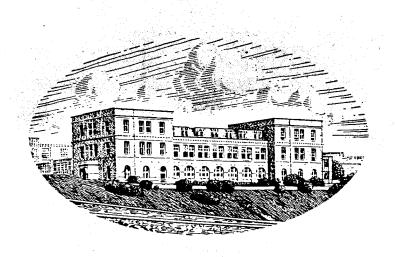
# MARINE BIOLOGICAL ASSOCIATION OF THE UNITED KINGDOM



HEAVY METALS IN THE FAL ESTUARY,
CORNWALL: A STUDY OF LONG-TERM
CONTAMINATION BY MINING WASTE AND
ITS EFFECTS ON ESTUARINE ORGANISMS.

by

G.W. Bryan and P.E. Gibbs

The Laboratory, Citadel Hill, Plymouth, Devon, England. •

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#### ABSTRACT

The Fal Estuary System in west Cornwall has, over many centuries, received inputs of heavy metals from various mining activities. In this context its most important tributary is the Carnon River, the acidic waters of which contain high concentrations of certain metals, notably Zn (mean concentration = 12400  $\mu$ g/l), Fe (9473), Mn (1792), Cu (689), As (233) and Cd (25.6). The Carnon River drains into Restronguet Creek where estuarine mixing occurs and concentrations of dissolved Zn typically range from 100 to 2000  $\mu$ g/l, Cu from 10 to 100  $\mu$ g/l and Cd from 0.25 to 5.0  $\mu$ g/l. The Creek sediments are highly contaminated, the levels of Cu, Zn, As and Sn being of the order of 1500 - 3500  $\mu$ g/g.

Analyses of organisms from the Fal Estuary have shown that some species contain abnormally high concentrations of Cu, Zn and As, especially in those living in Restronguet Creek. Levels of Cu in certain species, for example Fucus vesiculosus and Nereis diversicolor, exceed 1000  $\mu$ g/g, this level being two orders of magnitude higher than normal. However, tissue metal levels do not always reflect those of the environment: there is good evidence that some metals are regulated, including Zn, Cu, As, Mn and Fe, by particular species and in some cases these metals are utilised for specific purposes, for example, the hardening of the jaws of nereid and glycerid polychaetes. Cd is not usually regulated; although the dissolved Cd levels in Restronguet Creek are high, it is not accumulated appreciably by the biota, perhaps as a result of competition for uptake sites from other dissolved metals, especially Zn.

Experimental data indicate that the levels of Cu, Zn and recently-precipitated Fe oxide in the waters and sediments of Restronguet Creek would be expected to have a detrimental effect on the biota. Comparison of the Creek fauna with that of similar creeks in the Fal System shows the Creek supports only a sparse fauna; notably only one bivalve, Scrobicularia plana, survives within the creek and this population is confined to the margins. Evidently, bivalve larvae and juveniles are unable to withstand the toxic conditions. However, the flora and fauna is less obviously affected than might be predicted from experimental toxicity data. Several factors can be forwarded to explain this anomaly: first, the development of Cu or Zn tolerant strains in species such as Nereis diversicolor which enable the species to establish breeding populations within the Creek, and second, the development of increased tolerance with exposure to the conditions such as occurs when individuals are carried by tidal currents into the Creek.

Tolerant species often contain high concentrations of metals, particularly Cu; some of these species form the major food element of some predators inhabiting the Creek, such as fish and birds, which thereby have high metal intakes.

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#### GENERAL INTRODUCTION

During the 19th century the metalliferous mining region of southwest England (Fig. 1) was one of the most important in the world and in its heyday the productions of Cu, Sn and As sometimes amounted to 50% of the world supply. Output declined rapidly towards the end of the century and of more than 1000 mines in the area described by Dines (1969) only a handful of Sn mines are at present operational. However, drainage from the old mine adits and erosion of the spoil heaps by water still continues and is reflected by the high concentrations of metals observed in the sediments and waters of many streams and estuaries in the area (Hosking et al., 1965; Hosking & Obial, 1966; Bryan & Hummerstone, 1971; Thornton et al., 1975).

Included among the most heavily contaminated estuaries are the Hayle (Cu), Gannel (Pb) and Looe (Ag, Pb), but the highest levels of Cu, As, and Zn occur in Restronguet Creek, a branch of the Fal Estuary System. Via the Carnon River the Creek drains parts of what was formerly the most productive of the south-western mining districts, that of St. Day, Redruth and Camborne (Dines, 1969). In addition to receiving wastes from deep mining for several hundred years, Restronguet Creek has an association with the recovery of alluvial Sn probably stretching back several thousand years to the bronze age (Graves-Morris, 1979). Stream tin was originally recovered from the Carnon Valley, but later operations gradually extended down into the upper reaches of the Creek itself. When, in the 19th century, the task of excluding the tide and removing the silt to reach the underlying Sn became too great, the metal was extracted by mining beneath the sediments of the Creek (Taylor, 1873; Barton, 1971). Until recently, alluvial Sn was still being recovered in the Carnon Valley; not surprising that Restronguet Creek appears to be silting up rapidly; in medieval times the Creek was reputed to be navigable as far as Bissoe (Barton, 1971) and 19th-century photographs show ore ships alongside quays at Devoran (Fig. 2) which are now almost inundated with the sediments. Other 19th-century activities, including the refining of arsenic in the Carnon Valley and the smelting of Pb and Sn alongside Penpol Creek, have also undoubtedly added to the overall levels of contamination (Barton, 1971).

When Cornish mining was at its peak, O'Shaughnessy (1866) reported that oysters in the Fal Estuary were green in colour through absorbing large amounts of copper from the contaminated water. When some of these oysters were exported to France, the presence of Cu in them was shown to

be the cause of an outbreak of shellfish poisoning in Rochefort. The exact source of these oysters was not revealed, but green oysters from the vicinity of Restronguet Creek were studied by Boyce & Herdman (1898) and again by Orton (1923), who demonstrated that they were also contaminated with Zn and As. Analyses of sediments by the same author showed them to be heavily contaminated with As, Cu, Sn and Zn and this was confirmed more recently by Hosking & Obial (1966). The continued presence in Restronguet Creek of high sediment-metal concentrations and green oysters illustrates the long-standing nature of metal contamination in the area.

The present report describes observations on metal contamination in the Fal Estuary System carried out at intervals over the past 14 years.

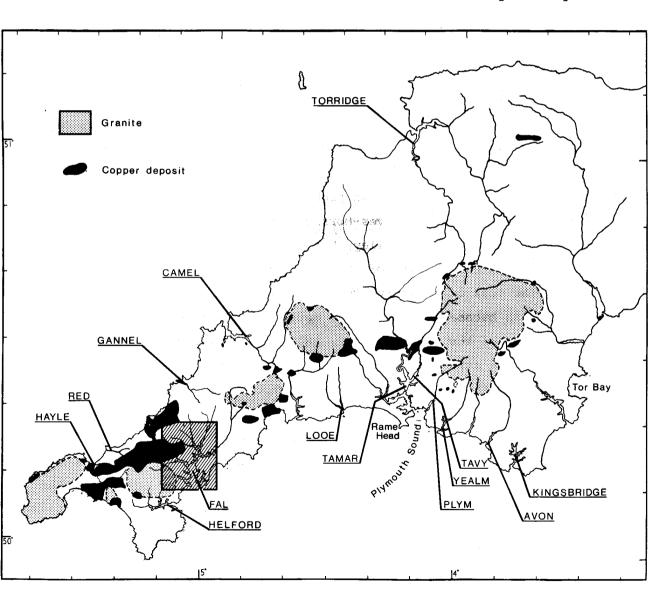


Fig. 1. South-West England: positions of estuaries and other features discussed in the text. Main study area is shaded and shown in greater detail in Figure 2.

Information from other contaminated and uncontaminated estuaries in the area has been used extensively to put conditions in the Fal Estuary into perspective. There are three main aspects to the Report: the first describes the input of metals to the area and some of the factors controlling their distribution in the environment; the second considers the bioaccumulation of metals by the macro-flora and fauna; the third covers observations on the biological effects of metals and their relation to the distribution of organisms in the estuary.

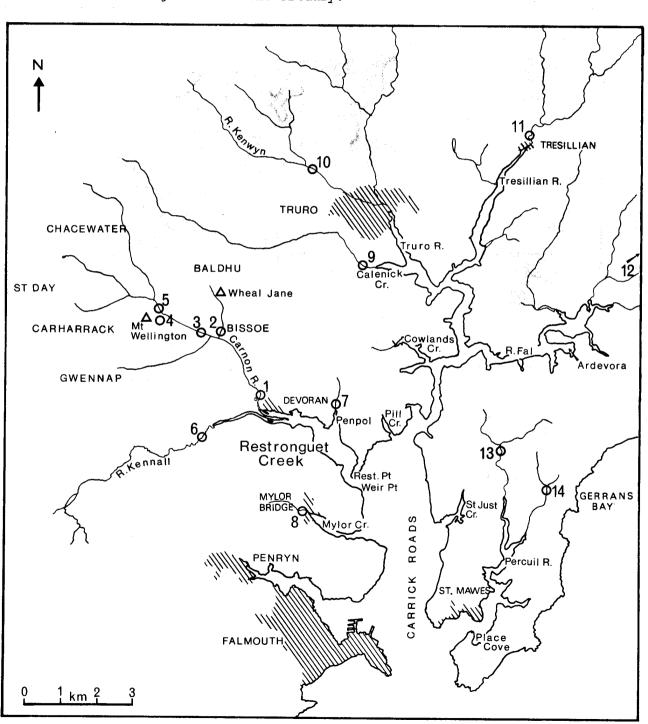


Fig. 2. Fal Estuary System: positions of freshwater sampling sites l-14 on the Carnon River and other tributaries.

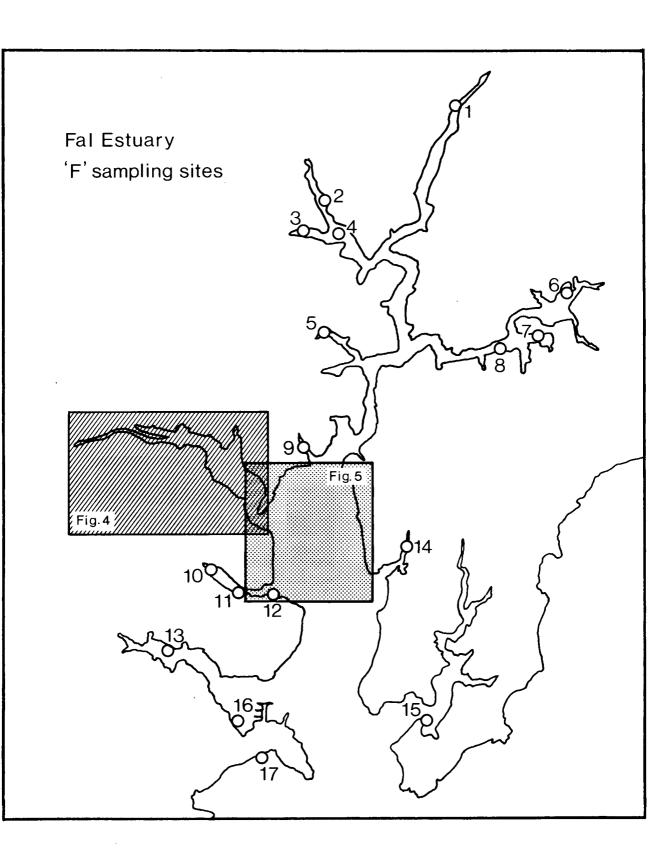


Fig. 3. Fal Estuary System: positions of 'F' sampling sites.

Details of shaded areas are shown in Figures 4 & 5.

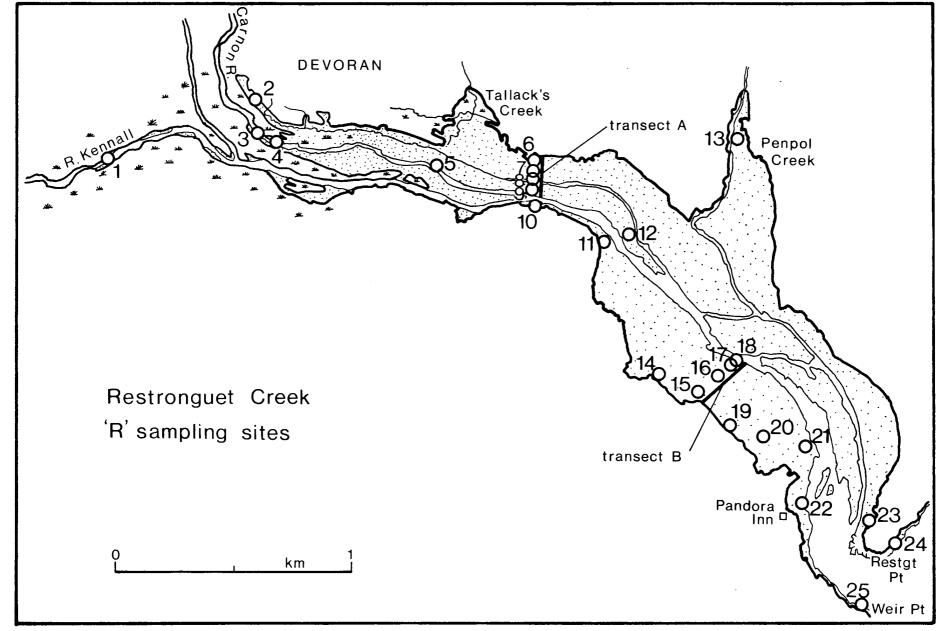


Fig. 4. Restronguet Creek: positions of 'R' sampling sites and 'A' and 'B' transects in the intertidal zone.

Areas exposed during spring tides are stippled

#### METHODS

The basic techniques employed in this study have already been published, but additional information is given in the individual sections. Details of methods for the pre-cleaning and analysis of organisms for heavy metals are given in Bryan et al. (1980), and the treatment of sediment samples is described by Luoma & Bryan (1981). Samples of water were filtered (0.45  $\mu m$ ) as soon as possible after collection and acidified with HCl: high metal levels were determined by flame atomic absorption and low levels by direct injection into a carbon furnace (Perkin-Elmer 76B).

In laboratory experiments, filtered (0.45  $\mu m)$  low-metal sea water from the English Channel was always used.

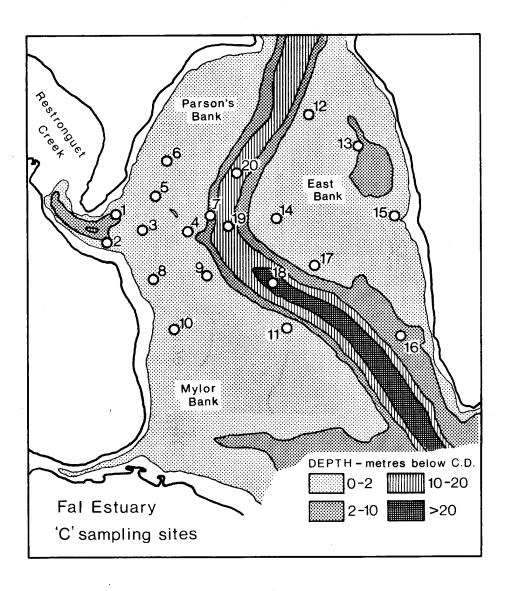


Fig. 5. Carrick Roads: positions and depths of 'C' dredge sampling sites off the mouth of Restronguet Creek.

#### HEAVY-METAL INPUTS TO RESTRONGUET CREEK AND FAL ESTUARY

#### Importance of the Carnon River

The principal source of heavy metals in Restronguet Creek is the Carnon River (Fig. 2) the catchment of which includes the Cu-and Sn-mining districts of Chacewater, St. Day, Carharrack, Gwennap and Baldhu (Hosking & Obial, 1966). Some mines were working in these localities in the seventeenth century and by the middle of the nineteenth they comprised one of the major copper-mining areas of the world. Copper production subsequently declined and by the turn of the century was almost negligible (Dewey, 1923).

Many of the old Cu mines are still drained by the County Adit (Fig. 2). Started in 1748 the Adit is some 30 miles long and joins the Carnon River at Mount Wellington Mine about 4 km from the head of Restronguet Creek (Barton, 1961). The acid (pH 4) adit water contains high concentrations of several metals, mainly in solution, and is a particularly important source of Cu (Table 1).

Mining for other metals, principally Sn, has continued intermittently in the Carnon Valley during the present century, the only active mine at present being Wheal Jane, although Mount Wellington mine reopened briefly in the nineteen seventies. The water draining from Wheal Jane, 2.5 km from the head of the Creek, contains a wide range of metals, the most significant being a high concentration of dissolved Zn (Table 1).

Until 1981, a plant at Bissoe recovered Sn from mine wastes which included tailings and alluvium carried down by the river and accumulated in the lower Carnon Valley. Particularly over the last 4 km of its course the Carnon River passes through ground dominated by metalliferous spoil heaps: being too toxic to support much vegetation, these are largely unprotected from erosion and thus provide additional inputs to the river.

Analyses of the Carnon River water before it enters Restronguet Creek show that it is quite acidic (pH 3.8) and contains high concentrations of Fe, Zn, Mn and Cu (Table 1; site 1). The last three named together with Cd are mainly in solution, but for As, Fe and Pb there is a significant insoluble component. A few determinations of metals not included in Table 1 have been carried out in water from site 1 and include 94000  $\mu$ g/l of Na, 69000  $\mu$ g/l of Ca, 10800  $\mu$ g/l of Mg and 8820  $\mu$ g/l of K. In addition, 6400  $\mu$ g/l of Al were measured in the water

#### TABLE 1

#### CONCENTRATIONS OF METALS IN FRESHWATER INPUTS TO THE FAL ESTUARY SYSTEM

Total and filtered (0.45  $\mu m$ ) samples acidified immediately to 0.025 N with HCl

Highest values underlined. Samples taken 4 Aug. 82 except  $\star$  - 21 Sept. 82 and  $\pm$  - 20 Sept. 82

Carnon River µg/litre

Sample site

Soluble

Sample Site	POTMOTE	ł			Cari	TOIL KT V	er µg/	TICLE		J	
(No.) in Fig. 2	or Total	As	Cđ	Со	Cu	Fe	Mn	Ni	Pb	Zn	рH
(1) Road Bridge	Soluble Total	82 200	10.1	37 60	474 493	18500 29410	2974 2971	135 135	28 39	12030 12070	3.8
(2) Wheal Jane	Soluble Total	22 380	$\frac{24.5}{24.3}$	52 72	2 334	44720 96730	6889 7238	142 181	31 <u>53</u>	25090 28560	5.7
(3) Bissoe	Soluble Total	31 30	6.7 6.5	79 111	680 684	17210 17680	1532 1528	172 167	18 18	6900 6680	3.8
(4) County Adit	Soluble Total	14 24	4.6 4.6	61 224	859 864	657 1049	882 873	137 132	5.6 6.8	2868 2774	4.1
(5) Twelveheads	Soluble Total	58 42	1.2 1.1	ND ND	54 53	45 137	97 94	66 47	1.7 2.1	953 929	5.6
					Other	fresh	water	input	s		
(6) Kennall	Total	3	ND	13	8	112	8	5	3	63	6.7
(7) Penpol	Total	11	ND	ND	9	129	72	26	3	27	6.8
(8) Mylor	Total	9	0.1	20	2	212	63	2	2	48	6.7
(8) Mylor*	Total	_	0.2	8	8	759	128	-	33	44	-
(9) Calenick*	Total	-	ND	7	14	744	139	-	15	130	-
(10) Kenwyn*	Total	-	ND	5	10	369	39	-	10	11	-
(11) Tresillian*	Total	-	ND	4	6	480	42	_	9	24	-
(12) Fal <sup>±</sup>	Total	-	0.7	6	9	1652	126	-	5	386	-
(13) Lanhoose 1	Total		ND	6	2	209	3	-	11	171	-
(14) Tregassa 1	Total	-	0.7	5	5	76	2	-	17	409	-
	Back	groun	d wate	r con	centra	ations	(Först	ner &	Wittm	ann, 19	79)
Fresh water		2	0.07	0.05	1.8	<30	<5	0.3	0.2	10	
Ocean sea water		2.1	0.01- 0.07	0.04	0.04-	- 1.3	0.2		0.001- 0.005		all-verification and the second
<u> </u>	ND = not detectable by direct furnace AA										

TABLE 2

ESTIMATES OF TOTAL METAL INPUT VIA CARNON RIVER

Analytical data for Sept. 80 - May 81 but

totals estimates for July 80 - June 81

	· · · · · · · · · · · · · · · · · · ·					
	•		μg/litre			
As	Cđ	Cu	Fe	Mn	Pb	Zn
		Total	concentrations a	and ranges	7	
233*	25.6	689	9473	1792	40 <sup>†</sup>	12400
<del>-</del>	(6.5-106)	(421–977)	(5560–13900)	(971-3317)	- -	(3630-57270)
		Dissolve	d concentrations	s and ranges		
_	24.8	593	5024	1777	29	12470
	(6.4-106)	(370–973)	(2670-10360)	(955–3315)	-	(3630-57230)
		Perce	entage dissolved	netal		
_	96.9	86.0	53.0	99.2	72.0	100
	Total	l annual inpu	ut from July 80	- June 81 (m	metric t	ons) ‡
9.3*	0.76	20.4	280	53.0	1.18	367
		Total annu	ual input for 19	971 (metric t	ons) +	
5.5	0.71	21.3	253	33.4	1.38	262

<sup>\*</sup>Langston (1983) †Fewer data; ‡Based on mean flow of 0.938 m<sup>3</sup>/sec, kindly supplied by South West Water Authority

on one occasion of which about 15% was soluble; levels of Ag are usually below 1  $\mu$ g/l, much of it being insoluble, and levels of Cr are of the same order. It is assumed that Sn occurs principally in suspension as the very insoluble oxide, cassiterite.

Metal concentrations in the Carnon River far exceed those of the similarly-sized River Kennall, which also enters the head of Restronguet Creek: levels in the stream entering at Penpol are also low (Table 1). Comparisons with other inputs to the Fal Estuary System (Table 1) suggest

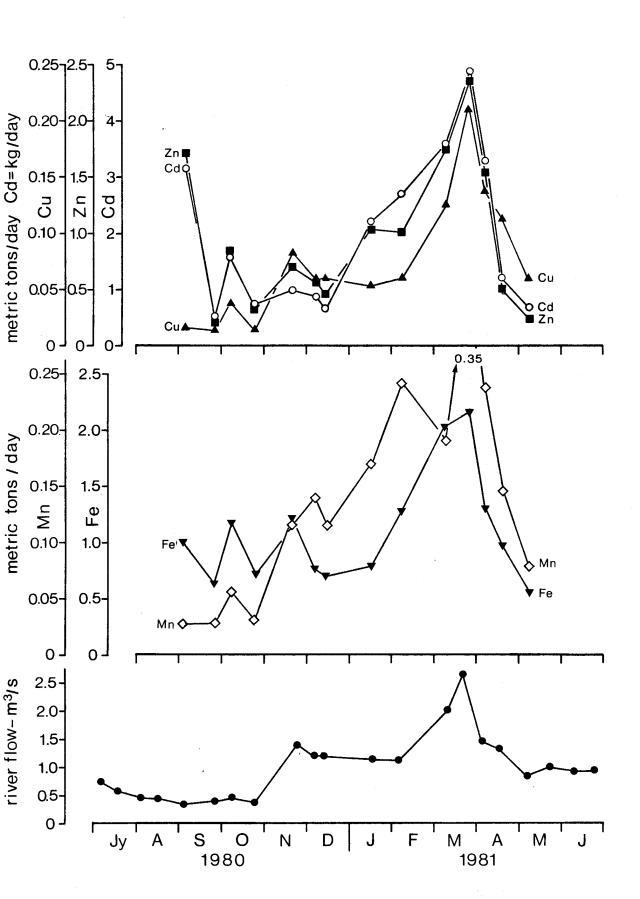


Fig. 6. Carnon River: variations in river flow and in total daily inputs of 5 metals. Flow data supplied by the South West Water Authority.

that even allowing for the greater flows of rivers such as the Fal, the Carnon River is, by a wide margin, the most important source of heavy metals in the system.

Table 2 shows the ranges and mean concentrations of total and

dissolved metals in Carnon River samples collected in 1980-81. Concentrations of Cu, for which the County Adit is a major source, vary less than those of Zn and Cd which are presumably under the influence of mining activity at Wheal Jane (see Table 1). Figure 6 shows how rates of input varied for five metals during 1980-81. Clearly, the river flow rate is a major influence on input rates; however, concentration changes are also important and in September 1980 exceptional levels of Zn  $(57270 \, \mu g/1)$  and

The annual input of metals between July 1980 and June 1981 is shown in Table 2 and a comparison with estimates from data for 1971 suggests that the present situation is not too different from that obtaining 10 years ago.

On entering the Creek the Carnon River water flows over the denser

sea water and, in calm weather, salinity stratification is very obvious. As the river water becomes mixed with sea water, the rise in salinity and pH

## Fate of heavy metals in the Creek

Cd (106  $\mu$ g/l) produced input peaks when the river was low.

leads to the flocculation of 'dissolved' Fe, probably as the hydrous oxide. Some other elements including Cu and As are associated with this process, and together with Fe tend to be removed from solution and deposited as sediment. On the other hand, Mn, Cd and Zn show much less evidence of removal from solution and their concentrations are largely dependent on the dilution of river water with sea water. Thus the dissolved concentrations of Mn, Cd and Zn are almost linearly related to salinity, and very little particulate metal is removed by filtration (Fig. 7). This contrasts with dissolved Fe, Cu and As (see Langston, 1983) where the formation of particulate material during mixing leads to more curved relationships

solution, the relative proportions of metals in the Carnon River water and the Creek sediments differ appreciably. Assuming that 100% of the Fe in the Carnon River is retained by the Creek sediments, the percentage retention of other metals needed to produce the present sediment composition can be calculated. The results in Table 3 agree with the

Because some metals tend to be deposited whilst others remain in

(Fig. 7).

direct observations on the waters of the Creek and show that whilst only small percentages of Co, Cd, Mn, Ni and Zn in the River input are retained, much of the incoming Ag, As, Cu and Pb is deposited. Presumably Sn should be included with the latter group, since it occurs in the sediment mainly as cassiterite and must enter the Creek in this very insoluble form (Hosking & Obial, 1966).

#### Composition of the sediments

Surface sediments in Restronguet Creek are light brown in colour due to the deposition of iron oxides. Particle-size measurements (British Standard 1377) showed 80% to be less than 20  $\mu m$  diameter and

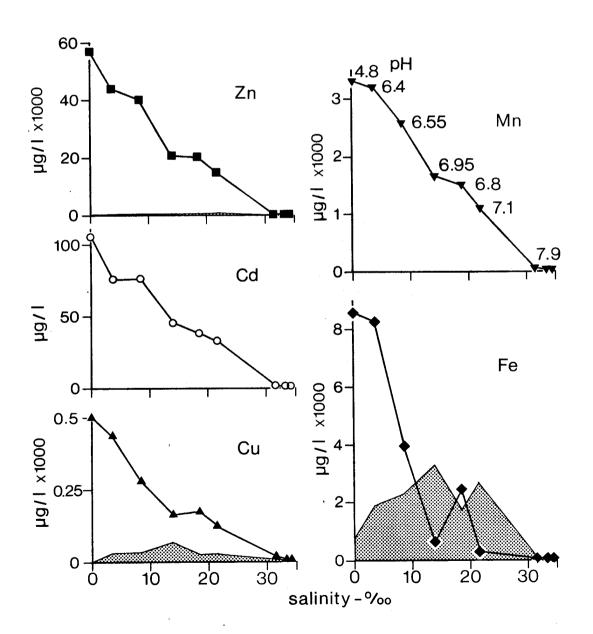


Fig. 7. Restronguet Creek: relationships between dissolved concentrations of 5 metals and salinity. Shaded areas represent particulate fractions of Fe, Cu and Zn, but were insignificant for Cd and Mn (4 Sept. 80).

RELATIVE RETENTION OF METALS FROM CARNON RIVER BY
RESTRONGUET CREEK SEDIMENTS

TABLE 3

Ag	As	Cđ	Со	Cu	Fe	Mn	Ni	Pb	Zn
	River	water co	ncentr	ations	(μg/litre)	from T	ables 1	and 2	
0.45	233	25.6	60	689	9473	1792	135	40	12400
Pı	edicted				ons (µg/g) ediment Fe			in Riv	er
2 <b>.6</b> 6	1377	151	355	4073	5.6%	10593	786	229	73303
Mean	observe	d sedime	nt con	centrat	ions (μg/g	)(from	Bryan <u>e</u>	<u>t al.,</u>	1980)
3.46	1732	1.1	18	2148	5.6%	475	31	297	2700
Per	centage	of meta	ls in	River r	etained by	sedime	nts if	Fe = 10	0%
130	126	0.7	5	53	100	4.	5 3.9	130	3.7
	·			·	<del></del>		· · · · · · · · · · · · · · · · · · ·	<del></del>	<del></del>

#### \*Mean of 2 values

40% less than 5  $\mu m$ . The organic content is about 6% and the low Ca level shows that the sediment contains at most only a few percent of CaCO $_3$  (Table 4).

In Table 4 metal concentrations in the Creek sediments are compared with those from other parts of the Fal Estuary. The results compare favourably with those of other workers (Orton, 1923; Hosking & Obial, 1966; Yim, 1972; Thornton et al., 1975) and show clearly that the Creek is the most heavily contaminated part of the Fal Estuary System. The influence of the Creek inputs on surface-sediment concentrations of Cu and Zn is shown diagrammatically in Figure 8. An interesting feature is the occurrence of very metallic sediments in Mylor Creek which lies to the south of Restronguet. The river input to Mylor Creek is small (Table 1) and the sediments clearly have their origin in the Restronguet input. Hosking and Obial (1966) noted the tendency for highly metallic water to persist between the two Creeks with little evidence of eastward migration. This

TABLE 4

TYPICAL ANALYSES OF SURFACE SEDIMENTS COLLECTED IN FAL ESTUARY SYSTEM (1976-80)

Positions of sites are shown in Figs. 3,4,5, . Highest values are underlined.

Results are for mitric acid digest of <100 \(mm\) fraction, but fusion used for Sn (Bryan et al., 1980)

†Ca soluble in 1N-HCl; \*see Luoma and Bryan (1981)

						oncent	ration	(ug/g	) exce	ot Fe	(%)			······································	% Ca <sup>‡</sup>	% Organic matter*
Estuary	Site	Ag	As	Cđ	Со	Cr	Cu	Fe	Нg	Mr.	Ni	Pb	Sn	Zn	* Cai	organic macter
							Restr	onguet	Creek							
Restronguet Cr.	R1	2.8	1076	0.9	14	21	1733	4.75	0.24	401	25	204	2672	1587	0.25	8.2
	R6	4.1	2520	1.2	22	37	2540	5.76	0.22	559	32	290	1730	3515	0.55	5.8
	R13	3.5	1600	1.3	18	23	2170	6.30	0.45	466	37	. 396	1350	3000	0.50	5.8
	R16	3.0	-	1.1	21	25	2145	5.39	-	571	26	220	-	2866	1.50	-
. 4.4	R22	2.6	: =	1.5	16	29	1785	3.92		441	27	198	. 7, .	1978	1.66	5.0
					<del></del>	Other	parts	of Fa	1 Syst							
Carrick Rds	Ci	1.9	, <del>,</del>	0.5	15	35	1808	4.73	<del>-</del> ,	406	27	201	-	1781		
	C20	0.9	-	0.6	9	36	490	2.49	-	254	23	119	-	494	-	5.5
· ·	C9	0.8		0.2	··· 7	31	341	2.29	-	254	20	91	-	380	-	-
Penryn Cr.	F13	0.7	-	0.3	12	47	322	3.70	, <del>-</del>	432	38	219	] <del>-</del>	440	-	
Mylor Cr.	F10	2.0	-	1.2	12	32	1117	3.45	-	393	29	179	-	980	0.80	6.2
Cowlands Cr.	F5	0.4	-	0.4	9	25	195	2.74	- '	344	20	85	-	361	0.37	5.4
Pill Cr.	<b>F</b> 9	0.8	-	0.2	11	43	527	3.42		252	34	219	-	613	-	-
Calenick Cr.	F4	√2.0	120	1.0	6	25	335	2.57	0.43	172	17	137	700	628	0.31	3.9
Truro R.	F2	2.7	1 <sub>2</sub> , 2,-	1.1	8	43	344	2.76	-	214	27	220	-	759	7.5	5.4
Tresillian R.	F1	1.1	88	1.0	8	23	256	2.21	0.61	260	21	100	591	400	-	4.9
R. Fal	F8	0.4	56	0.4	. 3	15	129	1.21	0.20	116	9	48	125	252	-,	1.9
St Just Cr.	F14	0.6	_	1.3	9	32	356	3.10	-	260	25	97		508	0.69	7.3
Place Cove	F15	0.1	<u> -</u> '	0.1	7	21.5	31	2.24	-	281	23	30	: <del>-</del>	106	4.30	1.6
						Othe	er cont	aminat	ed est	uaries						
Hayle	(upper)	.1.3	550	0.6	28	36	782	5.15	0.06	742	32	218	1750	942	3.10	4.4
Gannel	(upper)	2.9	233	3.0	40	29	217	3.32	0.09	1160	49	2175	305	1215	5.60	3.0
Tamar	(upper)	0.9	85	1.5	23	44	305	2.81	0.90	758	49	156	101	392	0.40	7.6
1							Contro	l estu	aries		<del></del>					
Yealm	(upper)	0.2	34	0.3	11	26	35	2.73	0.82	368	25	50	126	110	_	4.6
Avon	(mid)	0.1	13	0.3	10	37	19		0.12	417	28	39	28	98	-	4.2
Ratio: Restron	-	5.41	194	4.3	2.2	1.0	134	3.2	3.7	1.3	1.3	3 ं 10 ′	95	36		* 17 * * * * * * * * * * * * * * * * * *

tendency for metallic conditions to be confined to the western side of the Carrick Roads may also explain the presence of relatively high sediment levels in Pill Creek and Penryn Creek. Additional inputs of metals from various sources in the Truro and Calenick areas probably explain the relatively high levels of sediment zinc at the head of the Truro River. The generally lower concentrations in the Fal branch of the system may be the result of dilution with china clay wastes borne by the River Fal from the St. Austell area. Hosking et al. (1965) have drawn attention to the apparent failure of china clay wastes to adsorb Zn and thus assist in its deposition from the relatively high concentrations (386  $\mu$ g/1; Table 1) in the waters of the River Fal.

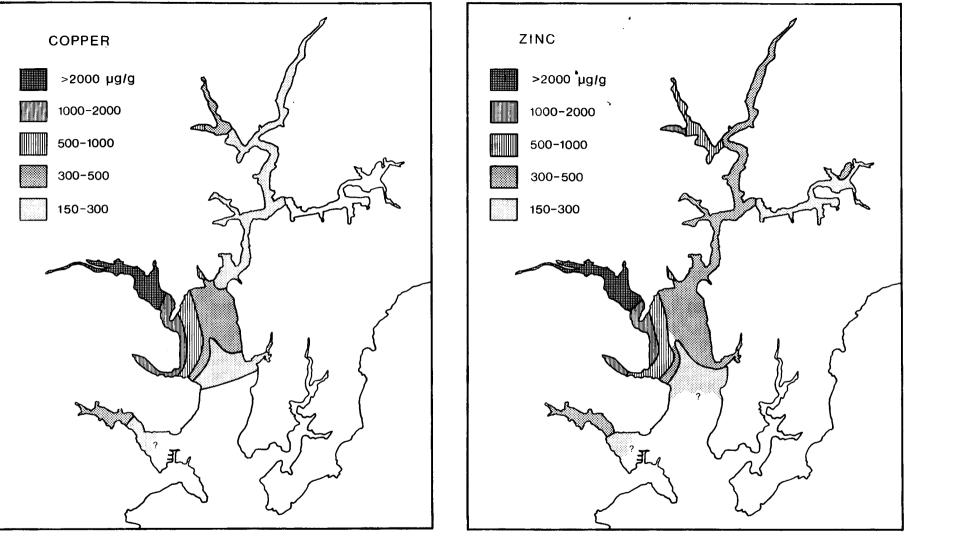


Fig. 8. Fal Estuary System: approximate distributions of Cu and Zn in <100  $\mu m$  fraction of surface sediment (HNO3 digested).

Compared with other estuaries contaminated by mining, such as the Hayle, Gannel and Tamar (Table 4), Restronguet Creek is most notable for its high levels of As, Cu and Zn, the contrast being less marked for Ag and Sn. The bottom line in Table 4 shows that the highest Creek values for As, Cu and Sn exceed those of the uncontaminated Avon Estuary by about two orders of magnitude, and a factor of about 40 separates the levels of Ag and Zn.

#### Conditions to which organisms are exposed in Restronguet Creek

#### Water

The hydrography of the Creek has not been investigated in detail but some observations on the chemistry of the water, related to the tidal cycle of conditions experienced by the biota, can be outlined.

At low tide the fresh water issuing from the Carnon and Kennall Rivers is channelled down the centre of the Creek and joined by several minor tributaries, notably from Penpol. On spring tides, most of the Creek bed is exposed at low tide but on neap tides a considerable area of the lower estuary remains immersed. On the flood tide the river water mixes with the sea water but being less dense forms a brackish layer on the surface of the incoming wedge of sea water, creating a marked vertical salinity gradient. This feature is well illustrated by some measurements made on 22 Mar. 71 at high tide: opposite Devoran (Fig. 4) the salinity of the surface layer (top 5 cm) was  $0.86^{\circ}/oo$  and at 40 cm depth the salinity was  $23.0^{\circ}/oo$ ; on the same occasion, near transect A these values were 7.9 and  $29.8^{\circ}/oo$  respectively.

Because the waters of the Creek are tidal and usually highly stratified, it is difficult to ascribe certain water concentrations to specific localities. Larval organisms at the sediment surface are likely to be vulnerable to even brief exposure to the very high metal concentrations which occur in the less saline surface waters. Thus on two occasions, one very calm and the other with a NW breeze blowing down the valley, samples were collected at the water's edge on the incoming tide along two transects A and B (Fig. 4). On both transects the clam Scrobicularia plana occurs only at the highest site, whereas the polychaete Nereis diversicolor is more widely distributed. The results for dissolved Zn and Cu in Figure 9 show that, as might be expected, the concentrations generally fall with distance from the river channel. In addition, particularly at transect B the decline in concentration was

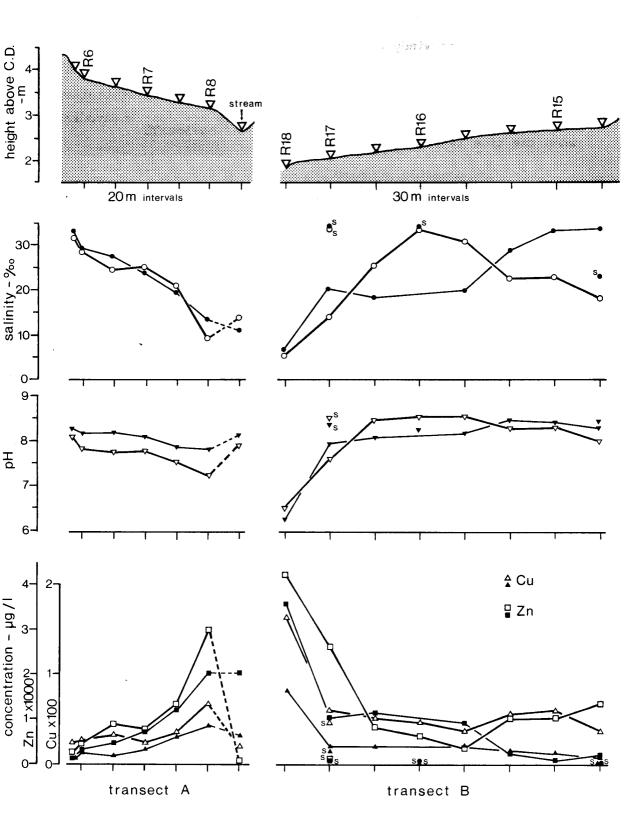


Fig. 9. Restronguet Creek: salinity, pH and dissolved Cu and Zn at the water's edge as tide advances across mudflats at transects A and B in Figure 4. Open symbols, calm weather (6 July 79); closed symbols, windy weather (19 July 79). (S) refers to samples of standing water collected before advance of tide. On transect A, low metal levels on lower shore reflect dilution, with low-metal stream water.

most obvious when windy conditions increased mixing. Samples taken from pools of standing water which remained from the previous tide were generally of high salinity and relatively low metal concentration: this suggests that the conditions on the mud flats are most unfavourable when the tide is rising.

Another possible approach to assessing average levels in the waters

of Creek is to assume that the salinity of the sediment pore water, below the immediate surface layer, reflects the average salinity of the overlying water. The salinity at site R5 (Fig. 4) in March, when inputs of water and metals are high, was about  $25^{\circ}/oo$  (Table 5) and from Figure 7 is equivalent to about  $10000~\mu g/1$  of Zn and  $100~\mu g/1$  of Cu. However, the concentrations of Zn (and Cd) shown in Figure 7 are exceptional and a more realistic value for Zn would be in the area of  $1000-2000~\mu g/1$ . Near the mouth of the Creek, concentrations would be expected to be 10~times lower ( $100-200~\mu g/1$  of Zn,  $10~\mu g/1$  of Cu). This is borne out by the work of Boyden et al. (1979) who sampled surface and bottom waters at low tide and high tide near the mouth of the Creek on four occasions during 1972-73. In surface waters, Zn values were  $28-300~\mu g/1$  and Cu  $5-26~\mu g/1$ . Bottom water values were  $17-192~\mu g/1$  for Zn and  $5-25~\mu g/1$  for Cu. A comparison with the baseline concentrations for sea water in Table 1 demonstrates that, even in the lower reaches of the Creek, metal levels are extremely

#### Sediment

high.

Table 5 shows that sediment-metal concentrations in soft mud decline only slightly in a downstream direction. However, lower concentrations are found in sandy areas near the mouth of the Creek (site R21). Sediment concentrations remain fairly constant down to a depth of 20 cm, although analyses of a longer core at site R2 showed that at a depth of 60-65 cm the level of Cu was double that at the surface. What period of time is represented by 65 cm of deposition can only be guessed but may be of the order of 100y and would therefore cover the final demise of the Cu mines.

The upstream limit of the deposit-feeding clam <u>Scrobicularia plana</u> occurs at the uppermost site (R6) on transect A (Fig. 4) and animals transplanted to sediment farther down the shore do not survive (p. 85). Along this transect, metal concentrations in surface sediments generally decrease with distance from the main channel (Table 6) and so also do the percentages of metals extracted from the sediments with hydrochloric

TABLE 5

METAL CONCENTRATIONS IN SEDIMENT CORES FROM RESTRONGUET CREEK

Unsieved sediment digested with nitric acid and residue

dissolved in dilute hydrochloric acid

Site and Date	Depth (cm)	Interstitial Salinity (%)	Concer Cu	ntration Fe	(µg/g)	except Pb	Fe (%)
(R1) Mar. 71	0 - 5 5 - 10 10 - 15 15 - 20	5.2 6.6 10.6 11.1	3200 3480 2960 3080	6.09 5.69 5.26 6.29	437 373 345 389	393 388 314 320	2290 2770 2410 2300
(R2) Jan. 71	0 - 5 5 - 10 10 - 15 15 - 20	19.7 17.8 20.5 23.8	3520 3610 3600 3690	6.51 6.36 6.17 5.88	412 414 420 422	385 359 372 421	2730 2800 2920 2930
(R5) Mar. 71	0 - 5 5 - 10 10 - 15 15 - 20	25.6 25.2 28.3 29.6	3560 3750 3500 2930	6.85 6.67 5.58 5.15	432 510 431 527	417 579 394 839	2800 3290 3160 2010
(R20) Dec. 70	0 - 5 5 - 10 10 - 15 15 - 20	35.0 30.4 28.2 24.5	2480 2960 3750 3730	4.93 5.99 7.47 8.35	331 438 541 708	319 - - -	1780 1640 2320 2660
(R21) Dec. 70	Coarse red sand (surface)	_	546	3.72	338	205	735

acid, acetic acid or ammonium acetate solution. Thus the potential availability of surface-sediment metals decreases with increasing distance from the river channel more markedly than the total concentration (Table 6). This might be expected, since the sediments on the upper shore are almost certainly older than those near the River Channel. Other work at site R6 showed that 1N ammonia extracts humic materials and 399  $\mu g/g$  of Cu from the surface sediment and this suggests that a significant fraction of the metal is organically-bound.

Measurements of metals in the interstitial waters of these sediments (Table 6) show that concentrations of Zn and Cu in the oxidized surface sediment are such as might be expected if they are influenced by levels in the overlying water (e.g. Fig. 9). Below depths of 1-2 cm negative Eh values are found: the lower levels of dissolved Cu and Zn in the deeper, black sediments indicate their removal, possibly as sulphides, whereas the

TABLE 6

EXTRACTABILITY OF METALS FROM SURFACE SEDIMENTS ON

TRANSECT 'A', AND INTERSTITIAL WATER CONCENTRATIONS

	•										
Site on transect	Sediment *	Sec	liment con (μg/		ion	Depth	Interstitial water concentration (µg/litre)				
'B'	extractant*	Cu	Fe	Mn	Zn	(cm)	Cu	Fe	Mn	Zn	
	HNO <sub>3</sub> (conc.)	2541	57600	559	3515	0	66	150	406	262	
(R6) Upper shore ( <u>S</u> . <u>plana</u> )	HCl (1N)	1920 (76%)	21800 (38%)	143 (26%)	2850 (81%)	10	30	8530	294	216	
	HAc (25%)	1534 (60%)	8600 (15%)	134 (24%)	3248 (92%)						
	AmAc (1N)	90 (3%)	8 (0.01%)	24 (4%)	185 (5%)						
(R7) Middle shore	HNO <sub>3</sub> (conc.)	2607	56400	579	4153	0	56	129	436	396	
(N. diversicolor)						10	7	8800	445	104	
	HNO <sub>3</sub> (conc.)	2568	76700	595	5414	0	83	106	520	390	
(R9) 5 metres from Carnon R.	HCl (1N)	2110 (82%)	54000 (70%)	276 (46%)	4730 (87%)	10	16	8920	350	67	
channel (no macrofauna)	HAc (25%)	2039 (79%)	33200 (43%)	295 (50%)	5354 (99%)		. •				
	AmAc (1N)	239 (9%)	13 (0.02%)	68 (11%)	440 (8%)						

<sup>\*</sup>Luoma & Bryan (1981)

high concentrations of Fe probably reflect the reduction and dissolution of Fe oxides.

### Summary

The principal input of heavy metals to Restronguet Creek and the Fal Estuary System is the Carnon River which receives drainage from various sources associated with metalliferous mining and extraction processes.

Carnon River water is acidic (pH  $\sim$  3.8) and contains high average concentrations of Zn (12400  $\mu g/1$ ), Mn (1792), Cu (689) and Cd (25.6) of which 86-100% is in solution. Levels of Fe (9473) and As (233) are also

high and roughly 50% is dissolved. Changes in metal inputs are mainly controlled by the river flow rate, but fluctuations in concentrations of Zn and Cd are sometimes important. Usually inputs are highest in the period November - April and reach maxima of about 2.5 metric tons/d for Zn and more than 0.2 for Cu, although the average levels are about 1 metric ton/d for Zn and 0.06 for Cu.

On mixing with sea water in Restronguet Creek, the behaviour of dissolved Cd and Mn from the Carnon River is almost perfectly conservative and that of Zn slightly less so. Thus water having a salinity of  $25^{\circ}/oo$  may contain more than 1000  $\mu g/l$  of dissolved Zn. Co and Ni also tend to remain in solution. Iron, on the other hand, rapidly flocculates and other elements tending to be removed from solution and therefore enriched in the sediments include Ag, As, Cu and Pb. Throughout all these processes, Sn probably exists largely as particles of cassiterite.

Restronguet Creek sediments contain levels of As, Cu and Sn ( $\sim 2500~\mu g/g$ ) which are two orders of magnitude higher than normal, whilst levels of Ag (4  $\mu g/g$ ) and Zn (3500  $\mu g/g$ ) are roughly 40 times normal. Apart from Sn, which occurs mainly as the very insoluble oxide cassiterite, these metals are readily extractable from the surface sediments and are therefore potentially bioavailable. In addition, the interstitial water in surface sediments contains significant levels of Cu and Zn.

In Restronguet Creek, the potential availability of heavy metals appears to fall with increasing distance from the head of the Creek and also with distance laterally from the Carnon River channel. Widespread metal contamination also occurs beyond the mouth of Restronguet Creek and is particularly obvious in the Carrick Roads and Mylor Creek.

The next section considers the bioaccumulation of metals by organisms in Restronguet Creek and compares the concentrations in their tissues with those of organisms from other parts of the Fal System and from other estuaries.

#### CONCENTRATIONS OF HEAVY METALS IN THE FLORA AND FAUNA

#### Introduction

In the following sections, concentrations of heavy metals in organisms from Restronguet Creek are compared with values from other parts of the Fal Estuary System and from other estuaries in south-west England. The locations of estuaries and sampling sites in the Fal System are given in Figures 1-5.

Several important points need to be stressed in considering these results:

- (1) Different types of organisms absorb metals from different sources: dissolved metals are accumulated by many species, but sediment-bound metals may be absorbed by deposit-feeding organisms and, particularly in larger animals, dietary sources may be pre-eminent. The total concentrations of metals in these various sources may not necessarily reflect their availability to organisms since this also depends on the chemical speciation of the metal.
- (2) Concentrations accumulated by organisms do not always change in relation to the availability of metals in the environment. In algae and some animals an approximately direct relationship does exist for a range of metals. However, other species are able to regulate the concentrations of some metals against environmental changes and this is more likely to occur if the element has an essential biochemical role. Some metals in this category enter the Fal Estuary System in appreciable quantities, notably Zn, Fe, Cu and Mn.
- (3) Metal levels that may be regarded as 'normal' vary, sometimes considerably, between species. Thus a concentration which in one organism would be considered unexceptional, might reflect gross contamination in another.
- (4) At a single sampling site, metal levels in an organism may change in response to factors such as time of year, size, age or reproductive condition. An attempt has been made in the present work to compare organisms of similar size, although this is not always possible.

#### Macroflora

#### Brown algae

 $\underline{\mathtt{Fucus}}$   $\underline{\mathtt{vesiculosus}}$  is widely distributed within the Fal System and

#### TABLE 7

BROWN SEAWEEDS: CONCENTRATIONS IN WEED FROM PAL ESTUARY SYSTEM COMPARED WITH THOSE IN OTHER ESTUARIES

Highest concentrations underlined

6.1		1.2	in section	. 7		4		414				· · · · · · · · · · · · · · · · · · ·		ببين لأوبت	الجهام منهات والأوال	سن جنسب	
	4				N IV		.3.√2		Fucu	s vesi	culosus	sampl μg/g d	48000 - 70	les grow	ing tips	)	
Estuary	, a	s:	ite		í c	ate	T. A.	Ag	Čđ	Có	Ċ <b>r</b>	is Cu	Fe	Mn	Ni	Pb	2n
			1 73	1 1			26	907	19313	, koj		Restrong	uet Cre	e <b>k</b>			
Restronguet	Cr.	R	10	1	Apr	. 81	giri (	2.21	1.41	15.7	~4.7	1450	13500	533	9.6	68.1	4200
	•	R	11		Apr	. 81	St. of	1.17	0.99	6.7	.3.5	938	6190	156	7.7	37.4	3230
•		R	12		Apr	. 81		0.60	0.95	4.9	2.8	919		<b>6</b> 8	7.1	28.3	2710
	inely	R	14	1	Apr	. 81	( A A )	0.79	0.81	3.8	1.6	ל <b>ג</b> ל	2030	134	4.2	15.6	2440
	4	R	19	1	Apr	. 81		1.17	0.91	<u>20.3</u>	2.2	717	2240	61	4.3	18.5	2670
Weir Pt	) <u>4</u>	a R	25	and the same	Apr	. 81	š	0.31	0.93	⊋a∵ <b>5.</b> 5	1.7	<b>19</b> 0	·	5 / <b>. 125</b>	3 4 4 A 2	6.6	2190
<sup>2</sup> 7 5x	77 X		\$31		Series .	< 0.0%	300	2,81 <b>%</b> \$	N a	i aci	Other	r parts	of Fal	System	q zedi		
Truro R.		F	2 *		201	4		1.05	1.11	2,4	54.35	_ ∵∋ე≉.,85	473				563
Calenick Cr.		F.	3		Apr	. 80		0.99	1.45	3.1	3.3	210	2508	279	4.8	57.1	788
Tresillian R	١.	ĵ <b>r</b> 1			Jan	. 80	1	0.28	0.90	2.4	3.4	56			2.9	14.5	585
Cowlands Cr.	47	F.	5	1	Apr	. 80	6 7	0.18	0.93	3.7	2.0	° 32	3270	672	2.4	15.7	475
Pill Cr.	. 95	FS	)		Jun	e 76	1	0.42	0.75	√ ∘ 3,8	2.8	119	1 26	3 144	3.4	24.8	556
St Just Cr.	4.51	F	14		May	80		0.22	4, 11,	5.3	4.0	94	1640	171	4.9	20.9	1180
Mylor Cr.		F	11		Mar	. 80	i ni	0.52	0.81	4.0	4.8	302	204	124	2.6	21.6	1120
Mylor Cr.		. F1	10	/5a	Mar	. 80	l fe	0.48	0.76	2.6	2.2	250	133	3 68	1.8	13.6	1010
Penryn Cr.		F			Jul	. 76		0.43	0.84	3.6	2.1	70	71	172	7.3	19.5	429
Falmouth	¥0.	F	17	33.1	Jun	e 76		0.27	1.00	0.6	0.8	7	5.	51	2.2	10.7	94
			****		3 (	are s		was de la			Other o	contamin	ated lo	calities	Application of		
Hayle	- 1	(uppe	er)		Apr	. 77		0.81	2.27	3.5	HIN SOL	436	- 8 N/F/N		21.7	32.3	1864
Red River		(mout			*J.	. 74	1 **	0.33	0.17	n (5 <u>1</u>	_	389	18 at 1800			6.3	919

Control estuaries

8

10

Cu

Ascophyllum nodosum (2nd vesicle from tip + first internode analysed)

0.24 0.81 2.3 7.7 227 631 79 1.6 10.5

94

193

Mn

ta choult

6.2

11.4

Ni

3.1

4.5

113

104

99

Zn

1400 1690 1070

1660

1010 106

121

746

Fe

Restronguet Cr	6000	R14	Aug.	79	0.79	0.24	546	129 29	1.5	2.3	
u propinské příhol	14	R19	் சுடி	79	<u>0.93</u>	୍ -0.09 ୍	<b>375</b>	136 103	1,400	1.6	
Pandora Inn		R22	Jul.	79	0.61	0.05	372	170 19	0.7	2.9	
Weir Pt		R25	Jul.	. 1	0.67	<u>0.31</u>	424	<u>355</u> 35	0.9	2.5	
	1				Other p	oarts of Fal	System	- Andrewski	4.84.853		
Mylor H.		F12	Jul.	79	0.50	0.20	138	<b>75</b> 19	0.6	1.4	
Falmouth ,		F17	Jul.	79	0.25	0.03	8	37 9	0,6	0.8	
	+1				7.79a+6.756		<del></del>	<del></del>			
penetrat	tes i	nto t	he upp	er rea	ches of Rest	ronguet C	reek b	eyond si	te RlO.		
Ascophyllum nodosum is less tolerant of low salinity but penetrates to											
mite D1/	1 in	+ha m	4 4 4 1 4	wa aaba	a of the Cree	ale Mah I.	- 7 -h	<b>-</b> b	1-	_	

0.6

2.3

1.39

1.18

Cd

0.6

2.2

Cr

0.37

0.29

May 82

Mar. 76

May 80

1753

(bim)

(mouth)

(Appledore)

Tamar

Looe

Torridge

site R14 in the middle reaches of the Creek. Table 7 shows that samples of both species from the Creek contain concentrations of Cu exceeding by roughly two orders of magnitude those of weed from site F17 at the mouth of the Estuary. Similarly, more than an order of magnitude separates levels of Zn in weed from the two localities. In F. vesiculosus, despite cleaning, a proportion of metals in weed from the Creek can be attributed to contamination of the fronds with sediment particles. Ιf it is assumed that, at worst, all the Fe in the weed stems from contamination with particulates, then the percentages attributable to contamination with other metals can be calculated from the composition of the local sediment: at site R1O these amount to about 20% for Cd, Mn and Zn, 30-40% for Ag, Co and Cu, 80% for Ni and over 90% for Pb and Cr. In A. nodosum from the Creek, metal concentrations, including that of Fe, are usually lower than in F. vesiculosus. It seems likely, therefore, that particulate contamination in F. vesiculosus accounts for some of the differences between the two species. No values for As are given in Table 7, but Langston (1980) found 63-160 µg/g in F. vesiculosus from Restronguet Creek compared with about 15 µg/g in 'normal' weed. addition, Klumpp & Petersen (1979) reported 38-184 µg/g in F. vesiculosus,

Based on earlier results from the Fal System, Bryan & Hummerstone (1973a) concluded that concentrations of metals such as Cu and Zn in F. vesiculosus give a reasonable reflection of their availabilities in solution. There is, however, some evidence from later work that Cu and Pb, for which fucoid polyphenols have very high selectivity coefficients, may also be scavenged by the weed directly from suspended particles (Luoma et al., 1982).

33-93  $\mu$ g/g in A. nodosum and 15-114  $\mu$ g/g in Enteromorpha.

#### Vascular plants

Salicornia, a salt-marsh plant, colonises many of the higher mudflats and in the upper reaches of the Creek (site R3) must be exposed to high concentrations of dissolved metals in addition to those in the sediments. Levels of Cu, Fe, Mn and Zn in the roots exceed those in the shoots and, in both tissues, concentrations are much higher in plants from the Creek than in those from an uncontaminated estuary (Table 8).

#### Macrofauna

#### Coelenterates

Actinia equina and Tealia felina from the Creek are comparatively uncontaminated (Table 9), although it is difficult to see how these

TABLE 8

SALICORNIA SP.: COMPARISON OF CONCENTRATIONS IN RESTRONGUET

CREEK WITH THOSE FROM AVON ESTUARY (JULY 1971)

Samples and sites	l	Cu	μg/g di Fe	ry wt Mn	Zn
Roots	etyt e .			. **	
Restronguet Cr.	(∿ R3)	571	4517	73	372
	(R6)	611	7779	117	359
Avon Estuary (mi	(b.	16	558	20	34
Shoots	e in species				
Restronguet Cr.	(∿ R3)	168	3168	49	289
	(R6)	169	1879	56	161
Avon Estuary (mi	d)	12	219	18	62

TABLE 9

CONCENTRATIONS IN SEA ANEMONES FROM RESTRONGUET

CREEK COMPARED WITH THOSE FROM OTHER AREAS

	μg/g dry wt										
	As	Cđ	Cu	Fe	Mn	Zn					
Actinia equina											
Restronguet Cr. (R15)	-	-	15.4	142	8.0	177					
S. Devon coast	_	0.23	10.3	278	9.8	185					
<u>Tealia</u> <u>felina</u>											
Restronguet Cr. (R24)*	55	0.40	7.7	-	-	289					
Southampton Water	72	0.07	_	-	-	200					
Irish sea <sup>±</sup>	-	0.66	57.0	730	9.3	280					
	<del></del>	·		·····							

<sup>\*</sup>Klumpp & Petersen (1979); Leatherland and Burton (1974)

<sup>&</sup>lt;sup>1</sup>Riley & Segar (1970)

anemones could avoid exposure to high ambient concentrations of Cu and Zn. The results imply that the metals are regulated, although more work is necessary to confirm this.

#### Polychaete Worms

Nereis diversicolor is probably the commonest and most widely distributed member of the Creek macrofauna and worms in the upper reaches of the Creek contain very high levels of Cu. Surprisingly, however, the highest concentrations, sometimes exceeding 2000  $\mu$ g/g, occur in worms at site Rl in the Kennall branch of the Creek, where the freshwater input is low in metals, rather than in the more obviously contaminated parts of the Creek such as site R4 on the bank of the Carnon River (Table 10).

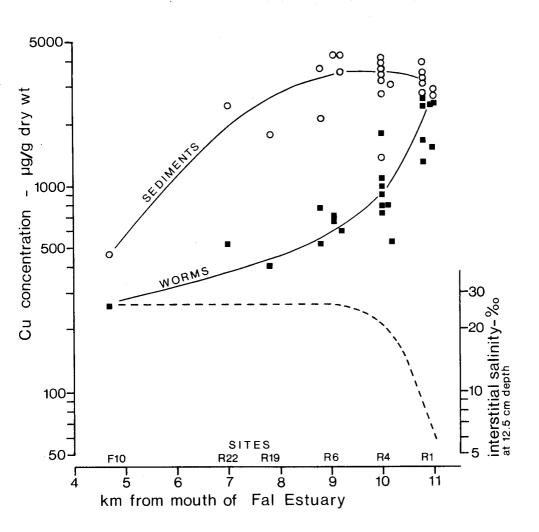


Fig. 10. Nereis diversicolor: changes in concentrations of Cu in worms and sediments (HNO<sub>3</sub> digest) with distance along Restronguet Creek. Positions of sites are shown in Figs. 3 & 4. Broken line shows sediment salinity (after Bryan & Hummerstone, 1971).

TABLE 10

NEREIS DIVERSICOLOR: CONCENTRATIONS IN WORMS FROM FAL ESTUARY SYSTEM COMPARED WITH THOSE IN OTHER ESTUARIES

	in gra		ijħ.	Highe	st conce	ntratio	ins unde	clined			4 04	্লেক ক	عاد شيد	etricie	1.
	and t	ološla		-27 -57	of also	V3.	135	<sub>. (3</sub> рид/	g dry	WEJ ALS	· Product	2.15 2.15			3.7
Estuary	Site	Date	Ag	As*	€ca	Co		Cu	Fe	Hg*	Mn	Ni	Pb	sn*	Zn
			-					Restro	nguet	Creek					
Restronguet Cr	7 R1 65	Mar. 77	5 is.0	23.	O3533	1.11	(1006)	14 30	. 554	ાળ.05	12.0	2.3	5.2	0.16	262
	R4	May 78	3.		1.8	14.2	0.,3	630	439	<b>-</b> . ,	8.3	6.5	1.9	_	405
	R6	Mar. 77	3.0	<u>87</u>	0.81	4.5	0.4	B 32	378	0.23	12.3	3.6	4.0		318
Penpol 37	R13	Max 17	1 6.36:2	57	0.97	7.5	0.70	C1932	268	0.18	14.1	3.9	9.8	0.46	302
Pandora Inn	R22	June 76	1.6	zau/d.	0.44	5.3		. 51	364	9 . G **	15.2	4.6	3.7	-	146
					- A					<u> </u>		3134 141	1 4 1 1 1 1 1 1 1 1		
*	noideí	umituqa	B287 268			计模型				al Syst	* ** · · · · · · · · · · · · · · · · ·	i di	Erei		
Truro Riv.	F2	Dec. 74		97,439	1.44	7.3	<0.3	196	424	- -	6.9	5.3	3.1	-	389
Calenick Cr.	F3	Apr. 90	25.1	• .	2.34	5.4	0.4	372	549	.o _ c	9.4	4.6	7.7	. <del>-</del> .	258
Tresillian Riv.	F <sup>1</sup> a.e.	Jan. 80	111.5	15	ા તુંત્ર છ	6.9	- ഉപ്പിന	84	735	0.21	11.9	s S Tua	2.7	1.6	298
River Fal	<b>F</b> 7	May 80	0.8	-	1.2	6.7	0.2	40	333	-	10.1	3.9	0.8	- '	259
Cowlands Cr.	F5	Apr. 80	0.9		0.17	4.9	0.2	59	497	804 L	ៈ <u>ខែ. 1</u>	3.2	2.2	-	218
Pill Cr.	<b>F</b> 9	June 76	9.8	.a5-	0,25	1.8	0.8	73	355	and the second	6.5	2.1	2.2		142
St Just Cr.	F14	May 80	0.3		0.71	1.4	0.13	44	284		10.4	1.9	2.2	- ,	156
Mylor Cr.	F11	Mar. 80	1.5		0.77	4.6	0.55	243	509		12.1	3.0	4.5	-	237
Mylor Cr.	F10	Mar. 80	ાં ⊲ુર.ક	Maria L	0.91	4.2	0.05	298	379	tall.	1117X	3.4	2.8		208
Penryn Cr	F13	July 76	, 0.4	lec	ੂ <b>0.</b> 05	2.8	0.31	18	294	DE SOL	10.3	1.9	8.9		120
			Other contaminated estuaries												
Hayle	(upper)	Nov. 74	5.3	84	0.47	10.3	<0.3	1210	734	0.22	5.7	9.1	4.2	0.08	260
Tamar	(upper)	Nov. 74	1		0.53	8.0	<0.3	130	591	0.14	12.8	4.3	7.0	0.34	179
24.1142	(appar)	1.00. 74	"."	••	<b></b> .	0.0	10.5	130	.391	0.14	12.0		7.0	0.34	1/3
- Annual Maria			1										<del></del>	<del></del>	
	, ÷,			4.4	0.44			Control							
Torridge	(lower)	Jan. 80	0.3	14	0.44	7.6	<0.3	21	604	0.28	13.9	4.4	2.0	0.09	163
Avon	(mid)	Dec. 77	0.1	7	0.14	5.1	0.5	19	564	0.07	11.8	3.3	5.4	0.09	197

\*analyses done between 1978-80 (Bryan et al., 1980)

Concentrations of Cu in sediments from the two localities are similar and the difference between the worms may in some way be related to salinity, that in the Kennall sediment being  $5-11^{\circ}/00$  compared with about  $20^{\circ}/00$  at site R4 (Bryan & Hummerstone, 1971). The overall effect is that concentrations of Cu in worms from the Creek fall rather more rapidly downstream than do the sediment levels (Fig. 10).

Appreciable concentrations of Cu are also found in  $\underline{N}$ . diversicolor from other parts of the Fal system, including Calenick Creek and Mylor Creek, and in other localities in south-west England, particularly the Hayle Estuary (Table 10). Results from a large number of estuaries have shown that, generally, a remarkably good relation exists between Cu levels in the ragworm and those of sediment samples digested with nitric acid or extracted with 1N hydrochloric acid (Luoma & Bryan, 1982).

 $\underline{\text{N.}}$  diversicolor from the Creek also contain abnormally high levels of Ag and As (Table 10) which can be related to the high sediment

concentrations (Bryan, 1974; Langston, 1980). On the other hand, despite the high concentrations of other metals in the waters (Zn, Mn, Cd) and sediments (Sn, Fe, Zn), levels in N. diversicolor from the Creek are comparatively 'normal'. Reasons for this include the ability of the ragworm to regulate concentrations of Zn, Mn and Fe in its soft tissues and also, for Zn, the presence of a high level in the jaws (~ 1.5%) which appears unrelated to environmental levels and in normal worms amounts to perhaps 25% of the body burden (Bryan & Hummerstone, 1973b, 1973c; Bryan & Gibbs, 1980). The limited accumulation of dissolved Cd by the ragworm probably results from competition from Zn for uptake sites, and was observed experimentally by Bryan & Hummerstone (1973b). Failure of the worm to absorb much Sn probably reflects its occurrence in the sediments largely as the insoluble oxide cassiterite.

Perinereis <u>cultrifera</u> is less tolerant of low salinities than N. diversicolor and occurs in coarse deposits in the lower reaches of

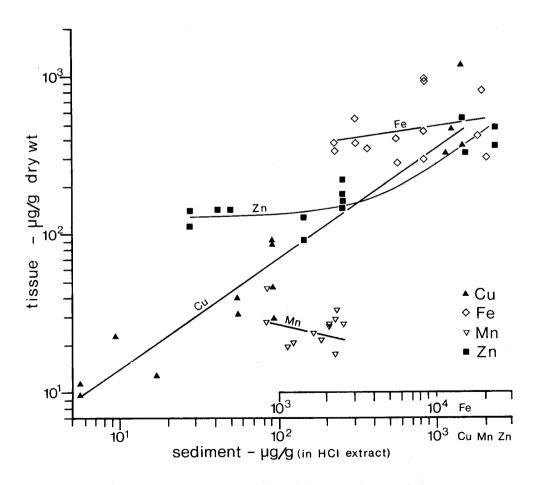


Fig. 11. Perinereis cultrifera: relationships between tissue concentrations and those of 1N HCl extracts of the < 100  $\mu m$  fraction of surface sediment.

TABLE 11

SYSTEM COMPARED WITH VALUES FROM OTHER LOCALITIES

Highest concentrations underlined

Cd

1.1

0.4

0.9

1.5

Cd

0.6

0.3

0.7

0.3

1.9

Cd

Ag

7.2

0.4

0.3

0.3

Ag

0.5

0.2

0.4

0.5

Ag

0.5

Cu

1210

687

329

38

12

12

Cu

2227

646

75

47

51

36

Cu

440

828

45

64

42

70

Perinereis cultrifera (µg/g dry wt)

Fe

Restronguet Creek

691

424

Other parts of Fal System

282

Other estuaries

380

347

Nephtys hombergi (µg/g dry wt)

Fe

Restronguet Creek

3263

1720

Other parts of Fal System

830

622

Other estuaries

1361

364

Glycera convoluta (µg/g dry wt)

Fe

Restronguet Creek

1371

1360

Other parts of Fal System

954

1064

Other localities

934

783

Mn

21

20

21

28

26

24

Mn

7.5

12.6

12.9

10.0

Mn

8.8

9.4

7.9

4.2

5.4

Pb

5.5

1.8

1.8

2.4

Pb

3.5

7.3

3.7

Pb

Zn

489

784

551

130

142

146

Zn

518

274

252

256

268

Zn

298

483

169

240

299

292

Site

R22

R23

R25

F15

(Salcombe)

(lower)

R6

R22

F5

F15

(lower)

(Salcombe)

R13

R22

F14

F15

Estuary

Pandora Inn

Place Cove

Kingsbridge

Restronquet Cr.

Pandora Inn

Cowlands Cr.

Place Cove

Kingsbridge

Tamar

Penpol

Pandora Inn

St Just Cr.

Place Cove

Whitsand Bay

Torbay

Yealm

Weir Pt

Restronguet Pt

ONCENTRATIONS	IN	ERRANT	POLYCHAETES	FROM	FAL	ESTUARY	

Restronguet Creek. At site R22, for example, metal levels in

P. cultrifera generally exceed those of N. diversicolor but, if anything,

the reverse is true of concentrations at uncontaminated sites (Tables 10

& 11). Relationships between tissue concentrations and those of sediment extracts are shown in Fig. 11. As with  $\underline{\text{N}}$ . diversicolor, body-Cu levels are clearly related to those of the sediments, whereas concentrations of

Fe and Mn show signs of being regulated against environmental changes.

Similarly, Zn appears to be regulated at low or moderate sediment

Similarly, Zn appears to be regulated at low or moderate sediment concentrations but, at the high levels found in the lower Creek, control is less effective in P. cultrifera than in N. diversicolor.

Nephtys hombergi from sites R6 and R22 in the middle and lower reaches

of the Creek contains appreciably higher concentrations of Cu, Fe and Zn than comparable samples of N. diversicolor (Tables 10 & 11). In these high-Cu worms the head end is blackened and X-ray microanalysis indicates that this is caused by the deposition of Cu sulphide in the body wall. A surface coating of oxide may account for the high level of Fe in the

A surface coating of oxide may account for the high level of Fe in the Creek animals. As in nereid polychaetes, concentrations of Cu in N. hombergi reflect environmental differences far more obviously than do body levels of Zn or Mn.

Glycera convoluta, a carnivorous polychaete, is found occasionally in the Creek and, as with the previous species, contains abnormally high levels

of Cu but less obviously enhanced concentrations of Zn and other metals (Table 11). In uncontaminated <u>G. convoluta</u> about half of the body-Cu is found in the jaws (Gibbs & Bryan, 1980). Copper levels in the jaws of worms from the Creek are unaffected by the environment and thus their contribution to the body burden of Cu falls to a few percent. It is thought that Cu may be essential to harden the jaws of glycerid worms, and in <u>G. gigantea</u> the jaw tips contain 130,000  $\mu$ g/g (13%) of the metal.

Cirriformia tentaculata occurs at site R22 in the lower part of Restronguet Creek (R22), near the low water mark, and contains higher-than-normal levels of Cu and Zn, but not Fe or Mn (Table 12).

Tharyx marioni collected from the same area of the Creek as <u>C. tentaculata</u> contains a remarkable level of As (Table 12). However, this feature seems to be unrelated to the high level of As in the Creek sediments, since equally-high concentrations are found in worms from uncontaminated sites

# TABLE 12

# CONCENTRATIONS IN SEDENTARY POLYCHAETES FROM FAL ESTUARY SYSTEM

F15

(lower)

(lower)

R22

F15

(lower)

(lower)

C5

C4

F4

F5

F15

(lower)

(coastal)

Place Cove

Pandora Inn

Place Cove

Carrick Rds

Calenick Cr.

Cowlands Cr.

Place Cove

Rame Head

\*Gibbs et al. (1983)

Tamar

Tamar

Yealm

Tamar

Yealm

## COMPARED WITH VALUES FROM OTHER LOCALITIES

Highest concentrations underlined

Estuary	Site	Ag	As <sup>*</sup>	Cd	Cu	Fe	Mn	Zn			
		Restronguet Creek									
Pandora Inn	R22	0.50	-	0.4	194	752	6.8	<u>176</u>			
	A. 19		ther pa	arts of F	al Syst	em					

84.0

2335

1512

2275

2183

As\*

26

male Cirriformia tentaculata (µg/g dry wt)

15

37

22

Tharyx marioni (µg/g dry wt)

Restronguet Creek

Cu

262

161

148

84

Cu

3124 2042

498

560

314

662

882

Other estuaries

Fal system

Melinna palmata (µg/g dry wt)

Other estuaries

0.2

Cd

Other parts of Fal system

Cd

Other estuaries

702

841

954

Fe

1183

1818

1602

1091

Fe

558

520

663

835

410

744

270

15.2

13.4

6.7

Mn

13.4

19.2

14.2

13.6

Mn

19.8

22.0

16.4

19.9

13.6

17.3

17.4

71

82

63

Zn

81

138

53

51

Zn

122

116

119

149

121

90

115

0.51 0.13

Ag

 $\frac{3.6}{1.9}$ 

0.7

0.2

3.2

0.04

1 - 3 - <u>Th</u> As\*

(Gibbs et al., 1983). Especially high levels of As, exceeding 10000  $\mu$ g/g, are found in the extensible feeding palps of <u>T</u>. marioni, but its

Levels of Cu are significantly increased in worms from the Creek, but those of Zn, Fe and Mn appear relatively 'normal' and are presumed to be regulated.

Melinna palmata dredged from the Carrick Roads off the mouth of

Restronguet Creek contains a high level of Cu (Table 12). Whilst some of this Cu may be a reflection of the high ambient levels in the area, worms from uncontaminated localities, some of them offshore, also contain large amounts of Cu. Around  $10000~\mu g/g$  of Cu, amounting to 30-40% of the body burden, are found in the branchiae and its accumulation is thought to function as a chemical defence against predation (Gibbs et al., 1981).

difference between levels in Carrick Roads animals and those from less-contaminated or offshore sites, again suggesting that these metals are regulated.

Evidence for Zn, Fe and Mn in M. palmata (Table 12) shows little

The presence of high levels of Cu in the waters and sediments of

### Polychaete summary

biochemical role is uncertain.

reflected by the presence of higher concentrations of Cu in polychaete worms. In species like <u>Nereis diversicolor</u> and <u>Nephtys hombergi</u>, which penetrate farthest upstream, Cu concentrations can reach 100 times 'normal'. In the lower reaches of the Creek, Cu levels in some species (<u>Perinereis cultrifera</u> and <u>Glycera convoluta</u>) may still be 10 - 100 times 'normal', but in the sedentary polychaetes <u>Cirriformia tentaculata</u>, <u>Tharyx marioni</u> and <u>Mellina palmata</u> the increases are less obvious. Where

Restronguet Creek and adjacent parts of the Fal Estuary is generally

they have been measured in worms from the Creek, levels of Ag are abnormally high: so also are values for As in N. diversicolor, but not in T. marioni in which exceptionally high concentrations are the norm. Although, generally speaking, levels of Zn and Fe are higher in polychaetes from the Creek, by comparison with Cu, increases are relatively small suggesting that these metals, together with Mn, are fairly efficiently regulated.

TABLE 13

SCROBICULARIA PLANA: TISSUE CONCENTRATIONS AT RESTRONGUET CREEK

SITE R13 (MARCH 80)

		μg/g	dry wt	
Tissue (6 clams)	Cu	Fe	Mn	Zn
Digestive gland	101	1925	25	7270
Kidney	168	1655	14	866
Mantle and siphons	56	2051	11.0	547
Gills	48	1218	9.5	912
Gonad/foot	25	647	7.7	543
Muscular foot	15	379	0.7	196
Adductor muscles	41	1211	7.2	339
Whole animal	46	733	6.6	1681

### Bivalve Molluscs

Scrobicularia plana, a deposit-feeding clam, is a characteristic species of intertidal estuarine muds and occurs around the margins of the middle region of the Creek, chiefly in muddy gravel deposits (Fig. 4). It is most common, however, in soft mud at the upper end of the Penpol area (R13) where densities of up to  $40/m^2$  have been recorded (see below). Clams from the Creek often reach a large size ( $\sim 5$  cm shell length) and a shell of 6.2 cm was found at Penpol.

Although concentrations of Cu and Zn in the Creek clams are abnormally high (Tables 13 & 14), they are not exceptional: similar or higher levels have been found in apparently less contaminated estuaries including other parts of the Fal System (Zn), the Gannel Estuary (Zn) and the West Looe Estuary (Cu). Among possible reasons for this anomaly are:

(a) the availability of sediment Cu may be limited by binding to the high level of Fe oxide in the creek sediment (Luoma & Bryan, 1982); (b) the availability of sediment-bound Zn may be similarly limited or the animal may be approaching saturation with the metal; (c) the clam might avoid the worst of the conditions by not deposit-feeding, and suspension-feeding only when dissolved-metal levels are not too high. Further evidence for this last possibility is considered on p. 87.

<u>Cerastoderma</u> <u>edule</u> is widely distributed in the Fal Estuary System and is particularly abundant in the River Fal where densities of > 10 mm animals were  $100-150/m^2$  at the Ardevora site (F7). Surveys of Restronguet

TABLE 14

# SCROBICULARIA PLANA: CONCENTRATIONS IN CLAMS FROM FAL ESTUARY SYSTEM COMPARED WITH THOSE IN OTHER ESTUARIES

Six animals of about 4 cm length cleaned for 1 week prior to analysis

Highest concentrations underlined. For further details see Bryan et al. (1980)

					μg,	/g dry v	wt		
Estuary	Site	Date	As	Cd	Cu	Fe	Mn	Pb	Zn
				Restro	nguet	Creek			
Restronguet Cr.	R6	Aug. 78	191	4.5	156	2700	17	50	3160
	R13	Mar. 79	190	2.3	89	2860	19	51	2580
	R16	Sept. 80	_	0.9	63	1195	17	20	2710
				Other	parts	of Fal	syster	m	
Tresillian Riv.	F1	Jan. 80	33	6.1	27	1460	12	40	3200
Calenick Cr.	<b>F</b> 3	Apr. 80	-	8.9	79	1450	28	57	2920
Truro Riv.	F2	Dec. 74	_	8.3	55	2410	20	101	4190
Cowlands Cr.	F5	Apr. 80	_	1.2	25	770	33	31	1970
River Fal	F7	Apr. 80	_	2.1	27	2030	33	17	2790
Pill Cr.	F9	June 76	-	0.4	39	902	18	22	9 39
St Just Cr.	F14	May 80	-	0.93	63	469	16	21	1043
Mylor Cr.	F10	Mar. 80	-	2.7	49	892	17	52	3010
Mylor Cr.	F11	Mar. 80	-	1.2	44	847	14	43	2130
				Other c	ontam	inated	estuar:	ies	
Gannel	(upper)	Apr. 77	_	13.6	81	1910	<u> 261</u>	991	<u>4810</u>
Tamar	(upper)	Feb. 80	-	3.3	39	2475	38	89	2181
West Looe	(upper)	Mar. 77	28	2.1	315	1310	70	489	2426
				Contro	ıl est	uaries			
Camel	(upper)	Jan. 80	27	0.4	19	989	18	8	309

Creek failed to reveal any cockles living in the sediments, but in January 1980 13 animals of 7-14 mm were found on the surface near site R16. Eight of these cockles died whilst being kept in clean water prior to analysis, and the high level of Fe observed in the survivors (Table 15) suggests that they were moribund and had not purged themselves of sediment particles. Correction of the results by assuming that all the Fe reflects contamination from sediment particles, reduces the tissue concentration of Cu by almost

0.9

52

798

126

23

539

(lower)

Torridge

CERASTODERMA EDULE: CONCENTRATIONS IN COCKLES FROM FAL ESTUARY SYSTEM COMPARED WITH THOSE IN OTHER ESTUARIES

Cockles cleaned for 2-3 days before analysis. Highest concentrations are underlined.

Estuary	Site	Date	No.	Size			μg/g d	dry wt		
ESCUALY	Site	Dace	cockles	(mm)	Cđ	Cu	Fe	Mn	Pb	Zn
						Re	estrong	uet Cree	ek	
Restronguet Cr.	R15-17	Jan. 80	5	11	2.1	486	5029	87.6	21.0	1082
3	R16	Apr. 81	1	35	3.0	174	1692	13.8	7.6	303
63d transplant <sup>‡</sup>	R18	Nov. 80	6	26	0.87	141	1258	21.9	-	317
						Other	parts o	of Fal S	System	
Carrick Rds *	(C8, 12, 15, 16, 17)	May 79	24	13	1.2	89	822	38.9	12.7	787
Mylor Cr.	F10	Mar. 80	5	36	1.4	91	1276	15.2	8.5	233
Mylor Cr.	F11	Mar. 80	1	47	1.3	59	1079	6.9	4.4	106
Pill Cr.	F9	June 76	1.	39	0.38	12.8	431	2.1	2.8	87
Cowlands Cr.	F5	Apr. 80	2	38	0.64	8.0	1189	8.6	3.3	99
River Fal	F7	May 80	5	30	0.67	6.6	748	7.2	2.0	166
St Just Cr.	F14	May 80	4	37	0.52	7.8	760	4.3	2.1	79
Penrhyn Cr.	F13	July <b>76</b>	5	34	0.52	4.7	328	3.3	6.5	92
Place Cove	F15	Mar. 79	1	41	0.40	5.0	572	3.2	2.5	79
					(	Other co	ontamina	ated est	tuaries	
Tamar	(lower)	Mar. 80	6	34	2.7	7.3	1051	4.1	4.5	71
Gannel	(mid)	Mar. 76	4	30	3.5	11.6	1422	210	69.0	180
Par	(beach)	May 81	3	20	0.38	12.9	497	6.1	3.2	125
E. Looe	(mid)	Mar. 76	5	28	0.69	9.7	565	6.2	5.3	54
						Co	ontrol e	estuarie	es	
Kingsbridge	(N. Quay)	June 74	5	36	0.45	6.0	305	3.0	4.3	40
Plym	(mid)	Mar. 80	5	33	0.67	3.7	412	1.6	1.8	38
Torridge <sup>‡</sup>	(Appledore)	Sept. 80	6	28	0.43	4.2	431	18.8	0.4	46

TABLE 16

OSTREA EDULIS: CONCENTRATIONS IN OYSTERS FROM THE FAL ESTUARY SYSTEM

COMPARED WITH VALUES FROM OTHER ESTUARIES

Animals cleaned for about 2 days before analysis. Highest values underlined

	· · · · · · · · · · · · · · · · · · ·								
				μg/	g dry	wt			
Estuary	Site	As	Cd	Cu	Fe	Mn	Pb	Zn	
				Restro	nguet	Creek			
Restronguet Cr	(R22-25)	19	-	1450	-	-	-	4150	Orton (1923)
		11	_	4000	-	-	-	5100	Orton (1923)
(extremely green	1)	_		16500	-	-	-	10500	Orton (1923)
(green oysters)		<u>39</u>	9.0	3874	157	8.1	-	14890	Sept. 1971
(pale oysters)		25	5.9	769	134	6.8	14	6004	Sept. 1971
(green oysters)		-	7.9	2614	219	16.7	2.5	17080	Feb. 1980
		-	-	1105	-	-	-	6290	George <u>et al</u> . (1978)
		17	3.0	2161	-	_		7167	Klumpp & Petersen (1979)
,			Oth	er part	s of	Fal sy	stem		
Carrick Rds	(C4,7)	-	3.9	957	386	15.9	2.8	4860	May 1979
	(C15,16,19)	-	3.5	912	294	13.0	2.4	5082	May 1979
	(C8,17)	-	3.6	609	246	8.8	2.2	3773	May 1979
St Just Pool			-	1450	-	_	_	3000	Orton (1923)
				Oth	er ar	eas			
Menai straits		<u>-</u>	5.2	392	223	<u>17.9</u>	6.2	3437	Boyden (1977)
Poole H.	(outer)	2.6*	5.9	86	394	7.0	8.0	1966	Boyden (1975)
Knysna	(S. Africa)	-	3.1	38	167	6.0	-	660	Watling & Watling (1976)
	1 1								

<sup>\*</sup>Leatherland & Burton (1974)

50% and that of Zn by about 25%. Even so, these cockles, contained higher levels of Cu and Zn than were found in a single 35 mm, apparently-healthy cockle found on the surface in the same area in March 1981, or in cockles transplanted to the Creek for 63 d (Table 15).

Cockles from other parts of the Fal System also contain abnormally high concentrations of Cu and Zn: this is seen in samples from Mylor Creek and is also apparent in the small cockle <u>Parvicardium exiguum</u> collected from the Carrick Roads off the mouth of Restronguet Creek (Table 15).

#### TABLE 17

### OSTREA EDULIS: TISSUE CONCENTRATIONS IN GREEN OYSTERS FROM

RESTRONGUET CREEK (SEPT. 1971)

Tissue	% dry wt	μg/g dry wt (from 5 oysters)											
115546	o dry we	As	Cđ	Cu	Fe	Mn	Pb	Zn					
Blood cells	11.3	-	2.7	23450	652	ND	6.2	61820					
Blood plasma	4.1	-	2.4	305	63	2.1	7.5	1225					
Muscle	26.1	38	8.3	1063	74	1.7	2.9	463					
Mantle	23.1	-	11.8	6043	293	25.2	4.5	19750					
Gills	20.2	66	8.9	6807	160	23.6	4.9	24250					
Palps	29.3	_	10.2	4585	138	7.7	ND	15920					
•													

Table 16

elsewhere. Since at least the middle of the last century, it has been recognised that Fal oysters sometimes assume a green coloration through the accumulation of Cu but are otherwise apparently unaffected (O'Shaughnessy, 1866). Later, Orton (1923) showed that oysters from the Creek also contain high concentrations of Zn and to a lesser degree As. These observations are borne out by more recent analyses of oysters from the Creek and other localities (Tables 16 & 17). The bottom line of

estuary contained relatively low concentrations of Cu and Zn, although

the spat originated in the United Kingdom.

shows that oysters grown in an uncontaminated South African

Ostrea edulis is common in the Fal Estuary System and there is a longestablished oyster fishery: some oysters are grown at the seaward end of Restronguet Creek and are subsequently decontaminated by relaying

The results for Creek oysters in Table 16 show great variability and reasons for this were examined by Boyden & Phillips (1981) who transplanted Pacific oysters, Crassostrea gigas, to the area and followed fluctuations in growth and metal content for 17 months in 1972-73. Mean concentrations of Cu and Zn ranged from around 7000 and

followed fluctuations in growth and metal content for 17 months in 1972-73. Mean concentrations of Cu and Zn ranged from around 7000 and 14000  $\mu g/g$  respectively during the winter months to 2000 and 5000  $\mu g/g$  in the summer. These fluctuations were attributed to various factors including the dilution of metals by tissue growth in the summer, metal

losses through spawning, and seasonal changes in input (see Fig. 6).

TABLE 18

MYTILUS EDULIS: CONCENTRATIONS IN MUSSELS FROM FAL ESTUARY SYSTEM

COMPARED WITH THOSE FROM OTHER ESTUARIES

Animals cleaned for 2 days before analysis. Highest values underlined

					μg/	g dry	wt		
Estuary	Site	Date	As	Cd	Cu	Fe	Mn	Pb	Zn
				R	estro	nguet	Creek	:	
6 month transplant*	R10	Apr. 81	-	6.6	<u>87</u>	310	10.6	43	1548
5 month transplant#		Oct. 74	-	1.6	∿50	201	5.4	14	264
4 month transplant*	R25	Feb. 81	-	4.9	40	332	9.8	_	368
Restronguet Pt <sup>†</sup>	R23	-	17	1.0	15			-	167
				Other	part	s of	Fal sy	stem	
Penryn Cr.	F13	July 76	-	2.2	7	274	4.7	<u>85</u>	323
		,			Other	estu	aries		
Tamar (transplant)*	(Saltash)	Oct. 80	-	2.4	7	186	11.6	21	145
Helford	(Bishop's Q.)	June 74	-	1.1	11	180	4.0	8	103
Plym	(upper)	June 74	-	23.2	13	175	22.0	37	330
Southampton Water**		· <b>-</b>	11	2.5	-	_	-	_	269
Poole H.‡	(outer)	Feb. 74	-	3.7	7	91	· _	-	97

<sup>\*</sup>Transplanted from Tamar to Restronguet Cr.; † Boyden (1977) transplant from Helford; †Klumpp & Petersen (1979); \*\*Leatherland & Burton (1974)

Mytilus edulis is not very common in the Fal System and is extremely rare in Restronguet Creek. However, Klumpp & Petersen (1979) analysed some mussels from Restronguet Point (R23) and found relatively low concentrations of Cu and Zn (Table 18). On the other hand, much higher concentrations were found in mussels transplanted to the same general area for several months by Boyden (1977) and the authors (Table 18; see also p. 89). Animals from Penryn Creek also appear to be contaminated with Zn but the level of Cu is almost 'normal'.

Macoma balthica was collected from the relatively uncontaminated Ardevora site (F9) on the Fal Estuary. Results from these animals in Table 19 show no evidence of Cu contamination but levels of Zn are comparable with those

TABLE 19

MACOMA BALTHICA: CONCENTRATIONS IN CLAMS FROM FAL SYSTEM

COMPARED WITH THOSE IN OTHER ESTUARIES

About 10 animals of ∿15 mm length cleaned for 1 week prior to analysis

	<del></del>		·								
Estuary	Site	Date	~ ~ .		μg/g (	dry wt					
ign v			Cd	Cu	Fe	Mn	Pb	Zn			
		:			Fal	system					
Fal River	(F7)	May 80	0.38	47	869	12.1	3.8	693			
		, , , , , , , , , , , , , , , , , , ,	Other contaminated estuaries								
Tavy	(mid)	Aug. 81	1.24	105	650	29.8	24.5	691			
E. Looe	(mid)	Mar. 76	-	338	788	24.4	60.6	1014			
-				Cor	ntrol es	stuaries	5				
Plym	(mid)	Jan. 80	0.96	74	626	9.1	9.1	559			
Torridge	(Appledore)	May 80	_	50	1131	33	6.2	337			
						<del></del>					

in animals from the Tavy Estuary which is moderately contaminated with metalliferous mining wastes.

### Bivalves from the Carrick Roads

Table 20 gives results for <u>Venus striatula</u>, <u>Venerupis pullastra</u>, <u>Venerupis aurea</u> and <u>Chlamys varia</u>: concentrations in <u>Parvicardium exiguum</u> have already been given in Table 15. Animals were dredged from a number of different sites off the mouth of Restronguet Creek (Fig. 5) and were pooled for tissue analysis. Comparisons with the same or related species from uncontaminated areas indicate that those from the Carrick Roads are significantly contaminated with Cu and Zn.

### Bivalve Summary

There is evidence that all nine species of bivalve collected in Restronguet Creek and the Carrick Roads are appreciably contaminated with both Cu and Zn. Oysters have a particular capacity for accumulating these metals and, occasionally Cu and Zn together account for about 2% of the dry tissue weight in animals from the mouth of the Creek. Cockles and

TABLE 20

CONCENTRATIONS IN BIVALVES FROM CARRICK ROADS (MAY 1979)

COMPARED WITH VALUES FROM UNCONTAMINATED LOCALITIES

Bivalves cleaned for 2-3 days and pooled from several sites

*									
Locality	Sites	No. of animals	Length (cm)	Cd	Cu	μg/g Fe	dry wt Mn	Pb	Zn
						Veneru	pis aure	a	
Carrick Rds	(C8,10,12)	10	3.1	1.2	111	400	5.3	2.2	199
					Ve	nerupi	s pullas	tra	
Carrick Rds	(C9, 12, 15, 17)	5	3.8	2.5		966	8.0	4.9	81
S. Devon Coast	(Wembury)	5	1.6	0.5	3.0	62	3.0	2.7	25
						Venus	striatul	a	
Carrick Rds	(C6,7,16,19,20)	8	2.1	1.1		725	7.7	- 10.4	177
Yealm	(Misery Pt)	3	2.6	1.1	19	660	6.6	32.0	68
						Ch l am	ys varia		
Carrick Rds	(C10,18)	3	4.5	4.0	54.4	214	51.2		2069
					Ch1	amys v	aria tis	sues	
Digestive gland	(C4,10,15,17)	5	4.7	29.0		601	9.2	7.2	251
Kidneys		. 5		106 <sup>-</sup>	704	325	1363	190	76300
Adductor muscles	fast slow	5 5		0.6 1.0		65 95	3.5 4.1	1.7 1.1	153 141
Mantle		5		2.2	9.5	263	8.1	2.0	119
Gills		5		6.4	16.5	357	8.4	1.9	173
Gonad/foot		5		1.9	17.5	197	28.7	3.1	506
				Ch.	lamys o	percul	aris (Br	yan 197	'3: )
Looe Bay	٠.	6-11	~6.0	5.5		113	158	12.0	462
_									

mussels are not usually found in the Creek, but concentrations of Cu and Zn in transplanted animals increased by approximately an order of magnitude. Curiously, <u>Scrobicularia plana</u>, the only fairly widely distributed bivalve in the Creek, does not accumulate such high concentrations of these metals as animals from several seemingly much less contaminated estuaries.

### Gastropod molluscs

<u>Littorina</u> <u>littorea</u> and <u>L. littoralis</u> are found in the seaweed zone in the lower one-third of Restronguet Creek and contain levels of Cu, Zn and As exceeding those of winkles from any other British estuaries (Tables 21 &

22; see also Bryan, 1983; Bryan et al., 1983).

Nucella lapillus, the dogwhelk, occurs at Restronguet Point (R23) and

accumulates higher concentrations of Cu and Zn than animals from other parts of the Fal System or other estuaries (Table 23).

Patella vulgata from outside Restronguet Point (R24) appear to contain

lower concentrations of Cu and Zn than limpets from Mylor Harbour (F12) and also from the mouth of the Red River which drains tin mines in the

## Gastropods from the Carrick Roads

Roads smaller increases are observed.

Camborne area (Table 24).

off the mouth of Restronguet Creek. Exceptionally high levels of Cu occur in <u>Nassarius reticulatus</u> and <u>Ocenebra erinacea</u>, and even under more normal conditions the former species contains a large amount of Cu. Some of this

Table 25 includes results for four species dredged from various sites

Cu almost certainly occurs as the blood respiratory pigment haemocyanin, but this is also true of gastropods such as <u>L. littorea</u> and <u>N. lapillus</u> which normally possess an order of magnitude less Cu than <u>N. reticulatus</u>

concentrations of both Cu and Zn are abnormally high, but in the slipper limpet Crepidula fornicata Zn, but not Cu, appears to be regulated.

(Tables 21 & 23). In the whelk Buccinum undatum from the Carrick Roads

### Gastropod summary

All eight species of gastropod collected in the Fal Estuary System have enhanced levels of Cu, which in <u>Littorina littorea</u>, <u>Nucella lapillus</u>

and <u>Patella vulgata</u> are about an order of magnitude higher than normal.

Levels of Zn are similarly enhanced in <u>L. littorea</u>, <u>L. littoralis</u> and

N. lapillus from the Creek, but in P. vulgata and species from the Carrick

TABLE 21

### LITTORINA LITTOREA: CONCENTRATIONS IN WINKLES FROM FAL ESTUARY

#### 30 ALESYSTEM COMPARED WITH THOSE IN OTHER ESTUARIES

Winkles cleaned for 2-3 days before analysis. Highest concentrations are underlined.

	- 3.403 school to 1	2 To 1 K TX	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	الله ال			1 /4		24 50 AL
Estuary	Site	Date	As	- ca	Ω <b>μg/g</b> Cu	dry Fe	wt Mn	Pb	Zn
		10 10	ļ.		Restron	guet	Creek		
Restronguet Pt	R23	Mar. 78	70.5	2.8	1069	492	158	3.0	956
Pandora Inn	R22 <sup>±</sup>		-	2.7	-,	498	54	9.0	250
e dito munitari ada	R22	Feb. 72		1.6	554	581	99	0.3	233
Weir Pt	R25	racorj 🙀	i git tārio	1.3	261	275	64	0.9	197
				Ot	her parts	of I	al Sy	stem	
Mylor H.	F12		- 2	1.3	464	268	49	-	179
Falmouth H.	F16	ા ાંવજ	±0¥E	1.2	<b>22</b> 2	279	20	2.3	121
Falmouth B.	F17		ii Tus	1.0	93	243	10	0.3	91
				Othe	r contami	nated	estu	aries	
West Looe	(upper)	Mar. 76	35.9	2.6	161	458	133	<u>70</u>	83
Bristol Channel	(Clevedon)		-	210	-		(4.2	@ [ ( <b>3</b>	520
Bristol Channel	(Penarth)*	<i>.</i>	- :	-	249	<b>-</b> 4	60	<b>া 15</b>	186
			<u>s</u>		Contro	l est	cuary		
Torridge	(Appledore)	May 80	19.0	2.0	129	399	42	2.2	75

Boyden (1977); Butterworth et al. (1972); Ireland & Wootton (1977); others Bryan et al. (1983)

#### TABLE 22

#### LITTORINA LITTORALIS: CONCENTRATIONS IN WINKLES FROM FAL ESTUARY

### SYSTEM COMPARED WITH THOSE IN OTHER ESTUARIES

Winkles cleaned for 2-3 days before analysis. Highest concentrations are underlined.

Estuary	Site	Date	As	ca 🗘	μg Cu	g dry Fe	wt.	Pb	 2an
	osto pro A			1951	Restr	onguet	Creek		TT J
Pandora Inn	R22	June 76	a C	5.6	841	332	233	9.3	1720
Restronguet Pt	R23*		<u>98</u>	-	-	-	-		
				Oti	er par		Fal Sy	stem	*****
Mylor Cr.	Fll	Mar. 80	-	6.0	1183	378	98	4.7	847
Pill Cr.	F9	June 76	-	4.7	649	431	197	5.9	607
Cowlands Cr.	F5	Apr. 80	-	1.2	244	418	90	3.4	163
St Just Cr.	<b>F14</b>	May 80	4.2. <b>_</b>	1.6	220	472	57	3.8	167
	i de la compa	n instal	1399	Othe	r cont	minat	ed est	uaries	
Severn	(Severn Beach)	-	12	178		-	-	-	312
Severn	(New Passage)	Oct. 76	-	171	131	311	54	4.9	296
Tamar ***********************************	(Cargreen)	Feb. 78	6 Te	15.7	726	314	188	16.7	176
₹Nata Lanta Eresata			. Terliga	Sa Tiliga, Sa a	Cont	rol lo	cality		18 97 - 495 <sup>5</sup>
S. Devon Coast	(Wembury)	May 78		4.5	98	234	20	3.7	123

Leatherland and Burton (1974). \*Klumpp & Petersen (1979);

#### TABLE 23

#### NUCELLA LAPILLUS: CONCENTRATIONS IN DOGWHELKS FROM FAL ESTUARY

### SYSTEM COMPARED WITH THOSE IN OTHER AREAS

Animals cleaned for 2 days before analysis. Highest concentrations are underlined.

Estuary	Site	Date			μд	/g dry	wt				
277337		Date	As	Cd	Cu	Fe	Mn	Pb	Zn		
	- EXTERIOR M	DE GEN			Restr	ongue t	Creek	e tonn	Sipli		
Restronguet Pt	R23	Mar. 79	- C - E	23	1002	383	37	5.0	3352		
	R23*	pu i	48	_	-	-	-	-7/			
Weir Pt	R25	Feb. 72	170	13.6	433	334	18.8	3.9	1615		
		Danker.		otl	ner par	ts of	Fal Sys	tem			
Mylor H.	F12	6 Lens		12.4	400	537	17.7	3.1	1956		
Falmouth H.	F16		-	6.5	305	281	15.1	6.3	503		
Falmouth B.	F17		1 2	13.1	177	327	13.8	1.5	822		
out loss that		80 15	Deb	Othe	er cont	aminat	ed estu	aries	131		
Red River	(mouth)	Mar. 72	-	4.7	809	185	12	1.0	323		
Looe	(max.)		-	13.0	110	214	17	5.1	416		
Bristol Channel	(Brean) 1		- 2	425	21	///2/11	-	27	3100		
					Con	trol a	reas		11		
Portland**			38	21		-		-	415		
South Devon	(coast)		-	23	66	234	13	5.0	351		

<sup>\*</sup>Klumpp & Petersen (1979); <sup>‡</sup>Bryan & Hummerstone (1977); <sup>†</sup>Butterworth <u>et al</u>. (1972); \*\*Leatherland & Burton (1974).

TABLE 24

PATELLA VULGATA: CONCENTRATIONS IN LIMPETS FROM FAL ESTUARY

### SYSTEM COMPARED WITH THOSE IN OTHER AREAS

### Animals cleaned for 2 days before analysis.

Highest concentrations are underlined.

Estuary

µg/g dry wt

Cd Cu Fe Mn Pb Zn

Restronguet Pt	R24*			37	16		ongue t	Creek	sia no		12
Meacronguet re	N29"	LANS		37	16	45		-		243	
aminakan Marai						Fal E	stuary	Syste	m		
Mylor H.	F12	Jan.	72	-	12.9	90	669	11.4	8.8	326	
Falmouth H.	F16	Jan.	72	· -	5.4	46	1070	3.7	32.0	401	
Falmouth B.	F17	Jan.	72		3.0	25	2660	24	10.2	225	
metalu ma net	being ubs	-14		993	Other	cont	aminat	ed est	uaries	+14-	
Red River	(mouth)	Mar.	72	-	24.0	147	750	15	19	323	
Looe	(max.)			100	21.0	27	2330	36	38	224	
Bristol Channel	(Portishead)	Die Ei			717	37	2594	91-7	14	434	
ALIAN CONTRACTOR						Con	trol a	reas			
Southampton Water**				13	2.7						
Portland**	Piles Yesira		V.	24	8.1	-	-		3-	95	
South Devon	(coast)			-	12	10	973	6	9	107	
*Klumpp & Petersen ( **Leatherland & Burt	1979); <sup>#</sup> Bryan	& Humn	ers	tone	(1977	); <sup>±</sup>	Boyden	(1977	);	- 176	

TABLE 25

CONCENTRATIONS IN GASTROPODS FROM THE CARRICK ROADS

(MAY 1979) COMPARED WITH VALUES FROM OTHER AREAS

Animals cleaned for 2 days before analysis.

Samples pooled from several sites.

Species		<del></del>	μg/g đ	ry wt		
and site	Cd	Cu	Fe	Min	Pb	Zn
Nassarius reticulatus						
Carrick Rds (C12, 6)	1.6	7290	5350	26.8	7.4	1385
(C8, 10, 15)	2.0	4080	3210	31.1	10.7	906
Cawsand Bay	2.1	2600	655	73.0	5.6	617
Plymouth Sound	2.5	1160	506	66.0	6.5	811
Ocenebra erinacea						
Carrick Rds (C17)	23.8	3770	762	12.4	8.3	2850
Buccinum undatum						
Carrick Rds (C15, 16)	4.0	510	338	4.8	2.8	3020
Looe Bay*	6.5	123	65	6.0	9.1	508
Crepidula fornicata						
Carrick Rds (C7)	0.5	433	223	21.5	2.8	84
Poole Harbour*	11.5	198	_	22.6	11.4	82
Southampton Water	1.4	_	~	-	-	116
S. Devon coast	1.1	132	376	130	2.3	111

<sup>\*</sup>Boyden (1977); \*Leatherland & Burton (1974)

### Crustaceans

Corophium volutator, a burrowing amphipod, was found in the summer of 1971 at site R3 on the banks of the Carnon River slightly farther upstream than the upper limit of Nereis diversicolor. Bearing in mind the high concentrations of dissolved metals to which this site is exposed, the differences in body concentrations of Cu and Zn between the Creek animals and controls from the Avon Estuary are remarkably small (Table 26). This is consistent with the presence of mechanisms for the regulation of these metals, and a degree of regulation was observed by Icely & Nott

(1980) in Cu-contaminated animals from Dulas Bay in Anglesey (Table 26). Copper is stored as large granules in the hepatopancreatic caeca of the midgut and may be voided through the gut following the

disintegration of the storage cells.

Carcinus maenas is common in the lower and middle reaches of Restronguet Creek where there is adequate cover. For the most part the population is composed of juveniles measuring less than 30 mm across the carapace, but in the summer some crabs twice this size are found at upstream sites. In crabs from site RlO, concentrations of Cu are less than three times

'normal' and those of Zn are less than twice 'normal' (Table 26). As with  $\underline{C}$ . volutator these relatively modest increases are consistent with the contention that both metal are fairly efficiently regulated (Bryan,

1968; 1971). With regard to As, Klumpp & Petersen found 62  $\mu g/g$  in crabs

from the middle reaches of the Creek and 22 µg/g near the mouth.

### <u>Fish</u>

the Creek: determinations of Cu, Zn and Fe in these flounders are compared with those for similar-sized fish from the uncontaminated Avon Estuary in Table 26. Apart from some enhancement of Cu in the liver, there is little evidence from the tissue levels that the Creek fish

Platichthys flesus was collected from site Rl in the Kennall branch of

were exposed to metal contamination. They were netted from the River Kennall at low tide when the water was fresh and therefore relatively uncontaminated (see Table 1). However, the sediments in this area are highly contaminated with Cu and Zn and are inhabited by the most heavily Cu-contaminated Nereis diversicolor in Restronguet Creek (Table 10; R1) although levels of Zn in the worms are not exceptional. Thus the absence of very significant accumulation by the flounder suggests that either metals are not being absorbed from the diet or are being

regulated in some way. Further studies on the accumulation of metals from contaminated N. diversicolor by fish were carried out using gurnards which will readily ingest whole worms.

When N. diversicolor from the flounder collection site (R1) were eaten by gurnards Trigla lucerna, there was similarly only slight evidence for the accumulation of Cu or Zn. Over a period of 22 days, fish of

20-30 g wet weight each consumed about 58 g wet weight of worms containing

TABLE 26

CONCENTRATIONS IN CRUSTACEANS AND FISH FROM RESTRONGUET

CREEK COMPARED WITH THOSE FROM UNCONTAMINATED AREAS

The state of the s		μg/g dry	wt
Species and site	Cu	Fe	Zn
Corophium volulator			
Restronguet Cr (R3)	499	700	254
Dulas Bay, Anglesey*	259	325	109
Menai Straits*	77	494	104
Avon Estuary, Devon	113	732	149
Carcinus maenas (small ∿ lg	wet wt)		
Restronguet Cr. (R10)	527	-	282
Tamar (lower)	181	_	167
Carcinus maenas (large ∿ 50c	g wet wt)		
Restronguet Cr. (R10)	191	<del></del>	149
Tamar (lower)	77	_	77
	1.		
Platichthys flesus (small 1.	.5 - 3.5g wet w	t)	
	ver 118		203
Restronguet Cr. (R1) vis	scera 28	302	123
rer	mainder 4.3	67	140
liv	ver 60	546	190
Avon Estuary (Devon) vis	scera 12	265	114
rei	mainder 3.2	35	130

<sup>\*</sup>Icely & Nott (1980)

about 300  $\mu$ g/g of Cu on a wet weight basis or 2000  $\mu$ g/g dry weight. If assimilated but not excreted, this level of input would increase the concentration of Cu in the fish by around 2000  $\mu$ g/g dry weight of Cu. Table 27 compares concentrations of Cu in these fish after 22 days with levels in gurnards in which the input of Cu from uncontaminated worms was 60 times lower. Although levels of Cu and Zn are higher in the livers of fish having the high-Cu diet, this may in part be explained by the fact that their livers were relatively smaller and apparently in a

TABLE 27

TRIGLA LUCERNA: COMPARISON OF CONCENTRATIONS IN GURNARDS

CONSUMING WORMS FROM RESTRONGUET CREEK OR CONTROL ESTUARIES

		<u> </u>	*.									
<b>-</b>	-		Liver			Visce	era	Remain	nder			
Fish wet wt at 22d (g)	in wt at 22d (%)	Wet wt of organ as % total wt	% dry matter	μg/g đi Cu	cy wt	μg/g di Cu	ry wt	μg/g di Cu	ry wt Zn			
				Die	t of Re	strongue (high me		ek worms	5			
19.4	-5.7	0.87	22.0	13.7	112	7.5	84	1.64	89			
27.4	17.7	1.40	31.8	14.3	77	11.5	88	2.66	88			
33.3	11.6	1.92	29.3	6.2	82	6.1	80	2.86	77			
12.9	_	1.56	21.3	10.9	-	6.8	-	3.62	_			
Mean	7.9	1.44	26.1	11.3	90	8.0	84	2.69	85			
	<u>+</u> 12.1	<u>+</u> 0.44	<u>+</u> 5.2	<u>+</u> 3.7	<u>+</u> 19	<u>+</u> 2.4	<u>+4</u>	<u>+</u> 0.81	<u>+</u> 7			
			Diet of Plym or Avon Estuary worms (low metal)									
13.7	14.6	3.00	39.2	1.9	39	7.4	82	2.40	109			
43.8	23.1	2.65	42.3	3.8	57	5.0	86	1.48	60			
21.7	-	2.69	31.7	6.1	-	6.0	-	1.02	-			
Mean	18.8	2.78	37.7	3.9	48	6.1	84	1.63	85			
	<u>+</u> 6.0	<u>+</u> 0.19	<u>+</u> 5.4	<u>+</u> 2.1	<u>+</u> 13	<u>+1.2</u>	<u>+</u> 3	<u>+</u> 0.70	<u>+</u> 35			
				Compa		f mean not si		s in t te cant)	est			
P	NS	<0.01	<0.05	<0.05	<0.1	NS	NS	NS	NS			

poorer condition than those in fish having a low-Cu diet (Table 27).

Faeces collected over the last 8 days of feeding contained levels of Cu 7.7 times higher than those of the ingested high-Cu worms. This suggests that much of the Cu (stored in phagolysosomes in the epidermal cells of N. diversicolor) passes through the gut of the fish without absorption: a lower faeces/worm ratio for Zn of 4.8 indicates that some Zn may be assimilated. Nbel-Lambot (1981) has shown that several species of teleost fish are able to limit metal uptake from the gut by the

formation of intestinal mucous corpuscles having the capacity to bind heavy metals. Whether the production of such corpuscles by gurnards in response to the high-Cu diet is related to the apparently inferior liver condition of these fish remains to be seen. In addition it would be interesting to see if the livers of flounders from Restronguet Creek are in any way affected. Köhler & Hölzel (1980) observed liver deterioration in flounders from the Elbe Estuary in which the sediments are contaminated with a range of substances including high levels of Zn, Cd and Hg.

### Summary

Although the crustaceans <u>Corophium volutator</u> and <u>Carcinus maenas</u>, and the flounder <u>Platichthys flesus</u> were collected in the more heavily contaminated parts of the Creek, their exposure to high concentrations of metals, particularly Cu and Zn, in waters, sediments and diet is belied by the relatively small increases observed in body concentrations. The main reason for this is the ability of these organisms to control concentrations of Cu and Zn in the tissues against environmental changes.

### General summary

The concentrations of As, Cu and Zn in the environment and biota of Restronguet Creek are compared with values from uncontaminated localities in Table 24: the contrast between these results is expressed as the ratio (Restronguet Cr./'Normal'). In all except two cases involving F. vesiculosus, ratios for the biota are far exceeded by those for the Carnon River input and the Creek sediments. The biota ratios are in part dependent on the site of collection and would be expected to decline downstream from area (1) to area (5). In addition, the ratios tend to reflect the abilities of various species to regulate metals. high ratios for Cu in plants, and some species of polychaetes and bivalve molluscs reflect the accumulation and storage of Cu rather than its regulation. On the other hand, low Cu ratios for crabs C. maenas and fish P. flesus are indicative of regulation. By comparison with the water and sediment ratios for As, those for the biota are much lower, possibly reflecting some regulatory ability. The same is generally true of Zn, although some groups including plants and molluscs often having comparatively CONCENTRATION RATIOS COMPARING VALUES FROM RESTRONGUET CREEK
AND VICINITY (RCr) WITH 'NORMAL' VALUES FROM BRITISH SITES (N)

Numbers in parentheses show approximate sample areas from head of Creek (1) to Carrick Roads (5)

RCr/N

1 100 m

116

194

12

12

1.5

7.1

-15

1.5

3.7

8.2

1.3

2.8

>2.8

	TABLE 28	
	LONG RELABITION	

RCr

2.33

2520

184

93

and 1885 and 1885 and

87

2335

191

39

17

70

98

48

37

Bivalves (\* = transplants)

Carcinus maenas (large) (3+2) 62 22 >2.8

13

15

33

7

1512

11.4

19

12

38

in the block of the elocated and

[21] 秦魏的 (1] [2 × 1] [34]

Fresh water (µg/litre)

Surface sediment (µg/g)

Sediment (max.) (1)

Fucus vesiculosus (2)

Coelenterate (µg/g)

Actinia equina (3)

Ascophyllum nodosum (3)

Nereis diversicolor (1)

Nephtys hombergi (2)

Tharyx marioni (4)

Melinna palmata (5)

Scrobicularia plana (2)

Cerastoderma edule (3)

Venerupis pullastra (5)

<u>Littorina littorea</u> (3)

Nucella lapillus (4)

Patella vulgata (5)

Buccinum undatum (5)

Crepidula fornicata (5)

Corophium volutator (1)

Platichthys flesus (liver) (1)

Littorina littoralis (3)

Nassarius reticulatus (5)

Ostrea edulis (4)

Mytilus edulis (4+2)

Venus striatula (5)

Gastropods

Crustaceans

Fisn

<u>Glycera convoluta (4)</u>

Perinereis cultrifera (4)

Cirriformia tentaculata (4)

Salicornia sp. (roots) (1+2)

Carnon River (1)

Plants (µg/g)

Polychaetes

on the home that is not too to be to be the second that the second of th

BLE 28

RCr/N

383

134

207

68

38

101 2 1.5

18 79

62

13

314 9.9

19 8.2

3.1

131

45

8.3

2.7

11

15

4.5

6.3

11

3.3

6.5

2.5

2.0

8.6

12\*

20

36

42

15

84

3.7

86

7.1

3

19

93

98

66

10

46

77

60

132

1163

RCr

12400

4220

1690

372

177

489

483

176

81

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3160

17080 1966

1082

1548

81

177

956

3352

243

1385

3018

84

254

203

THE WALL BE

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1720 - 123

122 90

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3515 98

10

99

34

106

185

130

169

51

309

38

97

25

68

75

323

95

617

373

104

190

82

63

318 120

518 252

RCr/N

1240

36

42

16

11

1.0

2.6

3.8

2.1

2.9

2.8

1.6

10

28

16\*

3.2

2.6

13

14

10

2.6

2.2

8.1

1.0

2.4

1.1

8.7

standing distance continued the distance

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689

2540

1450

546

611

15

1430

1210

828

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262

3124

156

486

3870

87

25

51

1069

841

1002

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510

433

499

118

191. 577

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45

2227

high ratios are less efficient regulators than polychaetes, crustaceans and fish in which consistently low ratios are observed.

Although concentrations of Cd in the waters of Restronguet Creek are high, this is not reflected by levels in the biota. Since Cd is not usually regulated, it is thought that competition for uptake sites from the high ambient concentrations of Zn, and possibly other metals, suppresses the absorption of Cd.

Levels of dissolved Mn in the Creek are also high and in some species including macroalgae and littorinid gastropods concentrations are higher than 'normal'. On the other hand, concentrations in polychaete worms show only small variations and appear to be regulated; this is not really surprising, since worms are often exposed to high concentrations of Mn in the interstitial waters of uncontaminated sediments.

The abnormally high levels of Fe and Ag in the Creek sediments are usually reflected by higher levels in the biota. However, with Fe, it is often difficult to separate that which has been absorbed by the organism from that deposited at the body surface as the hydrated oxide. In the Creek this deposition may occur from the overlying water or, in burrowing species, from the high concentrations of dissolved Fe in the sediment interstitial water (see Table 6). Regulation of Fe is evident in some groups, for example nereid polychaetes, but it is necessary to clean the worms thoroughly in acid-washed sand prior to analysis in order to remove Fe from body surfaces.

Generally-speaking, concentrations of Pb in the Creek biota are not much higher than 'normal'. In a number of cases, the presence of additional Pb in the organism seems to reflect its association with a high level of Fe which, as stated above, may not actually have been absorbed.

Although the Creek sediments contain more than 1000  $\mu$ g/g of Sn, concentrations in N. diversicolor only rarely exceed 1  $\mu$ g/g. This is perhaps not unexpected, since most of the sediment Sn appears to occur as the very insoluble mineral cassiterite.

## EFFECTS OF CARNON RIVER WATER AND RESTRONGUET CREEK SEDIMENTS ON ESTUARINE ORGANISMS

### Toxicity of Carnon River water

Examples from the literature showing the relative toxicities of metals to bivalve embryos, crab larvae and non-tolerant adult ragworms are given in Table 29: for comparison, the average levels of these metals in Carnon River water are also shown. Concentrations of Cu and Zn in the River water exceed the lowest toxic levels by more than two orders of magnitude and, on this basis, these two metals are the most likely by far to exert environmental effects. In Restronguet Creek also, concentrations of Cu and Zn in the water (Fig. 7) regularly exceed the levels shown to be toxic to embryos and larvae (Table 29). Furthermore, the toxicities of metals in the Creek are likely to be additive and may also be enhanced by the stresses produced by the extremes of salinity and temperature typically encountered in tidal estuaries (MacInnes & Calabrese, 1978, 1979).

TABLE 29

COMPARISON BETWEEN CONCENTRATIONS IN WATER ENTERING CREEK

AND TOXIC CONCENTRATIONS FROM LITERATURE

### Lowest effective concentrations underlined

	Concentrations		Lethal effec	Production of abnormal émbryos			
Metal	in Carnon River water entering Restronguet Creek (Table 3)	Oyster embryos* Crassostrea virginica (250/00; 260C) 48 h LC50 (µg/litre)	Crab zoeae† Cancer magister (340/00; 150C) 96 h LC50 (µg/litre)	Ragworm adults Nereis diversicolor (17.50/00; 130C) 192 h LC50 (µg/litre)	Oyster embryos‡ ©rassostrea	Mussel embryos <sup>†</sup> Mytilus edulis (34°/oo; 17°C) 48 h EC50 (µg/litre)	
Cu	689	103	49	270	5.3	5.8	
Ag	0.45	5.8	55	500	22	14	
Zn	12400	310	456	30000	119	175	
Pb	40	2450	575	>5000	758	476	
Cđ.	25.6	3800	247	100000	611	1200	
As	233	7500 <sup>3</sup>	2325	>25000 3	326 <sup>5</sup>	>3000 <sup>5</sup>	
Ni	135	1200	4360	130000	349	891	
Mn	1792	16000	-	-	<u>-</u>	· <del>-</del>	

<sup>\*</sup>Calabrese et al. (1973; 1977); †Martin et al. (1981) 3 = arsenite 5 = arsenate

Bivalve molluscs, particularly juveniles, appear to be among the most sensitive of estuarine organisms. The small-sized species Abra tenuis (Scrobiculariidae) has proved to be a convenient subject for use in toxicity experiments. Small individuals (2-3 mm) of this deposit-feeding bivalve from the Plym Estuary were used in groups of 30 to compare the toxicities of diluted Carnon River water with those of media containing different concentrations of Cu and Zn sulphates. Carnon River water diluted with filtered offshore sea water in the ratio of 1:3 killed 50% of the animals in 12 days, the end-point used being the failure of the shell to close when mechanically stimulated. The diluted River water contained 278  $\mu$ g/l of Cu and 3000  $\mu$ g/l of Zn. Comparable toxicity experiments with 75% sea water containing Cu and Zn sulphates in the ratio of 1:10 showed that 50% of the bivalves were killed in 12 days by somewhat lower concentrations (Table 30): on the other hand, higher concentrations were necessary when Cu and Zn were used singly.

TABLE 30

CONCENTRATIONS OF Cu AND Zn HAVING THE SAME TOXICITY

TO ABRA TENUIS AS DILUTED CARNON RIVER WATER

Salinity 26.25°/00; temperature 13°C; water changed regularly

12 day LC50 concentrations (μg/litre)									
•	ea water o 1:3		combined Oratio	Metals used singly					
Cu	Zn	Cu	Zn	Cu	Zn				
278	3000	250	2500	570	3750				

The results show that Cu and Zn in the diluted River water are rather less toxic than in the experimental mixture: this is probably to be expected, since a fraction of the Cu in the River water medium was probably associated with particles of Fe oxide which had not settled out when the water was allowed to stand for 8 days before dilution. Even so, the Carnon River water exerts much of the toxicity expected from its composition: the effects of Cu and Zn (and possibly other metals) appear to be additive, since if Cu and Zn are used singly, the toxic concentrations are much higher (Table 30). In A. tenuis the threshold

that of Zn is rather less than 1000  $\mu g/litre$ . Experiments with similar-sized (2-3 mm) juvenile Scrobicularia plana from Cowlands Creek (site F5) indicated a comparable threshold for Zn but one of about 50  $\mu g/litre$  for Cu. The 12 day LC50 concentrations were 325  $\mu g/litre$ for Cu and 8000 µg/litre for Zn: i.e. lower for Cu but higher for Zn than in A. tenuis. Toxicity of Restronguet Creek sediments

of Cu toxicity (used singly) appears to be around 100  $\mu g/litre$ , whilst

### In addition to considering the toxicity of the water in Restronguet

Creek it is necessary to establish the impact, if any, of the extremely metallic sediments. Before being used in experiments, surface sediments from different sites were sieved through 0.5 mm mesh and allowed to settle in seawater of 26.25°/oo salinity. Dishes containing different sediments were all placed in the same tank and completely covered with aerated seawater  $(26.25^{\circ}/\infty)$ . Thus, in theory, all the dishes were exposed to dissolved metals leached from the sediments. Groups of small bivalves

were introduced to the sediments and after 2-3 weeks the numbers of

survivors were counted. The results of such an experiment are shown in Table 31. Sediments from Restronguet Creek are obviously toxic to both

TABLE 31

TOXICITY OF RESTRONGUET CREEK SEDIMENTS IN MARCH 1980 TO ABRA TENUIS AND SCROBICULARIA PLANA

Site of surface sediment	Survival (	(%) after 18 d	Concentrations in				
	A. tenuis (Plym)	S. plana (Mylor)	S. plana (Tamar) (5 of	surviving Tamar S. plana (μg/g)			ar
	(30 of 1.6-3.2 mm)	(10 of 2.0-4.8 mm)	* · · ·	No.	Cu	Fe	Zn
Postvonguet Cx							

Restronguet Cr. 0 0 10 20 (C7) 2 440 3940 1590 50 40 (C17)7

1 298 2653 1322 20 (C15)10 40 3868 755 5 260 Mylor Cr. (F10) 100 100 100

Original concentrations

647

6

154

1909

A. tenuis and S. plana, whereas the Mylor sediments, although fairly heavily contaminated (Table 4), are not. The overlying water contained about 40  $\mu$ g/litre of Cu and 300  $\mu$ g/litre of Zn leached from the sediments, but presumably all the animals were exposed to this. Analyses of Cu, Fe and Zn in the larger surviving S. plana indicate that concentrations had more than doubled in some animals during the 18 days of exposure. Based on these analyses it would seem unlikely that the uptake of Zn could be responsible for death, since comparable levels are sometimes found under field conditions. On the other hand, toxicity experiments involving the exposure of larger clams to dissolved Cu showed that a net increase of 150-200  $\mu$ g/g in the tissue concentration was lethal: in Table 30 similar increases in the surviving clams suggest that Cu is the major toxic component in the surface sediments.

Additional experiments with Restronguet Creek sediments (site R7) have demonstrated their toxicity to other juvenile bivalves including cockles Cerastoderma edule and clams Macoma balthica.

### Summary

Comparisons between metal concentrations in the Carnon River input and toxic levels from the literature lead to the conclusion that Cu and Zn are potentially the most toxic metals in Restronguet Creek. Experiments with the small bivalve Abra tenuis show that in the diluted river water the toxic effects exerted by Cu and Zn are additive, the lower toxicity of dissolved Zn being counteracted by its much higher concentration.

Under experimental conditions, sediments from the upper reaches of the Creek are lethal to small bivalves and Cu may be the most important toxic component.

The next section considers the composition of the biota in the Fal Estuary System as a whole in order to determine whether the fauna and flora of Restronguet Creek differs appreciably from that in other comparable tributaries of the System.

#### MARINE BIOTA OF THE FAL ESTUARY

The biological survey of the Fal Estuary system can be divided into three sections: (1) investigations of the macrofauna of the intertidal mudflats within the creeks of the tributaries of the Fal ('F' sampling sites - see Fig. 3); (2) the main survey of Restronguet Creek, including both rocky substrates (stations A-T - Fig. 12) and the mud and sand flats (see Fig. 15 for locations of traverses); and (3) a dredge survey of the benthic fauna inhabiting the northern part of the Carrick Roads ('C' sampling sites - Fig. 5). The major part of the survey focussed on the biota of Restronguet Creek, the other areas of the Fal system being investigated for comparative purposes in order to assess the extent and possible effects of metallic contamination. of the observations are based on qualitative samples. From the outset it was apparent that a full-scale quantitative survey of the Fal system would not be a practical proposition since the area involved is extensive and quantitative sampling would involve transporting large amounts of sediment over considerable distances of the mudflats which, in many parts, are difficult to negotiate and, further, preliminary observations had shown that quantitative samples would not yield sufficient data to justify the time and effort involved in their processing. Intertidal macrofauna of the Fal mudflats

investigated in 1979-80 at 7 sites within the Fal system (see Fig. 4);

Excluding Restronguet Creek, the intertidal mud macrofauna was

these include the Truro River (F4), Cowlands (F5), Ardevora (F7), Philleigh (F8), Mylor (F10, F11), and St. Just (F14). For the most part, the areas sampled were between the levels of mid-tide and low water neaps; the fauna was assessed qualitatively by digging and hand-sorting the larger forms, the smaller-sized species being retrieved by washing through 0.25-1.00 mm meshes. Overall, the composition of the fauna inhabiting the mudflats proved to be fairly uniform and predictable throughout the estuary and therefore needs to be only briefly summarised.

As expected, Nereis diversicolor dominates the polychaete infauna, particularly above mid-tide level, but the small spionid Pygospio elegans is frequently also very numerous in small patches. Nephtys hombergi is generally common along with Melinna palmata and occasionally Ampharete acutifrons. Glycera convoluta tends to be widely scattered. Sieving of

the surface layers reveals the presence of small-sized worms such as Manayunkia aestuarina, Streblospio shrubsoli, Polydora sp and the oligochaete Peloscolex benedeni: these species have patchy, strongly-aggregated distributions. Bivalve molluscs are chiefly Scrobicularia plana and Cerastoderma edule: at Ardevora (F7) these two species number about 400-500/m² and 100-150/m² respectively. Macoma balthica can usually be found but tends to be sparse and Mya arenaria is erratic in its occurrence. Bivalve juveniles are common in the surface layers; frequently sievings yield many S. plana juveniles below 4 mm in length, with fewer C. edule and some M. balthica. Sieved samples reveal very few Abra tenuis in the Fal (one taken at site F11, 3 at site F14); this is curious since A. tenuis is quite abundant in similar habitats elsewhere, such as in the Tamar and Plym estuaries (noted by Gibbs, 1982).

Gastropod molluscs are the usual littorinids, L. littorea and L. saxatilis, plus Hydrobia ulvae, the latter occurring in typically dense clusters.

It can be concluded that the intertidal mud fauna of the Fal system is comparable to that found in other similar estuaries in southwest England such as the Tamar (see Spooner & Moore, 1940).

### Biota of Restronguet Creek

### Habitats

The substrates within Restronguet Creek may be conveniently divided into 'hard' and 'soft'. The hard substrates are chiefly found around the margins as low, mostly steep-sided, rock cliffs; exposed, mostly shaded, cliffs are fairly continuous along the south shore as far as opposite Devoran, extending down to MTL and beyond near the Creek mouth but only to about high water neaps in the upper reaches. Below the cliffs there is usually a band of loose rocks or shingle and this merges into the mudflat in a zone of muddy gravel. On the north shore, exposed rock cliffs extend only for a short distance inside the Creek (to about opposite transect B) and then banks of loose shingle and muddy gravel border the mudflats. The brown macroalgae and rocky shore fauna colonising the Creek margins were surveyed in April 1979 at selected sites along the south (stations A-H) and north (J-T) shores (see Figs. 12-14).

The 'soft' substrates composing the flats of the Creek can be broadly categorized as mud, muddy sand and coarse sand. Most of the

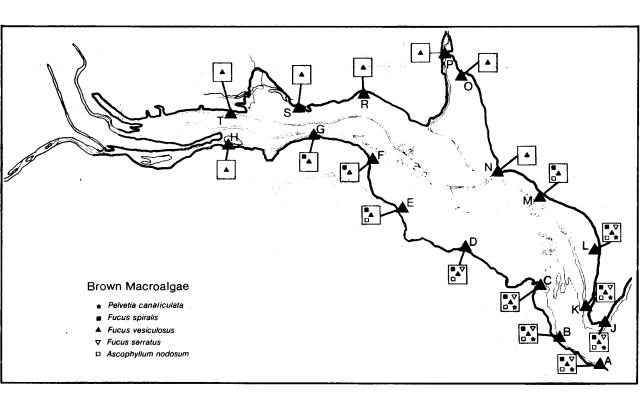


Fig. 12. Restronguet Creek: distribution of brown macroalgae.

area is covered by black mud, the consistency of which varies considerably; in some areas, particularly in the upper half of the estuary it is quite firm and easily traversed but in others, including most of the Penpol Creek, it is very soft and can be negotiated only with great difficulty and much effort. In contrast to these stable mudflats, at the mouth of the Creek there is a large area of clean, coarse sand that is maintained in a highly-rippled, mobile state by tidal currents. Between these two extremes, down the middle of the Creek, a narrow expanse of mixed deposit occurs as muddy sand; this sediment is far from uniform since digging often reveals a complex sequence of layered mud and sand, no doubt reflecting changes in river and tidal flow. The whole area of the Creek was surveyed in a semi-quantitative fashion by working transects of stations sited at intervals of 40-80 metres across the flats. At each station, areas of approximately 0.25 m<sup>2</sup> were dug out to a depth of 20 cm and the sediment sorted through by hand, noting each species present. Where possible, all individuals were counted but where a species was fairly numerous (>  $20/m^2$ ), as at many of the N. diversicolor stations, it was noted as common. With this method it was possible to occupy 131 stations sited throughout the Creek (see Fig. 15) during of spring tides in April 1979.

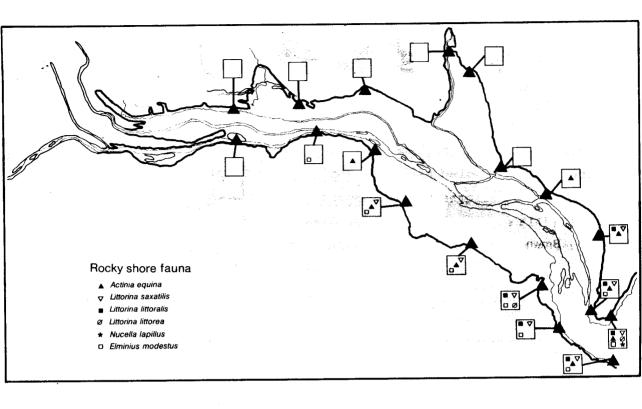


Fig. 13. Restronguet Creek: distribution of rocky shore species.

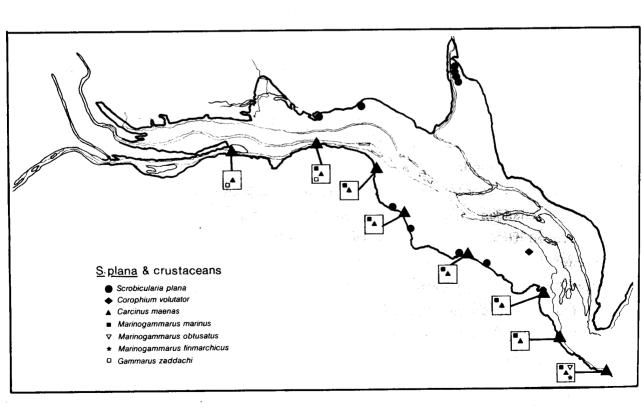


Fig. 14. Restronguet Creek: distribution of the bivalve <u>Scrobicularia plana</u> and crustacean species.

### Rocky shore species

Creek are illustrated in Fig. 12. All five of the common species - Pelvetia canaliculata, Fucus spiralis, Fucus vesiculosus, Fucus serratus and Ascophyllum nodosum - penetrate into the lower reaches and generally

The distributions of the principal brown macroalgae within the

show the well-defined pattern of zonation typical of sheltered shores.

On the north shore, four of the species die out rapidly leaving only

Fucus vesiculosus colonising the shingle banks beyond Station M. On the

south shore, however, the species less tolerant of estuarine conditions die out more gradually in the sequence P. canaliculata, F. serratus,

A. nodosum, F. spiralis. F. vesiculosus continues upriver on both shores as far as Devoran where it becomes very patchy, and the plants stunted, before dying out altogether a short distance above stations H and T.

The estuarine species <u>Fucus</u> <u>ceranoides</u> was looked for during the survey but was not recognised at any station; however, it may be present in the Creek.

are summarised in Fig. 13. Three littorinid gastropods are to be found

close to the mouth of the Creek - <u>Littorina saxatilis</u>, <u>Littorina</u>

<u>littoralis</u> and <u>Littorina littorea</u> - but only <u>L. saxatilis</u> penetrates any distance, being found to about Station E. The dogwhelk <u>Nucella lapillus</u> does not appear to be present in the Creek although it occurs just outside. The anemone <u>Actinia equina</u> is widely distributed and particularly common under stones along the south shore, occurring up to Station E. Three barnacles, <u>Chthamalus stellatus</u>, <u>Balanus balanoides</u> and <u>Elminius modestus</u> occur on the upper-shore rocks inside the Creek entrance; the former two species die out rapidly but E. modestus continues

The distributions of some animals associated with rocky habitats

over much of the Creek's length there is a continuous population of gammarids which is composed of several species showing a typical succession. Samples were collected from beneath stones at about the level

to the confluence (St. G) where it survives in small numbers on rocks

of high water neap tides along the south shore (Stations A-H). At the seaward end, three species occur - <u>Marinogammarus finmarchicus</u>, <u>Marinogammarus obtusatus</u> and <u>Marinogammarus marinus</u> (Fig. 14); the former two species are typically marine and do not appear to penetrate the Creek proper but <u>M. marinus</u> extends over much of the mid-estuarine region up to the confluence (St. G) where it overlaps in its distribution

with the brackish-water species <u>Gammarus zaddachi</u>. The upper limit of G. zaddachi was not investigated.

Carcinus maenas is abundant everywhere in the Creek (Fig. 14) where there is adequate cover in the form of weed and rocks and also man-made debris (such as corrugated iron). For the most part the population is composed of juveniles measuring less than 30 mm across the carapace.

Nereis diversicolor is the dominant species over much of the area

### Mud and sand infauna

of the Creek (Fig. 15); in the upper half the extensive high tide mudflats support a dense population of this worm reaching 4000 individuals/m<sup>2</sup>. The population extends along the banks of the tidal section of the River Kennall; the highest level at which N. diversicolor was found (Site 2) is about 1.4 metres above mean sea level, the level of mean high water neap tides; during some tidal cycles these worms would not be immersed for several days. Over the lower half of the Creek N. diversicolor is less abundant and more limited in its extent, presumably by a combination of tidal level and salinity regime but also the coarser grade and mobility of the sediment in the middle area of the estuary. Over large areas of the lower flats the population was found to be relatively sparse (less than 20/m<sup>2</sup>) and at many stations only burrows were noted. These empty burrows appeared to have been recently occupied since the sediment lining was in many cases lighter in colour and evidently still oxidised. After spawning, N. diversicolor dies; spent individuals were seen in some numbers on the mud surface in April and hence it is thought that the uninhabited burrows were those of recentlyspawned worms. Juvenile N. diversicolor (1-2 mm long) have been detected in the surface layers in both July and October and thus, whilst the main spawning of the Creek population may take place in spring, smaller spawnings probably occur during the summer months.

Nephtys hombergi and Nephtys cirrosa both occur in the Creek, the former is predominantly found in mud and muddy sand, the latter in clean coarse sand (see Clark & Haderlie, 1960). N. hombergi is probably the second most abundant polychaete in the Creek after N. diversicolor and is widely distributed over the lower half extending almost to Tallacks Creek (Fig. 16). In the survey the vast majority of specimens were small-sized (less than 30 mm long) and attained densities estimated at

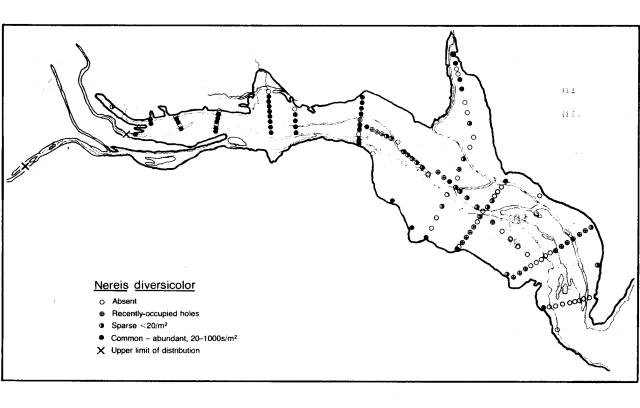


Fig. 15. Restronguet Creek: positions of survey transects and distribution of  $\underline{\text{Nereis}}$  diversicolor.

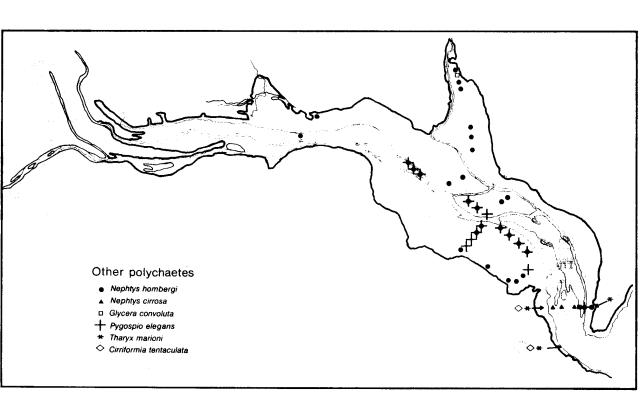


Fig. 16. Restronguet Creek: distribution of polychaete species other than N. diversicolor.

30-50/m<sup>2</sup>. From casual observations over several years it would appear that the abundance of this species in any particular area of the Creek is liable to fluctuate quite markedly, possibly because of localised population movements. Juveniles (0.6-1.0 mm in length) have been found in surface samples taken in October 1979. N. cirrosa was found only in the coarse sands at the tide-swept mouth of the Creek.

Glycera convoluta is uncommon in the Creek: in the survey two specimens of this species were recorded, one in Penpol and one at the Creek mouth. On an earlier occasion (15 Mar. 79), seven specimens were found in fine gravel at Restronguet Point. Because of its rarity, little can be said concerning the distribution of <u>G. convoluta</u> but it would seem that a breeding population of this essentially-marine species is not established in the Creek.

Pygospio elegans is found in the centre of the lower half of the Creek predominantly in the mixed mud and sand deposits (Fig. 16). Its sandy tubes are fairly conspicuous despite their small size, but in the survey were never found in any abundance. Examination of the tubes showed that in July some females were brooding eggs or larvae (up to about 1 mm in length) and evidently the population is an established one, not one maintained by larvae carried into the Creek by the incoming tide. Recently-settled juveniles have been found in surface samples taken in summer as far upstream as Tallacks Creek; thus the juveniles of the P. elegans appear to be widely distributed within the Creek by tidal currents.

Several other polychaetes occur in the muddy gravel along the shoreline at the mouth of the Creek in the vicinity of Pandora but do not penetrate the estuary to any extent. These include two cirratulids, Cirriformia tentaculata and Tharyx marioni, a nereid, Perinereis cultrifera, (all of which extend into the sublittoral off the Creek) and a capitellid, Notomastus sp.; the latter two species were not taken in the survey. The oligochaete Peloscolex benedeni also occurs in the Creek chiefly where there is any quantity of decaying organic material. Large numbers have been recorded in the vicinity of Tallacks Creek.

Corophium volutator is often present in high numbers in estuaries but proved to be very rare during the survey, only one specimen being taken in the lower half (Fig. 14). However, in previous years the species has been seen in moderate numbers burrowing in the stiff mud along the banks of the Carnon River upstream from Devoran (Site R3); the reason for its

scarcity in April 1979 is unknown.

Scrobicularia plana is seemingly the only bivalve penetrating the Creek to any extent. It is predominantly found around the margins of the middle Creek region, chiefly in muddy gravel deposits, but appears to be most common in the soft mud at the upper end of Penpol Creek: here densities of up to  $40/m^2$  have been recorded. The reason for S. plana being limited to the margins of the mudflats is not understood: large areas of the mudflats in the middle Creek region appear suitable for its colonization. Elsewhere in the Fal and in other estuaries, such as the Tamar, it occurs from the level of mean high-water to that of low-water springs although concentrated in the upper half of the tidal zone to below mid-tide level (Spooner & Moore, 1940). It is interesting to compare the size-frequency distribution of the S. plana population at Penpol with that of the population at Ardevora (Site F7) (a bay that is roughly comparable in situation and area). The Penpol population is composed solely of large individuals between 30 and 55 mm in length (Fig. 17) and to judge from the winter shell-growth-checks these animals are all fairly aged, probably 8-12 years old. However, in the Ardevora population large individuals are seemingly rare or absent but all sizegroups up to 35 mm in length are represented. A number of reasons can be forwarded to explain these differences but in the present context the point of interest is that the Ardevora population appears to have a fairly-regular annual recruitment whereas at Penpol no spat settlement would seem to have taken place for a number of years. Penpol individuals

spasmodic event.

<u>Cerastoderma edule</u> was not found in the Creek during the main survey.

However, in January 1980 some small individuals (7-14 mm long) were found scattered over the mud surface in the vicinity of transect B. All were

do appear to spawn: all specimens in a sample of 40 collected in July

mud sample taken in this area or in any other part of the Creek. features suggest that spat settlement within the Creek is a very

1980 had ripe gonads filled with seemingly-mature gametes. Nevertheless, no spat or small juvenile of S. plana has ever been found in a surface

lying exposed and did not appear to be thriving. Whilst it is possible these specimens represent the spat of 1979 it seems more likely that they had been transported from the outside grounds during rough weather. Two months later no live cockles were found in the area. No <u>C. edule</u> spat or juveniles have been found in surface mud samples from the Creek: it is

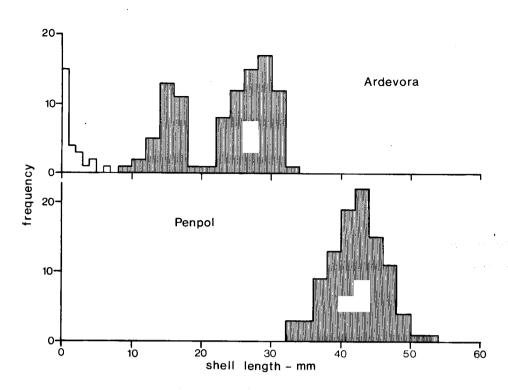


Fig. 17. Scrobicularia plana: comparison of size frequency distribution of populations in October 1979 at Ardevora (site F7) and Penpol (site R13). Open bars - juveniles from 250 μm sieved sediment sample (none taken at Penpol); hatched bars - adults hand-sorted from dug sediments.

therefore improbable the Creek supports a permanent population, unlike other similar inlets of the Fal.

### Benthic Survey of the Carrick Roads

From the biological viewpoint the Fal Estuary is of great interest by virtue of the fact that it is one of the few areas around Britain that supports an oyster fishery based on natural stocks. The fishery has been studied for many years, notably by Orton in the 1920's (Orton, 1923, 1926, 1927, 1940) and more recently by Waugh (1972) and Walne & Wood (1973). However, apart from casual observations, little has been published on the general fauna of the estuary.

The present survey was undertaken to assess the benthic fauna of the northern part of the Carrick Roads between Pill and Mylor Creeks in the area adjacent to the mouth of Restronguet Creek. The survey was carried out 1-2 May 1979 and a total of 20 stations were sampled with a small rectangular naturalist's dredge. This type of dredge effectively samples the surface and shallow-burrowing fauna to a depth of 5-10 cm depending on the hardness of the ground; deep-burrowing forms may be missed. For this survey the dredge was fitted with a fine stramin net

to prevent washing-out of the sample during hauling. At each station a part of the sample (about 10 litres of sediment) was washed through a sieve mesh of 1.0 or 2.0 mm diameter, the size depending on the deposit type, and the material retained on the sieve preserved with formalin to be sorted later in the Laboratory under a binocular microscope. The

remainder of the dredge sample (10-30 litres of sediment) was washed through a 4.0 mm mesh and the larger animals picked out on board. The

position, depths and sediment types of the sampling sites (Stations C1-

Cll on the west side, Cl2-Cl7 on the East Bank and Cl8-C20 in the main channel) are indicated on Fig. 5 and in Table 32.

Within the area surveyed, much of the bottom is flat and at shallow depths between 0.5-2.0 metres. These shoal areas are known locally as 'Parson's Bank' and 'Mylor Bank' on the western side, separated from the 'East Bank' by the steep-sided main channel which extends to depths of 12-20 m (Fig. 5). Over the whole area the bottom is composed of mud and muddy sand with varying admixtures of coarser material in the

form of fine to coarse shell gravel, lithothamnion (calcareous alga)

fragments and stones (see Table 32). Off the mouth of Restronguet Creek the mud is rather stiff whereas in the main channel it is soft and fluid. The widespread abundance of shell gravel, consisting of broken and complete bivalve shells (chiefly <u>Venerupis</u>, <u>Chlamys</u> and <u>Ostrea</u>), no doubt reflects to some extent the efforts of generations of oyster fishermen to encourage oyster spat settlement by laying large quantities of clean shell on the bottom to act as 'cultch'.

The commoner species and their relative abundance in the samples are listed in Table 32. Rarer species are listed in Table 33.

Over the whole survey area, including the main channel the infauna is dominated numerically by polychaete worms notably Melinna palmata,

Nephtys hombergi and Caulleriella spp. (chiefly Caulleriella caputesocis).

Nephtys hombergi and Caulleriella spp. (chiefly Caulleriella caputesocis Bivalves were taken in small numbers only, Abra alba being the commonest and most widespread. Venerupis pullastra, Venerupis aurea and Parvicardium exiguum all proved to be widely scattered but predominantly

found in the mixed shell-gravel deposits on the East Bank.

TABLE 32

THE DISTRIBUTION AND RELATIVE ABUNDANCE OF THE COMMONER SPECIES TAKEN IN THE SURVEY OF THE CENTRAL PART OF THE FAL ESTUARY

See Fig. 5 for sampling sites. Scale of abundance: to 1-5 individuals; to 6-20; the ->20.

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Venus striatula Venerupis aurea	**			+	+							+ +	+
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Abra alba Abra nitida	+	<b></b>	1475). J	+	+	* * <del>**</del> ** * *	+ ĺ∰u? •	- <b>+</b> 9/35#	k. 17.0+13% ►	∄5€	1 10	++ ' } ++	++ -
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Amphipoda spp.	* +	•		· · ·	+ +			*	+ +	+ ""+	+		
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Carcinus maenas  Macropipus arcuatus  Macropipus depurator	*	* 1		+	<b>₩</b>		+ +	+ +	,	+ ++			
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The juveniles of  $\underline{V}$ . pullastra, 3-6 mm in length and probably representing the 1978 brood, were fairly common and more widespread than the adults. A few species were taken in high numbers in restricted areas, for example, the polychaetes <u>Cirriformia tentaculata</u> and <u>Tharyx marioni</u>, both of which are abundant in the stiff mud off Restronguet Creek (and extend into the intertidal zone at the Creek mouth).

Since the dredge was not towed for any distance, the surface-dwelling forms, such as oysters and the gastropod Nassarius reticulatus, were not taken in large numbers. All three crab species captured appeared to be most common on the East Bank, especially Macropipus arcuatus. The epifauna attached to shells and stones was not studied in detail but the tube-worms Pomatoceros triqueter and Serpula

DREDGE SURVEY OF CARRICK ROADS : RARER SPECIES

NOT INCLUDED IN TABLE 32

TABLE 33

	,			7	<del>,</del>		
Species	Stations		ns	Species	Stations		
Coelenterate	18	19		Echiura			
Edwardsia callimorpha	10	19		Thalassema thalassemum	7		
Nemertea				Mollusca			
Nemertea spp.	4	19		Crepidula fornicata	7	14	
				Ocenebra erinacea	17		
Polychaeta	İ			Buccinum undatum	15	16	
Aphrodita aculeata	19			Philine aperta	18		
Pholoe minuta	11	15	17	Anomia ephippium	7		
Sthenelais boa	4	14		Thyasira flexuosa	20		
Phyllodoce spp	3	5	11	Mysella bidentata	14		
Ophiodromus flexuosus	11						
Syllidia armata	11	14	17	Crustacea			
Exogoninae sp.	15		fut d	Janira maculosa	15		
Platynereis dumerilii	11			Crangon crangon	4	15	
Magelona alleni	9	19					
Maldanidae sp	4	14	19	A second			
Myriochele sp.	5	19	20				
Megalomma vesiculosum	14	15					
Myxicola infundibulum	14		:				
Serpula vermicularis	7						
Pomatoceros triqueter	7		1. 38				

vermicularis were commonly seen on the shells of Chlamys varia. Of the common pests of oyster beds, several clusters of the slipper-limpet Crepidula fornicata, a few green crabs (Carcinus maenas) and one specimen of the tingle-whelk Ocenebra erinacea were noted. No starfish (Asterias rubens) was found.

In the survey samples about 70 species are represented. The great majority of these are widely distributed forms that are common in the Channel (see Marine Biological Association, 1957; Holme, 1961, 1966) and elsewhere. In terms of species composition the fauna of Fal Estuary can be compared to that of Plymouth Sound where, in suitable deposits, all of the Fal polychaetes, with one exception, can be found (see Gibbs, 1969). (The exception is Prionospio malmgreni which has not been recorded around South-West England.) The number of bivalves taken in the central Fal is lower than expected and it is possible that several deep-burrowing forms, such as Mya arenaria, were missed by the dredge but no dead shells of

these species were found. However, three bivalve species can be added to

the survey list: <u>Cerastoderma edule</u>, <u>Laevicardium norvegicum</u> and <u>Kellia suborbicularis</u>, all of which were found by Waugh (1972) on Parson's Bank in 1961-62 but were not taken in 1979.

One interesting feature of the sediments is the large quantities of <u>Bittium</u> shells present in certain areas (Stations 9, 11, 12 and 17). No live specimens of this gastropod were discovered; in view of the abundance of these shells it must be assumed that either this snail was once common in the estuary or the shells were introduced along with the cultch for the oyster spat.

## Discussion

Although more observations on the seasonal changes are required the present survey of the Creek has revealed several features of interest concerning the fauna of the intertidal flats.

Firstly, the bivalve fauna is very sparse both in numbers and variety. Only Scrobicularia plana occurs in any numbers and these are limited to the margins of the flats; in fact, in no area does this species appear to survive closer to the Carnon River than about 150 metres distance. It is perhaps surprising that Cerastoderma edule has no 'resident' population within the Creek; this species, which tolerates salinities down to 20°/oo (Tebble, 1966) is present in quantity on suitable grounds within the neighbourhood, and certainly the muddy sand areas of the lower half of the Creek appear to be suitable grounds for this species. The absence of Macoma balthica from the Creek (but found elsewhere in the Fal) is noteworthy but perhaps not significant: in South-West England this species is rarely abundant and tends to be rather patchy in its distribution between and within estuaries. Venerupis shells are abundant over the lower half of the Creek but it is suspected these may have been imported as 'cultch' for oyster spat settlement.

Secondly, no specimens of <u>Hydrobia ulvae</u> have been noted in the Creek; this small gastropod commonly occurs in high numbers in estuaries, where it forms an important food source for birds such as the Shelduck, and this is presumably the case at other localities within the Fal Estuary system.

Lastly, few polychaete species inhabit the muddy sand of the lower Creek: apart from <a href="Pygospio">Pygospio</a> elegans and <a href="Nephtys">Nephtys</a> hombergi, both of which are

common, several other estuarine species could be expected, particularly Melinna palmata, and also perhaps the cirratulid Caulleriella caput-esocis,

which is common in the Fal Estuary benthos.

In seeking the explanation for the absence of typical estuarine mud species in the Creek and the restricted distribution of Scrobicularia plana, some of the conditions imposed by the metal contamination need to be considered. Any organism settling on the sediment surface must be able to tolerate wide fluctuations in salinity and high concentrations of certain metals, particularly copper and zinc. For the spat of bivalves,

certain metals, particularly copper and zinc. For the spat of bivalves, such as <u>S. plana</u>, <u>C. edule</u> and possibly also <u>Macoma balthica</u>, these conditions are almost certainly lethal over long periods, depending also on the inflow from the Carnon River (see p. 15). However, <u>Scrobicularia</u> plana larvae do survive but, to judge from the distribution of adults,

only do so at the higher levels of the flats, i.e. around the margins; it seems possible that at these higher levels the length of time during

which the recently-settled spat are exposed to high metal concentrations is minimal whereas lower down the shore the metal concentrations and exposure times are lethal.

The toxicity of the Carnon River water may also explain the absence of Hydrobia ulvae in Restronguet Creek. As demonstrated by the data shown in Fig. 9, the surface water of the incoming tide contains the highest

in Fig. 9, the surface water of the incoming tide contains the highest metal concentrations and it is in this water that the <u>Hydrobia</u> would have to float whilst feeding on material trapped by their mucus rafts. The evidence suggests that <u>Hydrobia</u> is unable to tolerate or adapt to such high metal levels.

Although the polychaete fauna of Restronguet Creek is rather poor

in species, the widespread distribution of the spionid <u>Pygospio elegans</u> is an interesting feature. The species is known to tolerate estuarine conditions down to 12-14<sup>O</sup>/oo (Rasmussen, 1973). It has a rather complex breeding biology but briefly the eggs are laid in capsules within the burrow of the female and brooded so that the larvae are released at an advanced state of development. In the Creek these larvae appear to be widely distributed by tidal currents and have been found as far upstream as Tallack's Creek. During dispersal, these young stages, only 0.5-1.0 mm

in length, must be subjected to widely fluctuating conditions of salinity and to relatively-high metal concentrations. Their tolerance of copper and zinc must be high and it is likely that the  $\underline{P}$ . elegans population in the Creek has adapted to the metal contamination in much the same way as

the population of N. diversicolor (see below).

Whether or not the heavy-metal discharge from Restronguet Creek affects the distribution of benthic animals in the Carrick Roads remains to be investigated in detail but from the results of the present survey it would appear that the effect is minimal in that most of the species recorded in the survey area were found within the vicinity of the Creek mouth. The East Bank appears to be more productive than the west side but this may be simply a reflection of the sediment types.

### HEAVY-METAL TOLERANCE IN ESTUARINE SPECIES

## Tolerance in Restronguet Creek Species

Based on a comparison between concentrations of Cu and Zn in the waters of Restronguet Creek and levels observed to be toxic under experimental conditions, several species are much more widely distributed within the Creek than might be predicted.

The influence of exposure to dissolved Cu and Zn for 13 days on

## Fucus vesiculosus

the growth of small (3-4 cm) plants from Restronguet Creek and the Tamar Estuary is shown in Figure 18. Although the Creek weed is slightly affected by the addition of 100  $\mu$ g/litre of Cu, only 25  $\mu$ g/litre has a considerable effect on the Tamar weed. During a period of 12 days following exposure, the Creek weed regained its original growth rate at all concentrations: however, recovery of the Tamar plants was less complete and those exposed to 250  $\mu$ g/litre of Cu were dead. It was suggested by Bryan (1980) that tolerant weed is probably less permeable to Cu and that this, coupled with growth dilution, helps to limit the internal concentration and thus allows detoxication mechanisms more time to become effective. Tolerance to Cu may have a genetic basis since this

Restronguet Creek weed is especially tolerant to Zn, and  $1000~\mu g/litre$  had more influence on plants from the Creek than on those from the Tamar. This may be explained by the fact that, having a greater concentration of Zn originally, the Creek weed achieved a higher level during the experiment. Following the removal of Zn from the medium, the weed from both sites regained its original rate of growth (roughly 5% per day) and analyses after 12 days in clean water gave mean Zn concentrations of 1600 and  $1182~\mu g/g$  in the Restronguet Creek and Tamar plants respectively.

There is no evidence from the data shown in Figure 18 that the

has been observed in other seaweeds (Russell & Morris, 1970).

## Nereis diversicolor

the Avon Estuary (Tables 34 & 35).

Bryan & Hummerstone (1971, 1973b) observed that worms from Restronguet Creek are more resistant to the toxic effects of Cu and Zn than populations from less-contaminated estuaries such as the Avon (Table 34). Although tolerance is affected by salinity and temperature in both populations, worms from the Creek are consistently more metal-resistant than those from

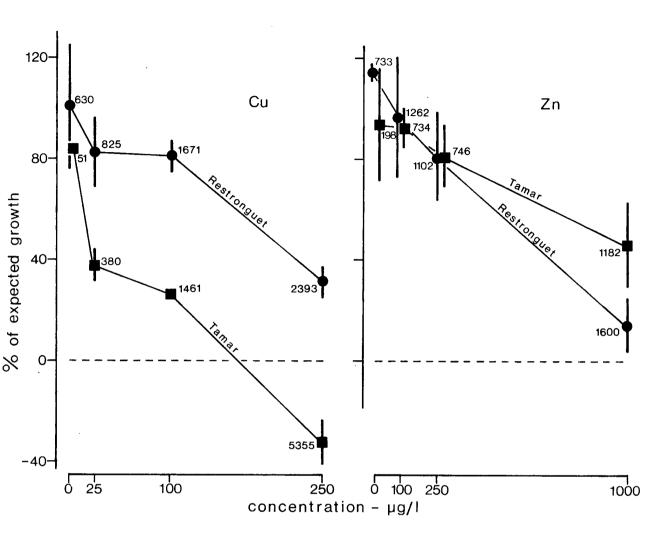


Fig. 18. Fucus vesiculosus: effects of Cu and Zn on the growth of small plants from Restronguet Creek and the Tamar Estuary. Plants were grown for 9 days in clean water and for 13 days with metals added. In the controls, growth was almost linear for the 22 day period and the effect of metals is assessed by comparing the measured increase in weight from 9-22 days with that predicted from the first 9 days of growth.

A period of 12 days in clean water was allowed for recovery and the numbers on the graphs refer to the final tissue concentrations after 34 days. Vertical lines show the range of results. Conditions were: salinity 17.5%; 13°C; continuous light; no nutrients added but media changed regularly.

NEREIS DIVERSICOLOR: COMPARISON OF LC50 CONCENTRATIONS

BETWEEN TWO POPULATIONS

TABLE 34

Metal	Salinity ( <sup>O</sup> /oo)	96 hr LC50 concentrations (μg/litre) at 13 <sup>O</sup> C			
		Restronguet Cr. worms	Avon worms		
Cu (citrate)	17.5	2300	540		
Zn (sulphate)	17.5	94000	55000		
	3.5	14600	11000		
0.35		2300	1500		

TABLE 35

NEREIS DIVERSICOLOR: INFLUENCE OF SALINITY AND
TEMPERATURE ON THE TOXICITY OF Cu TO TWO POPULATIONS

Salinity ( <sup>0</sup> /oo)	Temperature (°C)	Median survival time (hours) in 1000 μg/litre Cu (citrate) at pH 8.0			
		Restronguet Cr.	Avon Estuary		
35	13	156	79		
26.25	13	187	78		
17.5	13	250	78		
17.5	19	193	47		
8.75	13	160	48		
3.5	13	67	35		
1.75	13	8	4		

the lower permeability of Restronguet Creek worms to the metal (Bryan & Hummerstone, 1973b). In addition, these animals may possess a more efficient excretory system and are able to regulate the body concentration fairly efficiently despite the high ambient levels of Zn (e.g. Table 10).

Tolerance to Zn in N. diversicolor is based, in part at least, on

Unlike Zn, concentrations of Cu in N. <u>diversicolor</u> tend to reflect those of the sediments (p. 31) and the high concentrations found in Restronguet Creek worms are stored in membrane-bound vesicles in the epidermis (Bryan, 1976; Brown, 1982) and in the nephridia. Although the

capacity to immobilise Cu is important in the tolerant worms, this does not provide a complete explanation for their greater metal-resistance, since animals from some other estuaries store relatively high levels of Cu but are not especially tolerant. Preliminary experiments on this problem were described by Bryan (1976) and have since been repeated.

Juvenile worms (~ 10 mm long) from the Creek and the Avon Estuary (control) were grown in acid-washed sand for 4 months on a diet of yeast. The tolerance of the grown worms to two levels of dissolved Cu was then compared with that of freshly-collected animals of similar size. Table 36 shows that a large measure of Cu tolerance was retained by the grown Creek worms, although most of the tissues were laid down under Cu-free conditions and the body-Cu level was 19.3 times lower than in fresh worms.

NEREIS DIVERSICOLOR: COMPARISON OF Cu TOXICITY TO FRESH AND LABORATORY-GROWN TOLERANT AND NON-TOLERANT POPULATIONS

Estuary	Fresh or grown worms	Initial Cu level in worms (µg/g dry wt)	Median survival times (hours) in two concentrations of Cu (sulphate) at salinity 17.5 /oo and 13 C  500 μg/litre 1000 μg/litre	
Avon	fresh	15	88	68
Avon	grown	11	-	63
Restronguet Cr.	fresh	1100	>400	150
Restronguet Cr.	grown	57	∿400	103

With the aid of  $^{64}$ Cu, the absorption of Cu was studied in groups of grown and fresh worms exposed to different levels of dissolved Cu: uptake curves obtained at 100  $\mu$ g/l Cu are shown in Figure 19A. The results, expressed as concentration factors reached after 110 h (Figure 19B), show that similar levels are reached by both types of Avon worms over a range of Cu concentrations. This implies that the rate of uptake is directly proportional to the level of dissolved Cu. Results for the Creek worms are markedly different: the fresh animals absorb  $^{64}$ Cu most rapidly at low Cu concentrations, whereas the corresponding

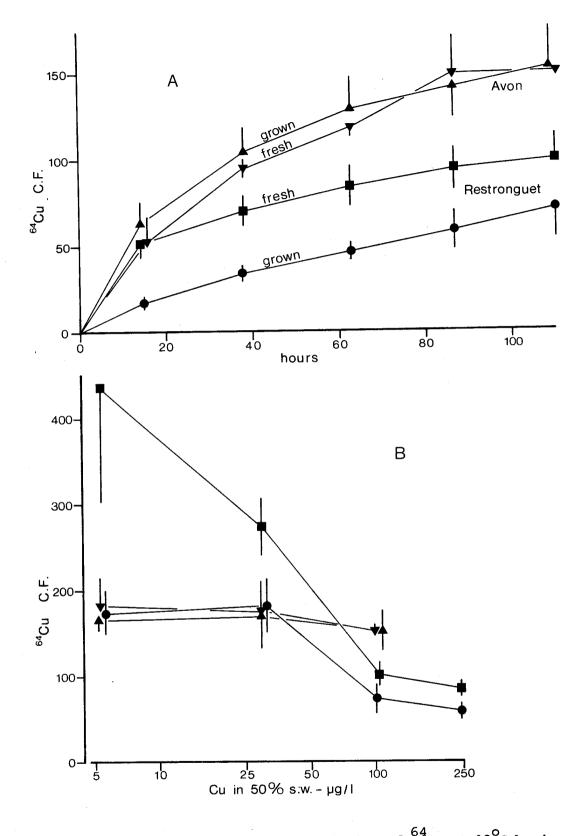


Fig. 19. Nereis diversicolor: (A) Accumulation of <sup>64</sup>Cu at 13 <sup>o</sup>C by 4 groups of worms from sea water containing 100 μg/l of stable Cu added as sulphate; (B) Relationships between the amount of Cu added to the water and concentrations factors (CF) on a wet weight basis reached after 110 hours. Values are means and standard deviations for 5 worms.

uptake of Cu by the grown animals resembles that of the Avon worms. Possibly the rapid uptake by the fresh Creek worms is a reflection of the additional binding or exchange capacity of their high-Cu epidermal cells. At 100  $\mu$ g/l of Cu, a level approaching the threshold of toxicity in Avon worms, the uptake of  $^{64}$ Cu by both groups of Creek animals is, significantly lower. Thus, reduced permeability to Cu appears to be an important factor in raising the threshold of toxicity for this population beyond 250  $\mu$ g/l. In addition, although not conclusive proof, the retention of tolerance by the grown Creek animals supports the idea that Cu-tolerance is genetically-based. The possession of tolerance is clearly a very important factor controlling the distribution of N. diversicolor in the Creek, particularly in areas of low salinity.

### Carcinus maenas

During hot weather large crabs are sometimes found at low tide under stones in the acid waters of the Carnon River (site R9). Not surprisingly perhaps, dead crabs have sometimes been seen in the river and others were found in the mud under a sheet of corrugated iron.

Tolerance to Zn. Experiments in which the resistance of Restronguet Creek crabs to Zn was compared with that of other populations showed that they were generally more tolerant. Table 37 compares the median survival times for different-sized crabs from three sites following exposure to  $10000~\mu g/l$  of Zn. Crabs from the Creek, particularly the larger specimens, are unusually tolerant to dissolved Zn. Analyses of dead crabs for Zn indicated that for the medium-sized animals a net uptake of  $440~\mu g/g$ 

TABLE 37

CARCINUS MAENAS: COMPARISON OF Zn TOXICITY TO DIFFERENT-SIZED CRABS FROM THREE POPULATIONS

Estuary	Median survival times for groups of 10 crabs in 10,000 μg/litre Zn at 35 /co salinity and 13 C. Also, net increase in body Zn level in dead crabs					
	Very small (^ 0.5g wet wt	Small ) (∿ 4g wet wt)	Medium (∿ 16g wet wt)			
	MST Net Zn up (days) (µg/g dry	_	- I			
Restronguet Cr. (R9) Falmouth H. (F16) Tamar (lower)	7.3 325 3.7 451 3.0 383	6.6 297 4.4 349 3.8 282	55* 256 <sup>±</sup> 7.8 433 6.8 440			

<sup>\*</sup>Projected value as experiment finished at 38 days. \*Dead crabs only - see text.

dry wt of Zn (control 77.5) killed the Plymouth crabs, 433  $\mu$ g/g (control 67.2) killed the Falmouth Harbour crabs and 256  $\mu$ g/g (control 136) killed 40% of the Creek crabs. However, the surviving Creek animals had absorbed more Zn, 520  $\mu$ g/g, in 38d without any obvious effect. If uptake of Zn by the crabs was linear, the net uptake of Zn per day based on the mean time of exposure would be: Plymouth 38.9  $\mu$ g/g/day, Falmouth

Table 38 gives the concentrations of Zn in the tissues of crabs which appeared unaffected by 38d exposure to 10,000  $\mu$ g/l of Zn and compares them with values for normal individuals from the lower Tamar Estuary.

28.1, Restronguet Cr. 20.2 (dead) and 13.7 (survivors).

TABLE 38

CARCINUS MAENAS: TISSUE Zn LEVELS IN CREEK CRABS SURVIVING IN sea water containing 10,000 µg/litre OF Zn FOR 38 DAYS

m:	Zn-tolerant c	reek crabs (3)	Tamar crabs (9)		
Tissue	μg/g wet wt	μg/g dry wt	μg/g wet wt	μg/g dry wt	
Urine	2.7	42.7	0.3	5.2	
Blood	68	1075	36	486	
Green gland	87	586	21	106	
Digestive gland	129	535	55	213	
Gills	493	3692	29	210	
Vas deferens	38	153	24	96	
Leg base muscle	68	314	44	201	
Dorsal carapace	269	370	2.7	3.6	

the tolerant crabs, including blood, muscle, vas deferens and digestive gland, accumulate remarkably little Zn. Higher concentrations in the carapace probably reflect surface adsorption, but levels in the green gland and especially the gills are thought to reflect the roles of these tissues in Zn excretion (Bryan, 1966).

Bearing in mind the high level of exposure, several tissues from

The results above indicate that tolerant crabs from the Creek may be less permeable to Zn, possibly better able to excrete the metal and require more Zn to kill them than non-tolerant individuals.

Previous work (Bryan, 1966) described the uptake and loss of <sup>65</sup>Zn by the tissues of the shore crab. Additional experiments were carried out in which the accumulation of <sup>65</sup>Zn was measured simultaneously in Restronguet Creek and Tamar animals exposed to different levels of stable Zn. A simple comparison of <sup>65</sup>Zn concentration factors achieved at different Zn levels (Table 39) shows that values for the Creek crabs

TABLE 39

CARCINUS MAENAS: COMPARISON OF Zn-65 CONCENTRATION FACTORS (WET BASIS) FOR INTERMOULT MALE CRABS FROM TWO POPULATIONS

Concentration of Zn added	Period of exposure (days)	Concentration factors for 1-3g wet wt crabs at 35 /00 salinity and 13 C				
to sea water (µg/litre)		Rest	ronguet Creek	Tamar		
	(4.670)	No.	C.F. <u>+</u> S.D.	No.	C.F. + S.D.	
o <sup>±</sup>	24	3	62.3 <u>+</u> 5.5	3	149 <u>+</u> 46	
100*	33	5	77.5 <u>+</u> 27.4	4	110 + 57	
250 <sup>±</sup>	24	3	28.0 <u>+</u> 4.5	3	46.3 <u>+</u> 16.3	
1000	24	3.	18.0 <u>+</u> 3.0	2	39.0 <u>+</u> 8.5	
1000*	33	6	36.7 <u>+</u> 9.2	5	54.6 <u>+</u> 15.8	
<sup>≟</sup> October	*Janua	ry		<u> </u>		

are consistently lower; this supports the contention that they are generally less permeable to Zn than normal individuals.

Unlike the situation for Cu in <u>F. vesiculosus</u> and <u>N. diversicolor</u>, where differences in tolerance between the Creek and other populations are very clear-cut, the results for Zn in <u>C. maenas</u>, a very mobile organism, show more tendency to overlap. Thus, rather than being members of a specially-tolerant population, it is possible that the animals

organism, show more tendency to overlap. Thus, rather than being members of a specially-tolerant population, it is possible that the animals acquire tolerance to high levels of Zn individually as they migrate into the Creek from less-contaminated areas. The gradual acquisition of tolerance may explain the remarkable resistance shown by some larger crabs to  $10,000~\mu g/l$  of Zn (Table 37).

Tolerance to Cu. Several toxicity experiments demonstrated that the Creek crabs are generally rather more tolerant to dissolved Cu than crabs from the Tamar Estuary. For example, when groups of 20 small crabs

from the Tamar Estuary. For example, when groups of 20 small crabs (0.4 - 4g wet wt) were exposed to 2000  $\mu g/\text{litre}$  of Cu (sulphate) at a salinity of  $35^{\circ}/\text{oo}$  and  $13^{\circ}\text{C}$ , the median survival times were 8.8 days for the Creek animals and 6.4 days for the controls. However, the former had

absorbed less Cu, net uptake 382  $\mu$ g/g dry wt (initially 260  $\mu$ g/g) whereas the controls showed a net uptake of 512  $\mu$ g/g (initially 81  $\mu$ g/g). Thus, there is an indication that the Creek animals are generally less permeable to Cu and the results of other toxicity experiments support this.

In addition, there is some evidence that the uptake of Cu from the

fed to both Creek and Tamar crabs indicated that the former absorbed only about 6% of the ingested metal compared with about 30% in the latter. As much as 25000  $\mu$ g/g dry wt of Cu was found in the crab faeces. In F. vesiculosus and N. diversicolor, the development of

diet may be limited in Cu-tolerant crabs. Unpublished experiments in which high-Cu ( $^{\circ}$  1500  $\mu g/g$  dry wt) N. diversicolor from the Creek were

tolerance to conditions in the Creek seems to be more essential for Cu than Zn, whereas the need to develop Zn-tolerance appears to be rather more important in  $\underline{C}$ .  $\underline{\text{maenas}}$ .

# Increased Cu-tolerance in other species

than some of the species already discussed.

than in those organisms already discussed. The amphipod  $\underline{C}$ .  $\underline{volutator}$  is normally very resistant to  $\underline{Cu}$  and thus it is not surprising to find that individuals collected at site R3 on the banks of the Carnon River show a comparatively modest increase in resistance. The polychaetes  $\underline{N}$ .  $\underline{hombergi}$  and the clams  $\underline{S}$ .  $\underline{plana}$  used in the tolerance experiments were from the

upper shore at site 6 and were rather less highly exposed to Cu and Zn

Evidence for increased tolerance to Cu has been observed in other

species from the Creek (Table 40) although its development is less obvious

# Summary

The possibility that organisms penetrating into the upper reaches of Restronguet Creek possess increased tolerance to metals has been examined in the seaweed <u>Fucus vesiculosus</u>, two polychaetes - <u>Nereis diversicolor</u>

and Nephtys hombergi, the clam Scrobicularia plana, and the crustaceans

TABLE 40

COMPARISON OF Cu (CITRATE) TOXICITY TO SPECIES FROM

RESTRONGUET CREEK AND OTHER ESTUARIES

	96 h LC50	168 h LC50 (μg/litre)			
Estuary	Nephtys hombergi (35°/00; 13°C)	Scrobicularia plana (17.5°/00; 13°C)	Corophium volutator (17.5°/∞; 13°C)		
Restronguet Cr. *Tamar; <sup>1</sup> Avon	700 250*	4600 2300 <sup>±</sup>	50000 32000 <sup>±</sup>		

Corophium volutator and Carcinus maenas. Increased tolerance to Cu is found in all six species and increased resistance to Zn is found in N. diversicolor and C. maenas but not F. vesiculosus. Since the area has been heavily contaminated with metals for more than 200 years, there has been plenty of time for metal-resistant populations to develop; and it is suggested that in N. diversicolor and F. vesiculosus, at least, increased metal-tolerance has a genetic basis. In C. maenas it is thought that tolerance may be acquired through exposure to increasing concentrations of Zn or Cu as the crabs migrate upstream. Similar conclusions may apply to other relatively mobile species including N. hombergi and C. volutator.

Although undoubtedly the mechanisms of tolerance vary in detail from species to species, the development of lower metal permeability seems to be a common feature which presumably allows more time for the detoxication of the metal.

## Uptake and effects of metals in transplanted organisms

Experiments were carried out to discover (1) whether organisms from other estuaries can survive at sites in the Creek occupied by native species possessing, initially at least, a greater degree of metal tolerance, and (2) whether in view of the absence of some species from the Creek and the limited distributions of others, adult animals (which are generally less sensitive than young stages) can survive at sites from which they are

absent but would be expected to occur if the Creek were 'normal'.

## Macroalgae

Fucus vesiculosus and Ascophyllum nodosum were transplanted from the Tamar Estuary (Torpoint) to the lower Creek (site R19) on two occasions (Fig. 20). Both Zn and Cu were absorbed more rapidly by F. vesiculosus than by A. nodosum and in each experiment the former species was in a very poor condition after 7 months compared with the Cu-tolerant native weed from the same site. A. nodosum was not so obviously affected by the conditions and this may be related to its much slower accumulation of both metals. Whether the native A. nodosum is a metal-tolerant strain, or whether the species can acquire metal tolerance, remains unknown. Concentrations of Zn and Cu in the native weed of both species show comparable annual fluctuations: these reflect the higher input during the winter months and also the high level of Zn input observed in the autumn of 1980 (Fig. 6).

## Scrobicularia plana

Uncontaminated clams from the lower Torridge Estuary were marked with waterproof ink and transplanted to site R6 which is the upstream limit of native <u>S. plana</u> in the Creek. The clams were unrestricted by netting. At least one animal survived for 280 d and its body levels of Cu and Zn approached those of the natives with Cu being more rapidly absorbed than Zn (Fig. 21). Curiously, in view of the exceptional levels of Cu and Zn in Restronguet Creek, concentrations in <u>S. plana</u> are not particularly remarkable and higher levels have been observed in animals from some other estuaries (Table 14).

Even a short distance down the shore from site R6, no S. plana are found and wide expanses of the Creek mud flats where they would normally be expected are devoid of clams. In the search for an explanation, clams from Penpol (site R13) were moved to sites in the upper and lower Creek where native clams are absent. At intervals the animals were recovered for metal analysis and note was made of the relative proportions of living and dead clams.

Table 41 summarises the results. Mortality was higher at the upstream sites (R7-R9) and was also increased at sites nearer to the channel of the Carnon River (R9 and R16 in Table 41). However, there is no clear evidence from analyses of the survivors (Table 41) that the transplanted clams were killed by the accumulation of Cu or Zn, since

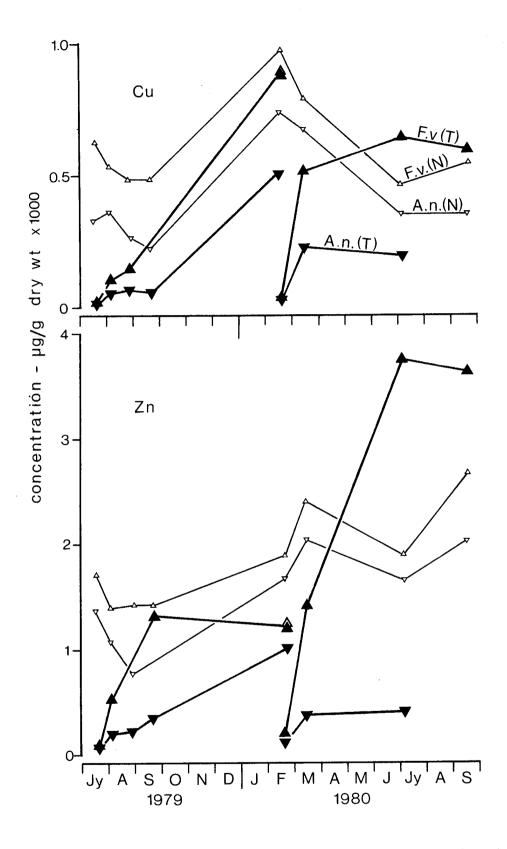


Fig. 20. Fucus vesiculosus (F.v.) and Ascophyllum nodosum (A.n.):

absorption of Cu and Zn at site R19 in Restronguet Creek

by plants transplanted from the Tamar Estuary (T) on 2

occasions (closed symbols). Open symbols show values for

native weed (N). Used tips and first vesicle of A. nodosum,

but older frond for F. vesiculosus

similar or higher values have been found in other, apparently unaffected populations (Table 14).

S. plana from the moderately-contaminated Tamar Estuary (Weir Quay) were also transplanted to two sites during these experiments and survived almost as well as the transplanted Penpol animals (Table 41). When, in a later experiment, clams from the relatively-uncontaminated lower Torridge Estuary were used they seemed to be more sensitive than the other populations. However, this may reflect the fact that the experiment

higher metal inputs, were reached sooner. There is no clear evidence from the analyses of Penpol  $\underline{s}$ .  $\underline{plana}$  transplanted within the Creek that mortalities are directly related to the accumulation of Cu or  $\underline{s}$ . In view of the high levels of  $\underline{s}$  and  $\underline{s}$  cu in

started later in the year and thus the stresses of winter, including

the accumulation of Cu or Zn. In view of the high levels of Zn and Cu in the waters and sediments of the Creek and their apparent availability to S. plana, it is remarkable that concentrations in these clams are not much higher (see also p. 37). This might be explained if, rather than deposit-feeding on the metallic sediments, the animals suspension-feed at

high tide when, because of stratification in the water, relatively clean sea water lies above the sediments. A possible reason for the high mortalities at the most upstream sites R7 - R9 may be that the clams spend so much time avoiding contact with high concentrations of metals in the overlying water that they die from a combination of anoxia and starvation. This is not always borne out by the condition (dry wt and shell length) of the active survivors in Table 41, but was certainly true of many specimens which were found to be moribund and therefore classed

as dead. Support for this idea comes from the work of Akberali & Black

(1980) who found that <u>S. plana</u> reacted to Cu levels of 10-100  $\mu$ g/l by closing the shell and only sampled the environment again 2-3h later. Shell closure was also effected by 500  $\mu$ g/l of Zn or more (Akberali <u>et al.</u> 1981). The fact that these levels of Cu and Zn are typical of Restronguet Creek, certainly gives credence to this explanation.

# Cerastoderma edule

Cockles of about 25 mm shell length were collected from the lower Torridge Estuary and placed in groups of 50 in the sediments at four sites (R15 - R18) along transect B in the Creek. Each group was covered with a cage of plastic-covered wire, the edges being buried in the sediment. The accumulation of Cu, Fe and Zn by the cockles is shown in

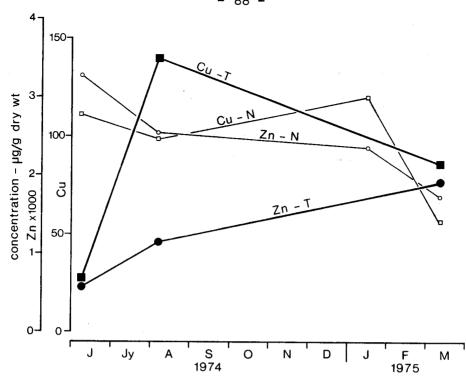


Fig. 21. Scrobicularia plana: changes in concentrations of Cu and

Zn in clams transplanted from lower Torridge Estuary to

Site R6 (T - closed symbols) compared with levels in native

clams (N - open symbols).

TABLE 41 SCROBICULARIA PLANA: CONCENTRATIONS OF CU AND Zn IN CLAMS TRANSPLANTED TO SITES IN RESTRONGUET CREEK FROM 3 DIFFERENT SOURCES INCLUDING THE CREEK ITSELF (PENPOL) 1431.330 Clams cleaned for 1 week before analysis Tissue dry Tissue dry Tissue dry Survival\* wt and Survival\* wt and Survival' wt and Shell length Site 11 13 X 3 length (μ**g**/g) au / shell length (µg/g) (1) (µg/g) Penpol ... 03 Day O (Feb. 80) Day 219 (Sept. 80) Day 419 (Apr. 81) R13 56 0.36/40 art 1515 1000 0.49/44 2082 0.43/42 62 1711 Penpol Day 219 Day 70 (Apr. 80) Day 385 (Mar. 81) transplants 19 0.37/41 2322 : ° :33 0.34/45 2577 of His 0.26/424 R7 0.32/41 2245 22 2273 R16 1 8 75 0.41/44 1635 100 0.47/43 91 2367 97 1952 0.417412 0.29/44 69 2438 1426 Day 0 (Feb. 80) : 99° T. Tamar 0.27/40 39 natives Tamar Day 219 (Sept. 80) Day 385 (Mar. 81) Day 70 (Apr. 80) transplants 0.22/434 R8 37 2779 O o. 35/42<sup>2</sup> R16 100 0.28/42 2842 36 0.34/40 101 3180 50 94 4344 Day O (Sept. 80) 60 m L. Torridge 0.32/37 40 477 native of. L. Torridge Day 42 (Nov. 80) Day 166 (Mar. 81) transplants **O** 1/1-2 30 R9 71 837 62 864 學的特 0.31/38<sup>1</sup> 0.25/38<sup>3</sup> R16 0.39/37 100 73 636 10 70 1739 0.40/37 37 100 35 91 651 1533 No. of animals used clams when all animals recover ed from a fraction of transplant area Fig. 22. After 63 days, concentrations of 141  $\mu$ g/g of Cu and 317  $\mu$ g/g of Zn were reached by cockles at site R18 nearest to the channel of the Carnon River and were comparable with levels found in an apparently

healthy native cockle of 35 mm found in the Creek (Table 15). Although only 10-15% mortality was observed after 63 days the remaining cockles died during the next two months (December and January, 1981). A second experiment in March and April 1981 when fresh water and heavy-metal inputs were particularly high (Fig. 6) was concluded after only 26 days.

experiment in March and April 1981 when fresh water and heavy-metal inputs were particularly high (Fig. 6) was concluded after only 26 days. Metal levels in the few surviving animals were similar to those observed previously after 63 days. In both transplant experiments it is thought that swamping by recently-deposited sediment may have contributed to the

little Cu or Zn from Creek sediments covered with flowing sea water. On the other hand, uptake was appreciable if the water was not changed since metals leached from the sediment remained available. This suggests that dissolved metals are the most important source in cockles. After 18 days in sediments covered with unchanged sea water, some cockles had died and levels of 242  $\mu$ g/g Cu and 404  $\mu$ g/g Zn were reached in the surviving animals. It appears, therefore, that the toxic body-burden of Cu is somewhere around 250  $\mu$ g/g. Support comes from the discovery of 486  $\mu$ g/g

of Cu in some moribund 11 mm native cockles (Table 15) of which sediment contamination may account for about 200  $\mu$ g/g (p. 38). Although probably

a contributory factor, it is assumed that Zn is less toxic to cockles than Cu, and this is perhaps borne out by the high value of 787  $\mu$ g/g of Zn found in the small cockle Parvicardium exiguum dredged from the Carrick

In laboratory experiments it was observed that cockles absorbed very

It is concluded that levels of dissolved Cu and Zn in the Creek are generally too high for the prolonged survival of adult cockles, although physical stresses produced by the fine iron oxide-rich surface-sediment may also be a contributory factor.

# Mytilus edulis

Roads (Table 15).

mortality of the cockles.

Groups of 30 mussels of 6-7 cm shell length collected from the Tamar Estuary (Saltash) were placed in cages of plastic-covered wire at 6 intertidal sites (R25, R19, R14, R12, R11, R10) extending from Weir Point to the confluence of the Carnon and Kennall Rivers. Samples,

usually of 5 mussels, were taken from each site at intervals over a

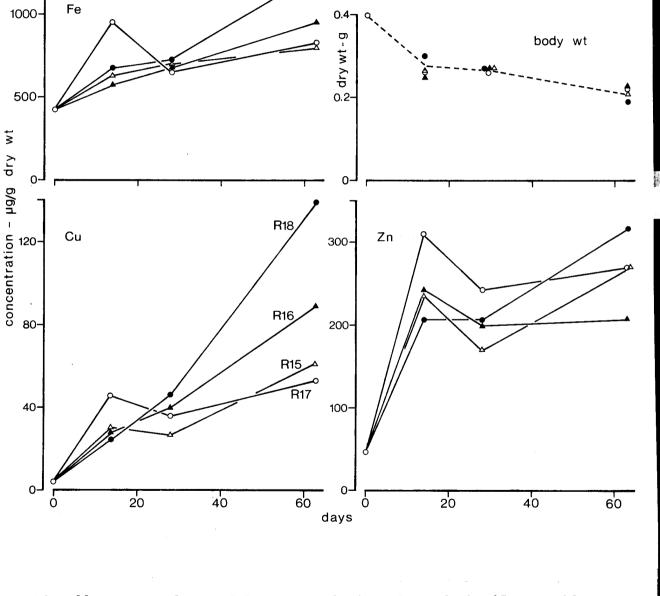


Fig. 22. <u>Cerastoderma edule</u>: accumulation of metals by 25 mm cockles transplanted from the lower Torridge Estuary to transect B (R15-R18) in Restronguet Creek in Sept. 80.

period of 7 months, except at Weir Point where the cage was washed away after 5 months. During the experiment, 33% of the mussels died at sites Rll and Rl4, 30% died at Rl0, 17% at Rl9 and 13% at Rl2. There was also a tendency for tissue weights to fall during the experiment, but this might be expected in the winter months. Concentrations of Cu, Zn and Fe increased considerably during the seven-month period, although at the end of the experiment, in May, there are signs that concentrations were falling from maxima reached in April when metal inputs were also highest (Figs. 23 & 6). Gonad development was observed in about 20% of the mussels sampled in April and 50% of those surviving until May. The highest values reached in April, after 6 months, are shown in Table 18

and the levels in the bodies and tissues of mussels at the end of the

Mussels survived in the Creek better than was expected, especially

at the more upstream sites where tissue-Cu concentrations exceeded the 60  $\mu$ g/g dry weight level estimated by Martin (1979) to be lethal. One reason for this almost certainly depends on the ability of the animals to avoid high levels of dissolved Cu by shell closure. Strömgren (1982) observed that 5  $\mu$ g/l of Cu induced shell closure in M. edulis, 6-7  $\mu$ g/l totally inhibited shell growth and 40-80  $\mu$ g/l represented the 14 day LC50 level: Zn was less toxic and 200  $\mu$ g/l reduced shell growth by 80%. However, these results refer to continuous exposure to metals whereas, in the Creek, stratification of the water means that exposure to the highest concentrations is intermittent. Sensitivity to increased Cu levels at certain states of the tide would also enable the mussel to avoid exposure to high concentrations of dissolved Zn, and freshly-precipitated Fe which is known to have a deleterious effect on mussels (Winter, 1972). Average ambient metal concentrations at the transplant sites were undoubtedly high, as is indicated by the levels in Fucus

# <u>Littorina</u> <u>littorea</u> and <u>L.</u> <u>littoralis</u>

vesiculosus from the same sites (Table 7).

experiment are given in Table 42.

were marked with a file and transplanted to site R19 in the Creek. This site is approaching the upstream limits of distribution of the native winkles. The accumulation of As, Cu and Zn by transplanted L. <u>littorea</u> is illustrated in Figure 24 and shows that uptake occurs mainly during the first two months. Following the uptake phase, fluctuations in concentration

More than 200 winkles of each species from the Tamar Estuary (Torpoint)

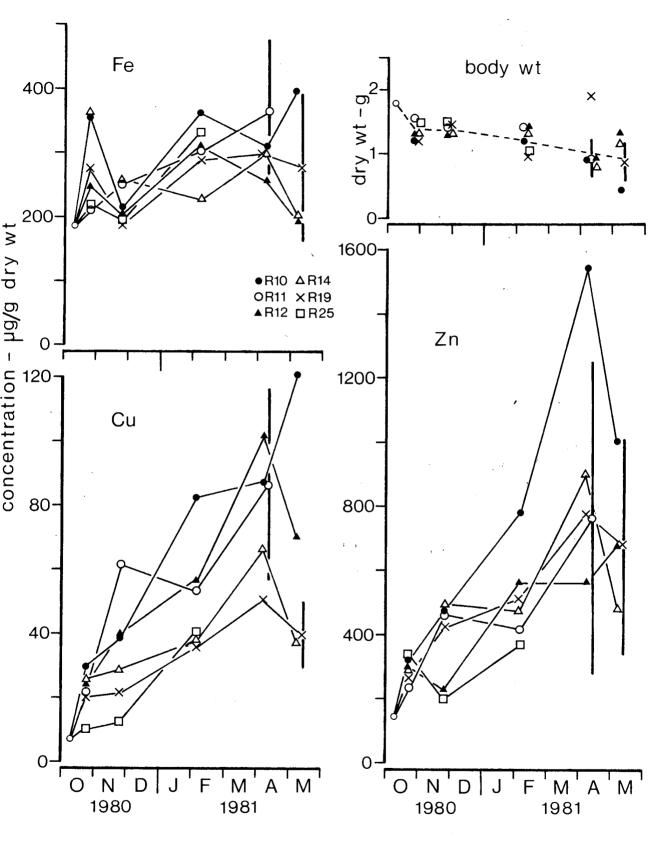


Fig. 23. Mytilus edulis: accumulation of metals in 6-7 cm mussels transplanted to 6 sites in Restronguet Creek from the Tamar Estuary. Vertical lines show standard deviations for 5 animals.

TABLE 42

## MYTILUS EDULIS: CONCENTRATIONS IN WHOLE ANIMALS AND TISSUES

### AFTER 7 MONTHS IN RESTRONGUET CREEK

Animals cleaned for 2 days before analysis.

Byssal threads removed.

	I					·	<del></del>
Site	No.	Cđ	Cu	μg/g dr Fe	y weigh Mn	t Pb	Zn
				whole	mussels		
RIO	1	7.1	121	399	15.4	31	1004
R12	3	4.1	50	193	6.0	28	670
R14	3	5.7	37	201	5.0	38	480
R19	5	6.5	40	278	9.5	37	674
Original concentrations	10	2.4	7	186	11.6	21	145
		Tissues (site Rl2)					
Kidneys		_	561	925	_	-	29160
Digestive gland		- -	53	573	_	-	146
Gills		-	259	304	_	_	138
Mantle		<del>-</del>	55	446	_	_	81
Foot & muscle	·	· -	21	150	_		110
Adductor muscles	,	<b>-</b>	5.7	130	-	_	114

were observed over the next 10 months. Comparable variations were observed for Cu and Zn in F. vesiculosus from the same site indicating that both species were responding to fluctuations in the input of dissolved metals to the Creek, albeit perhaps indirectly through the algal diet in the winkle. It appears that L. littorea from the Tamar Estuary can, to a large degree, adapt to the conditions in the lower Creek. This may indicate that the native animals do not represent an especially metal-tolerant strain of winkle but migrate into the Creek from less contaminated localities. More detailed, studies on the native winkles have been carried out recently (Bryan et al., 1983; Mason & Simkiss, 1983), but as yet no toxicity experiments have been carried out to see whether the native animals possess increased tolerance and whether this can be induced in transplants.

Transplant experiments involving L. littoralis gave essentially

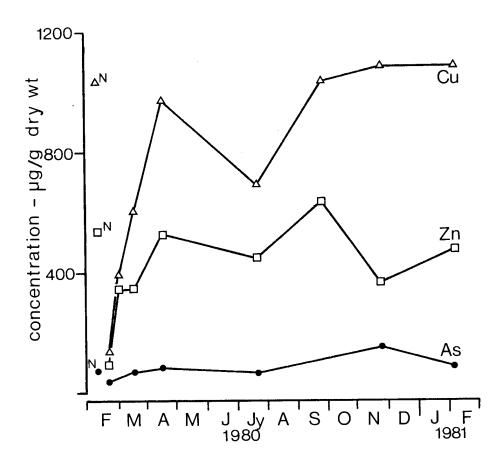


Fig. 24. <u>Littorina littorea</u>: accumulation of Cu, Zn and As by winkles transplanted from the Tamar Estuary to site R19 in Restronguet Creek. Levels in native winkles indicated by N.

the same results, but no animals definitely identified as transplants were found after 7 months. Since the movement of these smaller winkles was not restricted, it remains uncertain whether they migrated, were eaten by crabs or killed by the conditions. Additional work on heavy metals in this species from the Restronguet Creek and other estuaries has been described by Bryan (1983).

#### GENERAL DISCUSSION

## Heavy metals in the environment

Carnon River which drains acidic mine waste water into Restronguet Creek. Concentrations of metals in the River are abnormally high, but levels of Zn are exceptional and often exceed  $10000~\mu g/l$ . Interactions between River water and sea water in the Creek lead to the flocculation and

The most important source of heavy metals in the Fal System is the

deposition of Fe, probably as the hydrated oxide. Other elements, including Cu, As, Pb, and a small proportion of the Zn are also deposited probably due to adsorption by the Fe oxide and, in the case of Cu at least, by adsorption to humic substances (see p. 23). These elements, together with Ag and Sn which enter the Creek largely in the particulate phase, become enriched in the sediments and reach concentrations exceeding 'normal' estuarine levels by factors of about 10 for Pb, 40 for Ag and Zn, and 100 for Cu, As and Sn. Elements that tend to remain in solution in the Creek include Cd, Co, Mn, Ni and Zn but only Zn, by

A comparable study has been carried out by Foster et al (1978) in Dulas Bay, Anglesey, which receives acid mine wastes via the Afon Goch. They concluded that losses of Cu and Zn from solution occurred by adsorption onto hydrated ferric oxide above pH values of 4.5 and 6 respectively. As in the present work, Mn remained in solution and was not deposited.

virtue of its very high input, is appreciably enriched in the sediments.

sediments indicate that with the exception of Sn, which occurs mainly as cassiterite, most of the enriched elements are potentially bioavailable. In addition, concentrations of Cu and Zn in the interstitial water from surface sediments are comparable with the high levels found in the overlying water.

The use of chemical extraction procedures on the Creek surface

## Bioaccumulation of heavy metals

concentrations of Zn, Mn, Cu, Cd and probably Co and Ni in solution: it is also exposed to high levels of Fe, Zn, As, Cu, Sn, Pb and Ag in suspended particles and sediments. The availability of these elements

to the biota depends not only on chemical speciation in the waters and

The biota of Restronguet Creek is exposed to abnormally high

sediments, but also on the life-styles of different organisms: thus deposit-feeding bivalves are exposed to metals in a different way from macroalgae. In addition, the levels to which organisms accumulate metals depend not only on ambient metal concentrations but on their various

Bryan & Hummerstone (1973a) found that levels of Cu and Zn in Fucus vesiculosus from the Fal System tend to reflect the concentrations

metabolisms.

dissolved in the water. Experimental work with the same species has shown that, when the metals are used individually, concentrations of Cd, Co, Ni and Pb in the weed reflect those in the water (Bryan, 1983 and unpublished). However, although inputs of these metals to the Creek are abnormally high, they are not generally reflected by levels in the weed, if increased values for Pb due to particulate contamination are excluded. This point will be discussed with regard to Cd, but may apply to other metals also. The mean concentration of Cd in the Carnon River as it enters the Creek is about 26  $\mu$ g/l and, since its behaviour in the water is almost perfectly conservative, values of several  $\mu g/l$  are found even in the more saline waters. Levels of the same order in the waters of the Bristol Channel and Severn Estuary have led to Cd levels in F. vesiculosus at least an order of magnitude higher than those in the Creek (Morris & Bale, 1975). It has been shown experimentally that Cd absorption by the weed is reduced by high levels of Zn (Bryan, 1983),

Bristol Channel and Severn Estuary have led to Cd levels in

F. vesiculosus at least an order of magnitude higher than those in the Creek
(Morris & Bale, 1975). It has been shown experimentally that Cd
absorption by the weed is reduced by high levels of Zn (Bryan, 1983),
and this provides an explanation for the anomaly, since the ratio of
Zn to Cd in the Severn Estuary is about 10:1 compared with 400:1 in
Restronguet Creek. In addition to Zn, competition from dissolved Mn
and Cu in the Creek probably assists in suppressing the accumulation of
Cd by the weed. The contrast between levels of Cd in the biota of the
two estuaries seems to be general and applies at all trophic levels.
The differences are particularly obvious in gastropod molluscs, since
levels in animals from the Creek are lower by factors of 1-2 orders of
magnitude (Tables 21-24). These observations on Cd are very relevant
to the setting of emission standards for estuaries and support the
contention that if there are limits for metals they should not be uniform but
tailored to the capacity of the individual estuary to receive them.

The surface sediments in Restronguet Creek contain metals in

The surface sediments in Restronguet Creek contain metals in particulate and dissolved forms which are bioavailable to various species. For example, if the sediment is covered with clean, aerated sea

water, Cu and Zn are leached into the water and quite high concentrations are reached (see p. 58). There is good evidence that the sediment is an important source of Cu in N. diversicolor although it remains uncertain as to whether the body surface or the gut is the principal route for uptake. Concentrations of Cu in N. diversicolor (Luoma & Bryan, 1982) and Perinereis cultrifera (Fig. 11) relate very closely to sediment Cu levels and values exceeding 1000  $\mu$ g/g have been observed in worms from the Creek. On the other hand, Luoma & Bryan (1982) were unable to relate concentrations of Cu in the deposit-feeding clam Scrobicularia plana to those of the sediments, and animals from the Creek contain far less Cu

levels and values exceeding 1000  $\mu$ g/g have been observed in worms from the Creek. On the other hand, Luoma & Bryan (1982) were unable to relate concentrations of Cu in the deposit-feeding clam Scrobicularia plana to those of the sediments, and animals from the Creek contain far less Cu ( $\sim$ 100  $\mu$ g/g) than might be expected from the sediment levels ( $\sim$ 3000  $\mu$ g/g). This clam occurs only on the margins of the mudflats and probably avoids the worst conditions by shell closure, feeding only when a wedge of relatively uncontaminated water covers the mudflats. Similarly, it is thought that shell closure in response to high levels of Cu and Zn in the water enabled transplanted Mytilus edulis to survive for at least 7 months in the upper reaches of the Creek. Another reason for the relatively low level of Cu in S. plana may be the limited availability of this metal in the sediments despite its high total concentration. It is thought that high levels of hydrated Fe oxide in the Creek sediments adsorb some elements, including Cu,so effectively that their availability to S. plana in the Creek is lower than might be predicted from the total sediment concentrations (Luoma & Bryan, 1982). For example, it has been demonstrated that

extractable Fe increases, the availability of the other elements is reduced (Langston, 1980; Luoma & Bryan, 1978).

So far, only the influence of external factors on bioaccumulation has been considered. However, the metabolism of metals by the organisms themselves is very important in controlling the concentrations ultimately accumulated.

concentrations of As and Pb in S. plana are related directly to the

As/Fe and Pb/Fe ratios in 1N HCl extracts of oxidised surface sediments rather than to the levels of As and Pb alone : thus, as the amount of

Levels of Zn in the Carnon River as it enters the Creek are about 1000 times higher than 'normal'. However, this high level of contamination is reflected only slightly by increased concentrations of Zn in polychaetes, crustageans and fish because they are able to regular

Zn in polychaetes, crustaceans and fish because they are able to regulate the metal, i.e. increased absorption of Zn from the environment is counteracted by more efficient excretion. On the other hand, in macroalgae and bivalve molluscs, the regulation of Zn is less effective, since rather than being excreted with greater efficiency the metal is detoxicated and stored in particular tissues. In bivalves, for example, Zn is stored in the blood cells (amoebocytes) of Ostrea edulis (Table 17; George et al., 1978), in the kidneys of M. edulis and the scallop Chlamys varia (Tables 42 & 20), and in the digestive gland of S. plana (Table 13).

Generally-speaking, Cu is less effectively controlled than Zn, although its regulation is evident in several species including the shore crab <u>Carcinus maenas</u> and the flounder <u>Platichthys flesus</u>.

Exceptional concentrations of Cu are accumulated by other species, including macroalgae, some polychaetes, and molluscs, such as oysters, and reflect not only the high level of Cu contamination in the Creek but also the efficiency of the organisms' detoxication systems. Thus Cu is stored in the amoebocytes of oysters (Table 17), in the pore cells of <u>Littorina littorea</u> (Mason & Simkiss, 1983), and in the epidermis of Nereis diversicolor (Bryan & Hummerstone, 1971).

In addition to Zn and Cu, other elements which are regulated by some species include Mn and Fe, in polychaetes for example (p. 36). Further, Klumpp (1980) reported that winkles <u>Littorina littoralis</u> from the Creek are able to regulate body As levels at high levels of exposure. Regulation of As is also evident in other species including the worm <u>Tharyx marioni</u> in which concentrations of 2000 µg/g can be regarded as 'normal' (Gibbs et al., 1983).

It seems to be generally true that essential elements including As, Cu, Mn, Fe and Zn are better regulated than non-essential elements such as Ag, Cd and Pb. Thus studies on species from the Fal System have proved very useful in identifying tissues in which particular metals are regulated and may therefore have essential roles. As metalloproteins or metal-protein complexes, trace metals usually occur in enzymes or in oxygen carriers such as the Cu-protein haemocyanin. Recently, however, it has been shown that the jaws of nereid polychaetes contain about 1.5% of Zn and, since the concentration is unaffected by environmental levels in the Creek, it is postulated that Zn is involved in hardening the jaw surfaces (Bryan & Gibbs, 1980). A similar conclusion was drawn for the role of Cu in the jaws of glycerid polychaetes in which 13% of Cu was found in the jaw tips (Gibbs & Bryan, 1980). In the polychaete Melinna palmata, around 1.5% of Cu is found in the gills and appears to

be involved in a chemical defence mechanism for deterring small predatory fish (Gibbs et al., 1981).

It is concluded that concentrations of heavy metals in species from Restronguet Creek do not always reflect the high environmental levels to which they are exposed. There are various reasons for this, some of which relate to physico-chemical conditions in the Creek. Thus the accumulation of relatively low levels of Cd in the biota, despite its high input to Restronguet Creek, appears to result from competition for absorption sites from high concentrations of other dissolved metals in the water, particularly Zn. Other reasons relate to the characteristics of individual species. In molluscs, for example, exposure to the highest environmental concentrations can be avoided by shell closure. Also, some animals are able to regulate concentrations of metals such as Zn in the body against environmental changes. However, although this gives the impression that the organism is not exposed to contamination, it may in fact be struggling to excrete the metal from the body fast enough to balance increased absorption. Thus in species that regulate metals it

# Effects of metals in Restronguet Creek

and Zn ( $\sim$ 100-2000  $\mu$ g/l) occur at concentrations which are likely to produce significant environmental effects. In support, experiments on the toxicity

Of the dissolved metals in the waters of the Creek only Cu ( $^{10-100}\,\mu\text{g}/1$ 

may be difficult to judge from levels in the tissues whether or not the

organism is exposed to toxic concentrations.

of diluted Carnon River water to the small bivalve <u>Abra tenuis</u> indicate that its toxicity depends largely on the additive effects of Cu and Zn. Also, concentrations of several thousand  $\mu g/l$  of Fe, precipitated as the hydrated oxide, are suspended in the waters of the Creek and concentrations of this order have been observed to increase the mortality of <u>M. edulis</u> under experimental conditions (Winter, 1972). Other elements in the water, including As, Cu, Pb and Zn, are adsorbed by the Fe oxide and might considerably enhance its effect on filter-feeding organisms. Concentrations of Fe in the surface sediments are usually 5-6%, approximately double the values for less contaminated estuaries, and levels of Cu, Zn, As and Sn in the sediments are of the order of 1500 to 3500  $\mu g/g$ . Based on their

toxicities in solution (Table 29), sediment Cu would be expected to have far more impact than either Zn or As, whilst the presence of sediment Sn

largely as cassiterite renders it unlikely to exert any impact.

A comparison between the fauna of the Creek and that of other tributaries of the Fal System has shown clearly that it is impoverished in molluscs, especially bivalves. This is not surprising, since embryonic and larval bivalves are very sensitive to Cu and Zn at concentrations commonly found in the Creek (Table 29). In addition, surface sediments from the upper reaches of the Creek proved lethal to juvenile bivalves including S. plana and Macoma balthica under experimental conditions and Cu appeared to be the metal having the most impact. Although the tolerance of adult organisms to metal toxicity generally exceeds that of juveniles and larvae, transplanted adult C. edule were killed by exposure for several months in the lower reaches of the Creek, although whether accumulated Cu and Zn was the cause of death remains uncertain. Some individuals of M. edulis, transplanted to the upper reaches of the Creek, survived for at least 7 months despite losing weight and absorbing high concentrations of Cu and Zn. S. plana is the only bivalve occurring in any numbers in the Creek, but is confined to the upper margins of the mudflats and does not survive within 150 metres of the River Channel. When native clams were moved nearer to the River at transect A they died within a matter of weeks, but at transect B, in the lower reaches, some individuals survived for at least a year. The transplanted native clams showed little evidence for the accumulation of additional Cu and Zn, and it is postulated that mortality may have been caused by starvation and anoxia resulting from an attempt by the clam to remain closed and thus avoid the worst of the conditions. It is remarkable that larvae of S. plana ever became established in the Creek, although the predominance of large specimens in the population suggests that successful recruitment is Since S. plana in the Creek probably spawns mainly in July and August a dry autumn with minimal metal inputs might provide the most favourable conditions for settlement.

Of the gastropods that might be expected in the vicinity of the Creek, Hydrobia ulvae is the most obvious absentee. Nucella lapillus and Patella vulgata occur at, or just outside, Restronguet Point, but winkles Littorina littorea, L. littoralis and L. saxatilis occur in the lower reaches of the Creek.

Since the very young stages of organisms are usually most sensitive to metal toxicity, it is thought that many of the more mobile species including gastropods, some errant polychaetes, for example Nephtys hombergi and Glycera convoluta, and crabs Carcinus maenas colonise the

Creek by migration from less contaminated areas. Toxicity experiments have demonstrated that N. hombergi from the Creek possess greater tolerance to Cu than 'normal' individuals, whilst increased tolerance to both Zn and Cu has been observed in C. maenas. Although this might reflect the selection of the most tolerant individuals by the conditions in the Creek, it is thought that the greater tolerance may also be acquired through exposure as the organisms migrate into the Creek. Under experimental conditions, the induction of Cu tolerance through exposure to sublethal concentrations has been observed in the polychaetes Neanthes arenaceodentata (Pesch & Hoffman, 1982) and Eudistylia vancouveri (Young & Roesijadi, 1983).

The distributions of several species within the Creek appear to be virtually 'normal' and are thought to depend on the presence of metal-tolerant strains. One example is N. diversicolor which possesses increased tolerance to both Cu and Zn and is able to survive at upstream sites where salinities are low and dissolved metal concentrations are high. In this context it may be significant that the larvae of N. diversicolor undergo a direct development without a true pelagic phase (Dales, 1950): since the juveniles remain in the adult environment, selection for metal tolerance can be expected to be operative from an early stage. Similarly, the presence of a widespread 'resident' population of Pygospio elegans within the Creek may be attributed to this species' habit of larval brooding:, however, metal tolerance remains to be investigated in this small-sized species. F. vesiculosus, which survives in the upper reaches of the Creek despite accumulating several thousand  $\mu g/g$  of Cu and Zn, may be another example of an especially tolerant strain.

The occurrence of very high concentrations of metals in some tolerant species may pose problems to other organisms. Predation by birds on some invertebrates from Restronguet Creek (plus adhering sediment) could result in their ingesting high levels of Cu and sometimes Zn or As. For example, Redshank, Tringa totanus, are winter visitors to the Creek and feed almost exclusively on N. diversicolor containing a high concentration of Cu. Since its daily intake of worms is roughly equal to its body weight (Goss-Custard, personal communication), the Redshank may be at risk in the Creek, and this is being studied.

To summarise:-

Although Restronguet Creek is heavily contaminated with toxic metals

such as Cu and Zn, it has a flora and fauna which is less obviously affected than might be predicted from toxicity data in the literature. Among the most important reasons for this appears to be the development in some species of metal-tolerant strains, thus enabling them to maintain breeding populations in the Creek. In addition, other species although not necessarily breeding there are able to migrate into the Creek from other less contaminated areas of the Fal System. Some of these species show evidence of greater tolerance to Cu and Zn which may have been induced by increasing exposure to these metals. The most obvious absentees from the Creek macrofauna are bivalve molluscs, the larvae and juveniles of which appear unable to withstand the high concentrations of Cu, Zn, and perhaps recently-precipitated Fe oxide, in the waters and sediments of the Creek. An exception to this is the deposit-feeding clam S. plana, although its distribution is strictly limited to the upper margins of the Creek mud flats.

Many tolerant species occurring in the Creek contain much higher concentrations of metals than organisms from 'normal' estuaries. Thus predators (fish, birds) feeding within the Creek have high metal intakes.

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#### APPENDIX

### MARINE FAUNA OF THE FAL ESTUARY

The following is a summary list of those species identified from samples taken in 1979-80 in the northern and central parts of the Fal Estuary and which are mentioned in the text. Metal levels are given in the text for those species shown with an asterisk.

### COELENTERATA

Edwardsia callimorpha (Gosse)

\*Actinia equina L.

\*Tealia felina (L.)

Sagartiogeton undata (Müller)

#### **ECHIURA**

Thalassema thalassemum (Pallas)

#### PHORONIDA

Phoronis psammophila Cori

## ANNELIDA

Aphrodita aculeata L.

Sthenelais boa (Johnson)

Pholoe minuta (Fabricius)

Phyllodoce spp.

Eulalia spp.

Ophiodromus flexuosus (D. Chiaje)

Syllidia armata Quatrefages

\*Nereis diversicolor O.F. Müller

\*Perinereis cultrifera (Grube)

Platynereis dumerili (Aud. & M. Edw)

\*Nephtys hombergi Lam.

Nephtys cirrosa Ehlers

\*Glycera convoluta Keferstein

Scoloplos armiger (O.F. Müller)

Pygospio elegans Claparède

Polydora spp.

Prionospio malmgreni Claparède

Streblospio shrubsoli (Buchanan)

Magelona alleni Wilson

\*Cirriformia tentaculata (Montagu)

Caulleriella caput-esocis (St. Joseph)

Caulleriella sp.

\*Tharyx marioni (St. Joseph)

Notomastus sp.

Myriochele sp.

Ampharete acutifrons (Grube)

\*Melinna palmata Grube

Manayunkia aestuarina (Bourne)

Megalomma vesiculosum (Montagu)

Myxicola infundibulum (Renier)

Pomatoceros triqueter (L.)

Serpula vermicularis L.

Peloscolex benedeni (Udekem)

#### CRUSTACEA

Balanus balanoides (L.)

Eliminius modestus Darwin

Chthamalus stellatus (Poli)

Janira maculosa Leach

Gammarus zaddachi Sexton

Marinogammarus marinus (Leach)

Marinogammarus obtusatus (Dahl)

#### MOLLUSCA

- \*Littorina littorea (L.)
- \*Littorina littoralis (L.)

<u>Littorina</u> <u>saxatilis</u> (Olivi)

Hydrobia ulvae (Pennant)

- \*Crepidula fornicata (L.)
- \*Nucella lapillus (L.)
- \*Ocenebra erinacea (L.)
- \*Buccinum undatum L.
- \*Nassarius reticulatus (L.)

Philine aperta (L.)

Akera bullata Müller

Mytilus edulis L.

Ostrea edulis L.

Anomia ephippium L.

## PISCES

\*Platichthys flesus (L.)

Marinogammarus finmarchicus (Dahl)

\*Corophium volutator Pallas

Crangon crangon (L.)

Pagurus bernhardus (L.)

\*Carcinus maenas (L.)

Macropipus arcuatus (Leach)

Macropipus depurator (L.)

\*Chlamys varia (L.)

Thyasira flexuosa (Montagu)

Mysella bidentata (Montagu)

- \*Cerastoderma edule (L.)
- \*Parvicardium exiguum (Gmelin)
- \*Venus striatula (da Costa)
- \*Venerupis aurea (Gmelin)
- \*Venerupis pullastra (Montagu)

Abra alba (Wood)

Abra nitida (Müller)

Abra tenuis (Montagu)

- \*Scrobicularia plana (da Costa)
- \*Macoma balthica (L.)

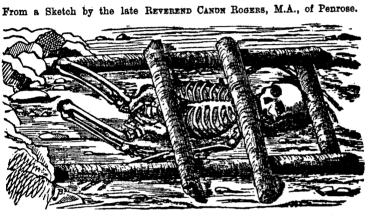
Mya arenaria L.

## SKELETON

Discovered resting on the TIN-GROUND

Between Tarnon-dean and the Arsenic-works, Perran-ar-worthal.

Drawn by Mr. H. M. Geofffici.



From Henwood (1873)