MODELING THE FATES OF METALS IN OCEAN-DISCHARGED WASTEWATERS

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ABSTRACT

Numerical models of the deposition of wastewater particulates and the mobilization of trace metals associated with the particulates were used to examine the fates of five metals (copper, zinc, chromium, lead, and cadmium) present in the submarine wastewater discharges of the Los Angeles County Sanitation Districts. The models predicted that the effluent-related deposition rates will exceed natural sedimentation rates for distances of up to 8 km from the outfalls and account for more than 80 percent of the variation in the metal concentrations observed in the sediments of this area. A discontinuity in the sediment metal distributions at about 3 km from the outfall was revealed by the models; this discontinuity was interpreted as the boundary between aerobic and anaerobic sediments and the position of a corresponding change in the metal mobilization rates. These predictions were compatible with earlier measurements of the physical, chemical, and biological characteristics of the sediments. The models also predicted that, although 90 percent of the metals discharged through the outfall system are associated with particulates, only 10 percent of the metals in the effluent would be retained in the nearby sediments. This prediction agreed with a budget estimated using a different technique.

INTRODUCTION

Most of the sewered wastewaters from the coastal regions of
southern California are eventually discharged into the ocean.
The major discharges, totaling approximately 1 billion gallons
per day (44 cu m/sec), undergo a minimum of primary treatment
prior to their introduction into the ocean through submerged
outfalls terminating in large multiport diffusers at a depth
of about 200 feet (61 m). These diffusers are designed to pro-
duce a wastefield that is "trapped" beneath the thermocline by
the density stratification that usually exists in the receiving
waters.

The generation of a submerged rather than surfacing wastefield
has markedly reduced many of the previous public health and
aesthetic problems associated with the discharge. As a result,
an increasing amount of attention has been devoted to the inves-
tigation of other potential, but often subtle, alterations of
the environment. The deposition of particulates suspended in
the effluent is an important consideration because communities
of benthic organisms are particularly susceptible to changes in
the quantity and composition of the sediments. It is only
recently that this aspect of ocean disposal has received appre-
ciable attention in the southern California area.

In addition to the input of organic material by wastewater par-
ticulates, recent studies (Galloway 1972a; Young et al. 1973),
have shown that many of the trace metals in wastewaters are
associated with this fraction of the effluent. Their concentra-
tion on these solids is frequently one to three orders of magni-
tude greater than the background levels found in sediments far
removed from outfall areas: As might be expected, field surveys
(Galloway 1972a and 1972b; Southern California Coastal Water
Research Project 1973) indicate significantly enhanced concen-
trations of these materials in the sediments near the major
southern California outfalls. The impact of these increased
metal levels on the marine biota has not been fully assessed;
nevertheless, there is concern that undesirable ecological con-
sequences may result.

Because the physical and chemical properties of the macro-
constituents of wastewater particulates and the chemical proper-
ties of the associated microconstituents may have significant
environmental manifestations, methods to predict the distribution,
concentration, and ultimate fate of these materials in the sedi-
ments are desirable. An approach that may assist in the eventual
attainment of this goal has been developed for the discharge of
Los Angeles County Sanitation Districts.

The Whites Point outfall system, located between the Los Angeles-
Long Beach Harbors and Palos Verdes Point, serves the Joint Water
Pollution Control Plant (JWPCP) of the Los Angeles County Sanita-
tion Districts. The system consists of three outfalls (a fourth
has been inoperative since 1965) that extend 5,000 to 12,000 feet
offshore; at the present time, only the two larger outfalls
(Figure 1) are in regular use.

The initial discharge (1937) was approximately 20 mgd. This flow
has steadily increased, and reached a level of about 380 mgd in
mid-1972. Approximately 60 percent of the volumetric flow is
carried by the 120-inch outfall, although, until recently, the
90-inch outfall carried the greater suspended solids load
($\sim$70 percent) as a result of the manifold structure between the
treatment plant and the outfalls. Because of this unequal pro-
portioning of the suspended solids and the length of operation,
the 90-inch outfall has been the single largest source of sus-
pended solids in the system.

Physical, chemical, and biological processes may all play impor-
tant roles in determining the fate of the various constituents of
effluent-related particulates. Each of these processes can, in
turn, involve mechanisms that encompass a wide range of time
scales. The development of a highly realistic model of sediment
processes, incorporating most of these mechanisms, could easily
result in a simulation in which the important features are
obscured by details, poorly understood mechanisms, and parameters
with values that are essentially unknown. The model described here,
which is admittedly a highly simplistic view of reality, represents
an attempt to simulate some aspects of the sediment system with the
minimum number of mechanisms necessary to provide quantitative
agreement with actual field measurements.

The model actually consists of two parts--a model of the physical
processes involved in sedimentation and a model related to the
chemical and biological changes occurring in the composition of
the effluent particulates.

SEDIMENTATION PROCESSES

The calculation of the final position of an effluent particulate
as it settles to the sea-sediment interface generally cannot be
made without invoking some simplifying approximations. In the
present model, these include the following assumptions:

1. Aggregation of the particulates subsequent to initial
   dilution can be neglected.

2. All of the discharged particulates start to settle from
   the same height above the ocean bottom.

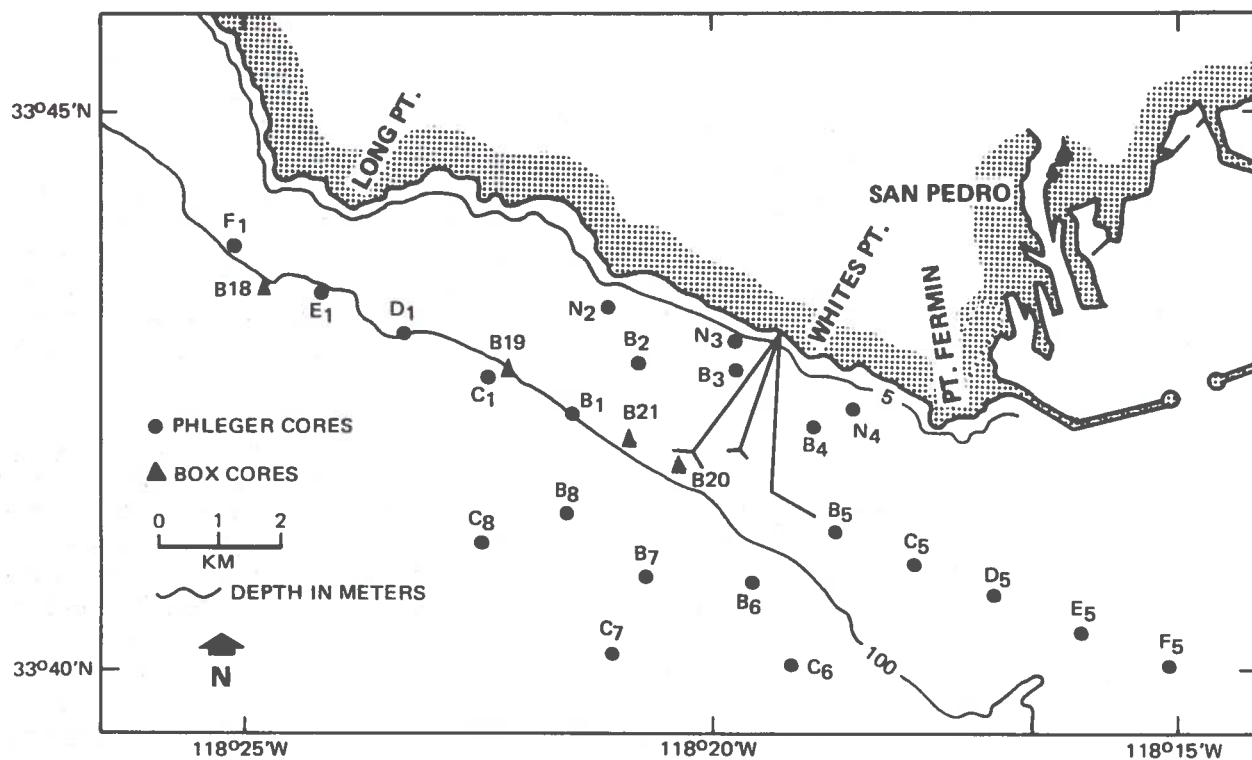3. Vertical advection and diffusion of particulates can
   be neglected.

Figure 1. Whites Point outfall system and sediment core locations. Pipes are (l. to r.) 90-in. outfall, 60-in. outfall, and 120-in. outfall.

4. Ambient turbulence does not affect the settling rates.

5. The horizontal velocity vector for a collection of particles at some depth, z, is identical to the ensemble average current velocity at the same depth.

Computations

The spatial deposition pattern in the outfall area was estimated by calculating the sediment deposition rates into a series of cells formed by dividing the area into 10-degree sectors intersected by rings 1 km apart, as shown in Figure 2. The center of this grid was located over the diffuser "wye" of the 90-inch outfall.

As a particle settles, it is carried by the local currents, which generally change in magnitude and direction with depth. The advective transport of the particulates was estimated, using 4,200 current measurements taken at 6 depths by Los Angeles County Sanitation Districts personnel between 1960-64. For simplicity, it was assumed that the water depth in the outfall area was constant and that each current persisted long enough for steady-state deposition patterns to be established. An "effective velocity vector," $\vec{v}_e$, was calculated for each set of measurements, using the measured current velocities at the depths through which the particle settled. As each particle was assumed to settle at a constant rate, the velocity vector could be obtained from the relation:

$$\vec{v}_e = \sum_n f_n \vec{v}_n \tag{1}$$

where f_n is the fraction of the total settling height, which is represented by the current velocity, $\vec{v}_n$.

The settling speed for a particle that reaches the sediments at the mth angular boundary is then given by:

$$|\vec{v}_s|_m = \frac{H}{r_m} |\vec{v}_e| \tag{2}$$

where

$|\vec{v}_s|_m$ = settling speed corresponding to the mth boundary,

r_m = radial distance to the mth boundary, and

H = settling height.

If the mass emission rate of the discharge and the distribution function of the settling speeds are known, the mass rate of input into each of the annular bands can be calculated. A settling velocity distribution function was not available for the Whites Point effluent; therefore, the results of a study (Hyperion Engineers 1957) of the settling properties of Hyperion sludge
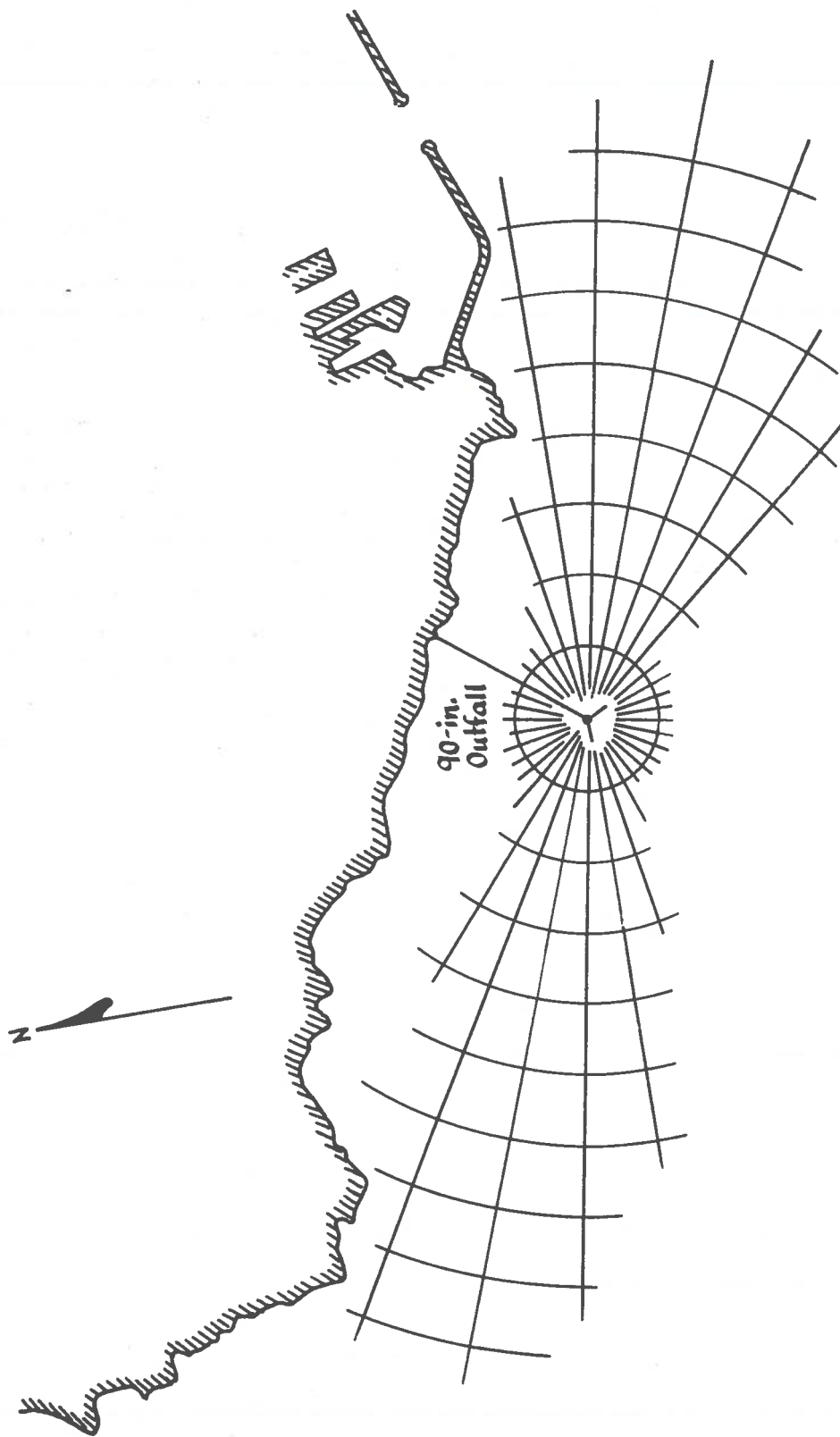
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Figure 2. Definition of deposition model grid. The cells are formed by dividing the area into 10-degree sectors and annular bands, each 1 km in width.

diluted 1:19 with seawater were used. An equation of the form

$$f(v_s) = 0.77 \frac{1}{1 + (1/12)(1/v_s)} + 0.23 \qquad\qquad (3)$$

where $f(v_s)$ is the mass fraction of particles with a settling speed of less than v_s, was found to give an analytical approximation of the discrete experimental data over the range of settling speeds encountered in the model (Figure 3).

Because the Whites Point effluent consists of supernatant from settling basins and centrate from sludge processing, it is likely to have proportionately less material with rapid settling velocities than Hyperion sludge. Therefore, the use of this approximate settling velocity distribution function will probably artificially increase the predicted deposition rates in the immediate vicinity of the outfall.

Diffusion processes in the ocean, which were also included in the model, were found to have a negligible effect on the resulting distributions. This is due, in large part, to the initial width of the wastefield and the increase in cell width with increasing distance from the outfall.

Predictions

Deposition distributions were obtained by calculating the deposition rates for each set of current measurements and then performing a cell-by-cell average over these values. The simulation results, which have been expressed in terms of the ratio of the effluent-related mass deposition rate to the natural mass deposition rate (0.009 dry g/sq cm/yr: Emery 1960), are shown in Figure 4. Because the model assumed a uniform depth over the area, only the results for the two bands that approximately satisfy this condition are shown.

It is readily evident that the discharge substantially increased the mass deposition rate over an area extending more than 8 km from the outfall. Approximately 50 percent of the discharged particulates are predicted to settle within 8 km of the outfall, with an additional 10 percent accounted for by extending the region to a 15-km radius.

The concentrations of many trace metals are substantially greater on effluent particulates than on natural sediments. Because effluent-related sedimentation rates exceed natural rates for distances of 8 km or more from the outfall, it might be expected that the sediments within 8 km of the discharge would exhibit enhanced trace metal concentrations. Figure 5 shows the distribution of copper in the upper 1 cm of the surface sediments around the Whites Point outfall as inferred from data taken at sampling locations shown in Figure 1 (Galloway 1972a). Natural copper concentrations are on the order of 20 mg/dry kg: The enhanced copper levels in the outfall area qualitatively confirm the deposition model predictions.
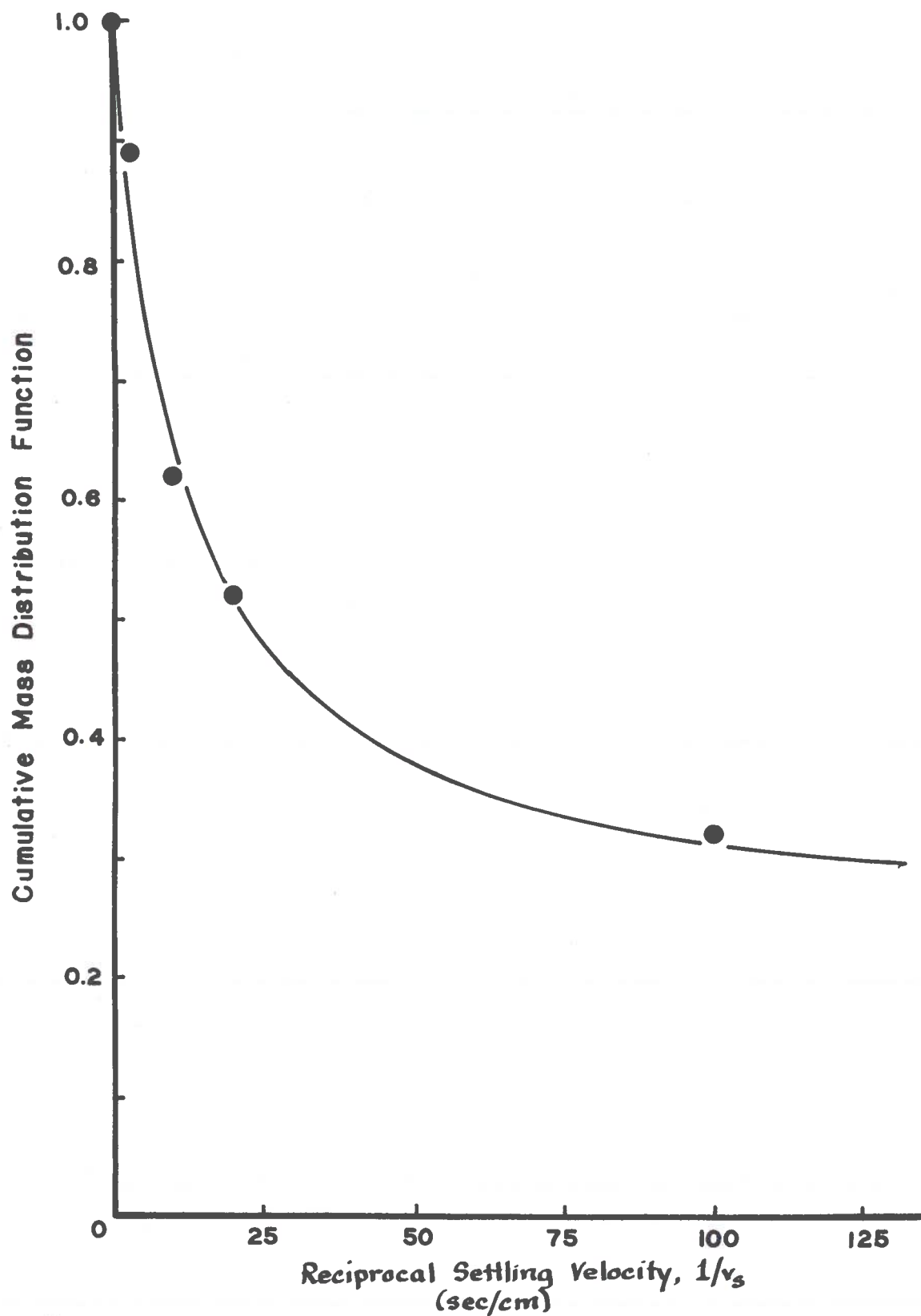
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Figure 3. Mass distribution function of effluent particulate
settling velocities. The ordinate represents the
fraction of the total particulate mass with a set-
tling velocity less than some value, v_s. The ab-
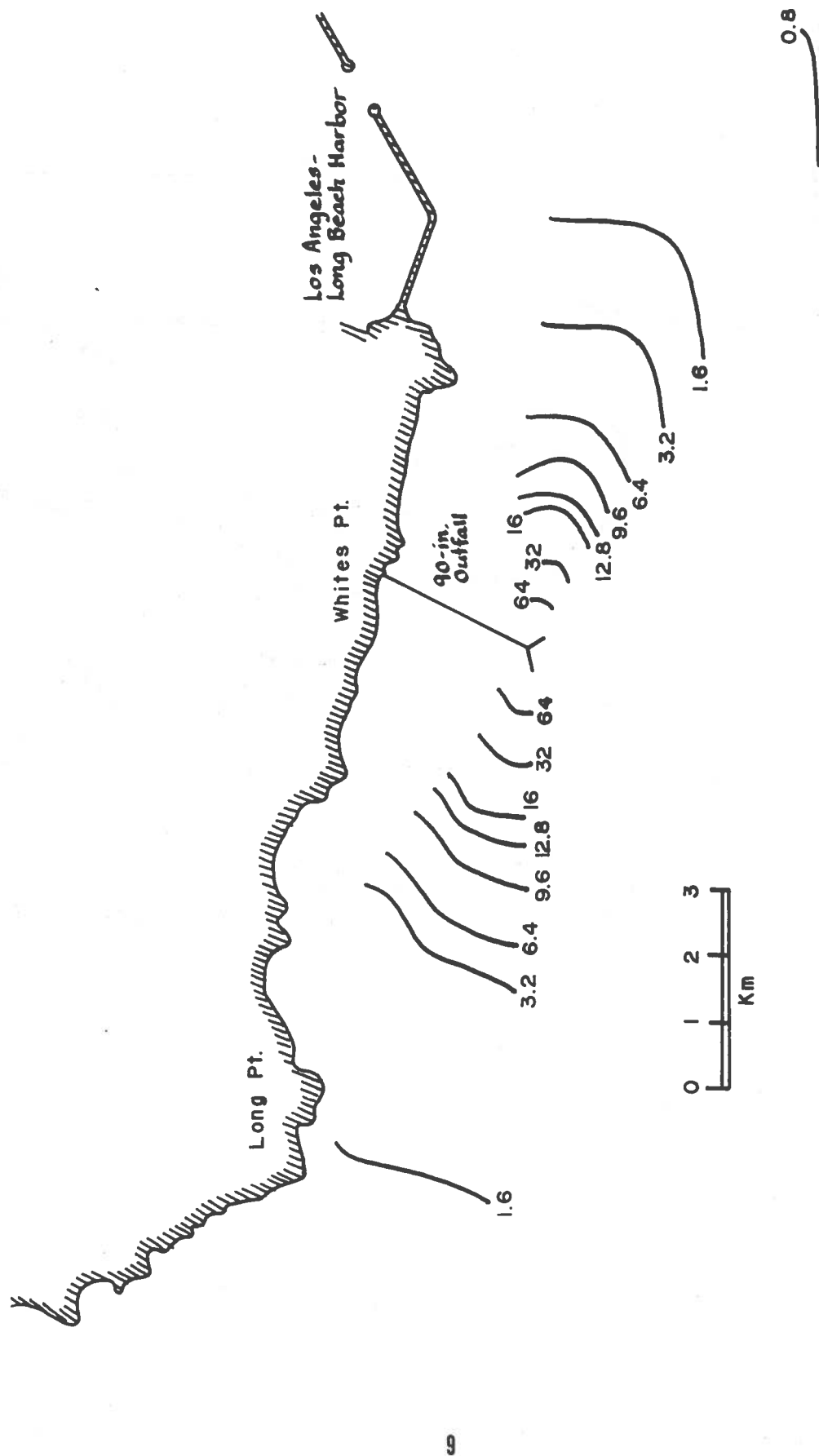scissa represents the reciprocal of this reference
settling velocity.

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Figure 4. Model-predicted isopleths of the sedimentation rate enhancement factor (defined as the ratio of the effluent-related deposition rate to the natural deposition rate).
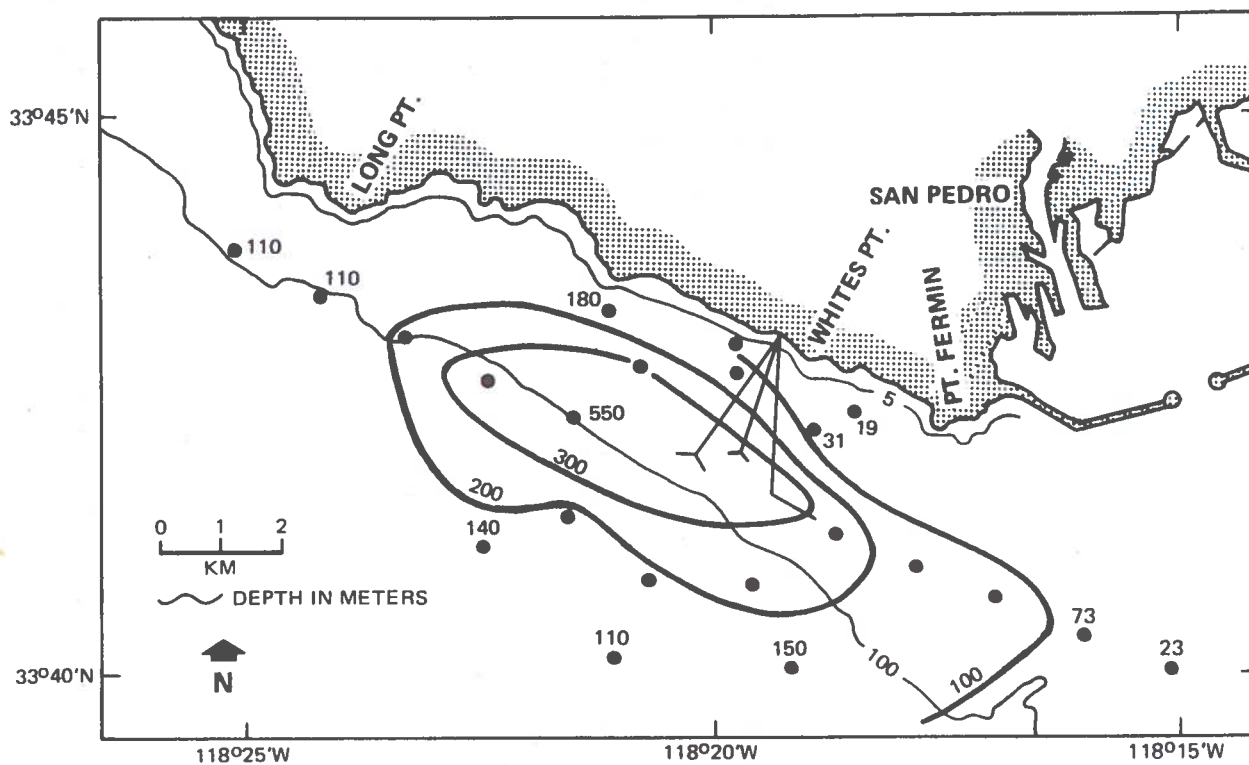
Figure 5. Copper concentrations (mg/dry kg) in the surface sediments around the Whites Point outfall system (Phleger cores, May 1970). After Galloway 1973.

The concentrations of many trace metals in the sediments near the outfall are substantially less than those on the effluent particulates--even in the immediate proximity of the outfall, where the effluent-related deposition rate may be more than 50 times the natural deposition rate. For example, Galloway (1972a) has shown that the concentration of copper on the effluent particulates is about 1,100 mg/dry kg; yet the highest copper concentration noted in the sediments around the outfall is less than 700 mg/dry kg. Because the effect of the decay of organic material in the settled particulates (without the desorption of copper) would be an increase rather than decrease in copper concentrations in the sediments, it is evident that additional processes must be included in the model before it can be used to make quantitative predictions of sediment trace metal concentrations.

A variety of mechanisms could result in lower levels of trace metals in sediments than on the effluent particulates; these include sediment mixing by benthic biota, a distribution of metal concentrations that is dependent upon particulate settling velocity (or size), or chemical and biochemical mobilization. Probably all of these processes play some role. For example, if benthic mixing alone was responsible for the differences between effluent particulate and sediment concentrations, the sediments would show an equal concentration reduction for each metal. Yet the observed sediment values ranged from a 5 percent increase over effluent concentrations for cadmium to a 40 percent decrease for copper.

No data on the effect of particulate size or settling velocity on the distribution of trace metals was available. An increase in concentration on the finer particles, as might be expected from surface absorption, would be reflected by an increase in the metal concentration in the sediments with distance from the outfall. There is a slight, but inconclusive, indication of such a feature at distances of 1.5 to 3.0 km from the outfall and at distances greater than 6 km, as shown in Figure 6. However, it seems unlikely that the substantial reduction in concentrations in the interval from 3 to 6 km could be explained by a correlation between metal concentration and particulate settling velocity.

In view of the inadequacy of benthic mixing alone to explain the observed reductions, and the lack of data on the effects of settling velocity on particulate trace metal concentrations, we have chosen to examine a suggestion by Galloway (1972a) that chemical and biochemical mobilization can provide an adequate, although possibly incomplete, explanation of the gross features of these distributions.
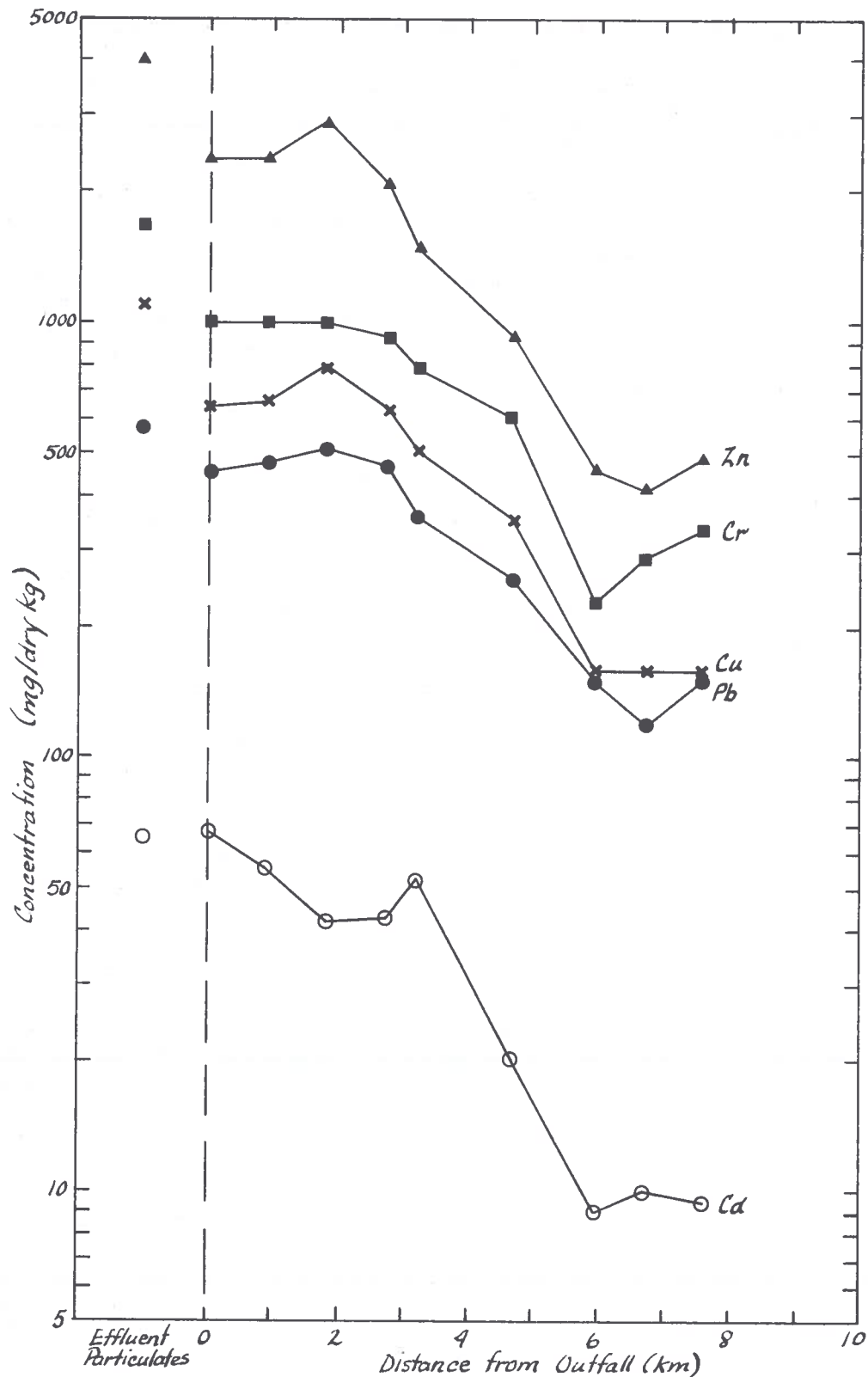
Figure 6.   Distribution of trace metals in surface sediments
along the 100-m depth contour to the northwest of
the 90-in. outfall. After Galloway 1973. Estimated
equivalent box core concentrations are shown for
the Phleger core samples.

MOBILIZATION OF METALS

Mobilization may take place in the water column, in the sediments, or in both. Prior to discharge, the particulates are in an essentially anaerobic environment; however, during the initial dilution process, the effluent is well mixed with ambient ocean water, which usually contains significant concentrations of dissolved oxygen, and mobilization may occur. An estimate of the time available for mobilization in the water column can be made using the results of the deposition model. As noted earlier, the model predicted that approximately 60 percent of the discharged particulates settle within 15 km of the outfall; hence (from Figure 3), most of the particulates should settle within 2 days after their release. Galloway (1972a) has conducted a preliminary laboratory study of chemical mobilization, using effluent particulates in well-stirred, refrigerated ($4^{\circ}C$) seawater. His results indicate that, in the water column, the reduction in the particulate trace material concentration during a 2-day period would probably be less than 10 percent (Figure 7). As this rate is insufficient to account for the observed reductions, most of the mobilization probably takes place in the sediments.

Computations

The chemical mobilization model assumes that the sediments can be divided into two parts--an upper layer in which the organic material may decay and trace metals may be mobilized from both the organic and inorganic fractions, and an underlying layer of nonreactive (permanent) sediments. Steady-state conditions are assumed, and the concentrations or mass of organic material, oxygen, and trace metals in a cell are calculated by mass balance equations, considering the transfer rates of these materials across the cell faces and the sources or sinks internal to the cell (Figure 8).

Mobilization Processes. It was assumed that the chemical mobilization processes in the sediments can be represented by two "lumped" reactions:

$$c + a \underset{k_2}{\overset{k_1}{\rightleftharpoons}} b \tag{4}$$

$$c + d \underset{k_4}{\overset{k_3}{\rightleftharpoons}} e \tag{5}$$

where

c = a trace material,

a = dissolved oxygen, and

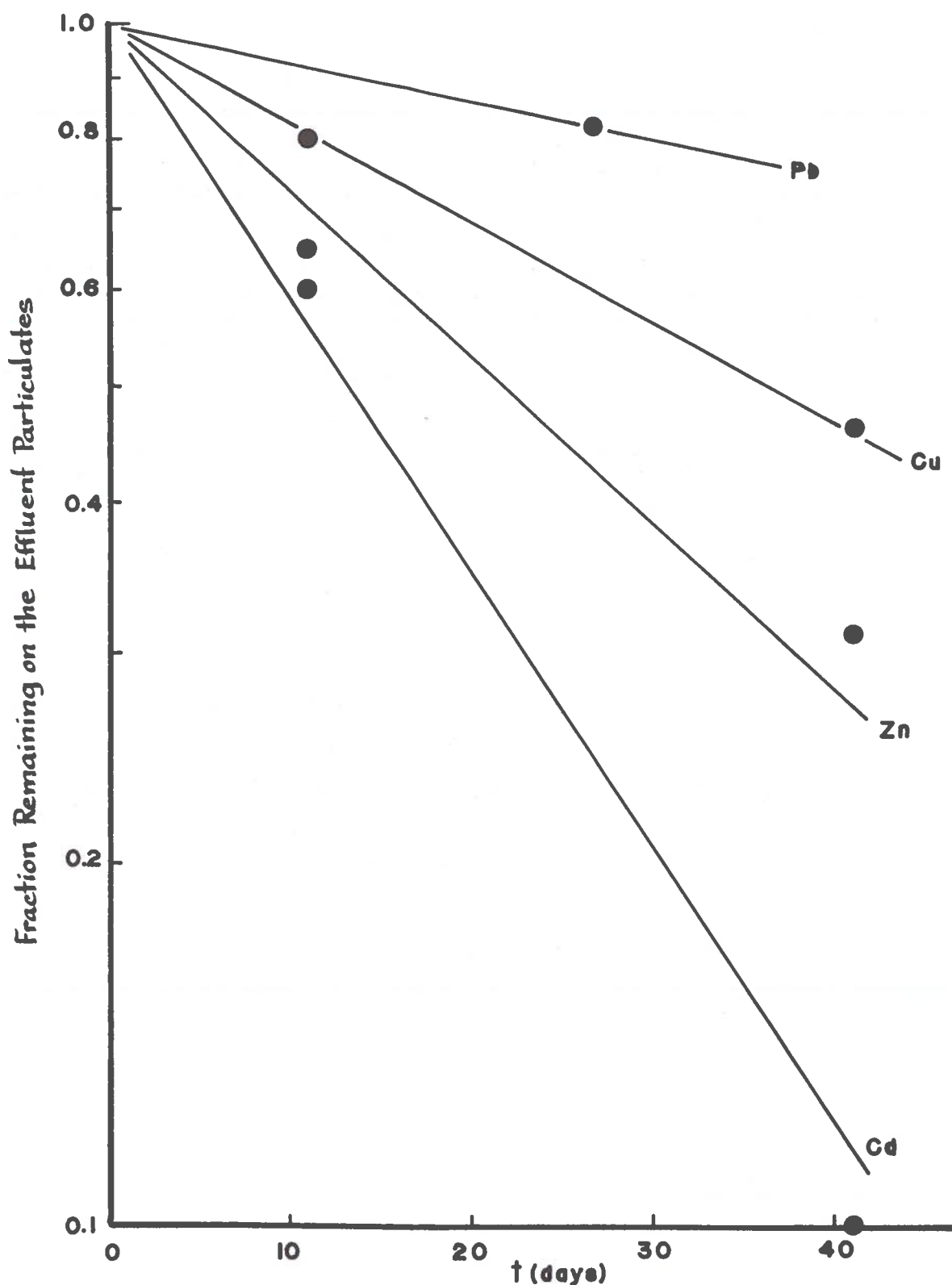b, d, e = unspecified reactants.

Figure 7. Observed decreases with time in particulate concentrations of trace metals in a 1:10 mixture of municipal wastewaters and seawater. Mixture was refrigerated and stirred continuously for 41 days. Analyses by Galloway (1973).
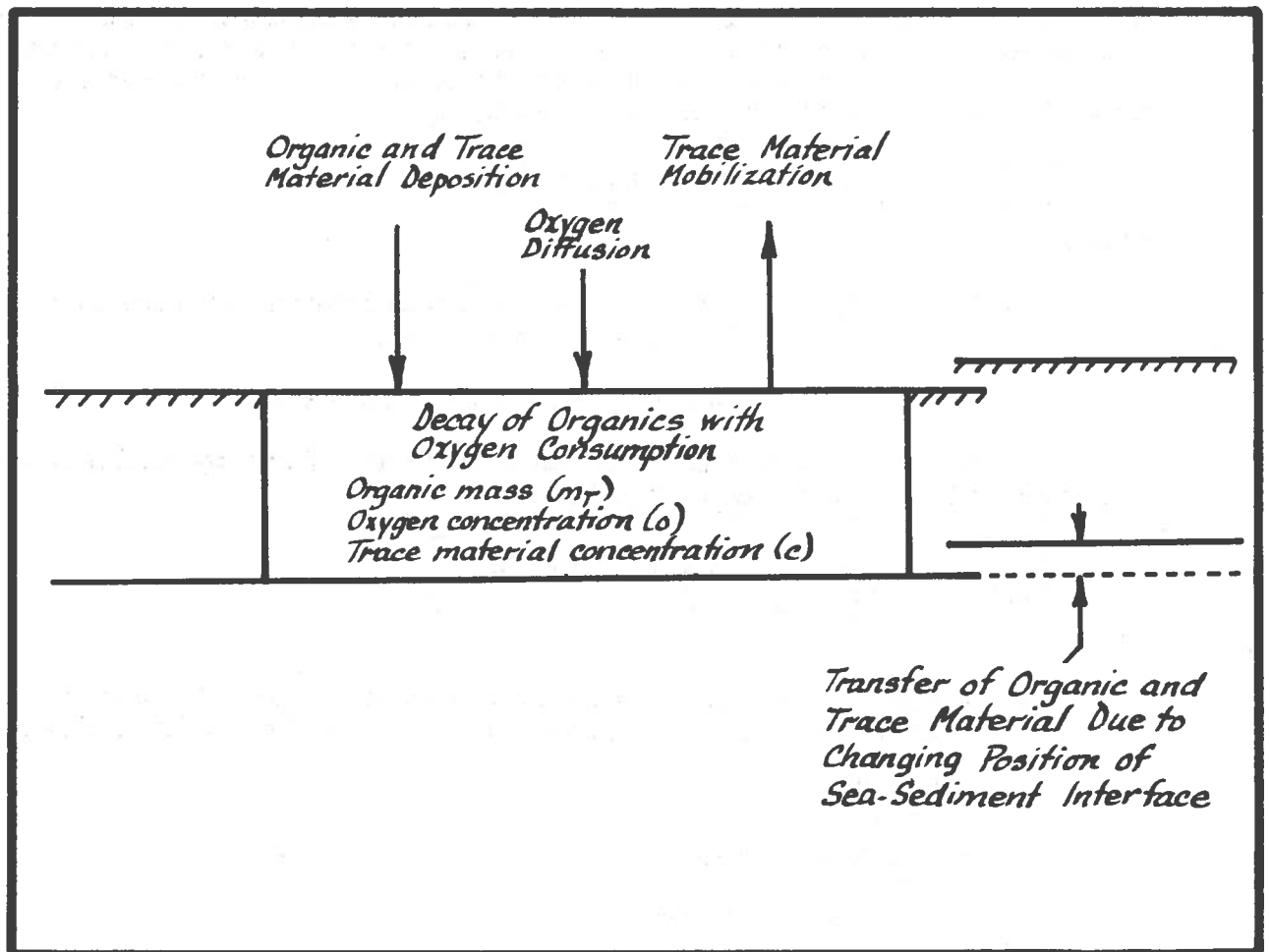
Figure 8. Processes incorporated into the mass balance calcu-
lations for the sediments.

The reactant "a", for the purposes of the model, need not be oxygen per se, but need only be some reactant with a concentration distribution in the sediments that is similar to that of oxygen. Similarily, Equation 4 could be replaced by a reaction in the form:

$$c \xleftrightarrow{} b + s \tag{4'}$$

where s represents some reactant with a concentration that is approximately inversely related to that of oxygen (e.g., sulfide). It was also assumed that the concentrations of a, b, d, and e are not significantly affected by the microconstituent (trace material) reactions, but are regulated by other macroconstituent processes. The time rate of change of the trace material concentration due to mobilization reactions is then given by:

$$\left.\frac{dc}{dt}\right)_m = -k_2 ca - k_4 cd + k_1 b + k_3 e \tag{6}$$

where

a, b, c, d, e = respective concentrations of substances a, b, c, d, and e, and

k_1, k_2, k_3, k_4 = appropriate rate constants.

Equation 6 can be written into an alternate form by defining the new variables λ_2, σ, a_o, and c_o*:

$$\left.\frac{dc}{dt}\right)_m = -\lambda_2 \left[c\left(\frac{a}{a_o} + \sigma\right) - c_o*(1 + \sigma) \right] \tag{7}$$

where

a_o = the dissolved oxygen concentration in the water column at some distance above the sea-sediment interface,

$\lambda_2 = k_2 a_o$,

$\sigma = k_4 d/k_2 a_o$, and

$$c_o* = \frac{k_1}{k_2} \frac{b + (k_3/k_1)e}{a_o(1 + \sigma)}.$$

The new variable, c_o*, can be interpreted as the equilibrium trace material concentration at the dissolved oxygen concentration a_o.

The oxygen concentration in the top sediments was estimated by assuming that the decay of organic material represented the principal oxygen demand, and that the rate of this decay was governed by the relation:

$$\frac{dm_T}{dt} = -\lambda_1 m_T \tag{8}$$

where

m_T = mass of sediments within some volume containing the decaying material, and

λ_1 = decay rate parameter.

If the rate of oxygen consumption is proportional to the decay rate, then

$$\left.\frac{da}{dt}\right)_{decay} = -\gamma(\lambda_1 m_T) \tag{9}$$

where γ is a constant of proportionality related to the oxygen demand per unit mass of sediments.

Oxygen consumed by decay is replaced by the diffusion of oxygen into the region of decay; the flux rate into this region given by:

$$J_a = -k_D \frac{da}{dz} \tag{10}$$

where

J_a = oxygen flux across a unit area,

k_D = diffusion coefficient, and

z = vertical distance.

The complete specification of this rate would necessitate solving the combined system of sediment decay and oxygen concentrations in the water column and sediments for each set of currents. To simplify the computation, it has been assumed that, on the average, diffusion takes place across a layer of thickness, t, so that J_a can be approximated by:

$$J_a \approx -\frac{k_D}{t}(a_o - a). \tag{11}$$

If these two rates are in equilibrium, then

$$a = a_o - \frac{t\gamma\lambda_1 m_T}{k_D}. \tag{12}$$

The decaying mass is calculated by a balance between the rate of deposition, the rates of decay, and the passage of material into the permanent (nonreactive) sediments, i.e.:

$$d_o + d_e = (\lambda_1 + \lambda_3)m_T \tag{13}$$

where

d_o, d_e = mass deposition rates of natural and effluent-related particulates, respectively, and

λ_3 = transfer rate of mass into the permanent sediments.

For simplicity, it was assumed that λ_3 was proportional to the deposition rate (and hence to the decay rate). Defining μ as

$$\mu = \lambda_3/\lambda_1 \tag{14}$$

and combining Equations 12 and 13:

$$a = a_o - \frac{t\gamma d_o}{k_o} \frac{1}{(1 + \mu)} \left(1 + \frac{d_e}{d_o}\right) \tag{15}$$

As the deposition rate increases, the average oxygen concentration in the volume of sediments will decrease. If d_e* is defined as the deposition rate at which the oxygen concentration becomes zero, then:

$$a = a_o \left[1 - \frac{1 + d_e/d_o}{1 + d_e*/d_o}\right] \qquad \text{for } d_e < d_e* \tag{16}$$

$$= 0 \qquad \text{for } d_e \geq d_e* \tag{17}$$

The corresponding chemical mobilization equations then become:

$$\frac{dc}{dt}\bigg)_m = -\lambda_2 \left[c\left((1 + \sigma) - \frac{1 + d_e/d_o}{1 + d_e*/d_o}\right) - c_o*(1 + \sigma)\right]$$
$$\text{for } d_e < d_e* \tag{18}$$

$$= -\lambda_2 \left[c\{(1 + \sigma) - 1\} - c_o*(1 + \sigma)\right]$$
$$\text{for } d_e \geq d_e* \tag{19}$$

If the sediment concentrations are independent of time (steady state), this mobilization rate must be balanced by the net rate of input of trace material into the volume containing the mass, m_T. This net input rate is the difference between the input of trace material through particulate deposition and the loss into the permanent sediments. Hence:

$$-m_T\left(\frac{dc}{dt}\right)_m = +\left[c_o d_o + c_e d_e\right] - (\mu\lambda_1)\left[cm_T\right] \tag{20}$$

where

c_o = concentration of trace material c on natural particulates, and

c_e = concentration of trace material c on effluent particulates.

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Combining Equations 18 and 20:

$$\frac{c}{c_o} = \frac{\lambda_2(c_o^*/c_o)(1+\sigma) + \lambda_1(1+\mu)x}{\lambda_1\mu + \lambda_2\left[(1+\sigma) - \dfrac{1 + d_e/d_o}{1 + d_e^*/d_o}\right]}$$

$$\text{for } d_e < d_e^* \qquad (21)$$

where

$$x = \frac{1 + (c_e/c_o)(d_e/d_o)}{1 + d_e/d_o} \qquad (22)$$

(and x equals c/c_o for conservative particulates).

If we apply the boundary condition that the concentration of trace metal in the sediments should approach the natural concentration as the effluent-related deposition rate goes to zero, it follows that:

$$\lambda_2/\lambda_1 = \frac{1}{(1+\sigma)(1 - c_o^*/c_o) - 1/(1 + d_e^*/d_o)} \qquad (23)$$

Combining this with Equation 21:

$$\frac{c}{c_o} = \frac{A + \left[(1-A) - B\right](1+\mu)x}{\left[(1-A) - B\right]\mu + \left[1 - B\eta\right]}$$

$$\text{for } d_e < d_e^* \qquad (24)$$

where

$$A = c_o^*/c_o,$$

$$B = \frac{1}{1+\sigma} \cdot \frac{1}{1 + d_e^*/d_o} = \frac{1}{1+\sigma} \cdot \frac{1}{\eta^*},$$

$$\eta = 1 + d_e/d_o, \text{ and}$$

$$\eta^* = 1 + d_e^*/d_o.$$

Similarly, for $d_e \geq d_e^*$, it can be shown that:

$$\frac{c}{c_o} = \frac{A + \left[(1-A) - B\right](1+\mu)x}{\left[(1-A) - B\right]\mu + \left[1 - B\eta^*\right]} \qquad (25)$$

Parameter Estimation. Equations 24 and 25 contain the four parameters c_o^*/c_o, σ, μ, and d_e^*/d_o, as well as the enhanced deposition ratio d_e/d_o. At the present time, the values of these quantities are unknown. Two of the parameters, μ and d_e^*/d_o, relate to the bulk properties of the sediments; the parameters c_o^*/c_o and σ are related to the chemical and biochemical properties of each trace material.

The trace material concentrations in the sediments around the Whites Point outfalls (Southern California Coastal Water Research Project 1973) have been used to obtain estimates of the values of these parameters. Direct measurements of effluent-related deposition rates at the sampling stations have not been made--this rate has been estimated using the deposition model predictions. As a result, only samples from stations within the region described by the deposition model (B1, C1, D1, E1, F1, B5, C5, D5, E5, F5, B18, B19, B20, and B21 as shown in Figure 1) were used in the analysis. Four of the stations (B18 through B21) were sampled using a box corer; a Phleger corer was used at the other stations. Because the characteristics of these two samplers differ to some degree, it was necessary to apply correction factors[1] to make the measurements comparable.

Predictions and Tests

All four parameters were evaluated for the zinc, copper, and chromium distributions by minimizing the sum of the squares of the deviations between the observed and predicted concentrations; the fitted values of the parameters are given in Table 1. The corresponding dependence of the trace material concentrations on the deposition rate ratio is illustrated in Figure 9.

It is immediately evident that the combined predictions of the deposition and chemical mobilization models yield substantially better agreement with the observed values than would be obtained if it was assumed that the particulates were conservative. In addition, if the oxygen-dependent reaction were neglected ($\sigma \to \infty$), the form of the predicted concentration curves would be essentially the same as for conservative particulates, but with a scaling factor. Because the resulting curves do not give as good agreement with the measured values, it is probable that the chemical mobilization process involves a reactant with a concentration variation in the sediments that is similar or identical to that of oxygen (or inversely proportional to it).

Table 1 gives the model-predicted values for the parameter f_s, the fraction of deposited material that subsequently becomes part of the permanent sediments. This is related to the parameter μ by the equation:

$$f_s = \frac{\mu}{1 + \mu} \tag{26}$$

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1. Box core/Phleger core average correction factors (and their standard errors) were obtained by comparing surface sediment concentrations in the two sample types from three regions near the 100-m contour to the northwest of the diffusers of the 90-inch outfall. The factors are Cd: 0.8 ± 0.06; Cr: 1.2 ± 0.1; Cu: 1.5 ± 0.2; Pb: 1.5 ± 0.2; and Zn: 1.6 ± 0.3.
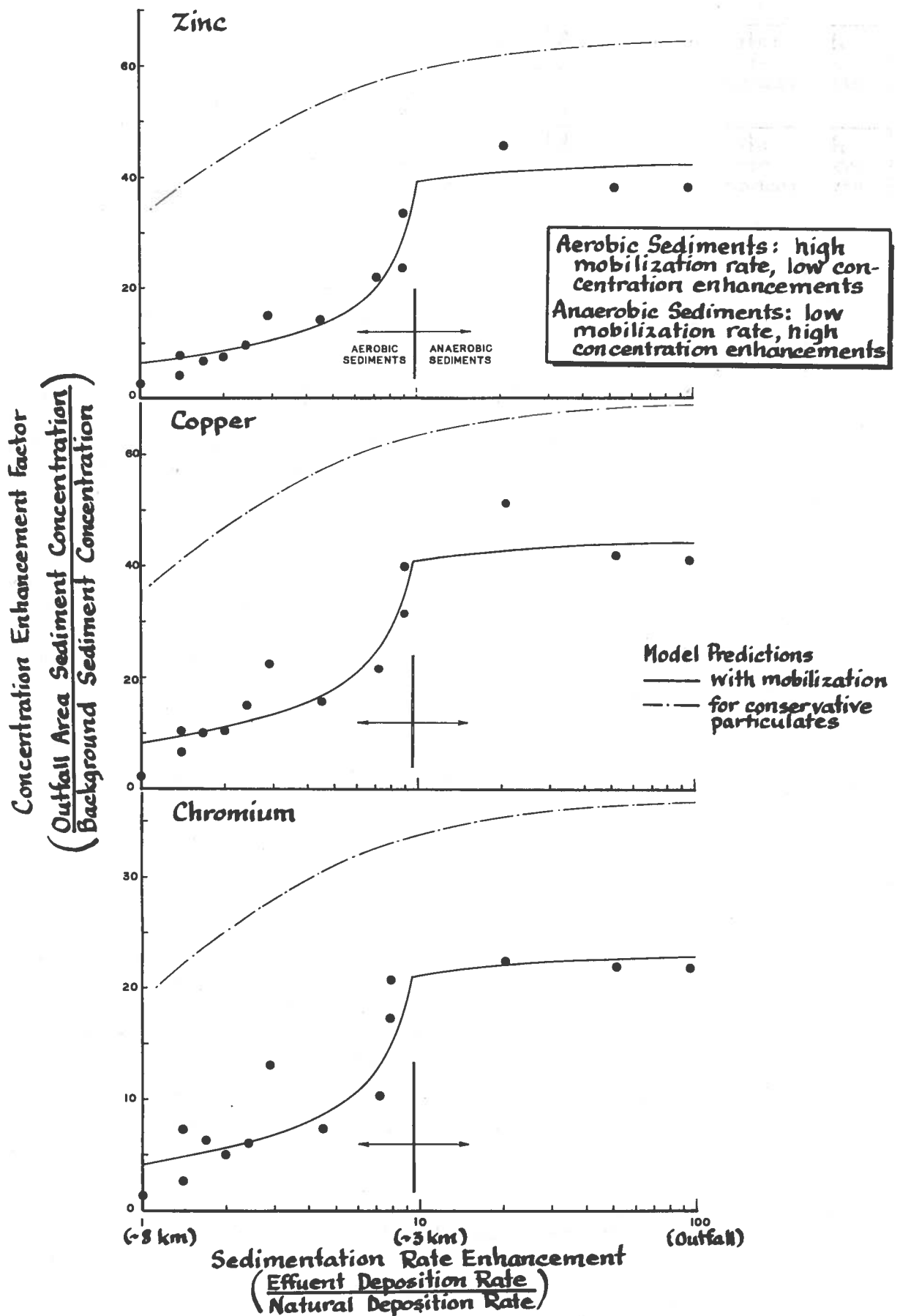
Figure 9. Predicted concentrations of zinc, copper, and chromium as a function of the enhanced deposition factors.

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Table 1. Fitted parameters.

Metal	$A = c_o^*/c_o$	$f_a = \dfrac{\sigma}{1 + \sigma}$	B	$f_s = \dfrac{\mu}{1 + \mu}$	d_e^*/d_o
Zinc	0.886	0.137	0.0784	0.77	10.0
Copper	0.876	0.179	0.0775	0.77	9.6
Chromium	0.887	0.175	0.0782	0.80	9.4
Lead	0.844	0.130	0.0798	0.77†	9.9†
Cadmium	0.876	0.038	0.0882	0.77†	9.9†

†Assumed value.

As noted earlier, because μ is a bulk property of the sediments, f_s should, in principle, be the same for all of the trace materials. This was found to be approximately true: f_s varied from 0.77 to 0.80, a scatter felt to be compatible with uncertainties in the measured values and the distribution of predicted deposition rates. Similarly, the parameter d_e^*/d_o was nearly the same for the three materials, ranging from 9.4 to 10.0.

Values of 0.77 and 9.9 were assumed for f_s and d_e^*/d_o respectively, and the observed concentration of lead and cadmium were then used to obtain estimates of the corresponding chemical parameters (resulting in a more restrictive two-parameter fit). These results are also contained in Table 1, and the predicted concentrations are illustrated in Figure 10. Again, a relatively good agreement with the measured values is obtained.

After the parameter-fitting procedures are applied, approximately 90 percent of the concentration variation[2] can be accounted for by the combined deposition-chemical mobilization model; the variation ranged from a low of 86 percent for cadmium to a high of 94 percent for zinc.

From the preceding discussion and illustrations, it is evident that the combined deposition-chemical mobilization model is capable of providing quantitative estimates of the distributions of several trace metals in the sediments around wastewater outfalls. However, this quantitative agreement may be merely a result of the parameter-fitting procedure, and the model may bear little relation to reality. To further test the model, we have also examined some of the model predictions and implications that follow from this parameter fitting. These comparisons include estimates of the buildup of effluent-related sediments, the relative rates of mobilization of trace metals in the water column, and the areal extent of a region of oxygen-depleted sediments.

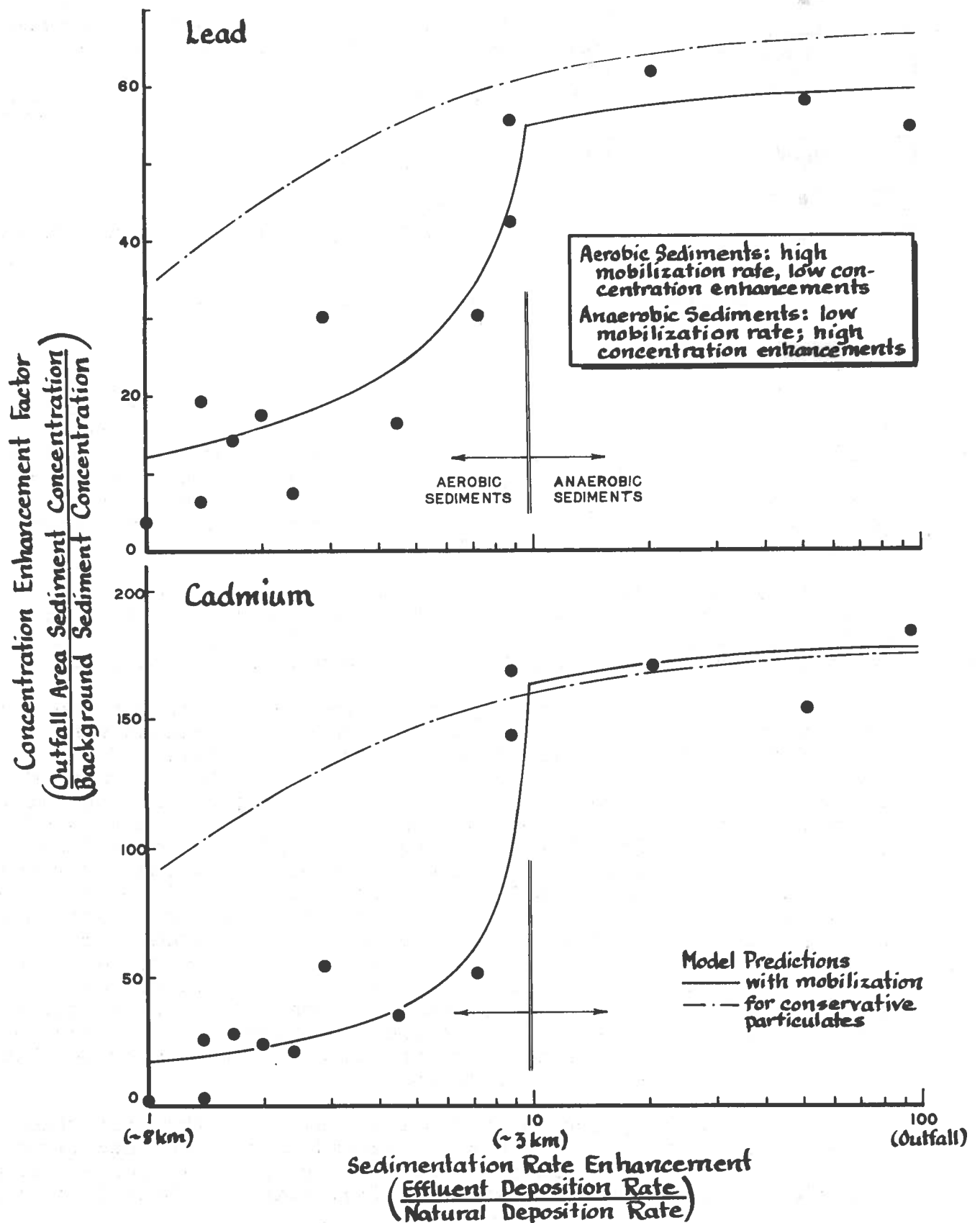2. As measured by the squared multiple correlation values.

Figure 10. Predicted concentrations of lead and cadmium as a function of the enhanced deposition factors.

<u>Sediment Buildup.</u> If biological mixing is neglected, the average[3] vertical velocity of the sea-sediment interface is given by

$$N_t = \left(\frac{\mu}{1 + \mu}\right)\frac{d_o + d_e}{\rho_s} = f_s\frac{d_o + d_e}{\rho_s} \tag{27}$$

where

N_t = sea-sediment interface velocity with respect to a fixed point, and

ρ_s = density of consolidated sediments

= 0.4 dry g/wet cu cm.

Hence, the total sediment thickness built up over the period of discharge could be calculated for a particular area if the total mass input of suspended solids was known. As these records do not exist, it was assumed that the suspended solids concentration remained constant; therefore, the average daily flow records over the period of discharge could be used. The resulting predicted sediment thickness at each of the four box core stations, shown in Table 2, ranges from 0.6 to 27 cm.

An alternate estimate of sediment thickness can be made using profiles of the concentrations of the trace metals in the sediments; profiles for copper are illustrated in Figure 11. The corresponding inferred depths are also contained in Table 2.

In general, there is relatively poor agreement. This outcome was, however, not entirely unexpected, because several mechanisms could reduce the deposition gradient near the outfall. For example, the model assumes that all the particulates discharged in the area originated from a single source--the 90-inch outfall. In fact, each of the four outfalls has made a significant contribution. This distribution of sources would tend to produce a more uniform sediment depth in the area near the outfall. A varying position of the wastefield in the water column, tidal currents, and scour would also tend to reduce the deposition rate gradients near the outfalls. The average depth predicted by the model for the three nearest stations is 15 cm, which is remarkably close to the 14.5-cm vlaue obtained by averaging the high and low values for the inferred thickness at these same stations. (The lower values are obtained by neglecting the region below the upper plateau in the concentration profiles; some motivation for this procedure is discussed in the following paragraph.)

The greatest discrepancy is at Station B18, where the predicted thickness is only 0.6 cm, yet the enhanced copper concentrations extend to at least 8 to 10 cm. This difference could result from sediment resuspension and mixing, or from mixing by benthic biota.

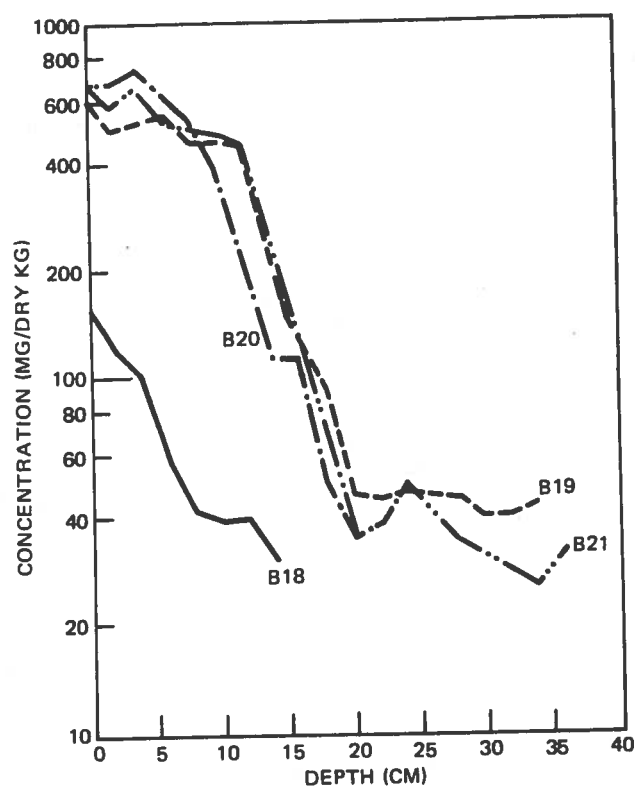3. Averaged over all measured currents.

Figure 11.   Vertical profiles of copper concentrations in sediments collected northwest of the Whites Point outfall system (box cores, July 1971).   After Galloway 1973.

Table 2. Sediment buildup resulting
from wastewater discharge.

Station Number*	Model-Predicted Thickness (cm)	Thickness Inferred From Metal Profiles (cm)
B20	27	8-20
B21	15	10-20
B19	2.5	10-20
B18	0.6	3-8

For example, the thickness of the layer of enhanced copper concentrations is almost identical to the thickness of the layer containing declining trace metal concentrations (depth interval: 10 to 20 cm) at the three stations nearest the outfalls; hence, the actual effluent-related sediments at these stations could correspond to the upper plateau region in the profiles.

Water Column Mobilization. The relative rates of chemical mobilization of trace metals in the water column predicted by the model can be compared with those observed in the laboratory study conducted by Galloway (1972a) if we make realistic assumptions about the water column chemistry. The two simplest assumptions are:

1. The chemistry of the sediments and water column are identical, but the water column oxygen concentration is given by $a = a_o$.

2. The oxygen-independent reaction (which may include biochemical processes related to bacteria, etc.) is absent in the water column.

The time-dependent concentration of trace metal on the the particulates can be obtained from Equations 18 and 23 by noting that $a = a_o$ and defining σ_w as the measure of strength of the oxygen-independent mobilization reaction in the water column:

$$\frac{c(t)}{c_e} = \left(\frac{c_o^*}{c_o}\right) + \left(1 - \frac{c_o^*}{c_o}\right)e^{-(1 + \sigma_w)\lambda_2 t} \qquad (28)$$

where

$$\lambda_2 = \frac{1}{(1 + \sigma)} \cdot \frac{\lambda_1}{[(1 - A) - B]}, \text{ and}$$

$$\sigma_w = \sigma \text{ for Case 1}$$

$$= 0 \text{ for Case 2}.$$

In Table 3, the relative mobilization rates for four of the trace metals predicted by the model for Case 1 and Case 2 are compared with the rates obtained from the laboratory study. The relative rates predicted by the model are found to be in the same order as those observed in the laboratory study, but the magnitudes are generally noticeably different. This may indicate a deficiency in the model or may reflect the fact that the laboratory environment differed from the marine environment (for example, in temperature and dilution).

Oxygen Depletion in the Sediments. By definition, the value of d_e^*/d_o is related to the critical deposition rate at which the sediments become anaerobic and ranged from 9.4 to 10.0 from fitting the trace metal distributions. Figure 4 shows that this result implies the existence of a region about 6.6 km long in which the sediments are depleted of dissolved oxygen.

In a 1957-62 study of formanifera in the area, Bandy et al. (1964) found a region of about 5.4 km extent in which no live benthic formanifera could be found. The position of this region was somewhat inshore of the oxygen-depleted area defined by the model and smaller in extent; however, the earlier observations could simply be a reflection of the influence of the two shorter out- falls (the 90-inch outfall did not begin operation until 1957) and their lower flow rates. Subjective measurements of sulfide odor and high organic content of the sediments were also made in conjunction with a Coastal Water Project study (1973) of benthic invertebrates; in Figure 12, the limits of these regions are compared with the anaerobic sediment boundaries predicted by the model. The general agreement is good.

Table 3. Relative rates of chemical mobilization of trace metals in the water column.

| Metal | Observed Rate* | Model-Predicted Rate** | |
		Case 1, $\sigma_w = \sigma$	Case 2, $\sigma_w = 0$
Lead	1.0	1.0	1.0
Copper	1.8	1.6	1.5
Zinc	2.8	1.6	1.6
Cadmium	4.4	2.1	2.3

*From Galloway 1972a.

**Given by $\dfrac{\{(1 + \sigma_w)\lambda_2/\lambda_1\}_{metal}}{\{(1 + \sigma_w)\lambda_2/\lambda_1\}_{lead}}$.

$$= \left(\frac{c_o}{c_e}\right) \frac{\sum\limits_{i}^{N}\left[\left(\frac{c_i}{c_o}\right)\left(\frac{\mu}{1+\mu}\right)\left(1 + \frac{d_o}{d_{e_i}}\right) - \frac{d_o}{d_{e_i}}\right] A_i \cdot d_{e_i}}{\sum\limits_{i} A_i \cdot d_{e_i}}$$

(33)

where A_i is the area of the $\underline{i}$th sector.

The results, which are in remarkable agreement with the estimates of Galloway (1972a), are contained in Table 4. Approximately 50 percent of the trace metals are lost on particulates that do not settle in the area. Of the remaining particulates, about 80 percent of the trace metals originally associated with them are lost by chemical mobilization: Only about 10 percent of the discharged trace metals remain in the area. The sediments therefore form a poor reservoir for the discharged metals in spite of the relative high concentrations observed on the sediments.[4] Thus, the sediment fields may act like a trace metal source of very large extent (essentially a 16-km diffuser), and this may account for the present inability to measure significantly enhanced dissolved trace metal concentrations in the area (Galloway 1972; Southern California Coastal Water Research Project 1972).

Other potential applications of the model are to predict the effects of treatment and discharge modifications on the concentrations of trace metals and oxygen in the sediments. For example, sediment trace metal concentrations may be altered by changing the biochemical oxygen demand of the suspended solids, the amount of suspended solids, and their settling characteristics as well as by reducing the heavy metal concentration on the effluent particles. With further refinement, the model may also prove useful in assessing the impact of discharging sludge into ocean basins and disposing of contaminated dredge spoils.

The present model should be used primarily to guide future research and to provide insight into the possible mechanisms governing physical and chemical sedimentation processes. For example, the model predicts that the suspended solids load (or the oxygen demand per pound of suspended solids) must be reduced by about a factor of 10 in order to eliminate anaerobic sediments from the Whites Point area. However, this factor depends critically on the form of the mass distribution of settling velocities

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4. Biological mixing cannot be incorporated into a steady-state model because the distribution of concentrations becomes time dependent due to the buildup of metals in the underlying sediments. We have attempted to incorporate an 8-cm mixing depth in the model and find that this predicts that 18 percent of the discharged metals will be retained in the previously defined area. Because of the nature of the approximation, this value should be an overestimate.

Table 4. Fraction of effluent trace metals
retained in sediments near the outfall.

Metal	Fraction of Particulates Settling within 8 km	Average Fraction of Metals Retained on the Particulates*	Overall Retention Factor
Zinc	0.50	0.18	0.09
Copper	0.50	0.18	0.09
Chromium	0.50	0.18	0.09
Lead	0.50	0.25	0.13
Cadmium	0.50	0.26	0.13
Average			0.11

*Average fraction initially on effluent particulates is 0.90
(Galloway 1972a).

for the particulates. As noted earlier, this function is highly
suspect (the required solids reduction is probably less).
Further research on benthic mixing, the effects of particulate
size on trace metal concentrations, particulate settling velocity
distributions, particulate resuspension, and direct deposition
measurements may, when combined with the features of this model,
provide an accurate and useful predictive capability.

CONCLUSIONS

The model-predicted distributions of five trace metals and dis-
solved oxygen in the surface sediments off Whites Point are
similar to those observed (or inferred) in past surveys. The
model results support the hypothesis that chemical or biochemical
mobilization of the trace metals off effluent particulates is the
dominant process in determining the fate of many metals near an
ocean outfall.

The model indicates that mobilization principally occurs as a
result of a reaction (or group of reactions) involving an oxygen-
like substance (or, conversely, the absence of a sulfide-like
reactant), except in regions where the dissolved oxygen concen-
trations are significantly reduced by the decay of organic
material. In the latter regions, the substantially slower
oxygen-independent mobilization reactions dominate and, as a
result, the trace metal concentrations in the sediments increase.

The concentrations of many metals in the sediments and water
column near an ocean outfall, or in the vicinity of the discharge
of dredge spoils, may, therefore, be determined by not only the
trace substance concentration in the waste but also the oxygen

demand of the waste and the availability of oxygen in the receiving waters. Because the ocean disposal of sewered wastewaters or dredge spoils and their associated trace substances may have important ecological consequences, it is recommended that additional tests of the model predictions and implications be made. These include field measurements of deposition rates and concentrations of various chemical properties of the surface sediments. The mobilization of trace metals off effluent particulates should also be measured under controlled conditions in a laboratory simulation of the marine environment.

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