Periodicity
in the trace metal content
of estuarine sediments

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ABSTRACT

Determinations of trace elements (Cd, Cu, Fe, Mn, Pb and Zn) have been made in Tamar Estuary sediments of 14 sites during 9 axial surveys. The sediments were analysed for total and acetic acid soluble metals, loss of weight on ignition and grain size. A statistical analysis of the total metal data showed distinct seasonal trends in the chemical composition of the sediments. In contrast, when similar tests were carried out on the acetic acid soluble data, there was no evidence of seasonality which showed that heterogeneous chemical reactivity is largely independent of the annual changes in the estuarine master variables. It was concluded that the major compositional changes were controlled by: 1) the fluvial input of new material; and 2) the recycling of existing material by seasonal oscillations in the river flow and tidal pumping. Since estuaries represent a major trap of trace elements, the temporal effects reported here are of relevance to the further refinement of geochemical models of trace metals.

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RÉSUMÉ

Périodicité des teneurs en oligo-éléments de sédiments estuariens

Des déterminations d'oligo-éléments (Cd, Cu, Fe, Mn, Pb, Zn) ont été faites sur des sédiments de l'estuaire du Tamar en 14 sites durant 9 campagnes. Dans les sédiments, les métaux totaux et solubles dans l'acide acétique, la perte au feu et la granulométrie ont été déterminés. Une analyse statistique des métaux totaux a révélé des changements saisonniers marqués dans la composition chimique des sédiments. Les mêmes tests pratiqués sur les données d'acide soluble n'ont pas révélé de changements saisonniers. Ce fait montre que la réactivité chimique hétérogène est en grande partie indépendante des changements annuels des variables principales de l'estuaire. En conclusion, les changements de composition majeurs sont contrôlés par: 1) l'apport fluvial de nouveau matériel; et 2) le recyclage de matériel en place lors des oscillations saisonnières des débits fluviaux et des actions de la marée. Puisque les estuaires sont un piège à oligo-éléments important, les effets temporels abordés ici sont très utiles à l'affinage futur des modèles géochimiques des oligo-éléments.

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INTRODUCTION

Cyclic changes in the freshwater and seawater conditions of temperature, pH, salinity, suspended solids and oxygen concentrations and their non-conservative interactions during mixing exert a major influence on heterogeneous chemical reactivity in estuaries (Morris, 1978; Morris et al., 1982 b; 1982 c). Assessing the chemical behaviour of trace constituents during estuarine mixing is fraught with difficulty because of the short-term variability of these controlling factors. Even so, many workers have attempted to define the chemical reactivity of an element on the basis of one survey (e.g. Burton, Liss, 1976) carried out under one, possibly unique set of hydrodynamic conditions. This approach
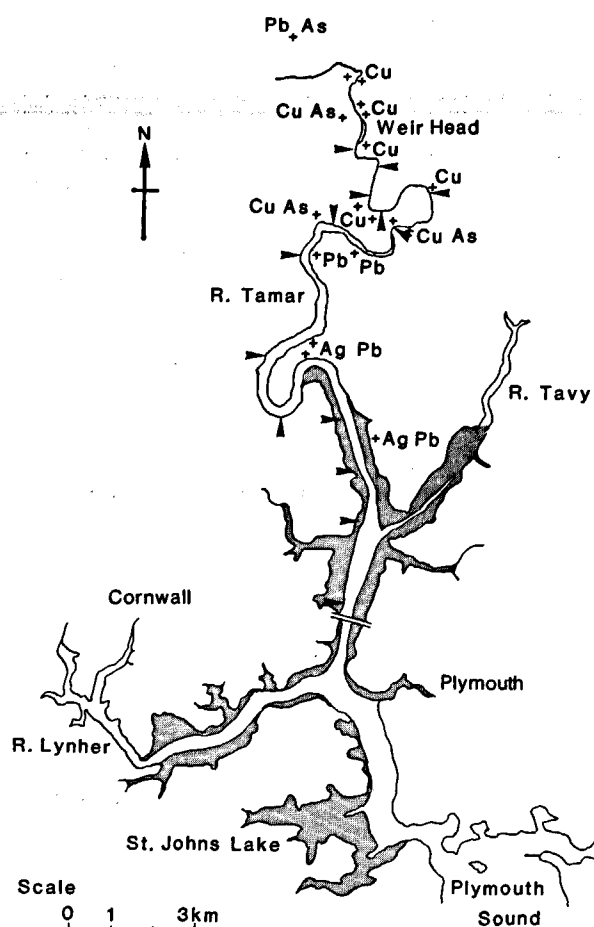
Figure 1

The Tamar Estuary. ▶-sediment sampling sites; +-disused mine and principal ore body.

can lead to unrepresentative conclusions and exemplifies the need for a coherent sampling strategy which covers both temporal and spatial variability (Morris, 1978), as has been shown in the case of heavy metals (Morris et al., 1982a; Ackroyd et al., 1986) and the nutrients (Morris et al., 1981).

Correspondingly detailed studies of estuarine sediments have hitherto not been attempted, presumably because the analytical requirements are considerably more demanding. Nevertheless, seasonal variability in estuarine sediment composition can be anticipated since variable internal net transports of material result from tidally induced upestuary movement with the turbidity maximum and downestuary movement during high river flow conditions (Allen et al., 1980; Bale et al., 1985). In this study, 9 separate surveys of the sediments were carried out at 14 sites in the Tamar Estuary (see Fig. 1) over a period of 20 months. The metals Cd, Cu, Fe, Mn, Pb and Zn were selected for study as there are major differences in their estuarine chemical behaviour (Loring et al., 1982; Morris et al., 1978) and the mineralised catchment area (Hamilton-Jenkin, 1974) and anthropogenic inputs constitute active sources of these elements.

EXPERIMENTAL

Sample collection

The sampling strategy was designed to cover a range of hydrographic conditions from the riverine end member, which included mine spoils, through the mid-estuarine region where large changes in the physico-chemical parameters are observed (Morris et al., 1982b), to a quasi-marine end member in the lower estuary. Samples of mobile, surface sediment (0-2 cm in depth) were taken from the low water mark using a "Teflon" spatula from a shallow draught vessel. A sample of sediment was taken at each of the 14 sites (shown in Fig. 1) during 9 axial surveys of the estuary, covering the period July 1980 to February 1982.

Sediment digestion and analysis

The samples were washed with distilled water (pH ~ 6) and then oven dried at 60°C to a constant weight (Holme, MacIntyre, 1971). The digestion procedures developed by Rantala and Loring (1973; 1975) and Loring and Rantala (1977) were used.

For total sediment analyses, approximately 1 g of the dried sediment was digested in a "Teflon" bomb using 6 ml of aqua regia, as a wetting agent, and 6 ml of "Aristar" HF. The reaction vessel was sealed and heated in an oven at 100°C for 1 h. The contents were then washed into a 250 ml volumetric flask containing "Aristar" H_3BO_3, which was then made up to the mark with deionised, distilled water.

Selective leaching experiments were carried out on 10 g portions of the dried sediment, which was digested using 50 ml of 25% v/v "Aristar" CH_3COOH (pH ~ 4) at room temperature for 12 h. The digests were then filtered through 0.45 μm filters and the solids washed with a small amount of deionised, distilled water. The filtrate was made up to volume in a 100 ml volumetric flask with deionised, distilled water.

The analyses for Cu, Fe, Mn, Pb and Zn in digests were undertaken by conventional air/acetylene flame atomic absorption spectrophotometry (AAS) on an Instrumentation Laboratory 151 spectrophotometer fitted with a deuterium background corrector. Cadmium was determined using the Delves Cup method (Delves, 1970; 1977). All the metal determinations fell within the linear response range and were calibrated using acidified standard solutions.

Reagent blanks were obtained by running the procedure without the sediment and the blank results for each metal were less than 1% of the measured values.

Two marine sediment reference materials, Miramichi Estuary Standard Sediment (MESS-1) and Baie des Chaleurs Standard Sediment (BCSS-1) were analysed in the same manner. The results obtained (Tab. 1) were in good agreement with the certificated values (National Research Council of Canada, 1981).

Table 1

The results of the analyses of standard sediments.

Element	BCSS-1		MESS-1	
	Standard ppm	This work ppm	Standard ppm	This work ppm
Cd	0.29±0.04	0.3±0.06	0.59±0.1	0.51
Cu	18.5±2.7	23.4±2.4	25.1±3.8	29.3±1.6
Fe	3.8%	2.66±0.56%	3.0%	2.75±0.31%
Mn	229±15	238±13	513±25	469±44
Pb	22.7±3.4	19.7±7.1	34.0±6.1	42.9±1.8
Zn	119±12	107±7	191±17	144±40

Loss of weight on ignition

The total carbon content was obtained as the percentage loss of weight of the dried sediment after ignition at 680°C for 6 h (Holme, MacIntyre, 1971). Loss of weight on ignition (LI) is known to give relatively high carbon contents due to loss of the carbonate fraction and remnant interstitial water bound to the clay matrix (Mook, Hoskin, 1982; Williams, 1985).

The values obtained using this method (7-14% LI) were usually higher than particulate organic carbon results (4-6% particulate organic carbon) obtained from Tamar Estuary sediments using a commercial combustiometric method (Watson et al., 1985).

Grain size

Sediment samples were fractionated into greater or less than 63 μm by wet sieving.

RESULTS AND DISCUSSION

The data base

The raw data base consists of over 1 000 determinations, which include total metal concentrations, acetic acid available metal concentrations, grain size and LI. The concentration data for each metal was plotted as the mean and one standard deviation at each of the 14 stations against distance downestuary from Gunnislake Weir (Ackroyd, 1983). As an example, Figure 2 shows total Mn concentrations in the sediments as a function of distance downestuary. The decline in Mn concentration can be explained in terms of the known chemistry of Mn in the Tamar estuary (Knox et al.,

1981; Morris, Bale, 1979; Morris et al., 1982 a). Dissolved Mn in the freshwater is taken up by the particulate phase in the vicinity of the turbidity maximum. During neap tides Mn accumulates in the sediment, only to be remobilised into the water column as Mn (II), during spring tides, following a period of benthic anoxia. Adsorption of Mn (II) onto particles in seawater is slow and the metal is mainly flushed from the estuary in the dissolved phase. This chemical cycling of Mn can only be significant if the element is taken up on the particle surfaces at the freshwater end-member. This study has shown that 80-100% of the Mn is removable by acetic acid and can, therefore, participate in surface reactions which give rise to the observed profile. In the case of the other metals the available fraction is in the sequence Mn (100%) > Zn (60%) > Cu (20%) > Fe (10%) which suggests that dissolved phase transport of these metals becomes less important down the series.

Statistical analyses

The total metal, LI and grain size data were subjected to a statistical analysis (Kendall, Stuart, 1961) and correlation matrices were produced to examine the inter-relationships between the variables (example for a summer cruise, see Tab. 2). Strong correlations between the metals Fe, Mn, Cu, Zn were not evident from
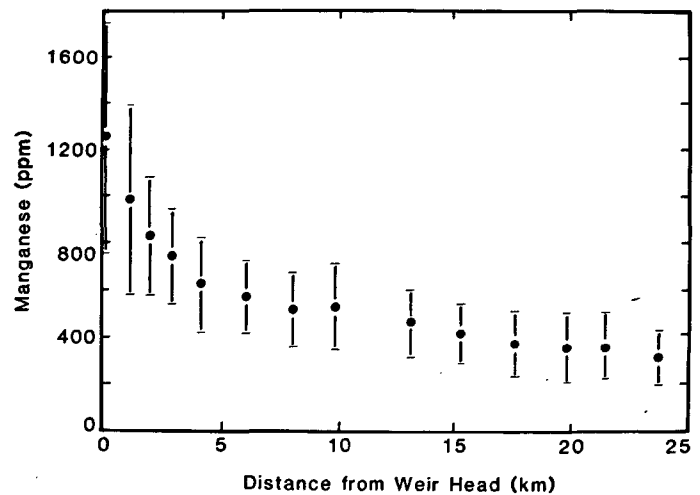

Figure 2

Total manganese concentrations in Tamar sediments as a function of distance.

Table 2

Correlation matrix for 22 July, 1980 hydrofluoric acid digestions.

	Mn	Cu	Fe	Zn	Pb	LI	Cd	Grain size
Cu	—0.58							
Fe	0.28	0.58						
Zn	—0.54	0.98	0.61					
Pb	—0.78	0.93	0.34	0.90				
LI	—0.45	0.83	0.53	0.79	0.75			
Cd	—0.28	0.73	0.59	0.81	0.59	0.50		
Grain size	—0.64	0.89	0.41	0.90	0.95	0.61	0.63	
Distance	—0.71	0.05	—0.64	0.02	0.38	—0.08	0.27	0.36

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence.

Table 3

Correlation matrix for 22 July, 1980 hydrofluoric acid digestions: normalised.

	Mn	Cu	Fe	Zn	Pb	LI	Cd
Cu	0.65						
Fe	0.93	0.87					
Zn	0.83	0.95	0.97				
Pb	0.13	0.81	0.48	0.63			
LI	0.78	0.96	0.95	0.98	0.71		
Cd	0.84	0.81	0.92	0.93	0.42	0.86	
Distance	—0.61	—0.47	—0.53	—0.50	—0.00	—0.42	—0.61

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence.

this analysis. However, a normalisation procedure, in which the total metal data set was standardised to 100% <63 µm grain size eliminated bias created by the grain size distribution and produced relationships between almost all the metals which were positive and significant at the 99% confidence level (*see* Tab. 3).
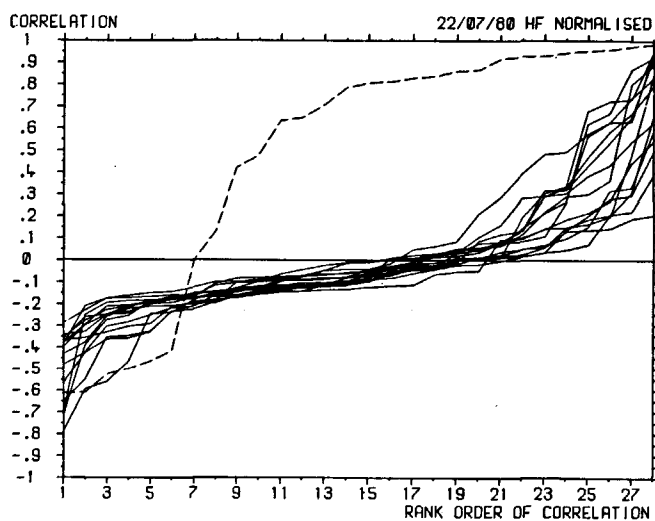

Figure 3 .
Rank order correlation profile for the total metal data of July 1980. The real data is represented by the broken line.

Further statistical tests were carried out in the form of rank order correlation plots (Kendall, Stuart, 1961), in which the correlation coefficients derived from the normalised data were plotted in ascending numerical order, with the most negative first and the most positive last, against the total number of coefficients (*see* dashed lines in Fig. 3, 4, 5). The second phase of the method was to randomise the raw data matrix, which consisted of columns of metal concentrations and LI values. The data in each column was reordered randomly and the correlation programme rerun. The correlation coefficients were then plotted on the rank order graph (full lines in Fig. 3, 4, 5) and the random reordering process was repeated 20 times. Figures 3, 4 and 5 show the actual and random rank order correlation profiles for summer 1980, winter 1980 and spring 1981, respectively. This sequence of diagrams indicates a seasonal progression. In summer, the real data differed significantly from the randomised data whereas the profile for the real data in winter approached the envelope of the random simulations (Fig. 4) and the spring profile (Fig. 5) showed an intermediate condition. These seasonal changes were linked to variations in river flow and the tidal transport of sediment within the turbidity maximum zone (Bale *et al.*, 1985; Uncles *et al.*, 1985). High energy resuspension and thorough mixing of inputs and surficial estuarine sediment occurs in winter,
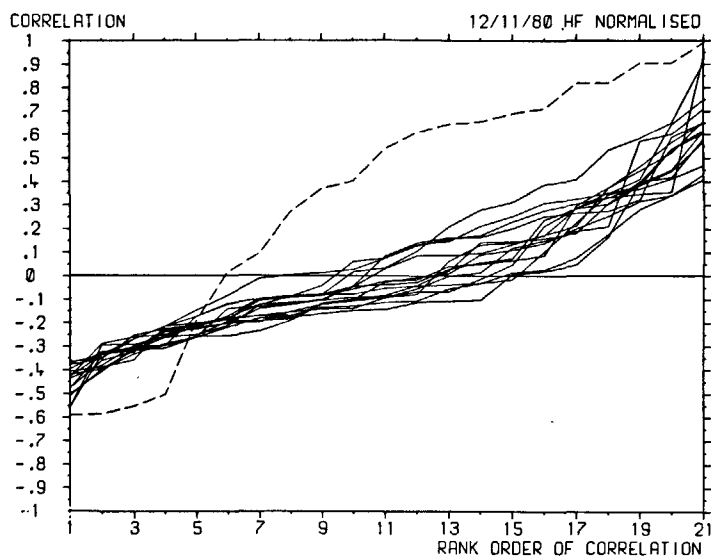

Figure 4
Rank order correlation profile for the total metal data of November 1980. The real data is represented by the broken line.
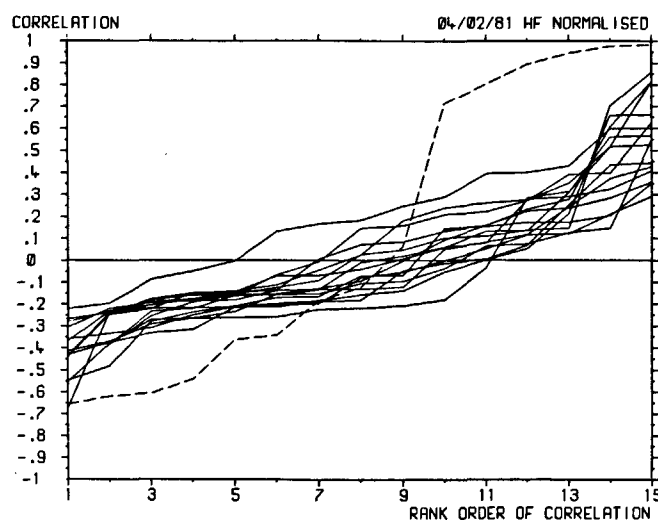

Figure 5
Rank order correlation profile for the total metal data of February 1981. The real data is represented by the broken line.
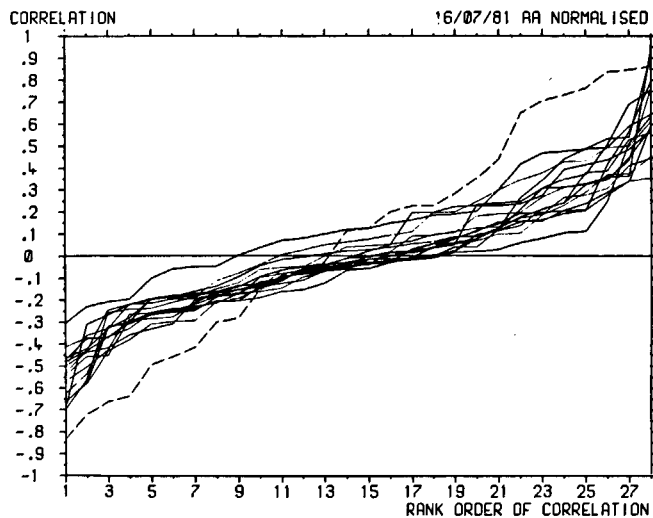
CORRELATION   '6/07/81 AA NORMALISED

Figure 6
Rank order correlation profile for the available metal data of July 1981. The real data is represented by the broken line.

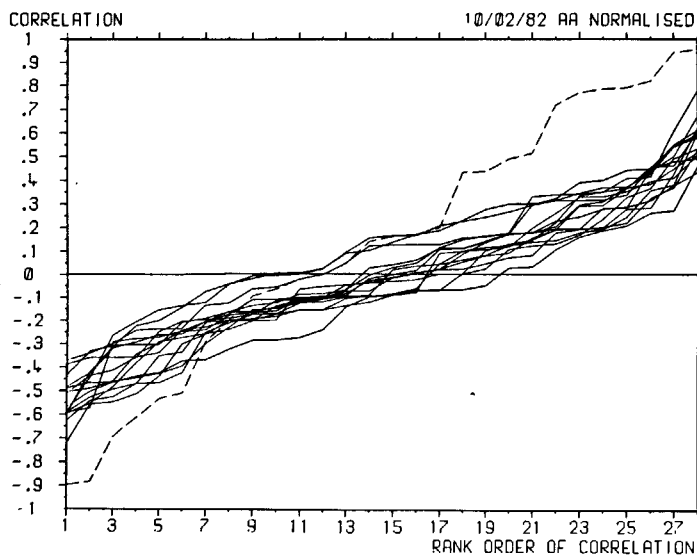CORRELATION   '0/02/82 AA NORMALISED

Figure 7
Rank order correlation profile for the available metal data of February 1982. The real data is represented by the broken line.

whereas in summer, with low river flows and low energy resuspension, a more quiescent sedimentary environment prevails. Additionally, the sediment input in summer is relatively low and constant whereas winter-time spate conditions introduce large quantities
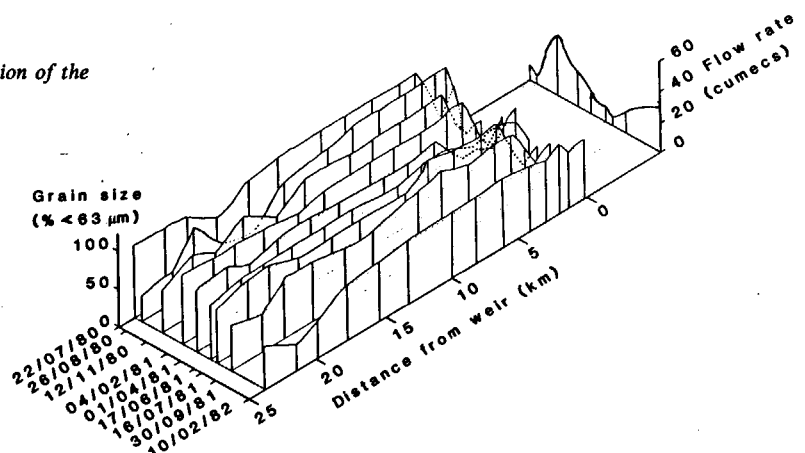
of new material episodically *via* streams and bankflows. Identical statistical analyses were carried out on the normalised concentrations from the acetic acid digestions and the results are shown in Figures 6 and 7. These plots showed no evidence of seasonal differences since the real data fell within the envelope of the random simulations. This lack of significant seasonality in the acetic acid soluble fraction of the metals suggests that the sorptive mechanisms controlling surface chemical composition are unresponsive to seasonal changes in the water column variables of temperature, pH and dissolved oxygen content. Therefore, the differences observed for the total metal data must be due to an influx of new material into the estuary which is smeared out along the estuary during conditions of high river flow.

Time series analysis of the data

The apparent seasonality in the data was further investigated using the normalised, total metal data and the grain size distribution. Figure 8 shows the grain size as a function of time and distance along the estuary. Under periods of low river flow, fine-grained material (<63 μm) accumulated at the head of the estuary and coarser material was found in the lower estuary (for example, in the profiles of 26 August, 1980 and 16 July, 1981). During the high river flows prevalent in winter the converse applied; the upper estuary was composed mainly of coarse-grained material and the mid to lower estuary was enriched in fine-grained material (for example, the profile of 1 April, 1981). This suggests that upestuarine mass transport of sediment was occurring in summer and downestuary in winter and that the mass transport was accentuated for the fine material. Subsequently, this hypothesis has been substantiated by a study of the seasonal cycle of accretion/erosion of sediment in the estuary (Bale *et al.*, 1985).

The tidal curve for the mid-estuarine region of the Tamar is asymmetrical (George, 1975; Uncles *et al.*, 1985) with a long ebb period and a short, high energy flood. This means that the flood period is characterised by high upestuary current velocities which move suspended sediment upestuary towards the turbidity maximum zone. The material deposited at slack water is only partially remobilised by the weaker ebb currents. This process is known as tidal pumping and accounts for the accretion of fine-grained sediment at the head

Figure 8
The 3-dimensional representation of the grain size composition of the sediments of the Tamar Estuary.

of the estuary during low to average river flows. By the end of summer, a large quantity of erodable material has accumulated at the head of the estuary. During high winter river flows, the turbidity maximum zone migrates downestuary exposing this material to erosion by river current and large tidal velocities occurring on the ebb current. Previously deposited bed sediment is resuspended under these high energy conditions and transported downestuary. The tidal asymmetry for neap tides is not so pronounced and major transport occurs during spring tides (Uncles et al., 1985). This process accounts for the net loss of sediment from the head of the estuary and the decrease in the proportion of fine-grained material in winter.

The normalised total metal concentrations and an average sediment density of $2650 \ kg \ m^{-3}$ were used to calculate the metal content per unit volume of sediment. Using this data as well as the time-distance information, 3-dimensional plots showing the temporal variations in the axial distribution of Fe, Cu, Zn and Mn in the estuarine sediment were constructed (Fig. 9-12).

The behaviour of the metals can be distinguished by their prevalence for participation in either chemical or physical processes. The Mn profile (Fig. 9) shows large inputs of particulate Mn at the head of the estuary in response to seasonal variations in the river flow. However, Mn is a highly reactive element (Morris et al., 1982a), with 80-100% of particulate Mn in the non-detrital form. In the 0-5 km region the concentration of Mn decreases significantly and lower estuary concentrations are about an order of magnitude lower than those in the upper sections. This arises because riverine particulate Mn undergoes internal chemical cycling in the region of the freshwater-brackish water interface and is eventually transported seawards in the dissolved rather than particulate phase. Furthermore, downestuary of 5 km the profile does not show any strong seasonal effects associated with the physically-dominated tidal pumping mechanism.

In contrast to Mn, the particulate Fe behaviour (Fig. 10) is less chemically dominated as may be expected for an element with typically <10% in an exchangeable form. There is evidence in Figure 10 that Fe is largely controlled by physical transport processes, including tidal pumping. Inputs into the upper sections coincided with increased river flows in the winter of 1980/81 with additional particulate Fe being derived from the mine spoil tips at the side of the estuary. In spring 1981, the metal levels decreased as the flow rate decreased but the Fe peak was smeared downestuary to about 10 km. However, during the low flow conditions in summer 1981, iron-rich material was brought from below the 0-5 km region as upestuary tidal pumping developed. Following this, the higher winter flow rates returned and the iron-rich material migrated downestuary as a prelude to the process being repeated. The sediment metal contents in the lower estuary essentially confirm this mechanism, since there was evidence of the loss of Fe to the upper estuary in summer 1981 and accretion in the winter of 1981/1982. This cycle is complicated by intermittent behaviour in the mid-estuarine region (approximately 15 km) where sediment divergence may occur (Uncles et al., 1985). Due to the shape of the estuary at this point tidal asymmetry is
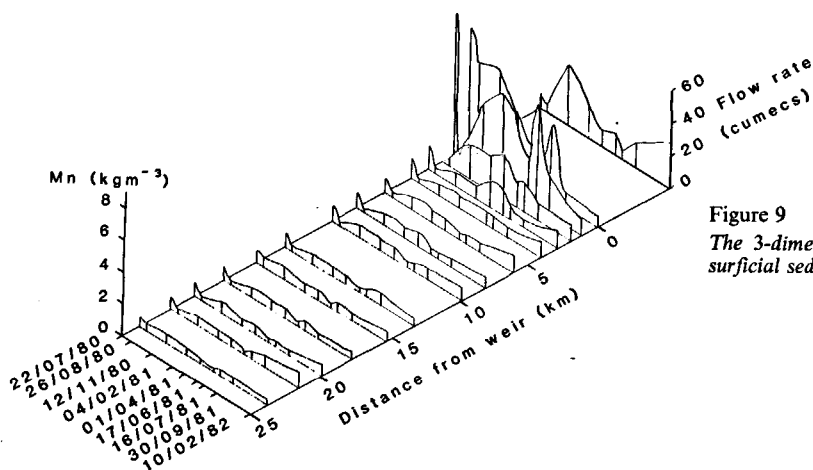

Figure 9
The 3-dimensional representation of total manganese content in the surficial sediments in the Tamar Estuary.
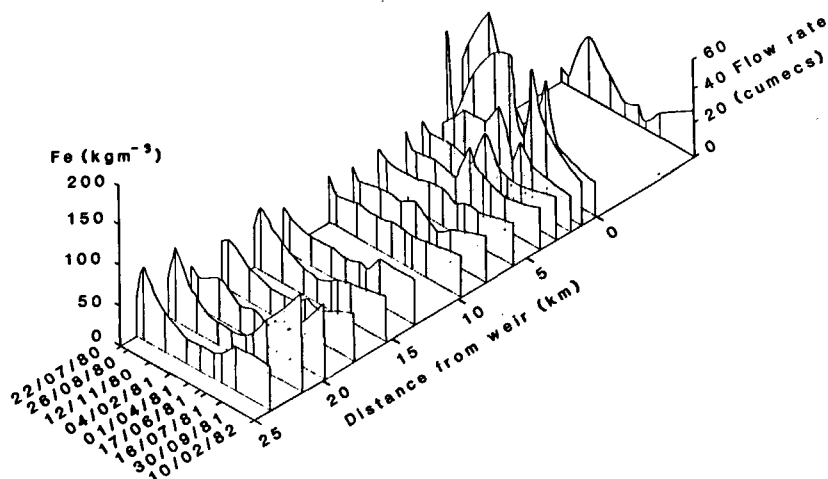

Figure 10
The 3-dimensional representation of total iron content in the surficial sediments of the Tamar Estuary.

Figure 11
The 3-dimensional representation of total zinc content in the surficial sediments of the Tamar Estuary.
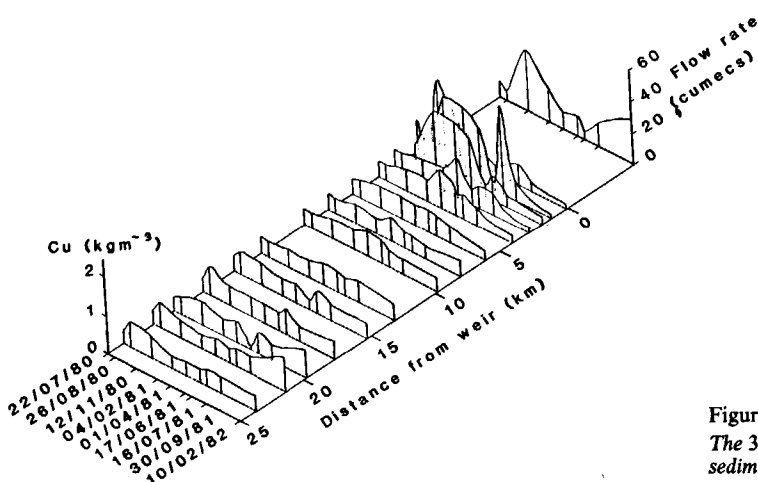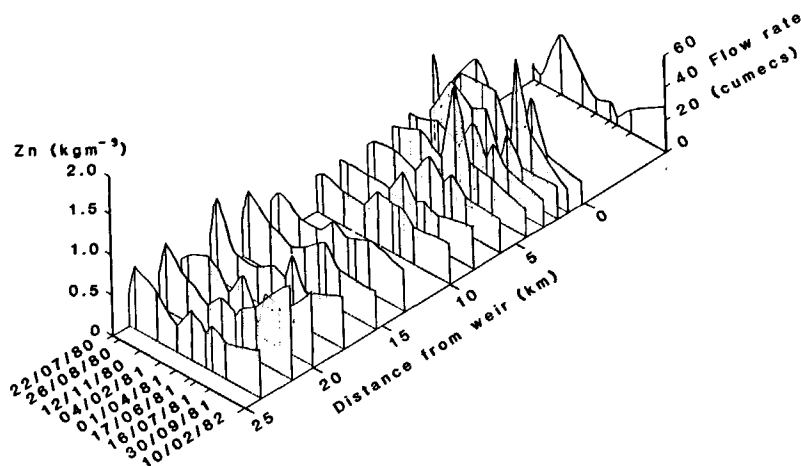

Figure 12

The 3-dimensional representation of total copper content in the surficial sediments of the Tamar Estuary.

very pronounced and sediment transport is almost always downstream seaward of 15 km, whereas upestuary the direction of movement is reversible depending on the magnitude of the river flux, *i.e.* a null point in the chemical composition of the sediments. The conclusion here is that sedimentary Fe, unlike Mn, is less susceptible to chemical transport mechanisms and is solely controlled by physical processes.

The time series plots for Zn and Cu are shown in Figures 11 and 12, respectively. The chemical analyses showed that the non-detrital Zn content was about 60%, with a uniform concentration (around 250 ppm) throughout the estuary. The zinc profile shows similarities to that of Fe and it does not compare well with the Mn profile, despite the high proportion of exchangeable metal. The reason for the apparently anomalous behaviour of Zn is that it has no redox chemistry and it is strongly adsorbed to Fe oxide phases. This means that Zn is dominated by the same physical transport processes as Fe. In contrast the Cu time series plot (Fig. 12) bears some similarities to that of Mn, even though only 20% of the Cu is in the non-detrital phase. However, the non-detrital Cu concentrations decrease by a factor of two from the head of the estuary to the seaward end. Thus, Cu behaviour is a combination of both chemical and physical processes.

In conclusion all the metals show upper estuarine distributions which are dependent on the input of new particulate material associated with the seasonal variations in river flow. In the lower estuary the Mn concentrations decreased to low values due to the chemical reactivity of this element. However, the seasonal variations of Fe and Zn are controlled by the tidal pumping mechanism. Copper was also responsive to this physical transport process but there was also evidence of desorption of copper from sediment particles. It is clear that the estuarine chemistry of Cu and Zn is poorly understood and further work is required.

Acknowledgements

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