TRACE METALS ON SUSPENDED PARTICULATES

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Our previous work had established the importance of sewered municipal wastewaters as sources of trace metals into southern California coastal waters. Many of these metals were also found to be strongly associated with the particulates in the effluent this association was reflected in the enhanced metals levels in the sediments around major outfall systems. However, an examination of the distributions and concentrations of these metals in the outfall areas indicated that we did not have sufficient information to predict these concentrations, estimate how they might change as the method of wastewater treatment was modified, or indicate how they might alter the marine environment.

We have undertaken both experimental and theoretical studies of the characteristics and properties of trace metals associated with suspended solids (the theoretical analysis is described in the previous article). The purpose of the experimental study was to explore some of the results of earlier work in greater detail; to obtain some idea of the changes that may result from additional treatment; to learn if the trace metals were preferentially associated with suspended solid particles of a certain size; to provide estimates of the rates of mobilization (release) or absorption of these metals on the particulates when the effluent is diluted with seawater; and to determine the concentrations of trace metals on suspended solids in selected rivers during periods of dry weather flow.

Nine metals (cadmium, chromium, copper, lead, mercury, nickel, zinc, manganese, and iron) were selected for study. The Hyperion Treatment Plant was selected as the source for all the samples (except river runoff) since several methods of treatment are employed there and the trace metal concentrations are typical of sewered municipal wastewater discharges from the major urban areas discharging into the coastal waters of southern California. Atomic absorption and differential pulse anodic stripping were used to measure the metals Concentrations' and the removal and sizing of suspended solids was accomplished with membrane filters.

We studied mobilization by diluting the sample with seawater and removing subsamples from a continuously stirred reactor at numerous intervals for trace metal analysis. Our analysis of primary effluent confirmed earlier results on the distribution of trace metals between the effluent particulates and the soluble phase. One major difference was noted: Earlier work indicated that more than 90 percent of the lead in primary effluent was associated with the particulates; but in this study, only about 20 percent of the lead was associated with the particulates. We do not know at the present time if this is the result of any changes in the method of treatment or in the type of lead being discharged into the sewers, or if it simply indicates that there is a wide variation in the partition of lead between these two forms.

About one third of the primary effluent from the Hyperion Plant is further treated by the activated sludge process (a form of "secondary" treatment). It has long been recognized that this additional treatment is effective in reducing the suspended solids concentration in the effluent (commonly by 90 percent or more), and we observed a reduction of 93 percent in this study; however, we did not find a corresponding reduction in the trace metal concentrations. Some metals (iron and chromium) were removed quite effectively, while others (nickel and manganese) showed only small reductions (Figure 1). An interesting discovery was that the concentrations of the soluble forms of the trace metals and the trace metal concentrations on the particulates are generally not reduced by comparable amounts, and in some cases, may actually increase, even though there was always a reduction in the total concentration expressed in terms of total trace metals per unit volume of effluent (Figure 2). We were also surprised to discover that, although the concentrations of many trace metals on primary particulates are much greater than those on natural sediments, the concentrations of cadmium, lead, and nickel in the suspended solids in dry weather river runoff from an urbanized area could be up to four times higher than those on Hyperion primary effluent particulates.

There are several mechanisms that might explain the association of trace metals with the effluent particulates, and these tend to fall into two categories. One attributes the association to the absorption of the trace metals on the surface of the particulates, and the second has the trace metal more or less uniformly distributed throughout the particulate. We roughly sized the particulates, using membrane filters of various sizes (Figure 3), and found no indication of the preferential association of trace metals with the finer particulates (which we would expect if the surface absorption mechanisms were involved). However, since the use of filters to size the particulates has some experimental perils, further study will be required before these results can be considered as conclusive. It might also be noted here that the activated sludge treatment apparently results in the production of larger particulates, since about 30 percent of the secondary effluent particulates could be retained on a 44 micron filter, while only about 10 percent of the primary effluent particulates were retained by this filter.

Our examination of the concentrations of various trace metals in sediments around the outfall suggested that mobilization of the metals from the particulates might be taking place. Some limited earlier data indicated that characteristic times for this mobilization to take place might be on the order of a few hundred to a few thousand hours. In that case, the release of metals from the particulates would principally occur after the particulates had been swept out of the outfall area, or after they had been deposited in the sediments. In contrast, the recent measurements indicate that a substantial fraction of some metals may be released into the water within the first hour following dilution with seawater (see Table 1), and hence might be available to the midwater biota as well as the benthic biota. At the present time, we cannot determine if the differences between these two mobilization studies are due to differences in the two effluents (Hyperion vs. Joint Water Pollution Control Plant, Los Angeles County) or in the experimental methods (the studies were not conducted under identical conditions), and additional work may be initiated. It should also be noted that additional mobilization might occur if the dilution were increased to levels comparable with those occurring in the ocean.

In summary, our recent work confirms that many of the trace metals are associated with suspended solids, but the concentration of trace metals on particles in Hyperion primary effluent does not appear to depend significantly on particle size. When we mixed particles from primary effluent, digested sludge, or river runoff with seawater, we found that up to 40 percent of the metals can be released within the first hour (different amounts may result from increased dilutions). Finally, although the concentrations of trace metals on primary effluent particulates are generally much greater than on natural sediments, even higher concentrations of some metals can be found on suspended solids in dry weather flows from urbanized areas, or on the particulates in effluent from an activated sludge treatment plant.

FIGURES

Figure 1.
Percent removal of effluent constituents resulting from the secondary treatment of primary effluent (Hyperion)

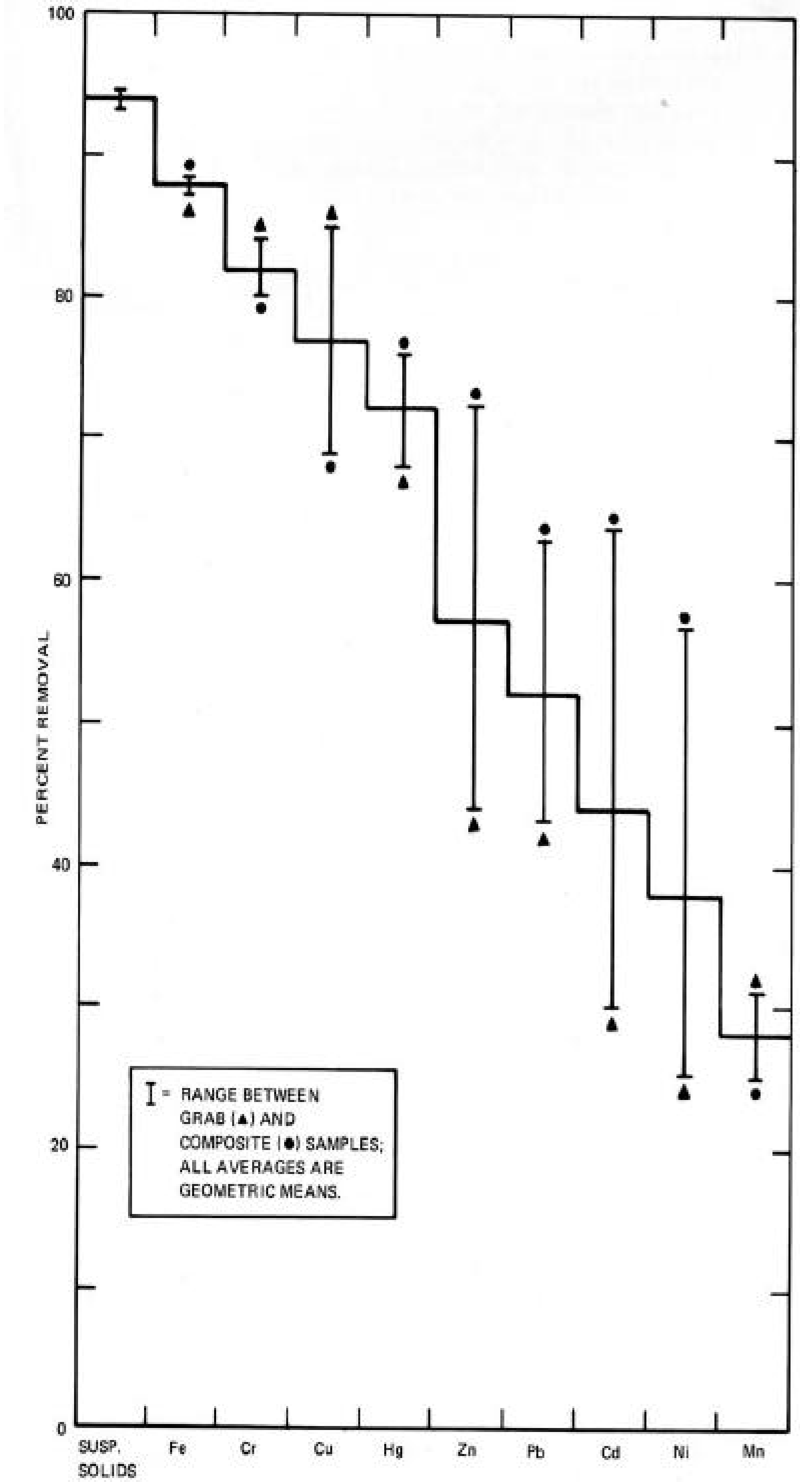


Figure 2.
Trace metal concentrations after secondary treatment relative to the concentrations in the primary effluent (Hyperion)

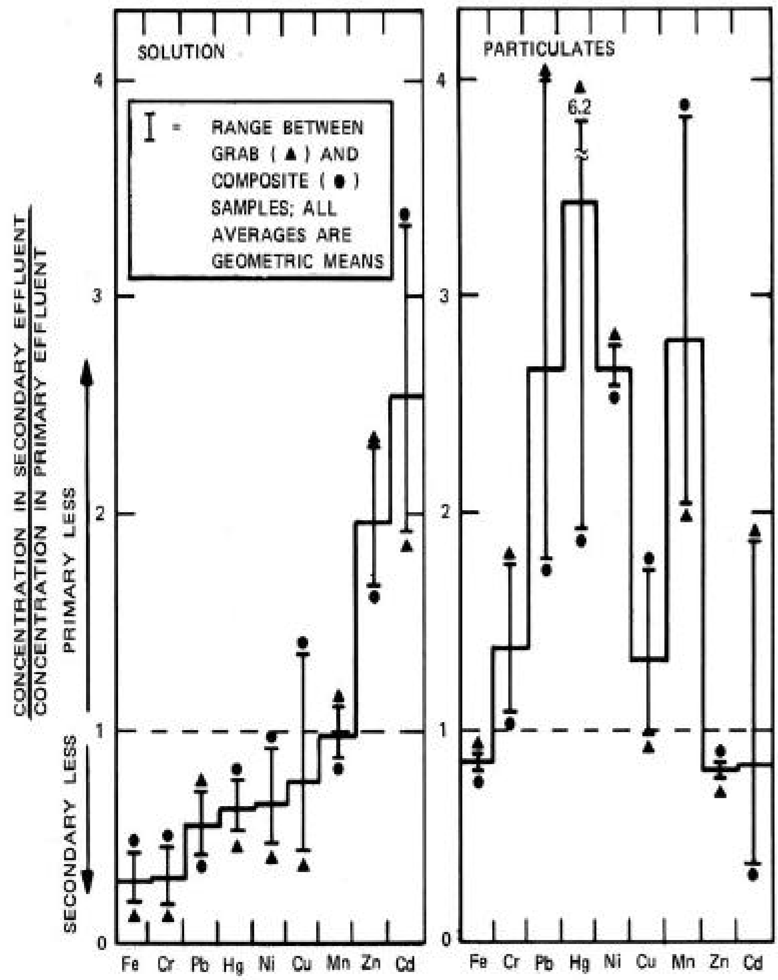
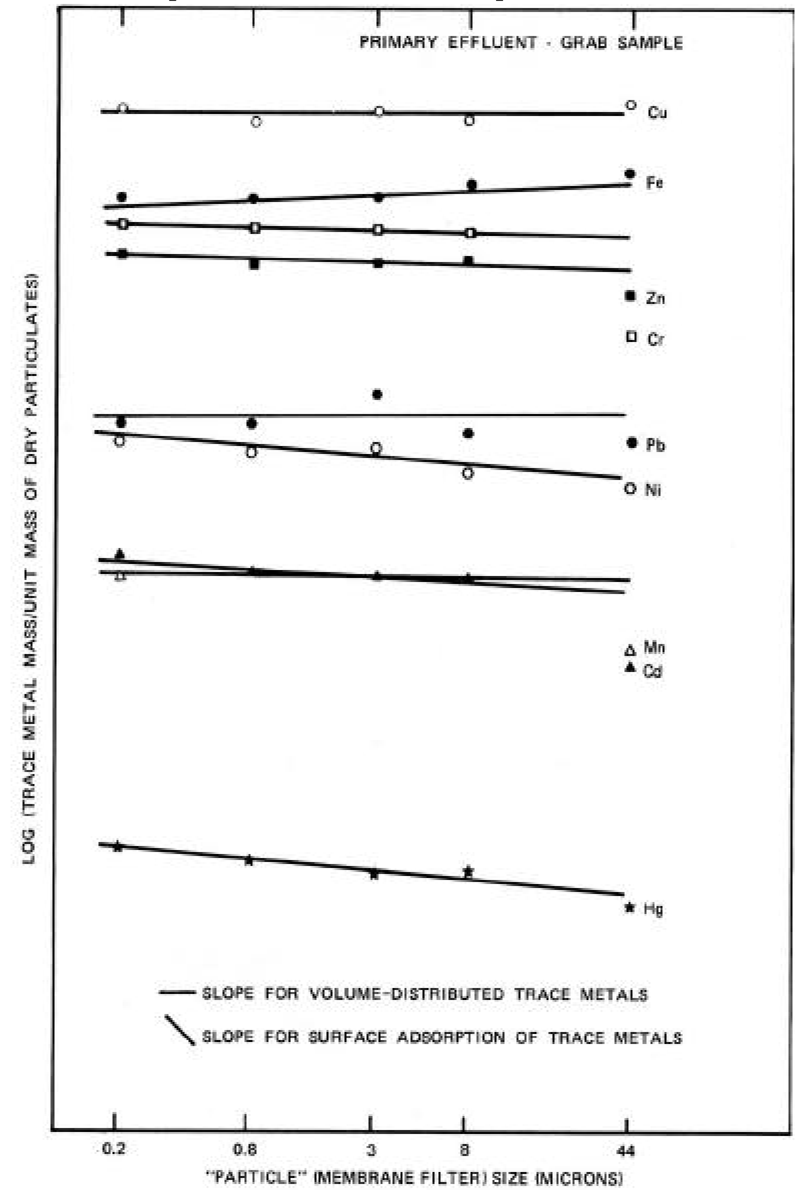


Figure 3.
Trace metal concentration of particulates versus inferred particle size



TABLES

Table 1.
Percent of trace metals released from primary effluent particulates following a 10:1 dilution with seawater

Metal	Percent Released After 1 Hour	Percent Released After 20 Days
Nickel	25	70
Cadmium	40	60
Copper	9	44
Zinc	16	26
Lead	7	19
Chromium	15	17
Iron	38	8
Manganese	78	6