

U.S. DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

POLLUTED SEDIMENTS

in

BOSTON HARBOR - MASSACHUSETTS BAY:

PROGRESS REPORT ON THE
BOSTON HARBOR DATA MANAGEMENT FILE

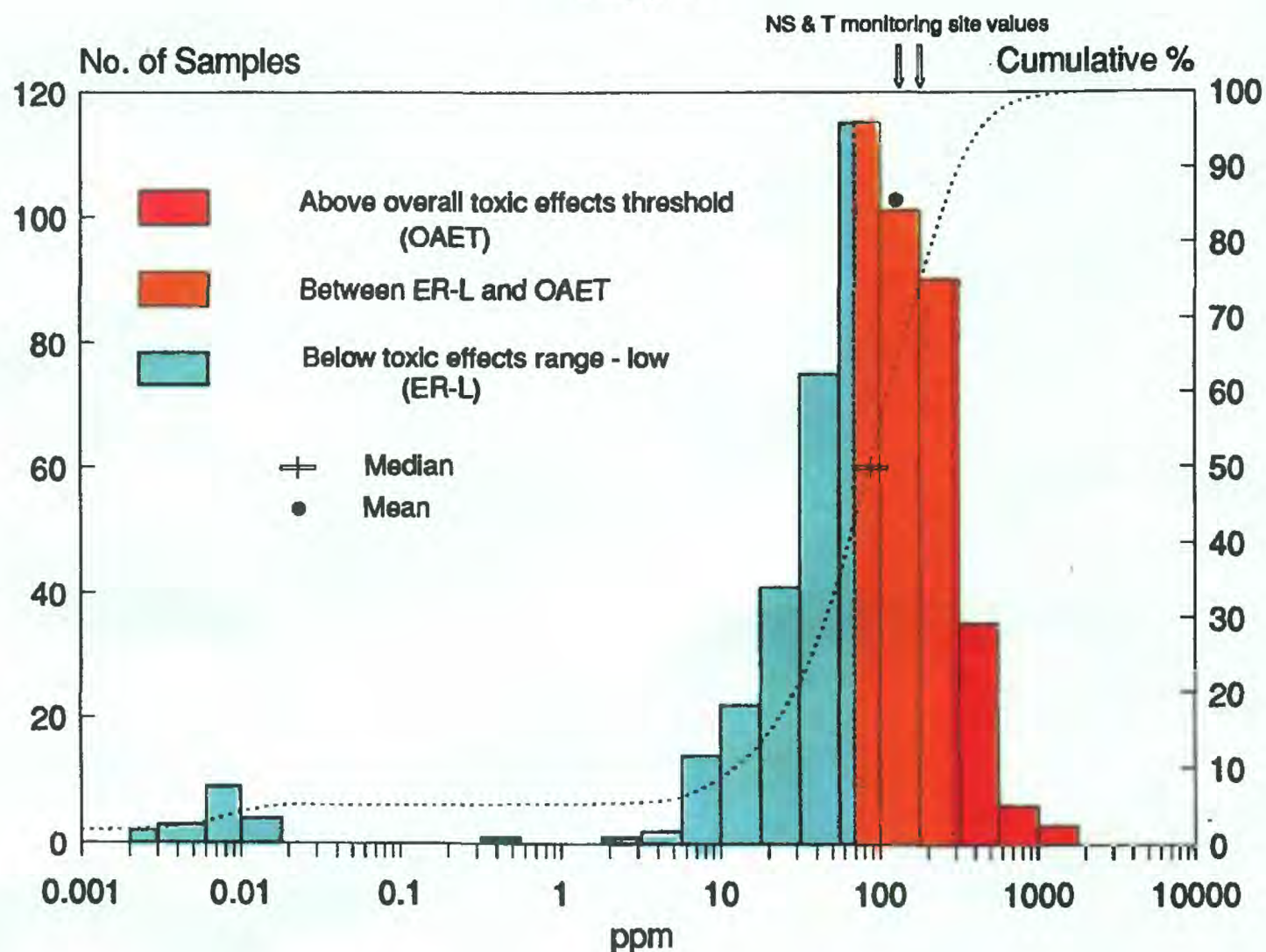
By

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U.S. Geological Survey
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Open File Report 91-331

Copper



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**POLLUTED SEDIMENTS IN BOSTON HARBOR - MASSACHUSETTS BAY:
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A substantial body of data bearing on sediment pollutants exists for the Boston Harbor-Massachusetts Bay region (Fig.1). The largest single source of data is the Boston Harbor Data Management File (BHDMF), sponsored by the U.S. Environmental Protection Agency and compiled by the consulting firm of Metcalf and Eddy(1984). This study was neither fully documented nor were the data synthesized at the time of creation of the file, but utilization of these data is now underway as environmental efforts intensify following the creation of the Massachusetts Water Resource Administration in 1985 (Battelle, 1991; MacDonald, 1991; MWRA, 1991; Butman et al, 1990).

This report describes an initial evaluation as part of an effort to validate the raw data and prepare it in a form readily accessible to interested members of the public, to decision makers, and to scientific investigators. In subsequent stages we plan to map metals and other selected sediment pollutants and interpret their distributions with special reference to geological, geochemical and geophysical parameters of the sea floor. The data cover Boston Harbor and Massachusetts Bay. We seek to complement the work of other Federal agencies, State and regional organiza-

tions, and researchers working in the overall effort.

We acknowledge the assistance of our colleagues in the Atlantic Marine Geology Branch of the Office of Energy and Marine Geology, C.M. Bostwick, now with the USGS Water Resources Division, Reston, VA, members of the Battelle Laboratories, Duxbury, special assistance by Susan Curran and Wendy Smith of the Massachusetts Water Resource Authority, Boston, Richard Taylor of the U.S. Environmental Protection Agency's STORET computer facility in Washington, and Donald McDonald of the Pacific Marine Environmental Research Laboratory, NOAA, Seattle.

Harbor Data Management File (BHDMF)

The BHDMF contains about 62000 sample records and lists 206 source documents (MWRA, 1988). It was transferred to the USGS INGRES¹ data management system and has been manipulated using spreadsheet and other software. The breakdown of total records in the BHDMF file is given in Table 1. Informal summaries by consultants and other reviewers, especially Mason(1984) and MWRA staff, have recognized several problems associated with the BHDMF. The main difficulties relate to (1) linking chemical and other parameters to well-defined samples, site locations, and other background information; (2) awkward file structure, making information retrieval cumbersome; (3) coding errors, discrepan-

¹ Mention of commercial tradenames in this report does not mean or imply endorsement by the U.S. Geological Survey

cies in locations and other typographical errors; and (4) the absence of quality control information on chemical parameters. These problems have been regarded by other investigators to be remediable to a considerable extent, but at the cost of searching out original sources, careful cross-checking, database design and of other time-consuming operations. Reviewers have also mentioned less remediable aspects, namely absence of some data sources, and location errors in the data, particularly from one important source.

Mason(1984) did not concur with those who apparently considered abandoning the database effort because of the above deficiencies. He pointed out that the coding of data and other work represented much effort, and that the database was the only large scale attempt to consolidate harbor-wide information on parameters which describe the marine environment. Moreover, Mason stated that he had not identified likely errors in the measured data; rather, the accuracy problems related more to the documentation process.

We have found some additional problems with the database as a means for effective characterization of the Harbor sediments. For example, data on physical properties, especially sediment texture, are reported for only a fraction of the samples having chemical data. Moreover, the coded data are lumped into only two categories: 1) "fine fraction", or "silt and clay", and 2) median grain size. As one may see in Fig. 2, even a three component, sand-silt-clay breakdown may yield a misleading description of

texture, which is the most critical factor in comparing and classifying sediments. Also, the inorganic chemical analyses show only a few data on major constituents such as aluminum and iron, as well as organic carbon and acid-volatile sulfides, which are used in environmental studies to help interpret the proportion of naturally-occurring metals vs. pollutant metals and to develop models of chemical affinity and bioavailability of the pollutants.

On the other hand, we agree with Mason about the value of the data base, not least because of some developments since his review such as: 1) the efforts of the Maguire Group and MWRA staff (MWRA,1988) have made available a virtually complete list of the codes used in the file; and 3) new types of synoptic surveys, especially sidescan sonar studies, which permit detailed mapping of bottom substrates (Bothner et al, 1990; Knebel et al, 1991.) Such mapping not only can quantify patchy sediment distribution in the Harbor and Massachusetts Bay but also offers a way to match sample parameters with their host bottom substrate types, providing a supplementary tool to investigate data outliers that create disproportionate noise or uncertainty in large data sets.

Major Distributional Features among the Analytical Data.

Table 1 presents the principal analytical components in the BHDMF data set. The number of records shown for sediments have special uncertainty in those cases where some attributes usually associ-

ated only with water-column measurements appear in records coded as sediments (e.g. chlorinity, salinity, and metal contents in units per liter, etc.). The lumping of analyses of dissolved metals in the water column with sediment data will obviously distort the descriptions both of the sediments and of the water column. In this study we have excluded the more obvious cases (e.g. very low concentrations listed in units that imply analysis of liquids, like mg/l). We have included in Figs. 4 - 6 some low-concentration values which appear as outlier populations. They have been included because they are reported in units (such as ppm) usually associated with analyses of sediments, but we suspect that these low concentrations are actually measurements made on water samples. This interpretation is justified because many of the data are below the concentrations in any known earth material (Handbook of Geochemistry, 1978). That the low levels do not represent solely analytical error is indicated by the fact that they correspond to the ranges of similar elements in records in the file that are coded as water column measurements. Evaluation of the validity of water column measurements is outside the scope of this study. Interstitial waters of sediments have taken on new importance in terms of establishing sediment quality criteria (USEPA, 1991), and any available information on this topic in the BHDMF will be included in our study.

Fig. 3 gives the distribution of records featuring all metals reported in sediments in Boston Harbor. The principal contaminant metals, lead, cadmium, chromium, and mercury, were determined in

roughly comparable numbers. Copper, which can be toxic in sufficiently large concentrations, nickel, and zinc are also reported for comparable numbers of samples. A smaller number of vanadium and arsenic values appear in the file. Other elements along with a few major constituents of sediments such as iron and aluminum are reported for relatively few samples.

Histograms (Figs. 4-7) of the frequency distributions of four of the most frequently analyzed elements, cadmium, mercury, lead, and copper, show that these metals fall into logarithmic distributions slightly skewed toward lower concentrations. These are consistent with patterns reported in the literature (see Long and Morgan, 1990; Lyman et al, 1987, and references cited). In part, the distributions can be explained as variable dilution in naturally occurring sediment of anthropogenic pollutants having fairly consistent concentration ranges. Where the sediment occurs in salinity-stratified estuaries, natural (but minor) enrichment of trace elements such as copper, zinc, cadmium, as well as organic matter and iron sulfides will occur (Folger, 1972; Kennedy, 1984).

The arrows along the tops of Figs. 5, 6, 7, and 8b denote the total concentrations (in dry weight) for samples within "effects-based" toxic ranges taken from Boston Harbor for the NOAA Status and Trends (NS&T) monitoring program (Long and Morgan, 1990). A total of four stations in Boston Harbor are monitored at yearly or multiyear intervals for this program. The dashed line represents the "Overall Apparent Effects Threshold" (OAET). It is the

metal content above which adverse biological effects consistently occur in a sediment. The threshold is determined by a variety of toxicity tests on various types of sediments. The threshold values are roughly comparable to "high" concentrations cited in O'Connor(1990). Long and Morgan (1990) acknowledge that in specific conditions "toxic bioavailability" the amount or form of material that actually induces mortality in organisms may be poorly correlated with total metal content, but they justify use of total metal concentrations in the absence of nationally adopted, official effects-based standards. The ER-M (Effects Range - Medium) toxicity threshold corresponds to an LC50, or 50 percentile mortality in experimental organisms, whereas ER-L (Effects Range - Low) corresponds to the 10 percentile of screened data.

Descriptive statistics for the frequency distributions are given in Table 2. These measures exclude outliers defined by samples differing from the logarithmic mean by more than three times the standard deviation. Inasmuch as arithmetic means and standard deviations could not be validly computed directly from the non-normal linear raw-data, we calculated means and standard deviations of the logarithms of the original values and reconverted these to linear (antilog) units.

The data show that for copper (cover and Fig. 2) most of the samples did not exceed the Overall Apparent Effects Threshold of toxic effects on organisms, reported by Long and Morgan, 1990. The two most concentrated samples from NOAA National Standards

and Trends monitoring program stations fall close to the mean and median values (50% mark on the cumulative curve). The lowest toxic effects threshold, ER-L, OAET threshold values, and the central tendency of concentrations was within the range of the NOAA NS&T monitoring stations.

Mercury was at the other extreme. Most samples exceed the NOAA toxic threshold limits, and all measures of central concentration tendency (mean, median, mode) exceed the value of the most concentrated NS&T station sample. Cadmium and lead fall between the relative toxicity ranges described by copper and mercury.

In general, except for copper, the concentration ranges included here are comparable to some of the most metal-rich U.S. harbor sediments reported (Anonymous, 1988).

The number of organic pesticide and other organic analyses is shown in Fig. 7 by compound. A frequency plot for the most frequently analyzed organic compound (or compound group), the polychlorinated biphenyls (PCB) (Fig. 8), shows a distinct bi-modal distribution and a mean and median that are within the range shown by the NS&T values. Fifty-three percent of the samples exceed the OAET toxic threshold limit.

Limited descriptive statistics for the above constituents are given in Table 2.

Discussion

The central tendencies among the metals displayed here show classical trace-element logarithmic distributions (Figs. 3-7; Table 2), with a slight skewing toward lower concentrations. Such a distribution, without significant polymodal distributions in the principal concentration range, could reflect variable dilution of a fairly consistent mix of anthropogenic contaminants by natural or metal-poor sediment. Values attributable to water or pore water analyses form secondary modes at extreme low values, well below those of any reported natural sediments (Handbook of Geochemistry, 1978). These are included because they were recorded as "sediment data" in the BHDMEF. The data compare in magnitude to values and inter-element relationships characteristic of seriously polluted environments in the United States as well as in Europe (see bibliographies in Lyman et al, 1987; Long and Morgan, 1990, and Salomons, cited in Van Pagee et al, 1988). These similarities to other data sets lend credence to the statement by Mason (1984) that he did not find significant errors in **measurement** in the BHDMEF sediment analyses. Moreover, the carefully controlled data of Bothner (1979), reported by Fitzgerald (1980), show general agreement with the central tendencies of metals reported here. However, further examination of the data file is required for two reasons, first to confirm analytical methodologies and validities, and second to make sure analyses are properly referred to the correct geographic positions. We have confirmed errors in the file in the form of misreported or

miscoded station positions (e.g. latitudes reported as 79' or 87', and longitudes half a continent west of Boston); the effects of these would not show up in the frequency plots of analytical data reported here, but will become an obvious problem in later mapping phases of our study.

The data in Fig. 7 suggest that mercury is the most serious pollutant in the general Harbor area. The high values may be partly attributable to antifouling paint, as well as concentrations from sewage, atmospheric and other sources. Mercury is known to have complex mechanisms for potential loss from contaminated sediments (Bothner et al, 1980). Assessing changes in mercury and other sediment metal levels with time is one of the current objectives of USGS estuarine studies in this area.

The values from contaminant analyses performed as part of the ongoing NOAA NS&T monitoring problem are shown by arrows on the sample distributions in the BHDMF that we have illustrated. The NS&T samples are designed to reflect **representative** locations rather than "hot spots" for the estuaries considered (anonymous, 1988). Although evaluations that incorporate extensive bottom sample information will clearly help to appraise the representativeness of monitoring sites, we draw no firm conclusions about the geographical or biological significance of the metal distributions at this phase of our study. In addition to the factors mentioned earlier, the data in the file represent samples collected before 1984, and time and geographic distribution of the samples remain to be examined. Many were taken before the

1980's, and loss or gain in contaminants, or subsequent redistribution of sediments in high energy events and storms may have occurred.

One should also note the recent EPA-sponsored studies reporting that acid-volatilizable sulfide concentrations (AVS) constrain solubilization of heavy metals in pore waters and affect organism toxicity (Di Toro, 1991; Hansen, 1991), in many cases this effect limits toxicity even where high metal concentrations are present. Seasonality of sampling may be a less complicating factor for total metal concentrations, since contaminated thicknesses have accumulated over many decades and net loss of metals can be expected to be slow. However, changes due to variable seasonal and associated physicochemical regimes for the bottom sediments could have implications for uptake in organisms (e.g. Luoma and Cain, 1979) and for AVS concentrations. In addition, very little is known about changes in and redistribution of sediment pollutants due to storms.

Conclusions

Frequency plots for about 600 samples of sediments in the Boston Harbor Data Management File show central tendencies consistent with well-established data sets from polluted coastal environments around the United States and in Europe. The means for copper (around 200 ppm dry matter) and for PCB's agree with values from the NS&T bottom sediment survey. However, the mean

and median for mercury are greater than the NS&T values and the apparent toxic effects threshold (OAET). The mean and median for cadmium cannot be compared with the NS&T values since no monitoring site values are given in the literature. The mean and median for lead are higher than the NS&T values for this component, but probably not significantly so, although we have not yet made tests for statistical significance in this phase of our study. Conclusions about the significance of the distributions for current Boston Harbor environmental conditions must await further evaluation of the data, including assessment of contaminant distribution in space, time, and especially linkage to sediment and bottom types, and to toxicity relationships, in succeeding phases of the study.

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Tables and Figures

List of Tables

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2. Descriptive statistics for frequency distributions of selected metal and PCB concentrations in the BHDMF, along with NOAA effects-based estimators of toxicity thresholds (from Long and Morgan, 1990). The data show linear conversions of logarithmic mean, standard deviations, upper and lower standard deviation bounds, and t-test confidence limits at the 95 percent confidence interval. The second bracket shows toxic effects ranges from Long and Morgan(1990). ER-L and ER-M refer to effects range low and normal [medium]?, respectively, and OAET refers to the "Over all Apparent Effects Threshold".

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1. Location map for Boston Harbor and Massachusetts Bay sediments currently under study. Sample positions are shown as solid dots. In addition to the BHDM file data, sources include Hathaway (1971) and unpublished laboratory data from the sediment database of the U.S. Geological Survey, Branch of Atlantic Marine Geology, Woods Hole, MA 02540. The data discussed in this initial phase of our study are primarily from locations within Boston Harbor proper.

2. Plot of textural data in a typical coastal sediment sample in a three-constituent (sand-silt-clay) histogram and in a standard textural analysis (ϕ) plot. ϕ is defined as the negative logarithm to the base 2 of grain size diameter in mm. Note that a large part of the silt fraction occurs in a narrow range, unpredicted by the 3-component plot.

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7. Frequency of concentration distributions for mercury in sediments in the BHDM file. Note high-value outliers. Other data as given in captions to Figs. 4 and 5.

8a. Number of sediment records for individual organic pollutants. Abbreviations: ALDE = Aldrin; AROHY = Aromatic hydrocarbons; ABHC = Alpha-BHC; BBHC = Beta BHC; CBNO = Gamma-PHC; DBHC = Delta-BHC; CHLOR = Chlordane; DDD = DDD; DDE = DDE; DDT = DDT; DIEL = Dieldrin; ENDI = Endosulfan I; ENDII = Endosulfan II; ENDR = Endrin; ENDRA = Endrin aldehyde; ENDS = Endosulfan sulfate; HEPTA = Heptachlor; HEPTE = Heptachlor-epoxide; HYDRC = unspecified (including polyaromatic) hydrocarbons; LIND = Lindane; MALA = Malathion; PARA = Parathion; PCB = polychlorinated biphenyls; PCB54 = polychlorinated biphenyls-54; TOXA = Toxaphene.

Fig. 8b. Frequency histogram for total PCB concentrations, in ppm; dashed line and arrows as in Figs. 4 and 5.

Table 1

**Analyzed Characteristics of Samples in the
Boston Harbor Data Management File
(BHD MF)**

I. Water column	Records
Physical Properties	10537
Chemical	15430
Nutrients	6880
Oxygen Demand	7302
Pesticides and other organics	793
Solids (particulates)	3310
II. Biological parameters	
Ecological community analyses	310
Bacteriology	9843
III. Sediments	
Physical properties	159
Chemical properties	176
Oxygen demand	135
Metals	4929
Nutrients	400
Pesticides and other organics	774
IV. Miscellaneous	
(e.g. oil + grease, chlorophyll, etc.)	1323
Total records	----- 62301

Table 2

Statistics* for Boston Harbor Data Management File

	Cd (.01 - 100ppm) ppm	Hg (.01 - 100ppm) ppm	Cu (0.5 - 2000ppm) ppm	Pb (4 - 2000ppm) ppm	PCB's (.001-100ppm) ppm
Mean =	2.46	1.07	85.9	110.	0.38
Median =	2.4	1.3	92.	129.	0.63
s.d. =	2.63	3.44	2.87	2.77	3.52
Mean + 1 s.d.	6.46	3.67	247.	306.	1.33
Mean - 1 s.d.	-0.933	0.310	30.0	39.9	0.106
n =	495	459	506	511	125
95% confidence interval {Mean \pm Student's $t_{.975}$ * (s.d.)}					
Upper limit		16.3	12.0	678.	813. 4.46
Lower limit		0.369	0.0948	10.9	15.0 0.0321

*Statistical measures were calculated using logarithmic data values, then reconverted to linear values.

	Cd		Hg		Cu		Pb		PCB's	
Toxic effects ranges	(ppm)	Percent samples > value	(ppm)	Percent samples > value	(ppm)	Percent samples > value	(ppm)	Percent samples > value	(ppm)	Percent samples > value
ER-L	5	24.	0.15	91.	70	62.	35	82.	0.05	86.
ER-M	9	4.6	1.30	49.	390	4.2	110	56.	0.40	53.
OAET	5	24.	1.00	59.	300	9.3	300	16.	0.37	53.

ER-L= Toxic effects range-low; ER-M= Toxic effects range-medium;

OAET= Overall apparent effects threshold; see text for definitions.

Comparative Toxic Effects Ranges for Various Elements
(from Long and Morgan, 1990)
(ppm)

ER-L	ER-M	OAET	
Sb	2	25	25
As	33	85	50
Cd	5	9	5
Cr	80	145	0
Cu	70	390	300
Pb	35	110	300
Hg	0.15	1.3	1
Ni	30	50	NA
Ag	1	2.2	1.7
Sn	NA	NA	NA
Zn	120	270	260
	(ppb)		
PCB	50	400	370

Fig. 1

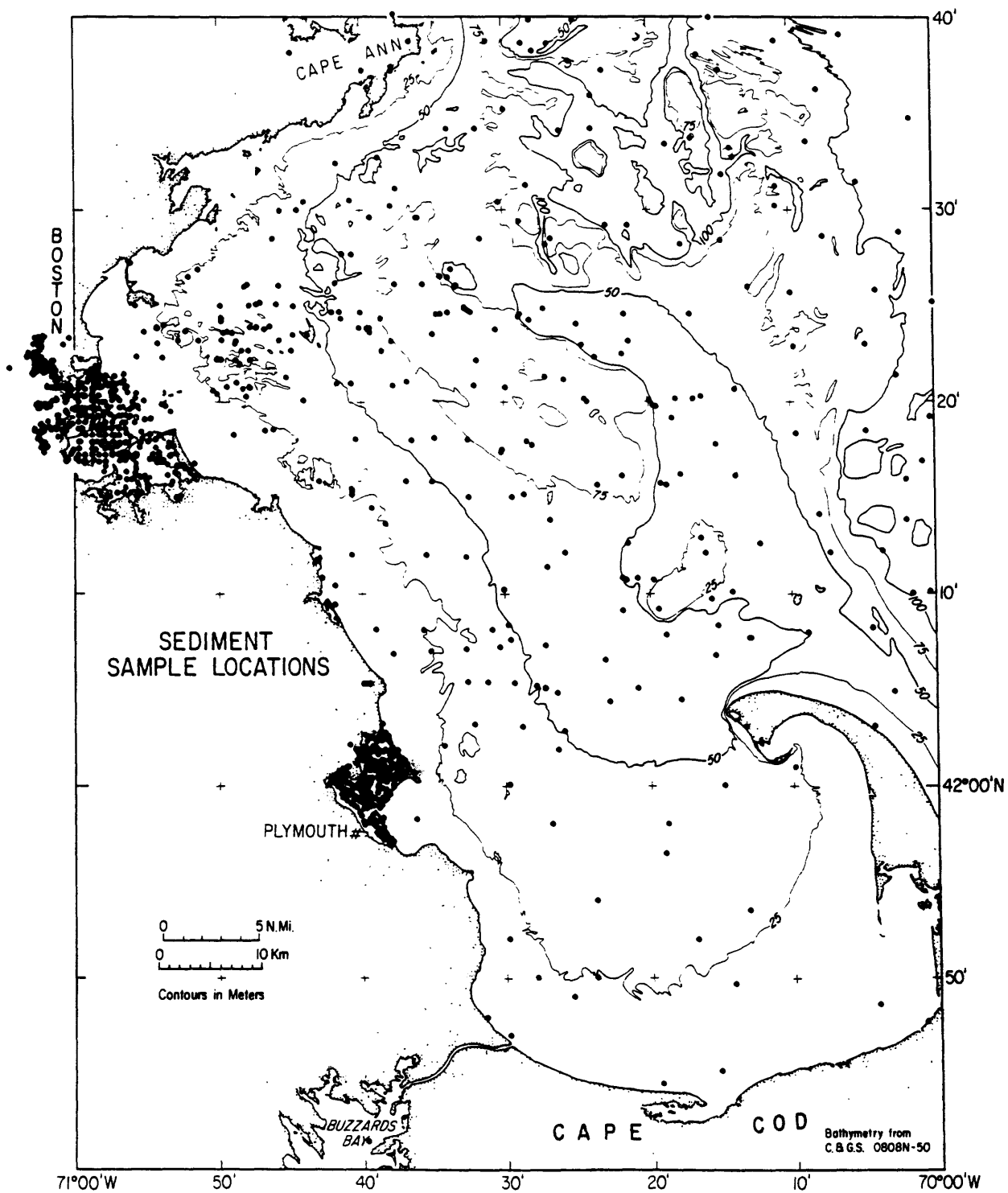


Fig. 2

Station 1721

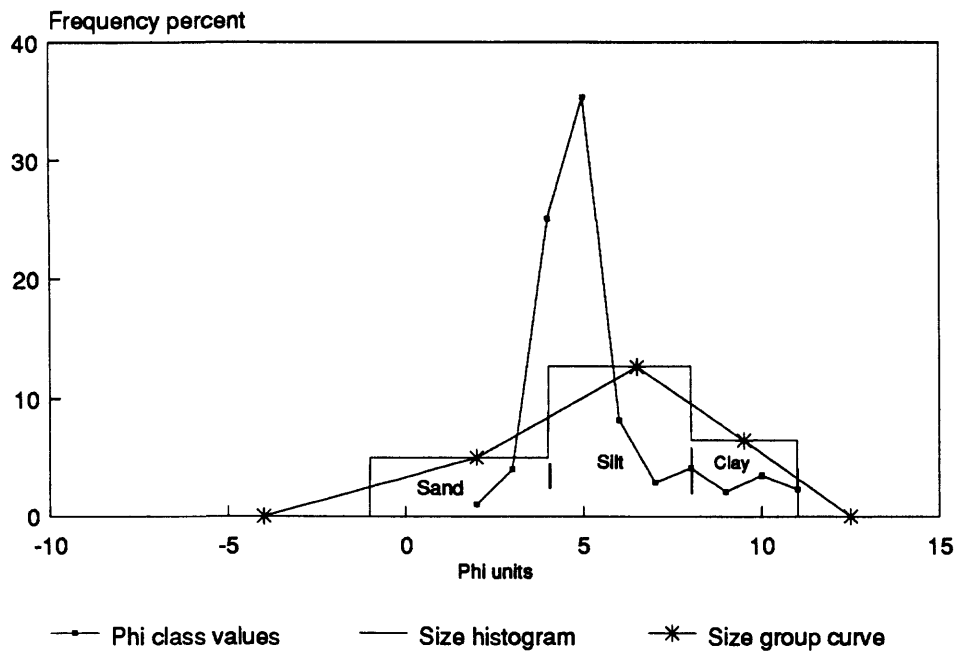


Fig. 3

Metal Analyses

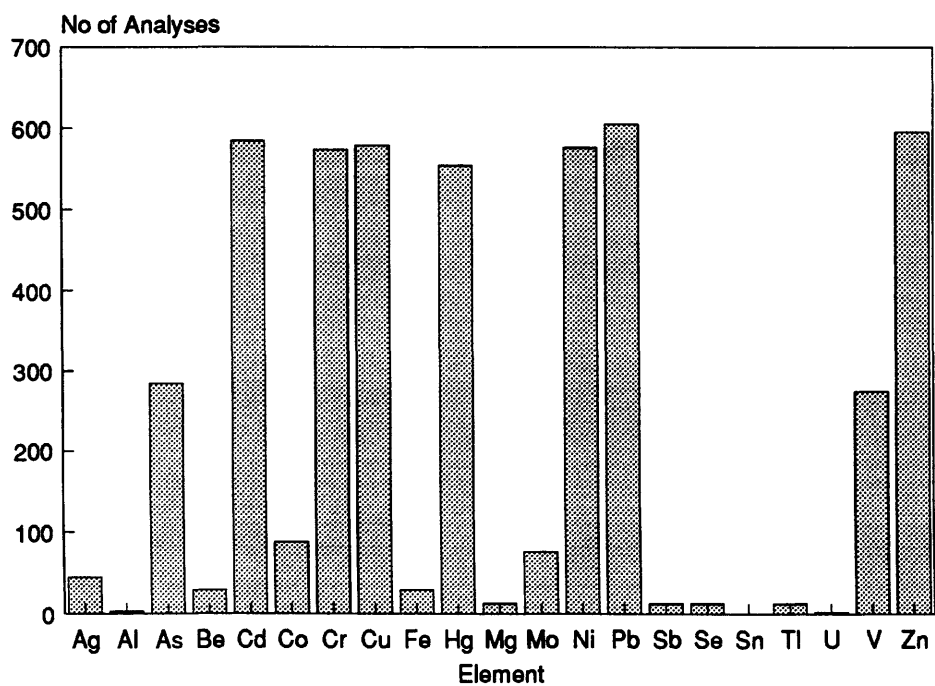


Fig. 4

Cadmium

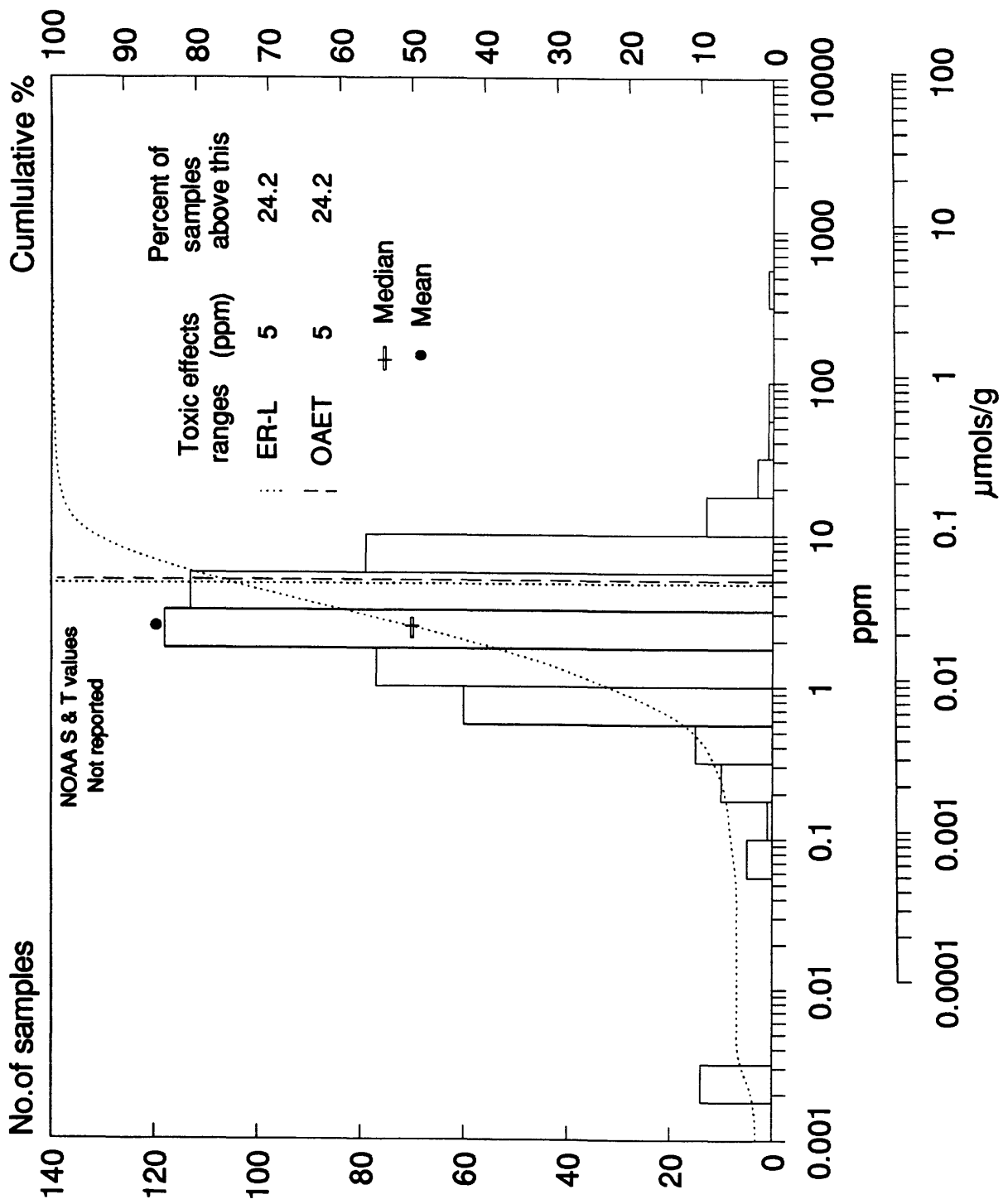


Fig. 5

Copper

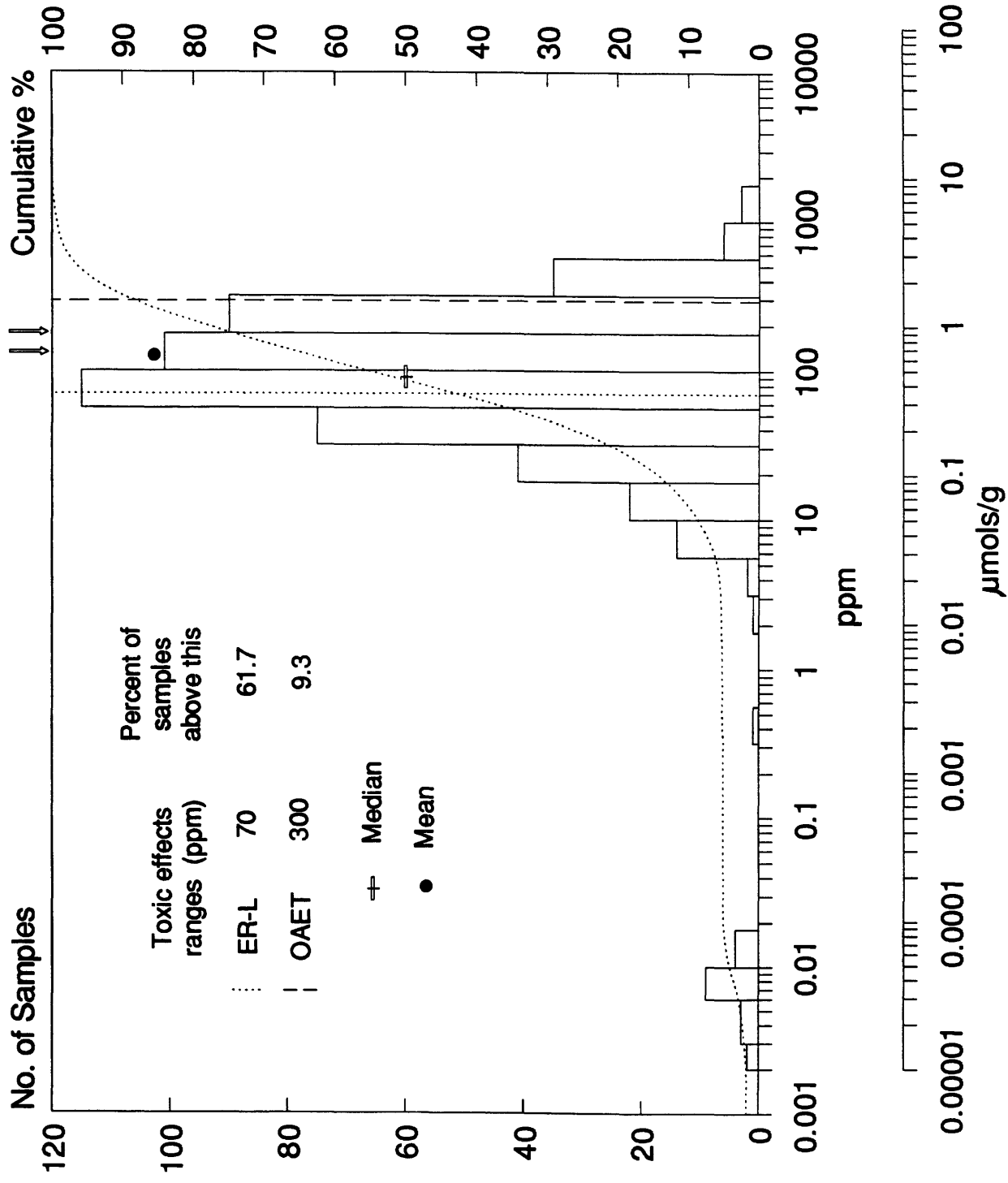


Fig. 6

Lead

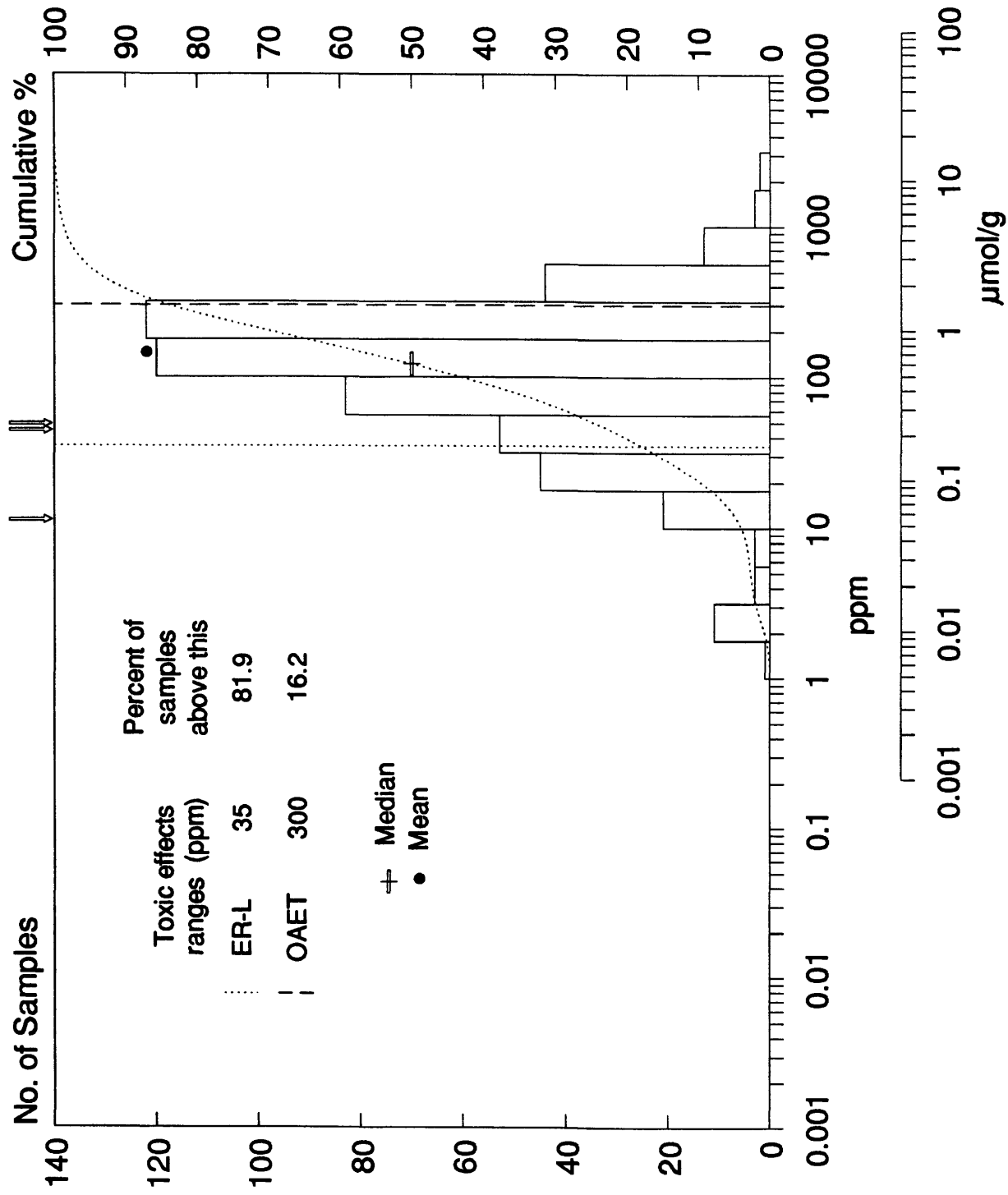


Fig. 7

Mercury

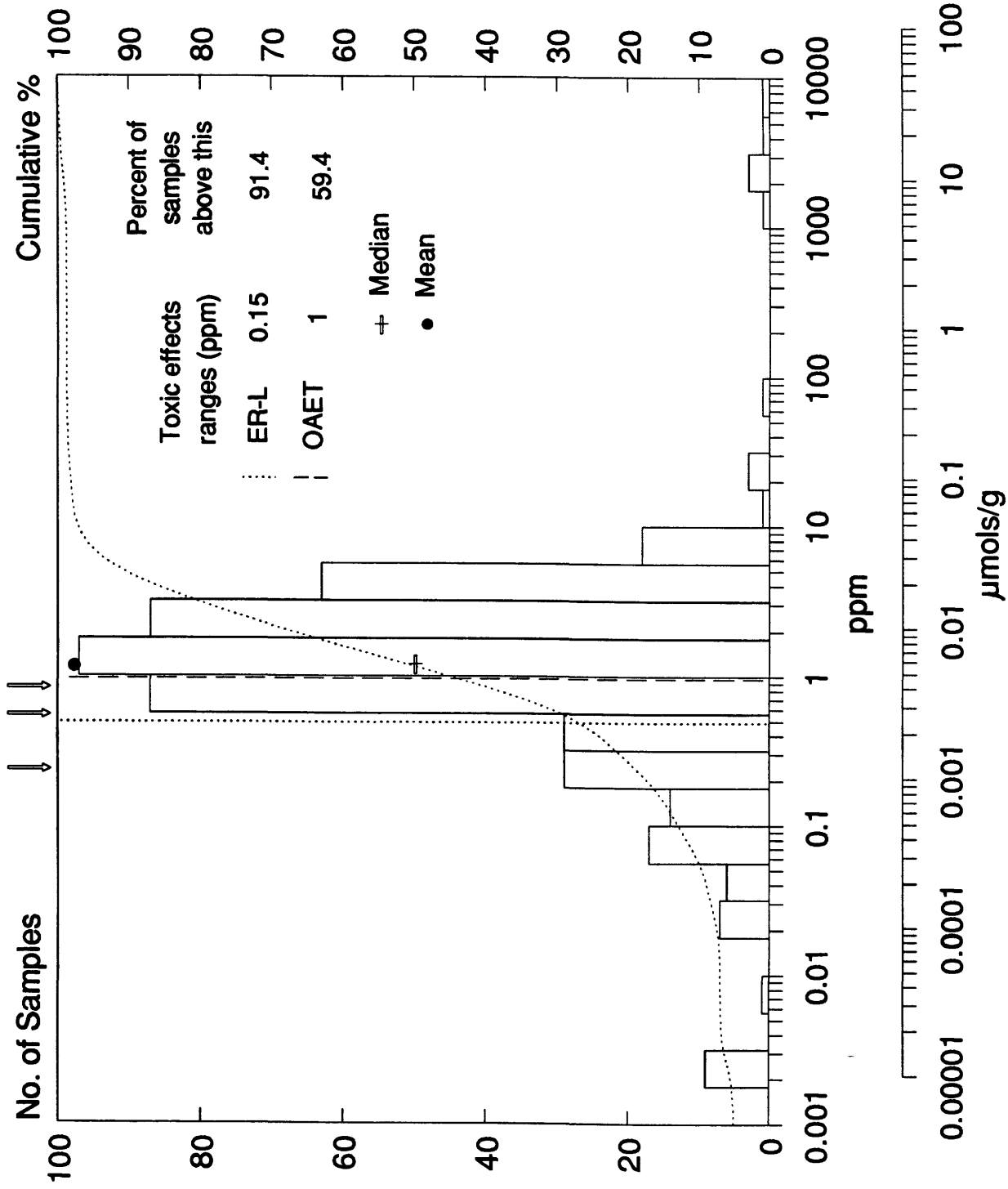


Fig. 8a

Pesticides and Other Organic Compounds

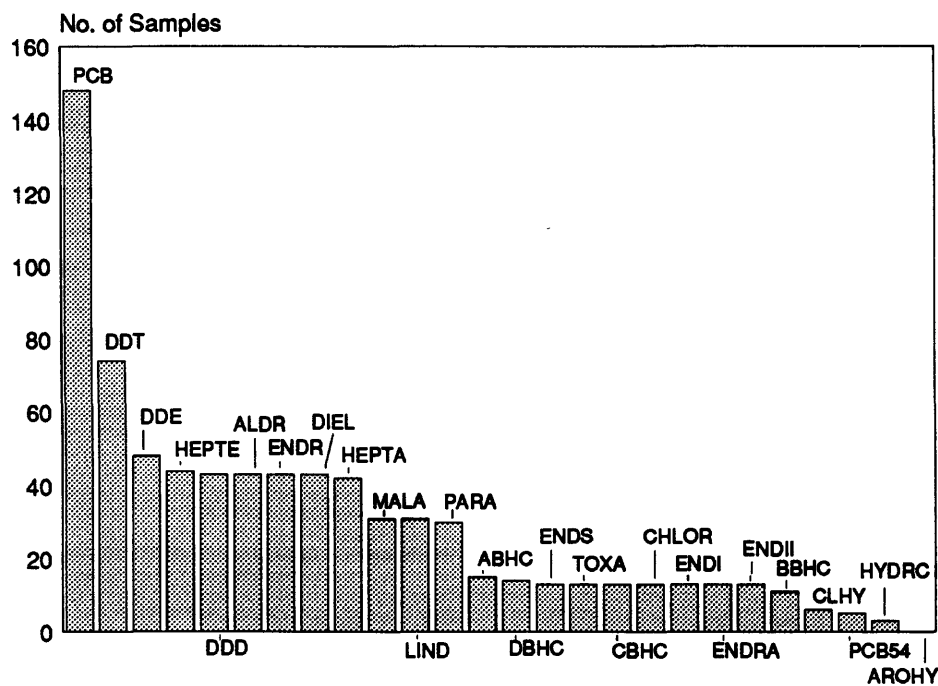


Fig 8b

PCB's

