

HEAVY METALS IN COASTAL SEDIMENTS

J. N. GALLOWAY
 University of California, San Diego
 San Diego, California

I would like to start by giving an historical perspective of pollution:

“In Kohln, a town of monks and bones,
 and pavements fanged with murderous stones,
 “And rags, and hags, and hideous wenches,
 I counted two and 70 stenches,
 “All well defined and separate stinks!
 Ye nymphs that reign o’er sewers and sinks,
 “The River Rhine it is well known,
 Doth wash your city of Cologne,
 “But tell me, nymphs, what power Divine,
 Shall henceforth wash the River Rhine?”

Samuel T. Coleridge (1772-1834)

A couple of years ago when I became interested in environmental research, I was reading the literature and found that very few studies were being done to study the problem from a geochemical perspective. Most of the studies were piecemeal and studied only part of the problem. Therefore, as a step toward solving that, I started investigating the alteration of the natural geochemical cycle of copper, zinc, cadmium and lead.

I will be talking today about Los Angeles County Sanitation District’s waste-water outfall. This outfall has a daily discharge of 370 million gallons (1.4 billion liters) of primary treated sewage. The concentration of particulate matter is about 325 ppm. The total concentrations of these four metals in the effluent and their annual rates of discharge from the outfall are shown below.

	Total Concentrates	Discharge Rate Grams/yr
Zn-----	1.2 ppm.	7×10^8
Cu-----	0.5	3×10^8
Cd-----	0.08	4×10^7
Pb-----	0.17	9×10^7

The concentrations of these metals in this effluent are 5-100 times above normal river concentrations.

Figure 1 is a map of the Los Angeles County outfall system showing the location of the two outfall pipes and the depth of water in fathoms. The sediment cores with which I worked (twenty-two gravity cores, fifteen centimeters long) were graciously taken for me by the Sanitation District of Los Angeles County at the positions shown on the map. The top surface centimeter of each core was analyzed for lead, copper, zinc and cadmium by atomic absorption spectrophotometry.

Figure 2 is a contour map of zinc concentrations in the surface sediment. The concentration measured at 5,000 feet away from the outfall was 1900 ppm and

as far away as 5 miles from the outfall the zinc concentration was between 50 and 100 ppm. In other words at 5 miles distance from the outfall you begin to approach natural concentrations (see below). One obvious fact from this data is that the sewage outfall is severely affecting the sediments. I also have contours like this for cadmium and copper, but to keep the talk short, people can see me later, if they wish to see them.

Figure 3 is a graph showing zinc concentration in surface sediments vs. distance from the outfall.

Figure 4 is a detailed study of one core taken 5,000 feet away from the outfall. Samples were taken every other centimeter in the core (core 22 cm. long) and analyzed for cadmium, copper, zinc and lead. The line at the bottom of the graph is what I call the *natural unpolluted concentration* in coastal sediment. For the present I have defined this quantity on the basis of the lowest concentration of each metal that I have found in the deepest sample of any core. The values so obtained are: zinc 70 ppm; copper 20; cadmium 1.5; lead 20.0. The vertical axis is variable, such that it is normalized to the natural concentration line for the different elements.

There are a number of ways that this data can be explained. One could conjecture that the top 10 cm. were deposited after the main sewer outfall of Los Angeles County was put in use in 1957. That assumption results in a sedimentation rate of 0.6 cm. per year. Or one can say that there is a mixing/stirring mechanism that accounts for this profile and, therefore, the time variable above will be distorted. Or you could say that above a depth of 10 cm. in the core the sediments became reducing and began concentrating the metals at some time in their history.

We are in the process of doing absolute age determination with the cores, so that we can better define the process going on.

The real function of this sediment study is to discover where the metals are going once they enter the ocean. The studies so far strongly suggest that some go into sediments, but I don’t have a concrete idea of how much because I have no independent measure of the rate of sedimentation.

But what happens once it is in the sediments? Are the metals easily mobilized? Is there biological uptake? In an effort to find how tightly bound these elements are in the sediment, I did a fractional dissolution of one sediment sample that was taken 5,000 feet away from the outfall and at 2 cm. from the top of the core. Table 1 shows the results of this work. One of the important things shown by this data is that large amounts of copper and lead are strongly bound,

possibly in an organic complex. For all of these elements, but most for copper and lead, if the sediment around the outfall becomes oxidizing, then the organic matter will be oxidized and these elements will perhaps be mobilized and escape into the sea water. Again, very preliminary and a lot of work has to be done.

The only reason I gave this paper was to talk to some people about the biological uptake. If anyone knows about the uptake of transition metals from the sediment-water interface, then I would enjoy talking to you afterwards.

TABLE 1
Los Angeles County

Frac-tion	Reagent	Percent of metal removed				Percent sediment dissolved
		Zn	Cu	Cd	Pb	
I	Boiling water.....	0.4	0.3	1.1	0.5	8.2
II	1:10 acetic acid.....	49.0	0.08	50.2	17.9	6.7
III	1:5 acetic acid.....	22.7	1.2	24.5	8.9	2.5
IV	1:2 acetic acid.....	10.5	0.5	10.7	7.6	2.3
V	Acetic acid.....	3.3	0.7	2.7	4.0	4.0
VI	1:10 nitric acid.....	11.7	82.3	7.6	40.7	17.5
VII	1:5 nitric acid.....	1.4	10.7	0.9	12.8	4.1
VIII	Nitric acid.....	0.4	2.2	0.7	2.2	1.5
IX	1:1 perchloric acid.....	0.4	1.9	0.7	3.1	4.4
X	Perchloric acid.....	0.3	0.2	0.7	2.2	1.0
XI	Hydrofluoric acid.....	0.4	0.4	0.3	0.2	47.8

Question: .6 cm. per year?

Galloway: That is what could be said.

Question: You were correlating this with the data when the effluent started going into the ocean. Was that 10-12 years ago?

Galloway: 1957, 13 years ago. Or it could be 1945 when the Los Angeles population started to increase rapidly.

Lasker: What kind of organisms do you find around that outfall?

Galloway: I've found only red worms and shrimp in my cores. But there are pictures of fish trying to swim into the outfall pipe presumably because the waste water is so rich in nutrient and organic matter.

Question: What happens if you treat these samples with sea water? I would think there might be some ion exchange going on.

Galloway: True, but these sediments have been in contact with sea water for a long time.

Question: You might get fresh sea water flowing over these at all times.

Galloway: I don't know. You can have 0.3 billion gallons of waste water per day coming out there.

Question: You also have California Current water.

Galloway: Yes, but California Current at depth here really doesn't have that much umph. This is a real tidal surge area here.

Question: Is the composition of the sediment different in here—size, distribution, etc.?

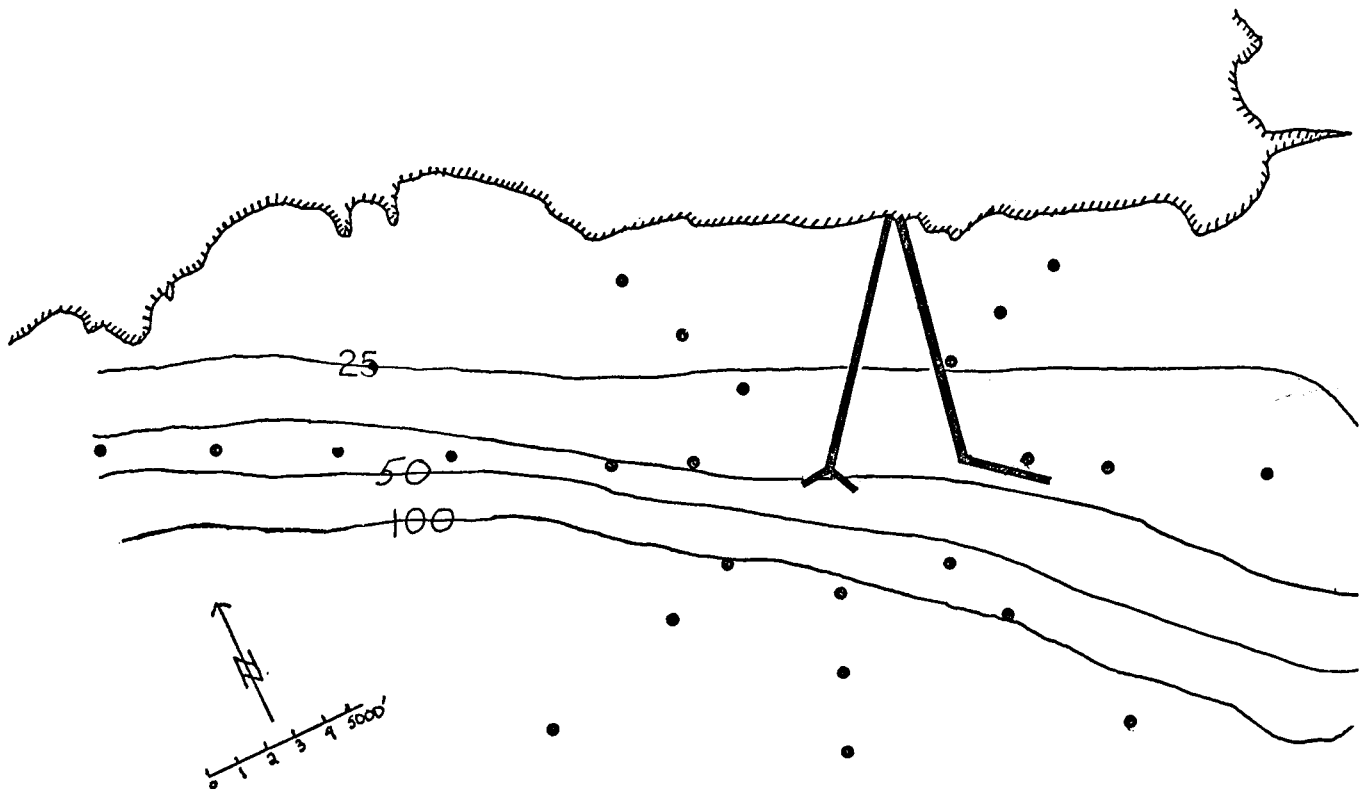
Galloway: Yes.

Question: Have you done a similar study on an area not affected by an outfall? Because your organic content could go up or down for natural reasons.

Galloway: No, but I would say that the best place to study background level is right in that area, at depth in the sediment column.

Question: Did you measure mercury?

Galloway: No. I tried measuring mercury by neutron activation, but you have to do some chemistry after radiation and I haven't had the time to go back. That is in the works.



LOS ANGELES COUNTY OUTFALL

FIGURE 1. Sediment core stations near Los Angeles County outfalls. Depths in fathoms.

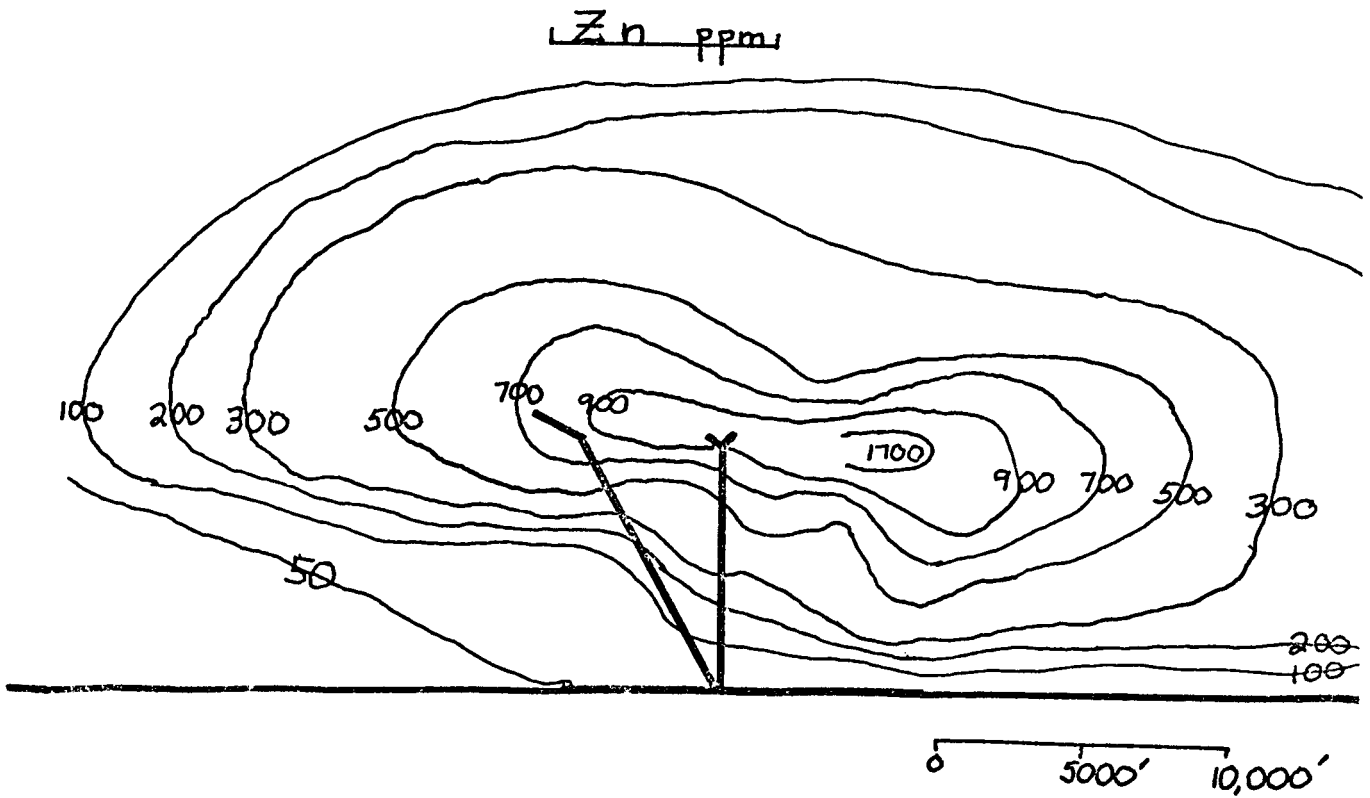


FIGURE 2. Generalized distribution of concentration of zinc in parts per million in surface sediments near Los Angeles County outfalls.

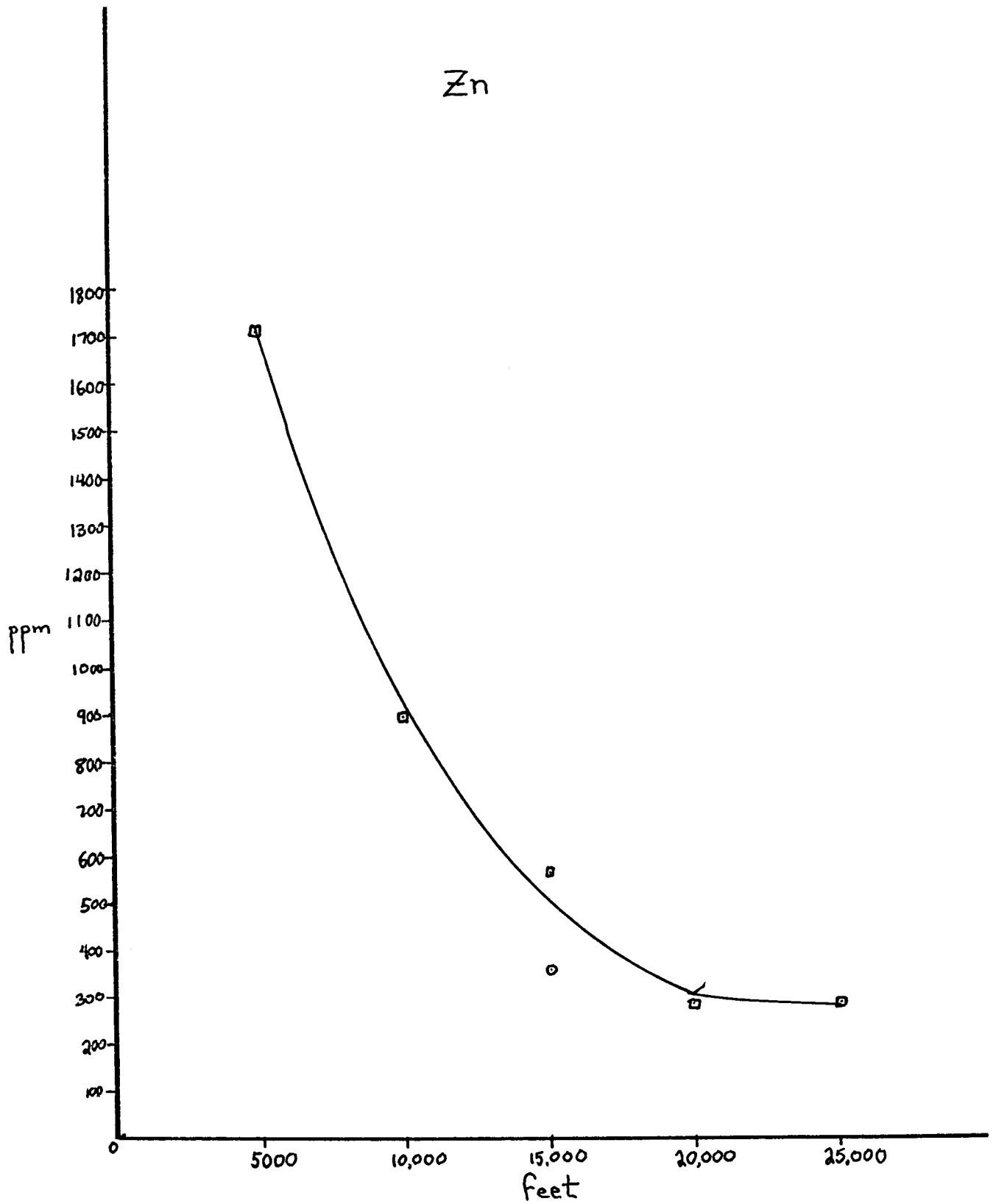


FIGURE 3. Relation of concentration of zinc in surface sediments to distance from outfalls. Concentration in parts per million. Horizontal distance in feet.

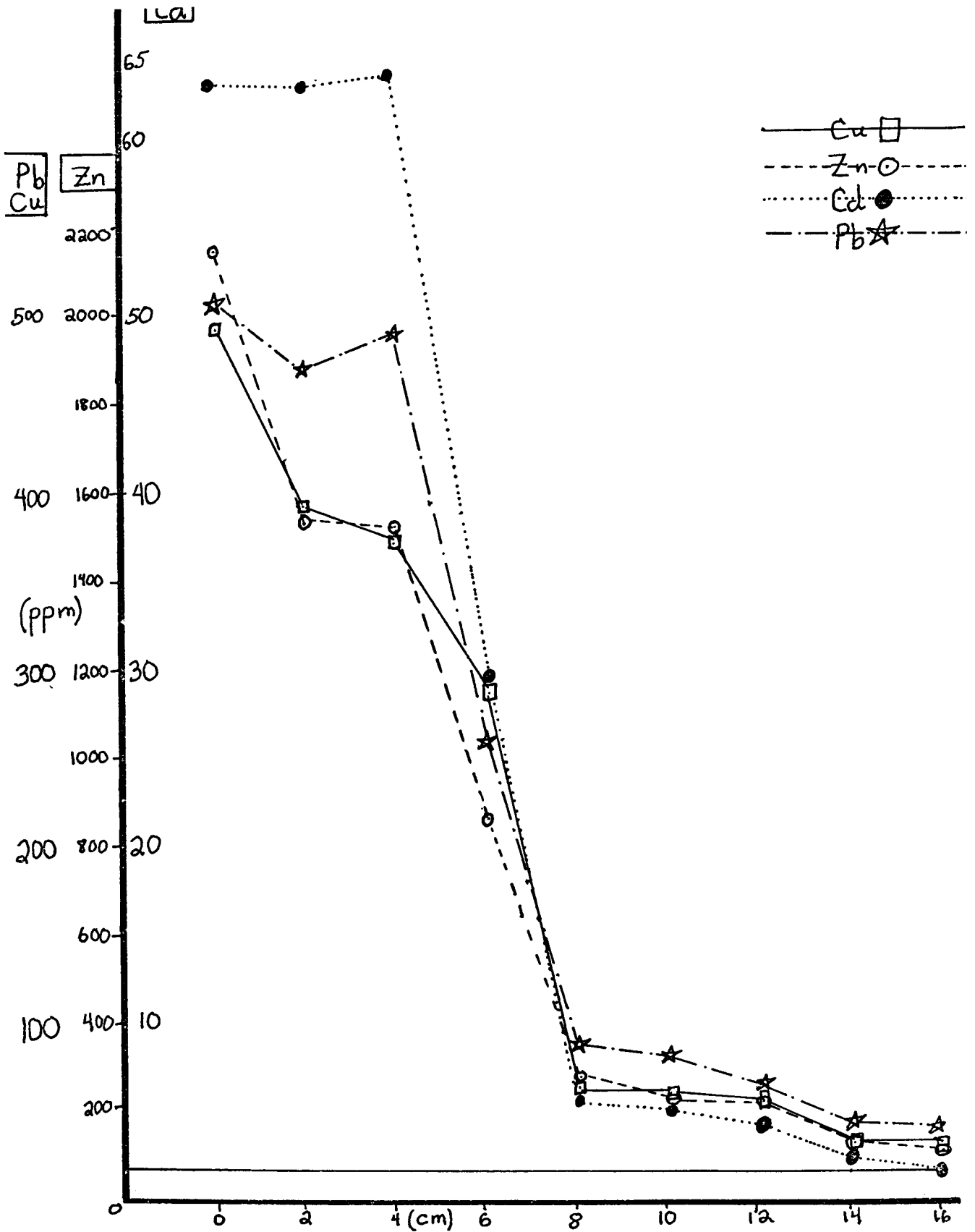


FIGURE 4. Relation of concentration of copper, zinc, cadmium and lead in a sediment core to depth below the sediment-water interface. Concentrations in parts per million are shown in the scales on the left. Depth in centimeters.