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HEAVY METAL POLLUTION INDUCED BY A FERRO-NICKEL SMELTING PLANT IN GREECE

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ABSTRACT

Seven heavy metals, Co, Cr, Cu, Fe, Mn, Ni and Zn, were measured in marine sediments, plants and invertebrates in the vicinity of a ferro-nickel smelting plant in Greece. The concentrations of metals in the sediment were higher than those found in the average unpolluted Greek coastal sediment. High levels of metals were observed in the gastropod molluscs, particularly *Cerithium vulgatum*, which concentrated metals more than other invertebrates.

INTRODUCTION

The smelting plant, which extracts iron and nickel from laterite ore, is situated on the south eastern shore of the Bay of Larymna in the northern Evoikos Gulf, Greece (Fig. 1). Sea water flows into the bay along the southeastern shore, passes the smelter and flows out along the north-western shore. The laterite consists primarily of the oxides of silica, iron and aluminium, with smaller quantities of calcium, magnesium, chromium, nickel and cobalt, and trace amounts of sulphur and arsenic. The by-products of smelting are dust, a small part of which escapes into the atmosphere, and slag, which is discharged into the Evoikos Gulf, 8 km from shore. Marine pollution in the bay occurs, in addition to atmospheric fall-out, through spillages of ore, coal (used in the furnaces), slag and the ferro-nickel product.

METHODS

A variety of invertebrates, plants and sediment was analysed for Co, Cr, Cu, Fe, Mn, Ni and Zn. The material was collected in July and November 1986 from four stations (Fig. 1) in the littoral zone, except for the towershell, *Cerithium*, the fan mussel, *Pinna*, the sea-grass *Cymodocea*, and the epiphytes, which were collected sublittorally at ~ 70 cm depth. The animals were brought alive to the laboratory where they were kept for 1 week in artificial sea water, periodically changed, to eliminate the gut contents; the plants were washed to remove

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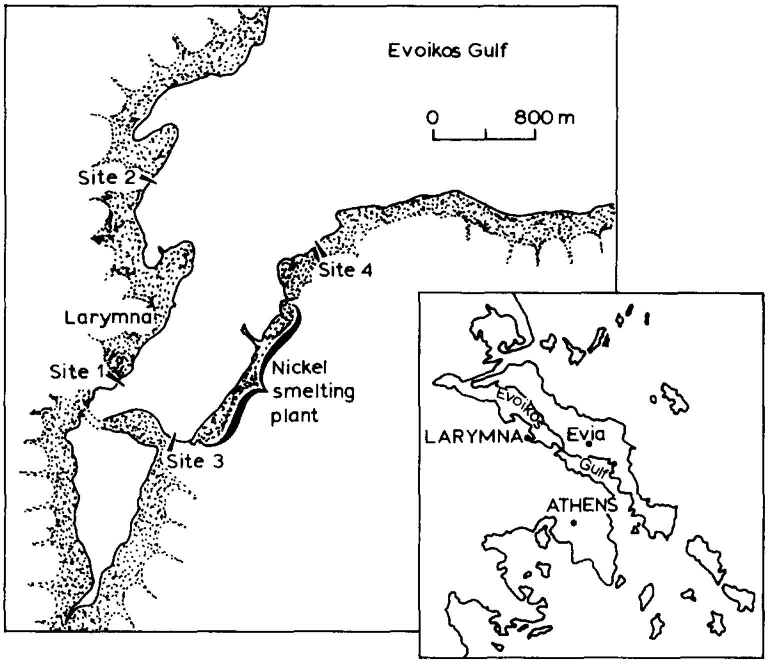

sediment. On some occasions, 5–8 specimens of each species were pooled to form one sample.

The preparation of samples was carried out according to the methods described by Bryan et al. (1985). The sediment was sieved through a 200 μm plastic mesh with 50% sea water (salinity, 34.3‰). After settling overnight, most of the water was decanted and the remaining sediment was air dried. The plant and animal tissues were dried in an oven at 80°C. Both sediment and tissues were digested in glass liquid-scintillation-counting vials with "Aristar" HNO_3. About 50 ml of acid was added to 1 g of dried material. The vial was then covered with a glass ball and heated on a hot plate for 1–2 days until a yellow solution was obtained. After removing the ball, the acid was slowly evaporated. The residue was dissolved in concentrated HCl and then diluted to give 10% or $\sim 1\,N$ HCl. The metals Cu, Co, Cr, Fe, Mn and Zn were analysed in a Perkin Elmer 603 flame atomic absorption spectrophotometer with a background correction for Co and Cr; carbon furnace atomic absorption was used for measuring Ni. The accuracy of the method used was established by analysing a NBS SRM 1577 Bovine Liver standard sample.

RESULTS

The observed concentrations of the standard sample together with the recommended values are shown in Table 1. The concentrations of metals in sediment and biota are shown in Table 2.

TABLE 1

Concentrations of metals in the NBS SRM 1577 Bovine Liver standard sample. NBS values taken from the certificates of analysis

	Concentration ($\mu g\ g^{-1}$ dry wt)	
	NBS	Present investigation
Ca	123	125.6 ± 3.1
Co	0.180	0.28 ± 0.01
Cr	0.65 ± 0.73[a]	0.13 ± 0.02
Cu	193 ± 10	185.9 ± 2.8
Fe	270 ± 20	277.4 ± 4.5
Mg	605	685.0 ± 30
Mn	10.3 ± 1.0	10.7 ± 0.1
Ni	0.4 ± 0.4[a]	0.08 ± 0.02
Zn	130 ± 10	141.7 ± 2.4

[a] Values taken from Gladney (1980).

Concentrations in the sediment of metals (except Cu and Mn) were higher than the average values for unpolluted Greek coastal sediments (Smith and Cronan, 1975; Voutsinou-Taliadouri et al., 1987); they are comparable to levels in polluted areas of Britain (Bryan and Gibbs, 1983).

The sediment in the Bay of Larymna is contaminated by the activities of the smelter. However, only 21% of the Ni and 37% of the Cr is extracted from the sediment with 10% HCl, which suggests that a large proportion of these metals may not be readily available to organisms. The concentrations of metals vary in the different species of invertebrates. The gastropod molluscs tend to concentrate the metals more than the bivalve molluscs. *Cerithium vulgatum* shows particularly high concentrations of Co, Mn, Ni and Zn. The cone shell *Conus mediterraneus* has the highest concentration of Cu together with the winkles *Monodonta* spp., which also show high concentrations of Cr. The levels of metals in *Monodonta* match those observed by Tuncer and Uysal (1982) in the polluted Bay of Izmir, Turkey. The mussel *Mytilus galloprovincialis* has lower concentrations than mussels from other coastal regions of Greece which are polluted by sewage (Grimanis et al., 1982). The carpet shell *Venerupis decussata* also has low metal concentrations compared with specimens from the Bay of Izmir (Tuncer and Uysal, 1982). In the beadlet anemone *Actinia* the levels are similar to those noted by Bryan and Gibbs (1983) for the same species from unpolluted sites in south Devon, with the exception of Mn which is more concentrated in specimens from Larymna. The relatively low concentrations of metals in the filter feeders (*Mytilus, Venerupis*) and the high concentrations in the herbivores (*Monodonta* spp) and detritus feeder (*Cerithium*) suggest that one pathway for the metals may be through the plants, which also show some high concentrations, i.e. *Cymodocea* leaves are rich in Mn, and the "epiphytes" in Cr, Mn and Zn. Direct comparison between all the sites is not possible since

TABLE 2

Concentrations ($\mu g\ g^{-1}$ dry wt) of metals in sediment and biota

Species	Date of collection	Part of animal	Site	No. of samples	Co	Cr	Cu	Fe	Mn	Ni	Zn
Actinia equina	Jul 86	Whole	2	4	0.4 ± 0.4	1.0 ± 0.4	5.2 ± 0.4	139.1 ± 44.2	156.1 ± 27.1		273.9 ± 18.7
Mytilus galloprovincialis	Jul 86	Whole	3	7	0.7 ± 0.5	3.0 ± 0.8	3.7 ± 0.6	191.7 ± 42.5	8.7 ± 3.4		67.9 ± 17.1
Venerupis decussata	Nov 86	Whole	1	3	3.1 ± 2.2	4.6 ± 0.8	9.1 ± 5.4	335.6 ± 160.5	9.4 ± 3.0	13.6	66.2 ± 4.3
Pinna nobilis	Nov 86	Muscle	2	1	0.8	10.2	7.4	348.6	435.1		144.6
Cerithium vulgatum	Nov 86	Whole	1	10	104.5 ± 35.9		71.0 ± 21.2	1698.4 ± 479.6	2131.0 ± 759.9	187.3 ± 94.3	2238.8 ± 561.4
	Jul 86	Viscera	1	1P[a]	75.8		71.1	1024.8	1396.3		4584.9
	Jul 86	Viscera	2	1P	27.9	102.9	35.9	2091.1	1307.0		2051.0
Monodonta articulata	Nov 86	Whole	3	10	1.4 ± 0.5	11.2 ± 2.1	125.4 ± 37.3	1360.1 ± 333.6	23.8 ± 13.9	10.5 ± 4.3	102.0 ± 19.4
	Jul 86	Viscera	3	2P	0.7	51.1 ± 1.9	214.3 ± 13.9	3661.8	64.6 ± 12.1		93.8 ± 4.0
M. mutabilis	Nov 86	Whole	4	10	1.1 ± 0.3	4.6 ± 1.9	136.6 ± 25.1	610.0 ± 142.2	39.5 ± 11.0	5.9 ± 0.9	98.8 ± 20.3
	Jul 86	Viscera	4	3P	1.1 ± 0.7	7.4 ± 2.5	161.6 ± 30.5	1453.0 ± 70.1	49.4 ± 12.1		65.8 ± 9.1
	Jul 86	Viscera	2	2P	1.7 ± 0.7	106.2 ± 25.7	119.5 ± 90.4	4771.5 ± 971.0	33.6 ± 8.4		90.0 ± 10.1
M. turbinata	Nov 86	Whole	4	10	2.3 ± 1.1	5.6 ± 2.4	109.1 ± 15.0	669.3 ± 216.6	36.4 ± 7.6	12.0 ± 0.2	65.7 ± 11.3
	Jul 86	Viscera	4	5P	3.1 ± 1.4	9.5 ± 5.8	128.9 ± 35.4	1073.0 ± 357.4	73.9 ± 23.5		90.8 ± 8.4
Conus mediterraneus	Nov 86	Whole	1	3	3.0 ± 0.8	1.0 ± 0.2	273.3 ± 57.8		10.1 ± 2.00	10.8 ± 4.1	121.3 ± 11.1
Cymodocea leaves	Jul 86		1	1P	9.6	5.5		694.1	650.9		135.3
Cymodecea roots	Jul 86		1	1P	1.2	5.1	10.4		33.2		59.3
Enteromorpha	Jul 86		4	1P		7.7	26.5	1526.9	22.2		44.5
"Epiphytes"	Jul 86		2	1P		138.9	14.2		974.2		176.6
Sediment (total metals)	Nov 86		1	4	33.3 ± 10.0	746.0 ± 145.0	13.9 ± 1.2		327.0 ± 6.9	600.0 ± 206.0	128.0 ± 2.1
Sediment (10% HCl extract)	Nov 86		1	2	14.8 ± 1.8	277.1 ± 17.5	8.7 ± 3.0		253.6 ± 9.8	127.5 ± 25.1	53.8 ± 21.0
% metal extracted with 10% HCl					44.4	37.1	62.6		77.5	21.1	42
Slag in smelter[b]					93	3130	9	20.50%	2330	1200	50
Average Aegean sediment[c]						49	13	1.3%	280	28	35
Average in Greek Coastal regions[d]					14	136	21	21.1%	878	105	52

[a]P = pooled samples.
[b]Voutsinou-Taliadouri and Varnavas, 1987.
[c]Smith and Cronan, 1975.
[d]Voutsinou-Taliadouri et al., 1987.

they do not contain the same species. However, comparison of the levels of metals in *Cerithium* suggests that Site 1 is more polluted than Site 2, while the levels in *Monodonta articulata* suggest that Site 2 is more polluted than Site 3.

CONCLUSIONS

It can be concluded that the smelting plant does contaminate the local environment with a variety of metals and that these are accumulated by marine organisms. However, different species accumulate different metals to a different extent and assessments of the effects of pollution must take this into account.

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REFERENCES

Bryan, G.W. and P.E. Gibbs, 1983. Heavy metals in the Fal Estuary, Cornwall: A study of long-term contamination by mining waste and its effects on estuary organisms. Mar. Biol. Assoc. U.K., Occas. Publ. No. 2, 111 pp.

Bryan, G.W., W.J. Langston, L.G. Hummerstone and G.R. Burt, 1985. A guide to the assessment of heavy metal contamination in estuaries using biological indicators. Mar. Biol. Assoc. U.K., Occas. Publ. No. 4, 92 pp.

Gladney, E.S., 1980. Elemental concentrations in NBS Biological and Environmental standard reference materials. Anal. Chim. Acta, 118: 385–395.

Grimanis, A.P., D. Zafiropoulos, C. Papadopoulou, T. Economou and M. Vassilaki-Grimani, 1982. Trace elements in *Mytilus galloprovincialis* from three Gulfs of Greece. VI[es] Journ. Etud. Pollut., Cannes, CIESM, pp. 319–322.

Smith, P.A. and D.S. Cronan, 1975. Chemical composition of Aegean Sea sediments. Mar. Geol., 18: M7–M11.

Tuncer, S. and H. Uysal, 1982. Etude des métaux lourds chez les mollusques dans les différentes zones de la Baie d'Izmir (Turquie). VI[es] Journ. Etud. Pollut., Cannes, CIESM, pp. 307–313.

Voutsinou-Taliadouri, F. and S.P. Varnavas, 1987. Marine mineral resources in the eastern Mediterranean Sea II: an iron, chromium and nickel deposit in the northern Euboikos Bay, Greece. Mar. Mining, 6: 259–290.

Voutsinou-Taliadouri, F., J. Satsmadjis and B. Iatridis, 1987. Granulometric and metal composition in sediments from a group of Ionian Lagoons. Mar. Pollut. Bull., 18: 49–52.