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INDICATORS OF HEAVY-METAL CONTAMINATION IN THE LOOE ESTUARY (CORNWALL) WITH PARTICULAR REGARD TO SILVER AND LEAD

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(Figs. 1–4)

The Looe Estuary in Cornwall has two equal branches, one receiving lead and silver from old mines and the other receiving silver from a presumed industrial source. Analyses of these and eight other metals have been made in seaweed (*Fucus*) as an indicator of levels in the water, in herbivorous gastropods (winkle *Littorina littorea*; limpet *Patella vulgata*), in filter feeders (mussel *Mytilus edulis*; cockle *Cerastoderma edule*) as indicators of contamination in suspended particles and in deposit feeders (bivalve molluscs *Scrobicularia plana* and *Macoma balthica*; ragworm *Nereis diversicolor*) as indicators of available metals in sediments.

There was little evidence of contamination with dissolved silver in the estuary but considerable evidence of contamination by particles of freshwater origin. Although the concentrations of particulate silver from the two sources were of the same order of magnitude, the influence of the non-mining source was much greater, a concentration of silver 425 times normal being observed in *Scrobicularia* at an upstream station. It was concluded that particles, perhaps of silver sulphide, from the mining source were of much lower biological availability than those from the other source where silver may be adsorbed on to particles.

Unlike silver, contamination with lead followed a similar pattern in different species. Of the other metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Zn) the most abnormal levels in the different species were observed for copper.

INTRODUCTION

A map of the Looe Estuary in south-east Cornwall is shown in Fig. 1. As it flows to the western branch of the estuary, the West Looe River passes through the Herodsfoot mining area which lies about 5 km above Sowden's Bridge. By Cornish standards, this was a productive area for lead and Dewey (1921) gives the output of Herodsfoot mine as 13470 tons of metal between 1848 and 1884 and more than 17 tons of silver between 1853 and 1884.

In 1972 a small survey of metals in sediments and benthic organisms showed that, as might be expected, the West Looe branch of the estuary was more heavily contaminated with lead than the East Looe branch. On the other hand, it was surprising to find the highest levels of silver in the East Looe Estuary since this river does not appear to be associated with mining.

Because silver is a rare contaminant of estuaries in south-west England, two surveys were conducted in December 1975 and March 1976 to see how the ability to accumulate silver, lead and other metals varies between different estuarine species which have been used or suggested as indicators of metal contamination.

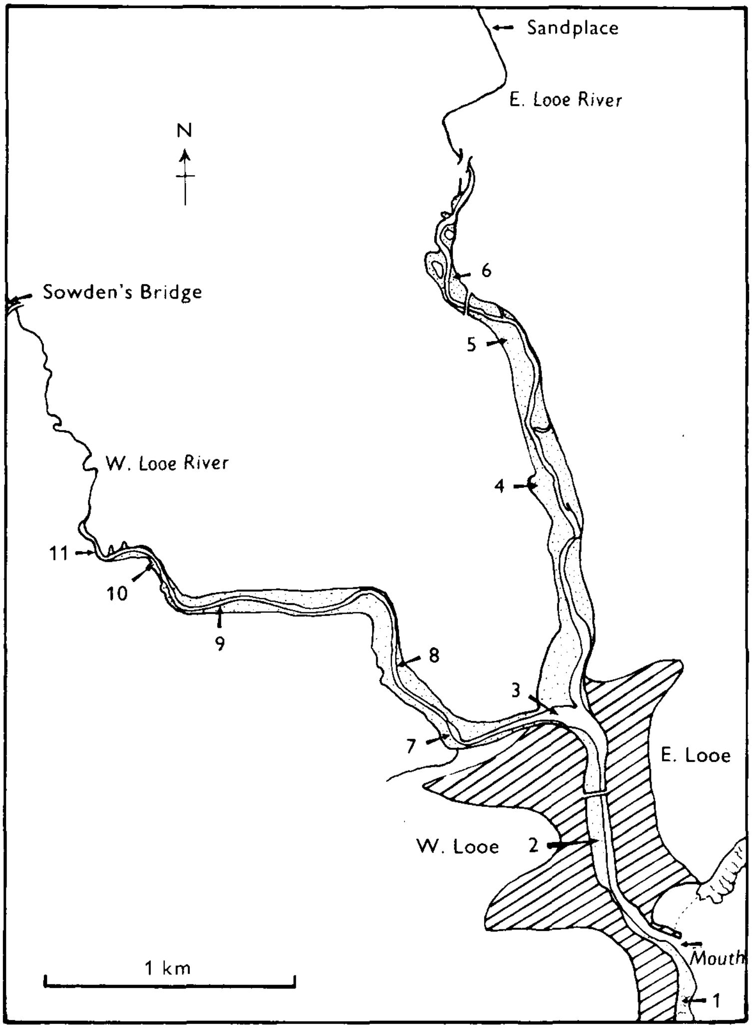

Fig. 1. Looe Estuary showing positions of intertidal sampling areas. Based on the 1:25000 Ordnance Survey Map with the sanction of the Controller of H.M. Stationery Office, Crown copyright reserved.

METHODS

Organisms and surface sediments were collected at 11 stations or areas which, as far as possible, were situated slightly above the mid-tide level in the intertidal zone (Fig. 1; Table 2). Before analysis, some sediment was air dried without sieving. The remainder was shaken with distilled water of pH 7 in a Gallenkamp Andreasen's pipette apparatus and, after settling for 15 min at 20 °C, a sample of fine particles ($\sim < 14$ μm) was withdrawn and dried. This was repeated several times to give sufficient sample for analysis. Seaweed was washed and samples were pooled from pieces taken from the older parts of several plants (Bryan & Hummerstone, 1973*a*). To remove most of the gut contents, animals were kept for a week in clean water before analysis. In the case of *Nereis diversicolor*, acid-washed sand was also used in the cleaning process (Bryan & Hummerstone, 1973*b*). The pooled soft parts from five or more animals were dried and, together with sediment samples, digested with Aristar nitric acid (20 ml for 0·4–1·0 g dry material) in flasks sealed with glass bubbles. After about 24 h the samples were evaporated to dryness and then dissolved in hydrochloric acid which was diluted to give a 1·2 N solution. Samples of river water were filtered through 0·45 μm membrane filters and, after adding a few ml of nitric acid, evaporated to dryness. The filters were digested with nitric acid and both residues dissolved in hydrochloric acid to give a 1·2 N solution. Analyses of samples and blanks were carried out with a Perkin-Elmer 306 atomic absorption instrument using background correction for Ag, Cd, Co, Ni, and Pb. Standard additions were used to check the recoveries of metals. This enabled corrections to be made for the effect of iron on chromium analyses of sediments and showed that analyses of silver in tissues were not seriously affected by lipids which are difficult to digest with nitric acid (Anderlini, 1974).

RESULTS AND DISCUSSION

Metals in the sediments

Thornton, Watling & Darracott (1975) have advocated the analysis of freshwater sediment as a means of recognizing areas of mineralization or metal contamination. Results for silver and lead in freshwater sediments are compared with those in the estuary in Fig. 2A–B. Differences between concentrations in the whole sediment and fine fraction reflect the texture of the sediment, the difference being greatest for coarse sediment. There were also differences between surface sediments in the estuary in December 1975 and March 1976 which were probably caused by seasonal changes in the tidal regime and in the capacity of the incoming fresh water to carry suspended sediments.

TABLE 1. CONCENTRATIONS OF METALS IN FRESHWATER SEDIMENTS

		Concentrations (ppm dry weight)									
		Ag	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
E. Looe River (Sandplace)	Total	15·3	1·3	19	59	65	37100	373	57	155	329
	Fine	14·9	—	—	76	64	44000	606	60	196	353
W. Looe River (Sowden's Bridge)	Total	2·8	0·1	17	37	60	35100	667	44	544	174
	Fine	6·9	—	10	48	131	56900	1200	58	1240	342

Concentrations of lead and silver in sediments from the West Looe River increased by almost an order of magnitude downstream of the Herodsfoot mine and then declined in the estuary as they were diluted by material from the other branch and from the sea. Particularly high concentrations found 3·6 km from the sea in the West Looe Estuary in December appear to have been caused by the river cutting into very metallic sediment which might have been deposited when the mines were working. Analyses of sediment cores from the West Looe branch showed concentrations of both metals increasing with depth. This indicates that input from the old mines is gradually falling.

In the East Looe River, concentrations of silver in the sediments increased by roughly an order of magnitude in the Liskeard area between Mooreswater and Trussel Bridge and the highest concentration of 15 ppm occurred in fine sediment at Sandplace which comes under tidal influence but is probably never saline (Fig. 2A; Table 1). From Sandplace the level of silver fell by about two orders of magnitude to the sea. Analyses of two cores in the East Looe Estuary showed that the highest levels of silver lay a few cm below the surface and judging from the Ag/Pb ratios, silver which was not introduced

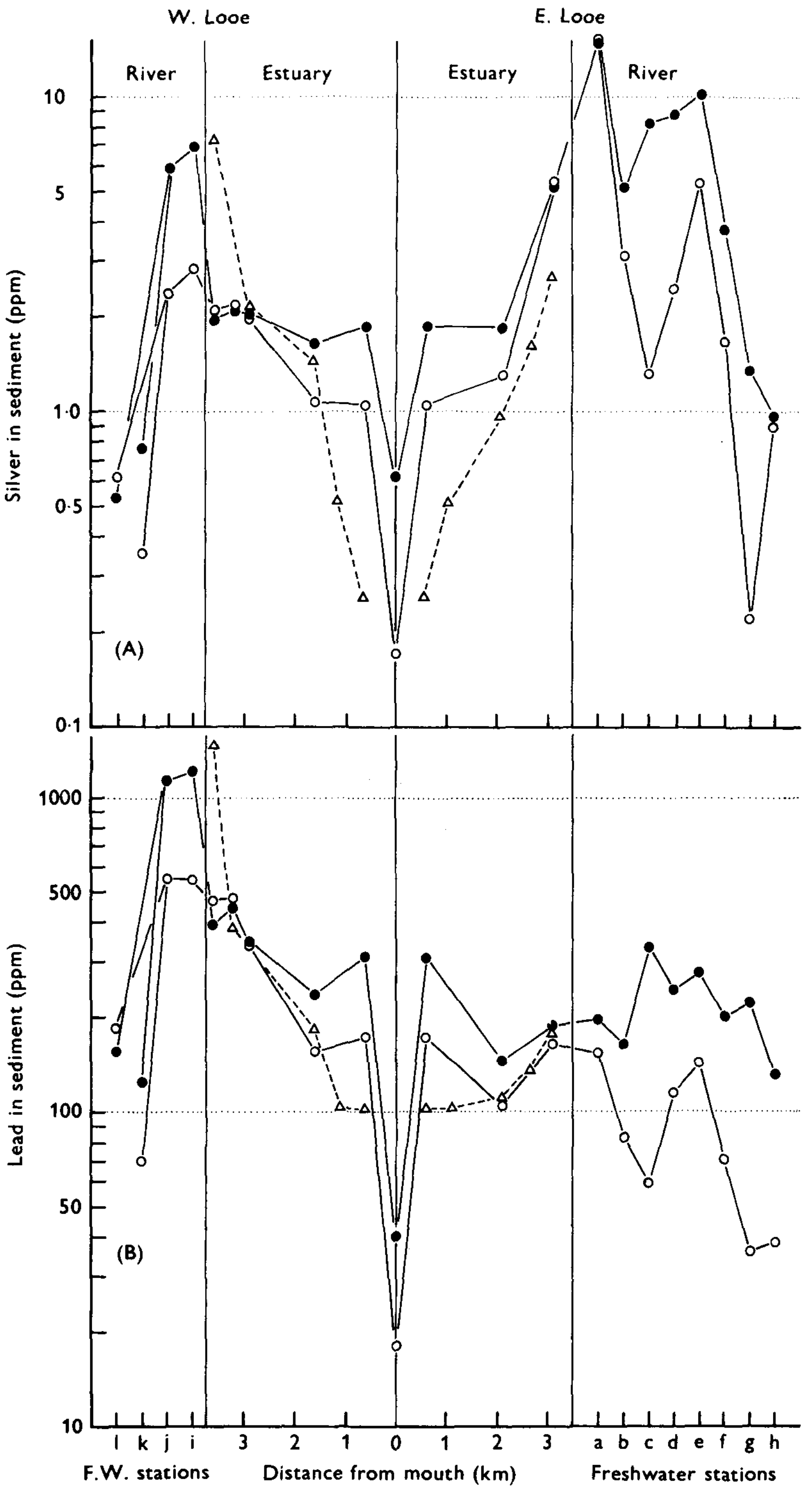

Fig. 2. (A) Concentrations of silver in surface sediments. (B) Concentrations of lead in surface sediments. △, total in December 1975; ○, total in March 1976; ●, fine fraction in March 1976. Freshwater stations: a, Sandplace; b, Plashford; c, Landlooe Bridge; d, Lametton Bridge; e, Trussel Bridge; f, Lodge Hill; g, Mooreswater; h, High Wood; i, Sowden's Bridge; j, below Herodsfoot; k, Cliver Wood; l, Connon Bridge.

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with lead from the West Looe branch occurred to a depth of at least 20 cm. To some extent this observation may be due to the mixing of sediments through the activities of the burrowing worm *Nereis diversicolor*, but it does suggest that silver contamination of this part of the estuary is of many years standing.

Concentrations of other metals in freshwater sediments from the stations nearest to the East and West Looe Estuaries are shown in Table 1 and values for the estuaries are summarized in Table 4. Over the sections of the two rivers which were sampled, there was no evidence for a marked increase in metal input other than that which was observed for silver in the East Looe River and for silver and lead in the West Looe River. Due to the mixing of sediments of freshwater and marine origin the estuarine sediments showed a general fall in concentration towards the sea although copper appears to be an exception since some of the highest levels were found in the harbour about 0·6 km from the mouth of the estuary.

Although the analysis of sediments serves as a very useful guide to metal contamination in the Looe Estuary, it gives little information about the biological availability of metals and their accumulation by organisms which is the basic cause for concern about contamination.

Metals in estuarine organisms

Table 2 summarizes the distribution of the more common species within the estuary and includes information about the salinity of the interstitial water from the sediment. The salinity of the surface sediment is thought to reflect recent conditions in the overlying water whereas that at depth may more nearly reflect average conditions during the year. Several of these species have been suggested or used as biological indicators of metal contamination and their occurrence together in this small estuary seemed to be a good opportunity to test their reactions to silver and lead in particular.

Some of the properties required in indicator organisms for analysis in estuaries include: (1) They should be common, accessible, relatively stationary and easily recognized. (2) They should be sufficiently tolerant of estuarine conditions to be distributed along a reasonable length of estuary and should be available at all times of year. (3) They should be large enough to provide a reasonable sample for analysis. (4) Organisms are required which are good accumulators of metals but do not regulate metals. That is, the concentration in the organism should change predictably with the availability of metals.

One object of this survey was to see whether species possessing the first three groups of properties possess the important fourth property, that of reflecting changes in the biological availability of metals. Another object was to see whether metallic contamination in solution, in suspension or in the sediments and interstitial water could be assessed separately by using a range of selective species. These points are considered particularly with regard to silver in subsequent sections.

Indicators of silver contamination

Silver in seaweed and solution

Concentrations of silver were measured in the brown seaweed *Fucus vesiculosus* from all areas except 6 and 11 (Fig. 1) where *Fucus ceranoides* was analysed. Brown seaweeds

TABLE 2. DISTRIBUTION OF SPECIES IN LOOE ESTUARY

Sampling area (Fig. 1)	km from mouth	S ‰ of sediment interstitial water in March 1976 (Depth)		Brown seaweeds		Herbivores		Filter feeders		Deposit feeders			Carnivore
		0–5 cm	15–20 cm	*Fucus vesiculosus*	*Fucus ceranoides*	*Littorina littorea*	*Patella vulgata*	*Cerastoderma edule*	*Mytilus edulis*	*Scrobicularia plana*	*Macoma balthica*	*Nereis diversicolor*	*Nucella lapillus*
1	.	~34	.	+	−	+	+	−	+	−	−	−	+
2	0·6	15·2	.	+	−	+	+	+	+	*	−	+	+
3	1·1	15·7	26·9	+	−	+	+	+	+	+	*	+	*
4	2·1	13·4	26·1	+	−	+	+	+	+	+	+	+	−
5	2·7	.	.	+	?	+	−	*	−	+	+	+	−
6	3·1	3·9	16·4	−	+	−	−	−	−	+	−	+	−
7	1·6	.	.	+	−	+	+	+	+	+	*	+	−
8	2·1	14·0	26·9	+	−	+	−	+	−	+	*	+	−
9	2·9	.	.	+	−	+	−	−	−	+	−	+	−
10	3·2	.	.	+	?	−	−	−	−	+	−	+	−
11	3·6	1·8	6·8	−	+	−	−	−	−	−	−	+	−

* Single or very few specimens.
? Lower limit unknown.

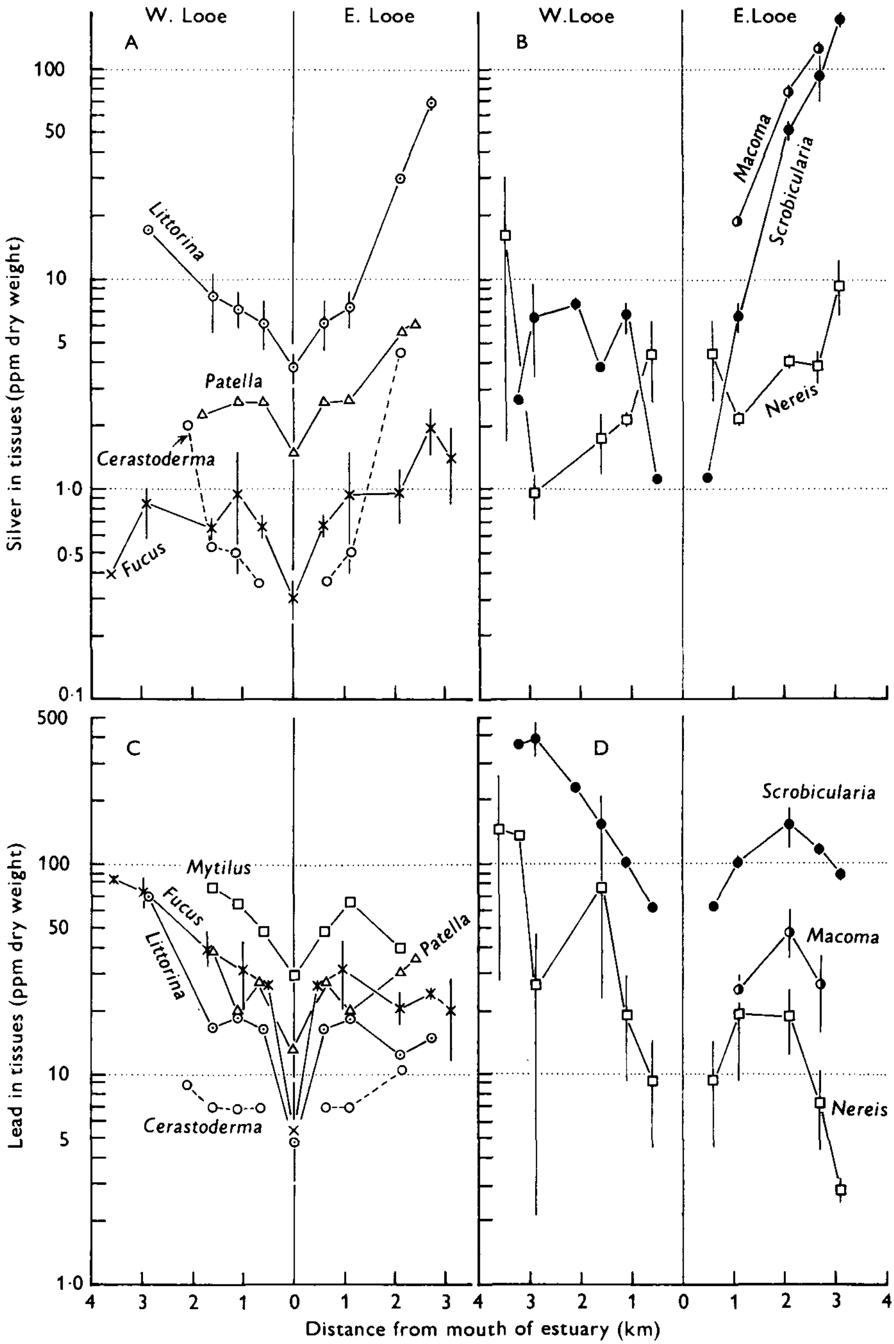

Fig. 3. (A, B) Silver in whole soft parts of estuarine organisms. (C, D) Lead in whole soft parts of estuarine organisms. Vertical lines show range of values from two surveys for some species. As far as possible, organisms of similar size were collected at each station.

are known to reflect changes in the soluble concentrations of some metals in the water (Bryan, 1969; Bryan & Hummerstone, 1973*a*; Morris & Bale, 1975) and unpublished work with *Laminaria digitata* suggests that this applies to silver also. The results in Fig. 3A imply that concentrations in the water were highest in the East Looe Estuary. Preston *et al.* (1972) found a concentration factor for *Fucus* in coastal regions of 5×10^3 (concentration in dry weed/concentration in water). Applying this factor to the results in Fig. 3A infers a concentration of 0·06 ppb (parts per billion) in water near the mouth of the estuary, which equals the value given by Preston *et al.*, and a maximum soluble concentration of 0·4 ppb in the East Looe Estuary. In the East Looe River soluble concentrations of 0·09–0·31 ppb were found at Sandplace (Fig. 1) and particulate concentrations of 0·07–0·4 ppb. Farther upstream at Lodge Hill soluble concentrations were 0·1–0·8 ppb and particulate concentrations 0·35–2·0 ppb. The soluble concentrations inferred by seaweed in the estuary are of the same order as those found in the river and probably represent average levels in the estuary over a period of several months. There is also the possibility that some of the insoluble silver in the river water may be released in the estuary, because Murray & Murray (1973) and Fukai & Murray (1974) have shown that, perhaps due to complex formation with chloride ions in sea water, silver adsorbed by particles of freshwater origin may be desorbed. Although analyses of the sediments pointed to silver contamination in both estuaries, this is not very evident from analyses of the seaweed and water.

Silver in herbivores

Species such as the limpet *Patella vulgata* and the winkle *Littorina littorea* which graze on small algae might be expected to indicate a pattern of distribution of silver in the estuary similar to that of the seaweed *Fucus*. This appears to be true for *Patella*, which contained higher levels than *Fucus* (Fig. 3A). Preston *et al.* (1972) calculated a concentration factor of $3 \cdot 1 \times 10^4$ for silver in *Patella* which divided into the present results would infer concentrations of 0·05 ppb in water near the mouth of the estuary increasing to 0·2 ppb in the middle reaches of the East Looe branch. These values compare favourably with those in the previous section.

Near the mouth of the estuary, *Littorina* contained about 13 times as much silver as *Fucus* but this factor increased to 20 in the West Looe branch of the estuary and 35 in the East Looe branch (Fig. 3A). Of many possible explanations, the simplest may be that this is caused by the greater contamination of ingested algae with sediment particles at the most upstream stations.

Silver in filter feeders

Bivalve molluscs such as the cockle *Cerastoderma edule* and the mussel *Mytilus edulis* feed on suspended particles and are generally thought to obtain a higher proportion of metals from this source than from solution (see for example, Pentreath, 1973). Results for *Cerastoderma* in Fig. 3A show that concentrations increased by more than an order of magnitude in an upstream direction in the East Looe branch. This pattern, as might be expected, more closely resembles the distribution of silver in the surface sediments in Fig. 2A than the distribution in the water as indicated by *Fucus* in Fig. 3A.

TABLE 3. COMPARISON BETWEEN CONCENTRATIONS OF SILVER AND LEAD IN LOOE ESTUARY WITH MORE NORMAL AREAS

Numbers of stations in Fig. 1 are shown in parentheses

	Concentrations (ppm dry weight)									
	Fucus sp.	*Littorina littorea*	*Patella vulgata*	*Cerastoderma edule*	*Mytilus edulis*	*Scrobicularia plana*	*Macoma balthica*	*Nereis diversicolor*	*Nucella lapillus*	Surface sediment
No. of samples	20	12	9	9	9	17	5	19	4	19
Silver										
Mean	0·82	19·6	3·0	1·52	0·23	40	85	5·2	2·7	1·5
Maximum	2·42 (5)	73 (6)	6·0 (4)	6·5 (4)	0·55 (2)	185 (6)	128 (5)	30 (11)	4·2 (2)	7·3 (11)
Minimum	0·24 (1)	3·2 (1)	1·5 (1)	0·11 (2)	0·10 (7)	1·1 (2)	19 (3)	0·7 (9)	1·3 (1)	0·17 (1)
'Normal'	0·2*	2·5†	1·7†	—	0·13†	0·4§	—	0·4‖	2·5†	0·1‖
Lead										
Mean	38	19	25	8·1	54	189	34	45	5·1	280
Maximum	86 (11)	70 (9)	38 (7)	15·6 (4)	105 (7)	473 (9)	61 (4)	261 (11)	7·1 (2)	2030 (11)
Minimum	3·1 (1)	3·7 (1)	5·1 (1)	4·7 (7)	30 (1)	62 (2)	15 (5)	2·1 (9)	1·9 (1)	18 (1)
'Normal'	2·1*	9·2†	8·6†	5·0‡	20†	13§	—	5·0‖	5·0†	50‖

* Preston *et al.* (1972).
† English Channel coast of S. Devon–similar size animals.
‡ Boyden (1975).
§ Camel estuary N. Cornwall–similar size animals.
‖ S. Devon estuaries.

On the other hand, *Mytilus edulis* showed no tendency to increase in concentration in an upstream direction and values remained low (Table 3). Tests were conducted to see whether any undigested lipids in the samples were affecting the analyses (Anderlini, 1974) or whether the metal was being lost during the week spent in clean water prior to analysis. Samples from station 4 in the East Looe Estuary were analysed, after wet digestion or dry ashing at 450 °C, 1 and 8 days after cleaning but the concentrations (~0·25 ppm) were not significantly different. The observed values come within a range for *Mytilus* summarized by Fowler & Oregioni (1976), but the value of this species as an indicator of particulate silver contamination seems to be very doubtful.

Silver in deposit feeders

The bivalve mollusc *Scrobicularia plana* feeds mainly on surface sediment and its response to the input of silver was so great that its concentration increased by more than two orders of magnitude in the East Looe Estuary (Fig. 3B). Over the same range of distribution, concentrations in surface sediments increased by perhaps one order of magnitude (Fig. 2A). In the upper reaches of the East Looe Estuary, the concentration of silver in the sediment (about 5 ppm) was 2–3 times that in the West Looe branch. By comparison, mean concentrations in *Scrobicularia* reached 170 ppm in the East Looe Estuary, almost 23 times the maximum of 7·5 ppm in animals from the West Looe Estuary (Fig. 3B).

The most likely explanation of this result is that silver associated with particles entering the East Looe Estuary was of far greater biological availability than that entering the West Looe branch. In the estuary as a whole, most of the silver probably exists as the very insoluble sulphide. Any silver temporarily or permanently buried in the sediments of the upper estuary, where reducing conditions are found near the surface, is likely to be converted to sulphide and to remain in this form unless reoxidized by bacterial action. The source of silver in the West Looe River appears to be the sulphide ores of the Herodsfoot area and so some silver may enter the estuary in this form. In the East Looe River, the form of particulate silver seems far less likely to be sulphide and much of it may be adsorbed on to particles.

The high availability of silver in the East Looe Estuary was also reflected by the deposit-feeding bivalve *Macoma balthica*. This is a much smaller animal than *Scrobicularia* but at the same stations contained even higher levels of silver (Fig. 3B). An experimental study of the availability to *Macoma* of radioactive silver from artificial sediments of different types has been made by Luoma & Jenne (1976). They observed that the availability of silver from association with the hydrated oxides of iron and manganese was high whereas its availability from an organic source was low. It seems quite possible that the readily available silver entering the East Looe Estuary is associated with the hydrated oxide layers of iron on particles. This availability will fall in a downstream direction in the estuary more rapidly than the total concentration of silver in the surface sediment, as the particles become temporarily buried and the silver reduced to sulphide which is assumed to be less readily available.

Silver forms complexes with ammonia and evidence for chemical differences between the sediments was obtained by shaking 0·3 g samples of dry sediment with 3 ml of 1 N ammonia solution for 5 h. About 36% of the total (HNO_3 extractable) silver was dissolved from the East Looe River sediment compared with 4·5% for sediment having similar texture from the West Looe River. For the estuarine sediments, which were finer, about 8% was extracted from the upper East Looe sample compared with 3·5% from the upper West Looe sample. These results are compatible with the idea that particularly in the East Looe branch the chemical form and availability of silver changes markedly when it enters the estuary.

The burrowing polychaete *Nereis diversicolor* is rather more widely distributed within the estuary than *Scrobicularia* and yet its concentration of silver varied by no more than an order of magnitude overall (Fig. 3B). With the exception of the 0·6 km station, concentrations in *Nereis* were more nearly related to the total concentrations in the sediments (Fig. 2A) and Bryan (1974) observed that concentrations of silver in *Nereis* are usually of the same order as those in the sediment. The much lower accumulation of silver in *Nereis* than *Scrobicularia* in the upper reaches of the East Looe Estuary could be explained if the worms were feeding on the walls of their burrows, where the silver would be present as sulphide, rather than on the surface of the sediment where the more readily available silver would be found. On the other hand, silver is absorbed fairly readily from solution by *Nereis* (Bryan, 1976) and it is possible that the animal reflects the availability of silver in the interstitial water rather than in the sediment particles.

Silver in carnivores

The dogwhelk *Nucella lapillus* which feeds mainly on barnacles was the only carnivore to be considered. However, it lacks tolerance of estuarine conditions and was common only at the two most seaward stations. Concentrations of silver are shown in Table 3 and were significantly higher in the estuary.

Summary

Contamination of the Looe Estuary with silver comes from an old mining source on the West Looe River and from a presumed industrial source on the East Looe River. There is little evidence of high levels of silver in solution and contamination is mainly confined to suspended particles and sediments. Analysis of deposit-feeding bivalves has indicated that silver is much more readily available from particles entering the East Looe Estuary than the West Looe, although, perhaps due to conversion to sulphide, availability falls rapidly downstream. The mean, maximum and minimum concentrations in the sediments and organisms are summarized in Table 3 and compared with values from uncontaminated areas. In species found near the mouth of the estuary, levels of silver were practically normal. This suggests that much of the silver is deposited in the estuary and any reaching the sea is rapidly dispersed. For estuarine species such as *Scrobicularia*, the lowest concentrations were abnormally high and the highest concentration was 425 times normal.

Although the toxicity of silver to marine organisms usually comes second to that of mercury, there is no definite evidence that the highest concentrations in Table 3 have had any toxic effects. Compared with animals from other estuaries in the area, *Scrobi-*

cularia grows to an appreciably smaller size in the Looe Estuary but it has not been shown whether this is related to metal contamination or to other factors such as overcrowding. Birds such as the oystercatcher *Haematopus ostralegus* are probably the main predators on the contaminated shellfish (Hughes, 1970).

Indicators of lead contamination

Concentrations in the sediments are shown in Fig. 2B and indicate that the West Looe Estuary receives far more particulate lead than the East Looe branch. Analyses of the brown seaweed *Fucus* in Fig. 3C suggest that levels of available lead in the water declined by more than a factor of ten from the upper reaches of the West Looe branch to the sea and also tended to fall upstream in the East Looe branch which has a much smaller input. The work of Preston *et al.* (1972) and Foster (1976) indicates a concentration factor for lead in *Fucus* of around 3×10^3 and this would infer concentrations in the water ranging from about 2 ppb near the mouth to about 28 ppb in the upper West Looe Estuary.

A pattern similar to that for *Fucus* was also shown by *Littorina* and *Patella*, the two herbivores (Fig. 3C). A concentration factor for lead in *Patella* of $5{\cdot}5 \times 10^3$ was found by Preston *et al.* (1972) and in the Looe Estuary would infer levels of 2·5 ppb at the mouth rising to about 7 ppb in the middle reaches of the West Looe Estuary.

Of the filter feeders, *Mytilus edulis* is a much better accumulator of lead than *Cerastoderma* and the pattern of distribution resembled that in the weed. Possibly in *Mytilus* more lead is absorbed from solution than from particulates. A similar argument might explain the lack of influence of particulate silver on concentrations in *Mytilus* (see p. 84). From experimental results, Schulz-Baldes (1974) calculated a concentration factor of $3{\cdot}5 \times 10^4$ for lead in *Mytilus* assuming that equal amounts were absorbed from food and water. This figure would give a soluble concentration of about 1 ppb near the mouth and more than 2 ppb in the West Looe Estuary. Agreement between the various estimates for the water is not unreasonable and a soluble concentration near the mouth of the estuary of 1–2 ppb is comparable with levels observed in other coastal regions (see, for example, Preston *et al.* 1972; Foster, 1976), although values in the open sea may be an order of magnitude lower than this.

Results for deposit feeders in Fig. 3D follow roughly the same pattern as the other species in Fig. 3C and the sediments in Fig. 2B, although there is a peak at the 2 km mark in the East Looe Estuary for these species which is not evident in the other results. Details of the hydrography of the estuary are unknown but these peaks suggest that at certain times particles from the West Looe Estuary are deflected into the other branch by the incoming tide. Concentrations of lead in *Scrobicularia* exceed those in all other species and values from the two surveys were remarkably similar. Unlike many molluscs, including *Mytilus*, *Cerastoderma* and *Patella*, where concentrations of lead tend to fall as the animal grows (Boyden, 1974), concentrations in *Scrobicularia* increase with increasing size or age, the metal being largely stored in the digestive gland. Although showing the same general pattern as the other species, concentrations in the worm *Nereis diversicolor* were remarkably variable, especially in the more contaminated areas. At the most upstream station in the West Looe Estuary this appeared to be caused by wide variations between patches of sediment caused by the erosion of old rather metallic deposits. In December 1975 animals containing 260 ppm were associated with surface sediment containing over 2000 ppm whereas in March 1976 animals containing 28 ppm were associated with sediment containing 400–500 ppm. Wide variation at other stations could not be explained in these terms. The variability in *Nereis* compared with *Scrobicularia* may be a function of diet and longevity as well as of changing concentrations in the environment. Judging from the way in which numbers of *Nereis* change with season, its life-cycle may occupy about 1 year. As a result, concentrations in the body are more likely to be influenced by factors such as rapid growth rate which can dilute existing concentrations. *Scrobicularia*, on the other hand, is fairly long lived and those analysed in the present work were estimated to be 6–7 years old. In addition, the uptake and loss of metals seems to be extremely slow with only small changes occurring over periods of several months. As a result, *Scrobicularia* may integrate levels of contamination over a period of years compared with perhaps a few months in *Nereis*. With regard to diet, *Scrobicularia* is mainly a deposit feeder (Hughes, 1969), but *Nereis* is regarded as omnivorous since it can feed on sediments, filter feed and use its jaws to ingest larger pieces of food (Harley, 1953; Goerke, 1971). As a result, variations in metal intake seem much more likely to occur in *Nereis*.

The distribution of lead in different species in Fig. 3C, D has a more consistent pattern than was observed for silver. Unlike silver, there is only one source of lead contamination and there is no evidence of differences in the availability of lead in the two estuaries. Lead sulphide seems likely to be a dominant particulate form since sulphide ores appear to be the source of contamination and other forms of lead are probably converted to sulphide under the reducing conditions just below the surface of some of the sediments.

The mean, maximum and minimum concentrations in the sediments and organisms are compared with values from uncontaminated areas in Table 3. Lowest levels of lead were found in species occurring near the mouth of the estuary and seem to be practically normal. However, the highest levels in species such as *Fucus*, *Scrobicularia* and *Nereis* from the upper Looe Estuary were 30–50 times normal. Thus lead contamination is largely confined to the estuary and any reaching the sea must be rapidly dispersed.

Concentrations of other metals in the estuary

The concentrations of eight other metals in the sediments and organisms are summarized in Table 4 and results for *Fucus* and *Scrobicularia* are shown in Fig. 4A–B.

Cadmium

The tendency for concentrations to fall in a downstream direction was least evident in *Fucus* but much more obvious in *Scrobicularia* and in the sediments where the metal was almost undetectable near the mouth of the estuary. Work by Preston *et al.* (1972), Morris & Bale (1975) and Foster (1976) suggests a concentration factor of around 10^4 in *Fucus*. This value would infer concentrations in the water ranging from about 0·09–0·18 ppb in the estuary, figures not much higher than that of 0·05 ppb considered typical of

TABLE 4. SUMMARY OF CONCENTRATIONS OF HEAVY METALS IN LOOE ESTUARY FROM BOTH SURVEYS

Numbers of stations in Fig. 1 are shown in parentheses.

	Concentrations (ppm dry weight)									
	Fucus sp.	*Littorina littorea**	*Patella vulgata*	*Cerastoderma edule*	*Mytilus edulis*	*Scrobicularia plana*	*Macoma balthica*	*Nereis diversicolor*	*Nucella lapillus**	Surface sediment
No. of samples	22	12	9	8	9	18	4	20	4	20
Cadmium										
Mean	1·30	1·38	8·6	0·84	1·78	1·62	0·67	0·53	12·8	0·2
Maximum	2·41 (9)	2·56 (9)	21·5 (4)	1·04 (7)	2·64 (1)	3·37 (6)	0·85 (4)	3·4 (6)	16·0 (2)	0·54 (6)
Minimum	0·86 (1)	0·49 (7)	3·3 (1)	0·48 (7)	0·84 (2)	0·60 (7)	0·21 (4)	< 0·1 (2)	5·5 (1)	< 0·1 (1)
Cobalt										
Mean	5·28	1·35	0·88	1·89	0·55	8·9	4·9	4·7	0·69	11·1
Maximum	10·5 (9)	3·04 (9)	1·56 (2)	2·93 (7)	1·07 (7)	17·7 (6)	6·8 (5)	7·9 (11)	1·16 (2)	16·6 (6)
Minimum	0·6 (1)	0·79 (7)	0·24 (1)	1·28 (8)	0·02 (2)	2·4 (2)	3·7 (4)	1·6 (2)	0·19 (1)	1·3 (1)
Chromium										
Mean	2·24	0·64	1·38	2·04	1·92	2·77	2·52	0·55	2·16	36
Maximum	3·54 (6)	0·98 (3)	2·62 (2)	2·46 (3)	2·74 (1)	3·89 (4)	3·30 (4)	2·39 (2)	5·61 (2)	55 (6)
Minimum	0·56 (1)	0·13 (7)	0·48 (4)	1·34 (2)	0·94 (2)	1·08 (7)	1·89 (5)	< 0·1 (10)	0·39 (1)	22 (1)
Copper										
Mean	17	124	19	9·8	9·5	133	300	44	110	63
Maximum	33 (2)	194 (5)	27 (3)	27·2 (4)	13·6 (3)	365 (4)	615 (3)	78 (11)	141 (2)	178 (11)
Minimum	3·5 (1)	62 (7)	10 (1)	5·2 (7)	3·9 (7)	16 (2)	96 (5)	22 (6)	51 (1)	13 (1)
Iron										
Mean	1450	446	1640	597	284	1090	997	362	214	27900
Maximum	3020 (6)	784 (3)	2330 (7)	991 (4)	401 (4)	3010 (6)	1540 (5)	462 (11)	270 (1)	31700 (6)
Minimum	121 (1)	272 (1)	891 (1)	406 (7)	152 (2)	559 (3)	502 (3)	260 (7)	193 (2)	17900 (1)
Manganese										
Mean	363	44	13·3	15·0	14·6	43	22	9·5	16·8	426
Maximum	692 (9)	133 (9)	36·0 (2)	44·6 (7)	35·4 (7)	100 (6)	24 (4)	12·5 (11)	23·3 (2)	778 (6)
Minimum	94 (1)	18 (2)	5·4 (7)	6·2 (4)	5·2 (4)	25 (4)	19 (3)	7·6 (3)	11·4 (1)	294 (8)
Nickel										
Mean	9·7	3·1	2·5	44	2·2	9·4	7·5	3·3	2·3	34
Maximum	13·6 (9)	4·1 (2)	3·7 (2)	62 (7)	3·5 (3)	13·9 (9)	7·9 (4)	5·2 (11)	4·1 (2)	51 (6)
Minimum	5·7 (1)	2·2 (7)	1·7 (3)	34 (3)	0·9 (2)	5·3 (2)	6·9 (4)	2·1 (2)	1·4 (1)	23 (3)
Zinc										
Mean	198	117	165	55	132	974	804	215	416	151
Maximum	340 (9)	284 (5)	224 (4)	66 (7)	199 (1)	1600 (9)	1160 (5)	258 (4)	520 (2)	250 (6)
Minimum	56 (1)	45 (7)	83 (1)	46 (8)	57 (7)	606 (3)	510 (3)	170 (3)	235 (1)	47 (1)
Range of dry weights of soft parts (g)	—	(0·18–0·36)	(0·38–1·2)	(0·26–0·6)	(0·16–0·75)	(0·14–0·3)	(0·04–0·06)	(0·02–0·03)	(0·15–0·22)	—

* Includes operculum.

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oceanic waters (Riley & Chester, 1971). Figures for the various species in Table 4 are comparable with values from other areas and there is no evidence of contamination in the Looe Estuary.

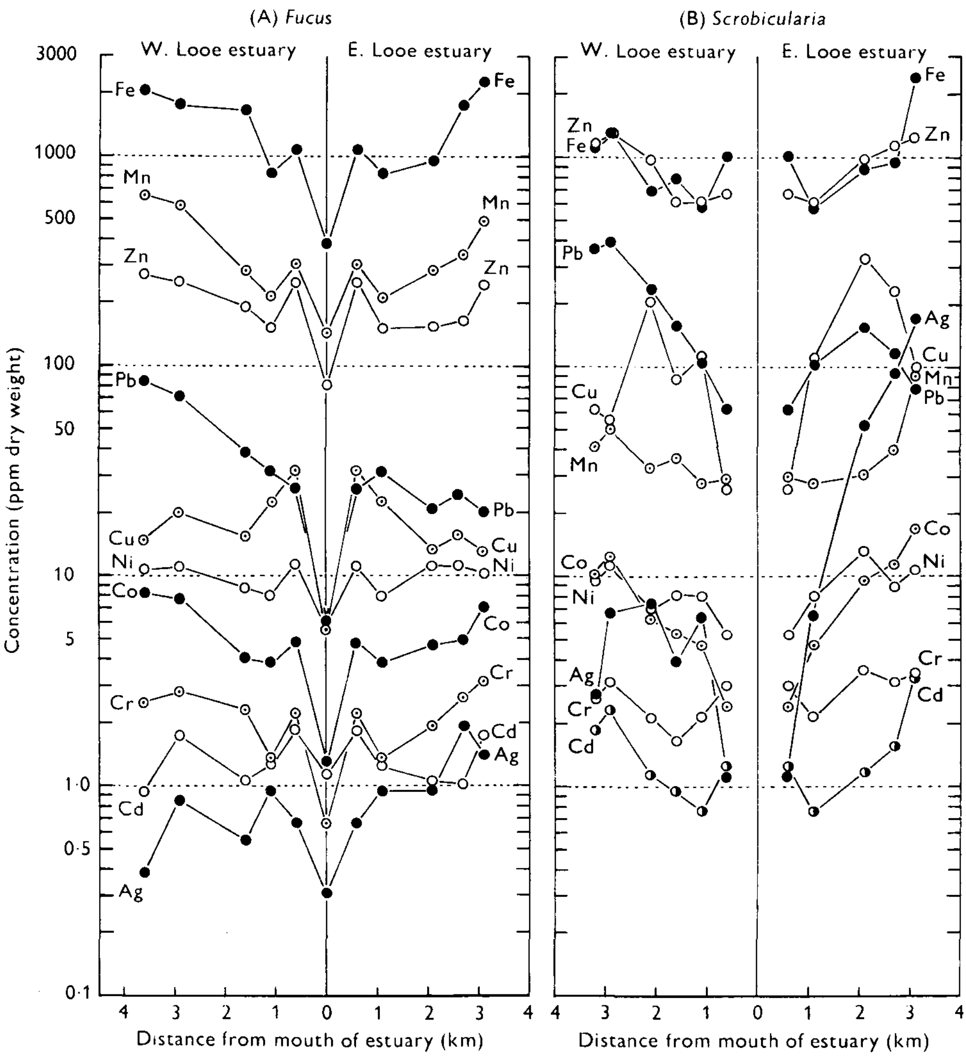

Fig. 4. (A) Concentrations of metals in older part of thallus in *Fucus*. (B) Concentrations of metals in soft tissues of *Scrobicularia* of about 34 mm shell length.

Cobalt

There was a very clear fall in all concentrations in a downstream direction (Fig. 4A–B). Assuming a concentration factor in *Fucus* of 6×10^3 similar to nickel, would indicate concentrations in the water of 0·1 ppb near the mouth increasing to 1·3 ppb in the upper reaches of the East Looe Estuary. Two samples of fresh water from the river contained 0·3 and 0·5 ppb in solution compared with the 0·2 ppb regarded as typical of river water (Riley & Chester, 1971). Concentrations for the sediments and organisms in Table 4 seem to be fairly normal for these species and there is little evidence of contamination.

Chromium

Generally speaking, concentrations fell towards the mouth of the estuary and this is clearly shown for *Fucus* in Fig. 4C. Using a concentration factor of 10^4 in *Fucus*, as suggested by the work of Foster (1976), infers concentrations in the water increasing from 0·06 ppb at the mouth to 0·3 ppb in the upper estuary. Values ranging from 0·35–0·9 ppb were found in the waters of the two rivers and compare favourably with the typical value of 1 ppb given by Riley & Chester (1971). Similarly, there is no evidence of contamination of sediments and organisms in Table 4.

Copper

In *Fucus* the highest level of copper was found in the harbour (Fig. 4A) which suggests an input from the town of Looe or conceivably from antifouling paints and ships' fittings. Additional evidence was provided by other species including *Nereis*, *Macoma*, *Patella* and *Mytilus* and, although patchy, concentrations of up to 174 ppm were found in the harbour sediments. There was little evidence for contamination in *Cerastoderma* or in *Littorina* which may be able to regulate copper since it contains haemocyanin. As Fig. 4B shows, high levels of copper occur in *Scrobicularia* from the middle reaches of both branches. Whether this is indicative of contamination is uncertain since these results do not appear to relate to the others and we have observed unusually high levels of copper in this species in other estuaries where there was no other evidence of contamination.

Assuming a concentration factor of 10^4 for copper in *Fucus* infers concentrations in the water ranging from 0·5 ppb near the mouth to 3 ppb in the harbour and 1·4 ppb in the upper reaches. The incoming river waters were found to contain about 1 ppb of soluble copper and there is no evidence of contamination from these sources. Although there is evidence for contamination in the harbour area, this is relative to the rest of the estuary. Higher concentrations of copper occur in the water, sediments and organisms from the Tamar Estuary which is regarded as being relatively unpolluted (Bryan & Hummerstone, 1971, 1973*a*).

Iron and manganese

In the majority of species concentrations of both metals fell towards the mouth of the estuary in a comparable way (Fig. 4A–B). This is not unexpected since concentrations of both metals in fresh water are usually much higher than those in the sea. In the two rivers we found soluble concentrations of 3–7 ppb for manganese and about 25 ppb of iron compared with less than 1 ppb for both metals in the English Channel given by Preston *et al.* (1972). By comparison with other species, concentrations of both metals varied least in *Nereis diversicolor* despite its very wide distribution. Bryan & Hummerstone (1971) suggested that *Nereis* regulates iron and this is strongly supported by the present results. Concentrations of manganese were also consistent with what has been found previously in *Nereis* (Bryan & Hummerstone, 1973*c*). No unusual concentrations of either metal have been found in the Looe Estuary.

Nickel

Generally speaking, concentrations of nickel in the various species showed less tendency to change within the estuary than those of other metals (Table 4; Fig. 4A–B). The highest levels were found in the cockle *Cerastoderma edule* and this seems to be quite normal since Boyden (1975) found similar concentrations in animals from the less contaminated parts of Poole harbour. Concentration factors for nickel in *Fucus* have been given as 2.8×10^3 by Preston *et al.* (1972) and 6.8×10^3 by Foster (1976). Using the higher value infers concentrations ranging from 0·9 ppb near the mouth of the estuary to about 1·7 ppb within the estuary and a similar level was found in the East Looe River. There is no evidence of contamination of the estuary with nickel.

Zinc

In most species and in the sediments concentrations of zinc fell towards the mouth, although the levels in *Nereis*, where regulation occurs, and in *Cerastoderma* remained remarkably constant. As with most other metals the results for *Fucus* in Fig. 4A hint at an additional slight input of metal in the harbour area (0·6 km). Using a concentration factor for zinc in *Fucus* of 6.8×10^4 (Bryan & Hummerstone, 1973*a*) infers concentrations of zinc in the water ranging from about 1·2 ppb near the mouth to about 4 ppb at upstream stations. Values for the two rivers were variable and ranged from 0·7–28 ppb in solution. The concentrations for various species which are summarized in Table 4 indicate that, for the most part, levels of zinc in the Looe Estuary are fairly normal.

It is concluded that of the ten metals studied, only silver, lead and perhaps copper occur in abnormal quantities in the Looe Estuary.

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