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FACTORS CONTROLLING THE AVAILABILITY OF SEDIMENT-BOUND LEAD TO THE ESTUARINE BIVALVE *SCROBICULARIA PLANA*

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(Figs. 1–4)

Concentrations of lead in the soft tissues of the deposit-feeding bivalve *Scrobicularia plana* have been compared with the physicochemical characteristics of sediments in 20 estuaries in southern and western England and one in north-west France. The results indicate that the biological availability of lead in the sediment is controlled mainly by the concentration of iron, and that the concentration of lead in the bivalve may be predicted from the Pb/Fe ratio in 1 N hydrochloric acid extracts of surface sediments.

INTRODUCTION

Realistic prediction of the impact of heavy metals in sediments upon aquatic biological resources will require an understanding of how physical and chemical factors affect metal uptake by organisms. In an attempt to obtain this, we have compared the concentrations of metals in the soft tissues of the deposit-feeding bivalve *Scrobicularia plana* (da Costa) in various estuaries with metal concentrations in extracts of the sediments. This paper describes our results for lead and shows that its biological availability in the sediment is strongly influenced by the level of readily extractable iron.

MATERIALS AND METHODS

Samples for the statistical analyses were collected from 17 estuaries in south and west England (see Table 1) during the high river-flow period between February and mid-May 1977. Sediment samples were collected from the oxidized surface layer of intertidal sediments and, as soon as possible after collection, were wet sieved through 100 μm polyethylene mesh using diluted sea water. Following overnight settlement, separate 2 ml subsamples of wet sediment were extracted for 2 h with 20 ml of 1 N ammonium acetate, 0·2 M ammonium oxalate in oxalic acid (Schwertmann, 1964) or 25 % acetic acid (pH adjusted to 2·2 with nitric acid) and for 30 min with 0·1 M hydroxylammonium chloride in 0·01 N nitric acid (Chao, 1972). Subsamples of 1 g of air-dried sediment were extracted for 2 h with 10 ml of 1 N hydrochloric acid or wet-ashed overnight with nitric acid to give a 'total' extract (Bryan & Uysal, 1978). The 30 min and 2 h extractions were carried out in 20 ml glass scintillation-counting vials, which were shaken at frequent intervals. The extract was separated from the sediment by filtration under pressure through a 0·45 μm membrane filter.

Animals were held in clean 50 % sea water for one week to allow depuration of undigested sediment; soft tissues were then pooled into 3–7 replicate samples, each made up of 3–5 similar sized individuals, and wet-ashed with nitric acid (Bryan & Uysal, 1978). Tissue samples and sediment extracts were analysed for metals using flame atomic absorption spectrophotometry. Background correction was used for all lead analyses but not for iron.

Most of the lead in *Scrobicularia* lies in the digestive gland, and the concentration is dependent upon the size of the organism (Bryan & Uysal, 1978; Bryan & Hummerstone, 1978). For this study, lead concentrations for each station were averaged from results for animals having lengths within 50 % of that of the largest. Size/age data from some estuaries suggested that this method probably compares levels in animals from a similar age range. This technique enabled more animals to be involved in the analyses than could be used when comparisons were restricted to animals of about 40 mm shell length (Bryan & Uysal, 1978), but the two systems usually give similar results. Lead concentrations in animals with ripe gonads were about 25 % lower than in normal animals from the same station. Corrections for this tissue dilution were applied on the comparatively few occasions when only ripe animals were encountered.

RESULTS AND DISCUSSION

Variations among estuaries

Concentrations of lead in both sediments and bivalves ranged through nearly two orders of magnitude (Table 1). The watersheds of the estuaries include agricultural lands, industrial/urban areas and former metal mining areas, thus providing diverse

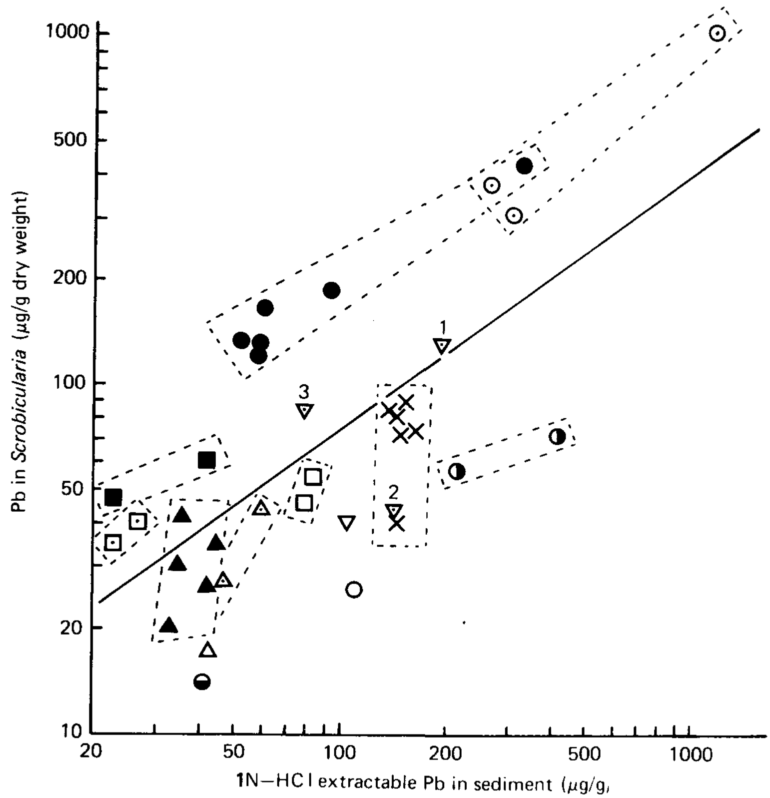

Fig. 1. Correlation between concentration of lead in soft tissues of *Scrobicularia plana* and concentration extracted from surface sediment with 1 N hydrochloric acid. Boxes enclose stations from each estuary and these are Torridge (⊡), Erme (■), Fowey (▲), Camel (◒), Beaulieu (△), Plym (△), Bristol Channel (□), Poole Harbour (▽), Hayle (○), Southampton area (▽), (1 Itchen, 2 Test, 3 Hamble), Tamar/Tavy (×), Looe (●), Restronguet Creek (◑), Gannel (⊙). Equation for line is $\log_{10}$ Pb animal = 0·728 $\log_{10}$ Pb sediment + 0·417 (n = 37, r = 0·69).

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Table 1. *Characteristics of estuaries sampled in south-west England: metal concentrations in sediments measured following extraction with* 1 N HCl

For positions of sampling sites see Appendix.

Estuary	Month of sampling	Range of Pb concentrations (μg/g dry wt) Sediment	Range of Pb concentrations (μg/g dry wt) *S. plana*	Range of Fe concentrations (mg/g) Sediment	Watershed characteristic
Torridge	May	22–26	35–40	4·2	Agricultural
Erme	Feb.	22–42	47–60	2·5–4·0	Agricultural
Fowey	May	33–44	20–42	2·7–3·5	Old mines in watershed
Camel	Apr.	41	14	3·7	Old mines in watershed
Beaulieu	Apr.	42	17	11·6	Agricultural
Plym	Feb.	46–60	27–44	2·8–2·9	Industrial/urban
Bristol Channel (Watchet and Minehead Harbours)	May	80–83	49–54	5·9–6·6	Urban/industrial
Poole (Inner Harbour)	Apr.	103	40	9·8	Industrial/urban
Hayle	Apr.	111	26	10·4	Old mines on river
Southampton area (Test/Itchen/Hamble)	Apr.	78–193	44–132	6·9–7·1	Industrial/urban
Tamar/Tavy	Mar.	139–162	40–88	7·2–10·0	Old mines on estuaries
Looe	Mar.	52–326	120–428	2·1–3·5	Old mines on river
Restronguet Creek (Fal)	Mar.	210–401	58–72	16·1–17·3	Old mines on river
Gannel	Apr.	264–1134	309–1016	4·2–6·0	Old mines on river

sources of lead contamination. When the concentrations of lead in the animals were compared with those of sediment extracts, significant correlations were found with the lead extracted by 1 N hydrochloric acid ($r = 0·69$), 25% acetic acid ($r = 0·68$) and the nitric acid digest ($r = 0·61$), but not with the lead concentrations in the other extractants. The concentration of lead extracted by hydroxylammonium chloride was affected by the carbonate content of some sediments and the amounts extracted with ammonium acetate were generally too low for accurate analysis. Concentrations extracted from the sediment with 1 N hydrochloric acid are compared with those of the animals in Fig. 1. Results for individual estuaries are fairly tightly grouped and within some, such as the Looe and Gannel, there is a clear relationship between levels in the animals and sediments. Between estuaries there is considerable variation. For example, at a sediment concentration of 400 μg/g, animals from Restronguet Creek contain about 60 μg/g whereas those from the Looe and Gannel Estuaries contain about 400 μg/g. These results suggested that reasons for such variation would be found by looking at inter-estuary differences between the characteristics of the sediments.

The physicochemical characteristics of the estuaries varied widely. Predominant sediment particle size ranged from sand to silt/clay; organic carbon ranged from 1·14 to 6·3% and calcium carbonate from less than 1 to 30%. There were also considerable differences between the average salinities at different sites. Although any or all of these factors may influence the biological availability of metals, none completely explains the variance in the relationship between acid-soluble lead in sediments and lead levels in *Scrobicularia*. There was also no significant correlation between concentrations in *Scrobicularia* and in the seaweed *Fucus vesiculosus* from the same sites ($r = 0·04$). Assuming that seaweed is an indicator of biologically available lead in the water column (Bryan & Hummerstone, 1973), it appears that concentrations of dissolved lead had little influence on those in *Scrobicularia*.

Influence of iron on the availability of lead

In lieu of a technique for extracting biologically available lead directly, relationships were sought between acid-soluble lead and other components of the sediment which might bind the metal, since the type of substrate to which a metal is bound may strongly affect the availability of the metal to the bivalves (Luoma & Jenne, 1977). Hydrous oxides of iron are an important component of oxidized sediments and are probably an important sink, binding heavy metals in sediments (Jenne, 1968).

The relationship between concentrations of lead and iron in hydrochloric acid extracts is shown in Fig. 2 (similar results were obtained with 25% acetic acid). Two types of correlation characterized the lead–iron relationship. The regression for the nine stations in the Gannel and Looe estuaries had a significantly different slope from that for the remaining stations. The latter slope probably implies a chemical relationship between lead and iron oxide in the sediments (Hem, 1970). The sediments in the Gannel and Looe Estuaries, which receive wastes from old lead mines, had much higher lead concentrations at a given iron concentration than did the other estuaries, and the slope of the lead–iron relationship implies that significant quantities of lead are bound to substrates other than iron oxide (Hem, 1970). Concentrations of lead in *Scrobicularia* from the

Gannel and Looe Estuaries were also higher than those in other estuaries (Fig. 1). When the concentrations of lead in animals from all stations were plotted against the Pb/Fe ratios for the 1 N hydrochloric acid extracts on logarithmic scales (Fig. 3) a highly significant correlation was obtained ($r = 0.88$). Using linear scales (Fig. 4), the value of r was increased to 0·99. Depending upon the method of statistical analysis, 78–94% of the variance in the lead levels of *Scrobicularia* could be predicted from

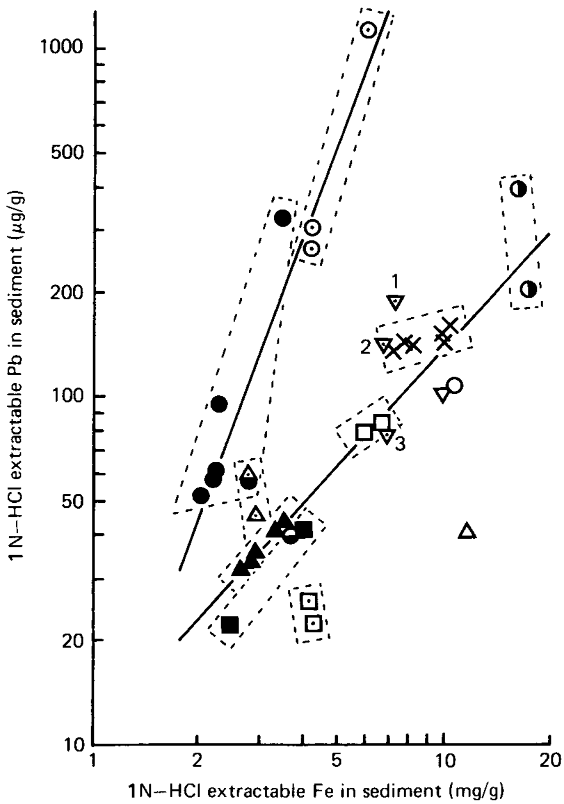

Fig. 2. Correlation between concentrations of lead and iron extracted from surface sediments with 1 N hydrochloric acid. Symbols as for Fig. 1. Equation for Gannel and Looe results is $\log_{10}$ Pb sediment = 2·79 $\log_{10}$ Fe sediment + 0·801 ($n = 9$, $r = 0.95$). Equation for other results is $\log_{10}$ Pb sediment = 1·097 $\log_{10}$ Fe sediment + 1·029 ($n = 28$, $r = 0.82$).

variations in the Pb/Fe ratio. Some variance remained unexplained among some of the lower lead concentrations in the bivalve (this was the cause of the weaker correlation for the logarithmically transformed data) but, in general, the relationship appears to provide a reliable predictive tool.

When concentrations extracted from the sediment by digestion with nitric acid ('total' extractable metal) were used in the Pb/Fe ratio, the correlation with lead concentration in *Scrobicularia* was inferior to correlations observed using the 1 N hydrochloric acid or 25% acetic acid extracts. The weaker acids remove much of the lead (45–92%) from the sediment, but a smaller proportion of the iron (15–40%).

Additional iron removed by the nitric acid includes large quantities of the more crystalline iron oxide phases, while the weaker acids remove primarily the more amorphous, heavy-metal reactive phases of the oxide (Jenne & Luoma, 1977). This readily extractable iron appears to be mainly responsible for controlling the biological availability of lead to *Scrobicularia*.

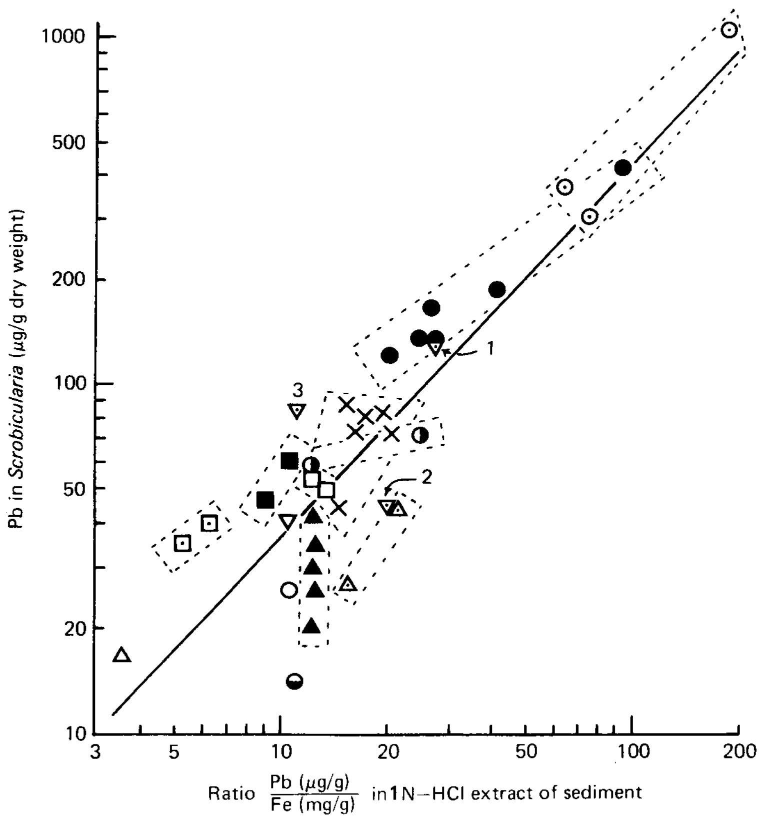

Fig. 3. Correlation between concentration of lead in soft tissues of *Scrobicularia plana* and ratio Pb/Fe extracted with 1 N hydrochloric acid. Symbols as for Fig. 1. Equation for results on logarithmic scales is $\log_{10}$ Pb animal = 1·071 $\log_{10}$ Pb/Fe + 0·496 (n = 37, r = 0·88).

Iron may influence the availability of lead to *Scrobicularia* in at least two ways. If both metals are released in the digestive tract, then iron may compete with lead for binding or transport sites, thus affecting its uptake. On the other hand, the concentration of iron in the sediment may also affect availability by influencing the physicochemical form of sediment-bound lead. To the extent that mass balance controls the partitioning of lead among different sinks in the sediment, increasing concentrations of iron may result in increasing lead partitioning to the iron oxide sink. If the biological availability of iron oxide-bound lead is low relative to forms such as organically bound lead, then the concentration in the animal could be inversely affected by increasing the iron content of the sediment. In the digestive tract, undigested iron oxide also may be competing for lead with other, possibly more digestible, components of the sediment and with the tissues. Although we have no conclusive evidence to indicate whether competition from soluble iron released into the gut or the binding capacity of insoluble iron oxide is the more important control on the uptake of lead, we tend to favour the latter explanation.

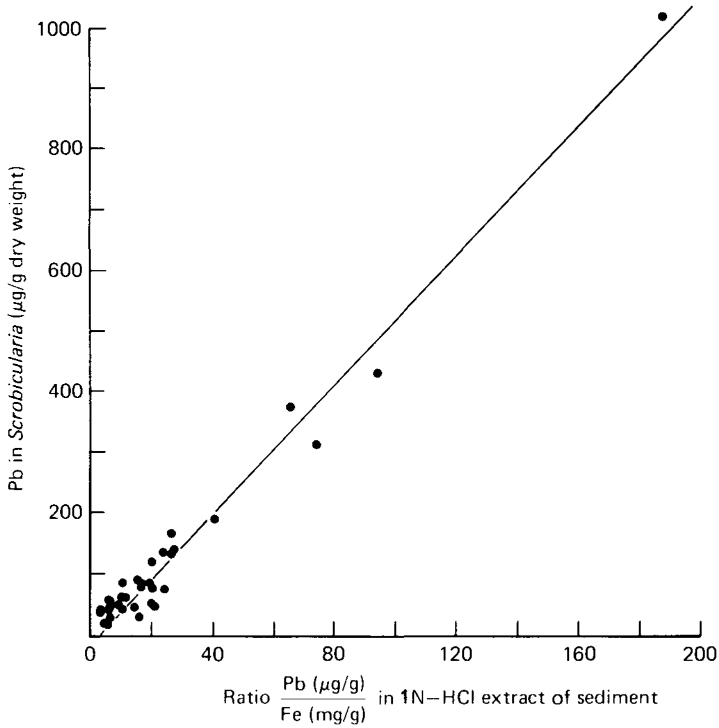

Fig. 4. Correlation between concentrations of lead in soft tissues of *Scrobicularia plana* and ratio Pb/Fe extracted with 1 N hydrochloric acid. Equation for results on linear scales is Pb animal = 5·32 Pb/Fe − 20 ($n = 37$, $r = 0{\cdot}99$).

Prediction of lead availability to Scrobicularia

The linear correlation

$$Y = 5{\cdot}32\,X - 20, \qquad (1)$$

where Y is the lead concentration in *Scrobicularia* and X is the Pb/Fe ratio (μg/g divided by mg/g) for 1 N hydrochloric acid extracts (Fig. 4), was used to predict lead concentrations in animals from some additional estuaries in different geographic regions (Table 2). These additional estuaries are the relatively pristine Otter and Axe (Devon) in south-west England; and the Thames in south-east England and the l'Elorn in north-west France, both of which receive appreciable amounts of urban and industrial waste. The concentrations of lead in *Scrobicularia* from all four estuaries agreed reasonably with the concentrations predicted from the Pb/Fe ratios in the sediments.

Table 2. *The concentrations of Pb observed in sediments (HCl extraction) and soft tissues of* Scrobicularia plana *from six estuaries compared with the concentration of Pb predicted for* S. plana *from the Pb/Fe ratio in the sediments*

Station numbers increase from the head to the mouth of the estuary.
For positions of sampling sites see Appendix.

Estuary		Month of sampling	Concentration of HCl-soluble Pb in sediment (μg/g)	Observed concentration of Pb in *S. plana* (μg/g dry wt)	Predicted concentration of Pb in *S. plana* (μg/g dry wt)
Axe	1	May*	25	8	9
	2		23	16	5
	3		22	29	20
Otter	1	May*	30	18	22
Thames	1	Nov.	57	25	36
	2		57	29	38
l'Elorn	1	Aug.	71	31†	34
	2		83	37†	42
E. Looe	1	Aug.	93	104†	128
	2		61	176†	97
	3		59	134	116
	4		63	165†	121
Gannel	2	Nov.	417 (wet)	327	330
			435 (dry)	327	322

* Sediment frozen until November. † Concentration corrected for ripe gonads.

To test the effect of seasonal changes on the usefulness of the relationship, sediments and animals were sampled from the Looe and Gannel Estuaries on a second occasion (Table 2). Again, the concentrations of lead predicted in the animals by the linear regression agreed reasonably with the observed concentrations, despite the fact that many of the animals had ripe gonads and a correction was necessary (see Methods). Results from the Gannel Estuary also show that the predicted concentration appears to be independent of whether dry or wet sediment is extracted with 1 N hydrochloric acid (Table 2). It is interesting to note that although the sediments of the East Looe and l'Elorn Estuaries showed similar degrees of lead contamination, the concentrations of lead in animals from the East Looe were 3–4 times those from the l'Elorn. Higher concentrations of weak acid-soluble iron in the sediments of the l'Elorn (7·1 mg/g) than in the sediments of the East Looe (2·3–3·3 mg/g) appear to greatly reduce the availability of lead to the l'Elorn animals.*

In about half of the estuaries we have studied, the regression equation

$$\log_{10} Y = 1{\cdot}071 \log_{10} X + 0{\cdot}496, \qquad (2)$$

gave slightly more accurate predictions of lead concentrations in *Scrobicularia* (Fig. 3). The use of the log-transformed data may be preferable at stations with very low Pb/Fe ratios, since the *Y*-intercept of equation (1) may result in predictions of negative values in such instances. However, equation (1) is preferable for higher values and was used for all predictions in Table 2.

In conclusion, the results indicate that the concentration of lead in *Scrobicularia* is largely controlled by the concentration in the sediment as modified by the inhibitory

* See note added in proof, p. 802.

effects of iron. The Pb/Fe ratio in 1 N hydrochloric acid extracts of sediments appears to reflect the availability of lead to *Scrobicularia*, since this value is almost directly proportional to the concentration of lead in the animal. Measurements of this ratio may be a useful way of assessing the biological availability of lead in estuarine sediments where *Scrobicularia* do not occur. Although this simple relationship works well for predictions of the availability of lead, preliminary results suggest that predictive relationships for other metals may be more complex.

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APPENDIX

Positions of sampling sites

Estuary	Locality	National Grid Reference
Bristol Channel	Watchet Harbour	ST072435
	Minehead Harbour	SS972471
Torridge	Westleigh	SS467289
Camel	Wadebridge	SW987730
Gannel	(1) Upper	SW809606
	(2) Middle	SW804607
	(3) Lower	SW798609
Hayle	Upper	SW547364

Estuary	Locality	National Grid Reference
Restronguet Creek	Point	SW805387
	Point	SW813386
Fowey	Newham	SX109578
	Newham	SX111574
	St Winnow	SX114570
	St Winnow	SX120566
	Cliff	SX127554
Looe (West)	(1) Upper	SX237544
	(2) Middle	SX245541
Looe (East)	(1) Upper	SX248557
	(2) Upper	SX251555
	(3) Middle	SX252548
	(4) Confluence	SX252540
Tamar	North Hooe	SX420657
	Halton Quay	SX412653
	Clifton Quay	SX422645
	Weir Quay	SX434645
	Saltash	SX432592
Tavy	Bere Ferrers	SX462636
Plym	Saltram	SX516560
	Laira Bridge	SX503544
Erme	Clyng Mill	SX627490
	Efford House	SX622493
Otter	(1) Budleigh Salterton	SY075823
Axe	(1) Upper	SY256916
	(2) Middle	SY254909
	(3) Seaton	SY253902
Poole Harbour	Inner	SZ005930
Beaulieu	Beaulieu	SU390023
Test	Totton	SU369133
Itchen	Northam Bridge	SU439130
Hamble	Lower Swanwick	SU495092
Thames	(1) Coalhouse Fort	TQ691762
	(2) Thorpe Bay	TQ916844
l'Elorn (Brest, France)	(1) 10·3 km } above Pont Albert Louppe (2) 3·5 km }	

Note added in proof:

In May 1978, *Scrobicularia* and surface sediment were analysed from the Humber Estuary into which large quantities of industrial and domestic wastes are discharged. A 1N hydrochloric extraction of the sediment gave concentrations of 191 μg/g of lead and 21 mg/g of iron; this latter value is the highest we have observed for iron. The Pb/Fe ratio predicted a lead concentration of 28 μg/g in *Scrobicularia*: 22 μg/g was observed. This result contrasts sharply with those for the Looe Estuary (Table 1) since, although the concentrations of extractable lead in the sediments of the two estuaries are of the same order, levels in the animals are an order of magnitude higher in the Looe Estuary where the concentration of extractable iron in the sediment is an order of magnitude lower.