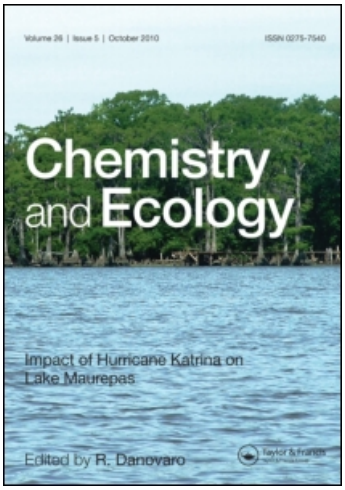

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Trace Metals and Organochlorine Pesticide and PCB Residues in Mussels from England and Wales, 1978

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Trace Metals and Organochlorine Pesticide and PCB Residues in Mussels from England and Wales, 1978

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As part of its work on marine environmental protection the Ministry of Agriculture, Fisheries and Food's, Fisheries Laboratory at Burnham-on-Crouch, undertook a mussel survey in England and Wales in 1978. Trace metal, organochlorine pesticide and PCB residue concentrations were determined. The survey comprised about 80 samples covering the whole of England and Wales.

The results of the survey showed that in general the contaminant concentrations reflected the expected environmental distributions of the compounds of interest. Samples from areas with significant anthropogenic inputs such as industrial estuaries generally contained the highest concentrations and samples from areas influenced mainly by natural sources usually contained much lower contaminant concentrations, although there were some notable exceptions. The survey indicates the usefulness of a mussel watch approach to monitoring in England and Wales and the suggestion is made that if used on a local more intensive scale the technique should be able to identify in greater detail the likely sources of pollution.

INTRODUCTION

Contamination of UK marine coastal waters by metals and organochlorine residues has been investigated for a number of years. Most of the substances of interest have sea-water concentrations in the range 10^{-9} to 10^{-12} g l^{-1} and although analytical techniques are available or being developed to measure these low concentrations few are suitable for routine use. Also, analysis of a single sea-water sample merely reveals what is present at the time of sampling, and gives a poor indication of general water quality. In order to overcome the problems associated with the analysis of sea-water containing low levels of trace contaminants, a number of workers have considered the

advantages of using selected benthic organisms which are able to concentrate a variety of contaminants and to act as integrators of exposure levels over a period of weeks or months (Goldberg, 1975; Goldberg *et al.*, 1978; Davies and Pirie, 1978, 1980; Holden, 1973; Morris and Bale, 1975; Bryan, 1979; Bryan and Hummerstone, 1973). While it seems unlikely that any one class of organism will satisfy all of the criteria required of an indicator organism, mussels possess many of the basic requirements, their biology is well understood and they have been used successfully in a number of studies (Goldberg *et al.*, 1978; Capelli *et al.*, 1978; Majori *et al.*, 1978; Phillips, 1976).

For a number of years, the Ministry of Agriculture, Fisheries and Food's, Fisheries Laboratory at Burnham-on-Crouch has been concerned with the protection of the marine environment and has produced reports on contaminant concentration in fish and shellfish landed in England and Wales (Portmann, 1979; Murray, 1979). As part of these investigations, a survey of accumulated substances in mussels (*Mytilus edulis* L.), taken from coastal sites around England and Wales, was carried out in 1978. This paper presents the results of this survey and comments on their significance and the form that any future mussel surveys should follow.

SAMPLING

In order to provide adequate coverage of the coastline, samples were collected at about 30-mile intervals along the coast. In certain areas of special interest however, such as the Bristol Channel, the sampling sites were much closer together.

Samples were collected from 20 commercially-exploited mussel beds and a number of other sites. As far as was possible, each sample was collected from mid-tide level and comprised at least 50 individuals of average size. The samples were placed in plastic bags, posted alive to the laboratory and kept for 24 h in settled sea water to allow evacuation of the gut contents and cleaning of the shell cavity, prior to extraction and analysis (Phillips, 1976).

EXTRACTION AND ANALYSIS

Metals

All the samples were analysed for mercury, cadmium, lead, zinc and copper using an atomic absorption spectrophotometric (AAS) technique and the manufacturers recommended conditions of operation of flame conditions, lamp current, wave length, etc. A wet-oxidation technique was used,

capable of oxidising methyl mercury to Hg^{++} yet suitable for normal flame AAS determination for the other metals. The samples were oxidised using a 1 : 1 mixture of concentrated nitric acid and 120 vol† hydrogen peroxide, 10 ml of which was added to 5 g of wet tissue. The sample was maintained at 60–70°C overnight and then the temperature was increased gradually until the mixture was boiling gently. Heating continued until the residue was reduced to 1 to 2 ml. The residue was diluted to 50 ml with 2N nitric acid.

Zinc and copper were determined directly on this solution by flame AAS. Mercury concentrations were determined by flameless AAS (Lawson and Kirkwood, 1980). Concentrations of lead and cadmium were determined by flame AAS following complexation with ammonium tetramethylene dithiocarbamate and extraction of the complex into 4 methyl-2-pentanone.

Pesticides and PCBs

Selected samples were analysed for α and γ hexachlorocyclohexane, dieldrin, ppDDT, including its degradation products ppDDD and ppDDE, and polychlorinated biphenyls (PCBs).

The samples were extracted with n-hexane in a soxhlet apparatus for four hours (approximately 120 cycles). The extract was then cleaned up to remove the co-extracted lipid material, using a column containing 3 g of partially deactivated alumina. The PCB residues were separated from the majority of the organochlorine pesticide residues prior to gas liquid chromatography (GLC) using a column containing 2 g of partially deactivated silica. Qualitative and quantitative analysis of the organochlorine pesticide and PCB residues was carried out by dual column GLC utilising electron capture detection. The methods of extraction, clean-up and analysis were based on that of Holden and Marsden (1969).

RESULTS AND DISCUSSION

The positions of the sampling sites are shown in Figure 1, and the results in Figure 2 and Tables I and II. The results of trace metal analysis are expressed on a wet weight basis, and the dry weight is shown as a percentage. The organochlorine residue data are presented on a wet weight basis together with the amount of lipid present.

Organochlorine residues

The results of the organochlorine pesticide and PCB residue analyses are presented in Table I. The results from earlier monitoring programmes (Portmann, 1979; Murray, 1979) showed that organochlorine residue

† Refers to concentrations of the hydrogen peroxide—1 vol H_2O_2 releases 120 vols of O_2 on decomposition to H_2O.

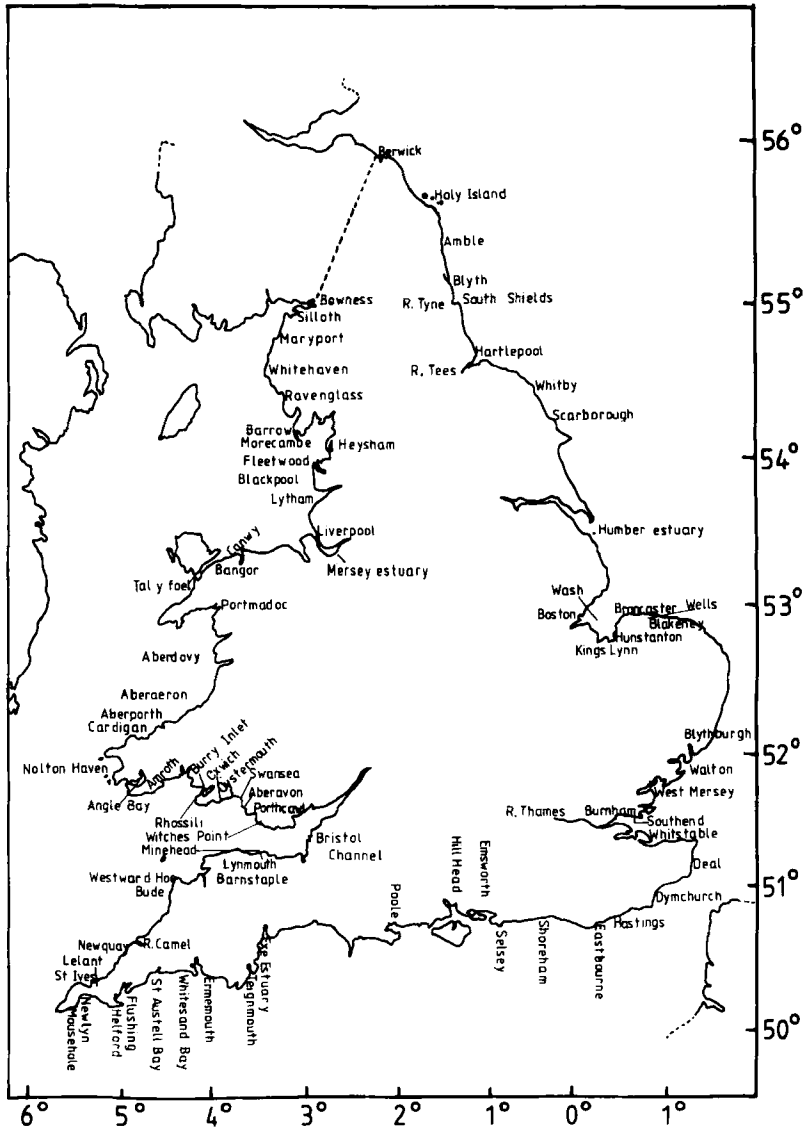

FIGURE 1 1978 mussel watch programme sampling sites.

TABLE I

England and Wales "mussel watch" programme 1978, organochlorine pesticide and PCB residue concentrations (mg kg^{-1} wet weight)

Area	No. analysed	Weight (g)	Size range (mm)	αHCH γ HCH	Dieldrin	DDE	DDD	DDT	PCB	% Lipid
West Mersea	51	94	34–36		0.008	0.004	0.008	<0.002	<0.05	1.0
Burnham-on-Crouch	50	93	18–35	All concentrations at or less than the limit of detection of 0.002 mg kg^{-1}	0.008	0.006	0.005	0.004	<0.05	1.0
Southend	50	111	35–50		0.010	0.005	0.008	0.005	<0.05	1.0
Whitstable	82	128	29–47		0.004	0.003	0.004	<0.002	<0.05	<1
Lee-on-Solent	52	231	47–70		0.003	<0.002	<0.002	<0.002	<0.05	<1
Poole	75	370	38–56	,, ,,	0.003	<0.002	0.004	<0.002	<0.05	<1
Whitesand	50	745	37–61	,, ,,	<0.002	0.013	<0.002	<0.065	<0.05	1.0
St. Austell	46	54	12–42	,, ,,	<0.002	0.004	<0.002	0.068	<0.05	1.0
Helford	50	83	10–38	,, ,,	0.006	<0.002	0.006	0.004	<0.05	1.0
Mousehole	50	30	5–28	,, ,,	<0.002	<0.002	<0.002	<0.002	<0.05	1.0
Newlyn	54	122	14–36	,, ,,	0.008	0.004	0.005	<0.002	<0.05	1.0
Minehead	50	38	26–39	,, ,,	0.008	<0.002	<0.002	<0.002	0.10	1.0
Swansea	50	63	35–52	,, ,,	0.004	0.006	0.005	0.005	<0.05	<1
Rhossilli (Worms Head)	50	50	34–45	,, ,,	<0.002	<0.002	<0.002	<0.002	<0.05	<1
R. Mersey (Princes Jetty)	72	74	24–37	,, ,,	0.031	0.023	0.060	<0.002	0.15	1.5
Lytham St. Annes	50	370	49–72	,, ,,	0.016	0.011	0.030	<0.002	0.05	1.5
Fleetwood	50	150	32–65	,, ,,	0.012	0.006	0.006	<0.002	<0.05	1.0
Heysham	50	160	30–50	,, ,,	0.005	<0.002	0.006	<0.002	<0.05	1.0
Morecambe	50	118	35–50	,, ,,	0.010	0.004	0.012	<0.002	<0.05	1.5

TABLE II

1978 "mussel watch" programme, details of samples analysed for trace metals.

Location	No. analysed	Total weight (g)	Size range (mm)	Date (1978)	Dry weight (%)
Berwick-on-Tweed	50	322	44–65	4.8	16.5
Holy Island	64	152	26–46	31.7	16.6
Amble Harbour	56	565	36–68	9.8	22.2
Ashington Blyth	53	180	35–49	31.7	13.9
South Shields	55	38	8–29	1.8	16.2
Hartlepool	52	170	30–46	31.7	15.9
Whitby	56	260	38–55	6.8	16.9
Scarborough	50	119	29–56	1.8	14.8
Boston	49	400	52–70	16.8	15.0
Kings Lynn	50	400	40–70	16.8	18.3
Hunstanton	50	343	45–67	21.8	21.7
Brancaster Harbour	53	256	48–64	21.8	17.3
Wells-in-Harbour	52	310	48–70	22.8	20.0
Blakeney Harbour	30	135	46–62	22.8	22.9
Blythburgh	52	230	33–64	8.8	21.6
Walton-on-the-Naze	56	351	39–56	1.8	21.0
West Mersea	51	94	34–46	1.8	18.2
River Crouch—Burnham	50	93	18–35	2.8	18.3
Southend	50	111	35–50	15.8	17.6
Whitstable Flats	82	128	29–47	21.9	18.2
Deal	41	15	18–30	7.9	22.4
Dymchurch—St. Mary's Bay	65	130	29–54	7.9	24.8
Hastings	54	190	43–53	7.8	20.7
Eastbourne	50	185	50–58	31.8	17.4
Shoreham	51	149	44–54	8.8	15.7
Selsey	50	96	28–48	29.7	15.8
Emsworth Channel	34	160	40–63	20.9	25.2
Hill Head—Lee-on-Solent	52	231	47–70	20.9	23.2
Poole	75	370	38–56	14.9	25.6
Exe Estuary	45	313	52–68	8.8	18.2
Teignmouth	50	386	56–74	5.9	25.8
Ermemouth—(Mothecombe)	50	99	15–40	3.8	22.3
Whitesand Bay—E of Rame Head	50	745	37–61	3.8	21.3
St. Austell Bay	46	54	12–42	4.8	19.4
Flushing	33	108	14–40	4.8	20.6
Helford Passage	50	83	10–38	4.8	24.8
Newlyn	54	122	14–36	5.8	18.5
Mousehole	50	30	5–28	5.8	17.7
St. Ives	50	111	22–40	5.8	20.7
Lelant—River Hayle	32	51	8–41	5.8	19.1
Newquay	52	110	22–38	6.8	19.7
Camel	33	26	6–24	6.8	21.2
Bude—Widemouth Bay	50	83	17–41	7.8	17.3
Westward Ho	49	140	22–38	7.8	17.1
Barnstaple—River Taw	51	437	57–81	7.8	25.9

TABLE II (Continued)

Location	No. analysed	Total weight (g)	Size range (mm)	Date (1978)	Dry weight (%)
Lynmouth	52	99	34–53	8.8	17.6
Minehead	50	38	26–39	8.8	17.2
Witches Point	50	33	25–36	9.8	16.9
Porthcawl	50	90	45–60	29.8	14.8
Aberavon	50	110	48–61	29.8	18.4
Oystermouth	53	112	42–60	15.8	15.2
Swansea	50	63	35–52	15.8	16.7
Oxwich	50	136	48–58	27.8	17.6
Rhossili	50	50	34–45	27.8	17.5
Burry Inlet	50	202	50–60	30.8	22.7
Amroth	50	153	46–55	26.8	25.0
Angle Bay	56	236	49–60	25.8	20.4
Nolton Haven	50	85	36–48	25.8	21.2
Cardigan	50	183	48–58	25.8	21.2
Aberporth	55	62	37–44	26.8	19.7
Aberaeron	56	55	37–46	26.8	15.7
Aberdovy	48	237	50–66	7.8	15.1
Portmadog	56	652	48–73	5.8	14.4
Tal-y-Foel	56	341	52–67	13.9	23.6
Bangor	69	389	56–71	15.9	19.6
Conwy	50	448	55–77	12.9	22.6
Liverpool	72	74	24–37	22.8	13.8
Lytham St Annes	50	370	49–72	23.8	21.2
Blackpool	70	422	43–66	22.8	22.4
Fleetwood	50	150	32–65	15.8	14.3
Heysham	50	160	30–50	15.8	14.6
Morecambe	50	118	35–50	15.8	17.3
Barrow-in-Furness	49	172	48–60	7.8	19.4
Ravenglass	50	170	35–50	14.8	14.4
Whitehaven	54	140	30–50	14.8	13.0
Maryport	48	104	24–55	14.8	14.1
Silloth	50	89	30–47	15.8	22.7
Bowness	55	221	34–57	15.8	23.4

concentrations in mussels were usually low and often less than the limit of detection (0.002 mg kg^{-1} for the organochlorine pesticide residues and 0.05 mg kg^{-1} for the PCB residues). On the basis of the earlier studies, organochlorine residue determinations were made on samples from 20 of the 80 sites. These sites were mainly in industrial estuaries, defined as areas where there are concentrations of urban development and associated industry, e.g. Thames, Bristol Channel/Severn and the Mersey. In contrast, samples were included from sites in the south-west of England, where contamination by direct discharges was likely to be small.

The organochlorine pesticide and PCB residue concentrations were low, usually less than 0.01 mg kg^{-1} and 0.1 mg kg^{-1} respectively and often less than the detection limit. There was some indication of elevated organochlorine residue concentrations in the samples collected from industrial areas, the maximum concentrations of dieldrin (0.031 mg kg^{-1}), DDE (0.023 mg kg^{-1}), DDD (0.060 mg kg^{-1}) and PCB (0.15 mg kg^{-1}) occurring in samples from the Mersey Estuary. The highest value of DDT however, occurred in samples from Whitesand and St. Austell (0.065 mg kg^{-1} and 0.068 mg kg^{-1} respectively), possibly reflecting the continued, albeit limited, use of this pesticide in agriculture.

By using mussels as indicators, it is therefore possible to distinguish between areas where there are major differences in anthropogenic inputs, but because of the relatively low concentrations of organochlorine residues found, small differences in environmental concentrations would probably be difficult to distinguish.

Trace metals

The results of trace metal analyses are presented in Table II and Figure 2. Elevated environmental concentrations occurred mainly in areas associated with industrial estuaries but some of the areas identified have not previously been considered to have a high trace metal content, e.g. copper at Hunstanton in the Wash. Another interesting feature was the absence of high trace metal concentrations in some areas associated with substantial anthropogenic inputs, e.g. Thames Estuary. Mercury and lead concentrations at Southend and Whitstable were very similar to those found along the east coast and south Kent coast and showed no sign of elevated concentrations caused by the known major inputs of these metals into the Thames Estuary.

The Mersey Estuary, the Tyne/Tees area, the Bristol Channel and, to a lesser extent, the Thames Estuary were clearly shown to be areas containing above average concentrations of a wide range of trace metals, probably of industrial origin. Mussels from Liverpool and Morecambe Bays and the north-east and south-east coastal areas of England also contained elevated trace metal concentrations which were probably of industrial origin. However, these concentrations were considerably lower than the peak concentrations found in mussels from the industrial estuaries.

Samples from some of the areas free from major anthropogenic inputs, such as the south-west of England also contained elevated concentrations of a limited number of trace metals, e.g. zinc and copper. Unlike the samples from industrial regions, the origin of these elevated concentrations is thought to be natural (Webb *et al.*, 1978), brought about by the weathering

of geological strata containing relatively high concentrations of trace metals. The cause of the high concentration of copper in the mussel samples collected from the Wash is unknown, however there is some doubt about the use of mussels as indicators of copper contamination (Phillips, 1976).

COMPARISON WITH TRACE METAL CONCENTRATIONS IN SEA WATER

The distribution of trace metal concentrations in sea water (Environment, Dept. of, 1980) shows some agreement with the trace metal concentrations found in mussels in this study. Where areas received significant industrial

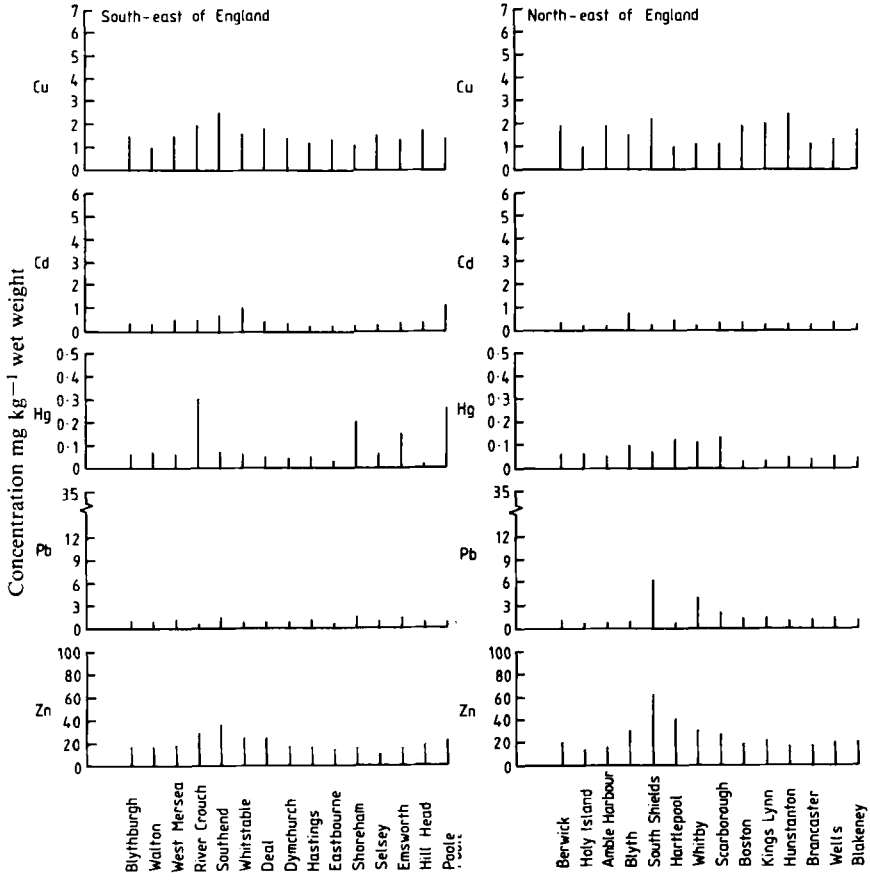

FIGURE 2 Concentrations of trace metals in mussels from England and Wales.

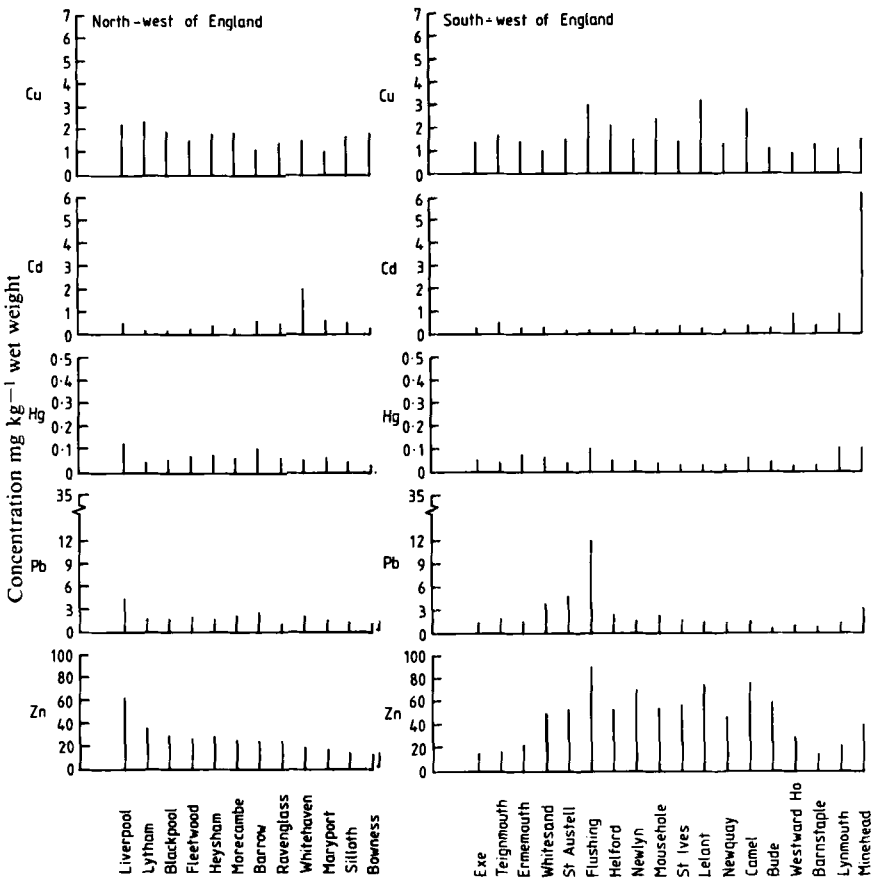

FIGURE 2 (Continued).

inputs such as the Thames and Mersey Estuaries, Liverpool Bay and the Bristol Channel, elevated trace metal concentrations occurred in both water and mussels. At a number of other sites where coastal samples of mussel indicated the presence of elevated environmental levels, the trace metal concentrations in offshore water were relatively low, e.g. the south-west of England.

Whereas the analysis of water samples provides only an instantaneous measurement of the levels of metals, mussel samples provide a means of assessing the environmental concentrations integrated over a longer period. They also give an indication of the biological availability of the trace metals. It is thus possible that analysis of mussel samples might provide a more useful way of determining the effects of polluting discharges on marine life.

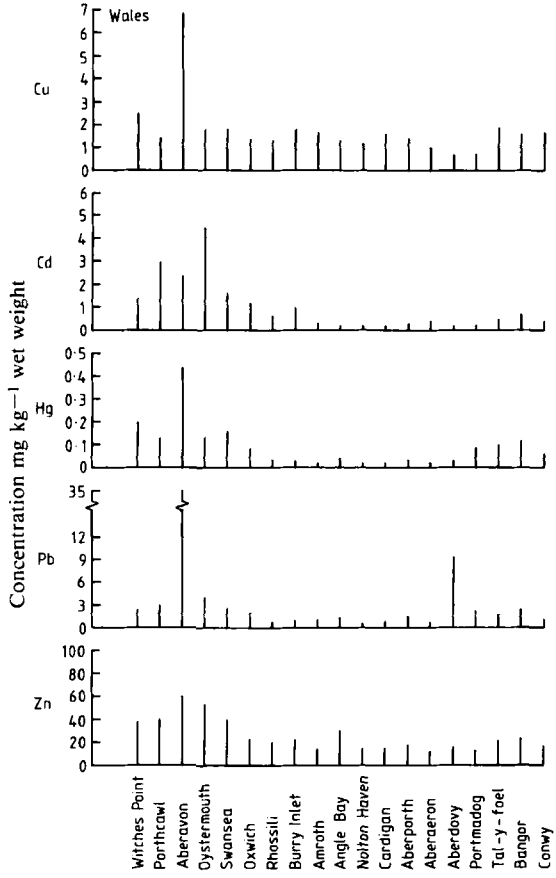

FIGURE 2 (Continued).

CONCLUSIONS

The mussel watch approach to monitoring in England and Wales has been shown by this survey to have a number of advantages over the direct study of trace contaminants in sea water. Analysis of water samples for trace contaminants is difficult and time consuming, the possibilities of contamination are high and the results only reveal what is present at the time of sampling.

The mussel survey provided a reasonably rapid sampling of the trace contaminant concentrations in the coastal marine environment of England and Wales. Such a picture is not available from the results of the regular fish and shellfish quality surveys because these samples are collected at different times of the year on a highly selective basis and cannot represent

the immediate coastal zone. In particular, the shellfish samples are limited to commercial stocks and hence the distribution is irregular.

It is unlikely that much would be gained by repeating such a large-scale mussel survey in the near future, as environmental levels of pollutants do not change quickly. However, if used on a local, more intensive scale, as carried out during this survey in the Bristol Channel, the mussel watch technique should be able to identify in greater detail the likely sources of pollution. The pathways followed by a contaminant when it enters the marine environment are as yet poorly understood. A clear understanding of at least the major pathways is essential for the development of a sound management policy for the control of industrial and domestic waste disposal. An intensive survey on a local scale using either indigenous mussel populations or introduced uncontaminated caged mussels from a single stock should provide a useful tool for the identification of biologically available contaminants (Davies and Pirie, 1978). Studies of this nature should be considered as a priority task in any future mussel watch type programme.

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