

## Historical Mining Signatures: Geochemical and Mineralogical Evaluation of Sediments in three Coastal – Estuarine Systems

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### Abstract

The X-ray fluorescence (XRF) of the inter-tidal sediments in Hayle, Gannel and Camel estuaries in southwest England's coasts are examined here to evaluate and compare the broad geochemistry of each of the three systems. The total base cation content (Na, Mg and K) of the samples in all of the estuaries is 5% while the Ca is ~20%. In terms of sub-environment significance, the estuarine and inlet sediments of Hayle exhibit a high content of Ca than the coastal/beach samples while both the Gannel's estuarine and beach samples exhibit ~25% of Ca composition. There is high variation in the dimension of Ca in the different sub-environments sampled in Camel estuary (outer-estuary – 25-28%, mid-estuary – ~20%, inner – 30%). The Al and Fe contents in all of the sites are below 2% except in Camel where Al is around 3.5%. There clear difference in the percentage of composition of trace elements among the estuaries is also evident. Sn's concentration in Hayle is higher than that of Camel and Gannel. Pb, Ba, Zr and Zn is significant in all of the estuaries at various degrees - Pb and Zn are abundant in Gannel, while Sn, W, Zr prominent in Camel. The significant effect of the release of the particulate mine waste are observed in the samples' mineralogical composition despite the cessation of the mine activities in the 19th/early 20th Century, suggesting that these elements are still bio-available and bio-active for riverine processes to transport/migrate in the estuary-coast interaction.

**Keywords:** XRF; Inter-tidal sediment; Major element; Minor element; Particulate mine waste; Hayle estuary; Gannel estuary; Camel estuary

### Introduction

Coastal and estuarine environments have had long and varied history of anthropogenic interference and these are being studied intensively because of the persistent presence of metals which pose environmental risks to both humans and ecosystems [1]. Indeed, many estuarine and coastal systems are increasingly affected by the release and deposition of heavy metals from the varied anthropogenic activities [2,3]. Most of the world's urban areas and economically active cities are located in the coastal zone and it is also the region to which anthropogenic wastes are discharged –including the release of trace metals in significant amount on many occasions [4]. It is argued that if humans had not sought to make use of the coastal-estuarine environment/zone, there would have been few environmental problems [5]. Thus the presence of humans in the coastal environment is argued to interfere and modify the coastal systems causing many environmental challenges in many parts of the world [6]. Toxic metals discharged into estuarine-coastal environments always settles and become incorporated into the sediments [7]. The sediments in the coastal/estuarine environments are often regarded as the prime reservoir of heavy metals in the coastal zone [8]. Geochemical investigations based on mineralogical and chemical analysis in coastal-estuarine environments are effective scientific tools with many applications [8,9]. Principally, such investigations were initially used as exploration tools [7,8] and of recent for environmental studies and purposes [8].

In the present study, the surface sediments from three distinct coastal-estuarine environments in southwest England are sampled for environmental investigations of impact of historical mining signatures on marine sediments. The purpose of this study is to confirm whether there is any strong sedimentary link between heavy metal contamination and historical mining activities in the region. Sediment's geochemical and mineralogical studies are useful in metal pollution investigation as they have long residence time in estuarine-coastal areas [1]. The present study complements the previous works in the region by exploring the sedimentary connectivity of the system through the evaluation of the geochemical composition of the intertidal sediments within the sedimentary environments in all of the three estuaries shortlisted for this study (the Hayle, Gannel and Camel estuaries respectively).

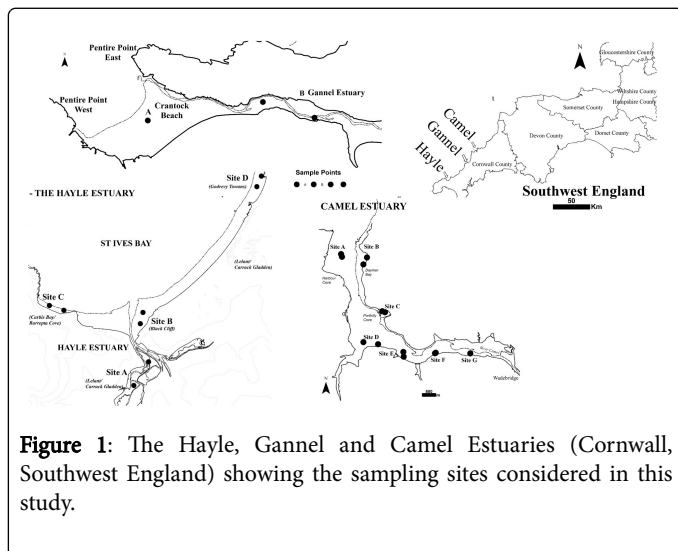
### Materials and Methods

#### Southwest England case study

United Kingdom (UK) is very rich in estuaries (over 160 according to Defra [10] with more than a quarter of the northwestern European estuaries occurring in the UK [10]. The Hayle, Gannel and Camel estuaries and their adjacent open-coast beaches (Figure 1), which are three neighbouring systems, provide an excellent opportunity to investigate the extent to which the diverse historical mining activities exhibit any regional coherence. The Hayle Estuary lies within St Ives Bay in the Penwith District of Cornwall in Southwest England (Figure 1). St Ives Bay is approximately 6.5 km wide, and the Hayle inlet lies just west of the centre of the bay. The bay is considered to be a closed sediment cell, suggesting that over the mesoscale, the sediment budget is balanced by morphodynamic adjustment across the estuary, inlet,

beaches and nearshore [11]. Site A, in the inner estuary (Lelant water/Carrack Gladden; Figure 1) is a broad intertidal flat while sites B and D are sandy planar upper foreshore which merge with a broader and flatter beach at the inlet of the Hayle estuary (site C).

The Gannel Estuary is 70% intertidal estuarine valley [12] situated in Newquay, between Pentire Point East and Pentire Point West, on the coast of Cornwall, South-West England (Figure 1).



**Figure 1:** The Hayle, Gannel and Camel Estuaries (Cornwall, Southwest England) showing the sampling sites considered in this study.

This coastline is macrotidal and the estuarine environment is a saltmarsh ria system comprising sandy intertidal sediments which merged through a narrow valley to a sandy beach-dune system (Crantock) seaward [13]. The Devonian slate/sandstone headlands of Pentire Points East and West ensure the system functions as a self-contained sediment cell [14].

The Camel Estuary, adjacent to Padstow, also in Cornwall, southwest England (Figure 1), is a shallow, predominantly sandy ria estuarine system formed as a product of post-glacial rise in sea level [15,16]. The main sedimentary environments in the estuary include sand dunes, saltmarsh, sand flats, mud flats, subtidal channels, and grazing marsh [15-17]. The Camel Estuary is also more sheltered, which enables the system to function as an important sediment sink [16,18].

### Field sampling

Surface sediments samples were collected from the intertidal zone of estuaries and along the beaches. Sample locations were located randomly within individual and key sedimentary sites in each system, and positioned using a hand-held Global Positioning System (GPS), ( $\pm 3$  m rms error). An effort was made to ensure that sufficient samples were collected from within the estuaries and along the beach areas, across the full intertidal zones. Samples acquired at low tide, were sealed, tagged and returned to the laboratory intact.

### XRF analysis

The XRF is used here to examine the sedimentological characterisation of sedimentary environments within, and connectivity between, the estuary and open coast system in Hayle, Gannel and Camel Estuaries respectively. X-ray Fluorescence Spectrometry (XRF) is used to determine the major oxide and trace element composition of sediment samples [19]. The major and trace elements in their oxidised

state are determined as percentage of composition. Major geochemical element analysed (XRF) here are: Ca (Calcium), Si (Silicon), Al (Aluminium), Fe (Iron), Cl (Chlorine), Mg (Magnesium), Na (Sodium), K (Potassium), Ti (Titanium), S (Sulphur), P (Phosphorus), Mn (Manganese), V (Vanadium), and Cr (Chromium). The trace elements analysed are: Ti (Titanium), Cr (Chromium), Co (Cobalt), Sr (Strontium), Se (Selenium), Sb (Antimony), U (Uranium), Zn (Zinc), Br (Bromine), Zr (Zirconium), Ba (Barium), Ce (Cerium), Pb (Lead), (Copper), Ga (Gallium), Ce (Cerium), As (Arsenic), Rb (Rubidium), Y (Yttrium), Mo (Molybdenum), Ag (Silver), Sn (Tin), Te (Tellurium), I (Iodine), Cs (Caesium), La (Lanthanum), Hf (Hafnium), Ta (Tantalum), W (Tungsten), Tl (Thallium), Bi (Bismuth), and Th (Thorium) respectively. The samples used in the XRF analyses were obtained from 0-5 cm sediment depth from a range of estuarine and open coastal sample locations (Figure 1). The major elements are determined as a percentage composition [20] while the minor/trace elements analysis are undertaken to obtain data in concentrations of one to several tons and parts per million (microgram-mg or a gram g).

The samples were freeze-dried at 60°C in MODULO 4k Freeze Drier for five days before the dried samples were pulverised into a fine powder using an agate mortar and pestle. Each pulverised ground sample was then weighed prior to analysis and the weight for each of the 21 samples ranged from 4 to 6 grams. These subsamples were analysed using a Spectro XLab Pro 2000 to produce the high X-ray intensity, which permits the quantitative analysis of elements in the *ng*-range.

The generated data were then analysed in Matlab and Paleontological Statistics (PAST) software [21] for comparison of major and minor/trace element composition across the three systems while the geospatial comparison of some major and minor elements composition were explored in ArcGIS. Major elements were measured in percentage (%) while trace elements were measured in  $\mu\text{g/g}$ .

## Results

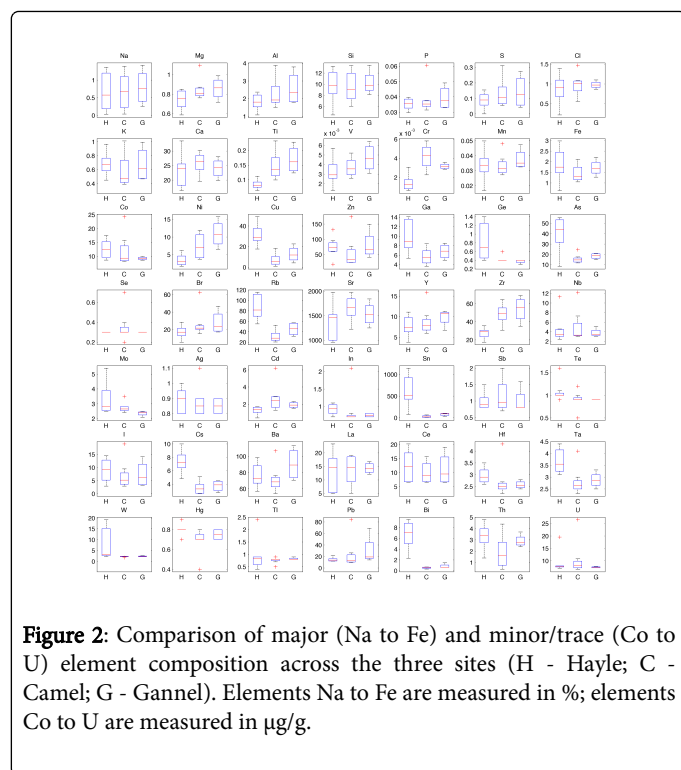
### Elemental composition of intertidal sediments

The comparative major and minor/trace elemental analysis of the samples in the systems are presented in Figures 2-5. The comparison of total base cation content (Si, Mn, P, Cl and Fe) of the Hayle estuaries is high compared to total content analysed for other estuaries while Mg, Al, S, and K of the major elements considered are, however, higher in Camel Estuaries (Figure 2).

The total base cation content (Na, Mg and K) is low (<5% in total) in all of the sites with the exception of Ca which is much higher ( $\sim$ 20%). Patterns in Ca distribution at the systems are broadly similar across the sites. Shell material was clearly present in the sediments sampled, and fragments are noted to contribute to the medium and coarse sand size populations. However, in all of the estuaries, Na, Mg, Si, S, and K have relative lower percentage (0.1-6%) of composition.

The summary comparisons of major elemental composition between the estuarine sediments and the beach/coastal sediments can be observed from the Figures 2 and 3.

The beach sediments in Hayle (Figure 3) have higher content of Si, Al and Fe ( $\sim$ 13%,  $\sim$ 2% and  $\sim$ 2%) than estuarine ( $\sim$ 8%,  $\sim$ 1.5% and  $\sim$ 1.5%) sediments respectively, while there is no significant difference in the elemental compositions of these major elements between the coastal and estuarine sediments in Gannel.

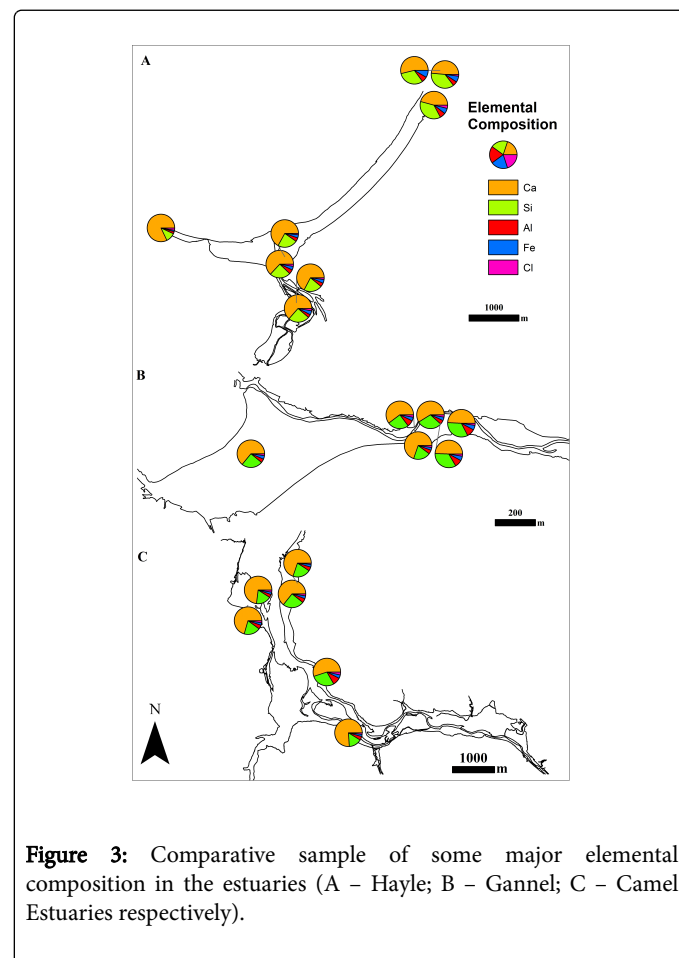


**Figure 2:** Comparison of major (Na to Fe) and minor/trace (Co to U) element composition across the three sites (H - Hayle; C - Camel; G - Gannel). Elements Na to Fe are measured in %; elements Co to U are measured in µg/g.

In another comparison, the beach sediments in Hayle have lower content of Ca (~20%) than its composition in the estuarine (~34%) sediments. Similarly, in Gannel, there is no significant difference in the percentage elemental dimensions of Ca in both estuarine (~20 - ~28%) and beach (~25%) sediments. In Camel estuary, however, the seaward sites (A - B) have lower content of Al, Si and Fe (~2%, ~8% and ~2%) compared to the mid-estuarine samples (Sites C & D, which are ~4%, ~12% and ~2%) and inner-estuarine samples (Site F, which are ~3%, ~13% and ~2%) respectively. Comparatively, in Hayle, the estuarine and inlet samples (Site A and C) exhibit a higher content (23-33%) of Ca than the open coast/beach sample (Site D) (16-19%) (Figures 2 and 3). In the Gannel, both the estuarine and beach samples exhibit the similar proportions of Ca (19-28%). Calcium in the Camel varies spatially: the outer estuary has a high percentage (sites A-C between 25-28%), the mid- and far inner estuary slightly less (~20% at sites D & F). Site E in the inner estuary has the highest concentration of Ca at around 30%. This is the opposite trends observed for Al, Fe and other related major elements. The Al and Fe contents across all sites are around 1-3% except in Camel Sites C, D & F where the Al is around 3.5-4%.

The geochemical profile of the trace elements sampled for analysis for the estuaries show Ti, Cr, Co, Sr, Se, Sb, and U are abundantly registered in Camel compared to Hayle and Gannel while V, Zn, Br, Zr, Ba, Ce, Hg, and Pb are higher in Gannel Estuary and Cu, Ga, Ce, As, Rb, Y, Mo, Ag, Sn, Te, I, Cs, La, Hf, Ta, W, TI, Bi and Th in Hayle respectively (Figures 2 and 4). Trace elements such as Zn, Rb, Sn, Sr, Zr, Ba, Pb, Ce, La, have high concentrations in all of the samples when compared with other elemental dimensions. There is over 55% concentration of Zn in all of the samples in Hayle and Gannel (>70 µg/g), which are higher than the concentrations in the outer-estuarine samples of Camel estuary (Sites A - B, (~ 25 - 28 µg/g), Figures 2 and 4). It is only the mid-inner estuarine samples in Camel (Sites C - F) which exhibit a significant composition of these elements (~70 - >170

µg/g). The coastal/beach sediments of Hayle Estuary have higher composition of Rb (>100 µg/g), than estuarine samples (~75 µg/g), while they are of low content in Gannel (<60 µg/g) and Camel (<50 µg/g) estuaries respectively (except at site F, the inner estuary in Camel).



**Figure 3:** Comparative sample of some major elemental composition in the estuaries (A - Hayle; B - Gannel; C - Camel Estuaries respectively).

The composition at the coastal sediments of site D in Hayle is lower than that of other concentration in the samples. The Zr composition in Gannel and Camel estuaries are higher (>35 µg/g), than sediments' composition of this element in the Hayle Estuary (<~35 µg/g), while it is a different scenario for the Sn concentration as there are higher concentration of this element in Hayle (>400 µg/g), than in the Gannel (<~107 µg/g) and Camel (<30 µg/g) estuaries. Ba and Pb are also of notable composition (>50 and >10 µg/g respectively) in all of the sites with the significant dimension of concentration recorded in Camel's inner estuarine samples at site F (>106 and 84 µg/g respectively) (Figure 2).

Sr is strongly associated with Ca and it is therefore strongly present where Ca is apparent in all of the three systems (Figure 4).

Sr content in sediments are highly controlled by combination of parent rock materials and climate, and therefore its concentration is higher with a range of 50-1000 mg kg<sup>-1</sup> [22]. Here, the composition of Sr is higher in all of the sample sites (>1000 µg/g) except at Hayle beach Site D where it is less than (<) 1000 µg/g. Although Sr is easily mobilised and derived during weathering processes, notably in oxidising acidic environments, it can also be incorporated in clay materials and fixation of organic materials [22]. The anthropogenic

sources from industrial waste, especially from Zn refineries, incineration ash and disposal of coal ash are other possible derivation of Sr in sediments [23]. The samples in all of the sites exhibit a reasonable high percentage of Si dimension with Si being prominent at samples across the seaward/coastal zones, reflecting the importance of the quartz component. The proportions associated with the other major elements, for these samples, are minimal (Figures 2 and 4).

The result of the Principal Component Analysis (PCA), using the correlation-type in Paleontological Statistics (PAST) software is presented in Figure 5. The first three main eigenvalues (12.09, 8.9, and 3.79) of the nineteen values in the analysis correspond to 35.6%, 26.2% and 11.2% of the total variance respectively.

Thus the first two principal components (PC), presented as Biplot in Figure 5, provides the basic information about the differences in the elemental composition. The x-axis presents the PC1 while the y-axis indicates the PC2 of the elemental composition. Quite a lot of the minor elements are at/just above detection level and therefore are ignored in the detailed analysis. Here, the difference between the Hayle and the other two estuaries are obvious. Specifically, the Hayle is much higher in metal pollutants than the other estuaries, and much lower marine carbonates (Ca, Sr) (Figures 2-4).

The inclusion of the grain size statistics did not really change the pattern of results (in the PCA analyses), but it shows that coarser grain sizes in the Hayle are rather more strongly associated with the metals Cu and Sn, but not associated with the metals Pb and Fe.

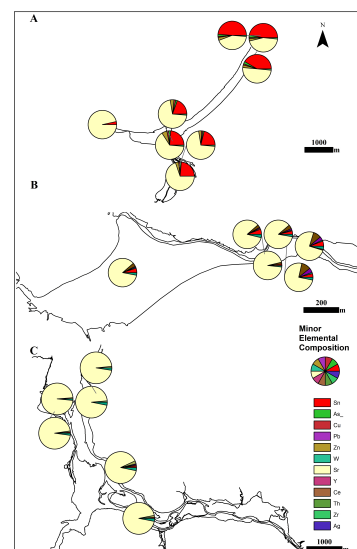
## Discussion

### Geochemical and mineralogical composition of sediments

The mineralogical and geochemical investigation of sampled sediments, in addition to other similar previous studies in the region (e.g., [24-29], etc.) showed that the estuaries have retained sediments which are significantly enriched in Si, Al, Na, Fe, Cl, K, Sn, Sr, Zn, Zr, Ba, Rb, Y, and W. These geochemical and mineralogical compositions in the sedimentary systems indicate the signature of historical impact of industrial activity on the sedimentary environment [29]. The intertidal sediments of the three estuaries clearly show the release of mine waste tailings into the estuarine catchments leading to and resulting in enhanced siltation [28]. Sn, Cu, As and Zn are significant in the Hayle estuary, Pb and Zn are important in the Gannel estuary and Sn, W and Zr are enriched in the Camel estuary respectively. Specifically, the Hayle is much higher in metal pollutants than the other estuaries, and the proportion of marine carbonates is much reduced (Ca, Sr).

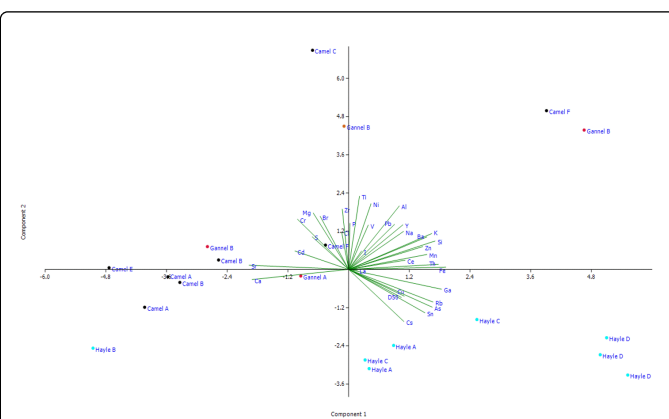
The history of mining activities in the region and their impact are well-documented. Despite the cessation of mining activities in the region in over 100 years ago [29], the geochemical and mineralogical of the intertidal sediments clearly retain the legacy of these human activities.

The presence of mining contamination at the beaches and the open coast indicates that there is a sedimentary connection between the estuary and the beach, and also attest to the historical impact of the anthropogenic activities on the estuarine sediment systems. The evidence from the geochemical analyses of the sediments is an indication of the reworking of waste derived originally from the past mining activities through the riverine inputs [28,30].



**Figure 4:** Comparative sampling of some minor elemental composition in the systems (A – St Ives-Hayle; B – Crantock-Gannel and C – Padstow-Camel systems respectively).

Findings in the data indicate that mine waste tailings have been deposited within the estuaries but hydrodynamically transported to the estuary mouth and open coast. The geochemistry and mineralogy of sediments from the sites here can be compared with other estuaries in Cornwall where hard-rock mining activities have resulted in siltation, for example in the Fowey Estuary [28] and Fal Estuary [31].



**Figure 5:** Principal Component Analysis (PCA, using correlation-type in PAST) of the elemental (XRF) composition (%) of intertidal sediments and the grain-size (represented as D50). (Note: colour representation: Hayle – light green dot, Gannel – Red dot, and Camel - Dark brown dot).

The geochemical signature of the elements composition in the estuaries, as evidenced from the XRF analysis of some of the samples and other previous works on the study sites, confirmed that sediments



supplied to the estuaries and coastal zones of the region were derived either from (i) the offshore during the early Holocene as a result of the sea-level rise which flooded the region [28]; (ii) onshore as a result of terrestrial transportation of sediment through the hydrodynamic action of the river system [25,32]; or, (iii) most recently, through the human activity as a result of the release of particulate waste from major historical mining which contributed immensely to the siltation and supply of the sediments in the region [25]. However, considering the geochemical elements of both beach and estuarine environments' sediment samples, there is a possibility that the beach and coastal sands in the vicinity of the bays (especially those at the entrance channels) are caught up by the ebb and flood of the tide, then carried in and out of the estuaries.

### Evidence for sediment sources

The current coastal and estuarine sediment build-up is as a function of either onshore or offshore supply of natural sediments coupled with supplies arising from human activities [26]. Cornish estuaries have received considerable attention regarding sediment geochemistry - principally as a result of past mining activities in the region. The distribution of Sn and other heavy materials in the superficial portion of the sediments in Hayle Beach area can be attributed to the transportation of mine waste by the River [33]. Although the River Hayle is very active in the estuary and drains a significant part of the mining area, Pirrie and Camm [25] observed that River Hayle alone could not have supplied much of such sediment to Hayle's beach as the estuary acts as an "efficient sediment trap". The major mining operation areas, numerous smelting/mineral processing plants and tin processing plants contributed to the discharge of large volumes of fine sediments enriched in Sn, Cu, As and Zn [28]. Hayle was important sites for Cu, Sn and large scale tin smelting and iron foundry in the eighteen and nineteen century, the cessation of which contributed to the release of particulate mine waste to the estuary [29].

Camel estuary is significantly enriched in Sn, W and Zr, sourced from the release of particulate mine wastes directly from the hard-rock mining activities at Mulberry and Lanivet region where large quantities of cassiterite were discharged into the estuary through local streams [27]. The geochemical elemental profile of the estuarine sediments in this study indicates the composition of mining related sediment supplied to the estuarine system.

Of all the estuaries, the Gannel is recognised to contain the highest Pb contamination of any estuary in the South-West England [27]. The geochemical parameters of the sediments analysed here indicate that the sediment might have been sourced from particulate waste from mining activity centred on cross-course mineralisation [26]. Previous work in the estuary [25,26] clearly suggest that Gannel Estuary received highly significant particulate wastes from mines working with "Pb-Ag-Zn lodes" [26].

From the results presented in this study, it can be stated that the elemental composition of the geochemical of both the estuarine and beach/open coast sediment samples show that the build-up of the inter-tidal sediments in the estuaries are as a result of offshore sources combined with the onshore sediments transported into the estuaries (which have been impacted as a result of human activities, notably mining). The almost equal concentration of the major biogenic elements in all of the estuaries supports the view that the valleys of the estuaries, with the infilling of sediments of similar geochemical content at almost equal proportion, are derived as a result of flood of the early Holocene in forming the present/modern estuary [26]. Aluminium,

potassium, manganese and iron (Al, K, Mn, and Fe) are the dominant signals for the terrestrial/onshore inputs into the sediments in the region. The sedimentary concentrations of these elements follow similar pattern in all of the estuaries. This indicates, here, that both onshore and offshore contributions (evidenced by the concentration of marine elements such as Mg, Sr, and so on) also interplay in supplying sediments to the estuaries. In addition, one of the most important contributors to the siltation of the estuaries in the 19th and 20th century is the release of particulate waste from upstream mining.

### Conclusion

The XRF geochemical and mineralogical compositions of sediment show the levels of mine waste tailings in the estuarine system analysed here which is as a result of major historical mining activities with Sn, Cu, As and Zn as predominantly significant in Hayle, Pb and Zn in Gannel and Sn, W, and Zr in Camel estuaries respectively corresponding with the historical mining industries in each of the systems. The effects of the release of these particulate mine waste are still significantly observed in the sample sediments' mineralogical composition despite the cessation of the mine activities in the 19<sup>th</sup>/early 20<sup>th</sup> Century suggesting that these elements are still bio-available and bio-active for riverine processes to transport/migrate in the estuary - coast interaction. This study has shown, therefore, that the signature of anthropogenic activities (e.g. mining) has effects that is beyond the years of their operation and cessation, and has also confirmed that there is a strong sedimentary link between heavy metal contamination and historical mining activities in the Southwest England coastal-estuarine environment.

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