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Levels and Interactions of Selenium with Group IIB Metals in Mussels from Swansea Bay, South Wales, U.K.

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Swansea Bay is an inlet (approximately 270 km^2) located on the northern coastline of the Bristol Channel, U.K. Past and present urban and industrialized development has led to the direct or indirect input to the bay, the latter from rivers, of various industrial and domestic waste discharge containing appreciable amounts of metal effluents (Chubb et al. 1980; Bird 1987). This area also supports a small commercial fishery (Shackley et al. 1980). In an aquatic dynamic system such as this, the fate of a single chemical is complicated by possible interaction with other elements. In this study the results of a survey of the Group IIB metals, zinc, cadmium and mercury in the mussel, *Mytilus edulis*, from the Swansea bay area are presented. In addition, selenium concentrations are reported since it has been reported that this micronutrient can exert an antagonistic effect on these metals (Magos and Webb 1980). Correlations between the different elements are included.

MATERIALS AND METHODS

In keeping with the guidelines of the U.K. Mussel Watch Programme (Mance 1987), mussels were collected in early February from seven sites along the coastline of Greater Swansea Bay (Fig. 1). Thirty-five individuals of 30-35 mm length (the dominant size in the different populations sampled) were collected from the mid-tidal zone at each site and returned to the laboratory for metal analysis. Prior to the metal analysis encrusting organisms were removed, the animals held for 48 hrs in 30 µm filtered sea-water for gut purging. Soft tissues were dissected out, homogenized, stored in acid washed tubes and frozen until required for metal analysis. Zinc and cadmium were determined by flame atomic absorption on oven dried material at 105°C following nitric acid digestion. Mercury was determined by the cold vapour technique. Selenium was determined by electrothermal atomisation based on the method of Shum et al. (1977). Both of these methods have been previously described (Micallef and Tyler 1987). Wet weights were taken for selenium and mercury. Aliquots were dried

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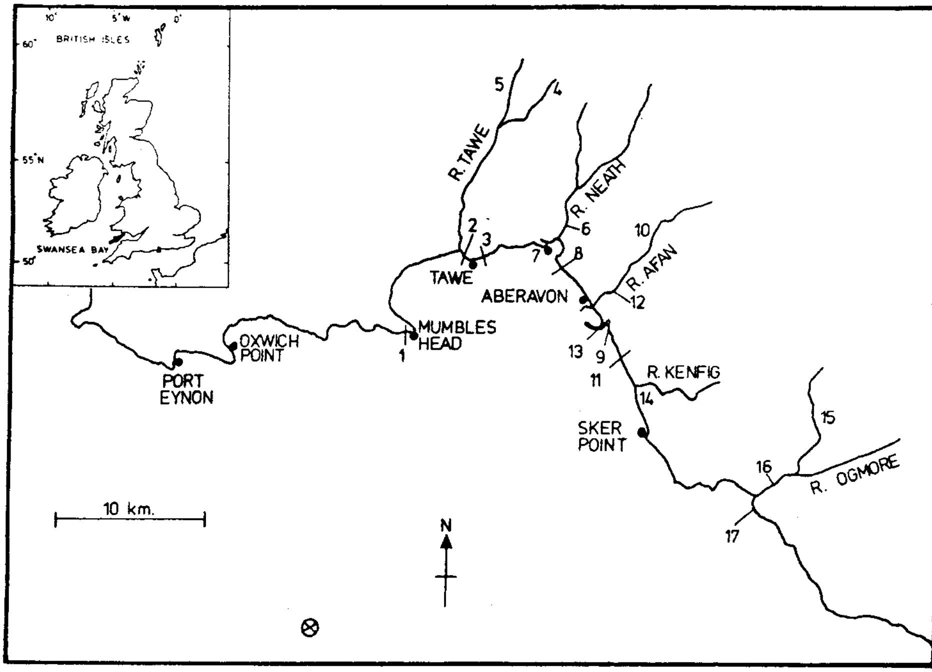

Figure 1. Inputs to Swansea Bay (after Chubb et al. 1980)

Table 1. Total average mass input of metals (kg/day) per major discharge. (After Chubb et al. 1980). For location of discharge see Fig. 1.

Discharge No.	& Name	Zinc	Cadmium	Mercury
1	Mumbles Head Outfall	12.10	0.09	0.01
2	Industrial Outfall	0.15	0.001	0.0003
3	Queens Dock	6.95	0.01	0.001
4	Nant-y-Fendrod	230.00	2.50	0.03
5	River Tawe	131.00	0.63	0.35
6	Industrial Outfall	2.82	0.01	0.006
7	River Neath	33.60	0.37	0.27
8	Neath Outfall	18.60	0.02	6.0*
9	Industrial Outfall	124.00	0.11	0.02
10	River Afan	7.42	0.12	0.03
11	Industrial Outfall	122.00	0.13	0.02
12	Industrial Outfall	1.05	0.04	0.001
13	Glyncorrwg Outfall	3.26	0.008	0.006
14	River Kenfig	0.53	0.005	0.01
15	River Ogmore	9.18	0.11	0.06
16	Penybont STW Effluent Outfall	1.83	0.01	0.02
17	Penybont STW Sludge Outfall	2.40	0.012	-
⊗	Sludge Dumping Ground			
●	Mussel Sampling Sites			

Figures underlined represent largest single source.
* W.W.A. (1982) reported that the total mass input of mercury had decreased to 2.02-3.6 kg/day at discharge 8 which ceased operation in 1982.

at 105 ° C to obtain dry weight conversion factors. All results were expressed in ppm (d.w.). Each metal analysis was done in triplicate and all performed using a SP9 Pye Unicam atomic absorption spectrophotometer. Mean concentrations and standard error for each element were calculated, whilst for each metal, differences among means were assessed by one-way analysis of variance and, where appropriate, Duncan's mutiple range test. Correlation between the means of the different metals was assessed by Spearman's rank correlation coefficient. A level of $P \leq 0.05$ was used in all comparisons.

RESULTS AND DISCUSSION

The results are presented in Fig. 2. The mean zinc values varied from 276 ppm at the mouth of the River Tawe to 175 ppm at Oxwich Point. It is thought that the kidney plays an important role in determining the whole soft tissue concentration in mussels (Lobel 1986).

The highest contamination was found in the inner part of the bay at the mouths of the rivers, Tawe and Neath. These data are the same order of magnitude as that reported by Shackley (1986) for littoral infauna taken from the same area during a survey conducted in 1976 indicating that no substantial reduction in zinc contamination has taken place in the last ten years. These high levels are attributed to the high input of zinc from the run-off of the river Tawe (Table 1) and its tributaries, which contribute to 39% of the total zinc discharge to the bay (Chubb et al. 1980). Inputs from the river Neath (discharges 6, 7), and its proximity (discharge 8), contribute a relatively small amount (Table 1) of zinc to the bay yet the levels of zinc in the mussels were high and not significantly different from those levels obtained in mussels from the river Tawe area. These high levels could be explained by the anticlockwise tidal pattern (Moran and Collins 1979) and sediment transport paths (Collins et al. 1980), the latter mainly in a south-west to north-east direction across the bay bringing zinc contaminated outflow into close proximity with mussels sampled from the Neath area.

The second highest zinc contaminated mussels (Fig. 2) were found at Aberavon, Sker Point and at Port Eynon (Fig. 1). The mean levels of zinc were significantly lower than those found at the mouths of the rivers Tawe and Neath. These levels, particularly those recorded at Aberavon, are coincident with the second major inputs (discharges 9, 11; Table 1). It is important to note that mussels sampled from the Port Eynon location, the furthest site removed from any direct industrial influence, contained elevated zinc levels.

The lowest mean levels of zinc were recorded in mussels taken from Mumbles Head and Oxwich Point with no significant difference between the two locations.

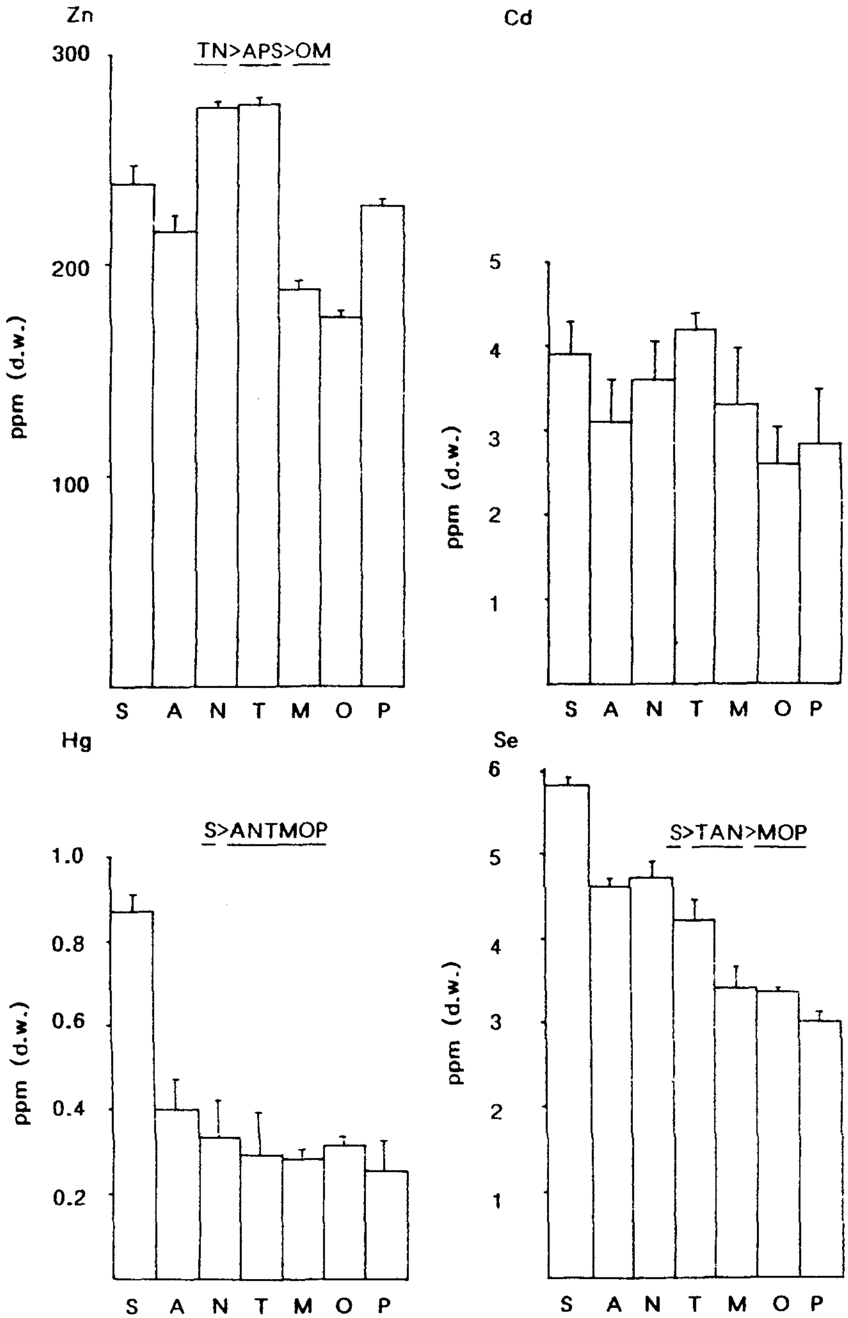

Figure 2. Mean concentrations (±SE) of zinc, cadmium, mercury and selenium in mussels from different sites: S = Sker Point; A = Aberavon; N = Neath; T = Tawe; M = Mumbles Head; O = Oxwich Point; P = Port Eynon. Significant differences indicated by >; Non-significant differences are underlined.

The mean values for cadmium varied from 2.58 ppm at Oxwich Point to 4.22 ppm at the mouth of the river Tawe. Although no significant differences were observed among the mean concentrations of cadmium in the soft-tissues from the different sites, mussels taken from the mouth of the river Tawe contained the highest cadmium levels. The same trend was observed by Shackley (1986) for indigenous littoral fauna from this area. Again, as in the case of zinc, the largest discharge of cadmium to the bay occurs via the Tawe River outflow as a result of input from Nant-y-Fendrod tributary (discharge 4; Table 1). Since cadmium has a close geochemical association with zinc, any leaching of wastes from past metalliferous mining facilities would contain cadmium. Similarly to the situation with zinc, mussels taken from sites not directly influenced from river run-off, Oxwich Point and Port Eynon still contained high levels.

Mean mercury levels in the mussels also showed small intersite variation. The highest mean value obtained was 0.87 ppm in mussels taken at Sker Point which was 2 to 3.5 times greater and significantly different from those mean values obtained for mussels from other sampling locations. The principal source of mercury contamination in the bay was from a chlor-alkali outfall (discharge 8, Table 1) whose operation has ceased since 1982 (W.W.A. 1982). In fact a comparison with earlier work shows that mercury contamination in mussels is now reduced at least in the immediate vicinity of the past main point source at Aberavon (Table 2).

Table 2. Mean total Hg tissue concentrations in indigenous mussels (ppm d.w.). ND = Not determined

Site	W.W.A. (1982)	Present Study
Sker Point	0.28	0.87
Aberavon	1.35	0.40
Neath	ND	0.32
Swansea Flats/Tawe	0.37	0.29
Mumbles Head	0.40	0.28
Oxwich Point	ND	0.31
Port Eynon	ND	0.25

The relative high levels of mercury in the mussels at Sker Point could be the result of two factors: either the direct influence of run off from the river Ogmore, including discharge from the Penybont Sewage treatment plant (W.W.A. (1982) report a level of 0.55 ppm d.w. in mussels taken from the Ogmore area) or in view of the sediment transport paths described earlier, it is possible that contaminated sediment found in the immediate vicinity of the past mercury point source has been displaced to the south-east direction. Thus sediments which previously were a sink for mercury have now become a major source for the littoral fauna (Hodson 1987).

Selenium levels in the mussels showed a similar trend to those of mercury, but, with more intersite variation (Fig. 2). The highest mean selenium concentration recorded (5.78 ppm) was in mussels taken from Sker Point. There are no known data for selenium input into the bay but natural and anthropogenic sources together with atmospheric deposition as a result of fuel combustion could contribute to the observed levels. The range of mean selenium values reported here (2.96 - 5.78 ppm) are similar to mean values (2.9 - 5.6 ppm) reported by Karbe et al. (1977) for mussels sampled from the Baltic and North Seas.

Correlations coefficients between the different elements were calculated (Table 3). There was no significant correlation between the mean levels of zinc and selenium, possibly because both these two elements are micronutrients and their uptake mechanisms are independent of each other. There was also no significant correlation between cadmium and mercury. These two metals are generally considered the more toxic of the four elements analyzed. Since displacement of essential metals from SH-groups of biological molecules is one reason to explain the toxicity of non-essential metals, it is possible that cadmium and mercury are competing for the same common ligand hence explaining the lack of mutual dependence in bioaccumulation. Laboratory experiments with mussels have shown that simultaneous exposure to cadmium and mercury has no effect on mercury accumulation but decreased that of cadmium (Breittmayer et al. 1980).

Table 3. Correlation coefficient between the different elements in the soft tissues of mussels. $P \leq 0.05$ for coefficients which are underlined. NS = Not significant

Zn	Cd	<u>0.714</u>	
Se	Cd	<u>0.714</u>	
Se	Hg	<u>0.857</u>	
Zn	Hg	0.143	NS
Zn	Se	0.500	NS
Cd	Hg	0.393	NS

A significant positive correlation was found between the two micronutrient elements and cadmium. Laboratory experiments have shown that prolonged selenium exposure increased cadmium uptake in the hemolymph of the shore crab, Carcinus maenas, resulting in an equimolar ratio of Se:Cd (Bjerregaard 1985). In this study the most significant correlation was obtained between mercury and selenium. There is evidence to show that complementary accumulation of selenium and mercury sometimes in a 1:1 molar ratio takes place in marine mammals, birds and fish (Koenam et al. 1973, Leonzio et al. 1986, Mackay et al. 1975). However evidence of a lack of dependent co-accumulation in fish does exist (Luten et al. 1980).

The literature for this co-accumulation of selenium and mercury in bivalves is also conflicting. Whereas field studies have shown that positive correlation exists between selenium and mercury levels in M. edulis from North and Baltic Seas (Karbe et al. 1977), laboratory experiments have shown that selenium uptake was not significantly affected by mercury in M. galloprovincialis (Fowler and Benayoun 1976), although Pelletier (1986) found that simultaneous exposure of M. edulis to selenium and mercury increased the uptake rate of selenium but had no effect on that of mercury.

It seems that intersite variation exists in the levels of the essential elements taken from this industrial embayment and that contamination still remains a problem, at least with respect to zinc. Geographical differences exist for the most toxic metal, mercury, although it seems that the situation with mercury pollution has improved in recent years. Finally, although the mechanisms for interaction have still to be completely elucidated, interaction can be implied to take place where correlation exists for some of the elements.

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