HEAVY METALS POLLUTION OF BARCELONA HARBOUR SEDIMENTS

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INTRODUCTION

Barcelona is an industrialised city on the northeast part of Spain's Mediterranean coast. It has been an important port in the region for many years and much heavy industry is sited there. Two rivers discharge into the Mediterranean in the region of Barcelona. To the north is Rio Besos, to the south is Rio Llobregat, both flow through heavily populated areas and receive domestic, agricultural and industrial effluent. The main sewage outfall for the Barcelona area is located to the south of the harbour, just north of the mouth of Rio Llobregat (see map). The harbour of Barcelona is protected from onshore winds by the eastern dike and therefore the body of water contained within is a low energy area prone to the deposition of fine sediments. Hence the main channels within the harbour are regularly dredged to maintain a navigable depth for shipping. These dredgings are then dumped in the Mediterranean within Spanish national waters.

Industrial inputs frequently cause dredgings to be highly polluted with heavy metals. In recent years much attention has been focussed on the toxicity of dredging spoils and their effects on receiving environments. The majority of Rotterdam dredgings, for instance, are considered to be too polluted to dump in the sea or to spread on agricultural land and are therefore treated as toxic waste by the Netherlands authorities (Nijssen 1988). Rotterdam harbour is situated in the estuarine region of the heavily polluted Rhine river and receives contaminants from the Rhine and the Maas. The dredgings are grouped into four classes according to contaminant levels, class four being the most polluted with heavy metals and persistent organic contaminants. The long term policy for these dredgings is to reduce pollutant loading of the sediments from source so that Class 4 waste is no longer produced.

Cadmium, chromium, lead and soluble copper compounds are included in the EEC list of priority pollutants. The toxicity of these metals is well documented (Brown & Kodama 1987) and this has prompted many investigations into their distribution in the environment (Bridges 1989, Nriagu 1990). This study was commissioned by Greenpeace Spain to investigate a range of heavy metals in sediments from Barcelona harbour and surrounds.

SAMPLING AND METHODS

Sediment samples were obtained using a Van Veen grab operated from the Greenpeace vessel MV Sirius in May 1992. The location of these samples is shown on the map. The samples were transported to the Greenpeace Exeter Laboratory at Exeter University, UK, where they were analysed for a range of metals. The metals investigated were nickel (Ni), manganese (Mn), iron (Fe), chromium (Cr), zinc (Zn), copper (Cu), cadmium (Cd), cobalt (Co), lead (Pb) and titanium (Ti).

Subsamples of the sediments were oven-dried and their moisture content thereby determined. The sediments were qualitatively examined for sand/shell/clay content. While analytical measurements of particle size distribution would have been preferable, this method of macroscopic rating of sediment composition was justified since the only intent was to separate sand/shell-dominant samples from clay-dominant samples. In fact all of the sediments in this study were dominated by clay. Preparation of the sample digests was by microwave digestion in a CEM MDS2000 sample preparation system. Approximately 1 gram of sample was weighed accurately into an acid washed teflon sample vessel and 20mls of 1:1 nitric acid:single distilled deionised water added. The samples were microwaved at full power for one hour and pressure controlled to a maximum of 150psi. Duplicate samples were analysed for each sampling location and an average value thus obtained.

A blank was included in each sample run of twelve individual sealed Teflon vessels. Nitric acid was used for the digestion. Although this method does not produce a complete digestion of the sediment, it has been shown by Pavoni *et al* (1987) to be satisfactory in determining heavy metal concentrations for environmental investigations. The remaining metals are more firmly bound to the mineral matrix of the sediment and therefore less bioavailable. Analysis was by Varian Liberty 100 ICPAES (Inductively coupled plasma atomic emission spectrometer). The ICPAES was calibrated against commercially available ICP standards (MBH analytical U.K.) and standard quality control checks were carried out on each batch of samples. The results are shown as table 1.

Sample Location Map of Barcelona Harbour and Surround

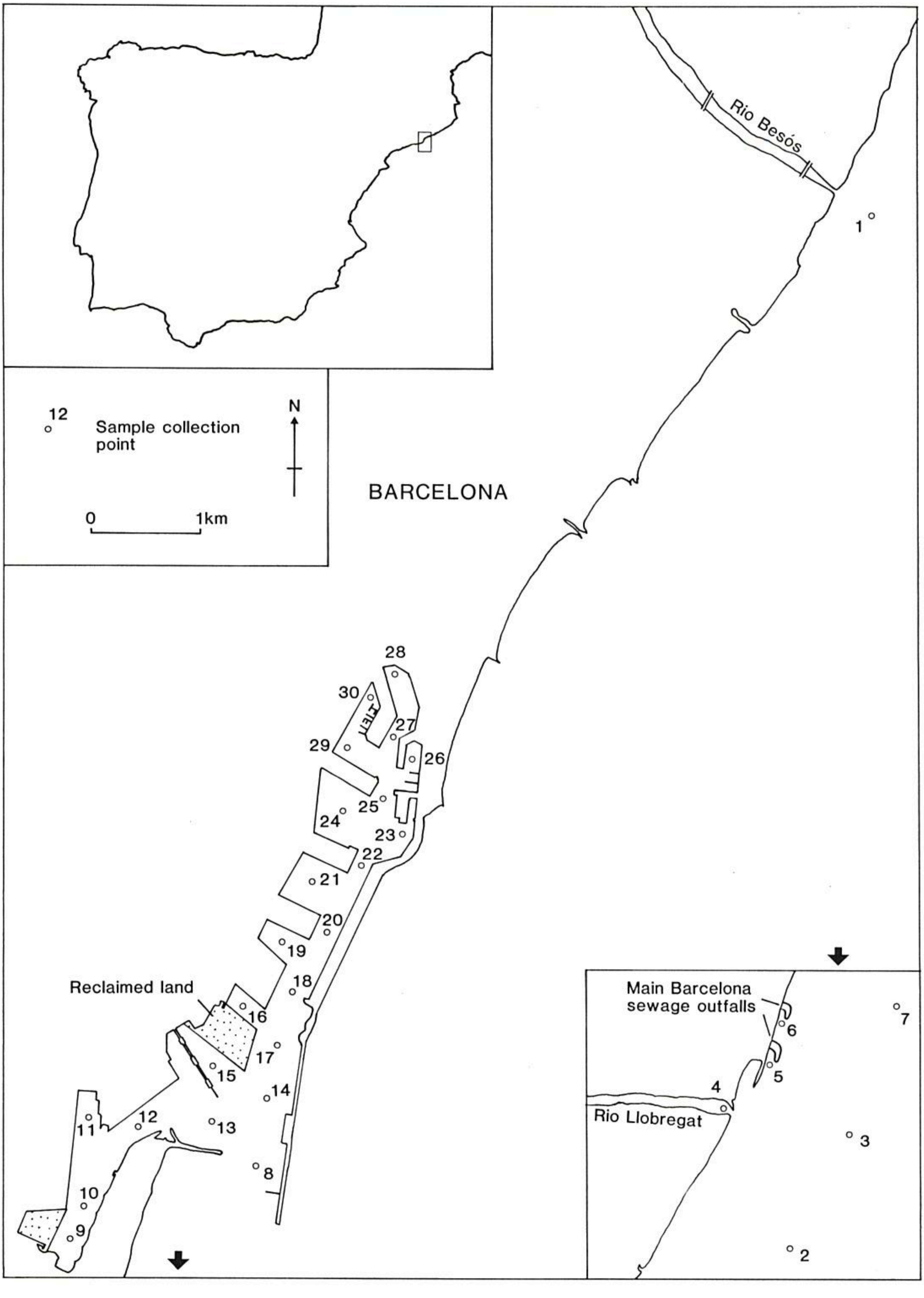

TABLE 1

Concentrations of metals in sediments from Barcelona

SAMPLE NUMBER	CONC. IN DRY SAMPLE (ppm) Ni	CONC. IN DRY SAMPLE (ppm) Mn	CONC. IN DRY SAMPLE (ppm) Fe	CONC. IN DRY SAMPLE (ppm) Cr	CONC. IN DRY SAMPLE (ppm) Zn	CONC. IN DRY SAMPLE (ppm) Cu	CONC. IN DRY SAMPLE (ppm) Cd	CONC. IN DRY SAMPLE (ppm) Co	CONC. IN DRY SAMPLE (ppm) Pb	CONC. IN DRY SAMPLE (ppm) Ti
:1	23.5	272	22900	256	355	158	6.65	8.92	156	947
:2	9.35	266	13200	42.4	77.2	21.6	3.71	4.28	24.3	218
:3	21.4	289	19600	91.9	184	76.8	5.1	7.32	41.6	370
:4	15.6	336	16700	75	216	44	4	6.12	47.4	353
:5	10.2	202	10100	97.8	113	32.2	2.62	3.67	52.4	208
:6	37	168	11000	102	324	161	2.93	5.25	109	340
:7	7.41	271	13700	48.1	81.5	23.6	3.24	3.7	29.6	373
:8	18.1	311	17900	151	318	79.5	5.68	7.74	116	364
:9	17.7	348	18100	30.5	63.3	15.4	4.69	7.82	11	321
:10	19.5	286	17100	70.8	259	95.9	4.94	6.99	82	389
:11	38.4	263	22600	111	555	197	5.89	14.93	236	593
:12	16.8	232	15900	80.9	191	76	4.18	5.86	77.6	396
:13	12.7	290	18600	94.7	187	69.8	4.76	5.95	73.7	389
:14	17.5	295	19800	126	254	96.5	5.16	6.24	103	476
:15	16.4	319	20500	96.6	205	81.3	5.43	6.75	75.5	403
:16	19.4	309	21100	96	308	112	6.19	6.96	140	486
:17	16.9	316	18800	91.4	217	82	5.13	6.92	80.4	432
:18	20.3	294	19700	104	259	98.4	5.85	7.07	101	461
:19	28.7	241	20900	127	617	212	5.32	7.35	195	501
:20	17.4	227	17100	77.9	264	102	4.36	5.99	88.2	468
:21	22.8	242	19600	108	375	151	5.22	6.65	159	538
:22	15.8	204	15900	63.6	256	102	4.14	5.85	106	476
:23	22.6	213	18700	84.3	517	256	2.41	6.46	178	501
:24	13.8	181	13600	47.2	245	115	4.21	4.21	108	500
:25	16.1	188	14200	53	192	133	2.12	4.99	122	462
:26	30.9	214	27800	109	1100	775	7.37	7.96	585	500
:27	10.1	186	13200	38.4	235	105	2.95	4.24	97.3	478
:28	16.1	223	19800	70	884	234	3.71	6.82	244	559
:29	12.1	189	14600	37.5	342	135	3.13	4.69	195	475
:30	21.2	181	17000	62.1	588	223	3.64	4.22	286	468
mean *	19.2	250	18400	84	367	154	4.63	6.64	150	462

* mean of samples 8-30 i.e. sediments from within the harbour wall

RESULTS AND DISCUSSION

The concentrations of metals found in the sediments in the region of Barcelona harbour are consistent with substantial anthropogenic input. Table 2 gives a comparison of some Barcelona harbour metals concentrations with those in dredgings from Rotterdam harbour and with background levels. Concentrations of lead, cadmium and zinc are comparable to those found in areas of Rotterdam harbour whereas nickel and chromium concentrations are lower. The mean copper concentration in Barcelona sediments is higher than the highest concentration found in Rotterdam. Rotterdam is an exceedingly polluted harbour because contaminants carried by the Rhine and Maas are deposited on the fine sediments of the harbour when fresh and sea water mix. Barcelona harbour does not have such a riverine input of pollutants and therefore the concentrations of metals in the sediments indicate a large anthropogenic input in the environs of the harbour itself.

TABLE 2.
HEAVY METALS IN SEDIMENTS FROM ROTTERDAM COMPARED TO BARCELONA

	Rotterdam# [mg/kg]	Background* level [mg/kg]	Barcelona$ mean [mg/kg]
Pb	80-240	30	150
Cd	3-13	0.3	4.63
Cr	97-187	73	84
Cu	39-142	20	154
Ni	24-63	26	19.2
Zn	256-1079	76	367

#figures for 1984 dredged material, here the heavy metals have been extrapolated to a 50% fraction smaller than 16micrometres. in: Nijssen (1988)
*in: Driel & Nijssen (1988)
$this mean figure is calculated from samples 8-30

There is considerable variation in metal concentrations found in the sediments of this study, different metals predominate in different parts of the harbour system. This variation is suggestive of several point sources of pollutants within and without the harbour. For example, sample 11 from the southwestern section and 26 obtained from the northeastern section of the inner harbour contain elevated concentrations of several metals investigated in this study. This is indicative of point source discharges in both these regions of the harbour. Sample 1 taken near the mouth of Rio Besos, to the north of Barcelona harbour, contains elevated concentrations of all the metals investigated in this study. In a study of both Rio Besos and Rio Llobregat Gomez-Belinchon *et al* (1991) found that these rivers carry a heavy burden of volatile organic pollutants, including considerable quantities of petroleum hydrocarbons and chlorinated compounds, into the coastal zone. It is therefore probable that much of the heavy metal loading in sample 1 originates from the Rio Besos also. As the fresh water from Rio Besos mixes with the sea much

of its pollutant loading will associate itself with sediments in the mouth of the estuary.
Cadmium was found at elevated concentrations in several locations. The presence of cadmium in the sediments at these levels warrants further investigation. Cadmium does not occur freely in nature and there are no specific ores from which it is mined, it is of concern to human health and has been demonstrated to have adverse effects on aquatic ecosystems. Some recorded effects of exposure to cadmium include renal tubular damage, structural and functional liver damage and anaemia. In aquatic organisms, cadmium is directly toxic and can exert sub acute effcets upon growth and reproduction. Copper is toxic to a wide variety of marine organisms and the high concentrations observed in this study will undoubtedly be modifying the local benthic community.

The United States EPA have maximum advisory levels for heavy metals in sludge which can be applied to agricultural land without causing toxic effects to plants (EPA 1981). These concentrations are Pb 500 mg/kg, Zn 250 mg/kg, Cu 125 mg/kg, Ni 62 mg/kg and Cadmium 2.5 mg/kg. All of the sediments in this study contain more cadmium than the EPA maximum recommended concentration of 2.5 mg/kg for application of municipal sludge to medium-textured croplands to prevent phytotoxicity. Many of the sediments from Barcelona also exceed these advisory levels for zinc and copper.

CONCLUSION

From the results it is clear that Barcelona harbour is heavily contaminated with heavy metals due to insufficient regulation of diverse inputs. Concentrations of cadmium, lead and copper are sufficiently high to be a cause for concern. The enclosed and shallow nature of the harbour only serves to emphasise this problem. Dredging the harbour and dumping these dredgings into the Mediterranean is hence a "back door" route for the disposal of toxic waste. There is no incentive for waste reduction. It is likely that these dredgings are modifying the marine life at the site of dumping. Some of the metals examined in this study are toxic and liable to bioaccumulate. It is possible that the practice of dumping these dredging spoils into the Mediterranean will have a detrimental effect on the quality and viability of local fisheries. A long term policy to reduce pollutant loading of the sediments from source should urgently be considered for the Barcelona region so that such polluted sediments are no longer produced.

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