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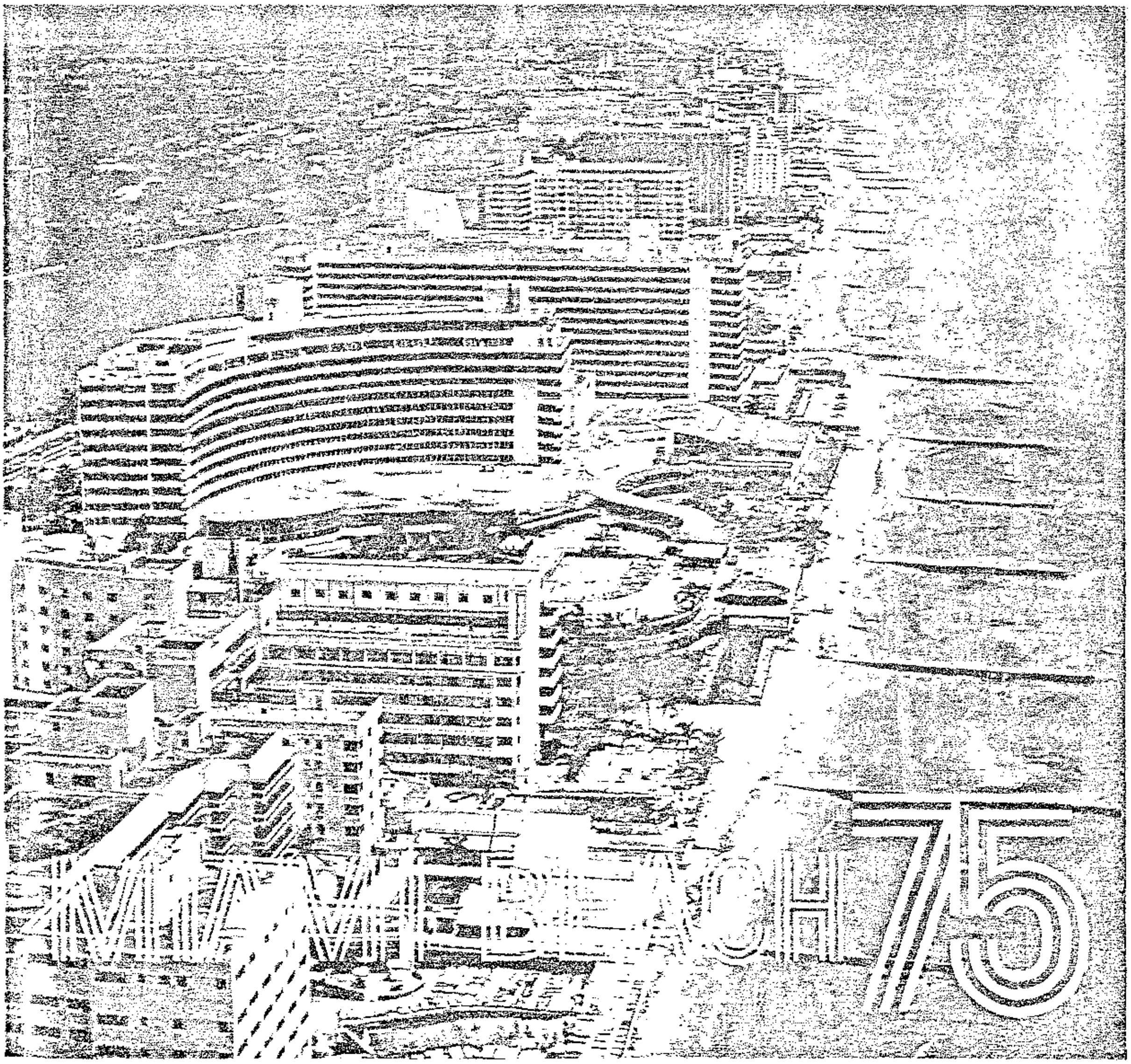

Transport of trace metals by suspended particulates on mixing with seawater

Naresh Rohatgi and Kenneth Y. Chen

A large fraction of trace metals in wastewater effluents and surface runoff is known to be associated with suspended solids (ss) and with nickel and manganese to a lesser degree.[1] On entering the ocean, a portion of the trace metals in ss may be incorporated into sediments through various physicochemical interactions. The remaining portions may go through various chemical changes in the presence of high concentrations of sodium chloride. The localized enrichments of trace metals in sediments around discharge areas may represent only a small fraction of the metal input from freshwater sources.

Galloway [2] studied trace metal accumulations around the outfalls of major discharges in Southern California and found that, on the average, less than 15 percent of the transported metals could be accounted for in the adjacent sediments. The remaining fraction may be widely dispersed because of high dilution and mix-

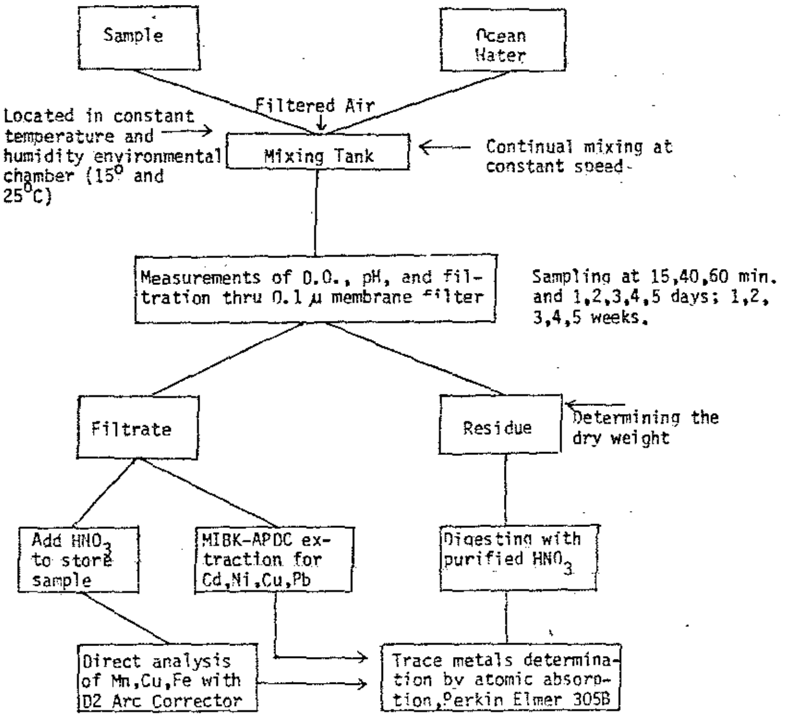

FIGURE 1.—Flow diagram of experimental procedure.

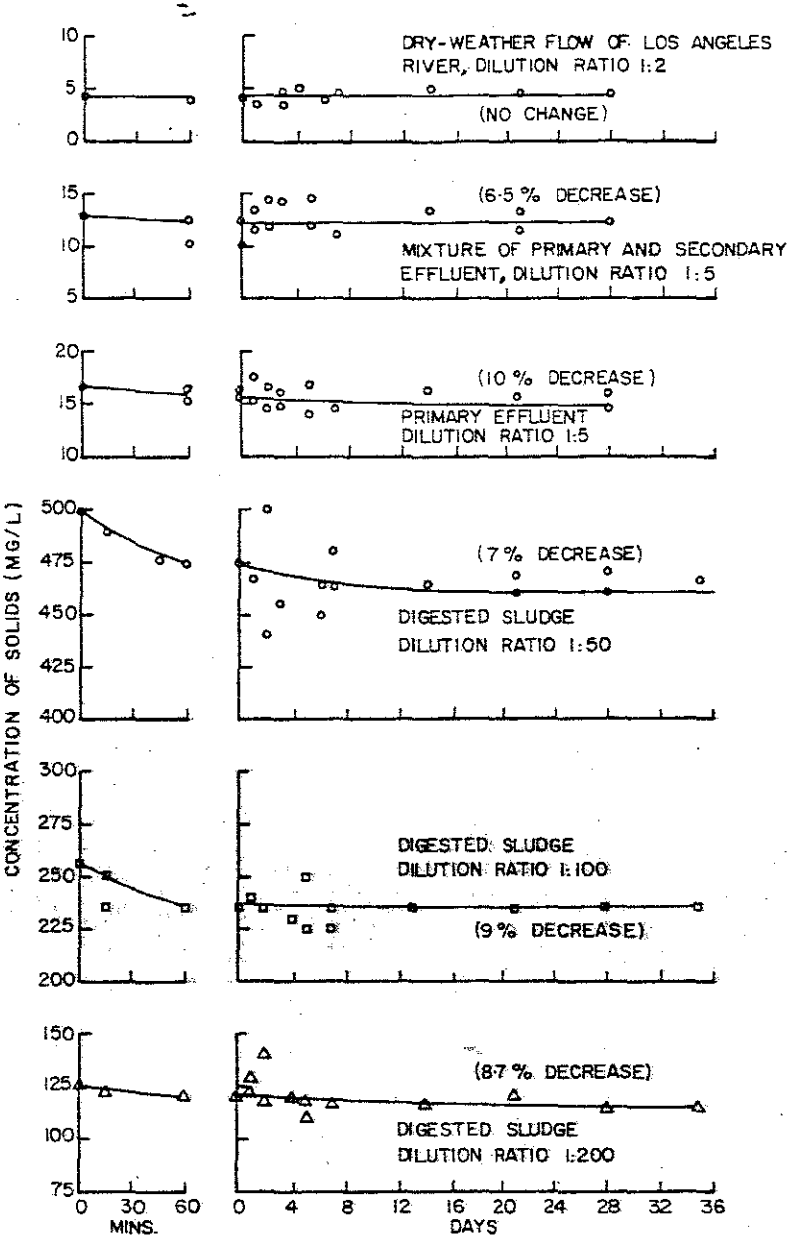

FIGURE 2.—Variation of solids concentration in sludge and waste effluents on dilution with seawater.

ing, or the trace metals may be mobilized in solution, resulting in the long-distance transport of trace metals in the ocean.

de'Groot[3] studied the behavior of mercury in the organic particulates of the Rhine and Ems Rivers and demonstrated the release of mercury from the organic particulates as they enter the saline environment of the ocean. It was suggested that the oxidation of organic matter might

TABLE I.—Sampling Data for Hyperion Treatment Plant

Waste Effluent	Date	Seawater: Effluent Dilution Ratios
Digested sludge	7-1-74	200, 100, 50
Primary effluent	8-15-74	10, 5
Mixture of primary and secondary effluent	8-15-74	10, 5
Dry weather flow from Los Angeles River	8-18-74	2

TABLE II.—Release of Trace Metals from Digested Sludge Particulates After Dilution with Seawater

Element	Total Concentration of Trace Metals Before Dilution (mg/l)	Initial Concentration of Trace Metals in Residue (mg/kg)	% of Trace Metals Released at 1 hr (1:50)	% of Trace Metals Released at 1 hr (1:100)	% of Trace Metals Released at 1 hr (1:200)	% of Trace Metals Released After 5 wk (1:50)	% of Trace Metals Released After 5 wk (1:100)	% of Trace Metals Released After 5 wk (1:200)
Cd	5.62	234	24.8	37.2	20.5	93.0	95.0	96.0
Cu	61.9	2,579	1.0	3.3	7.1	5.0	5.6	9.0
Cr	59.7	2,441	0	6.0	14.4	2.0	2.0	3.8
Fe	326	13,298	0	0	0	0	0	0
Mn	2.75	111	0.9	4.5	7.7	31.8	34.7	35.7
Ni	14.86	603	3.4	2.5	10.9	49.0	58.0	64.0
Pb	21.5	875	48.6*	45.1*	53.1*	37.8	35.4	35.4
Zn	115.24	4,256	8.6	9.8	14.5	18.0	24.4	38.7

* Percentage of trace metals released after 15 min.
Note: Temperature = 15°C.

TABLE III.—Release of Trace Metals from Suspended Solids in Primary Effluent After Dilution with Seawater at 5:1

Element	Total Concentration of Trace Metals After Dilution (μg/l)	Initial Concentration (mg/kg)	Concentration After 90 min (mg/kg)	Concentration After 28 days of Equilibrium (mg/kg)	% of Trace Metals Released After 90 min	% of Trace Metals Released After Reaching Equilibrium	% Trace Metals Released After Reaching Equilibrium (Temperature = 25°C, Dilution Ratio = 10)
Cd	1.8	75.0	60.5	4.0	19.3	94.7	60.1
Cu	48.4	2,819	2,802	933	6.0	67.0	43.9
Cr	45.0	2,695	2,695	2,695	0	0	—
Fe	110	5,999	6,688	6,666	0	0	—
Mn	11.3	51.6	51.0	50	0	0	6.0
Ni	31.0	960	924	413	3.75	57.0	69.8
Pb	3.15	155.7	133.7	73.3	14	52.9	19.0
Zn	19.5	1,140	1,178	640	0	43.86	25.7

Note: Temperature = 15°C, except in the last column.

TABLE IV.—Release of Trace Metals from Suspended Solids in Mixture of Primary and Secondary Effluent After Dilution with Seawater at 5:1

Element	Total Concentration of Trace Metals After Dilution (μg/l)	Initial Concentration (mg/kg)	Concentration After 90 min (mg/kg)	Concentration After 28 days at Equilibrium (mg/kg)	% Trace Metals Released After 90 min	% Trace Metals Released After Reaching Equilibrium	% Trace Metals Released After Reaching Equilibrium (Temperature = 25°C, Dilution Ratio = 10)
Cd	1.8	87.3	72.0	6.25	17.5	92.8	57.5
Cu	30	2,182	2,000	667	8.34	69.4	53.0
Cr	42.3	3,296	3,296	3,296	0	0	—
Fe	69.3	5,277	5,344	5,283	0	0	—
Mn	7.6	51.4	52.0	50.0	0	0	8.42
Ni	37.0	896	848	333	5.4	62.8	44.6
Pb	2.1	140.3	120	58.3	14.5	58.4	42.8
Zn	19.8	1,481	1,456	917	1.7	38.1	17.6

Note: Temperature = 15°C, except in the last column.

TABLE V.—Release of Trace Metals from Suspended Solids in Dry Weather Flow from Los Angeles River After Dilution with Seawater at 2:1

Element	Total Concentration of Trace Metals After Dilution (μg/l)	Initial Concentration (mg/kg)	Concentration After 90 min (mg/kg)	Concentration After 28 days at Equilibrium (mg/kg)	% of Trace Metals Released After 90 min	% of Trace Metals Released After Reaching Equilibrium	% Trace Metals Released After Reaching Equilibrium (Temperature = 25°C, Dilution Ratio = 2)
Cd	< D.L.*	—	—	—	—	—	—
Cu	7.0	1,063	837	362	21.3	65.9	60.0
Cr	2.0	452	452	452	0	0	—
Fe	53.3	12,167	12,167	12,167	0	0	—
Mn	3.4	498	498	475	0	0	0
Ni	6.0	407	181	113	55.5	72.2	21.5
Pb	3.5	516	475	430	7.9	16.7	31.9
Zn	4.8	905	814.5	362	10.0	60.0	21.9

* Below detection limit (0.2 μg/l).
Note: Temperature = 15°C, except in the last column.

be the major mechanism for the release of mercury into solution.

Kharkar *et al.*[4] studied the flux of Ag, Co, Cr, Cs, Mo, Rb, and Sb entering the ocean in the dissolved state. They conducted adsorption-desorption experiments with standard clay minerals to estimate the amount of each trace metal adsorbed on the suspended particulates that might subsequently be released on contact with seawater.

A recent study showed that cadmium in the dredged sediment will desorb more in solutions of high ionic strength than in those of low ionic strength under aerobic conditions; in the case of copper, the effect was found to be opposite.[5] Galloway[2] also reported the release of trace metals under similar conditions. On the other hand, Windom[6] reported that dredged sediments in the reduced state are oxidized on release to oxygenated water, resulting in the precipitation of ferric hydroxide. The precipitated ferric hydroxide in turn scavenges trace metals from solution.

The Hyperion Treatment Plant of Los Angeles, Calif., which discharges about 340 mgd (1,292 mil l/day) of partially treated wastewater effluent into the Pacific Ocean, was chosen for studying the fate of trace metals associated with suspended particulates on discharge. Principal interest was given to digested sludge, primary effluent, and a mixture of primary and secondary effluent. Dry weather flow from the Los Angeles River was also selected because of the past practice of discharging industrial wastes into this river.

The main objective of this paper is to determine whether trace metals such as Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn are released from waste effluent particulates after discharge into a saline environment and, if so, to what extent they are released and what the possible mechanisms are for their mobilization from particulates, which can enhance the long-distance transport.

EXPERIMENTAL

Samples of primary effluent, digested sludge, and mixtures of the primary and secondary effluents were obtained from the Hyperion Plant.

Samples of dry weather flow were collected from the surface water of the Los Angeles River. Special care was taken to avoid the collection of sediments along with the water sample. The samples were collected at least 3 to 4 miles (4.8 to 6.4 km) inland from the ocean to avoid dilution by seawater. Seawater samples were filtered through a 0.1-μ membrane filter before mixing with waste effluents.

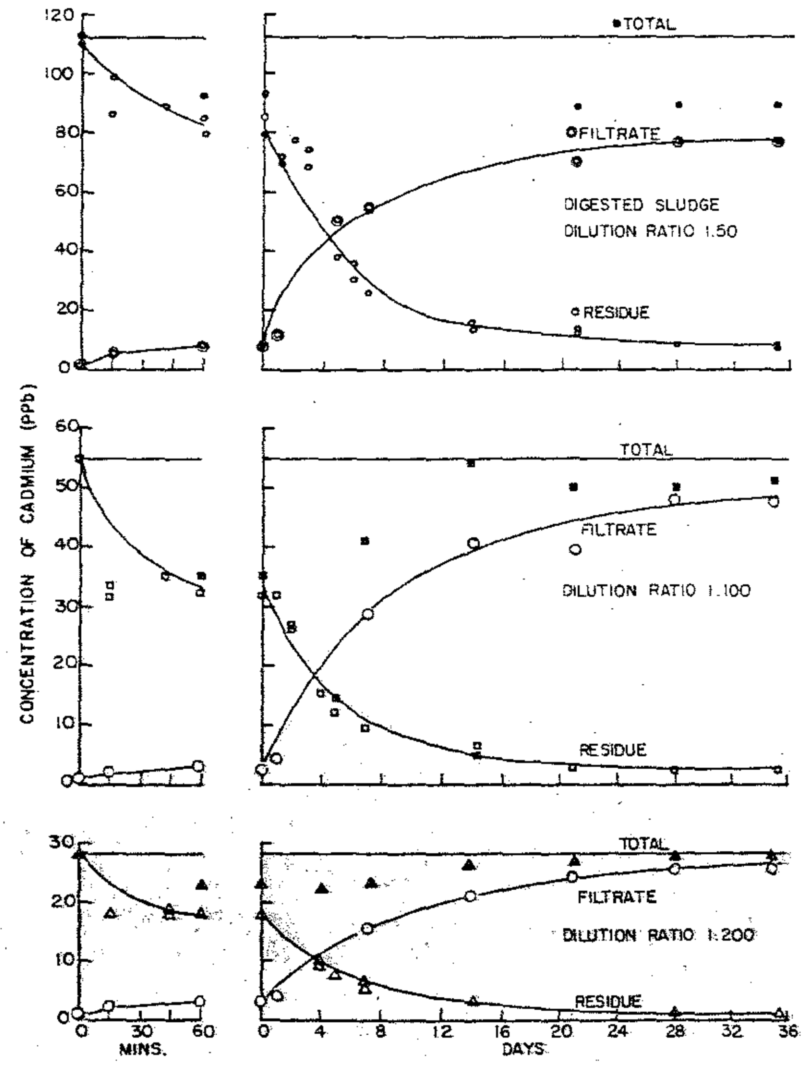

FIGURE 3a.—Distribution of Cd in solid and solution phases after mixing digested sludge with seawater.

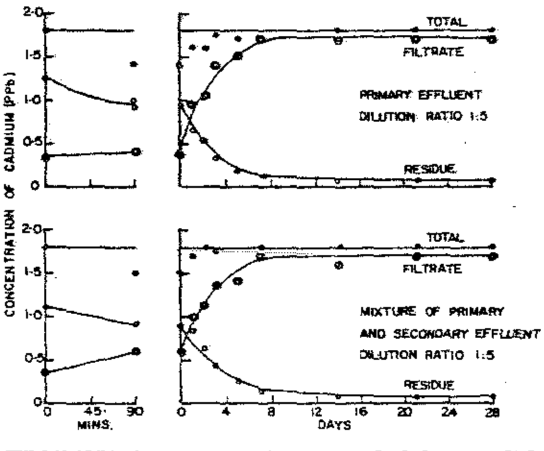

FIGURE 3b.—Distribution of Cd in solid and solution phases after mixing different waste effluents with seawater.

Table I lists the sampling dates for different waste streams and the ratios of dilution with seawater for experiments conducted at 15°C. Samples for experiments at 25°C were collected in the early part of 1974. All samples from the Hyperion Plant were collected at the regular sampling outlets of each unit.

A flow diagram of the experimental procedure is shown in Figure 1. The mixing tanks were located in a constant temperature, constant humidity chamber. Two temperature ranges were used: 15° and 25°C. Samples were stirred throughout the experiment at constant speed. High dissolved oxygen (DO) concentration was maintained by diffusing filtered com-

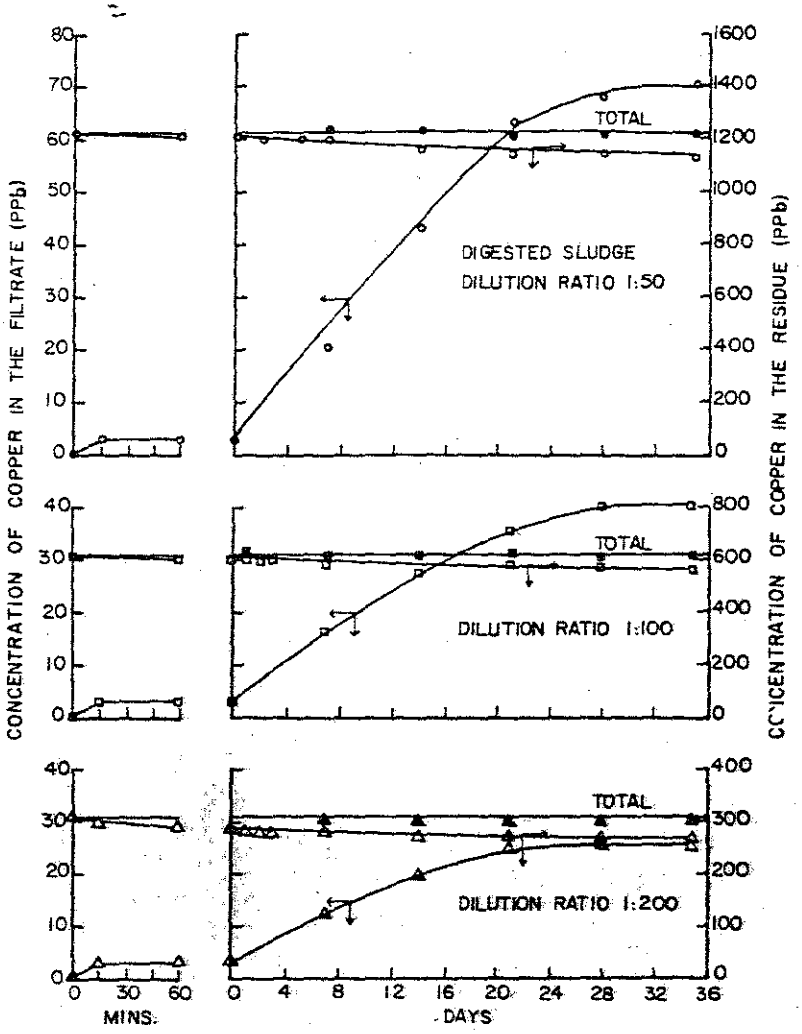

FIGURE 4a.—Distribution of Cu in solid and solution phases after mixing digested sludge with seawater.

pressed air from time to time to ensure the existence of aerobic conditions in the mixing tank.

The partitioning of trace metals between liquid and solid fractions was accomplished by passing the mixture through a 0.1-μ Sartorius membrane filter. Residues on the membrane were digested with ultrapure nitric acid and analyzed for trace metals. Backgrounds of trace metals in these membranes were properly compensated. Filtrates were analyzed for Cd, Cu, Ni, and Pb by the MIBK-APDC extraction method for seawater.[7] The MIBK was distilled twice before use, and the trace metal contamination from APDC was removed by extracting with purified MIBK. Iron, Mn, and Cr were determined by direct injection. An atomic absorption spectrophotometer[a] equipped with graphite furnace atomizer and D_2 arc background corrector were used for metal determinations.

RESULTS AND DISCUSSION

All results reported herein were obtained at 15° and 25°C with seawater obtained outside of the Los Angeles-Long Beach

[a] Model 305B, Perkin-Elmer, Norwalk, Conn.

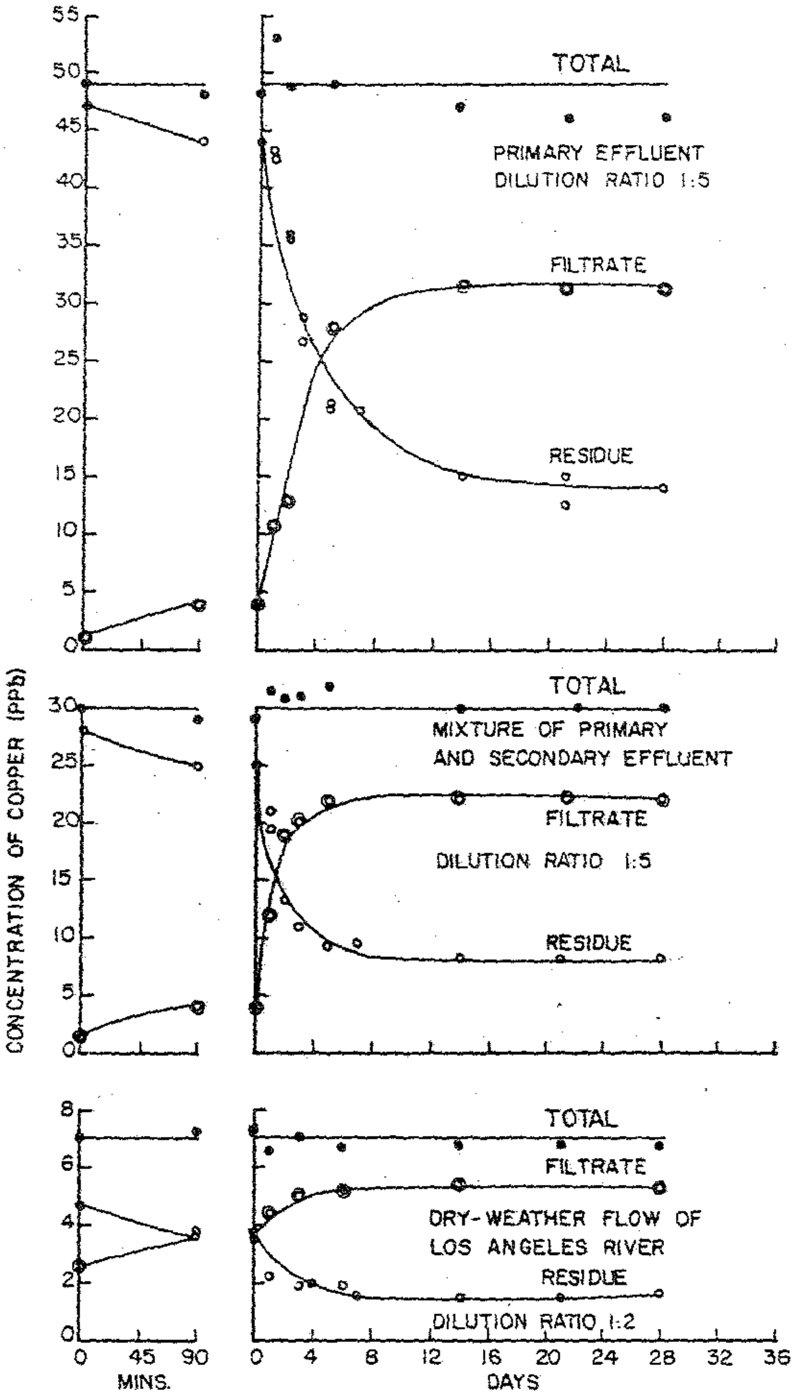

FIGURE 4b.—Distribution of Cu in solid and solution phases after mixing waste effluents with seawater.

Harbors. The change in concentration of trace metals in the solid phase is regarded as the release to the seawater. In a few cases, mass balances were made between the concentrations in the whole suspension and the sums of the trace metals contents of both particulate and solution fractions. These comparisons were made to verify

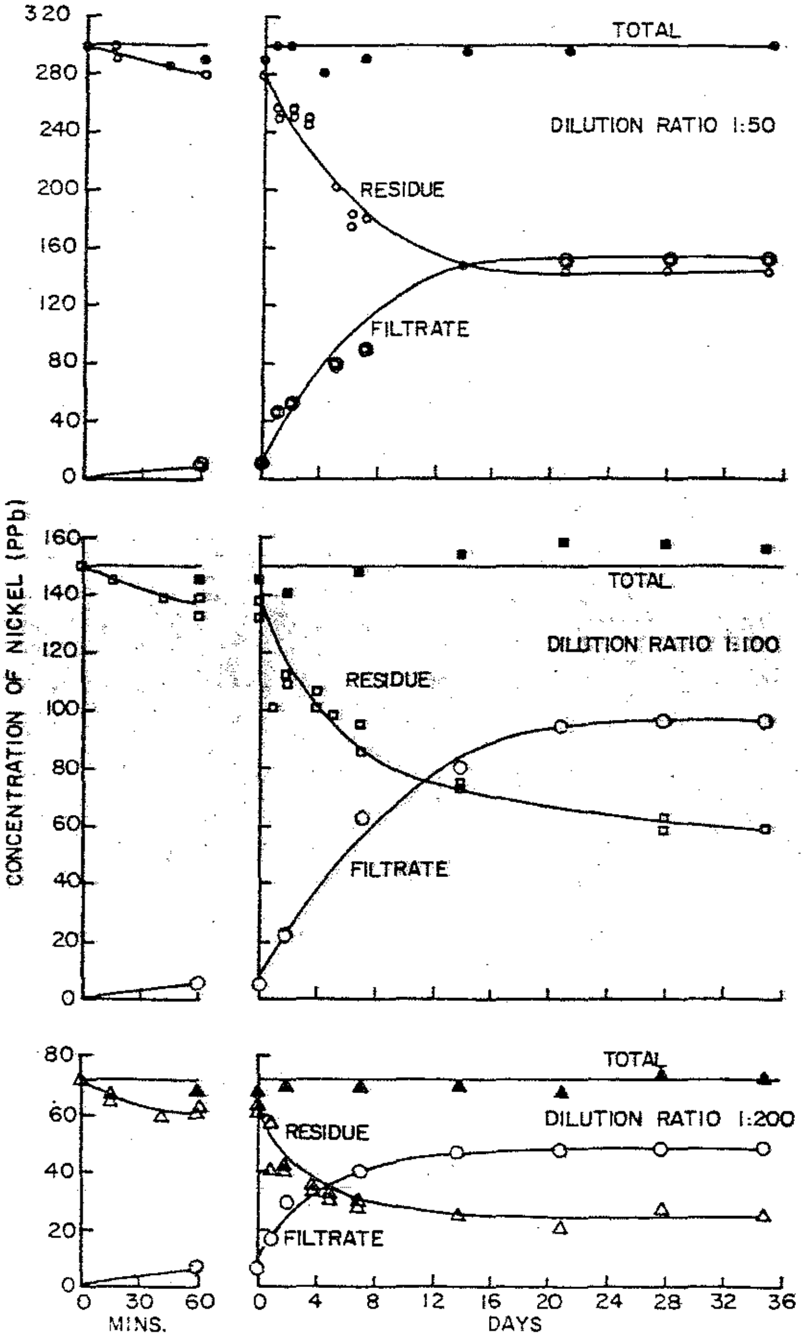

FIGURE 5a.—Distribution of Ni in solid and solution phases after mixing digested sludge with seawater.

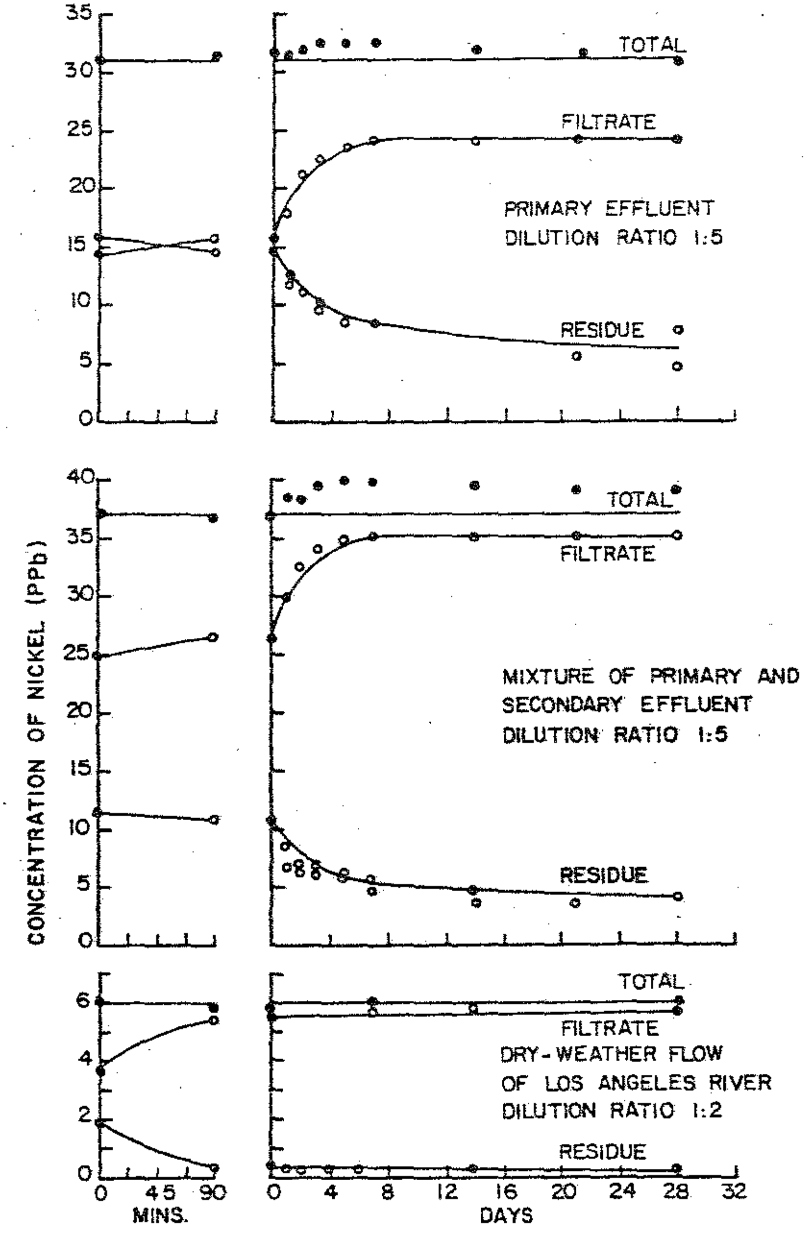

FIGURE 5b.—Distribution of Ni in solid and solution phases after mixing different waste effluents with seawater.

the accuracy of analytical techniques (Figures 3 to 10). The percentage of trace metals released was calculated as the change in trace metals associated with suspended particulates based on the dry weight of solids.

During the experiment, pH values for all mixtures ranged between 7.6 and 8.2. The DO was kept relatively constant at 6 to 8 mg/l, depending on the types of effluent, by allowing filtered compressed air to diffuse into the mixing tank.

Variations in SS concentrations were found to be within 5 to 10 percent throughout the experiment; in the case of the dry weather flow from the Los Angeles River, no detectable change in solids concentration was observed (Figure 2). The decrease in ss concentrations in wastewater effluents and digested sludge may be a result of both chemical and biological oxidations of particulates in reducing states. After 1 wk, the ss concentration seemed to reach an apparent equilibrium because of the refractory nature of the remaining solids. For the dry weather flow from the Los Angeles River, there might not be enough reduced particulates present to cause any change in solids concentrations.

Results on the release of trace metals from the suspended particulates of wastewater effluents, sludge, and dry weather flow from the Los Angeles River are listed in Tables II through V. In most cases, Cd, Cu, Ni, Pb, and Zn were found to be released to a greater extent than the rest. Chromium, Fe, and Mn were not found to be released except in the case of digested sludge, in which 2 percent of the chromium and 35 percent of manganese were found to be released from solid phases.

Up to 95 percent of Cd was released from suspended particulates. At different dilution ratios of both wastewater effluents and digested sludge with seawater, no significant difference in the release of cadmium was observed. During the initial phase, a significant amount of cadmium was found to be released from suspended particulates. In digested sludge, an apparent equilibrium was reached after 3 wk at higher dilution ratios. At lower dilution ratios, equilibrium was reached more slowly; a small amount of cadmium was observed to be released even after 3 wk (Figure 3a). Figure 3b shows that for wastewater effluents apparent equilibrium was reached after 2 wk.

Release of copper from digested sludge particulates was found to be very low, 9 percent at most. However, release of copper from other waste effluents generally falls in the range of 65 to 70 percent. In the case of digested sludge, a lower percentage of copper was observed to be released with a decrease in dilution ratios. Apparent equilibrium conditions were reached within 3 to 4 wk for the suspension of seawater and digested sludge (Figure 4a), while for the other effluents, equilibrium was observed within 2 wk (Figure 4b).

Dilution ratio seems to play an important role in the release of nickel and zinc from suspended particulates. It was found that, with a decrease in ss concentration, the release of nickel and zinc increases to a considerable degree. Figure 5a shows that about 64 percent of the Ni was observed to release from suspended particulates of digested sludge at a dilution ratio of 200; apparent equilibrium conditions were reached within 2 to 3 wk. For other effluents, a major portion of the nickel was initially present in the solution phase. The release of nickel from suspended particulates was observed to reach apparent equilibrium conditions within 1 wk (Figure 5b). The release of zinc from suspended particulates follows the same pattern as that of nickel. Figures 6a and 6b show that a considerable amount of zinc was released during the initial phase.

In the suspension of digested sludge and seawater, lead was found to release immediately after mixing, followed by a slow reduction of soluble lead. Apparent equilibrium was reached within 2 wk

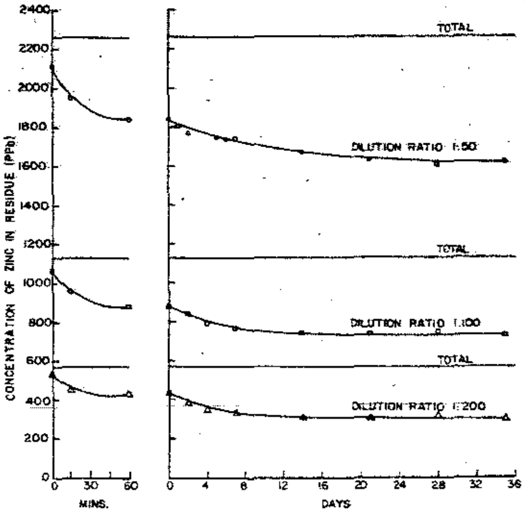

FIGURE 6a.—Concentration of Zn in solid phase after mixing digested sludge with seawater.

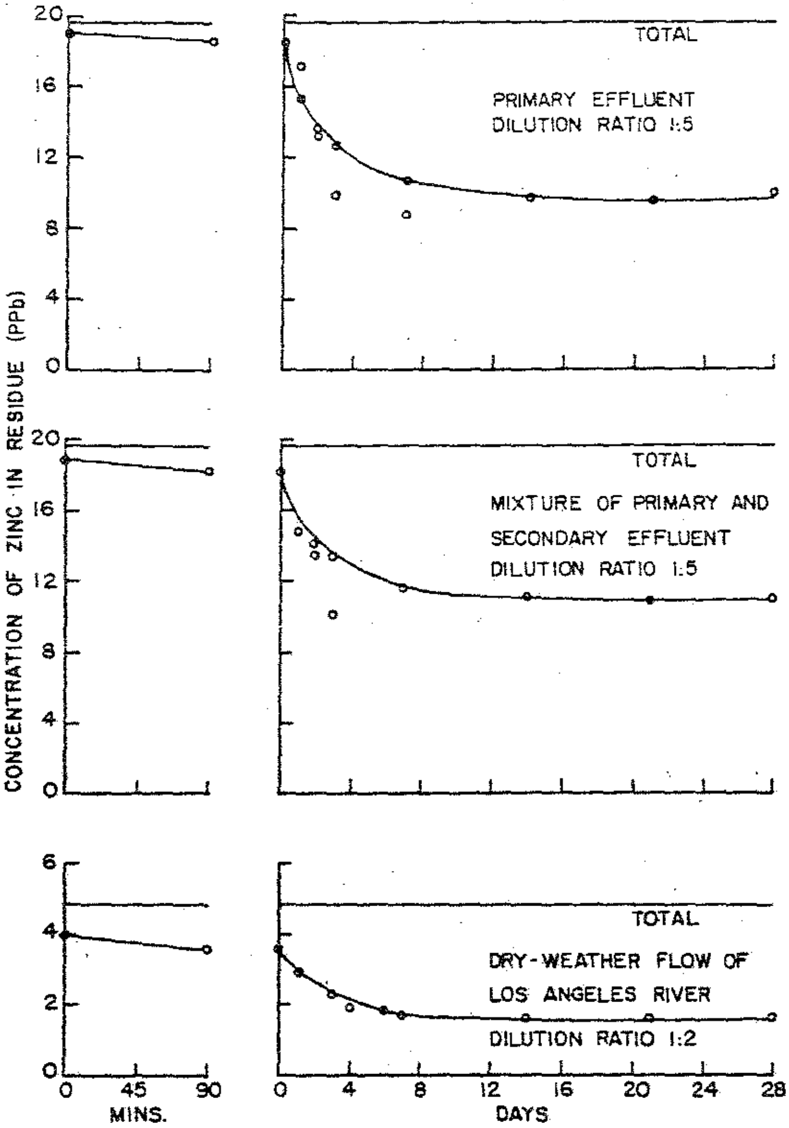

FIGURE 6b.—Concentration of Zn in solid phase after mixing different waste effluents with seawater.

(Figure 7a). In other effluents, an apparent equilibrium condition was found to be reached within 1 wk (Figure 7b.)

Table VI shows the percentage release of trace metals from suspended particulates after an apparent equilibrium was reached in each case. The dilution ratios for digested sludge were 50 and 200; the dilution ratios for primary effluent and dry weather flow from the Los Angeles River were 5 and 2, respectively.

It is quite obvious that the characteristics of ss from primary effluent and the mixture of primary and secondary effluent are quite similar. In general, the ss of dry weather flow from the Los Angeles River, the primary effluent, and the mixture of primary and secondary effluent were observed to release a higher percentage of trace metals in comparison with digested sludge ss, except in the case of lead.

The difference in results may be attributed to the nature of the ss present in the different effluents as well as to the forms and locations of trace metals in the solids, for example, easily oxidizable or refractory organo-metallic compounds; precipitates as metal oxide, hydroxide, or sulfide; adsorption on the surface of ss; or in the crystalline structure of ss.

In general, the release of trace metals was observed to occur in two stages: a rapid initial release, followed by a slower, long-term release. During the initial rapid stage, Cd and Pb concentrations in the suspended particulates were observed to decrease considerably, while Cu, Ni, and Zn were released to a lesser degree. These observations may be attributed to

1. The release of trace metals as bare ions as a result of (*a*) the oxidation of organic particulates containing trace metals, (*b*) the oxidation of metal sulfides, and (*c*) the surface desorption of trace metals caused by high dilution ratio; and
2. Complexation of trace metals to form soluble complexes of (*a*) inorganic ligands such as Cl^-, and (*b*) organic ligands, possibly resulting from the oxidation of organic particulates.

The particulate matter from wastewater effluents and sludge is composed of organic matter and inert materials. Trace metals may be either adsorbed on the surfaces of these particulates or chemically bonded as organo-metallic compounds. On mixing

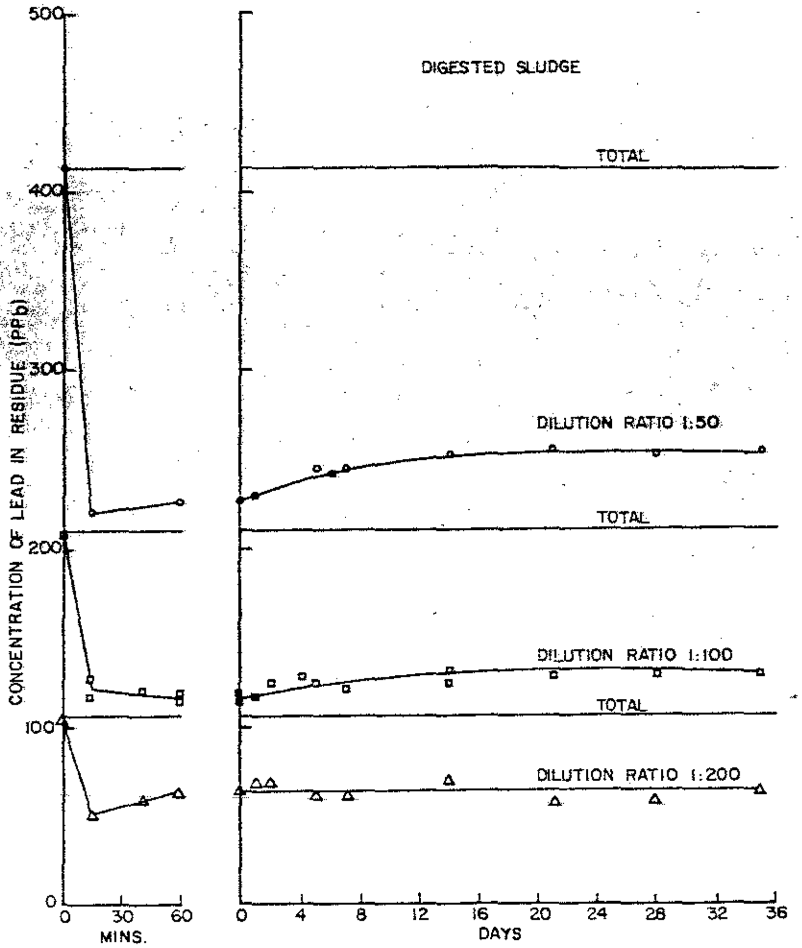

FIGURE 7a.—Concentration of Pb in solid phase after mixing digested sludge with seawater.

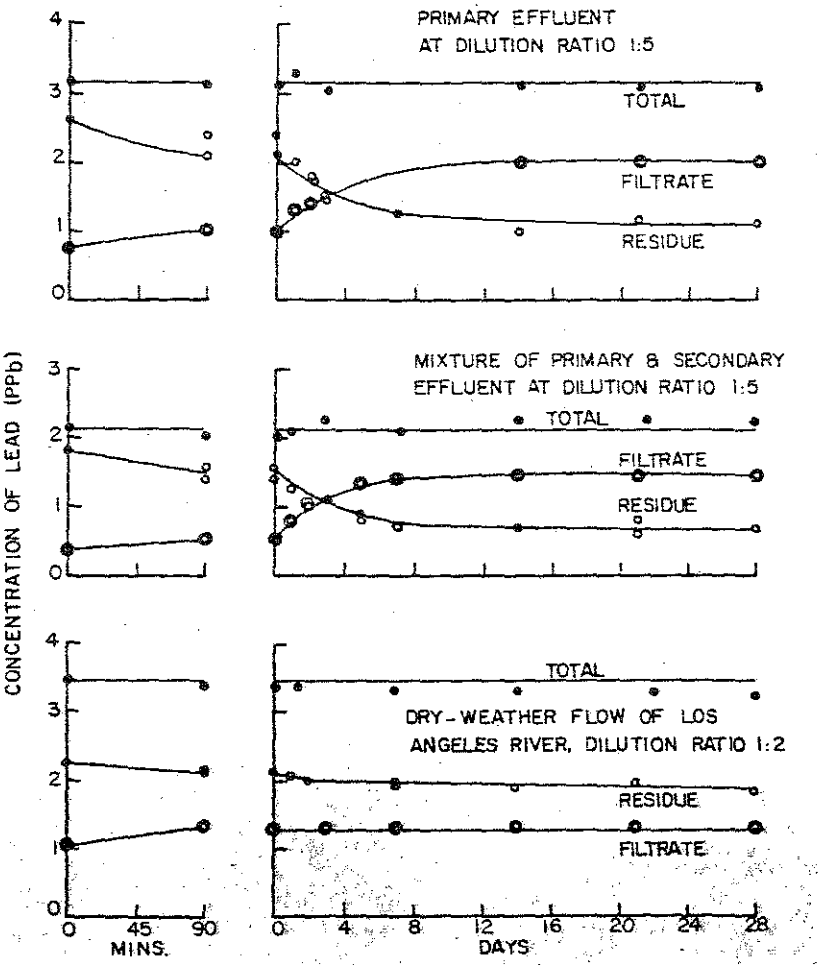

FIGURE 7b.—Distribution of Pb in solid and solution phases after mixing different waste effluents with seawater.

with aerated seawater, the organic matter may be oxidized further to result in the release of trace metal ions in solution. It is quite possible as well that a large fraction of trace metals could be present as metal sulfides. These metal sulfides could be oxidized in the well aerated water and form more soluble complexes.

Concentration of trace metals on the surface of suspended particulate interfaces is a reversible process; thus, adsorbed material may be released into solution as the particles are carried from one environment to the other. The extent of surface desorption at solid-solution interfaces also depends on the dilution ratio. The release of trace metals by surface desorption may be expressed by the following equilibrium equation:

$$\text{Metal} - (\text{Suspended Particles}) \leftrightharpoons \text{Metal Ion}^{2+} + (\text{Suspended Particles})$$

Because the release of trace metals by surface desorption is not necessarily an instantaneous process, it is quite possible that this phenomenon is one of the mechanisms responsible for the slow, long-term release of trace metals. The extent of release from the solid phase is time dependent and seems to reach an apparent equilibrium after 20 days.

The effects of dilution ratios are shown in Table II. Digested sludge was observed to release more of the trace metals as dilution ratios were increased. The effect was particularly strong for Ni and Zn.

The release of trace metals from suspended particulates is probably enhanced by the formation of soluble complexes with the anions that are abundantly present in aerated seawater.[8] The major anions, Cl^-, SO_4^{2-}, and HCO_3^-, may compete with adsorption on the surfaces of the hydrous oxides of Fe and Mn. Because the concentration of chloride ions is much higher than that of the other anions present in the seawater, metal-chloride complexes are probably the predominant species, with hydroxyl complexes playing a minor role.

In seawater, Cd will form Cd^{2+}, $CdOH^+$, $CdCl_3^-$, and $CdCl_4^{2-}$, as well as undissociated $CdCl_2$. The concentrations of $CdCl^+$ and $CdCl_2$ are much higher than

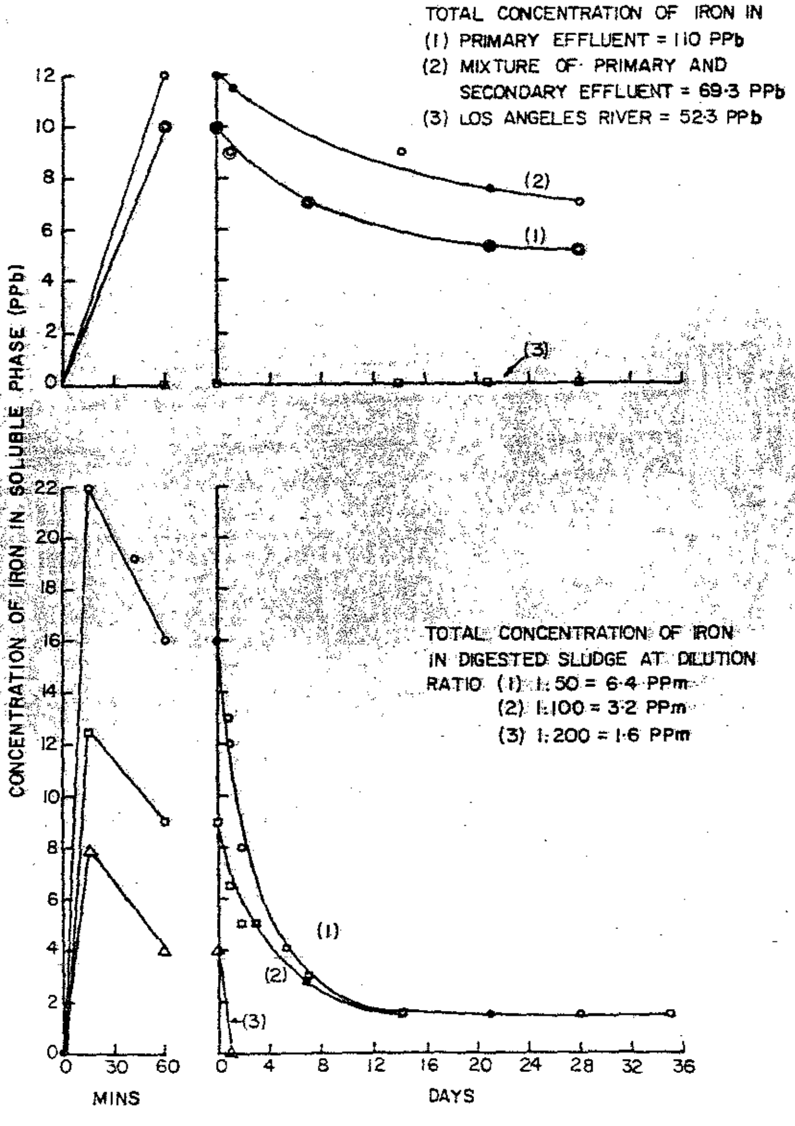

FIGURE 8.—Concentration of Fe in solution phase after mixing different waste effluents with seawater.

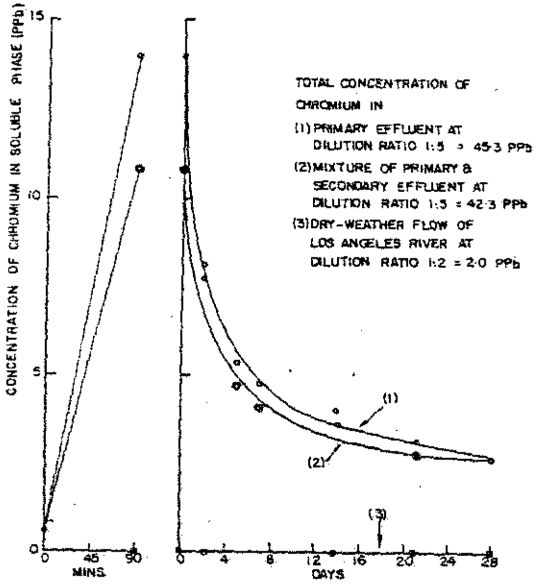

FIGURE 9a.—Concentration of Cr in solution phase after mixing different waste effluents with seawater.

TABLE VI.—Percentage Release of Trace Metals from Suspended Particulates at Equilibrium

	Digested Sludge	Primary and Mixture of Primary and Secondary Effluents	Dry Weather Flow from Los Angeles River
Cd	93–96	93–95	—
Cu	5–9	67–69	66
Ni	49–64	57–63	72
Pb	35	53–58	17
Zn	18–39	38–44	60

those of $CdCl_3^-$ or $CDCl_4^{2-}$.[8, 9] Cadmium was observed to be released to a great extent from these particulates, up to 95 percent in digested sludge. It may be suggested that complex formation is more important than adsorption in determining the fate of Cd. The same phenomenon was observed in the case of Zn.

The forms in which copper can exist in solution are Cu^{2+} and $Cu(OH)_2$ as ion-pair

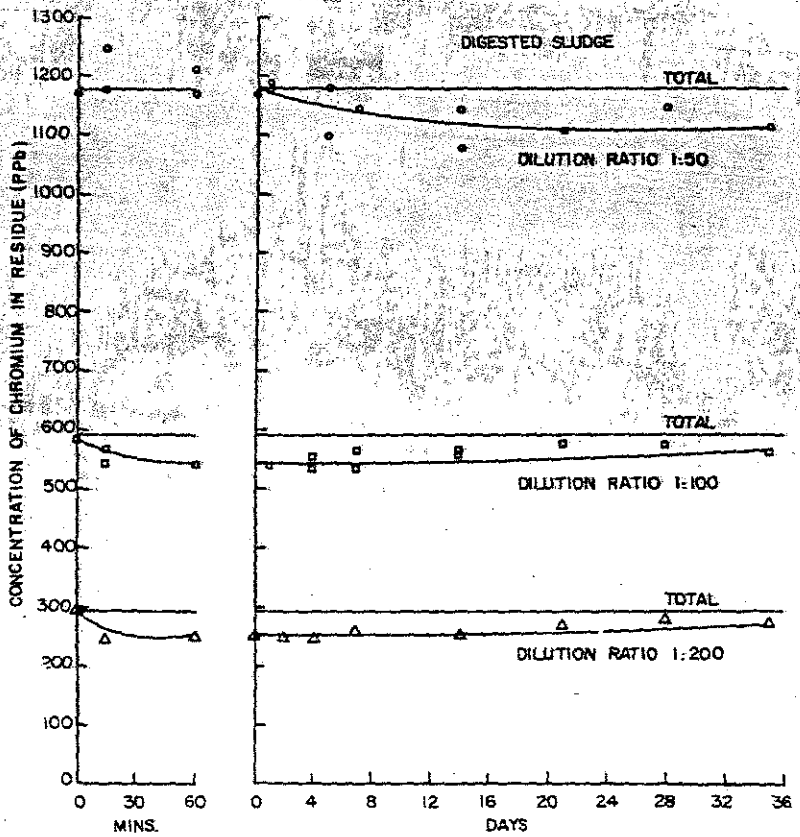

FIGURE 9b.—Concentration of Cr in solid phase after mixing digested sludge with seawater.

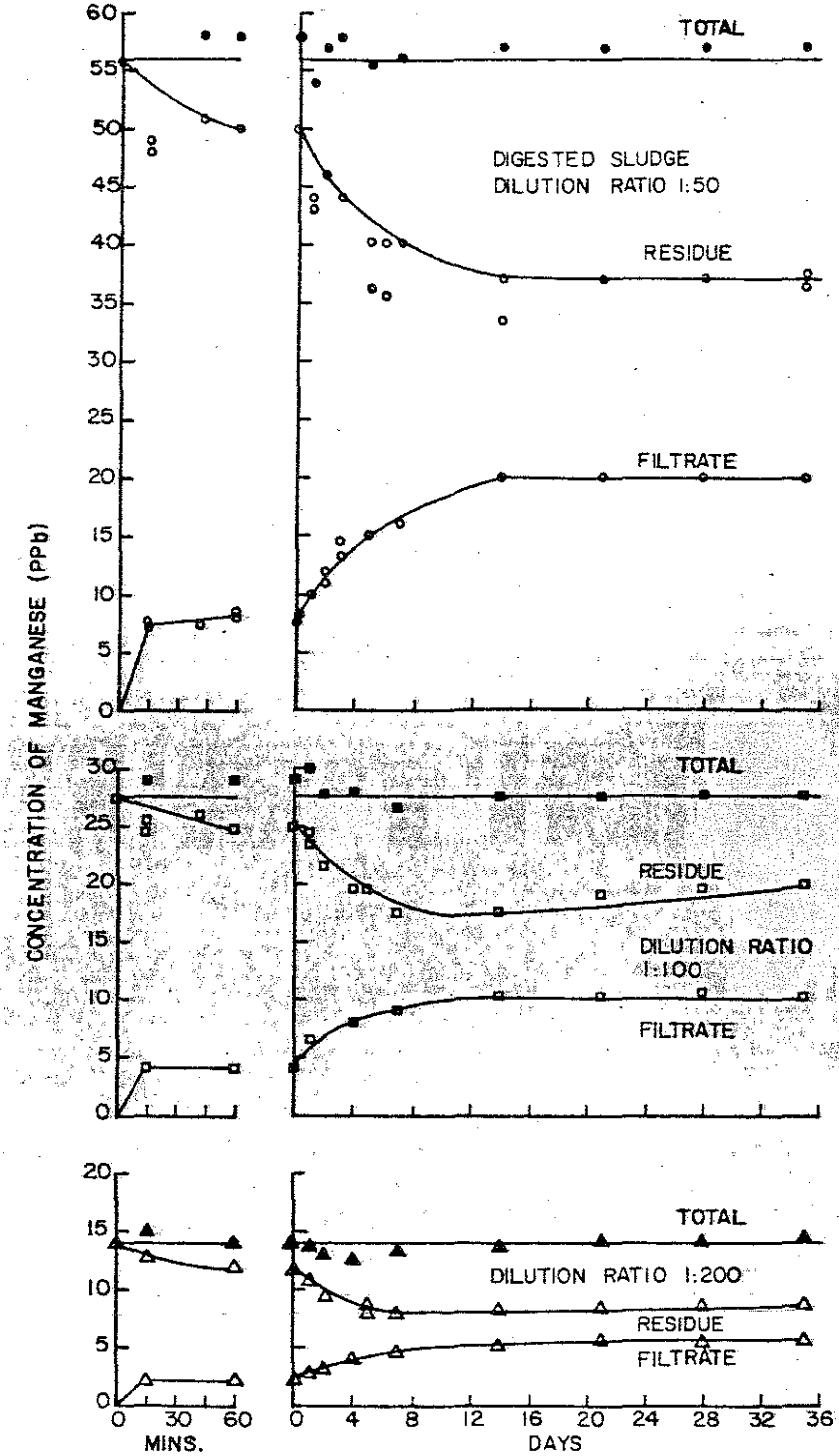

FIGURE 10a.—Distribution of Mn in solid and solution phases after mixing digested sludge with seawater.

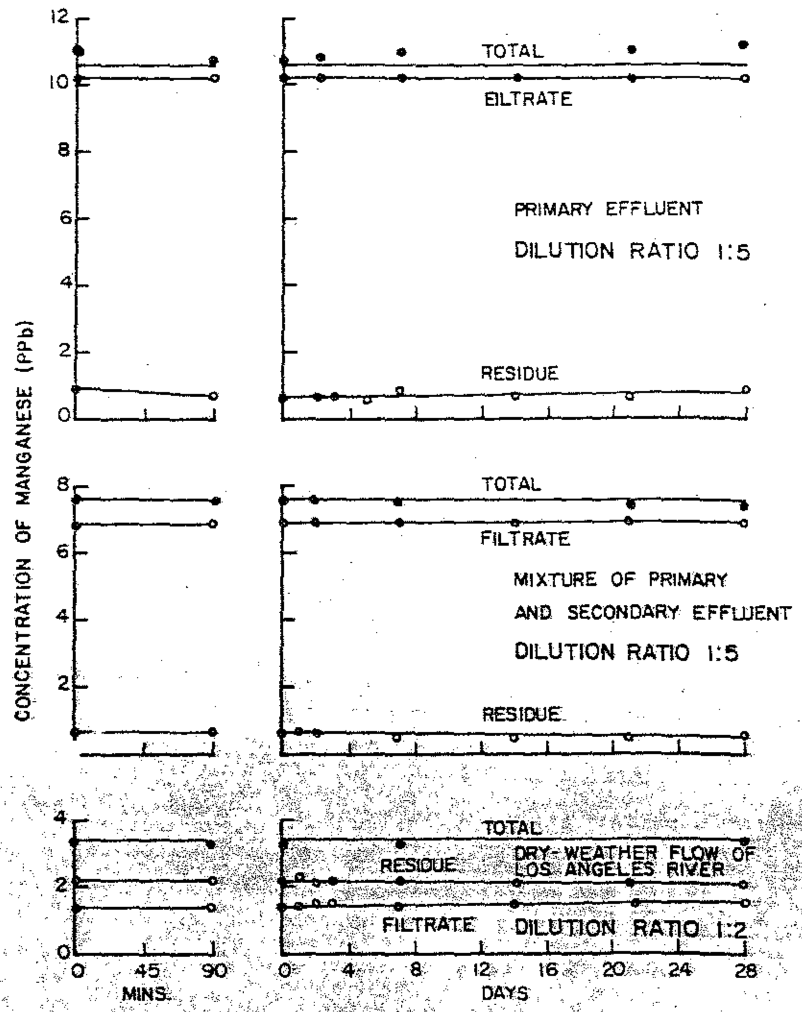

FIGURE 10b.—Distribution of Mn in solid and solution phases after mixing different waste effluents with seawater.

complex. Chloride complexes are relatively small. Copper is found to be released up to 70 percent in wastewater effluents and dry weather flow; however, the release in digested sludge is negligible.

The forms in which Ni can exist in seawater are Ni^{2+}, $NiOH^+$, $NiCl^+$, and $NiCl_2$. There is no evidence for the presence of negatively charged nickel chloride complexes under seawater conditions. It was found that about 60 percent of Ni can be released from suspended particulates. Iron was found to be released initially; however, soluble Fe was reduced greatly to very low levels after about 1 wk of contact, as shown in Figure 8. Initially, Fe was probably in the more soluble reduced state. The subsequent disappearance from the aerobic solution may be explained by the oxidation of the ferrous form to the ferric state, characterized by insoluble oxides and hydroxides. The same results were obtained for chromium, as shown in Figure 9a, except in the case of digested sludge. Figure 9b shows that very little Cr was found to be released from suspended digested sludge solids throughout the experiment. This is probably a result of the absence of soluble complexes.

Figure 10a shows that about 35 percent of the manganese was found to be released from digested sludge particulates. In the primary effluent and in the mixture of primary and secondary effluents, most of the manganese was found to be in solution. No substantial change of concentration was observed in the solid at a dilution ratio of 5, as shown in Figure 10b. At a dilution ratio of 10, the initial response was observed to be a decrease in the concentration of manganese in the ss. Later, the concentration in the solids increased again (Figure 10c). This may be the result of the early oxidation of manganese sulfide to release Mn^{2+} into solution with subsequent oxidation of Mn(II) to Mn(IV), which resulted in the formation of insoluble manganese oxides. Similar results were found in the case of dry weather flow from the Los Angeles River. Formation of organometallic complexes may account for many of the unexplained phenomena in this study.

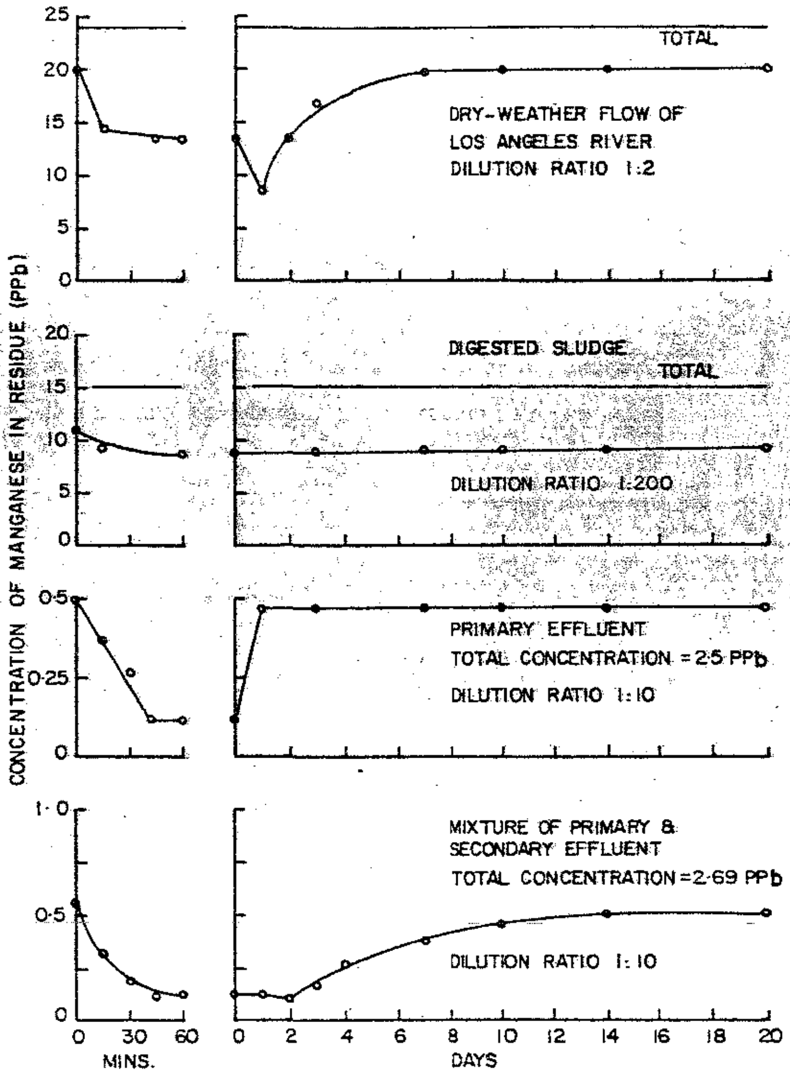

FIGURE 10c.—Concentration of Mn in solid phase after mixing different waste effluents with seawater (temperature = 25°C).

SUMMARY

Under aerobic conditions with seawater salinity, trace metals were observed to be released from suspended particulates, especially in the cases of Cd, Cu, Ni, Pb, and Zn. The release of trace metals was observed to occur in two stages: an initial rapid release, followed by a slower, long-term release. Release of trace metals may be attributed to (*a*) the oxidation of organic matter or metal sulfides; (*b*) desorption from ss, which depend mostly on the dilution ratio and pH of seawater; and (*c*) the formation of metal chloride as well as organo-metallic complexes.

ACKNOWLEDGMENTS

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REFERENCES

1. Chen, K. Y., *et al.*, "Suspended and Dissolved Trace Metals in Wastewater Effluents." *Jour. Water Poll. Control Fed.*, 46, 2663 (1974).
2. Galloway, J. N., "Man's Alteration of the Natural Geochemical Cycle of Selected Trace Metals." Ph.D. thesis, Univ. of California, San Diego (1972).
3. de'Groot, A. J., *et al.*, "Contents and Behavior of Hg as Compared with Other Heavy Metals in Sediments from the Rivers Rhine and Ems." *Geologie en Mijnbouw*, 50, 393 (1971).
4. Kharkar, D. P., *et al.*, "Stream Supply of Dissolved Silver, Molybdenum, Antimony, Selenium, Chromium, Cobalt, Rubidium and Cesium to the Oceans." *Geochim. et Cosmochim. Acta*, 32, 285 (1968).
5. "Characterization of Pollutants Availability for San Francisco Bay Dredge Sediments." Pacific Northwest Lab., Battelle Memorial Inst., Rept. to U. S. Army Engineer. Dist., San Francisco, Calif. (Nov. 1973).
6. Windom, H. L., "Environmental Aspects of Dredging in Estuaries." *Jour. Waterways, Harbors, & Coastal Engineering Div., Proc. Amer. Soc. Civil Engr.*, 475 (Nov. 1972).
7. Brooks, R. R., *et al.*, "APDC-MIBK Extraction System for the Determination of Trace Elements in Saline Waters by Atomic Absorption Spectrophotometry." *Talanta*, 14, 809 (1967).
8. Zinno, A., and Yamamoto, S., "A pH-dependent Model for the Chemical Speciation of Copper, Zinc, Cadmium, and Lead in Seawater." *Limnol. & Oceanog.*, 17, 5, 661 (1972).
9. Sillen, L. G., and Martell, A. E., "Stability Constants of Metal Ion Complexes." Spec. Publ. No. 17, The Chemical Soc., London (1964); Suppl. No. 1, Spec. Publ. No. 25 (1971).