in solution through mine drainage or as a result of the discharge of particulate waste (usually referred to as tailings). Whilst the management of mine drainage is one of the main environmental challenges for the present-day mining industry (e.g. Salomons, 1995), the release of mine waste tailings during historical mining activity has had the most significant long term effect (e.g. Hudson-Edwards *et al.*, 1999; Leblanc *et al.*, 2000; Borrego *et al.*, 2002). The estuaries of Cornwall, UK, provide an ideal area to examine the long term impact of the release of particulate mining waste on the environment because: (a) different estuaries have received waste streams from different mining operations, (b) the contaminated sediments have been in the environment, in many cases for >100 years, without subsequent remediation, and (c) there have been limited subsequent industrial operations impacting upon the coastal sediments which could otherwise obscure the mining-related signatures.

Mining of metalliferous minerals in Cornwall, extends back 3000 years to the Bronze age (Penhallurick, 1986; Gerrard, 2000). Tin, copper, lead, arsenic, zinc, tungsten and iron were all extracted on a large scale with smaller scale operations extracting a variety of other metals, including silver and uranium. The industry left the environment contaminated from centuries of sustained mining-related discharges. Particulate waste products from mining activity and related processing and smelting were routinely discharged into the fluvial catchments which flow into estuaries around the Cornish coastline. Consequently, Cornish estuaries such as the Fal (Pirrie *et al.*, 1997, 1999a, 2003), Camel (Pirrie *et al.*, 2000), Gannel (Pirrie *et al.*, 2000), Fowey (Pirrie *et al.*, 2002a), Helford (Pirrie *et al.*, 2002b) and Hayle (Copperhouse) (Yim, 1976; Merefield, 1993; Healy, 1995; Pirrie *et al.*, 1999b) (Figure 1a) are highly contaminated and preserve a record not only of the extent and timing of historical mine waste contamination but also the type of mining activity in the respective fluvial catchments. For example, particulate contamination in the Fowey Estuary can be attributed to placer tin mining activity prior to 1880 (Pirrie *et al.*, 2002a) whilst contamination within the Fal Estuary is attributed to polymetallic hard rock mining during the late 1800s (e.g. Pirrie *et al.*, 1997, 2003). When the levels of mine waste contamination in Cornish estuaries are compared with other mining-related contaminated areas globally (Table 1), the extent of the impact in Cornwall can be appreciated. Today, the estuaries are important marine habitats but are also key sites to understand the long-term fate of mining related particulate contaminants in the environment. In this paper, a geochemical and mineralogical study of the impact of mining on sedimentation in the Hayle Estuary, UK is presented. This estuary records the impact of the release of tailings from both Cu and Sn mining operations, and allows an understanding of the longevity of the environmental impact of this historical mining activity.

Location	Sn (ppm)	Cu (ppm)	As (ppm)	Pb (ppm)	Zn (ppm)	Reference
Hayle Estuary UK	7041	29,869	6348	867	10,571	This paper
Fal Estuary UK	3400	5073	2803	902	6600	Pirrie *et al.* (2003)
Fowey Estuary, UK	1210	527	144	131	420	Pirrie *et al.* (2002a)
Gannel Estuary UK	200	411	975	16,000	3500	Pirrie *et al.* (2000)
Camel Estuary UK	842	241	283	53	207	Pirrie *et al.* (2000)
Rio Tinto, Spain	n.d.	4300	5500	2500	1300	Hudson-Edwards *et al.* (1999)
Aznalcollar, Spain	22	2120	6100	8500	21,200	LeBlanc *et al.* (2000)
Fenice Capanne, Italy	n.d.	7500	1090	10,100	13,600	Mascaro *et al.* (2001)
Daduck, South Korea	n.d.	1280	n.d.	3886	40,000	Kim *et al.* (2001)

Table 1. *Comparison of the levels of mine waste contamination in the Hayle Estuary compared with other estuaries in Cornwall and also other mine waste contaminated areas in the World. The Rio Tinto in Spain has been significantly contaminated as a result of mining activity (LeBlanc* et al.*, 2000). In 1998 a tailings dam at Aznalcollar failed resulting in the catastrophic release of pyritic mine waste tailings into the local environment (Hudson-Edwards* et al.*, 1999); these values are analyses of the tailings deposited in the adjacent river valley. Fenice Capanne is an area of tailings waste from polymetallic mining operations in Tuscany, whilst Daduck is an area of mine waste tailings in South Korea (Mascaro* et al.*, 2001; Kim* et al.*, 2001). n.d. – not determined.*
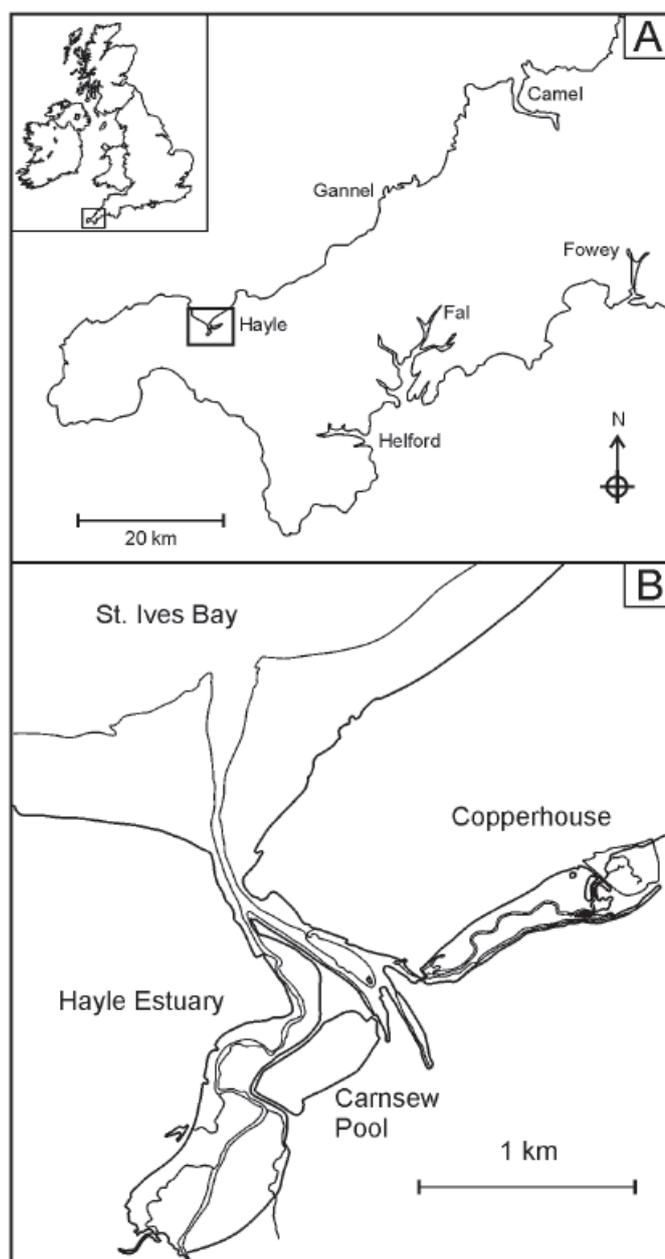

Figure 1. (**a**) *Map showing the location of the major estuary systems of Cornwall, UK, all of which have received significant sediment supply as a result of mining activity.* (**b**) *Simplified map of the Hayle Estuary, which is composed of two branches, Copperhouse and Hayle. This study examines the Hayle branch of the estuary.*

STUDY AREA

The Hayle Estuary on the north Cornwall coast UK, comprises two discrete branches, Copperhouse to the north-east and Hayle to the south-west (Figure 1b), that meet before flowing into St. Ives Bay (Figure 2). This study examines the Hayle branch of the estuary which comprises four major discrete fluvial catchments (Hayle, Trencrom, Canonstown and Lelant) along with other minor catchments which together drain an area in excess of 70 km². The Copperhouse branch to the estuary comprises two fluvial catchments (Angarrack and Mellanear) which drain an area of 22 km². The natural geomorphology of the estuary has been extensively modified with, for example, the construction of Carnsew Pool in 1834 as a deep water pool with sluice gates (Figure 2); opening the sluice gates at low tide effectively eroded sediment and maintained the important deep water navigable channel (Firth and Smith,1999). Management of the tidal channel was important as historically Hayle was a port for the export of copper ore, and for the import of coal. Today much of the estuary is managed as a nature reserve, particularly for migrating wading birds.

REGIONAL GEOLOGY

The regional geology of the Hayle Estuary catchment area is dominated by Devonian metasedimentary rocks assigned to the Mylor Slate and Porthtowan formations into which are intruded the Lands End, Tregonning-Godolphin and Carnmenellis granites (Figure 3). The Frasnian Porthtowan Formation comprises mudstones, muddy siltstones and sandstones (Leveridge *et al.*, 1990), whilst the younger, Famennian, Mylor Slate Formation is dominated by dark grey to black slates with thin silt laminae and subordinate sandstones (Goode and Taylor, 1988; Isaac *et al.*, 1998). Some 10-20% of the Mylor Slate Formation comprises originally basaltic rocks altered to metabasites during regional lower greenschist facies metamorphism during the Variscan Orogeny (Isaac *et al.*, 1998). The Lands End Granite is the youngest pluton within the Cornubian Batholith (Chen *et al.*, 1993; Clark *et al.*, 1993) and is a composite body predominantly composed of biotite granite (Goode and Taylor, 1988). The Tregonning-Godolphin Granite is also a composite body comprising biotite granite, postdated by lithium mica granite (Goode and Taylor, 1988). The Carnmenellis Granite is dominantly a coarse grained, porphyritic, muscovite-biotite granite (Leveridge *et al.*, 1990).

Extensive mineralisation within the catchment area to the Hayle Estuary is characterised by main stage WSW-ENE trending high temperature hydrothermal veins or lodes, cross cut by younger, lower temperature, NW-SE trending veins, locally termed cross courses. The dominant main stage ore minerals include cassiterite and arsenopyrite and chalcopyrite whilst the cross course mineralisation comprises chalcopyrite, sphalerite and galena (Goode and Taylor, 1988; Scrivener and Shepherd, 1998).

Figure 2. *Oblique air photographs of the Hayle Estuary area. (**a**) View southwest towards the Hayle branch of the estuary. The mine waste contaminated sediments form the intertidal areas at the head of the estuary. (**b**) View north showing Carnsew Pool, constructed in 1834 as a means of maintaining the narrow active channel which flows out into St. Ives Bay.*

Figure 3. *Schematic geological map of the Hayle Estuary area. Solid line depicts the catchment area to the estuary. TGG – Tregonning Godolphin Granite. Minor exposures of Tertiary and Quaternary sediments are omitted for clarity.*

The Mylor Slate Formation is locally unconformably overlain by limited exposures of late Pliocene sediments assigned to the St Erth 'Beds' (Goode and Taylor, 1988). These comprise fluvial conglomerates in turn overlain by marine sands which have yielded a diverse molluscan and microfossil assemblage (Mitchell *et al.*, 1973). Quaternary sediments, typically comprising raised beach deposits overlain by Devensian periglacial slope deposits also crop out in the area, but are best exposed in the coastal sections (Scourse, 1999; Campbell *et al.*, 1999). Associated with Quaternary fluvial sediments are extensive cassiterite placer deposits, which based on geophysical studies, can be mapped extending offshore (Camm, 1999).

MINING HISTORY

The metal mining industry of Cornwall extends from the early Bronze age through until the closure of the last tin mine in 1998 (Penhallurick, 1986; Gerrard, 2000). Early mining involved the working of cassiterite placer deposits, a process referred to as tin streaming (Gerrard, 2000). Tin streaming in the catchment area to the Hayle Estuary is documented from the Medieval period onwards, and was also carried out strategically in the early 1940s (Buckley, 1999; Camm, 1999). Earlier, Prehistoric, tin streaming activity in the area is also
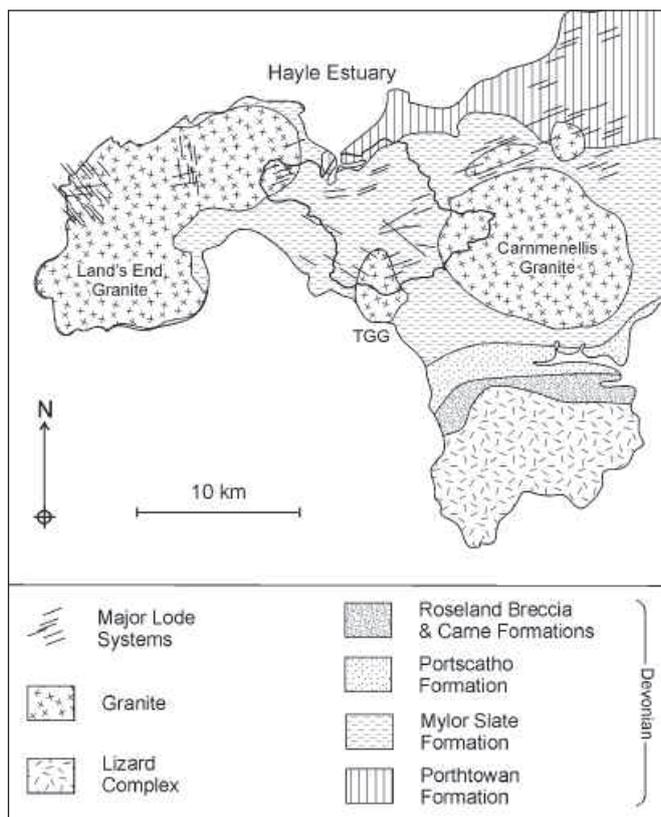
possible (Buckley, 1999). Hard rock mining commenced in about the 13th century, initially for tin and then copper. Copper production peaked in the 1860s and then rapidly declined; tin production peaked in the 1890s and then also declined. Over 60 hard rock mines are documented from the catchment area of the estuary (Table 2; Figure 4), most of which were operational in the late 1700s and 1800s.

In addition to the metal mines, there were numerous mineral processing plants and smelters (Firth and Smith, 1999)
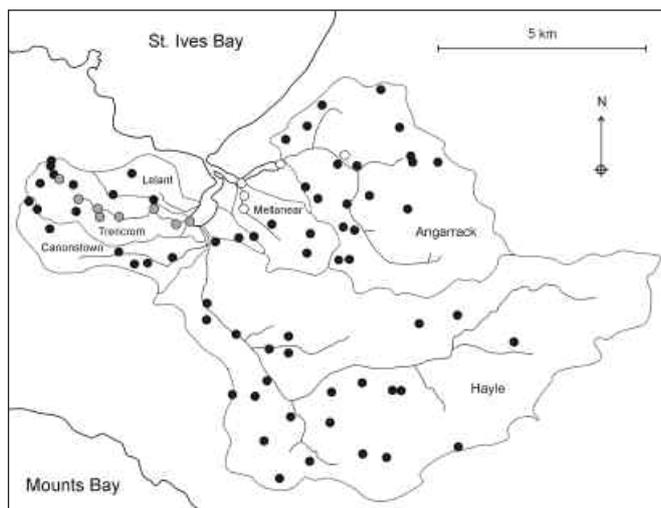

Figure 4. *Diagram showing the catchment areas for each of the rivers discharging into the Hayle Estuary along with the location of the recorded major hard rock mining operations in the area (black circles), smelting plants (open circles) and tin processing plants (grey circles).*

Mine name	Date	Recorded production
Alfred Consols/Great Wheal Alfred	1801-1832 1846-1864	135,000 tons Cu ore, 245 tons Zn ore
Manor Mine	1756-1864	32,980 tons Cu ore, 172 tons Sn ore, 110 tons Zn ore
Relistian Mine	1751-1846	12,151 tons Cu ore
Wheal Ann	1805-1865	16,462 tons Cu ore, 3.5 tons Pb ore, 30 tons Zn ore, 28 oz Ag
Mellanear	1815-1890	66,410 tons Cu ore, 80 tons Sn ore, 1400 tons Zn ore
Wheal Sisters	1825-1900	24,930 tons Sn ore, 17,536 tons Cu ore
Penberthy Crofts	1789-1907	19,411 tons Cu ore, 73 tons Sn ore
Halamanning/Retallack	1781-1858	30,420 tons Cu ore
Great Work	1540-1902	6250 tons Sn ore, 1020 tons Cu ore
Binner Downs	1758-1838	51,100 tons Cu ore, 100 tons Fe ore
Crenver/Abraham	1815-1876	134,184 tons Cu ore, 975 tons Sn ore, 4.9 tons Pb/Ag ore

Table 2. *Summary of the main hard rock mining operations in the catchment area of the Hayle Estuary. Data are summarised from Gregory (1947); Dines (1956); Hamilton-Jenkin (1961, 1963, 1965); Noall (1982, 1984, 1993); Burt et al., (1987); Firth and Smith (1999).*

(Figure 4). The mineral processing operations resulted in the discharge into the fluvial catchments of large volumes of fine grained tailings, and the inefficiency of the processing ensured that the tailings were still enriched in Sn, Cu, As and Zn. Hayle was an important site for Cu and Sn smelting from the 18th century onwards, and an important iron foundry was also established in 1779. Copper smelters were established in 1721 and 1758. Blocks of black slag from the smelter at Ventonleague were used in the construction of local houses and bridges. Large scale tin smelting commenced in 1816 and continued through until 1908, although smaller scale local tin smelting operations, known as blowing houses, were probably present in this area significantly predating the documented industrial activity.

PREVIOUS STUDIES

There are a limited number of previous studies on the estuary. Hosking and Obial (1966) collected 38 superficial sediment samples (26 from the active channel and 12 from the intertidal mudflats) and analysed them for Sn, Cu, W and As. The highest Sn and Cu values for sediments from the main active channel were both 1000 ppm, with 1000 ppm Sn and 2000 ppm Cu in the intertidal mud banks. Yim (1976) recovered two cores from the Hayle River channel in the estuary using a bucket auger and found up to 10,000 ppm Sn, 2760 ppm Cu, 1920 ppm As, 3450 ppm Zn and 600 ppm Pb in association with red-brown laminated silts and clays. Within the catchment area for the Copperhouse branch of the estuary, stream sediment samples have up to 3000 ppm Sn, 483 ppm Pb, 1004 ppm Zn, 1057 ppm As and 1650 ppm Cu (Merefield, 1993). Brown (1977) examined the water and sediment chemistry and the invertebrate biology along the River Hayle and suggested that there was abundant copper and zinc both within the particulate sediment and also in solution as a result of mine drainage discharge.

Cores recovered from Copperhouse by Pirrie *et al.* (1999b) comprise finely laminated red brown clays and silty clays overlying carbonate sands. The clays and silty clays contain abundant grains of cassiterite, chalcopyrite, Fe oxides, arsenopyrite, sphalerite, polymetallic slags, pyrite, ilmenite, monazite, zircon, wolframite, galena, chalcocite/bornite and pyromorphite (Pirrie *et al.*, 1999b). In addition, a range of diagenetic As sulphide and Cu sulphide phases, including chalcopyrite were recognised (Pirrie *et al.*, 1999b). These sediments are interpreted to be mine waste tailings that have been partially chemically remobilised as a result of oxygenated pore water flowing through the underlying carbonate sands (Pirrie *et al.*, 1999b).

ANALYTICAL METHODS

Nine undisturbed sediment cores varying from 13 cm to 99 cm long were recovered from the estuary (Figure 5) all of which were taken from the intertidal sediments. A handheld GPS with an accuracy of ±5 m was used to record sampling locations. The recovered cores were photographed, logged, and subsampled for geochemical and mineralogical analysis. Each core was subdivided into 5 cm stratigraphic intervals; 50 g subsamples were ground to a fine powder in a chrome steel tema mill and prepared as pressed powder pellets using elvacite binder and a boric acid jacket. 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 ppm with an analytical error of ± 10 ppm, and are summarised in Table 3. One core (Core 5) was analysed by XRF for a wider range of elements including Zr, Ce and Th (Table 4). In addition, 43 surface (uppermost 5 cm) sediment samples were collected throughout the area (Figure 5) and were also analysed by XRF for Sn, Cu, Zn, Pb and As (Table 5).
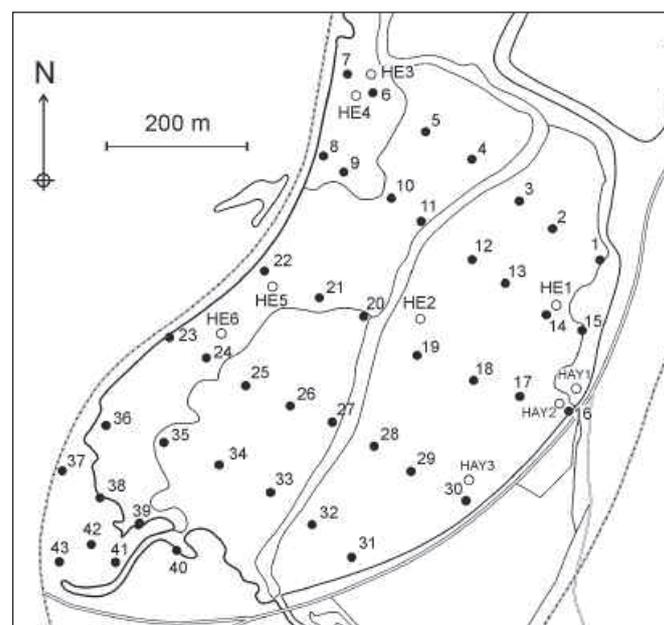

Figure 5. *Diagram showing the core sample locations within the Hayle Estuary (open circles) and also the location of the surface sample points (black circles).*

	No.	Cu Min.	Cu Max.	Sn Min.	Sn Max.	As Min.	As Max.	Pb Min.	Pb Max.	Zn Min.	Zn Max.
Core HE1	11	106	10598	<10	4108	21	3790	<10	867	122	2928
Core HE2	15	527	1714	1881	4085	311	816	125	261	445	984
Core HE3	18	204	1673	61	4626	56	578	19	218	113	1047
Core HE4	19	284	1317	1095	4437	167	479	63	200	329	865
Core HE5	19	634	3157	2233	7041	262	1447	137	373	512	2430
Core HE6	19	469	2727	1280	6019	181	851	129	362	433	2835
Core HAY1	7	457	12554	364	5861	113	4018	37	930	931	4398
Core HAY2	10	1269	29869	2258	6299	674	6348	173	1457	1594	10571
Core HAY3	3	1052	1802	2473	4355	548	897	175	304	622	981

Table 3. *Summary of the down core geochemical data for the Hayle Estuary. All values are in ppm.*

Sample depth (cm)	Cu	Sn	As	Pb	Zn	W	Sr	Y	Zr	Ce	Th
0 - 3	779	3882	y	178	549	69	205	40	117	128	28
3 - 8	1329	4954	577	307	744	85	119	45	109	130	46
8 - 13	1580	5503	712	373	804	84	115	45	100	173	66
13 - 18	1623	5612	720	304	817	80	119	43	89	170	83
18 - 23	1832	5907	994	312	1010	86	106	51	109	156	54
23 - 28	2338	7041	1447	321	1164	100	100	55	125	179	59
28 - 33	2187	6859	1063	310	1480	87	109	58	112	228	46
33 - 38	2668	6866	870	355	2000	75	257	46	81	176	63
38 - 43	3157	6010	788	347	1995	75	231	38	67	128	77
43 - 46.5	3001	6165	978	325	1918	71	299	40	65	114	70
45.5 - 50.5	3107	5717	803	295	2430	66	373	42	68	143	59
50.5 - 55.5	1842	4207	625	208	1437	61	635	33	25	100	35
55.5 - 60.5	1397	4027	496	171	1382	62	644	33	25	127	25
60.5 - 65	1569	6184	564	221	1899	79	476	39	52	152	29
65 - 70	880	2765	323	160	947	44	475	26	16	67	<10
70 - 75	689	3025	262	138	695	46	438	34	24	109	<10
75 - 80	634	2988	291	147	759	47	422	29	17	80	<10
80 - 85	770	2233	274	137	690	41	340	26	17	60	<10
85 - 91	705	3273	340	159	512	51	339	25	20	60	<10

Table 4. *Down core geochemical data for Core HE5 from the Hayle Estuary. All values are in ppm.*

The samples with the highest concentrations of Cu and Zn as determined by XRF were then analysed by atomic absorption spectrophotometry (AAS) for Cd. In total, 166 samples have been analysed by XRF in this study. Although many sediment geochemistry studies utilise ICP-MS or ICP-AES as the preferred analytical method, the standard digestions used do not effectively digest cassiterite. As cassiterite is a major tracer mineral for mining activity throughout SW England, the accurate determination of Sn is essential, hence XRF is the preferred analytical method. 35 undisturbed sediment core plugs were taken from the remaining half of the cores and prepared as polished blocks following gentle resin impregnation under vacuum. The heavy mineral content of the blocks was analysed using reflected light microscopy and using a JEOL 840 scanning electron microscope fitted with a Link System (Oxford Instruments) AN10000 energy dispersive spectrometer. Bulk mineralogical analysis at 5 cm stratigraphic intervals was also carried out on 19 samples from Core 5 using a Seimens D5000 X-ray diffractometer (XRD) using CuKα radiation.

Three cores (HE1, HE3 and HAY1) were dated using the ^{210}Pb and ^{137}Cs methods. ^{210}Pb (half-life = 22.3 years) is a naturally produced radionuclide that has been extensively used in the dating of recent sediments. Dating is based on determination of the vertical distribution of ^{210}Pb derived from atmospheric fallout (termed unsupported ^{210}Pb or ^{210}Pb$_{excess}$) and the known decay rate of ^{210}Pb (see Appleby and Oldfield, 1992 for further details of the ^{210}Pb method). ^{137}Cs (half-life = 30 years) is an artificially produced radionuclide, introduced to the study area by atmospheric fallout from nuclear weapons testing and nuclear reactor accidents, and via licensed discharges from nuclear facilities. Global dispersion of ^{137}Cs began in AD 1954, with marked maxima in the deposition of ^{137}Cs occurring in the northern hemisphere in AD 1958, AD 1963 (from nuclear weapons testing) and AD 1986 (from the Chernobyl accident). Discharges from BNFL Sellafield in north-west England have also released ^{137}Cs into UK coastal waters, mainly in the 1970s. Under favourable conditions, periods of peak fallout/discharge provide subsurface activity maxima in accumulating sediments which can be used to derive rates of sediment accumulation (e.g. Ritchie and McHenry, 1990; Cundy and Croudace, 1996). Subsamples from the upper 20-30 cm of each core were counted for 8-24 hours on a Canberra well-type ultra-low background HPGe gamma ray spectrometer to determine the activities of ^{137}Cs, ^{210}Pb and other gamma emitters. Detection limits were ca. 3 Bq/kg.

CORE SEDIMENTOLOGY AND DATING CONTROL

All of the cores recovered from the Hayle Estuary are comparable, with red-brown bioturbated silts and clays at the present day sediment surface overlying finely planar laminated red clays and silts (Figure 6). Thin sand laminae also occur within the laminated clays and silts in some of the cores. The laminated clay-silts are typically up to 40 cm thick and lack bioturbation. The clay-silts overlie medium grained light grey carbonate sands. In some of the cores the sands immediately below the laminated clays are charcoal grey in colour. Thin clay laminae are interbedded with the carbonate sands in some of

Sample	Cu	Sn	As	Pb	Zn
1	2231	3265	985	271	895
2	3192	4692	768	354	1090
3	414	1421	185	85	508
4	195	1070	108	53	296
5	88	910	57	30	172
6	888	2751	365	139	517
7	594	2991	382	162	463
8	330	1557	158	90	326
9	458	2748	229	123	407
10	186	1832	146	67	281
11	197	632	98	46	319
12	548	2453	276	121	507
13	1333	2575	527	200	754
14	4139	3480	1484	439	1301
15	2116	2308	820	261	1145
16	4520	3061	2292	522	1777
17	710	2300	410	153	523
18	1786	4303	835	255	987
19	994	3480	491	185	620
20	393	1339	212	91	464
21	308	1705	183	90	387
22	1229	3685	535	207	729
23	1158	2646	666	204	586
24	985	3093	489	171	587
25	710	2907	338	161	493
26	383	2199	239	124	480
27	609	2013	290	133	676
28	1966	5455	1015	309	958
29	2009	5336	1162	344	1194
30	1168	2561	546	173	742
31	1025	2481	611	202	685
32	1398	3815	680	238	960
33	1229	2980	666	247	791
34	412	2422	128	64	220
35	995	2452	532	173	434
36	1759	5222	664	260	562
37	628	1479	190	122	320
38	496	2768	676	203	389
39	941	2750	649	212	516
40	566	2238	375	192	430
41	711	3237	384	177	496
42	563	2302	368	154	379
43	455	1499	92	114	246

Table 5. *Summary of the surface sediment geochemistry in the Hayle Estuary. Values for Cu, Sn, As, Pb and Zn are in ppm. Sample locations are shown on Figure 5.*

DOWN CORE GEOCHEMISTRY

The down core variation in the concentrations of Cu, Sn, Pb, Zn and As in representative sediment cores is shown in Figure 7 and summarised in Table 3. Four cores (cores HE3, HE4, HE5 and HE6) were collected from the western side of the estuary and are broadly comparable, with very high levels of Sn contamination, typically >3000 ppm and up to >7000 ppm. In most of the cores Sn values are relatively low at the base of the core, increase rapidly, then decrease, then increase again and either remain at a relatively uniform high level of contamination up to the present day sediment surface or show a decrease in contamination towards the sediment surface. This profile is mirrored by the down core variation in Cu and Zn, although the absolute levels of Cu and Zn do not exceed 3000 ppm, and are commonly less than 1000 ppm. Arsenic concentrations partially follow this profile, although commonly show peak levels of As contamination stratigraphically above the main pulse in Sn, Cu and Zn. Pb contaminant levels are relatively low and generally relatively invariant throughout the sediment profile. Core HE2 from the centre of the estuary shows a comparable geochemical profile to the cores from the western side of the estuary (Figure 7). Core HE5 was also analysed by XRF for Sr, Y, Zr, Ce and Th (Figure 8; Table 4). Sr values are >300 ppm at the base of the core, increase to >600 ppm and then decrease rapidly to >100 ppm. The high Sr values correlate with the carbonate sands at the base of the core, whilst the low Sr values correspond with the red laminated silts and clays. Th and Ce are co-variant,
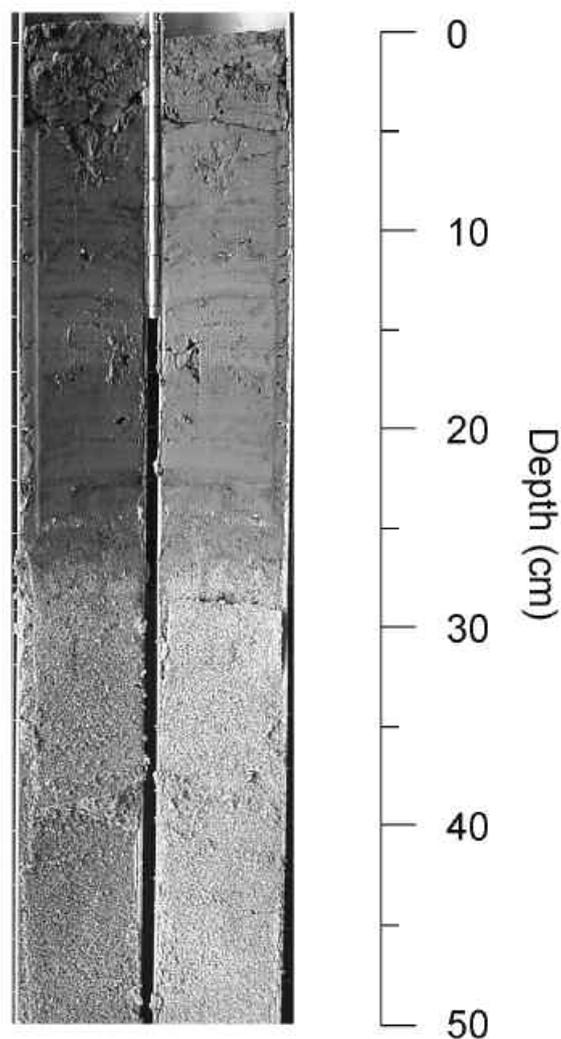
the cores. Diffuse bioturbation is present in the sand-dominated intervals. Towards the base of Core HE3 there is a thin pebble bed composed of granitic rock fragments and feldspar grains.

In the three dated cores, ^{210}Pb showed relatively uniform activities of 0.05 to 0.09 Bq/g in all samples. While some slight variations in ^{210}Pb activity occur (which are most likely the result of minor compositional variability in each core), there is no clear decline in ^{210}Pb activity with depth in any of the cores examined. [137]Cs was not detected in any of the samples analysed. The absence of ^{137}Cs and the presence of near constant ^{210}Pb activity with depth is typical of sites where prolonged erosion or repeated dredging has completely removed recent sediments (i.e. sediments labelled with ^{137}Cs and [210]Pb$_{excess}$), exposing older deposits (e.g. Cundy *et al.*, 2003). Based on the absence of ^{137}Cs, the surface sediments in each core analysed here are older than 1954 (the date of first widespread dispersion of ^{137}Cs from above ground nuclear testing (Ritchie and McHenry, 1990)), and are probably pre-1880 (i.e. greater than 120 years old, which is the time taken from [210]Pb$_{excess}$ to decay to insignificant activity levels). As there is no dredging activity in this part of the estuary, it is assumed that these sediments have been exposed as a result of prolonged natural erosion.

Figure 6. *Photograph of Core HE1 from the Hayle Estuary. Note that the finely laminated unbioturbated clays-silts in the upper part of the core sharply overlie carbonate sands below.*
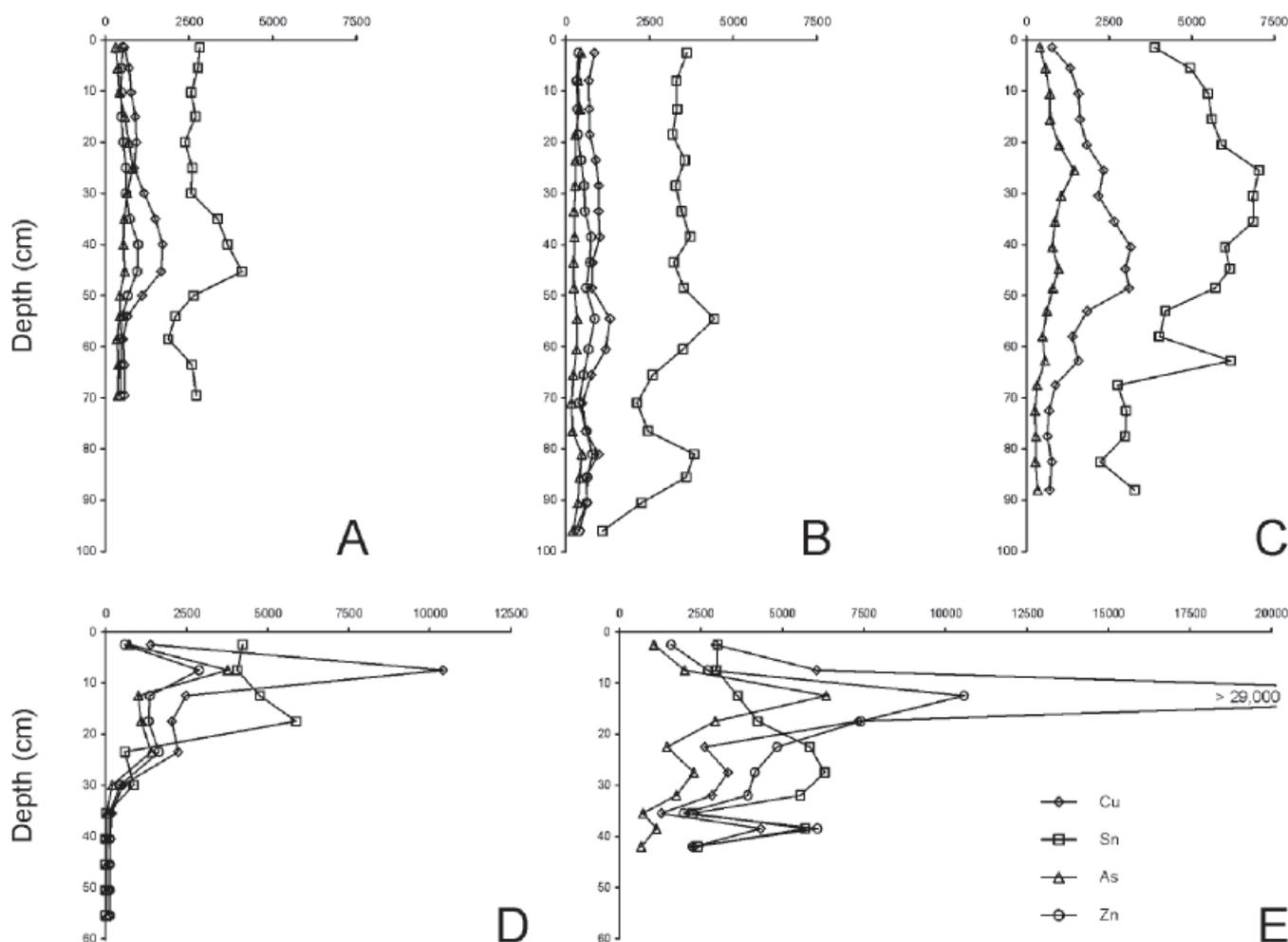
Figure 7. *Down core geochemical variation in sediment geochemistry (ppm) throughout the Hayle Estuary. Cores (A) HE2, (B) HE4 and (C) HE5 are from the western and central part of the estuary and show a major pulse in Sn contamination which co-varies with Cu and Zn. Cores (D) HE1 and (E) HAY2 are from the eastern side of the estuary and show a major peak in Cu, Zn and As contamination within the upper 15 cm of the sediment profile.*

increasing significantly at the base of the laminated clays and silts and then decrease slightly towards the present day sediment surface (Figure 8). Zr and Y show a gradual increase in concentration towards the present day sediment surface.

Cores HE1, HAY1 and HAY2 recovered from the eastern side of the estuary show a different down core geochemical profile (Figure 7). The lower part of the sediment profile is comparable with profiles from the western side of the estuary with a clear peak of 4000-5000 ppm Sn. However, in each of these cores, this is followed by an abrupt and extreme increase in Cu between 5 and 15 cm below the present day sediment surface, with Cu values in core HE1 of >10,000 ppm, >12,000 ppm in core HAY1 and an extreme concentration in excess of 29,000 ppm Cu in core HAY2. Maximum concentrations of Cd in Core HAY2 are 26 ppm.

When the down core geochemical variation in contamination is compared with the core sedimentology, there is a clear correlation between the lower levels of contamination and the carbonate sands at the base of the core. The highest levels of contamination in the cores recovered from the western side of the estuary correlate with the base of the laminated red muds, with decreasing levels of metal contamination in the uppermost part of the sediment profile. However, the very high levels of contamination in the cores from the eastern side of the estuary occur between 5 and 15 cm below the present day sediment surface.

SURFACE GEOCHEMISTRY

To examine in more detail the apparent spatial variation in contamination with localised extreme Cu contamination on the eastern side of the estuary, 43 samples of the uppermost 5 cm of the sediment profile were collected across the estuary with a sample spacing of approximately 50-100 m (Figure 5, Table 5). The results are summarised in Table 5 and are shown graphically as contoured geochemical maps showing the spatial distribution of Cu, As, Zn and Sn in Figure 9. The geochemical maps for Cu, As and Zn clearly show a discrete area of highly contaminated sediment on the eastern side of the estuary extending approximately 200 m to the north and 100 m to the west. The distribution of Sn within the surficial sediments is rather different with an area with up to 4000 ppm Sn in the intertidal areas to the east of the main active channel and also an area with >3000 ppm Sn in the south-west corner of the estuary (Figure 9).

SEDIMENT MINERALOGY

SEM and reflected light microscopy examination of 35 resin impregnated polished blocks showed that the dominant detrital heavy minerals present are chalcopyrite, sphalerite, cassiterite, arsenopyrite and pyrite along with more minor galena, monazite, zircon, stannite, wolframite, plumbogummite,
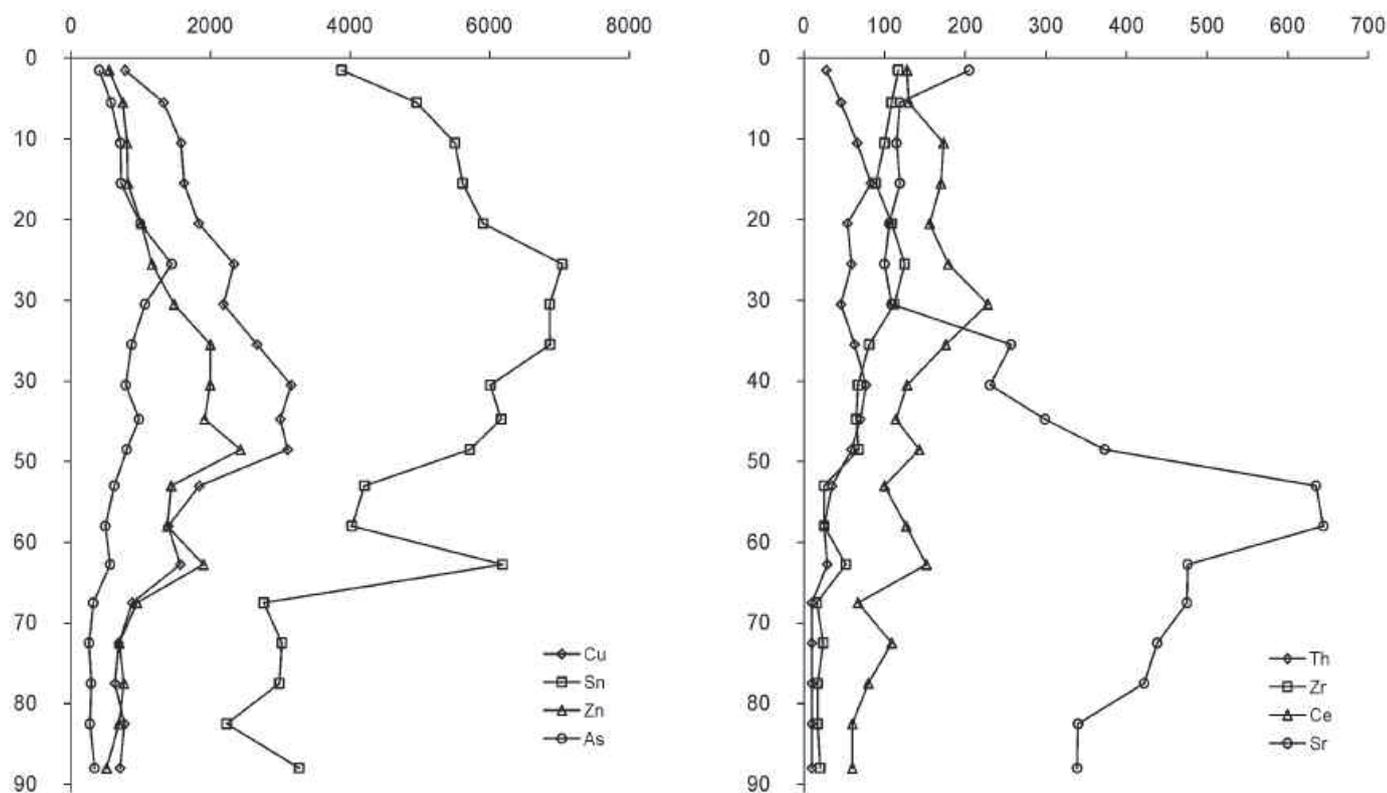
Figure 8. *Variation in Cu, Sn, Zn and As for Core HE5 compared with the down core variation in Th, Zr, Ce and Sr; all values are in ppm. The increased concentration of Sr corresponds with the carbonate sands at the base of the core whilst the increased concentrations of Sn, Cu and Zn correlate with laminated silts and clays.*

covellite, bornite and ilmenite (Figure 10). The heavy minerals occur as both discrete liberated grains and also grains locked within larger silicate hosts (Figure 10a). Grain size ranges from 500 µm to <10 µm (Figure 10b). In addition to the naturally occurring ore minerals, man made slag and smelt products are also present in all of the samples examined including tin metal and Si-Fe-Al slags. Diagenetic framboidal pyrite is also a common component, typically nucleated within shelter porosity in bioclasts. In addition to pyrite framboids, there are also framboids composed of chalcopyrite, which show no textural evidence for alteration. Detrital chalcopyrite grains commonly show Cu-poor, Fe-rich alteration rims (Figure 10c) interpreted to be due to oxidation. Fe-rich rims also occur around detrital grains of bornite and arsenopyrite (Figure 10d, e). Locally atacamite ($Cu_2Cl(OH)_3$) occurs as a diagenetic phase (Figure 10f). The bulk mineralogy of core HE5 was examined by XRD and showed that quartz, chlorite and mica occurred throughout the sediment profile; calcite was present in the uppermost 5 cm but absent within the laminated clay-silts, occurring again at the base of the core. Feldspar is present sporadically throughout the core.

INTERPRETATION

The down core sedimentology, geochemistry and mineralogy are all consistent with the interpretation that the laminated clays-silts are mine waste tailings, discharged into the estuary during historical mining and mineral processing activity. All of the cores on the western side of the estuary show co-variance in Sn, Cu and Zn, although the Sn values are considerably higher throughout (Figure 7). This co-variance in the metals is consistent with sediment supply from polymetallic hard rock mining activity. Three river catchments drain directly into this part of the estuary; the Trencrom catchment with an area of 5.2 km², which had a number of mines but also extensive tin

processing plants, the Canonstown catchment (4.9 km²) which also had several mines and the much larger River Hayle catchment (58 km²) which drained an area with a number of very large copper mines; the Hayle River was also extensively worked for placer tin. Merefield (1993) analysed stream sediment samples in both the Trencrom and Hayle rivers. Sn values were up to 3859 ppm in the Trencrom River, but Cu values were low (maximum 166 ppm). In contrast, in the Hayle River Sn values were up to 11,527 ppm and co-varied with Cu and As, with up to 2993 ppm Cu and 2065 ppm As. Based upon the stream sediment chemistry and the historical record of mining activity, it is interpreted that the main source of the contaminants seen in the estuary was from the release of particulate waste from mining and mineral processing operations in the River Hayle catchment; hard rock mining operations in this area peaked in 1860 and had largely ceased by 1900. The Trencrom and Canonstown catchments were probably more minor sources of contaminants. Although there may have been some contamination as a result of mine drainage, the majority of the contaminants are interpreted to be particulate grains of the ore minerals and associated gangue minerals themselves (cf. Pirrie *et al.*, 2003)

In contrast with the cores on the western side of the estuary, cores on the eastern side show an extreme pulse in Cu contamination between 5 and 15 cm below the present day sediment surface (see Figure 7). This area of increased Cu contamination appears to correlate with an area of increased Cu, As and Zn which can be mapped in the surface sediment samples extending into the estuary from a stream draining a small area of land on the eastern side of the estuary (Figure 9). This low lying area of land was part of the estuary until the 1920s and received sediment supply from the River Hayle and also a small stream, referred to on the UK 1877 Ordnance Survey topographic map of the area as 'Water Lane', which drained two large scale Cu mines, including West Wheal Alfred
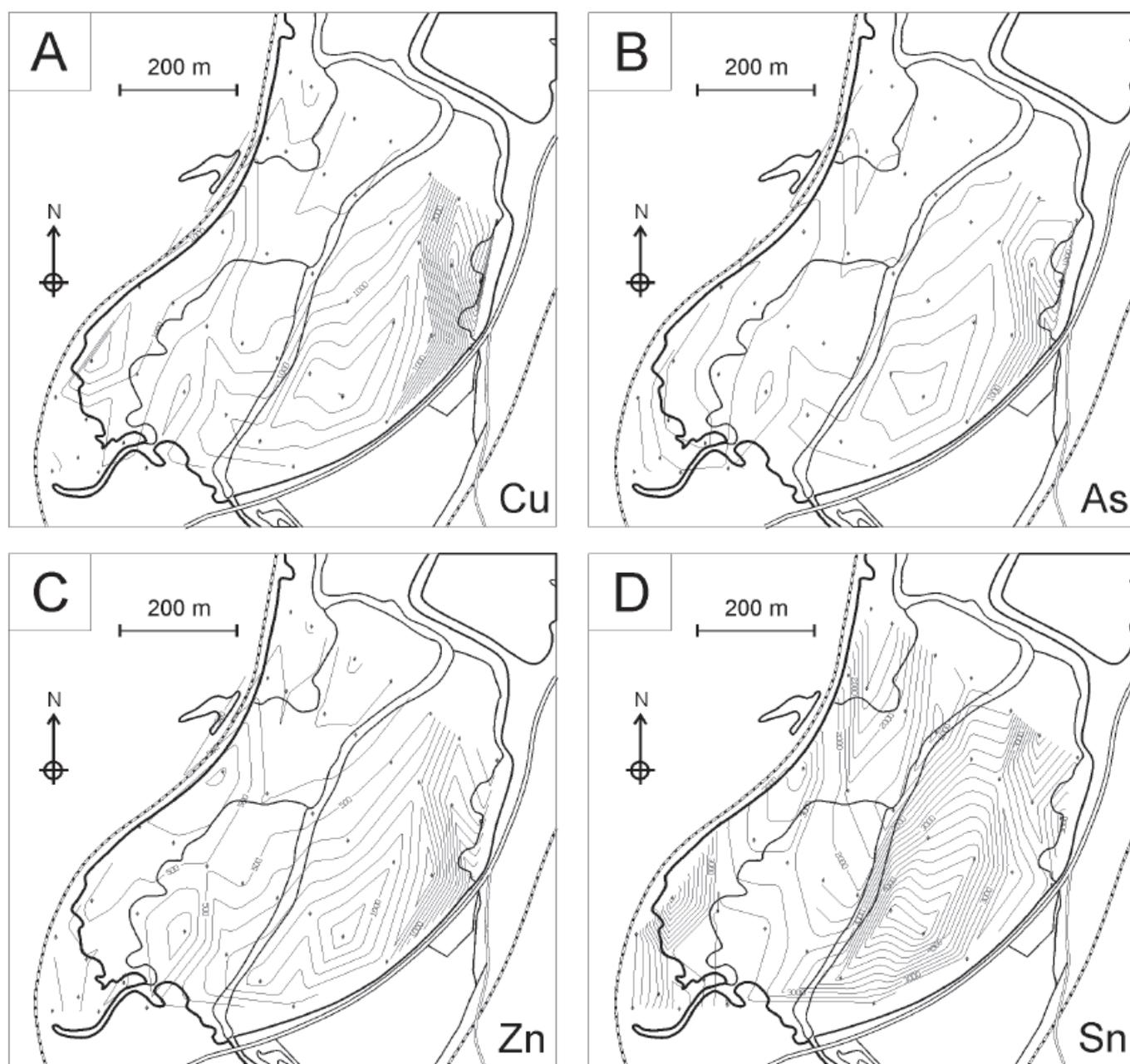
Figure 9. *Contoured geochemical maps for the surface (uppermost 5 cm) sediments in the Hayle Estuary for (**A**) Cu, (**B**) As, (**C**) Zn and (**D**) Sn; all values are in ppm. The geochemical maps for Cu, As and Zn all show a plume of contamination on the eastern side of the estuary, associated with the small stream entering the estuary on this side. The geochemical pattern for Sn shows an area to the east of the main active channel and in the SW corner of the estuary with elevated Sn concentrations.*

(1805-1865) and Wheal Music which was part of Mellanear Mine, operational between 1815 and 1890. It is highly likely that these mines discharged Cu tailings into this stream with resultant siltation along the edge of the estuary, effectively forming a natural tailings pond with some disharge out into the eastern side of the estuary.

The mineralogy of the laminated clay-silts is consistent with the interpretation that there has been significant sediment supply as a result of mining. In the cores recovered from the western side of the estuary there is a clear correlation between the sediment geochemistry and the mineralogy, with abundant grains of the common ore minerals chalcopyrite, cassiterite and sphalerite. In many cases the sulphide mineral grains show minimal evidence for alteration. However, particularly on the eastern side of the estuary, the chalcopyite commonly has clearly developed reaction rims around the grain margins with apparent loss of Cu relative to Fe. In addition, in this area diagenetic Cu minerals including chalcopyrite framboids and

atacamite cements are present. Thus locally the oxidised sulphide mine waste has altered and released metals in solution; in some cases leading to the precipitation of diagenetic Cu phases, but it is also likely that some of the metals remained in solution and may also have been adsorbed or absorbed on to the surface of other mineral grains. In addition to the mine waste tailings, man made slag and smelt products also occur throughout the area. These were probably derived from smelting activity in the Trencrom and Mellanear catchments (Fig. 4).

The sands which occur at the base of most of the cores and also locally interlaminated with the clay-silts are dominated by marine-derived skeletal carbonate grains. Merefield (1982) noted that samples from the Hayle branch of the estuary contained between 42 and 56% carbonate, with approximately equal proportions of aragonite and low Mg calcite, together with high Mg calcite, with Sr values of up to 2000 ppm. This is consistent with the elevated levels of Sr seen at the base of core HE5 (Figure 8).
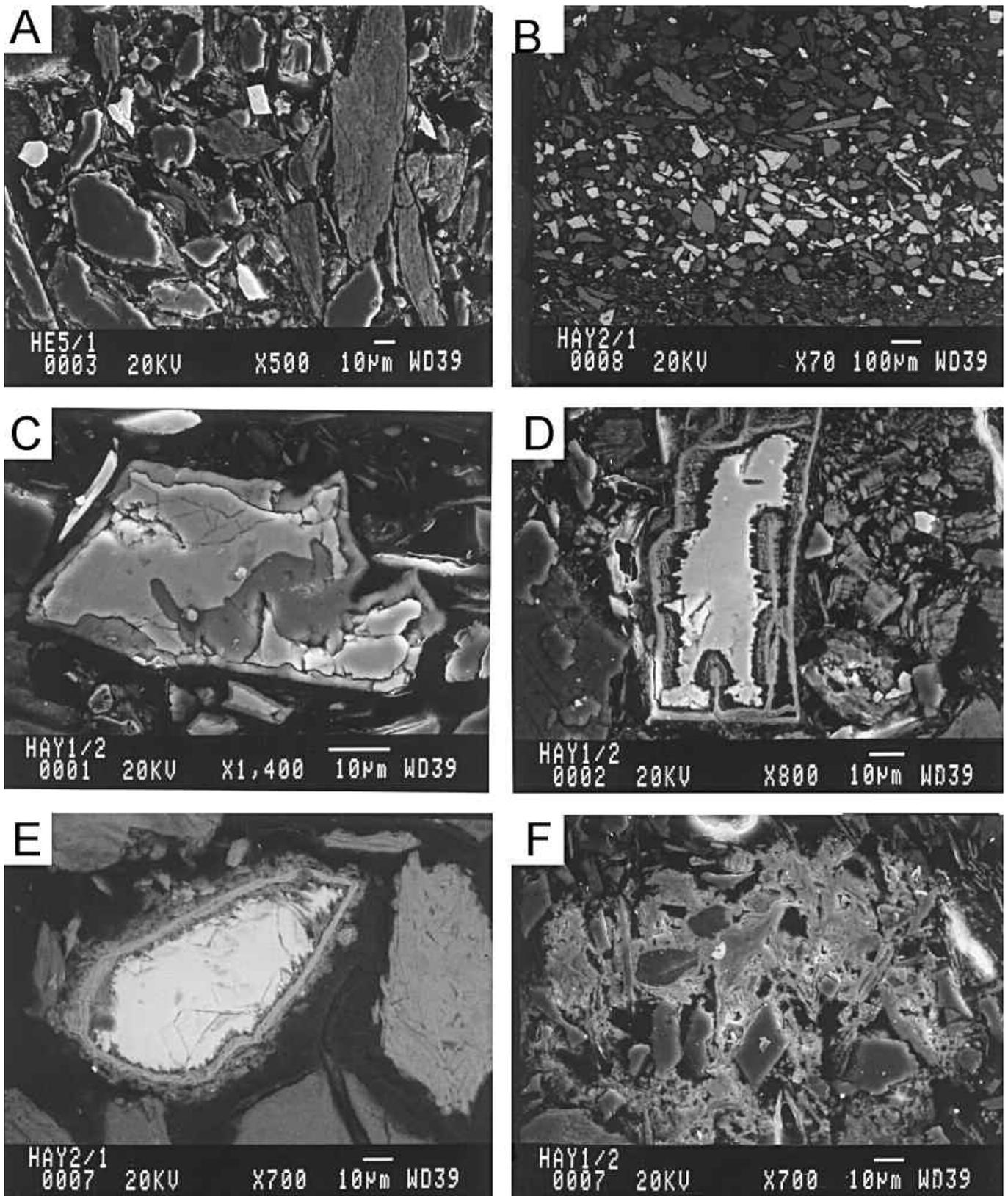
Figure 10. *Representative scanning electron microscope images. (**A**) Small grains of liberated cassiterite (bright phase) within the sediments from the western side of the estuary. (**B**) Backscatter electron image showing a laminae within the sediments on the eastern side of the estuary with very abundant sulphide grains dominated by chalcopyrite along with sphalerite, arsenopyrite and pyrite (bright phases). (**C**) Detrital grain of chalcopyrite with a clearly developed reaction rim with decreased Cu and increased Fe relative to the grain centre. (**D**) Detrital grain of bornite with a well-developed rim of Fe oxide surrounding the grain. (**E**) Backscatter electron image showing a grain of arsenopyrite surrounded by an Fe oxide reaction rim. (**F**) Diagenetic atacamite cements infilling available pore space within a sample from the eastern side of the estuary.*

DISCUSSION

The deliberate release of metallic mine waste into the environment in the Hayle Estuary, Cornwall, largely ceased over a 100 years ago and the geochemical and mineralogical profiles within the intertidal sediments clearly reflect this major period of contamination. However, there is a considerable environmental legacy to the mine waste, which can subsequently be remobilised physically, chemically or as a result of human activity. Physical reworking of the particulate waste may be the result of tidal flow, migration of the intertidal channels, or through the action of burrowing invertebrates or wading birds. Once sulphide grains are exposed to an oxidising environment they can be chemically remobilised and the contaminants potentially become bioavailable. Human activity may also lead to the accidental reworking of the contaminated sediments causing chemical and physical remobilisation of the contaminants such that they can become bioavailable. Mapping the distribution of historical mine waste contaminants can significantly reduce the risk of un-intensional remobilisation of mine waste and the subsequent environmental impact. In addition, the mineralogy of the original tailings waste is critical in the long term environmental impact. For example, the high Sn values on the western side of the estuary are largely related to the presence of cassiterite and as such do not pose an environmental threat. However, the tailings waste on the eastern side of the estuary is dominated by chalcopyrite, sphalerite and arsenopyrite with a much higher potential for diagenetic alteration and the release of metals in solution. This is reflected by the localised distribution of secondary diagenetic Cu minerals within the estuarine sediments.

ACKNOWLEDEMENTS

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