Vlaams Instituut voor de Zee

Distribution and Abundance of Heavy Metals in Finfish, Invertebrates and Sediments Collected at a Deepwater Disposal Site

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Analyses of deep water finfish to several heavy metals indicate that deep water fish have less metal in muscle tissue than do fish taken from the continental shelf. Liver tissue from deep water fish also, generally, contain less metals. Sediments and a single invertebrate collected at deep water stations have also been analysed for heavy metals.

In recent years some scientists have become increasingly concerned about the accumulation of toxic heavy metals and other contaminants in marine finfish and their forage species. Several papers and reports have indicated the possible extent of heavy metal buildup or accumulation in invertebrates and finfish taken from estuaries and the coastal zone (Wright, 1976; Fowler & Oregioni, 1976). Suspected movements of metals from the coastal zones to the deeper seas beyond the shelf-slope break have not been conclusively demonstrated, however, and very little is known about metal contamination of organisms in deeper waters. Barber et al. (1972) reported on mercury concentrations in axial muscle removed from benthopelagic fish caught in 1971 and 1972 as well as preserved specimens taken in 1883 and 1886. Gibbs et al. (1974) discussed problems inherent in analysing tissues which have been fixed or preserved in standard preservatives. The present paper presents values for nine metals measured in four species of deepwater demersal finfish and one benthic invertebrate, the red crab (Geryon quinquedens). In addition, data are given for three species of pelagic or surface-dwelling finfishes taken in a general area of deepwater disposal site No. 106 (bounded by 38°40′N, 39°00′N, 72°00′W and 72°30′W). Depths range from 1550 m in the northwest corner of the disposal area to 2750 m in the southeast corner.

Finally, data are presented on the distribution and abundance of six heavy metals in surficial sediments collected from nine benthic sampling stations located in or near the deepwater site. This site is utilized for disposal of arious industrial wastes deemed too toxic for inshore disposal operations. Some of these wastes are known to contain heavy metals and other toxic materials.

Materials and Methods

Samples of organisms were collected by bottom trawling devices and surface nets utilized in the general area of the deepwater disposal site No. 106. Sediment samples were collected from the submersible Alvin using metal-free core liners. After collection, fish and invertebrates as well as sediments were frozen until chemical analysis could be completed. All samples were kept as free as possible of contamination by metals and metal containers. Latitude and longitude of the collection site for each sample is given in Table 1.

Chemical analyses for heavy metal content of the organisms and sediments were conducted as follows: Biological samples were stored frozen in plastic bags until dissection. Tissues were removed and ground with

stainless steel and glass equipment. These were then refrozen in plastic containers until analysis. For analysis for Ag, Cd, Cr, Cu, Ni, Pb, and Zn concentrated HNO₃ was added repeatedly to the samples which were being charred on a hotplate. A white ash resulted which was dissolved in 10% HNO₃, filtered and analysed directly. Arsenic was isolated by preliminary wet ashing in concentrated HNO₃ and subsequent dry ashing in a muffle furnace. This was followed by dissolution in HCl and analysis by arsine generation. For mercury analysis the sample was digested in a concentrated solution of H₂SO₄ and HNO₃ and was further oxydized by KMnO₄. The solution was reduced and aerated to reduce free mercury and then analysed by a flameless technique.

Sediments were stored frozen in plastic cores until work-up. The cores were thawed and the top 4 cm removed. Detritus was physically removed from the samples which were then dried at low temperature, ground and stored in plastic containers under a desiccated atmosphere until analysed. For analysis for Cd, Cr, Cu, Ni, Pb, and Zn the sample was wet-ashed in concentrated HNO₂ and H₂O₂, taken up in a solution containing HNO₃, HCL, NH₄Cl and Ca (NO₃)2.4H₂O and filtered. The resulting solution was analysed directly with the Perkin-Elmer Model 403 atomic absorption spectrophotometer. Analysis for mercury was done by adding dilute agua regia to the samples which were heated, further oxydized with KMnO4 and reheated to complete the digestion. The mixture was reduced, aerated and analysed by a flameless technique.

It should be emphasized that our heavy metal analyses have been intercalibrated with those of other laboratories using similar techniques as well as through neutron activation methodology for certain metals (Greig, 1975).

Results and Discussion

The results of our analyses of finfish are given in Tables 1 and 2. We were able to examine only one deepwater crustacean for body burdens of metals, the red crab, *Geryon quinquedens*. When compared with Wright's findings (1967) for Cd, Cu, Ni and Zn in muscle and gills from the coastal green crab, *Carcinus maenas*, red crab has 0.10 ppm Cd, 8.3 ppm Cu, 0.48 ppm Ni and 69.0 ppm Zn in muscle vs 0.51 ppm Cd, 6.00 ppm Cu, 6.20 ppm Ni and 43.24 ppm Zn in muscle of the green crab. Gills from the red crab has 0.81 ppm Cd, 31.3 ppm Cu, 0.50 ppm Ni and 20.2 ppm Zn; the green crab gills contained 0.63 ppm Cd, 10.90 ppm Cu, 6.70 ppm Ni and 14.16 ppm Zn. These comparisons indicate that Ni was significantly higher in the coastal green crab but other metals occurred within the same orders of magnitude.

As noted by Barber *et al.* (1972) a knowledge of the present abundance and distribution of mercury and other metals in the ocean is necessary to understand the natural biogeochemical flux of these elements through the coastal and deepwater ecosystems and to document and possibly predict the impact of man's activities in the world ocean.

TABLE 1

Metal concentrations (ppm, wet weight) in fish and crabs collected in the vicinity of a deep water dump site (No. 106) in the Middle Atlantic Right.

Species	Latitude N	Longitude W	Tissue	No. of animals	Average length (mm)	Average weight (g)	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1. "Antimora	38°53°	70°42	Muscle	10	430	706.0	< 0.09	21.1	< 0.09	<0.52	< 0.50	0.62	< 0_51	<1.00	2.40
rostrata			Liver	10	430	706.0	0.13	4.8	0.32	< 0.52	3.34		< 0.48	~ 1.00	43.00
	38°27	73°03'	Muscle	.5			0.15	_	< 0.12	< 0.61	< 0.51	0.49	< 0.51	< 0.80	2.84
			Muscle	5			0.12	_	< 0.12	< 0.61	< 0.51	0.32	< 0.51	< 0.80	3.15
			Liver	5			0.11	_	0.36	0.59	1.96	_	< 0.45	0.70	12.20
			1_iver	.5			0.11		0_33	0_57	1.86	_	< 0.47	1.20	11.10
2. *Nematonurus	38°53°	70°42'	Muscle	10	355	189.0	< 0.10	20.0	< 0.10	< 0.52	< 0.50	0.28	< 0.60	1.00	2.9
armatus			Liver	10	355	189.0	_	10.4	1.33	0.52	0.70	0.31	< 0.50	< 1.00	50.00
			Muscle	7	609	217.0	< 0.10	10.0	< 0.10	< 0.52	< 0.50	< 0.10	< 0.50	<1.00	1.4
			Liver	7	609	217_0	_	_	1.21	< 0.86	4.80	_	< 0.82	<1.6	16_2
			Muscle	4	007	21.10	0.11	_	< 0.11	< 0.53	< 0.44	0.30	< 0.44	< 0.7	3.13
			Muscle	4			0.14	-	0.14	< 0.68	< 0.57	0.44	< 0.57	0.9	3.19
3. * Halosauropsis	39°45"	70°43	Muscle	3			< 0.12	_	< 0.12	0.98	1.49	0.09	< 0.48	<0.7	2.45
macrochir	38°27′	73°03'	Muscle	3			0.12		< 0.12	1.17	1.65	0.10	< 0.50	0.8	2.37
4. *Synaphohranchus kaupi	39°52	70°55	Whole animal	10	_	32.4	< 0.09	8.0	0.12	< 0.42	1.62	< 0.15	< 0.49	< 1.00	6.8
5. *Gervon	39°52	70°55'	Muscle	7	93	227.0	< 0.13	1.6	< 0.10	< 0.51	8.3	0.23	< 0.48	< 1.00	69.00
quinquedens			Gills	7	93	227_0	0.43	9.1	0_81	< 0.52	31.3	< 0.16	< 0.50	< 1.00	20.2
6. Seriala	38°33'	72°10′	Muscle	6	145	63.6	< 0.10	1.2	< 0.10	< 0.52	< 0.63	< 0.10	< 0.50	< 1.00	3.7
			Liver	6	145	63.6	0.24		0.24	< 1.26	1.96	-	< 1.20	< 2.4	15.5
7. Hygophum	38°47	72°38'	Wholeanimal	10	_		< 0.09	_	< 0.11	< 0.49	< 0.47	_	< 0.47	< 0.95	7.4
hygomi	38°271	72°10′	Whole animal	15	_		0.08		0.11	< 0.35	0_64	_	0.74	1.0	8.5
	38°42'	72°44'	Whole animal	15	-	_	< 0.07		0.09	< 0.31	0.57	_	0.37	< 0.60	7.7
	38°48'	72°26′	Wholeanimal	15	_		< 0.10	-	< 0.07	< 0.37	0.73	_	0_53	< 0.75	6.9
8. Stephanolepsis	38°27′	72°10′	Whole animal	6	_	_	< 0.07		0.14	< 0.36	< 0_90	_	0.48	1.0	
hispidus	38°53'	72°11'	Whole animal	5		21.5	< 0.09	1.5	< 0.13	< 0.52	0.89	< 0.11	< 0.49	<1.07	10.3

^{*}Species generally regarded as bottom dwellers.

As noted by the aforementioned authors it is a popular assumption that the deeper parts of the oceans have been the least affected by chemical contaminants. However, certain elements of society advocate using the deep seas for waste disposal; it is believed that wastes, even highly toxic materials, will be sufficiently diluted or isolated in the hadal and abyssal regions of the oceans. Others argue that the deepsea benthic communities are particularly subject to any stress and waste disposal may have extensive effects on these stable populations which have evolved through long periods of time within narrow ranges of physical and chemical variation.

Since Barber et al. (1972) presented data on a single metal, Hg, in several fish, our comparisons with their values must be limited to Hg. They noted that Hg in axial muscle increased with the standard length of the fish and reported that Hg (ppm wet weight) ranged from 0.24 in a fish 33.5 cm long to 0.76 in one 52.2 cm long. These fish were taken either on 28 July 1971 or 5 July 1972. These authors also analysed a single fish of the same species, Antimora rostrata, of approximately the same length (45.7 cm) but collected in 1883. The fish contained 0.50 ppm of Hg. We analysed the homogenated muscle tissues from ten A. rostrata, averaging 43.0 cm in length,

and found 0.62 ppm of Hg (Table 1), a similar value to those found by Barber et al. (1972) in fish of similar length.

The Hg content in axial muscle and liver from other species of finfish is shown in Table 1. Data are also given for eight other metals from most finfish species analysed.

Although both the recent and 1883 fish of Barber et al. (1972) were collected southeast of Cape Hatteras in an area less likely to be contaminated with materials similar to the industrial wastes disposed of at site No. 106, the values they report for Hg in axial muscle were similar to those we found in fish of the same species collected at deepwater disposal site No. 106 off the New York Bight.

Because there seems to be no significant variation in Hg in deepwater fish taken off New Jersey and Cape Hatteras, or for that matter, in fish collected almost a century apart, it is possible that other metals shown in Table 1 represent normal levels in deepwater fish.

A recent study (Greig et al., 1975) of Hg concentration in fish taken in 1971 from North Atlantic offshore waters, indicates that the deepwater fish reported upon here generally have about the same concentrations of Hg as fish taken from the continental shelf. The highest values in the previous study were 0.49 ppm in the muscle of cusk (Brosme brosme) and 0.53 ppm in spiny dogfish (Squalus

TABLE 2

Elemental concentrations (ppm, dry weight) in sediments obtained from a deepwater dumpsite in the New York Bight.

Latitude (N)*	Longitude (W)*	Field code	Sampling date	Depth (m)	Cd	Cr	Cu	Hg	Ni	Pb	Zn
38°31.9′	72°10.5′	584	26/7/75	2812	<1.25	16.7	25.8		29.7	13	47.8
38°31.2'	72°12.1'	585	27/7/75	2818	<1.25	16.7	23.0		33.1	15	47.0
38°46'	72°30.2'	586	28/7/75	2351	< 1.25	14.6	17.2		19.8	14	40.2
38°49.9'	72°34.1'	587	29/7/75	2027	< 1.25	15.8	18.7		22.2	14	42.5
38°52.7'	72°16.6'	589	31/7/75	2452	< 1.25	14.7	14.9		17.4	13	39.1
38°56.7'	72°25.1'	590	01/8/75	1688	< 1.25	16.2	17.9		20.8	13	44.3
38°55'	72°05.5'	591	02/8/75	2477	< 1.25	13.0	13.8		15.8	8	32.0
39°09.9'	71°54.8'	592-1	03/8/75	1959	<1.25	13.5	13.9		16.3	15	36.7
39°10′	71°55.1'	592-2	03/8/75	1982	<1.25	6.0	6.5		< 7.4	7.5	19.5

^{*} Latitude and longitude given are for the tending vessel Lulu only. § Values indicated are averages of either two or three replicates.

acanthias) muscle. The greatest concentrations of Hg noted in deepwater finfish were 0.62 ppm in Antimora rostrata and 0.44 ppm in Nematonurus armatus. We found an average of 0.30 ppm for all deepwater fish muscle sampled compared to an average of 0.154 ppm reported by Greig et al. (1975) for muscle from offshore continental shelf finfish.

Values for metals other than Hg in coastal finfish have recently been reported by Peden et al. (1973), Hardisty et al. (1974) and Wright (1976). The latter noted metal values comparable to those reported by Peden and Hardisty. A comparison of our data with data from the above papers indicates that Cd, Cu, Ni and Zn were generally higher, sometimes much more so, in coastal fish from Great Britain, with coastal fish showing Cd concentrations 3 to 10 times those of deepwater fish. Copper was also generally higher in muscle from coastal fish when compared with deepwater species. Nickel was 5 to 14 times more abundant in muscle tissue from coastal fish and Zn was as much as 60 times more abundant in coastal finfish (Wright, 1976).

The foregoing indicates that deepwater finfish have less metal in muscle tissue than do fish taken from the continental shelf. Comparisons of metals in liver tissues indicate that, generally, coastal fish have somewhat greater concentrations of Cd and Cu. Ni and Zn were somewhat more elevated in liver tissues from coastal fish. However, Zn was high in the liver of the deepwater Antimora and Nematonurus but was less than half that found in the English sprat.

Additional analyses of organisms from deepwater and midwater trawls are being made to increase our baseline measurements. We are also analysing tissues from additional midwater and surface finfish collected at the deepwater dump site No. 106 to determine if surface or midwater dwelling fish become contaminated with metals in wastes disposed at the site. Certain fish are known to move from surficial waters to deeper benthic environments; such fish may provide a 'link' whereby toxic heavy metals and other contaminants are moved from surface waters to great depths.

In addition to analysing animal tissues for heavy metals, we have examined two collections of sediments taken at stations in or near the dumpsite. Table 2 gives the amounts of metals found in sediments collected at benthic stations located near the deepwater disposal site No. 106. These values are very similar to those previously found in sediments collected from similar stations in 1973 (Pearce et al., 1975). Future collection of sediments from these stations can be analysed to provide data on possible accumulations of metals due to ocean disposal operations and terrigenous export seaward via the Hudson Shelf Valley.

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Barber, R., Vijayakumar, A. & Cross, F. (1973). Mercury concentrations in recent and ninety-year-old benthopelagic fish. Science, 178, 636-639.

Fowler, S. & Oregioni, B. (1976). Trace metals in mussels from the N.W. Mediterranean. Mar. Pollut. Bull., 7, 26-29.

Gibbs, R., Jarosewich, E. & Windom, H. (1974). Heavy metal concentrations in museum fish specimens: effects of preservatives and time. Science, 184, 475-477.

Greig, R. (1975). Comparison of atomic absorption and neutron activation analyses for the determination of silver, cadmium, and zinc in various marine organisms. Analyt. Chem., 47, 1682–1684.

Greig, R., Wenzloff, D. & Shelpuk, C. (1975). Mercury concentrations in fish, North Atlantic offshore waters—1971. Pest. Monit. J., 9(1), 15-20.

Hardisty, M., Huggins, R., Kartar, S. & Sainsbury, M. (1974). Ecological implications of heavy metal in fish from the Severn Estuary. Mar. Pollut. Bull., 5, 12-15.

Pearce, J., Thomas, J. & Greig, R. (1975). Preliminary investigations of benthic resources at deepwater dumpsite 106. In: May 1974 Baseline Investigation of Deepwater Dumpsite 106. NOAA Dumpsite Evaluation Report 75-1. pp. 217-228.

Peden, J., Crothers, J., Waterfall, C. & Beasley, J. (1973). Heavy metals in Somerset marine organisms. *Mar. Pollut. Bull.*, **4**,7-9.

Wright, D. (1967). Heavy metals in animals from the North East coast. Mar. Pollut. Bull., 7, 36–38.

An Assessment of the Pollution of Cornish Coastal Waters

A detailed survey of pollution was undertaken in five areas around the Cornwall coast in south-west England, at St. Austell and Mevagissey Bays, Falmouth Bay, Mounts Bay, St. Ives Bay and Portreath. The aim of the study was to establish baseline values against which subsequent changes could be detected and their importance evaluated. Three major investigations were undertaken in each area involving seawater sampling and analysis, heavy metal analysis of seaweed specimens and quantitative surveys of intertidal fauna and flora. In general, the areas studied showed few signs of being exposed to significant levels of industrial or sewage pollution.

The county of Cornwall is fortunate in possessing an exposed and scenically attractive coastline free from large areas of industrialization and urbanization. The importance of fisheries and tourism, both of which occupy a significant part in the economic development of the area, demand, however, that the quality of the coastal waters be maintained at a high level and that the effects of pollution by sewage discharges and activities associated with the mining of china clay and other minerals are kept to a minimum.

Recognising the importance of water quality to the sea fisheries for which they are responsible, Cornwall Sea

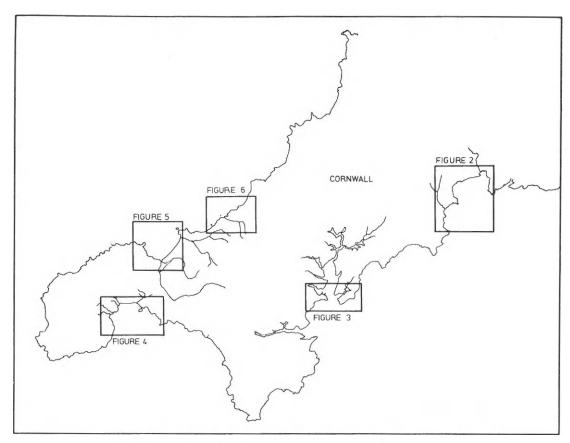


Fig. 1 Map of the county of Cornwall showing locations of the study areas.

Fisheries Committee requested Atkins Research and Development to undertake an appraisal of the existing state of coastal waters under its jurisdiction. A preliminary study showed that five coastal areas appeared to be most at risk from the effects of industrial and/or sewage waste (Atkins Research and Development, 1974). These areas were St. Austell and Mevagissey Bays; Falmouth Bay; Mount's Bay; St. Ives Bay and the Portreath area (Fig. 1 and Table 1).

From late 1974 to the autumn of 1975, three major investigations were undertaken in the above areas involving:

TABLE 1Major sources of pollution in the five study areas

	Coastal sewa	ge discharges			
Study area	Number of outlets		Major types of industrial waste		
St. Austell & Mevagissey Bays	5	6600	China clay waste—1.5 m tonnes in 1972, but progressive reduction to near zero in 1976.		
Falmouth Bay	4	6400	China clay waste (residue recovery schemes have reduced loads); mining waste particularly via Carnon River.		
Mounts Bay	15	9500	_		
St. Ives Bay	3	5100	500 m³/d of creamery waster mining waste via Red River; 327,300 m³/d cooling water.		
Portreath area	2	6400	Mining waste; processing wastes.		

Data from South West Water Authority (pers. comm.) and Department of the Environment and Welsh Office (1973).

- (i) the establishment of water quality monitoring stations, collection of water samples and analysis of their chemical and bacteriological quality;
- (ii) the collection of samples of the brown seaweed *Fucus vesiculosus* and their analysis for heavy metal content; (This investigation was carried out in collaboration with the Institute for Marine Environmental Research and forms part of their work on the accumulation of trace elements in brown aglae);
- (iii) the establishment of permanent shore transect sites and surveys of the fauna and flora of these sites.

The main purpose of these investigations was to provide a baseline against which subsequent changes could be detected and their importance evaluated. Consequently their full value will only be realised when they are repeate and the results compared with the situation in 1974/75.

This paper summarises the main findings of these investigations, full details of which have been reported to the Sea Fisheries Committee (Atkins Research and Development, 1976).

Sample Sites, Methods and Analysis

Seawater Thirteen water quality monitoring stations, generally 1-1.5 km offshore, were established within the 5 survey areas (Figs. 2-6). At each station, during August 1975, seawater samples were taken every 3h over a complete tidal cycle and at varying depths, depending on whether or not a thermocline or halocline was present. All samples were analysed for nutrients, particulate matter, Escherichia coli and faecal Streptococci. In addition, a proportion of the samples were analysed for a range of heavy metals using atomic absorption spectrophotometry.

