Reprinted from ENVIRONMENTAL SCIENCE & TECHNOLOY, Vol. 11, Page 819, August 1977

Copper and Other Heavy Metal Contamination in Sediments from New Bedford Harbor, Massachusetts: A Preliminary Note

Peter Stoffers[1], Colin Summerhayes[2]*, Ulrich Förstner[1], and Sambasiva R. Patchineelam[1]
Woods Hole Oceanographic Institution, Woods Hole, Mass. 02543

■ The clay fraction of bottom sediments near the head of New Bedford Harbor, Massachusetts, contains more than 1% of Cu, Cr, and Zn combined. These and other heavy metals are industrial wastes that were discharged into the harbor over the past 80 years or so. They are located mainly in the clay fraction of the sediments, and their concentration warrants consideration of their recycling potential. Metal concentrations decrease exponentially seaward into Buzzards Bay, where surface sediments contain three times as much Cu (the main contaminant) as buried sediments. Clearly, the harbor is a leaky sink for contaminants. The effect on marine life of this widespread metal contamination is not yet known.

Marine sediments from bays and estuaries near large industrial and urban areas are typically contaminated with heavy metals like Cu, Pb, Zn, Cr, and Cd, which may be present in amounts 5–10 times higher than they were 50–100 years ago (*1–5*). Most of this recent concentration of metal is due to discharge of industrial wastes into the sea. During a study of sediment dispersal in the Massachusetts coastal zone, we have found that the bottom sediments of New Bedford Harbor, on the estuary of the River Acushnet, contain large amounts of heavy metals, and it appears that these have an industrial source. A detailed report of this study is currently being prepared (*6*).

In Figure 1 we show the distribution of Cu in the clay-sized (smaller than 2 μm) fraction of surface sediments collected from the seabed by grab (92 samples) and gravity core (20 samples). We deliberately focused on the clay-sized fraction to eliminate chemical variations that may have been caused by variations in the grain size of the sediments (*7*). Copper concentration gradually decreases seaward from values of more than 6000 ppm near the head of the harbor to less than 100 ppm at the edge of Buzzards Bay.

We used 19 short gravity cores to study the history of metal contamination in the area (*6*). Samples were taken at 2-cm intervals in the top 10 cm of each core and at 20-cm intervals below that. In Table I we compare the metal concentrations in the upper 5–20 cm of three selected cores with the background metal concentrations that we measured near the bottoms of the cores; core locations are given in Figure 1. Maximum amounts of metal enrichment are ×150 for Cu,

---

[1] Present address, Laboratorium für Sedimentforschung, Universität Heidelberg, Germany.

[2] Present address, Exxon Production Research Co., P.O. Box 2189, Houston, Tex. 77001.

WHOI 3893

×100 for Cd, ×30 for Pb and Cr, and ×10 for Zn (Table I). Marked increases in the concentration of metal above background levels occur at burial depths of 60–80 cm in core A, at 40–60 cm in core B, and at about 10 cm in core C. The sediments are organically enriched black silts that smell of hydrogen sulfide; therefore, it seems highly unlikely that a significant amount of the metal found near surface results from diagenetic processes operating within the sediment column.

By analyzing different grain size fractions, we are able to show that the metals are associated with fine-grained particles. The largest amounts of Ag, Cd, Cr, Cu, Pb, and Zn were measured in the clay fraction smaller than 2 μm, and Cu reached 8500 ppm (or 0.85%) in the very fine clay fraction smaller than 0.63 μm. Almost 40% of Cu and Zn were located in the leachate-resistant fraction that consists largely of insoluble mineral detritus (Table II). We do not know yet in what mineral form these metals occur. About 20% of these same elements were located in authigenic phases that were leachable with an acid-reducing agent solution (Table II); in the highly reducing sediments from this area, iron sulfides are the main authigenic minerals (*8*). The remainder of the Cu and Zn was associated with the organic fraction of the sediment (Table II), probably because of the sorption of dissolved Cu and Zn onto organic phases. Chromium showed a different distributional pattern, most (85%) being located in the authigenic fraction, or in the leachate-resistant fraction (8%) (Table II). We suspect that Cr may have entered the harbor mainly as chromate anions rather than in solid form.

Our data suggest that the source of metals is in the harbor, where rates of sediment and metal accumulation have been highest (*6*). Here four of our samples contain more than 1% of Cr + Cu + Zn in the clay fraction, and away from the harbor there is an exponential seaward decrease both in absolute metal concentration and in the thickness of the contaminated surface layer of sediments. Seaward diffusion of metalliferous waste therefore appears to have been very limited, although even the surface sediments at the seaward edge of the study area, and in Buzzards Bay, appear to be slightly contaminated, having Cu levels of more than 60 ppm that are three times higher than the background Cu levels of subsurface sediments in the same locality.

Inspection of publicly available EPA records suggests that industrial discharge of Cu-rich waste is concentrated close to the Cu maximum shown in Figure 1, and that Cu discharge may have reached 200 lb/day in recent years. Knowing the history of maintenance dredging in the harbor and the

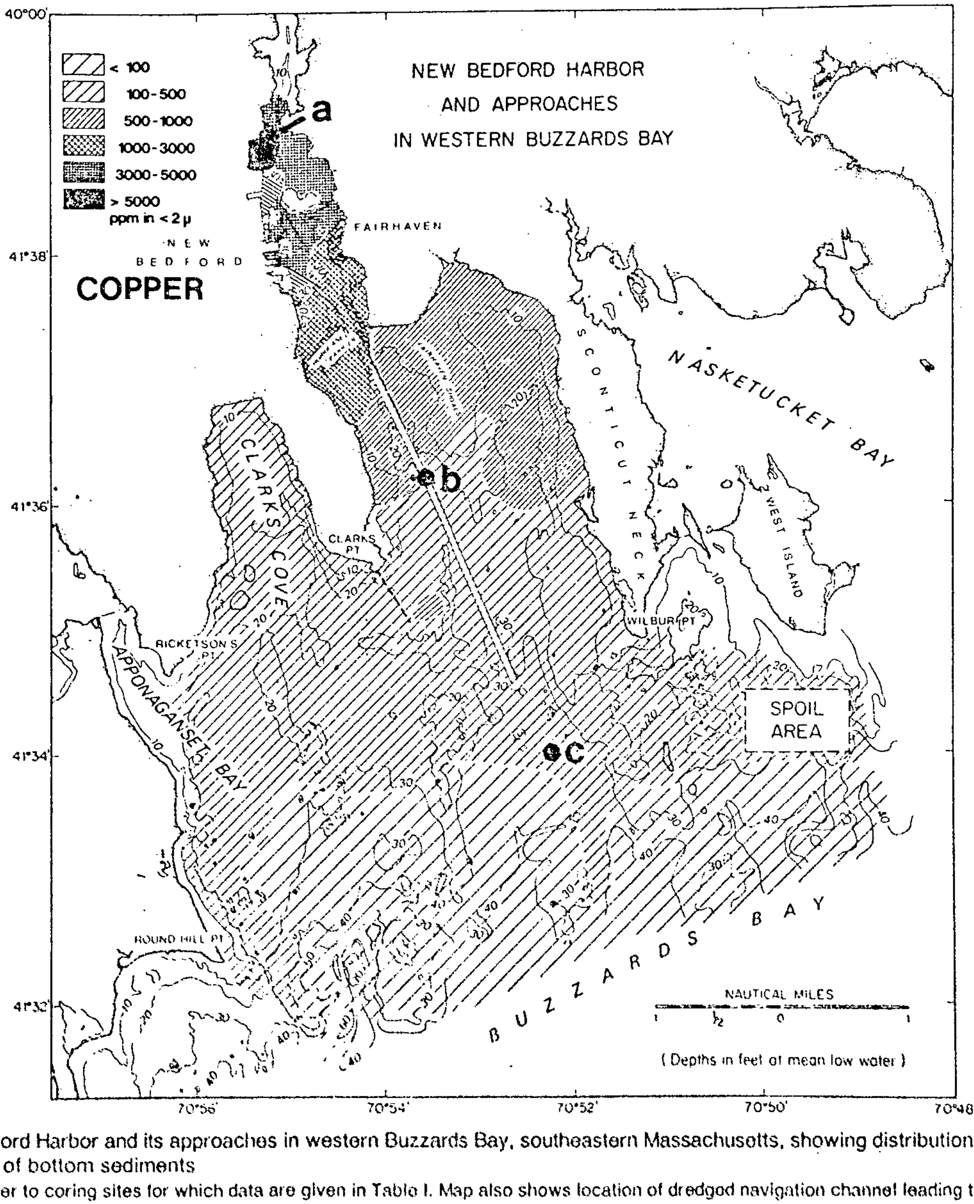

Figure 1. New Bedford Harbor and its approaches in western Buzzards Bay, southeastern Massachusetts, showing distribution of Cu in the smaller than 2-μm fraction of bottom sediments

Letters a, b, and c refer to coring sites for which data are given in Table I. Map also shows location of dredged navigation channel leading to harbor, and of areas of recent dredging within harbor (diagonal hatching). Sample locations on which this map is based are given by Summerhayes et al. (*6*)

Table I. Mean Abundances of Different Metals in ppm in Clay Fraction (Smaller than 2 μm) of Sediments from Tops of Three Representative Cores (n = Number of Samples Analyzed), Compared with Mean Abundances of Metals in Uncontaminated Sediments (Background) Found at Bottoms of Cores (Core Locations Given in Figure 1)

	Cu	Cd	Pb	Cr	Zn
Core A					
0–20 cm (n = 6)	3136	52	616	2146	1550
Core B					
0–10 cm (n = 5)	580	6.6	210	439	484
Core C					
0–5 cm (n = 3)	117	1.4	104	218	315
Background	20	0.4	20	100	150

Table II. Distribution of Metals in Percentages in Different Fractions of Clay Fraction of Sample, as Determined by Different Chemical Leaching Techniques (S. Rao, Analyst). Method of Chester and Hughes (*14*) Used for Authigenic Mineral Extraction

Leaching method	Cu	Cr	Zn
Bitumen extraction with 1:1 alcohol: benzene mix	6.29	0.21	8.06
Cation exchange with 0.2 N $BaCl_2$ triethanolamine	17.6	0.01	21.38
Humic acid extraction with 0.1 N NaOH	1.36	1.57	0.2
Fulvic acid extraction with 0.1 N NaOH + H_2SO_4 (pH 3)	17.28	4.86	4.28
Authigenic mineral extraction with acid-reducing agent	18.27	85.04	27.66
Resistant mineral (residue after extractions completed)	39.2	8.32	38.42
Total concn of metal (ppm)	2500	1850	595

thickness of Cu-rich sediment (up to about 70 cm), Summerhayes and others (*6*) calculate that metal-rich mud has been accumulating at rates of about 3 cm/yr in the deepest parts, and at rates of about 4 mm/yr in the shallower parts of the harbor. The history of waste metal accumulation covers a period of about 80 years, which is in good agreement with the known history of Cu discharge from industrial plants in this area.

Contamination of bottom sediments by Cu and associated elements in amounts similar to those reported in the harbor is common for marine sediments in mining districts rather than industrial areas (*9–12*). The amounts of metal in the sediment are sufficiently high to raise the intriguing possibility that they may be extracted profitably by some recycling process. Calculations suggest that there are about 3500 metric tons of Cu + Cr + Zn in the harbor muds; the possible value of this deposit, at current market values, is about $5 million. Mining the muds, which are about 0.5 m thick on average, would not present any problem. Further work is needed to ascertain what difficulties might be encountered in extracting different metals from the sediment.

From the exponential seaward decrease in metal concentration away from the harbor, and the seaward thinning of surface sediment contaminated with metal waste, it appears that the estuary of the Acushnet does operate as a pollutant sink preventing the transfer of solid and adsorbed metal waste to the open ocean. This particular sink, however, appears to be slightly leaky, since the top 10–20 cm of sediments from the edge of the study area and from further seaward in the center of Buzzards Bay contain about three times as much Cu as buried uncontaminated sediment from this region. Further studies should take account of the possibility that some of the waste metals may accumulate in the aquatic food chain in Buzzards Bay by way of deposit and filter-feeding organisms (*9*). It should also be pointed out that, like nutrients (*13*), some of the metals in these waste deposits may be reintroduced into the water column by natural chemical, biological, and geological processes (as well as by dredging); further work is needed to establish the importance of these remobilization processes and their effects on food chains in this region.

Acknowledgment

Samples were collected from *R. V. ASTERIAS,* with the assistance of Dick Colburn (master), Jeffrey P. Ellis, and Scott R. Briggs, all of Woods Hole Oceanographic Institution. K. O. Emery and D. A. Ross, Woods Hole Oceanographic Institution, critically reviewed a draft of this report.

Literature Cited

(1) Harlow, W., et al., *J. Mar. Biol. Assoc. UK,* **53,** 721 (1973).
(2) Erlenkeuser, H., et al., *Geochim. Cosmochim. Acta,* **38,** 823 (1975).
(3) Förstner, U., Reineck, H. E., *Senckenbergiana Marit.,* **6,** 175 (1974).
(4) Bruland, K. W., et al., *Environ. Sci. Technol.,* **8,** 425 (1974).
(5) Thomson, J., et al., "Estuarine Research", Vol 1, p 28, Academic Press, New York, N.Y., 1975.
(6) Summerhayes, C. P., et al., Tech. Rept., Woods Hole Ocean. Inst., Woods Hole, Mass., in preparation.
(7) Förstner, U., Müller, G., "Schwermetalle in Flussen und Seen", Springer-Verlag, Berlin, Germany, 1974.
(8) Moore, J. R., *J. Sediment. Petrol.,* **33,** 511 (1963).
(9) Bryan, G. W., Hummerstone, L. G., *J. Mar. Biol. Assoc. UK,* **51,** 845 (1971).
(10) Brown, M.J.P., *Geoforum,* **18,** 9 (1974).
(11) Elderfield, H., Thornton, I., Webb, J. S., *Mar. Pollut. Bull.,* **2,** 44 (1971).
(12) Thornton, I., et al., *Sci. Total Environ.,* **4,** 325 (1975).
(13) Rhoads, D. C., *Am. J. Sci.,* **273,** 1 (1973).
(14) Chester, R., Hughes, J. M., *Chem. Geol.,* **2,** 249 (1967).

Received for review December 9, 1976. Accepted March 30, 1977. One of us (C.P.S.) was supported for this program by funds from the U.S. Dept. of Commerce, National Oceanic and Atmospheric Administration, Sea Grant Office; the others were supported by the German Science Foundation.