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Heavy Metal Accumulation in Estuarine Sediments in a Historical Mining of Cornwall

Sediments in the Hayle estuary in a historical mining area of Cornwall have been found to contain exceptionally high concentrations of tin, arsenic, copper, lead, tungsten and zinc. In this study, the distribution of these heavy metals is correlated with pollution from past mining activity through mine waste discharge into streams, and changes which took place at the time of the development of the Upton Towans.

The Hayle estuary is bottle-neck shaped and has an area of approximately 2 km^2 (Fig. 1). Near the mouth of the estuary on the inland side, the Hayle Harbour splits up the estuary into a north-eastern offshoot and a south-western offshoot. The construction of the Hayle Harbour which has included a canal in the north-eastern offshoot has led to an acceleration in silting rate of the estuary away from the harbour channels. On the seaward side, the estuary connects up with St. Ives Bay, splitting the Upton Towans, a stretch of blown sand deposit formed during two storms in 1750 and 1869 (Salmon, 1973) into two bodies.

The hinterland of the Hayle estuary consists essentially of shales and sandstones of Devonian age intruded by granite. Associated with the granite are numerous mineral lodes in which occur minerals rich in tin, arsenic, copper, lead, tungsten and zinc. Among these metals, tin and copper have been mined in the past. In the St. Hilary area, where wastes from ore dressing operations were discharged into the River Hayle, the mines date back at least to the eighteenth century (Dines, 1956). Losses in the treatment of Cornish tin ores during the early twentieth century must have exceeded 33% (Thomas, 1913), and in some cases it approached 60%. Since all the mines utilize stream water in ore concentration, waste material discharged into streams can find their way down into the estuary.

In this study, the main objective was to determine the vertical distribution of tin and its associated heavy metals in the estuarine sediment, and to evaluate their significance in reflecting past mining pollution. The disposition of the Hayle estuary makes it an effective sediment trap for the land detritus. Most of the resistate ore-minerals and also those originally mobilized ore elements which have been transported by the river as absorbed components of colloids are trapped (Hosking & Ong, 1963–4).

Methods

Vertical sections of estuarine sediments were sampled using a 15 cm diameter bucket auger during low tide at three selected locations (Fig. 1). Because of the design of the bucket auger, some sample mixing was unavoidable and special care was taken during the lowering and removal of the auger from the drill-hole to avoid scrapping material from another horizon. At each auger station, sediment was split according to variations in grain size and/or colour, and the splits were transferred into polythene bags *in situ.*

In the laboratory, entire sample splits were sieved with an 8-mesh sieve (BSS) to remove gravel. After drying at 60°C, samples were split with a Jones riffle down to about 100 g before grinding and homogenization using an agate Tema mill. Tin and lead were determined by optical emission spectroscopy (Nichol & Henderson-Hamilton, 1965). Copper, iron, manganese, zinc and calcium were determined by atomic absorption spectroscopy following digestion with a 4:1 nitric–perchloric acid mixture. The

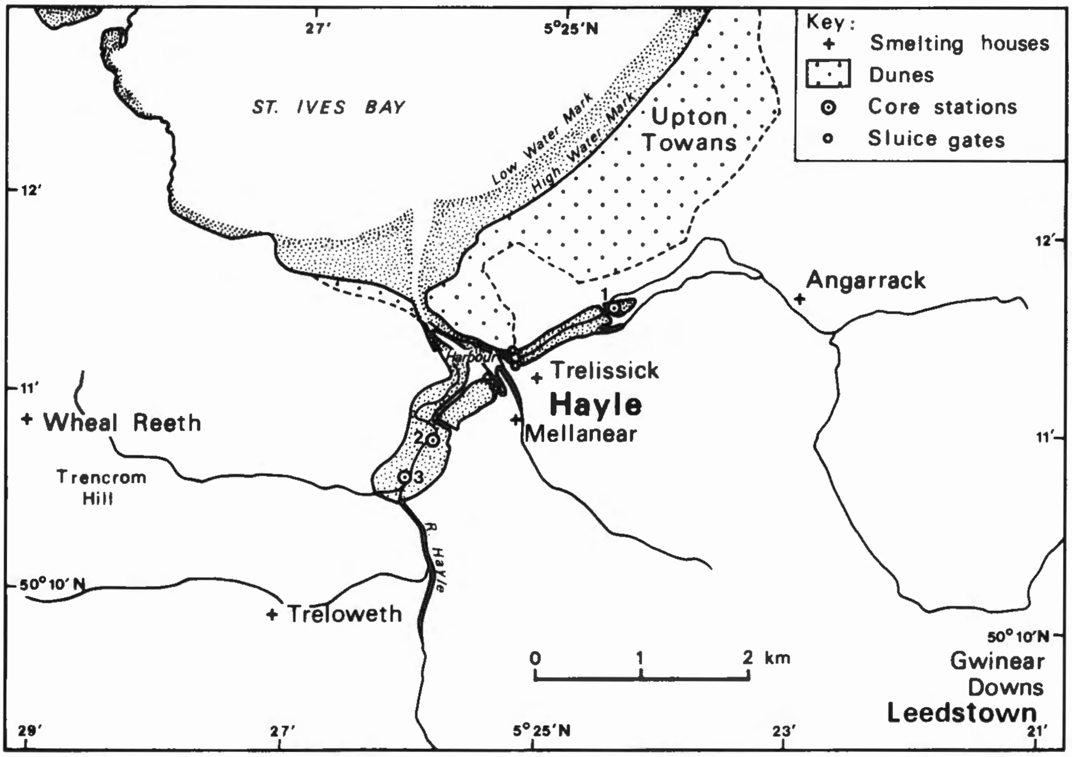

Fig. 1 The Hayle estuary and its hinterland including the location of core stations and principal tin smelting houses.

ppm calcium found was used to estimate the percentage of shells in the sediments, on the assumption that all the calcium present are shells. A colorimetric technique similar to that of Almond (1953) and Stanton (1966) was used for arsenic. Tungsten was also determined colorimetrically using the zinc dithiol method (Stanton, 1970).

Results and Discussion

Descriptions of sediment type in the cores are shown in Fig. 2 and the geochemical results are shown in Table 1. Although the geochemical results are for the minus-8-mesh fraction of samples, the majority of sediments in the cores falls within the fine sand to clay size range. Since vertical changes of sediment type are related to the environment of deposition, it is advantageous to examine the bulk sediment removed of gravel in order to cut down sampling error.

The main interest in these cores is in the shell-poor sediments, since they represent undiluted land derived detritus. However, because of the presence of blown sand deposits in the vicinity of the estuary, wind transported shells originating from the sand dunes fringing the coast are blown into the estuary during storms and dilute the land derived detrital sediments. Core 1 was taken from the

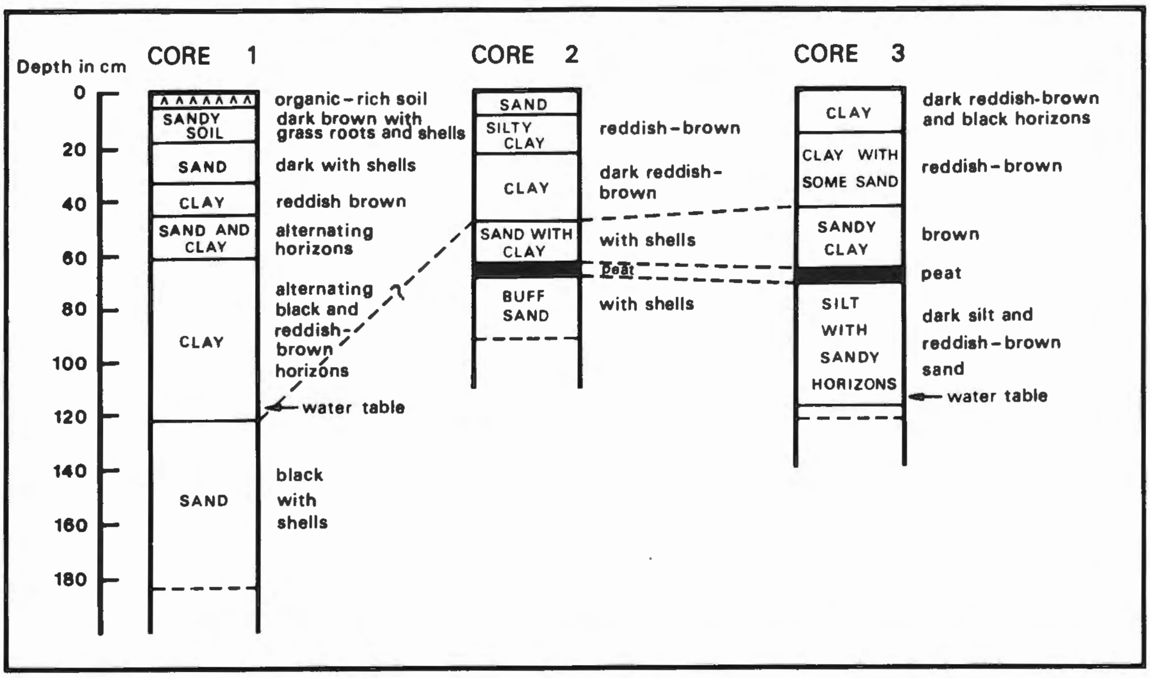

Fig. 2 Vertical distribution of sediment type in the Hayle estuary cores.

TABLE 1
Distribution of tin and other heavy metals in the minus-8-mesh fraction of Hayle estuary sediments (ppm).

Core No.	Depth (cm)	Shells (%)	Sn	As	Cu	Fe	Pb	Mn	W	Zn
1	5 - 8	11.0	1000	768	570	35 520	200	768	350	900
	20 - 30.5	17.3	850	720	430	22 320	300	1020	44	900
	35.5- 45.5	7.3	1000	1680	1260	55 680	400	864	32	2290
	45.5- 61	14.5	1000	960	810	34 080	400	504	220	930
	61 - 91.5	0.3	10 000	3600	2000	96 000	850	1368	320	1590
	106.5–122	0.3	10 000	4080	2600	93 600	850	1512	360	1880
	122 –152.5	24.8	1600	240	270	17 760	40	312	350	560
	Below 152.5	23.3	2000	360	290	21 120	60	336	650	730
2	0 - 20.5	1.0	5000	720	1700	54 720	400	792	56	690
	25.5- 45.5	0.4	10 000	1920	2060	77 760	500	1080	56	1220
	51 - 66	24.2	1300	240	890	21 360	70	336	9	640
	71 - 91.5	31.2	50	12	68	3840	20	48	4	80
3	0 - 15	0.8	1600	840	1240	55 200	400	696	56	740
	20.5- 40.5	0.2	1300	720	1090	45 600	400	624	56	470
	45.5- 61	0.2	1300	720	1750	48 960	400	720	44	710
	66 - 71	1.0	10 000	840	2760	53 760	600	648	52	3450
	71 - 91.5	0.2	10 000	240	540	26 880	85	336	24	440
	96.5–112	0.4	10 000	120	480	26 400	30	360	28	540
	Below 112	0.5	1600	300	480	28 080	50	336	28	460

eastern branch of the estuary on the bank of the main river channel which has its source in the Gwinear Downs mining district. This part of the estuary has been used as part of a sluicing system (Fig. 1), as a sluice pool for trapping seawater at high tide which is released through the sluice gates at mid-tide to wash the channel of the main harbour free of sand (Spring, 1974, personal comm.). Cores 2 and 3 were taken from near the banks of the River Hayle channel on the western branch of the Estuary. Both these cores show an organic-rich peat horizon approximately 5 cm thick which may relate to a former lower stand of sea level.

In core 1 the highest concentration of tin, arsenic, copper, iron, lead and manganese are all found in the alternating black and reddish-brown clay horizons at 61–122 cm, which coincide with the lowest shell concentrations. The high concentration of these metals together with the nature of the sediment suggest that they may be fine mine tailings transported into the estuary by fluvial processes downstream from the Gwinear Downs mining district, and the tin smelter at Angarrack 1704–1881 (Barton, 1967) (Fig. 1). If the relatively shell-rich sediment in the upper horizon of the core originated during the second great storm in the formation of the Upton Towans in 1869, then these clay horizons must have been formed during an earlier period. If this is the case, then there is good agreement with the mining records which show that the peak production period in the Tremayne group of mines of the Gwinear Downs mining district and the Angarrack tin smelter predated 1869. In this district, the Providence Mine 1820–1862 produced 14 450 tons of black tin while between 1848–1868 in the Tremayne Mine proper, the output was 1492 tons of black tin, giving a total of just under 16 000 tons of black tin for the group of mines (Dines, 1956). With such large scale mining activity on the hinterland of this part of the estuary, the poor recovery of fine tin associated with this period and the efficiency of the estuary in acting as a filter for the land derived detritus, the high concentration of all the elements within these horizons can be explained. The decrease in concentration of tin, arsenic, copper, iron, lead, manganese and zinc at depths of greater than 122 cm is accompanied by an increase in shells. If these shell fragments have derived from the first great storm in 1750 during the formation of the Upton Towans, then the distribution of elements would correlate very well with the much smaller scale mining activity on the land prior to this period.

Core 2 shows a marked increase in shell content towards the basal horizon at depths of greater than 51 cm which is also poorer in all the metals in comparison to the sediment above. Core 3 on the other hand, which is located nearer to the present High Water Mark and to the main channel of the River Hayle in the intertidal zone of the estuary shows less than 1% shells throughout its length. This low shell content may be explained by its protected position from wind blown shells originating in the coastal dunes, or shells washed into the estuary on a rising tide. The peat horizons encountered in core 2 at 63.5–68.5 cm and in core 3 at 66–71 cm indicate rapid burial probably related to a recent change in condition within the estuary. Both horizons may have the same age and origin, on the basis of their thickness and depth of occurrence. The construction of the second sluice pool and the harbour probably at around 1830 (Cotton, 1974, personal comm.) has effectively reduced the intertidal area within the western branch of the estuary by over a quarter. Consequently, the reduction in area within this part of the estuary has led to rapid silting and the formation of the peat horizon. If this is the case and the peat horizons in cores 2 and 3 do correlate in age, then the high shell concentration below 68.5 cm in core 2 may be related to the first great storm in 1750 during the formation of the Upton Towans. On this basis, the sediment below the peat horizon in core 3 may be related to mining contamination from the pre-1830 mining era, and likewise the sediments above the peat horizon in both cores are likely to post-date 1830.

In the surficial horizons of both cores 2 and 3, the sediments are found to be enriched in all the metals. The tungsten concentrations in both cores are much lower in comparison to core 1 which suggests that the source rocks in the hinterland differ in tungsten enrichment. However, the sediment with highest concentration of tin in core 3 at 96.5–112 cm is not as enriched in other metals as compared to the sediment above. The mining records (Dines, 1956) indicate that most of the mines in the vicinity between Leedstown and St. Hilary, north of the Godolphin Granite, whose tailings were discharged into the River Hayle, are very old. The peak activity in the Leedstown area seems to have declined before 1850 and many of the mines in the St. Hilary area date back at least to the eighteenth century. In the Trencrom Hill area, tailings were discharged down the small but steep gradient stream valley draining into the Hayle estuary, which has been shown in a follow-up minus-80-mesh stream sediment reconnaissance survey to contain tin in excess of 35 000 ppm (Fig. 3). The peak production in mines of this area was reached after about 1830 with 13 000 tons of black tin since about 1825. Therefore the high tin concentration with relatively low concentration of other elements below the peat horizon in core 3 may be related to tailings from the River Hayle catchment area. On the other hand, the high element concentrations above the peat horizon may be the result from tailings of the Trencrom Hill mining district where the peak production period was reached after 1830. However, the sediment within this portion of the estuary is also complicated by the contribution of wastes from three smelting houses located in the vicinity

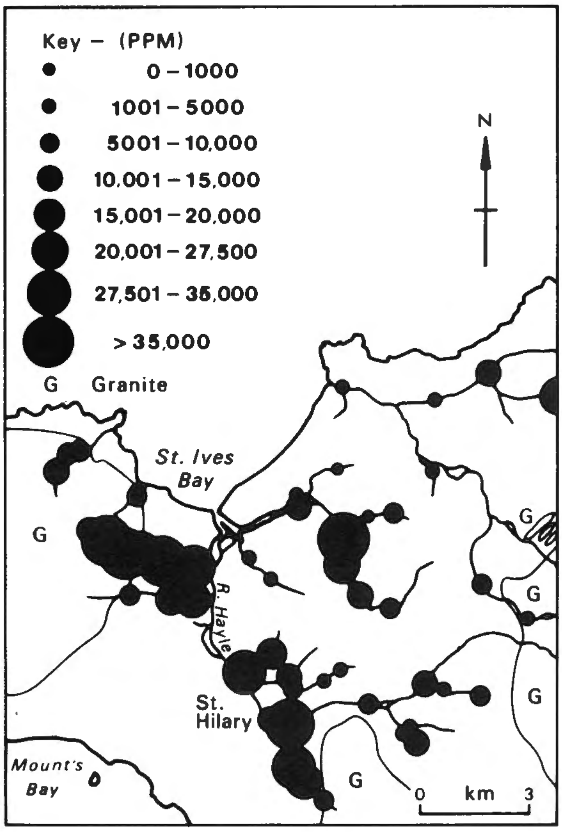

Fig. 3 Distribution of tin in the minus-80-mesh stream sediment in streams draining into Hayle estuary.

at Mellanear 1837–1905, Treloweth 1715–1883 and Wheal Reeth 1823–1824 (Fig. 1), and more recently by the establishment of an iron foundry near the harbour.

Tin distribution studies made on stream sediments in streams draining into the estuary (Fig. 3) have given further support that tin has originated from mines in the hinterland. The waste products of these mines including minerals containing arsenic, copper, iron, lead, tungsten and zinc, liberated through ore dressing have been transported by streams into the estuary. Due to the efficiency of the estuary as a sediment trap, high concentration of these heavy metals have been able to build up.

Conclusions

This study has demonstrated the important role played by the Hayle estuary in trapping land derived detritus due to mining operations. In the past, marine pollution through tin and copper mining on the hinterland has significantly altered the composition of the estuarine sediments. Here, it is shown that variations in the vertical distribution of tin and other associated heavy metals may be correlated with changes in the intensity of mining activity and changes taken place in the geomorphological evolution of the estuary.

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Long-term Chemical Effects of Petroleum in South Louisiana Wetlands—I. Organic Carbon in Sediments and Waters

The chemical effects of chronic petroleum input into a shallow water marsh were examined by measuring hydrocarbon levels and dissolved organic carbon content of sediments associated with two active oil fields in south Louisiana. Annual levels of total organic carbon in the surface waters of the oil fields were higher by 1 mg C/l. in the salt marsh and 5 mg C/l. in the fresh marsh than the respective control sites. Average dissolved organic carbon concentrations in the interstitial waters of cores taken within the oil field environments were 105% higher than the control in the salt marsh and 43% higher than the control in the fresh marsh. Significantly lower ratios of C_{17} to pristane occurred in both oil field sediments; however, average odd-even predominance values were not indicative of petroleum contaminated sediments. The results indicate that microbial processes are responsible for