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MERCURY IN SEDIMENTS

In recent years, the Coastal Water Research Project has conducted surveys of the distribution of certain trace substances in sediments around the major municipal wastewater outfalls off southern California. Because of high levels of heavy metals found in sediments near Los Angeles County Sanitation Districts outfall system off Whites Point in 1970, detailed surveys of the Palos Verdes shelf were conducted in 1972 and 1973. This article presents the results of the 1975 survey for total mercury in surface sediments in this same area.

From previous data, we estimated that there are approximately 4 metric tons of anthropogenic mercury in the upper 30 cm of the Palos Verdes sediments. Because of the threat this mercury could pose to the local marine life, our studies have been aimed at determining its ultimate fate. Organic mercury compounds, which exhibit higher chronic toxicities and a strong affinity for animal tissues, are generally considered to be the most deleterious of the various forms of mercury. Other researchers have shown that organic mercury can be produced from inorganic forms by microbial methylation in the sediments: In Minamata, Japan, organic mercury taken up by marine animals via the sediments and subsequently ingested by humans was responsible for the poisoning of local inhabitants. Therefore, in 1975, we measured the total organic mercury content of the sediments for the first time. Other parameters related to sediment geochemistry were determined as well.

With the aid of the Los Angeles County Sanitation Districts ocean monitoring group, we obtained replicate Shipek grab samples over the entire standard benthic sampling grid (Figure 1) during August 1975.. The sediments were homogenized, placed in acid-cleaned polystyrene vials,.and frozen immediately to avoid loss of volatile organomercurials. The samples were subsequently analyzed for total mercury, organic mercury, and total volatile solids. (Details on the analytical procedures are given in Eganhouse 1975).

As a part of their routine monitoring activities, the Sanitation Districts personnel measured the oxidation-reduction potential (Eh), pH, and total sulfide ion activity ($\Sigma S^{=}$) of interstitial water samples from the same grabs. Hydrogen sulfide odor was recorded.

The conditions of the sediments off Palos Verdes appear to have changed between 1972 and 1975. The hydrogen sulfide field, which covered about 16 sq km in 1972, has constricted to patchy areas in the immediate vicinity of the outfalls, and the previously reducing surface sediments appear to have become aerobic. Coincidentally, the levels of total mercury in surface sediments have decreased slightly during this period. Comparisons of the sediment mercury data for 1972 Phleger cores, 1973 Shipek grabs, and 1975 Shipek grabs are given in Table 1. The 1973 grab samples were analyzed again in 1975 for comparison, and the results are listed on the table as "1973 reanalysis."

We used the Wilcoxon signed-rank test to determine if there were differences between data sets and found no statistically significant difference between the 1972 and 1973 data.

However, the 1975 results were lower on the average than 1972 and 1973 values by 25 and 9 percent,* respectively. The mercury concentrations of the Los Angeles County effluent particulates have not changed dramatically since 1971 (Table 2). Assuming that the differences are not due to systematic sampling error, this decrease may mean that (1) more mercury was mobilized from the particulates during (and/orsubsequent to) the sedimentation process, (2) the surface sediments were preferentially diluted by "natural" particulates during this period, or (3) that both of these events occurred. The reduced mass emission of total suspended solids—and, hence, total mercury—since 1971 may account for some of the observed lowering of surface sediment mercury levels.

Data on the presence of organic mercury provides indirect evidence of a potential for a long-term, low-level release of mercury by the sediments. The 1975 data for total mercury, organic mercury, and percent organic mercury are plotted in Figure 2. It is clear that small but significant quantities of organic mercury, up to 2.3 percent of the total mercury, were present in the surface sediments. Along the 60-m contour—the region of most highly enriched sediments—the levels of total and organic mercury appear to be similarly distributed with proximity to the outfalls. However, there was a depression in the organic mercury levels at the stations close to the outfall termini (Stations 6E and 7C). This depression may have resulted from inhibition of the methylating factors in the sediments, presumably governed by the prevailing environmental conditions. A high conversion rate of organic mercury to inorganic forms, that is, demethylation, is another possible explanation for the depressed values. The relatively low and constant concentrations of organic mercury found in surface sediments at 30, 150, and 300 m indicate that the organic mercury found along these contours is released more quickly to overlying waters and/or that it is being produced at slower rates than at the 60-m stations. Further study is required to understand the transfer mechanisms for organomercurials in these sediments.

A convenient method for estimating the degree of trace metal release by sediments has recently been suggested by Robert Sweeney and Emil Kalil of UCLA. The method consists of comparing the measured total volatile solids as a function of the total mercury content of the sediments with a line representing ideal dilution of sewage particulates by natural particulates. Figure 3 is an example of this type of plot using the 1975 data. In general, the data points fall well below the ideal mixing curve and even below the curve that represents a 25 percent reduction of organic matter with no loss of mercury. The implication is that mercury is retained in the sediments while degradable organics experience appreciable bacterial decomposition. In a relative sense, this is correct. But because the data reflect the state of affairs at some time after sedimentation, the importance of bioturbation and resuspension is obscured in the graphic approach. Moreover, it is impossible to know with certainty that all the mercury is retained by the sediments or that the sediments are not acting as a sink for reactive mercury in overlying waters as the data reflect a net result at one point in time. The plot does show, however, that the sediments are significantly enriched with mercury relative to the organic matter. The fact that enhanced uptake of mercury by benthic animals off Palos Verdes has not been observed indicates that the mercury there is probably in some form(s) essentially

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*In this analysis. Station 3A was excluded due to extreme bias.

unavailable to the biota or that the uptake is counterbalanced by equivalent losses. Thus, the present data suggest that most, if not all, of the mercury is bound in the refractory phase of the sediments. Changes in sediment conditions with time, however, may affect the activity of mercury off Palos Verdes.

In summary, our results show that levels of total mercury in the surface sediments on the Palos Verdes shelf droppedslightly between 1972 and 1975, although the exact cause of this decrease is still uncertain. Organic mercury, constituting up to 2.3 percent of the total mercury in Palos Verdes sediments, appears to have been concentrated in the regions where total mercury values were highest, except for two stations near the outfalls, where organic values dropped. The highest level observed for total organic mercury was 0.021 p.g/dry g. Data on the relationship between total volatile solids and total mercury showed that mercury in the surface sediments is probably trapped in the refractory component and is largely unavailable to the benthic animals.

The Project's studies of mercury are reviewed in a technical memorandum released this year (Eganhouse et al. 1976). Studies are now underway to determine how the metal is partitioned among the various sediment phases.

REFERENCES

Eganhouse, R.P., Jr. 1975. The measurement of total and organic mercury in marine sediments, organisms, and water. TM 221, Coastal Water Research Project, El Segundo, Calif.

Eganhouse, R.P., Jr., J.N. Johnson, D.R. Young, and D.J. McDermott. 1976. Mercury in southern California waters: Inputs, distribution, and fate. TM 227, Coastal Water Research Project, El Segundo, Calif.

Table 1. Concentration of total mercury (µg/dry g) in sediments collected from the Palos Verdes Shelf, 1972, 1973, and 1975.

Station*	1972 Phleger Cores	1973 Shipek Grabs	1973 Reanalysis	1975 Shipek Grabs
1A	–	0.69	–	0.50
1B	0.64	0.64	0.71	0.59
1C	2.08	1.87	1.85	2.20
1D	0.22	0.21	0.26	0.52
2A	–	0.99	–	0.99
2B	–	1.39	–	0.87
2C	–	3.02	–	2.09
2D	–	0.73	–	0.13
3A	–	0.11	–	1.12
3B	–	1.10	0.54	1.51
3C	3.42	2.70	2.83	3.01
3D	0.71	0.63	0.50	0.25
4A	–	1.26	–	0.98
4B	–	2.53	–	3.22
4C	–	4.35	–	3.30
4D	–	1.48	–	0.30
5A	–	0.55	–	0.55
5B	3.24	3.12	4.05	2.74
5C	–	3.66	3.80	3.75
5D	0.95	0.74	0.35	0.50
6A	–	0.84	–	1.64
6B	2.92	3.03	2.30	2.82
6C	–	8.45	–	4.42
6D	2.35	0.99	1.17	0.58
7A	–	2.33	–	0.79
7B	–	2.79	–	5.37
7C	–	6.40	–	3.92
7D	–	0.74	–	0.31
8A	–	0.66	–	1.12
8B	–	3.60	–	4.45
8C	–	2.40	–	3.68
8D	–	1.78	–	1.72
9A	–	0.66	–	1.01
9B	4.78	4.67	3.61	2.58
9C	2.54	2.77	2.90	1.58
9D	0.88	1.76	0.87	0.43
10A	–	0.61	–	0.20
10B	0.71	0.43	0.54	0.42
10C	0.84	2.08	1.92	0.39
10D	0.96	0.91	0.98	0.37

*Station locations shown in Figure 1.

Table 2. Flow, total suspended solids, and mercury data on Joint Water Pollution Control Plant effluent, 1971 to 1975.*

	1971	1972	1973	1974	1975
Flow (mgd)	371	351	359	346	341
Total suspended solids (mg/l)	330	290	258	276	278
Total mercury (mg/l)	0.0014	0.0011	0.0012	0.0011	0.0011
Particulate mercury (μg/dry g)**	4.24	3.79	4.65	3.98	3.95
Mass emission rate for total suspended solids (10^6 kg/yr)	169.0	140.5	127.9	131.8	130.9
Mass emission rate for mercury (10^3 kg/yr)	0.72	0.53	0.59	0.52	0.52

*Data from Los Angeles County Sanitation Districts annual summaries for Joint Water Pollution Control Plant effluent.

**Calculated based upon mercury being 100 percent in the solid phase.

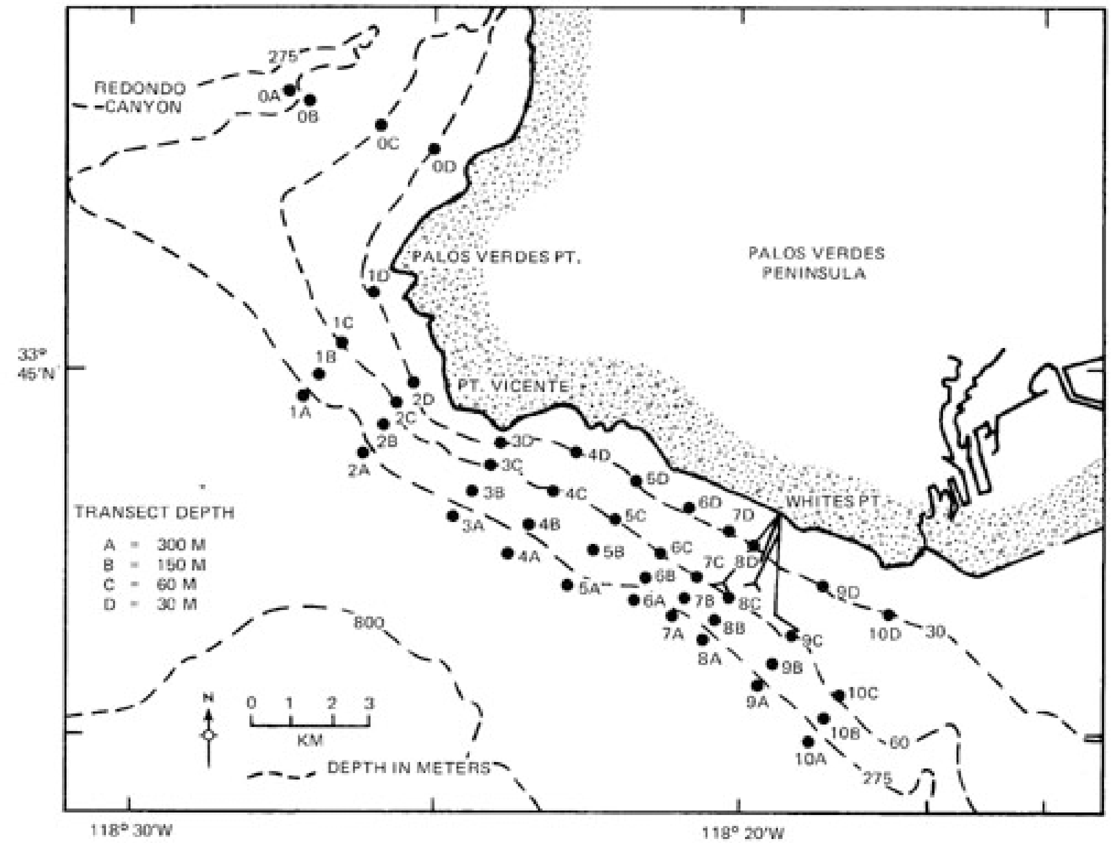

Figure 1. Stations for survey o mercury in sediments.

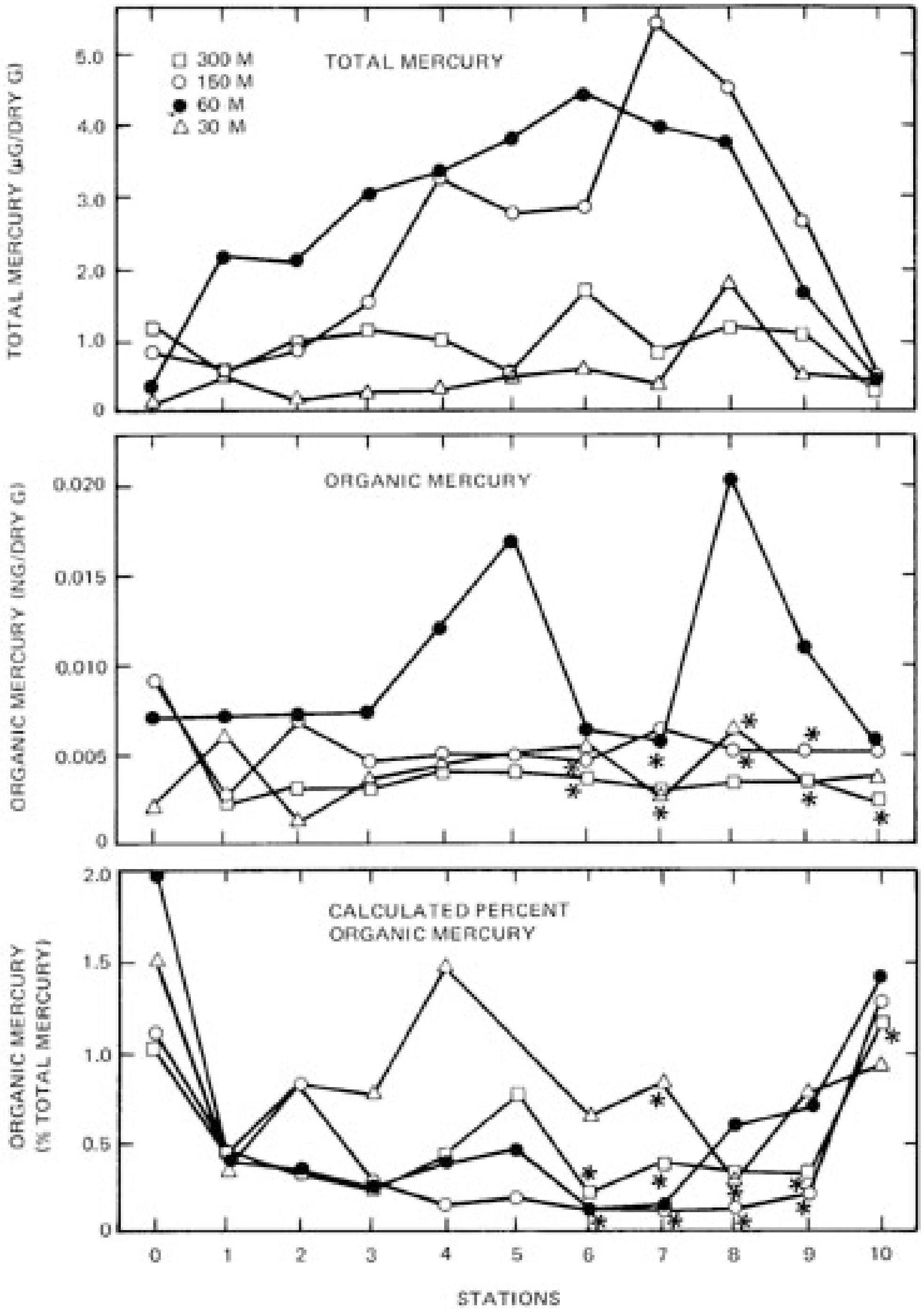

Figure 2. Mercury in surface sediments off Palos Verdes. Asterisks near organic mercury values indicate samples in which no mercury was detected (levels shown are limits of detection given sample size).

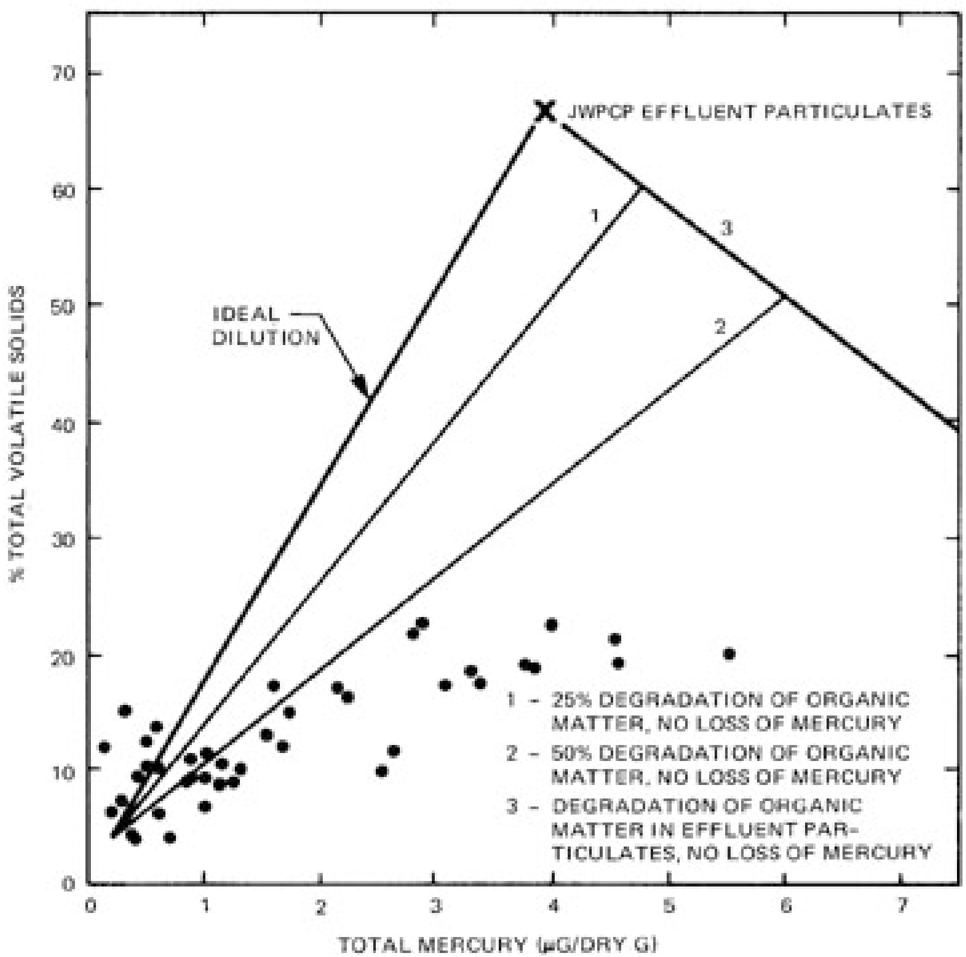

Figure 3. Total volatile solids vs. total mercury in surface sediments from the Palos Verdes Shelf, August 1975.