DIGESTED SLUDGE:
DELINEATION AND MODELING FOR OCEAN DISPOSAL

Thesis By

William Karl Faisst

In Partial Fulfillment of the Requirements
for the degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

May 10, 1976

ACKNOWLEDGMENTS

The author wishes to express his thanks to his advisor, Professor Jack E. McKee, for providing pragmatic guidance and timely prodding, to Professor James J. Morgan for always asking the right question, and to Professor Norman H. Brooks for valuable suggestions regarding the disposal of sludge to the ocean.

Dr. Robert Koh's help on data analysis and computer programming was invaluable and is greatly appreciated. For technical and laboratory assistance, sincere thanks are extended to Ms. Sylvia Garcia and Messrs. Elton Daly, Joe Fontana, Larry McClellan, Phil Naecker, Ly Cong Truong, Dave Byrum, and Ed Moniz. Operation of the Coulter Counter would not have been possible without the help of Gordon Treweek. Valuable criticism of this manuscript was provided by Jasenka Vuceta, Gordon Treweek, James Hunt, Thomas Holm, and Donald Herron.

Many current and former members of the Caltech community also aided this work along the way. Particular thanks go to Carol Sibley, Susan Rottschaefer, Michael Hoffmann, George Jackson, Tom Sibley, Elaine Granger, Helen Fabel, Katie Foley, Joan Mathews, and Shirley Hughes.

Financial support for this research was provided by the people of California through the California State Fellowship Program and the people of the United States through training and research grants from the Environmental Protection Agency. Additional summer support and the actual production of this manuscript were sponsored by the Environmental Quality Laboratory of the California Institute of Technology.

This manuscript would never have been completed without the expert work of Pat McCall and Pat Rankin. Their good humor and helpful comments carried the author through the roughest times.

Finally, the author thanks his sisters, Julie van Houten and Justine Faisst, for their technical help and moral support and his parents for their help and encouragement throughout his educational career.

ABSTRACT

Experimental work was performed to delineate the system of digested sludge particles and associated trace metals and also to measure the interactions of sludge with seawater. Particle-size and particle-number distributions were measured with a Coulter Counter. Number counts in excess of 10^{12} particles per liter were found in both the City of Los Angeles Hyperion mesophilic digested sludge and the Los Angeles County Sanitation Districts (LACSD) digested primary sludge. More than 90 percent of the particles had diameters less than 10 microns.

Total and dissolved trace metals (Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were measured in LACSD sludge. Manganese was the only metal whose dissolved fraction exceeded one percent of the total metal. Sedimentation experiments for several dilutions of LACSD sludge in seawater showed that the sedimentation velocities of the sludge particles decreased as the dilution factor increased. A tenfold increase in dilution shifted the sedimentation velocity distribution by an order of magnitude. Chromium, Cu, Fe, Ni, Pb, and Zn were also followed during sedimentation. To a first approximation these metals behaved like the particles.

Solids and selected trace metals (Cr, Cu, Fe, Ni, Pb, and Zn) were monitored in oxic mixtures of both Hyperion and LACSD sludges for periods of 10 to 28 days. Less than 10 percent of the filterable solids dissolved or were oxidized. Only Ni was mobilized away from the particles. The majority of the mobilization was complete in less than one day.

The experimental data of this work were combined with oceanographic, biological, and geochemical information to propose and model the discharge of digested sludge to the San Pedro and Santa Monica Basins. A hydraulic computer simulation for a round buoyant jet in a density stratified medium showed that discharges of sludge effluent mixture at depths of 730 m would rise no more than 120 m. Initial jet mixing provided dilution estimates of 450 to 2600. Sedimentation analyses indicated that the solids would reach the sediments within 10 km of the point discharge.

Mass balances on the oxidizable chemical constituents in sludge indicated that the nearly anoxic waters of the basins would become wholly anoxic as a result of proposed discharges. From chemical-equilibrium computer modeling of the sludge digester and dilutions of sludge in anoxic seawater, it was predicted that the chemistry of all trace metals except Cr and Mn will be controlled by the precipitation of metal sulfide solids. This metal speciation held for dilutions up to 3000.

The net environmental impacts of this scheme should be salutary. The trace metals in the sludge should be immobilized in the anaerobic bottom sediments of the basins. Apparently no lifeforms higher than

bacteria are there to be disrupted. The proposed deep-water discharges would remove the need for potentially expensive and energy-intensive land disposal alternatives and would end the discharge to the highly productive water near the ocean surface.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF TABLES (continued)

LIST OF NOTATION AND ABBREVIATIONS

English

aq = aqueous

b = diffuser length

c = chemical concentration

c_{max} = center-line concentration of c

c_o = c_{max} at $x = 0$

C_i = molar concentration of the ith constituent

cfs = cubic feet per sec

cm = centimeter

D = diffusion coefficient

D_x, D_y, D_z = values of D in the x, y, z directions respectively

$D_{x,o}$ = initial x-component of D

D.O. = dissolved oxygen

e, e^- = an electron

f = log base

g = acceleration of gravity

G = standard free energy

ΔG_{ads} = change in the free energy of adsorption

ΔG_{coul} = change in the coulombic free energy

ΔG_{solv} = change in the solvation free energy

ΔG_{chem} = change in the chemical free energy

j = stoichiometric equivalents of ligand in a metal-ligand complex (Me_kL_j)

LIST OF NOTATION (continued)

$K_{a,1}$ = dissociation constant for the removal of the first H^+ from H_2S

k = stoichiometric equivalents of metal in a metal-ligand complex (Me_kL_j)

K = 10^3

K_{ads} = constant of adsorption

K* = equilibrium constant of the reduction reaction

ℓ, l = liter

L = any ligand

m_i = grams of metal captured on the ith filter

$\bar{m}$ = average metal capture

M = moles/liter

Me = any metal

MGD = million (10^6) gallons per day (1.547 cfs or 43.8 liter/sec)

mg = milligram

mm = millimeter

n = number of filters

pε = log $\{e^-\}$

pH = log $\{H^+\}$

pH_{pzc} = pH of zero surface charge

R = gas constant

$\underline{R}$ = Reynolds number

rpm = revolutions per minute

s = solid

s_i = grams of solids captured on the ith filter

$\bar{s}$ = solids specific metal capture

LIST OF NOTATION (continued)

sec = second

t = time

T = temperature

v_s = particle settling velocity

$\bar{V}$ = velocity field

y = plume height of rise

yr = year

Z_i = the electrical charge of the ith constituent

Greek

α = dissipation parameter

η = particle number concentration

μ = micron, 10^{-6} meters

$\underline{\mu}$ = absolute viscosity

ρ = fluid density

ρ_s = density of particles

σ = a unit of fluid density, $(\rho - 1) \times 10^3$

Other

[ ] = concentration in moles/ℓ

{ } = chemical activity in moles/ℓ

LIST OF NOTATION (continued)

Abbreviations

FROE = fixed residue on evaporation (see Section 2.3.1)

M.W. = molecular weight

NROE = nonfilterable residue on evaporation (see Section 2.3.1)

TROE = total residue on evaporation (see Section 2.3.1)

VROE = volatile residue on evaporation (see Section 2.3.1)

W/ = with

CHAPTER 1

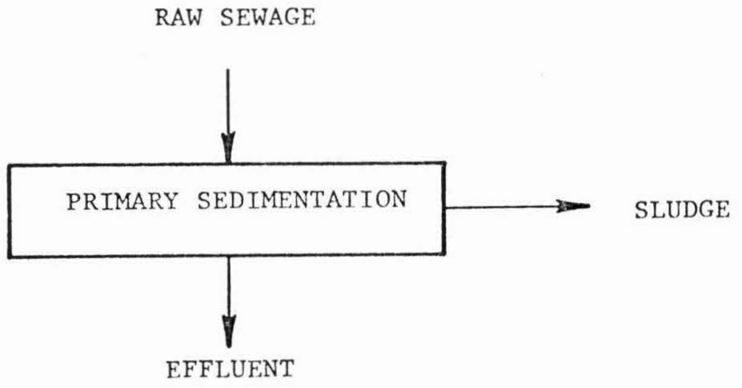
SEWAGE SLUDGE AND THE ENVIRONMENT

1.1 The Sludge Problem

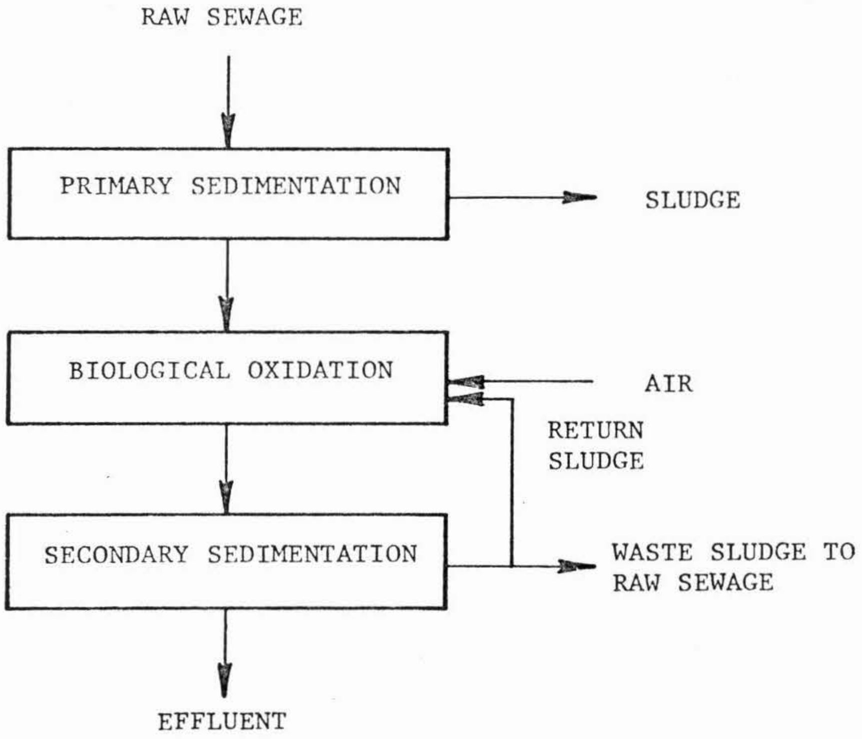
Sewage sludge, the liquid-solids suspension resulting from the sedimentation phase of wastewater treatment, presents a serious disposal problem of increasing magnitude in the United States today. Sewage sludge contains recognizable matter--grains of sand, vegetable seeds and skins, and hair--as well as large concentrations of particulate organic matter, trace metals, pesticides, chlorinated hydrocarbons, and other residues of our modern municipal and industrial society. National awareness of water pollution problems and other environmental degradation contributes to the inherent problems of sludge disposal. Existing treatment plants are upgraded to improve the effluent and associated receiving-water quality; new plants are constructed where no wastewater treatment was previously practiced. A direct product of such amelioration is more sludge. All sludge disposal must comply with stricter government regulations than have existed in the past.

In absolute terms, sewage sludge quantities are staggering. Digested sludge from primary treatment amounts to an average of 12.4 kg (27.4 lbs)/capita annually. With activated-sludge secondary treatment, the annual per capita average rises to 23.2 kg (51.1 lbs), an increase of 87 percent (Metcalf and Eddy, 1972). If tertiary treatment such as biological denitrification is mandated, an additional sludge increment can be expected. Primary treatment of sewage from approximately seven million people in Los Angeles County would result in 8.7×10^7 kg or 8.7×10^4 metric tons of sludge annually using the average figures quoted above; the total would increase to 16.2×10^7 kg or 16.2×10^4 metric tons annually with secondary treatment. Actual sludge production for all of Los Angeles County is already in excess of 14×10^4 metric tons for a combination of complete primary and partial secondary treatment. Over 10.6×10^4 metric tons of this sludge are currently discharged into the ocean. Of the total wastewater solids discharged from Los Angeles County into the ocean, almost 47 percent is digested sludge.

Schematics of typical sewage treatment processes are shown in Figure 1.1 with sludge sources as indicated. Once produced, sludge should be treated in some manner, e.g. anaerobic or aerobic digestion, dewatering, heat drying, direct incineration, wet oxidation, etc., and disposed of to some final sink, the ocean or the land (as fill or fertilizer). In some instances raw sludge is dewatered and disposed of directly by landfilling. The possible treatment and disposal schemes for sludge are summarized in Figure 1.2. Sludge flows usually constitute less than two percent of the total flow in a treatment facility, but sludge processing and disposal represent 30 to 60 percent of the capital and operating costs for most plants.



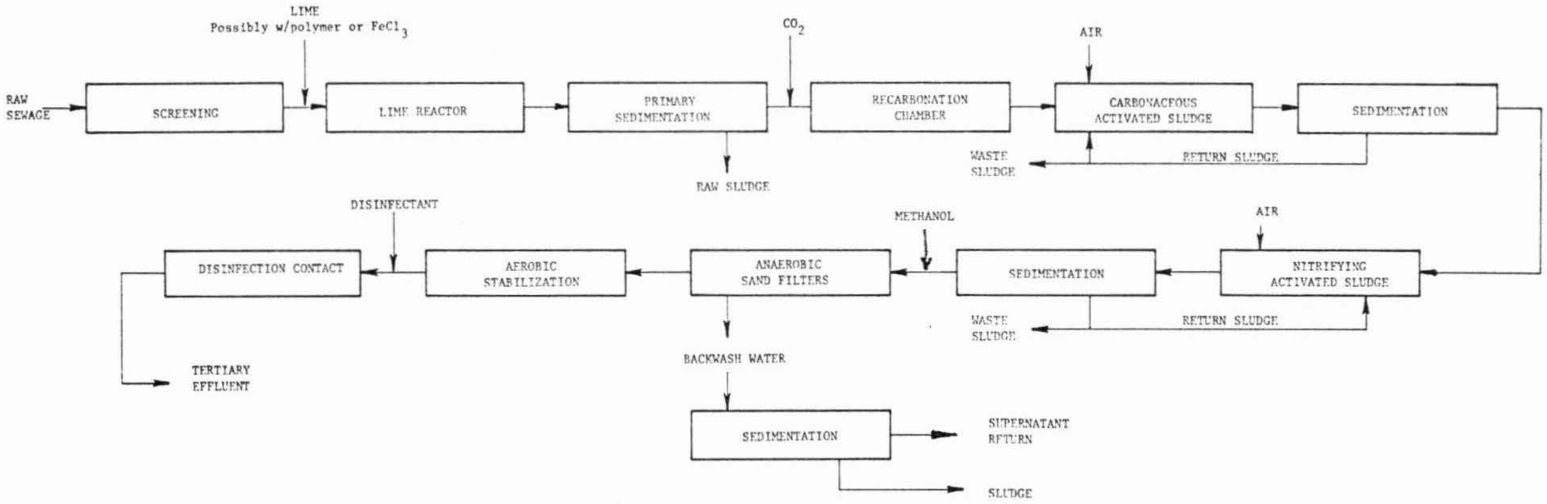
a. Primary Treatment



b. Secondary Treatment

FIGURE 1.1

Typical Sewage Treatment Processes



c. Tertiary Treatment

FIGURE 1.1c

Typical Sewage Treatment Processes

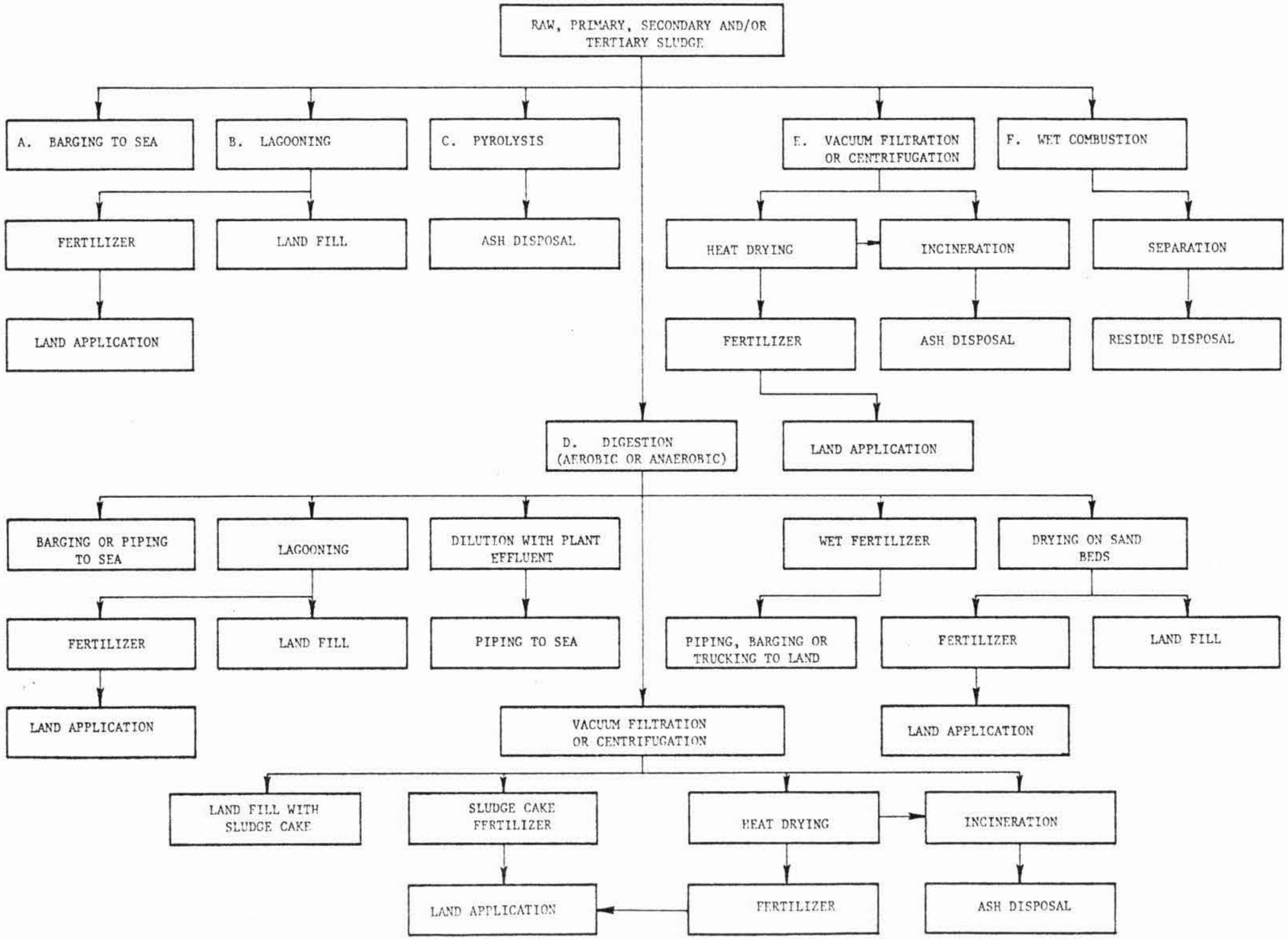


FIGURE 1.2

Sludge Processing

1.2 Environmental Impacts

Once sludge is placed in a final sink it may be "out of sight" and "out of mind", but many of its constituents are potentially harmful. Direct adverse environmental impacts from sludge disposal are difficult to document. Many sludge trace metals, e.g. cadmium (Cd) and mercury (Hg), can cause illness or death to man or other organisms. Industrial discharges of Cd and Hg in Japan have been connected with the tragic "Itai-Itai" and Minamata diseases, respectively. In the case of mercury, the methyl mercury species entered the human food chain through fish which were subsequently eaten by the natives.

It cannot be overemphasized, however, that trace metal toxicity is a function of concentration. Many metals, e.g. calcium (Ca), magnesium (Mg), and sodium (Na) are macronutrients necessary in large concentrations for life; others, micronutrients, e.g. iron (Fe), copper (Cu), zinc (Zn), and vanadium (V), are necessary in small amounts. Still others, e.g. Cd, lead (Pb), and gold (Au), are not known to be requirements, of any life form. For those metals with identified requirements a deficiency develops if background levels are below such requirements. At higher concentrations, the ecosystem may still be in balance, while at extremely high levels toxicity occurs. Copper is a classic example, appearing as an alternate to iron (Fe) in the blood of some vertebrates. Copper is also a favored algacide.

Halogenated organics, e.g. DDT (dichlorodiphenyltrichloroethane) and PCB (polychlorinated biphenyls), are also present in sludge. DDT has been linked to reproductive failures of bald eagles, osprey, and peregrine falcons (Hickey and Anderson, 1968), and of brown pelicans (Anderson and Hickey, 1970). PCB or trace contaminants remaining from its manufacture have been toxic to chick embryos (Vos, et al., 1970).

The particulate matter in sludge can have many environmental impacts. A substantial portion of the particulates are oxidizable forms of organic carbon. Myers (1974) found that 34 percent of centrate particles discharged from the Los Angeles County outfalls at Whites Point are organic carbon and 35 percent of that 34 percent (12 percent of the total) were easily decomposed. The biochemical degradation of these organics may deplete dissolved oxygen (D.O.) in the water column with a corresponding alteration of biochemical pathways and of the oxidation-reduction (redox) potential of ocean waters or sediments. The depletion of D.O., an essential element for all life forms higher than bacteria, can cause serious alteration of marine communities. Solubility of many trace metals may also be drastically changed in the receiving sink.

Upon discharge into the ocean the particulates from sludge may attenuate light as it penetrates through the water column, thereby decreasing the euphotic depth. Peterson (1974) measured such light attenuation by the sewage effluent field off Whites Point. The euphotic depth was reduced 30 to 60 percent. The discharge there, which is a mixture of primary effluent and digested sludge centrate, increased in quantity from 1934 to 1969 (see Figure 1.3). The kelp beds once quite extensive in this area disappeared by 1958. These

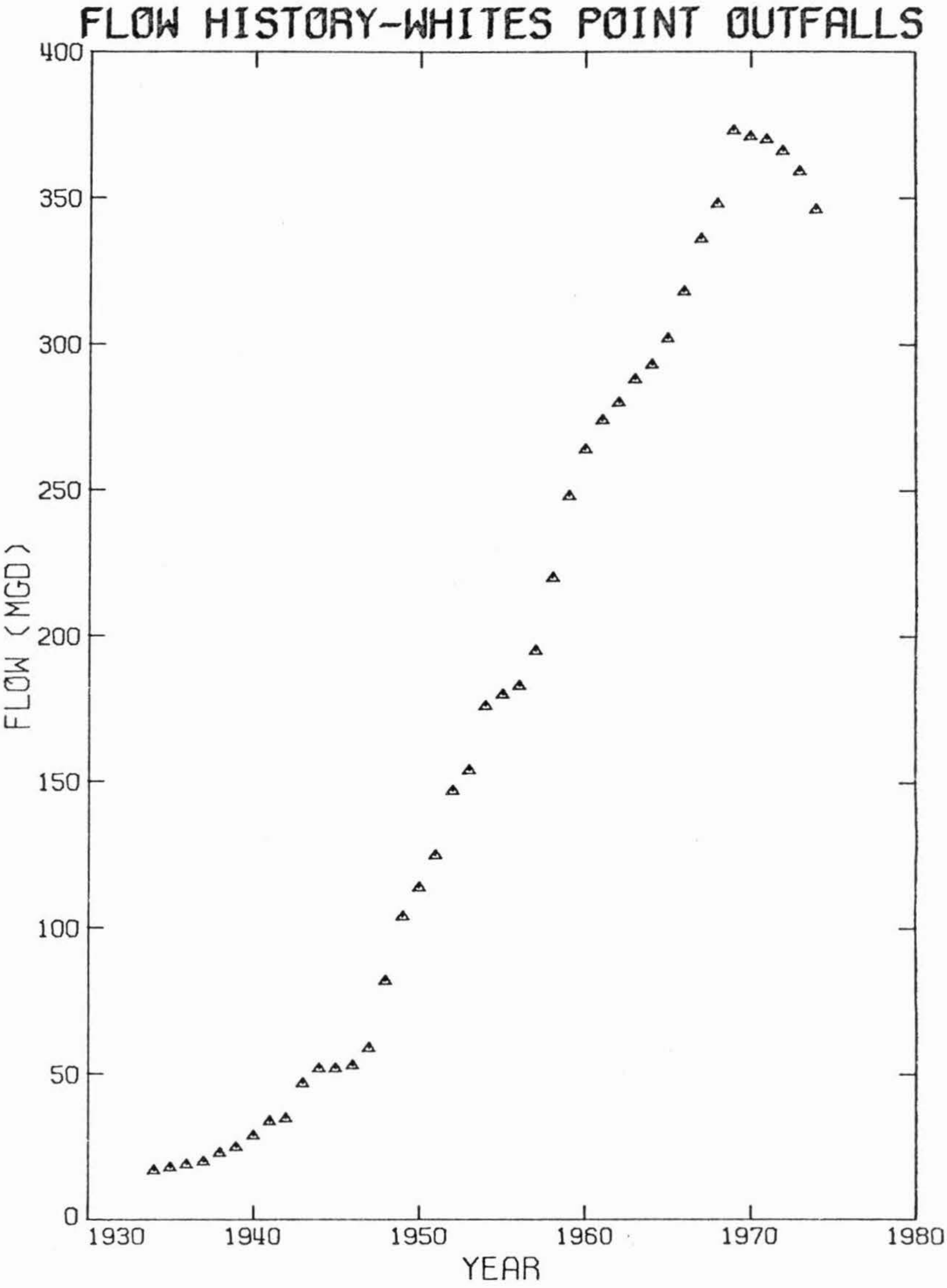


FIGURE 1.3

Flow History From the LACSD Whites Point Outfalls
Data from North (1972) and SCCWRP (1975)

beds, made up of the giant kelp Macrocystis pyrifera, are important to the coastal ecosystems of southern California because they form the basis for a diverse and highly productive marine community. The giant kelp is also harvested commercially.

There are two implications of the reduced euphotic depth. First, the absolute amount of light available for photosynthesis is reduced, decreasing the total possible productivity. Second, decreased light penetration also reduces the bottom area with adequate light to establish kelp plants, thus reducing the total habitat.

Myers also detected an accumulation of organic carbon of terrestrial origin in the sediment adjacent to the outfalls. The Southern California Coastal Water Research Project (SCCWRP) (1973) reported an extensive anaerobic sediment zone around the same outfalls as shown in Figure 1.4. The accumulation of sewage particulate matter has apparently "blanketed" local areas with rocky bottoms, Grigg and Kiwala (1970) postulated that the kelp and other organisms requiring rocky bottoms for attachment or shelter might be unable to propagate under these conditions.

Large populations of sea urchins have also been reported adjacent to the Whites Point outfall (North, 1972). Urchins normally eat the detrital fallout from the kelp forests. If urchin populations expand extensively and the detritus is inadequate to support all the population, they will attack the kelp plants directly, severing the holdfasts which anchor the kelp to the bottom. The detached adult plants drift away and thus provide no spores to replenish the local

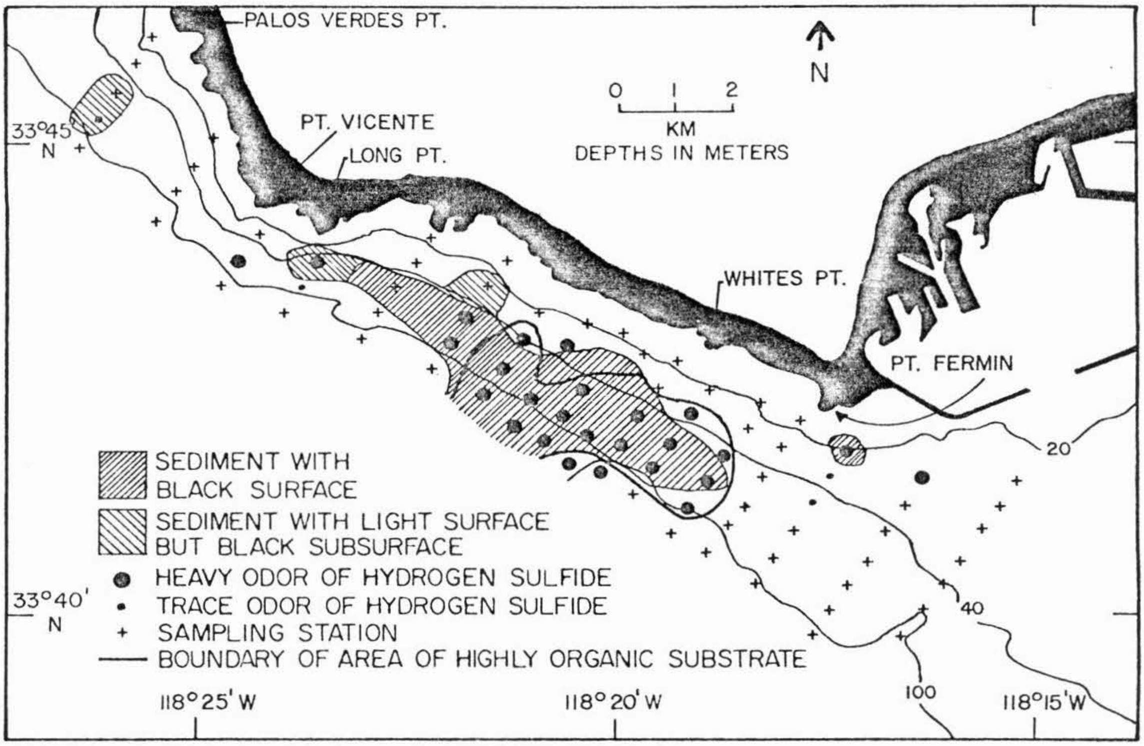


FIGURE 1.4

Qualitative Analyses of Sediments off Palos Verdes, July, 1971

Source: SCCWRP, 1973.

Note: More recent qualitative analyses of sediments (1973, 1974, and 1975) indicated that the zone of anaerobic surface sediments and strong hydrogen sulfide odors may have decreased substantially in size. (U.S. EPA and Sanitation Districts of Los Angeles County, 1976).

kelp population. Any spores that do settle from nearby plants may be devoured before they are large enough to reproduce; thus the forests die off or disappear.

Once the kelp is gone, the urchin population decreases owing to the lack of food. Without the local urchin overpopulation the kelp may naturally re-establish itself. In the area off the Palos Verdes Peninsula, however, young urchins apparently graze on the sludge blanket covering the ocean bottom or directly absorb limiting nutrients of sewage or sludge origin from the water. There is then a constant semi-starved urchin population that effectively prevents kelp reproduction.

The trace metals in sludge that are mainly associated with particles may also have important environmental implications. As will be discussed later, sludge particle size and density affect the settling velocity of the sludge and hence the lateral spread of the sludge following marine discharge. The sludge and effluent discharges by both the City of Los Angeles and County Sanitation Districts of Los Angeles County behave as buoyant plumes in the ocean. (See Chapter 3 for a more detailed discussion of this subject.) Advection and diffusion move the "clouds" away from the outfalls while flocculation and sedimentation act to deposit the sludge.

Organisms in the marine environment such as zooplankton and bivalves may also affect the sewage particles. These organisms are suspension feeders which extract nutrients from the water by removing suspended particulate matter. Large particles are physically filtered by cilia or other appendages. Smaller particles may be sieved onto or impacted (adsorbed) by mucous nets secreted by the organism. The nets are subsequently eaten by their producer. Some suspension feeders consume all material they catch, expelling the inedible portion with the waste products of the edible fraction. Others "sort" the edible from the inedible before ingestion, expelling the inedible as pseudofeces.

Jørgensen and Goldberg (1953) found that the ascidran *Ciona* (a tunicate) and the clam *Mytilus* retained all one- to two- micron graphite particles while the oyster *Crassostrea virginica* retained two to three micron particles but passed one to two micron particles. The echiuroid worm *Urechis caupo*, which feeds with a mucous net, completely retained *Palinurus* hemocyanin (M.W. 450,000). Later work by Haven and Morales-Alamo (1970) used the Coulter Counter to check particle-size distributions over the size range one to 12 microns of both natural and artificial suspension filtered by oysters (C. *virginica*). The oysters retained natural particles in the range one to three microns with one-third the efficiency of larger particles; with clays the efficiency was one-half that for one to two micron particles as for larger particles.

The distance between latero-frontal cilia is assumed to be the factor which determines the smallest particle size that can be completely retained by suspension feeders. If trace metals in sludge particles are associated with particular size fractions, the uptake of these metals may exceed by many times their actual levels in the total water column. Trace metals may thus be concentrated biologically. Particle-size specificity by important marine organisms might point toward removal of certain particle-size fractions or the breakdown of sludge into smaller particles before discharge.

Trace metal build-up has been noted around both the Whites Point outfalls of the County Sanitation Districts of Los Angeles County and the City of Los Angeles Hyperion outfalls in Santa Monica Bay. (These facilities and their associated sludges will, hereafter, be referred to as LACSD and Hyperion, respectively.) Galloway (1972) found abnormally high concentrations of Cd, chromium (Cr), Cu, Pb, and Zn at Whites Point. Typical surface isoclines for Cu are shown in Figure 1.5. A decrease in concentration with depth for copper (see Figure 1.6) indicated that the buildup of Cu increased as flow from the outfall increased. Similar surface concentrations were documented by SCCWRP (1973) near the Hyperion sludge outfall as shown in Figure 1.7. Burland, et al. (1974) have also suggested that wastewater flows may contribute a significant portion of the silver (Ag), Cd, Cr, Cu, Pb, and Zn entering the sea off southern California.

1.3 Research Objectives and Thesis Organization

1.3.1 Research Objectives

The preceding sections have outlined the magnitude of the digested sewage sludge problems and documented known, probable, and

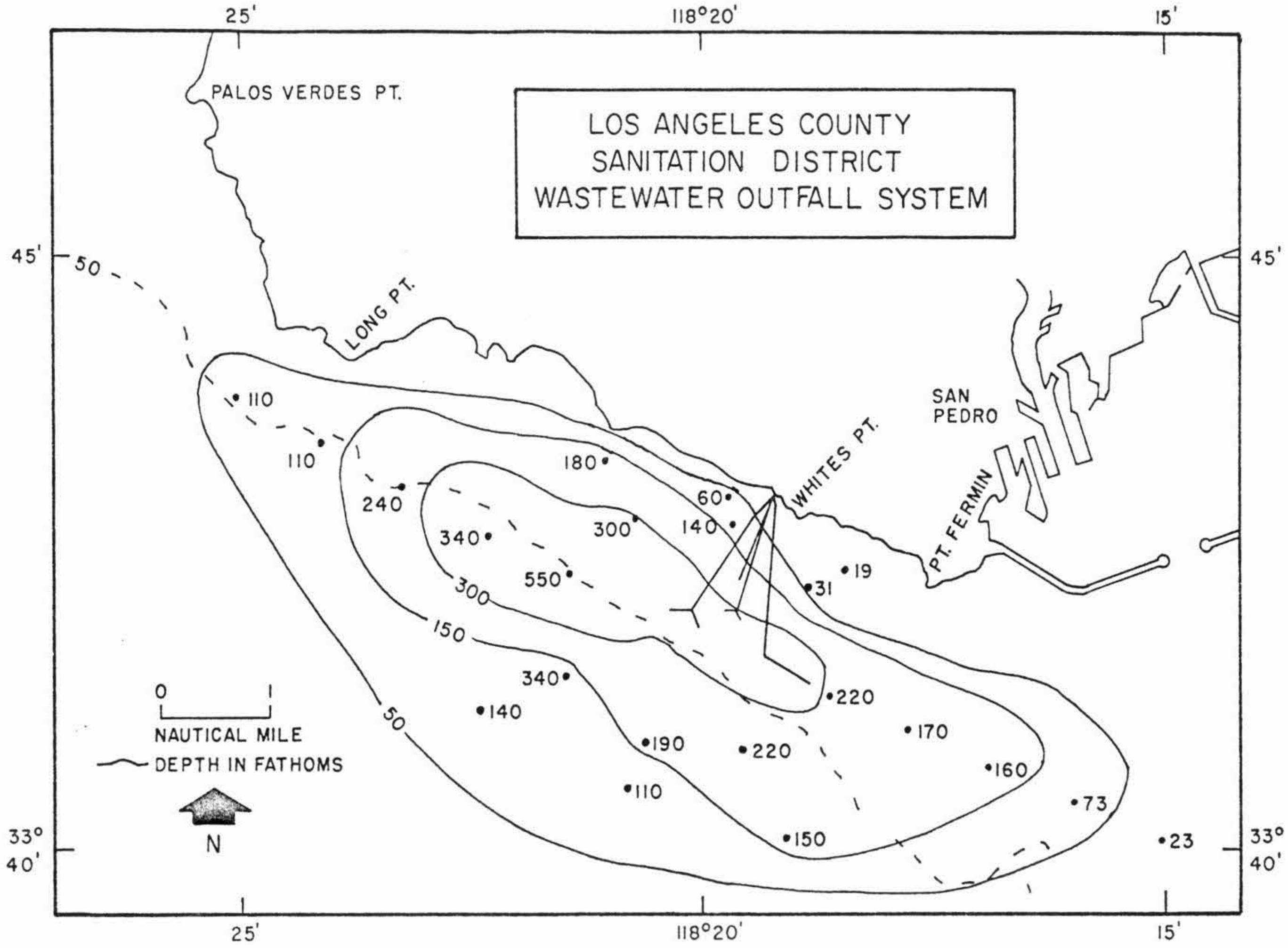


FIGURE 1.5

Copper Concentrations (mg/dry kg) in the Surface Sediments Adjacent to the Whites Point Outfalls of LACSD

Source: Galloway, 1972.

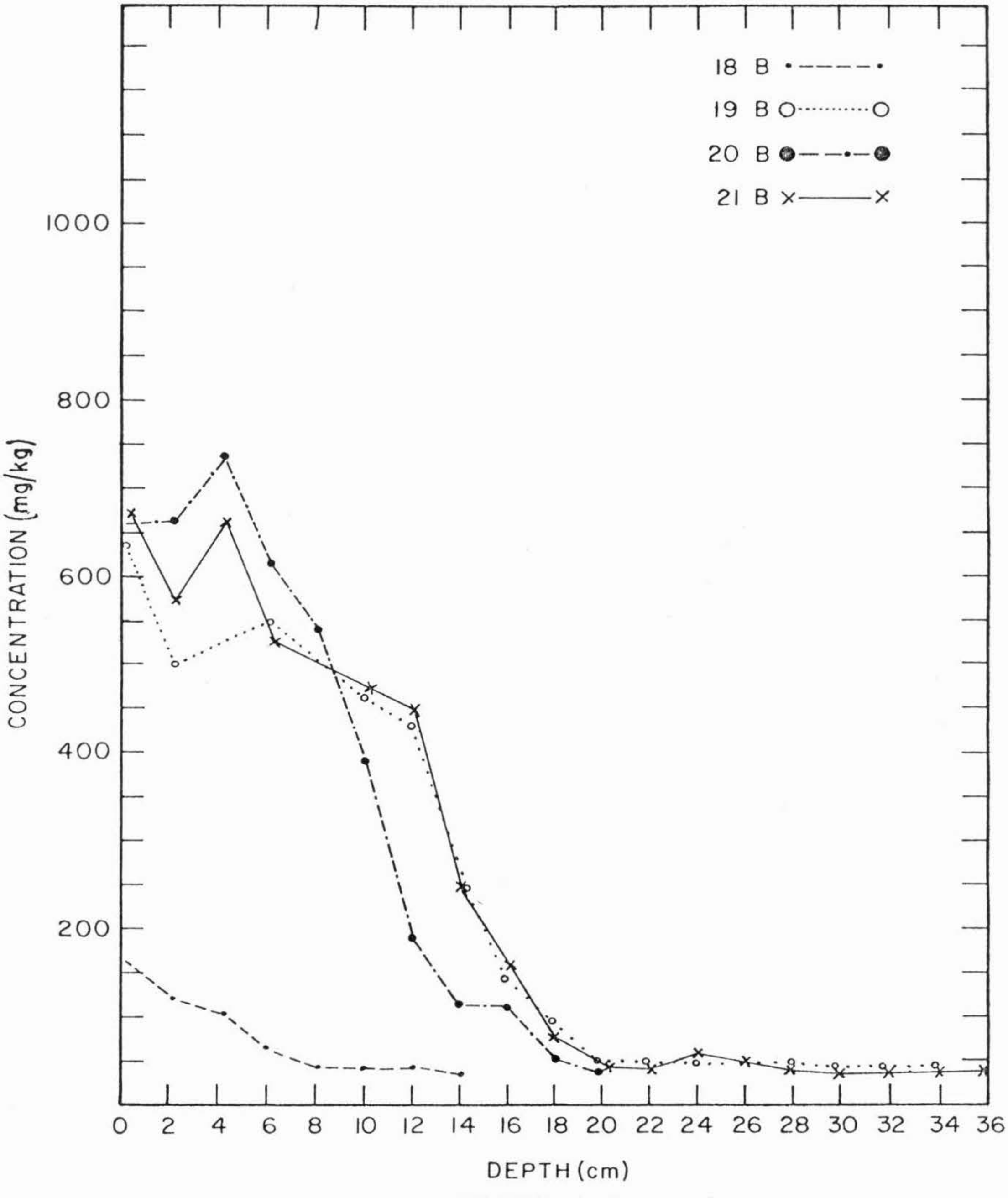
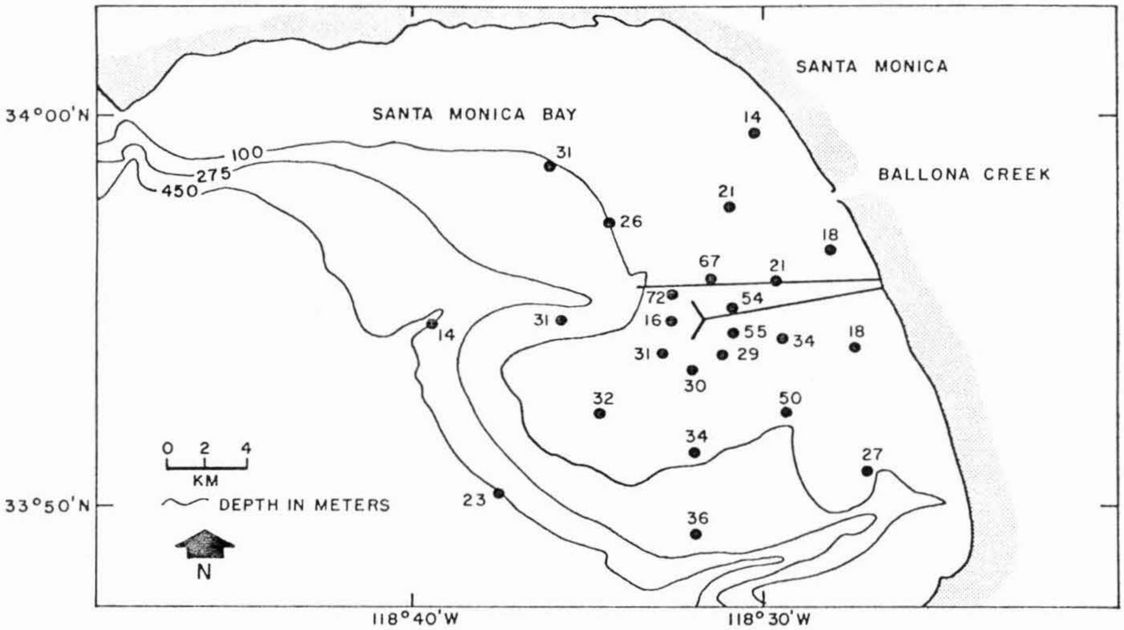


FIGURE 1.6

Copper Concentrations in Four Sedimentary Columns Adjacent to the Whites Point Outfalls of LACSD

Core 18B is furthest from the discharge (∿ 7 km), 19B about 3 km, 21B, about 1 km, and 20B at the 90-in outfall. Water depth for all samples was ∿ 90 m. Source: Galloway, 1972.

a. Phleger Cores, June, 1970.



b. Box Cores, July, 1971.

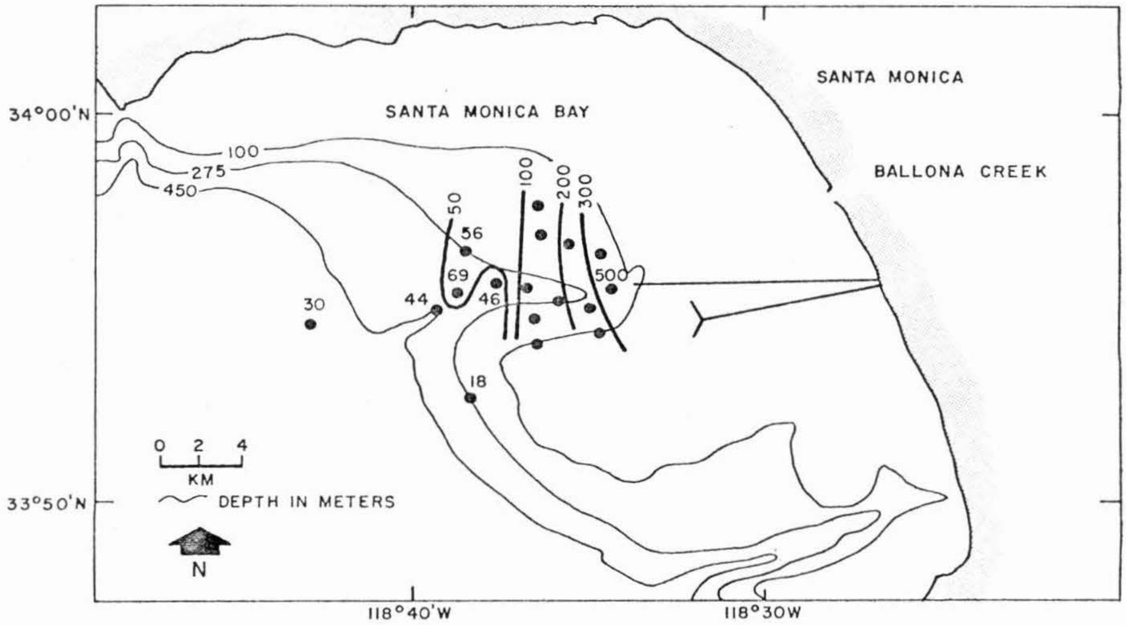


FIGURE 1.7

Copper Concentrations (mg/dry kg) in Surface Sediments Around the Hyperion Outfall System

Source: SCCWRP, 1973.

possible sludge environmental impacts. The objectives of this research are twofold:

I. Experimental

1. To determine the size distribution of representative samples of digested sewage sludge and estimate the specific-surface area of such sludge.

2. To measure the trace metal concentrations associated with different particle-size fractions.

3. To measure the physical-chemical interactions of sludge particulate matter and trace metals during oxic mixing with seawater and during sedimentation in seawater.

II. Modeling

1. To use the results of the experimental work together with available oceanographic data to propose disposal schemes for sludge off southern California.

2. To predict the hydraulic and physical-chemical behavior of sludge solids and trace metals.

3. To assess the major environmental impacts of such schemes.

It should be noted that sludge disposal to the ocean is at odds with current state and federal regulations and laws, particularly Public Law 92-500. Sludge disposal to the ocean is, however, a cost-effective low-energy means of permanently ridding society of wastewater solids. Alternative disposal schemes will probably require large outlays of capital and high operating costs while using energy in a manner that must contribute to the already significant local air pollution.

If an environmentally sound plan for ocean disposal can be developed, the benefit to southern California will be substantial.

Trace metals and particle-size distribution were chosen as system parameters because they are essential model inputs for any simulation of ocean disposal of sludge. Neither of these important properties has been measured adequately by previous researchers. A fine-scale examination of particle-size distribution has potential significance for such difficult tasks as sludge dewatering and for other disposal practices, such as landfilling and land spreading. In past experiments dewatering sludge has generally been treated as a black box, to be manipulated only from the outside without considering what is actually happening at the particle level.

1.3.2 Thesis Organization

In the presentation that follows, digested sludge will be characterized in Chapter 2. This delineation includes a review of previous work, chemical and particle-size measurements, and the results of experiments on physical-chemical interactions of sludge with seawater. The proposed plan for ocean disposal is presented and modeled in Chapter 3, followed by an assessment of environmental impacts. Chapter 4 includes a summary, conclusions, and recommendations for future work. A series of Appendices contains operational techniques and experimental data.

CHAPTER 2

THE DIGESTED SLUDGE PARTICLE-TRACE METAL SYSTEM:
I. SLUDGE CHARACTERIZATION—A REVIEW
II. PHYSICAL AND CHEMICAL MEASUREMENTS
III. SLUDGE INTERACTIONS WITH SEAWATER

The environmentally sound disposal of digested sewage sludge requires a detailed knowledge of sludge constituents and the biological processes of sludge digestion. In Part I of this chapter, existing information about the sludge particle-trace metal system is reviewed. The measurements from this work on sludge particle-size distributions and sludge trace metals are presented in Part II. Experiments conducted to measure the physical-chemical interactions of sludge solids and trace metals with seawater are described and the results discussed in Part III.

PART I. CHARACTERIZATION OF DIGESTED SEWAGE SLUDGE: A REVIEW

2.1 Introduction

The following section summarizes the biological process used to treat raw sludge that originates from the sources noted in Figure 1.1. The physical and chemical properties of the resulting digested sludge are then tabulated, and the physical-chemical interactions of sludge solids and trace metals are also reviewed.

2.2 Sludge Digestion

Primary and/or secondary sewage sludge can be digested aerobically or anaerobically. Both methods result in a reduction of total solids for disposal and in an improvement of dewatering and other handling properties. The anaerobic pathway is chosen most frequently because of low biological solids production, a high degree of waste stabilization, zero oxygen demand, and methane fuel production. Slow bacterial growth and low biomass in the anaerobic digesters are possible shortcomings owing to low resistance to process upset. (McCarty, 1964a,b,c,d).

With conventional anaerobic digestion, a hydraulic retention time in the reactor of 10 to 30 days is typical. The reactor temperatures are maintained at 37°C (99°F) for the mesophilic range or 55°C (131°F) if thermophilic digestion is practiced. As can be seen in Figure 2.1, the minimum retention time (equivalent to maximum system efficiency) occurs near these temperatures. Different strains of bacteria apparently predominate at these local optima (Rowe, 1971).

The biological processes of anaerobic digestion are summarized in Figure 2.2. The two-step system depends first on facultative and anaerobic bacteria (Pseudomonas, Flavobacterium, Alealigenes, Enterobacter) to decompose complex fatty acids, proteins, and carbohydrates into organic acids, alcohols, aldehydes, ammonia, and a refractory humus residue. A second group of bacteria (Methanobacterium, Methanosarcina, Methanococcus) converts the organic acids (including amino acids) into methane (CH_4), carbon dioxide (CO_2), ammonium ions (NH_4^+), bicarbonate, and bacterial bodies. The most important reaction pathways for CH_4 formation are acetic acid cleavage (70%) and CO_2

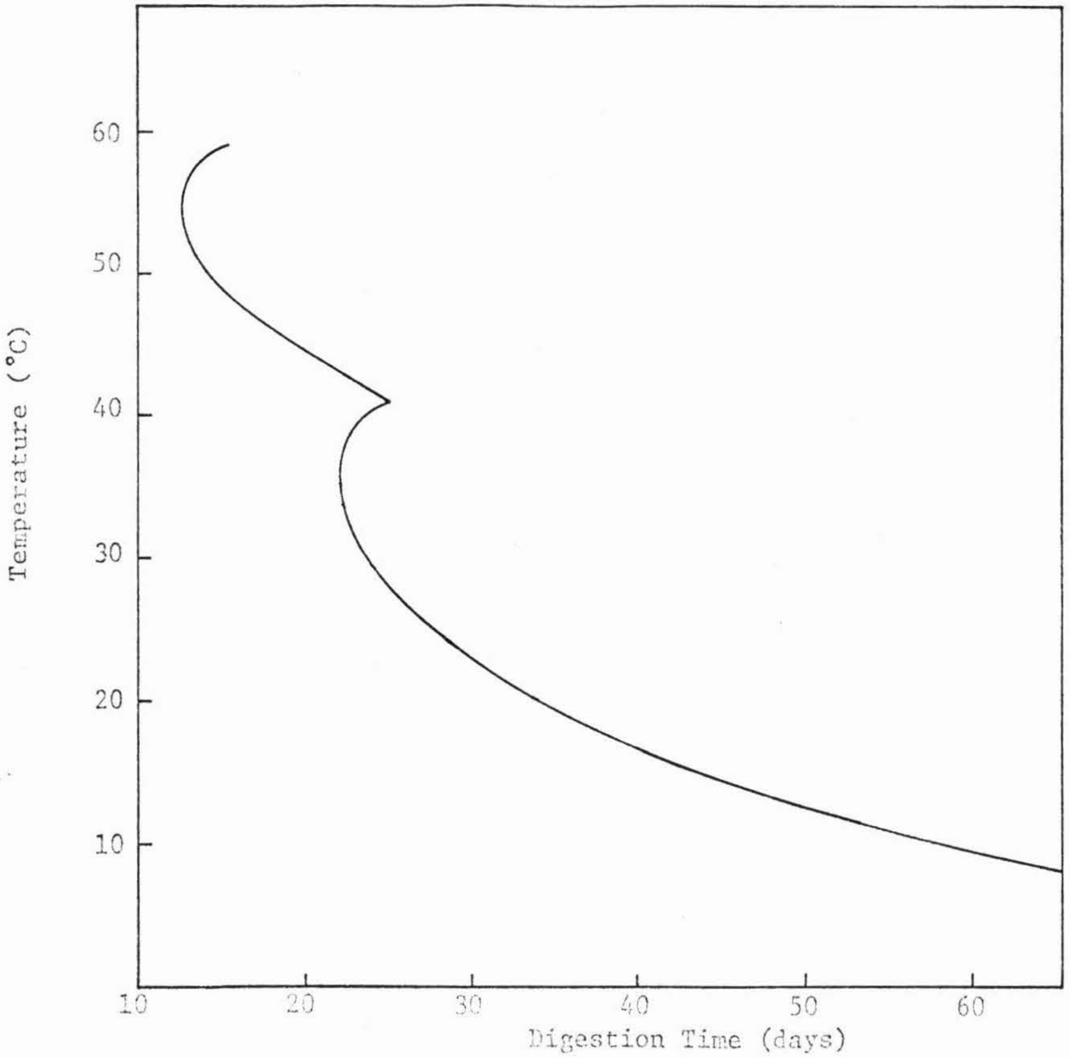


FIGURE 2.1
Time Required for Sludge Digestion

Source: Rowe, 1971.

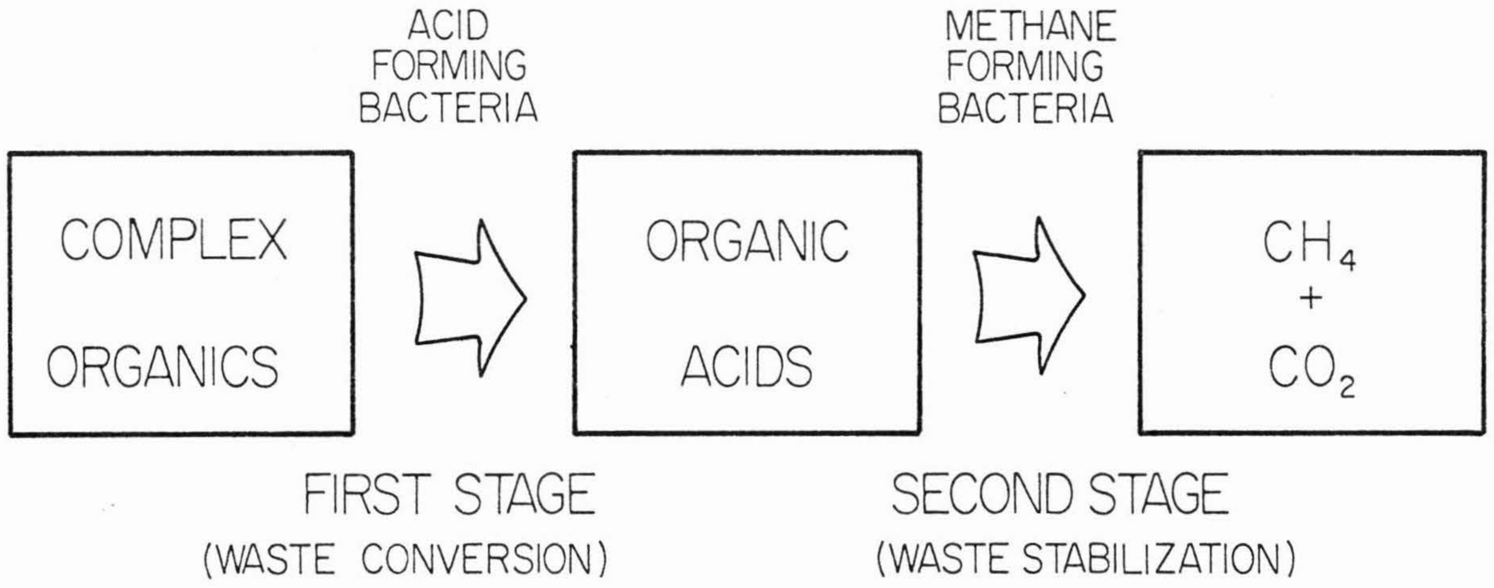


FIGURE 2.2

The Two Stages of Anaerobic Treatment Consist of Waste Conversion by Acid Forming Bacteria Followed by Stabilization with Methane Forming Bacteria

Source: McCarty, 1964a.

reduction (30%). Typical organic acids are listed in Table 2.1 and the major methane formation pathways are shown in Figure 2.3. Some production of hydrogen sulfide (H_2S) also occurs with sulfur from protein and sulfate ion (SO_4^{2-}) reduction serving as the principal sulfur sources.

In the two-step reaction described above, the methane producing step is rate limiting; the bacteria involved at this stage are also more sensitive to toxic materials (trace metals, cyanides, etc.), pH changes, and temperature alterations. [Recent work on methane formation by Finney and Evans (1975) has indicated that methane production may be limited by transfer processes at the cell surface rather than by slow biological growth.] Any disruption of methane production is followed by an accumulation of organic acids forcing the pH to drop. This pH change further inhibits methane conversion.

2.3 Physical Properties of Sludge

2.3.1 Water Content

The water content of sludge is typically measured by evaporation to constant weight at 105°C. The remaining solids, known as total residue on evaporation (TROE), include both suspended and dissolved matter. The dissolved matter is known as non-filterable residue on evaporation (NROE). TROE ranges for typical sludges are:

- raw primary sludge: two to seven percent by weight (20,000 to 70,000 mg/l)
- unthickened activated sludge: 0.2 to 1.0 percent by weight (2,000 to 10,000 mg/l)
- trickling filter sludge: four to seven percent by weight (40,000 to 70,000 mg/l)

TABLE 2.1

Typical Organic Acid Intermediates

Acid	Chemical Formula
Formic Acid	$HCOOH$
Acetic Acid	CH_3COOH
Propionic Acid	CH_3CH_2COOH
Butyric Acid	$CH_3CH_2CH_2COOH$
Valeric Acid	$CH_3CH_2CH_2CH_2COOH$
Isovaleric Acid	$(CH_3)_2CHCH_2COOH$
Caproic Acid	$CH_3CH_2CH_2CH_2CH_2COOH$
Alanine	$CH_3CH(NH_2)COOH$
Cysteine	$CH_2(SH)CH(NH_2)COOH$
Leucine	$CH_3CH(CH_3)CH_2CH(NH_2)COOH$

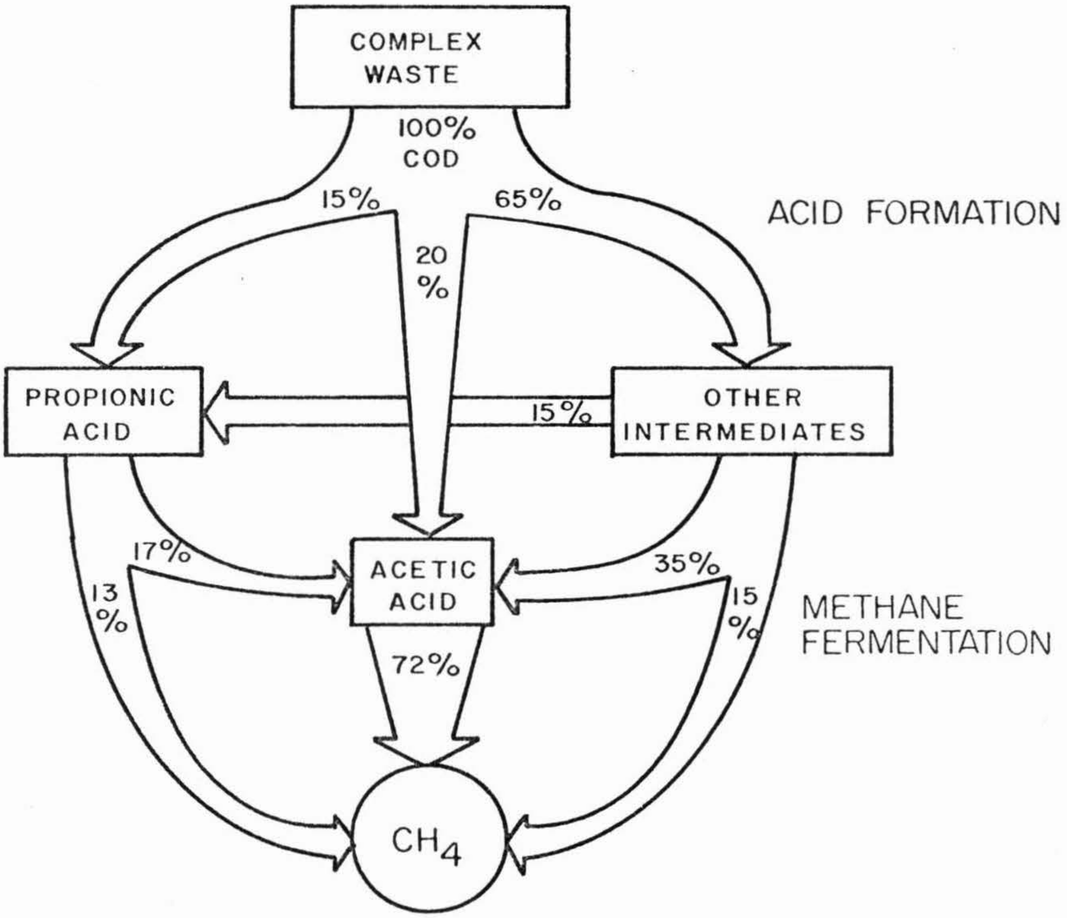


FIGURE 2.3

Pathways in Methane Fermentation of Complex Wastes such as Municipal Waste Sludge

Percentages represent conversion of waste COD by various routes.

Source: McCarty, 1964a.

- digested primary sludge: two to six percent by weight (20,000 to 60,000 mg/l)

The TROE of raw sewage will usually be less than 2,000 mg per liter.

When solids are measured by evaporation, volatile compounds such as ammonium bicarbonate (NH_4HCO_3), ammonium carbonate ($(NH_4)_2CO_3$), and some organics are lost. Solids volatilized by combustion at 550°C (VROE, volatile residue on evaporation) vary from 60 to 80 percent for raw sludge to 30 to 60 percent for digested sludge. The remaining solids are fixed residue on evaporation (FROE).

The main importance of sludge water content is its influence on handling ease and transportation costs in disposal schemes. Separation of sludge solids from the liquid phase is typically done by air flotation, vacuum filtration, centrifugation, or drying on sandbeds. At five percent solids by weight, 19 tons of water must be hauled to a disposal site to dispose of one ton of solids. Since sludge is often generated some distance from viable disposal sites, the energy costs for hauling non-dewatered solids can be prohibitive. Liquid sludge can also be piped to suitable sites for disposal or utilization. For disposal schemes such as sanitary landfilling, a fairly-high solids content facilitates handling procedures.

The liquid fraction of the sludge contains a substantial biochemical oxygen demand (BOD), a large share of the nitrogen and phosphorus in the sludge, and the fine solids (particles) not captured by dewatering. If the solids and liquids are separated, the liquid stream must also be treated. In such separation, the sludge loses the nutrients most needed if the sludge is to be used as anything more than a soil conditioner when applied to the land.

2.3.2 Particle Size and Particle Density

An introduction to the importance of particle size distribution for sludge has already been presented in Chapter 1. Particle size together with particle density also affect the terminal settling velocity of particles released in the water column. For particles settling in environments where the Reynolds number

$$\underline{R} = \frac{\rho d v_s}{\mu} \tag{2.1}$$

is less than 0.5, Stokes Law holds.

$$v_s = \frac{g}{18} \frac{\rho_s - \rho}{\mu} d^2 \tag{2.2}$$

where v_s = particle settling velocity

g = acceleration of gravity

ρ_s = mass density of particle

ρ = mass density of fluid

μ = absolute viscosity

d = particle diameter

Both ρ and μ vary with temperature as will be discussed in Chapter 3. For natural materials, ρ varies from close to 1.0 g/cm^3 for some biological growths to 2.65 g/cm^3 for typical siliceous minerals to about 4.0 g/cm^3 for garnet sands. For Stokes Law settling, $v_s \alpha d^2$ and particle diameter is the more sensitive parameter. The importance of the density term $(\rho_s - \rho)$ on sludge sedimentation is difficult to evaluate. The density difference will be discussed further in Section 2.6.2.

The solids in sewage have been classified by size according to Rudolfs and Balmat, (1952) as:

1.	settleable solids	>100 μ
2.	supracolloidal solids	1 μ to 100 μ
3.	colloidal solids	1 mμ to 1 μ
4.	soluble solids	< 1 mμ

Typical sedimentation processes in sewage treatment remove the settleable and some supracolloidal solids. Biological treatment and/or chemical coagulation can be used partially to remove colloidal and soluble solids. The fractions removed by sedimentation and/or biological treatment are raw sludge.

Information about the particle-size distribution of digested sludge is very limited. Raw and digested sludges from the City of Los Angeles Hyperion Treatment Plant have been wet-sieved, apparently using standard soil sieves. The data from this work appear in Table 2.2 (Garber and Ohara, 1972) and in Figure 2.4 (Garber, et al., 1975). The visible matter was listed as seeds, vegetable skins, fibers, bits of plastic sheeting or film, bits of bone, pieces of metal foil, fish scales, particles of soap, and bits of rubber and hair. With the possible exception of metal foil and bone, all of these materials should be volatilized by the standard volatile-solids testing (combustion at 550°C). Bits of egg shell, grains of sand, and glass chips are also common among the gritty matter found in sludge. Cigarette filters, coarse cellulose, and bits of plastic foam are representative of additional combustibles in the visible sludge fractions. Wet screening of sludge prior to ocean disposal effectively removes all visible matter.

TABLE 2.2

Sieve Analysis of Hyperion Digested Sludge(1)

Sieve Mesh Size	Opening Size (mm)	Percent Retained (by weight)
8	2.38	0.87
10	1.68	0.51
20	0.841	5.60
48	0.297	4.89
65	0.210	1.60
100	0.149	3.62
150	0.105	0.65
200	0.074	1.57
passing 200 mesh		80.69

(1) Source: Garber and Ohara, 1972.

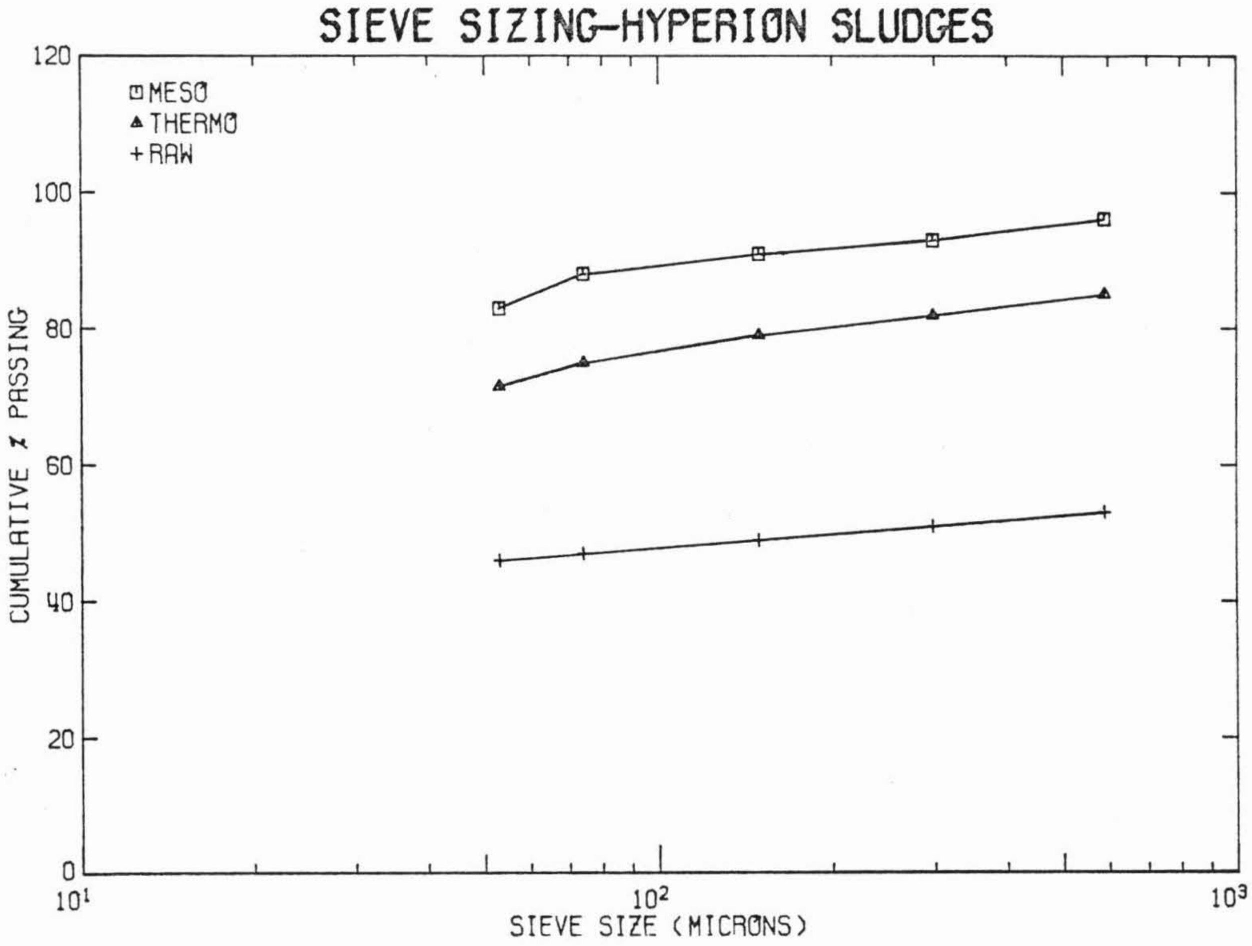


FIGURE 2.4

Sieve Sizing of Hyperion Sludges: Raw, Mesophilic, and Thermophilic

Source: Garber, et al., 1975.

Two important facts can be drawn from Table 2.2 and Figure 2.4. First, the process of sludge digestion at Hyperion clearly reduces the sludge mean particle size. Since one of the chief goals of sludge digestion is to stabilize the raw sludge, the particle size reduction, probably caused both by bacterial action on and degradation of components of the sludge and by mixing, is expected. While less than 50 percent of the raw sludge at Hyperion will pass a 53-micron hole, 70 to 80 percent of the digested sludge, depending on sludge digestion temperature, will pass the 53-micron screen.

Second, the majority of digested sludge particles is less than 100 microns in diameter, and thus is slow to settle and difficult to remove by sedimentation processes. The particulate specific surface area, which varies as the diameter of the particle squared, should be high. These smaller particles should include bacterial cell bodies, fine cellulose, clay material, and mineral precipitates, such as metal sulfides, Fe_3O_4, etc. These smaller particles also have important biological significance, as was discussed in Chapter 1.

2.3.3 Techniques for Particle Sizing and Counting

The precise counting and sizing of sludge particles is possible using several techniques, including light and electron microscopy and electronic particle counting apparatus. Microscopic methods are limited, however, because of difficulties in sample preparation and handling. Electronic particle counting and sizing with a device such as a Coulter Counter allow for the rapid and accurate sizing of particles such as sludge on a repetitious basis over a large particle size spectrum. Sizing of the particles by Coulter Counting has been used for approximately 20 years on such diverse substances as blood cells, clays, pollens, plastic beads, water-treatment floc, and oil droplets. Extensive reviews of Coulter Counter applications and theory are available in Kubitschek (1960), Wachtel and LaMer (1962), Strickland and Parsons (1968), and Treweek (1975).

2.3.4 Particle Sizing by Filtration

The classic technique for particle sizing in geology and soil mechanics is sieve analysis (either dry or wet). This method, generally applied to the larger-sized particles greater than 400 mesh or 37 microns, is reasonably fast and gives good results for particles that are nearly spherical in shape.

An attempt has been made to use Millipore cellulose ester membranes to size sewage and sludge particles (see Chen, et al., 1974). However, previous work on marine particle filtration (see Sheldon, 1972; Sheldon and Sutcliffe, 1969; and Cranston and Buckley, 1972) clearly shows that cellulose ester membranes are unsuited for such separation. Sheldon and Sutcliffe point out that one manufacturer of such membranes, Millipore, actually recommends that their product not be used in such applications.

Sheldon and Sutcliffe (1969) and Sheldon (1972) used a Coulter Counter to examine the particle retention of nylon and stainless steel meshes, Whatman glassfiber filters, and Nuclepore and Millipore membranes. With light particle loading and low vacuum (12-13 cm of mercury), the Millipore and glassfiber filters retained particles of much smaller diameter than the manufacturers' stated pore size. The meshes and Nuclepore membranes showed 50 percent retention of particles (by number) at their manufacturers' reported pore sizes.

Cranston and Buckley (1972) examined the retention of latex beads, kaolinite clay, dissolved organics, and dissolved inorganics on five different membrane and fiber filters. Their interest was to select filters that gave the best particle retention and the most consistent gravimetric results. The Nuclepore membrane performed best except for retention of dissolved humic materials; Nuclepore membranes were particularly good for not retaining dissolved salts from seawater filtration.

Chen, et al. (1974) used centrifugation (up to 740g relative centrifugal force) to fractionate Hyperion digested sludge. Eighty-two percent of the sludge solids and 60 to 80 percent of the trace metals (Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) were removed with centrifugation times of at least 10 minutes. The centrate was then filtered through 8.0μ, 3.0μ, 0.8μ, and 0.22μ Millipore filters. Two percent (Cr and Zn) to thirty percent (Mn) of the trace metals remained in the fraction that passed the 0.22-μ filter. Eighty percent of the centrate solids by weight passed the 8.0-μ Millipore filter but all were retained by the 0.22-μ filter. The estimation of sludge particle size distributions from the data is crude at best. The initial centrifugation should remove some percentage of all particle size fractions. The capture efficiency of the Millipore filters should also increase with filter loading.

2.4 Sludge Chemical Constituents

Knowledge of sludge chemical constituents is essential for the evaluation of potential sludge environmental impacts, for the selection of environmental parameters for monitoring efforts, and for attempts at modeling the chemical behavior of sewage sludge. The heterogeneous nature of sludge prevents the characterization of a typical sludge, but sufficient information is available to list typical concentration ranges for chemical constituents. The order of presentation that follows will be sludge metals, inorganic ligands, and organic ligands.

2.4.1 Sludge Metals

The data on metal in sludge have been arbitrarily separated into two categories--major constituents, e.g. Na and Ca, which are usually present as more than one percent (10,000 mg/kg) of the TROE and minor or trace constituents, e.g. Ag and Pb, that individually make up less than one precent of the TROE. Trace constituents occasionally may be measured at concentrations greater than 10,000 mg/kg, but such values are clearly exceptional. (As mentioned in Chapter 1, the importance of particular metals is poorly understood. Measurements for any given metal often become available only after that metal is recognized as potentially dangerous in the environment. This situation has imposed a further limitation on the availability of sludge metal information.)

2.4.1.1 Major Constituents

The major metals found in sludge are Al, Ca, Na, Mg, and K; concentrations for these metals expressed as mg/kg dry solids appear in Table 2.3. The sources to sewers and hence to sludge include water supply systems, groundwater infiltration, surface runoff inflows, industrial discharges, and domestic waste. The metals' importance is probably most pronounced in determining the ionic strength in the sludge digester and, for Ca, in the effect on alkalinity through the precipitation of calcium carbonate ($CaCO_3$).

Magnesium can also form an important solid, $MgNH_4PO_4$, in sludge digesters. Precipitation of this material in the piping at the Hyperion treatment plant has caused severe plumbing problems (Garber and Ohara, 1972).

2.4.1.2 Trace Metals in Sewage Sludge

The trace metals studied in this research, Ag, Cd, Cr, Cu, Fe, Ni, Mn, Pb, and Zn, were chosen to cover a spectrum of oxidation states that was as broad as possible in natural systems (i.e. $MnCO_3$, $Fe(H_2O)_6^{3+}$, FeS, FeS_2, Cu_2S, CuS, etc.). These metals, known to be present in sludge, can be measured with reasonable ease using Atomic Absorption Spectrophotometry (AAS) or X-ray techniques. Several of the metals, e.g. Cd, Pb, and Cu, have been identified as toxic in the environment.

Reported concentration ranges for the nine metals are summarized in Table 2.4. The large variations can be traced directly to sewage sources. The lowest concentrations were found in sludges resulting from the treatment of domestic sewage. The highest levels were the consequence of industrial waste discharges to sewerage systems.

TABLE 2.3

Major Metals Found in Digested Sludge
(mg/kg dry solids)

Metal	Concentration Range
Al	5500 - 57500
Ca	2500 - 52600
K	1900 - 10900
Mg	5000 - 14000
Na	6600 - 16200

Source: East Bay Municipal Utilities District, 1975; Orange County Flood Control District, 1974; Shipp and Baker, 1975; Van Loon, et al, 1973.

TABLE 2.4

Trace Metal Concentration Ranges(1)
(mg/kg dry solids)

METAL	CONCENTRATION RANGE	TYPICAL RANGES
Ag	4 - 150	10 - 50
Cd	2 - 1500	20 - 1000
Cr	16 - 40000	100 - 1000
Cu	52 - 10400	400 - 2000
Fe	6000 - 74000	10000 - 30000
Mn	73 - 39000	100 - 500
Ni	7 - 5300	100 - 500
Pb	52 - 26000	200 - 2000
Zn	570 - 49000	1000 - 3000

(1) The extremes of concentration on the high side can be traced directly to industrial discharges. The low values generally come from plants receiving only domestic sewage. More typical values are shown in the third column.

Source: Camp, Dresser, and McKee, 1975; East Bay Municipal Utilities District, 1975; Page, 1974; Shipp and Baker, 1975; Van Loon, et al., 1973; Van Loon and Lichwa, 1973.

2.4.1.3 Dissolved Trace Metals in Sewage Sludge

The division between dissolved and particulate trace metals in digested sludges is a strong indicator for the pε, a measure of the redox potential, within the sludge digester. (The implications of the pε parameter will be discussed more completely in Section 3.6.) The fraction of trace metals in solution is important to any disposal scheme because dissolved metals are more immediately and directly able to influence biological processes. In sludge dewatering, dissolved metals obviously remain in solution and should be considered in the treatment of the liquid side stream.

Few data on the partition between dissolved and particulate metals are available. The results of analyses done on the City of Los Angeles Hyperion sludge as a part of a dewatering study are shown in Table 2.5. For the digested sludges the fraction of metals in solution falls into two categories: those less than one percent--Cd, Cr, Cu, Zn--and those less than seven percent--Ni and Pb. The Cu sample for mesophilic sludge shows 34 percent in solution while that for raw sludge is 21 percent in solution, both at extreme variance from the other measurements.

Measurements on dissolved and particulate trace metals have also been made on a number of southern California sewage treatment plant effluents by Galloway (1972). Galloway's values for LACSD effluent (Table 2.6) are very similar to those for Hyperion sludge digesters, on a basis of percentage of dissolved metals, probably reflecting the combination of digested sludge centrate with the effluent from the primary sedimentation tanks in the LACSD system. It should be noted that the total metal concentrations in the sludge are far higher than those in the effluent. The effluent from Hyperion's five-mile outfall (Table

TABLE 2.5

Partition Between Suspended and Dissolved Trace Metals in Hyperion Sludge (1),(2)

	Ag	Cd	Cr	Cu	Ni	Pb	Zn	MEAN % TROE
PRIMARY SLUDGE	2.40(3)	0.02 2.48(4)	0.09 45.18(4)	11.00 52.00(4)	0.67 10.83(4)	8.00(3)	1.55 119.45(4)	6.40 %
DIGESTED MESOPHILIC	3.30(3)	0.02 2.98	0.06 50.26	11.00 32.00	0.36 9.14	0.50 7.50	0.06 77.34	2.12 %
DIGESTED THERMOPHILIC	2.40(3)	0.02 2.78	0.15 52.52	0.27 36.73	0.45 11.05	0.45 7.55	0.20 67.80	2.35 %
WASTE ACTIVATED	0.30 2.00	0.30 0.77	0.70 16.00	0.50 11.50	0.38 1.42	0.25 2.25	0.25 12.75	0.69 %

(1) Dissolved fraction separated from solids by membrane filtration.

(2) All concentrations in mg/1

(3) Total content

(4) Key: Dissolved
Suspended

Source: Mitchell, 1974.

TABLE 2.6

Partition Between Dissolved and Particulate
Trace Metals in Two Effluents

METAL	LACSD Effluent(1)				Hyperion 5 - mile Outfall(2)			
	CONC IN SOLUTION	CONC IN PARTICLES	TOTAL CONC	% SOLUBLE	CONC IN SOLUTION	CONC IN PARTICLES	TOTAL CONC	% SOLUBLE
Ag	.0004	120	.010	4.7	.0045	130	.020	25
Cd	.0010	65	.022	4.7	.0014	108	.012	12
Co	.001	8	.004	28	.0004	4	.0008	50
Cr	.032	1700	.61	5.2	.082	1440	.22	36
Cu	.040	1120	1.1	3.6	.026	1500	.18	14
Fe	.067	20000	7.3	9.2	.14	5400	.68	20
Mn	.030	150	.080	40	.023	108	.033	66
Ni	.087	220	.16	55	.10	520	.15	65
Pb	.0062	570	.19	3.2	.003	320	.035	10
Zn	.130	4100	1.4	9.0	.036	2300	.27	14

(1) All concentrations in mg/1 for solution and mg/dry kg for particles. Concentration of particulate greater than 0.45 μ is 325 mg/1.

(2) City of Los Angeles Hyperion Plant particulate concentration is 100 mg/1.

Source: Galloway, J. N., 1972.

2.6) shows far larger percentages of dissolved trace metals, reflecting the secondary treatment given to about one-third of that plant's flow and also to the discharge of Hyperion's sludge through a separate sludge outfall. Mitchell and Schafer (1975) reported the following percentages of trace metals associated with the particulate phase for the effluent from the Hyperion sludge outfall:

Cd	99 percent	Ni	96 percent
Cr	94 percent	Pb	61 percent
Cu	94 percent	Zn	89 percent.

2.4.2 Sludge Inorganic Ligands

The inorganic ligands in sludge come from the water supply, infiltration and runoff, and domestic and industrial discharges. The process of anaerobic digestion breaks down organics in the sludge, releasing bicarbonate, phosphate, ammonia,and sulfur from the fats, proteins,cellulose,and other matter. Amino acids and sulfate in the raw sludge are reduced to ammonia and sulfide during digestion while ligands such as chloride, fluoride, and bromide should be unchanged. The concentrations of ligands are important for the behavior of the trace metals, both in the digester and during disposal operations, owing to the formation of metal-ligand precipitates and complexes.

Concentrations or concentration ranges for sludge inorganics, with the exception of NH_3, orthophosphate, CN^-, and Cl^-, are not readily available. Since inorganic ligands in general have far lower toxicities than trace metals and many organic ligands, this dearth of information is anticipated. Anderson (1956) reported phosphate (P_2O_5), as percent dry solids, ranging from 0.9 to 5.0 with an average of 2.7. For sludge at 25,000 mg/l total solids the range is equivalent to 225 mg/l to 1200 mg/l, with an average of 675 mg/l ($pP_{total} = 2.32$*). Anderson also reported total sulfur concentrations of one percent dry solids ($pS_{total} = 2.11$).

Chloride data for sludges are sparse, with reported values around 300 mg/l. Cyanide concentrations are much smaller, on the order of 0.1 to 0.5 mg/l for Los Angeles area sludges. The low concentrations of CN^- are far more significant, however, because the strong complexes that CN^- forms with Ag, Cu, Ni, and other metals greatly increase the fraction of such metals not bound to the particulate phase.

2.4.3 Sludge Organic Ligands

Organic ligands in digested sludge are important because many organics complex trace metals strongly, in competition with precipitation and surface adsorption reactions. Metal-organic complexes are soluble in the sludge and thus increase the fraction of dissolved metals. Any organic compound that enters the sewage system, or that is produced by the bacteria present there, will be found in the sludge digester. This heterogeneous mass includes common compounds such as proteins, carbohydrates, cellulose, fats, and fatty acids as well as more exotic substances--e.g. halogenated hydrocarbons and polychlorinated biphenyls (PCB).

---

*The notation $p[X] = -\log$ (molar concentration of X) throughout the text.

The characterization of organics in digested sewage sludge has been mainly limited to organic acids, the main methane precursors in anaerobic fermentation. Acetic, propionic, butyric, pyruvic, formic, lactic, valeric, and succinic acids have all been identified by chromatographic methods. (See Kaplovsky, 1952, and Mueller, et al., 1956). Acetic, propionic, and butyric acids are generally the predominant organics. The total concentrations of volatile acids for stable mesophilic digesters, expressed as acetic acid, are 50 to 200 mg/l; for thermophilic digesters, a value of 500 mg/l is expected.

Phenolic compounds in LACSD sludge centrate were reported at 1.8 mg/l (Sanitation Districts of Los Angeles County, 1973). Total DDT flows from Hyperion sludge outfall (SCCWRP, 1975) were 0.0026 mg/l (16.9 kg/year) and for PCB's, 0.0030 mg/l (21.5 kg/year).

2.5 Physical-Chemical Interactions of Sludge Solids and Trace Metals

2.5.1 A Review

Consideration of sludge only on a physical basis or only on a chemical one is informative but falls short of reality because the chemical constituents are intimately connected with the particles. Two processes that collectively approximate the behavior of sludge in contact with seawater, oxic mixing and sedimentation, are considered in the next section.

2.5.2 Sedimentation Experiments

Extensive work on the theory and use of sedimentation columns with both flocculant and nonflocculant suspensions has been done by McLaughlin (1958, 1959). Single and multidepth sampling from columns up to 1.2 m deep was made on sand, clay, and sewage-particulate suspensions. Sweep flocculation was postulated to occur when faster particles overtake slow ones and the particles with different initial fall velocities become attached. Not surprisingly the effect of flocculation was found to increase with depth in the column. Experiments made with several different sewage-treatment-plant effluents showed great variation in velocity distribution between samples. However consistent results from samples from one source at one point in time were possible.

Previous work on the sedimentation of sludge or sewage effluent solids in seawater or seawater-like liquids has been done by Brooks (1956), Myers (1974), and Morel, et al., (1975). Brooks conducted experiments with Hyperion digested sludge, diluted 20:1 with seawater. Solids were collected with Gooch crucibles. His data (see Figure 2.5) showed that 50 percent of the solids had a settling velocity, v_s, of less than 2.8×10^{-2} cm/sec. (These data have been adjusted from 31.5°C, the experimental temperature, to 12°C.) Rapid flocculation of the sludge was observed visually.

Myers diluted a 24-hour composite of Los Angeles County Whites Point effluent 1:1 with filtered seawater and captured the falling solids on Whatman type GF/C glassfiber filters. The composite sample contained primary effluent and centrate from digested primary sludge. The sludge centrifuges in the treatment plant captured 25 to 35 percent of the solids as sludge cake. The remaining fine solids were retained

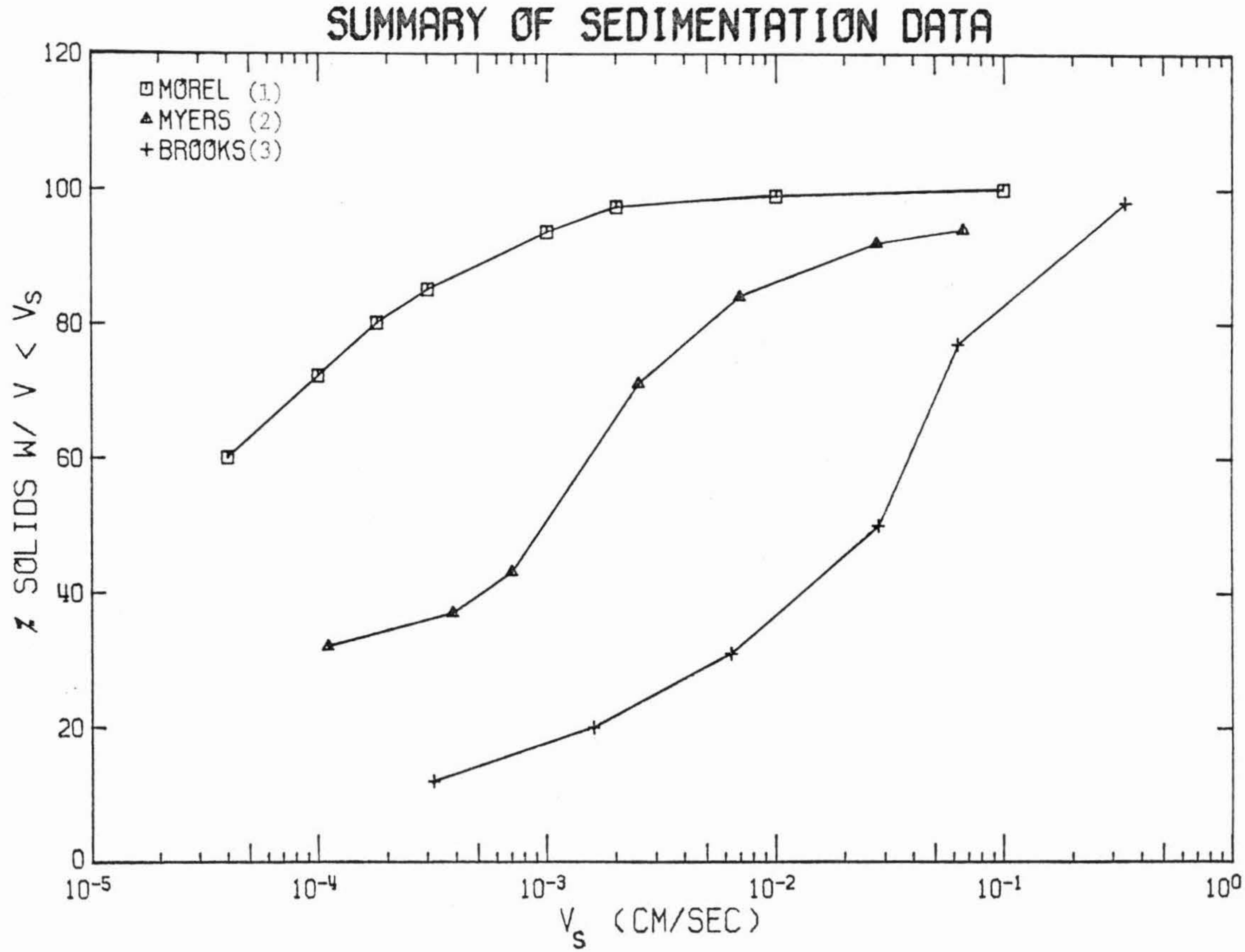


FIGURE 2.5
Sedimentation Data for Wastewater Solids in Seawater-like Media

Source: (1) Morel, et al., 1975 (Effluent in NaCl); (2) Myers 1974 ; (3) Brooks, 1956 .

in the centrate. The 50-percent v_s reported by Myers was 1.0×10^{-3} cm per second (see Figure 2.5).

Morel, et al. (1975) reported sedimentation experiments run on a 24-hour composite of sewage particulates and on the same composite diluted 10:1 with 0.5 M NaCl. Solids were captured on membrane filters; trace metal analysis was done for Cr, Cu, Fe, and Zn on the captured solids. Raw sewage showed a 50-percent v_s of 1×10^{-3} cm/sec. For the sewage/NaCl mixture the 50-percent v_s was less than 1×10^{-5} cm/sec. To a first approximation trace metals sedimentation paralleled that of the suspended solids.

A direct comparison of the three experiments listed above is difficult because the solids-capture techniques were not the same, different solids were used, and the sedimentation media and the temperature varied. However, a range of sedimentation velocities (1×10^{-5} to 3×10^{-2} cm/sec) can readily be identified. The importance of experimental conditions and their control is evident for future work as is the choice of sedimentation fluid and the solids-separation technique. For example, in the experiments by Morel, et al. (1975) the use of sodium chloride as the sedimentation fluid may not stimulate flocculation as would the use of seawater which has a large concentration of divalent metal ions.

2.5.3 Sludge in Oxic Seawater

Any model of sludge discharges to the ocean must consider the interaction of sludge solids with seawater. The sludge comes from an anoxic environment, the digester, and enters one that is at least mildly oxic. A change in the redox potential is coupled with a sharp change in the ionic strength of the surrounding medium.

Oxic mixing experiments have been run previously on Hyperion sludge by Rohatgi and Chen (1975) and Mitchell and Schafer (1975). Mitchell and Schafer reported that "...very little change in the discharge particulate composition occurs even after 11 days of mixing with aerated seawater."

Rohatgi and Chen mixed 50:1, 100:1, and 200:1 dilutions of sludge with filtered natural seawater at 15°C for periods of up to five weeks. They monitored suspended solids and trace metals (Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn) by AAS. The measured decrease of suspended solids with time was seven to nine percent. The percent decrease of trace metals in the particulate form is summarized in Table 2.7, below. The fraction of trace metal released or mobilized increased with increasing dilution for Mn, Ni, Zn, and Cu.

TABLE 2.7

Percentage of Trace Metals Released After Five Weeks
From the Particles in Digested Hyperion Sludge

Metal	50:1 Dilution (1)	100:1 Dilution (1)	200:1 Dilution (1)
Cd	93.0	95.0	96.0
Cu	5.0	5.6	9.0
Cr	2.0	2.0	3.8
Fe	0	0	0
Mn	31.8	34.7	35.7
Ni	49.0	58.0	64.0
Pb	37.8	35.4	35.4
Zn	18.0	24.4	58.7

(1) Sludge was diluted with filtered natural seawater.

Source: Rohatgi and Chen, 1975.

PART II. MEASUREMENTS OF PHYSICAL AND CHEMICAL PROPERTIES OF DIGESTED SLUDGES: PARTICLE SIZE DISTRIBUTIONS, TRACE METALS, AND INORGANIC LIGANDS

2.6 Measurements: Sludge Physical Properties

2.6.1 Water Content

The water content of all sludges used in this work was measured according to Standard Methods (1971). The TROE values ranged from 2.4 to 2.9 percent by weight, with 50 to 60 percent volatile on combustion. (See Table A.1 for the actual results and Section 2.3.1 for a definition of terms.) A NROE of 1270 mg/l was measured for Hyperion sludge; 59 percent of the NROE was volatile on combustion.

2.6.2 Particle Density

Direct density measurements of sludge particles were not made as a part of the research but circumstantial evidence indicated that the fine material had a density substantially greater than 1.0 gm/cm^3. During the final stage of the separation procedure for the dissolved and particulate sludge fractions (see Appendix A.5), sludge that passed an 8.0-μ Millipore filter was spun at 20K rpm in an ultracentrifuge. Two distinct layers collected in the bottoms of the centrifuge tubes. The heavier layer was black like the majority of the sludge particles; the overlying layer was white.

Since the sludge was later found to be supersaturated with $CaCO_3$ (see Section 2.7.1), there was a strong indication that the white layer was hydrated calcium carbonate ($CaCO_3 \cdot 6H_2O$), a white solid with ρ_s = 1.77 gm/cm^3. Since the majority of the sludge particles, by both weight (Section 2.6.4) and number (Section 2.6.3), was less than 8.0-μ microns in diameter and since the apparent density of the small particles was high, the sensitivity of the settling velocity v_s to $(\rho_s - \rho)$ should be low.

2.6.3 Particle Sizing by Coulter Counter

2.6.3.1 The Coulter Counter

The Coulter Counter depends upon the conductivity difference between particles and the surrounding electrolyte for particle detection. The suspension is drawn through an orifice in the wall of a non-conductive tube by an advancing mercury column. A current is passed between electrodes inside and outside the tube; the passage of a non-conducting particle causes a voltage pulse which is proportional to the particle volume. This proportionality holds for particles with diameters from about two to 40 percent of the aperture diameter. The voltage pulse is amplified by the Coulter Counter electronics and then scaled and sorted with a pulse height amplifier/multi-channel analyzer (PHA/MCA). The 128-channel output from the MCA is then viewed visually on an oscilloscope and can also be transferred automatically to paper punch tape with an attached teletype terminal. The output from the Coulter Counter for sludge is for spheres of volume equivalent to the randomly-shaped particles in the suspension.

Particle suspensions must be fairly dilute to avoid problems of coincident passage of several particles through the aperture. The volume sampled is set by electronic probes in the mercury column, which trips start and stop switches as the mercury passes. The instrument used for this work had settings for sample volumes of 50 microliters, 500 microliters, and 2,000 microliters. Four apertures, 30 μ, 70 μ, 140 μ, and 280 μ, were used in this work. The Coulter Counter was calibrated with polystyrene latex (PSL) spheres as described in Appendix B.

The paper tape output from the MCA was transferred to card images which were subsequently edited to remove spurious data, especially data points for particles much larger than 40 percent of the aperture and for electronic noise. A computer program was then employed to convert channel counts and calibration information to particle diameters, surface areas, and volumes. Particles were assumed to be solid spheres. This assumption was necessary considering the heterogeneous composition of sewage sludges.

The particle spectra were purposely taken with overlap, both to check the correspondence among apertures and to provide continuous spectra over a large range of particle diameters. The plots of raw spectra generally showed similarly curved shapes; total particle counts were also within a factor of two to four for adjacent spectra, but at no point were the curves exactly coincident.

The matching of spectra was a multistep process. The spectra for the original plots represented the average results of three to five runs on the Coulter Counter. The data were also smoothed using a simple running average on sets of five adjacent points. The number versus diameter plots were then examined visually. Two types of errors prevented coincidence of the curves. Dilution errors would increase or

decrease the number of counts and lead to vertical displacement of the curves. Horizontal displacements would be caused by errors in the log base measurements or in the identification of correct channel numbers for the calibration particles. In reality both types of errors probably occurred making simultaneous adjustments more realistic.
(See Figure 2.6 for a schematic summary of error corrections.)

Other sources of error would be non-uniform response of a given aperture to the particle suspension and physical changes in time of the particle system such as flocculation or sedimentation. Such physical changes would alter the size distribution while measurements were being made.

The possibility of flocculation in the high ionic strength of the sodium chloride solution was countered by frequent agitation of particle solutions and sonification of samples before measurements were taken. Stirring the suspension between sampling runs was done for the 140-μ and 280-μ apertures to prevent losses by sedimentation. The teletype output for successive runs on given samples was examined and showed losses or variations of less than 10 percent.

2.6.3.2 Coulter Counter Results

For data-matching, the errors were attributed to both variations in dilution and in the log-base setting. Adjacent spectra were compared by overlaying one curve on the other and appropriate correction factors were then calculated. The fitted particle number versus diameter and resulting volume versus diameter plots for both LACSD primary and Hyperion mesophilic sludges appear in Figures 2.7 through 2.10.

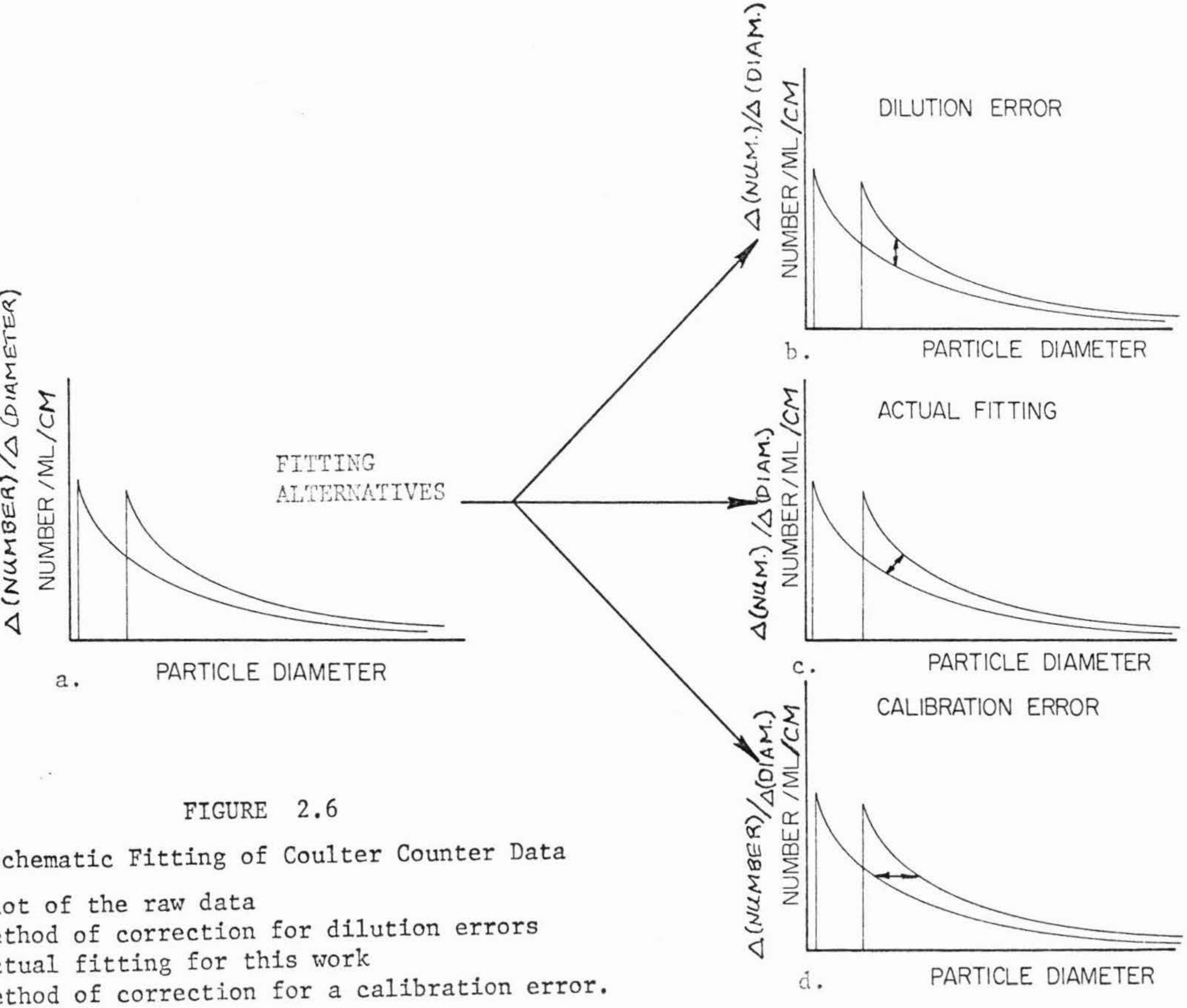


FIGURE 2.6

Schematic Fitting of Coulter Counter Data

a. Plot of the raw data
b. Method of correction for dilution errors
c. Actual fitting for this work
d. Method of correction for a calibration error.

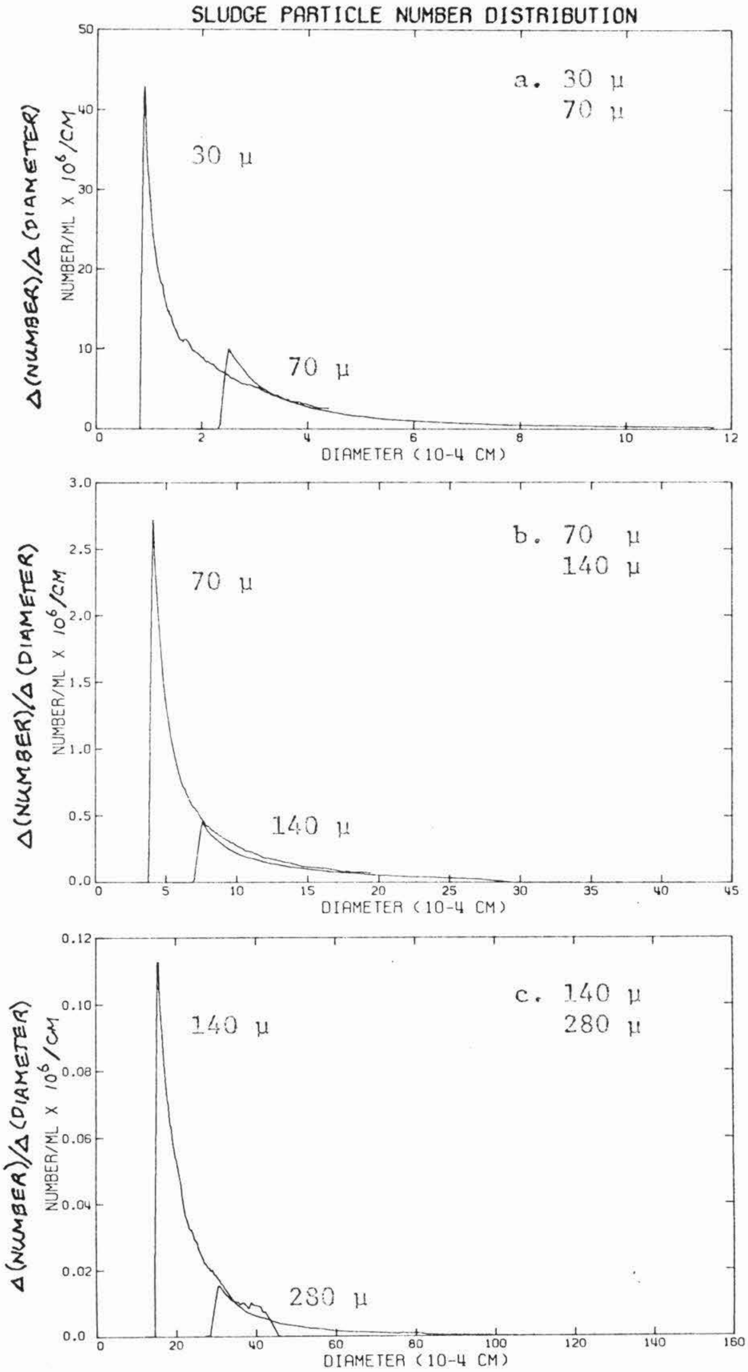


FIGURE 2.7

Particle Number Distributions as Measured with a Coulter Counter - LACSD Sludge. Apertures used are as shown.

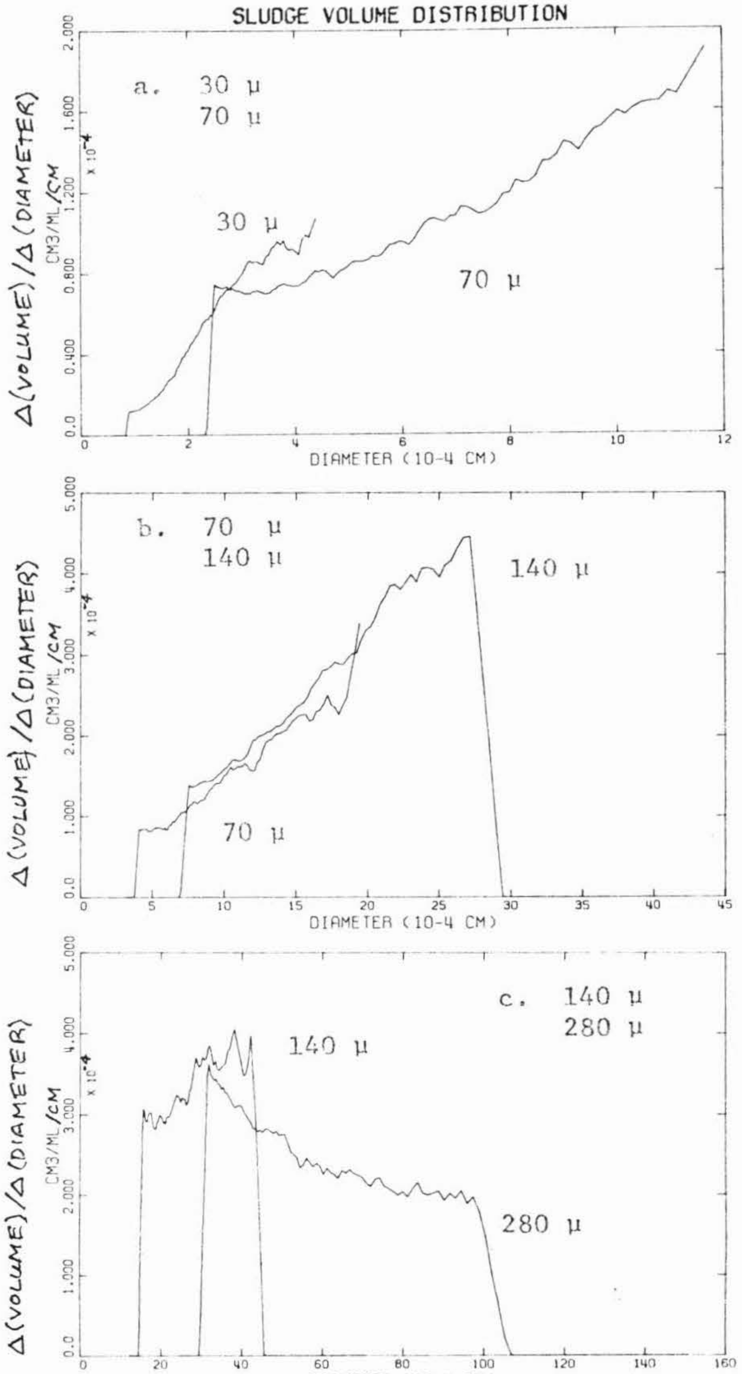


FIGURE 2.8

Volume Distributions for LACSD Sludge Calculated from Number Distributions in Figure 2.7. Apertures used are as indicated.

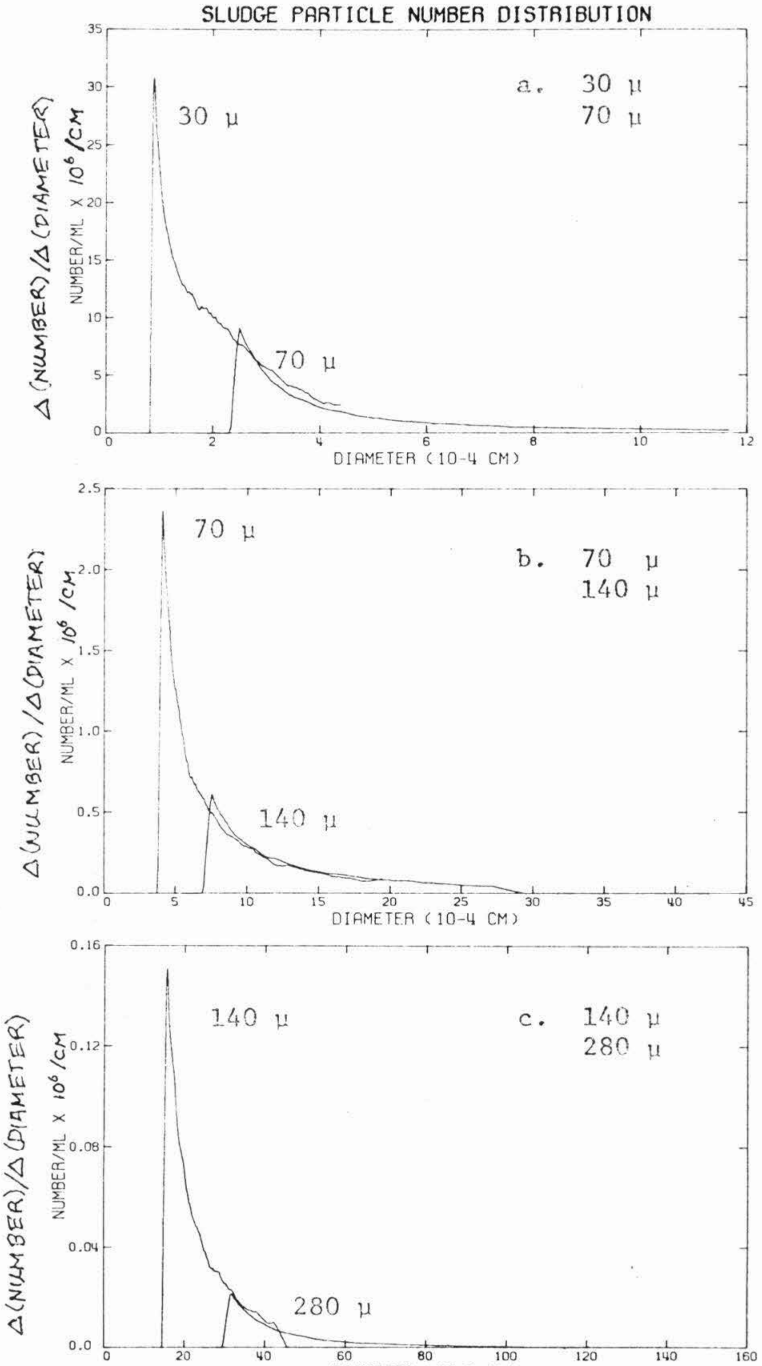


FIGURE 2.9

Particle Number Distributions as Measured with a Coulter Counter - Hyperion Mesophilic Sludge. Apertures used are as indicated.

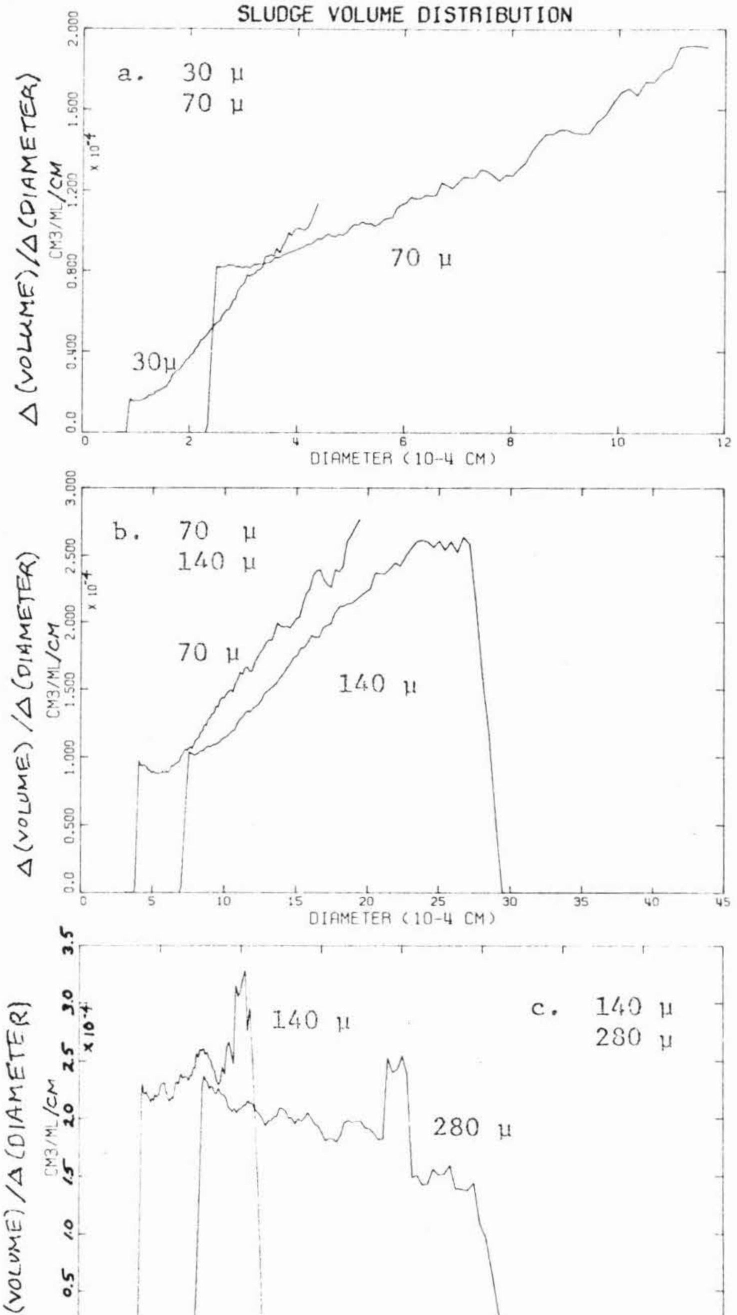


FIGURE 2.10

Volume Distributions for Hyperion Sludge Calculated from Number Distributions in Figure 2.9. Apertures used are as indicated.

Six variations of aperture and instrumental settings were used to get a particle-size distribution over the entire size range. The particle-number and particle-volume curves are presented in adjacent pairs for comparison.

The volume distributions, which are proportional to diameter cubed, were neither as smooth nor as well-fitted as the number distributions. The "roughness" in the volume distribution curves, especially at the large diameter end of the spectrum, for any given aperture is attributable to statistical uncertainty in the Coulter Counter data. For higher channel numbers (larger diameters) the particle-number distributions clearly show that total counts per channel were lower. If the number of counts per channel is lower, the statistical significance is also lower and the fluctuations in the volume distribution result.

Number, surface area, and volumes for the entire sludge spectra are summarized in Table 2.8. As expected, the number counts are very high, especially for small diameter particles. The particles less than 6.0 μ in diameter constitute more than 97 percent of the total counts while contributing only 19 percent of the measured volume. These smaller particles are in the size fraction that most seriously affects the penetration of light in the water column (see Section 1.2), and hence are potentially the most deleterious if discharged to the productive upper layers of the ocean. The total volumes measured, 4.15×10^{-2} cm^3/ml for LACSD sludge and 3.68×10^{-2} cm^3/ml for Hyperion sludge, are somewhat higher than would be expected based on the total solids in the sludge. The bulk of this volume, 45 to 50 percent, comes from the two largest diameter intervals recorded with the Coulter Counter. These

TABLE 2.8

Particle Size Distributions by Coulter Counter

LACSD Digested Primary Sludge

Diameter Interval	Aperture(1,2)	Number Sum	Volume Sum	Area Sum
0.89 to 2.72	30	1.06×10^{12}	2.34×10^{-3}	7.17
2.75 to 6.04	70	1.48×10^{11}	4.35×10^{-3}	6.47
5.99 to 12.72	70	2.08×10^{10}	6.69×10^{-3}	4.50
12.43 to 20.55	140	3.96×10^{9}	8.53×10^{-3}	3.05
20.10 to 32.62	140	1.44×10^{9}	10.65×10^{-3}	2.77
33.22 to 60.35	280	3.30×10^{8}	12.58×10^{-3}	1.76
Totals		1.24×10^{12}	4.51×10^{-2}	25.72

City of Los Angeles Digested Mesophilic Sludge

Diameter Interval	Aperture(1,2)	Number Sum	Volume Sum	Area Sum
0.89 to 2.72	30	1.17×10^{12}	2.20×10^{-3}	7.73
2.75 to 6.04	70	1.78×10^{11}	5.65×10^{-3}	8.13
5.99 to 12.72	70	2.06×10^{10}	6.61×10^{-3}	4.44
12.43 to 20.55	140	2.85×10^{9}	5.92×10^{-3}	2.20
20.11 to 32.63	140	1.04×10^{9}	8.48×10^{-3}	2.01
32.22 to 62.99	280	2.55×10^{8}	9.88×10^{-3}	1.36
Totals		1.37×10^{12}	3.88×10^{-2}	25.33

(1) Units:
Diameter Intervals - μ
Apertures - μ (10^{-6} meters)
Number Sums - Number of particles/liter
Volume Sums - cm^3/ml
Area Sums - meters^2/liter

(2) Aperture used to measure a given diameter interval.

larger sizes may represent some flocculated material, in essence a duplicate counting of the smaller particles. If particle volume is assumed to be directly proportional to particle weight, a substantial fraction of the sludge should settle rapidly. This result was not observed in the sedimentation experiments (see Section 2.8) and flocculation of the sludge is more suspect.

The surface area of the sludges, approximately $25m^2/l$, is high compared to natural system such as the ocean, where surface areas of more than 1.0 m^2/l are considered large. Since in the Coulter Counter measurements all particles are treated as spheres of equivalent volume, the calculated surface areas are conservative for a material as heterogeneous as sludge. The fraction of particles smaller than approximately 0.9 μ also was not measured in this work and may contribute an additional significant surface area input since the specific surface area of these particles is very high. The similarity of the particle-size distributions for the two sludges measured in this work should be noted. The TROE's for the two sludges are within 15 percent of each other, the number counts within 10 percent, and the surface areas within two percent.

2.6.4 Particle Sizing by Vacuum Membrane Filtration

In the original plan for this research, particle fractionation by sieving (see Section 2.3.4) i.e. using microscreens (10, 20, or 30 micron) and Nuclepore membranes, was anticipated to be a viable means for particle sizing. Microscreens are available in both nylon and stainless steel. The Nuclepore membranes are thin polycarbonate sheets with very uniform round holes etched through them; available pore diameters decrease in size from eight microns.

Microscopic examination of dilute sludge suspensions revealed the majority of particles, at least by number, were less than 10 microns in diameter. Since trace metal analysis as well as particle sizing was planned, the use of stainless-steel meshes was ruled out. Nuclepore membranes were selected, but there was a possibility that solids loading per unit filter area large enough to allow for metal analysis by X-ray techniques might alter the sieve-like properties of the membrane.

Microscopic examination of 8.0-μ membranes loaded with both 1.1-μ and 15.8-μ PSL spheres showed some capture of 1.1-μ beads. (All filtration was done with vacuums of up to 74 cm of mercury.) Calculations were then made to determine the percent open area on the membranes and the theoretical loading of spheres necessary to clog all the pores. If a randomly-shaped particle larger than a pore is lodged across a pore, fluid will continue to be drawn through the remaining opening, but the effective pore size is significantly decreased. (See Figure 2.11, below).

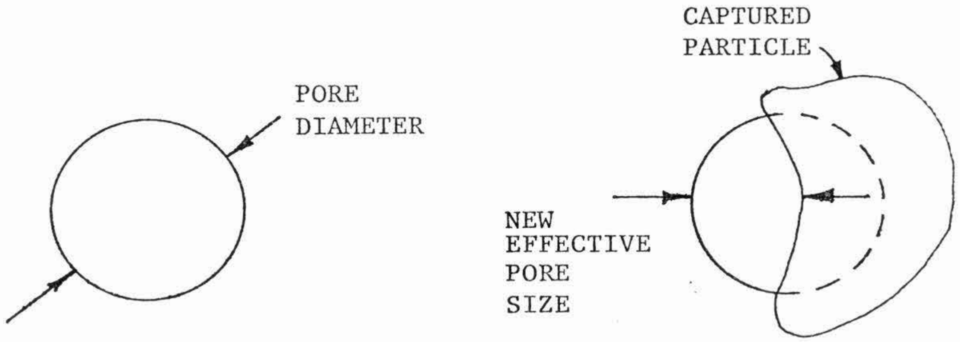


FIGURE 2.11

Effects of Filter Clogging

The sample calculations of Table 2.9, where it is assumed one particle per pore causes clogging, emphasize this point. Even if several particles per pore are necessary for clogging in vacuum filtration situations, less than one milligram of material should be sufficient for complete clogging of a filter surface with a 3.5 cm diameter.

The actual performance of Nuclepore membranes was tested in this research using a 100:1 dilution of LACSD primary sludge with sludge-filtrate. The sludge-filtrate dilution was applied in increasing volumes to sets of three membranes, mounted on a Millipore filter head, and the fluid drawn off by the vacuum. The membranes were then dried and the solids measured by weighing. The results, shown graphically in Figure 2.12, demonstrate the 8.0-μ membrane efficiency increases with increasing solids loading. The efficiency for the 1.0-μ membrane is constant (correlation coefficient for the linear best fit is greater than .99). At the lowest loading the capture on the 8.0-μ membrane is 46 percent of that on the 1.0-μ membrane. The total solids captured were 0.338 mg on a 8.0-μ membrane (weight = 14 mg) and 0.734 mg on a 1.0-μ membrane (weight = 20 mg). At any lower total solids loadings, it is doubtful that accurate and reproducible weight determinations could be made. (The linear weight-capture per volume added for the 1.0-μ filter confirms the choice of these filters for use in solids capture during mixing and sedimentation experiments, where total loading per filter varied up to a factor of 10.)

Photomicrographs of 8.0-μ and 1.0-μ membranes (Figures 2.13 and 2.14) were made to illustrate the rapid clogging at low loadings and thus their unsuitability for particle fractionation using vacuum

TABLE 2.9

Theoretical Clogging of Nuclepore Membranes

PORE DIA	PORE DENSITY(1) (per cm^2)	# OF PORE PER 3.5cm DIA TARGET	VOL/PARTICLE(4) (cm^3)	VOL FOR CLOGGING(2) (cm^3)	WT RANGE FOR(3) CLOGGING (mg)	% OPEN AREA
8 μ	1×10^5	9.6×10^5	2.68×10^{-10}	2.57×10^{-4}	.257 → .684	5 %
5 μ	4×10^5	38.5×10^5	6.54×10^{-11}	2.52×10^{-4}	.252 → .668	7.8%
3 μ	2×10^6	19.2×10^6	1.41×10^{-11}	2.71×10^{-4}	.271 → .718	14.2%
1 μ	2×10^7	19.2×10^7	5.24×10^{-13}	1.01×10^{-4}	.101 → .267	15.6%

(1) As reported by the manufacturer.

(2) Assuming 1 particle/pore causes clogging.

(3) Assuming particle density extremes are 1.0 gm/cm^3 to 2.65 gm/cm^3.

(4) Volume of a spherical particle that would just clog the pore.

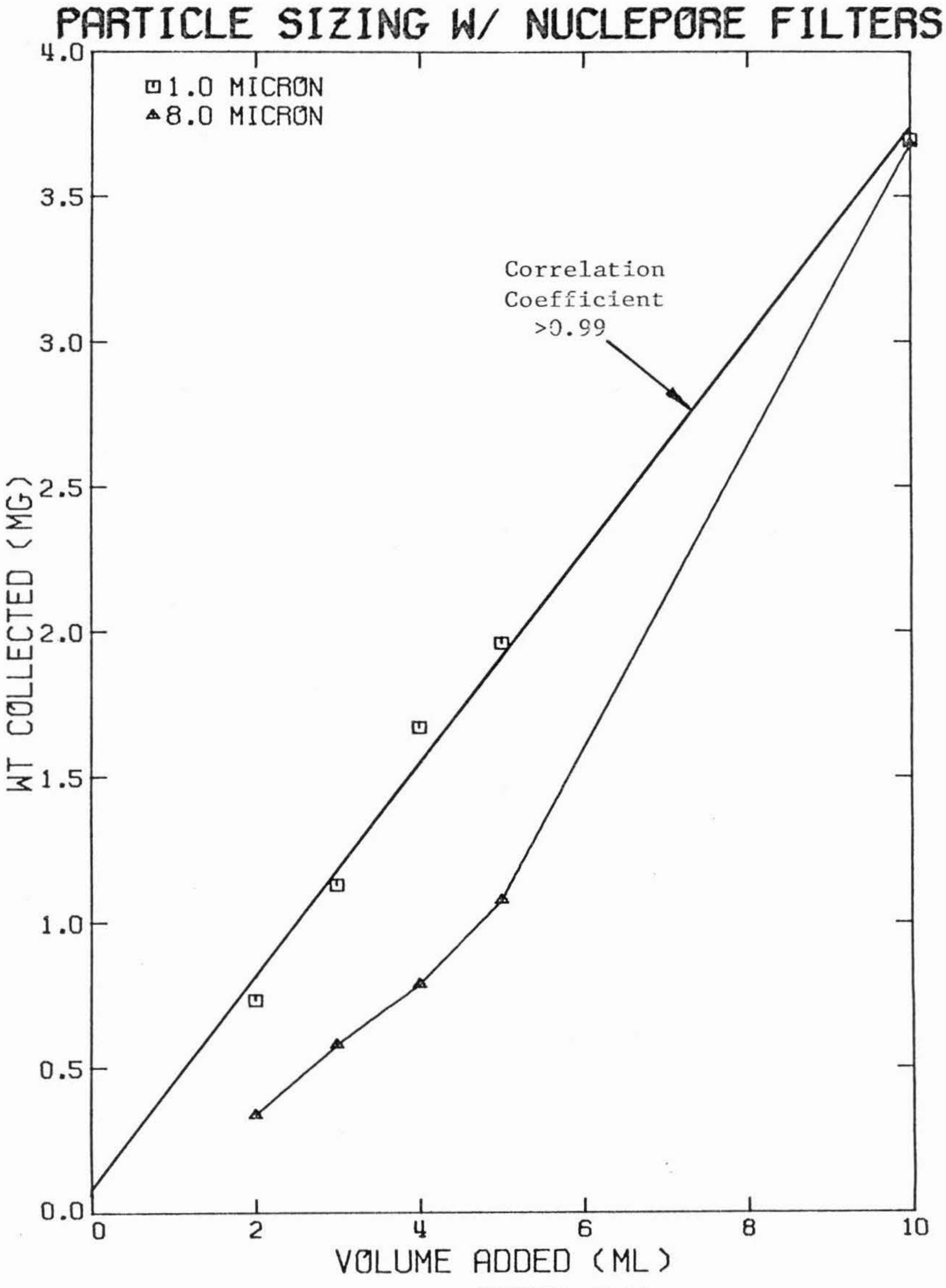
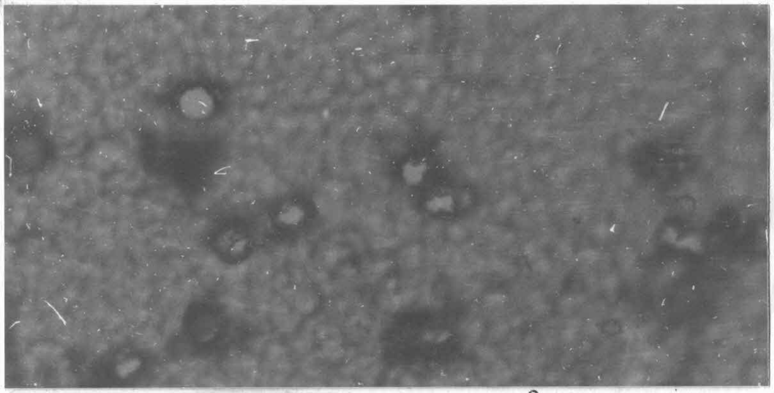
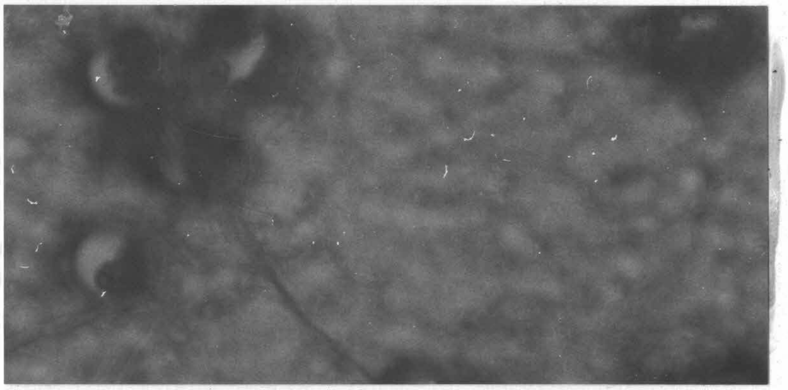


FIGURE 2.12

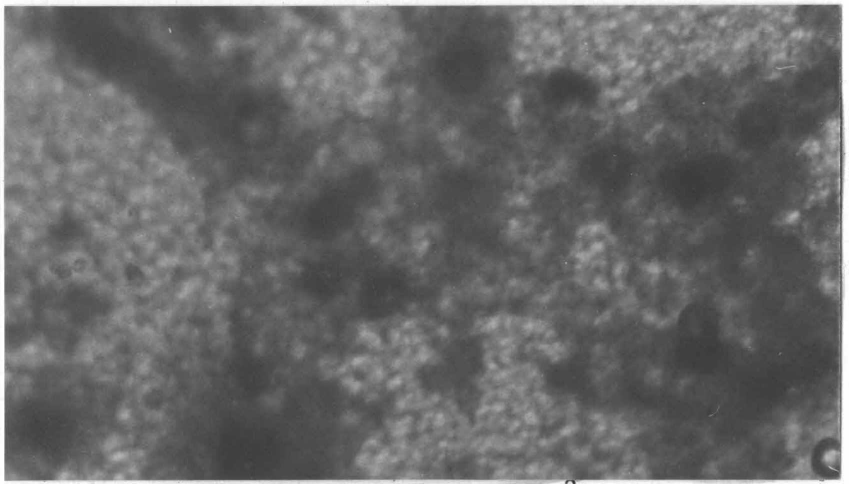
Solids Retention by Nuclepore Membranes Loaded With A 100:1 Dilution of Sludge with Sludge Filtrate



a. Lightest loading (.03 mg/cm^2) - Note partially clogged pores.



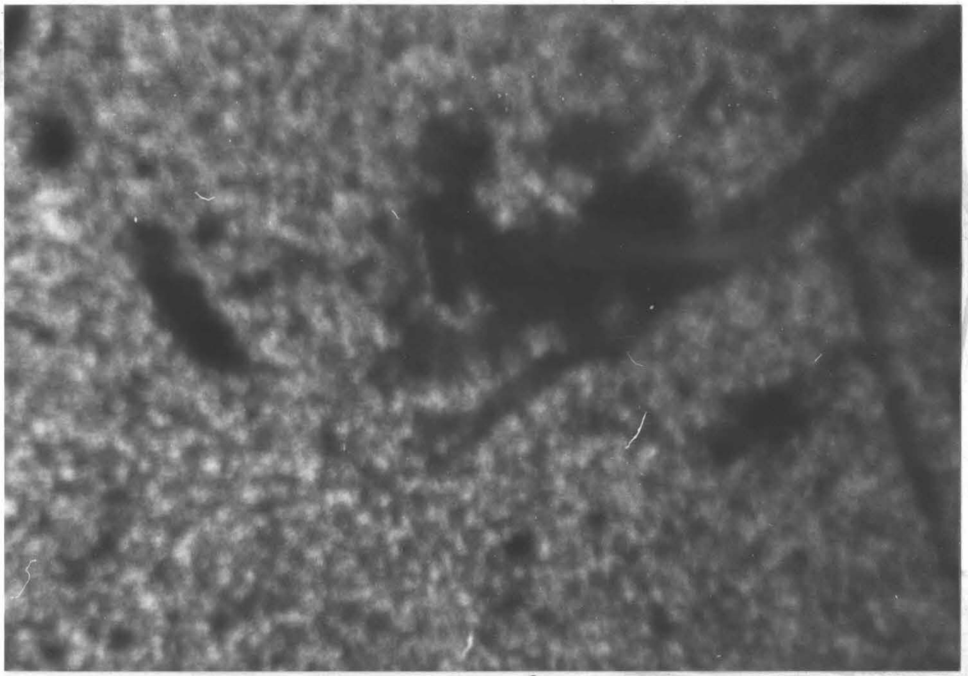
b. As in a. above, higher magnification



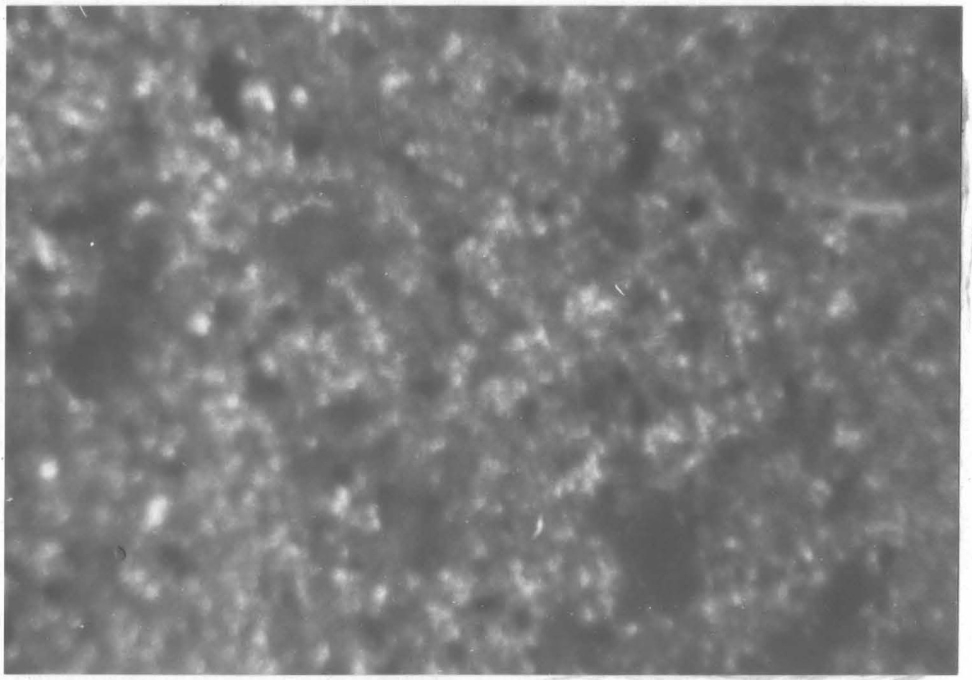
c. Heaviest loading (.34 mg/cm^2) pores clogged.

FIGURE 2.13

Micrographs of Sludge on 8.0-μ Nuclepore Membranes
Pores have a Diameter of 8.0-μ



a. Lightest loading (.07 mg/cm^2) (1 cm = 30 μ)



b. Loading as in a. above (1 cm = 3 μ)

FIGURE 2.14

Micrographs of Sludge on 1.0-μ Nuclepore Membranes techniques. Both clogged and unclogged pores can be clearly seen in the 8.0-μ photos at different magnifications. As the loading was increased the number of unfilled pores decreased. The time for filtering with 10-ml loadings increased dramatically. The same phenomenon is evident for the 1.0-μ filters but the number of unclogged pores in the most lightly loaded filter is considerably smaller. At higher loadings, the pores are no longer distinguishable.

2.7 Measurements: Sludge Chemical Constituents

2.7.1 Major Metals

Typical concentration values for the major metals in digested sludge were previously listed in Table 2.3. Regular analysis for Ca, Mg, etc. was not done in this research, but evidence for the importance of Ca was found when an attempt was made to separate the dissolved from the particulate matter in sludge (See Appendix A.5). The dissolved phase, after separation and filtration through a 0.45-μ Millipore filter, was stored in a constant temperature room at 4°C. Within two to three days the previously clear solution became cloudy; after sitting for a period of several weeks, small crystals had formed in the sludge filtrate. A check was then made of a sample of sludge filtrate that had been sitting for approximately three months at 4°C. Clear crystals up to several millimeters long were found in a bottle of this filtrate. Spectrographic analysis and X-ray analysis of these crystals indicated they were calcium carbonates present as both aragonite and calcite. Since $CaCO_3$ solubility increases with decreasing temperature, the precipitation of

$CaCO_3$ indicated that the sludge filtrate was greatly super-saturated with respect to $CaCO_3$.

2.7.2 Total Concentrations for Some Trace Metals in Sewage Sludge

Analyses for total trace metal concentrations in sludges were done for Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn by flame AAS after an acid/ peroxide digestion of the samples. The analytical techniques are summarized in Appendices A.3 and A.4. The metal concentrations for Hyperion and LACSD sludges are reported in Tables 2.10 and 2.11. Comparing these values to those in Table 2.4 it is evident that the metal concentrations in Los Angeles sludges fall at the upper end of the concentration scale, reflecting the industrial inputs to sewage flows. Source control programs could probably reduce the total metal present, as has already been done for Hg discharges to the City of Los Angeles sewerage system (Bargman and Garber, 1972). However, studies by Davis and Jacknow (1975) on data from New York City; Allegheney County, Pennsylvania; and Muncie, Indiana, and by Klein, et al. (1974) in New York City have shown that 10 to 90 percent of the total metal (depending on the metal and the region) originated from residential and commercial sources. Such sources are far less amenable to control programs.

2.7.3 Dissolved Trace Metals in LACSD Sludge

The dissolved trace metals in a sample of LACSD digested primary sludge were measured as a part of this research. The separation of the liquid sludge fraction from the particles is described in Appendix A.5 and the metal analysis technique in A.6. The fraction of dissolved

TABLE 2.10

Trace Metals in Digested Hyperion (Mesophilic) Sludge Analysis by Atomic Adsorption Spectrophotometry (1)

Metal	gm Me/gm wet sludge(2)	gm Me/gm Tot solids	moles/1(3)
Ag	4.31×10^{-6} ± 1.38	1.82×10^{-4}	4.02×10^{-5}
Cd	4.80×10^{-6} ± .30	2.03×10^{-4}	4.30×10^{-5}
Cr	6.04×10^{-5} ± .15	2.55×10^{-3}	1.17×10^{-3}
Cu	5.48×10^{-5} ± .18	2.32×10^{-3}	8.68×10^{-4}
Fe	3.80×10^{-4} ± .15	1.60×10^{-2}	6.85×10^{-3}
Mn	4.05×10^{-6} ± .22	1.71×10^{-4}	7.42×10^{-5}
Pb	1.88×10^{-5} ± .22	8.12×10^{-4}	9.14×10^{-5}
Zn	7.75×10^{-5} ± .76	3.27×10^{-3}	1.19×10^{-3}

(1) Based on complete acid digestion of 10 gm of wet sludge, 2.5% TROE.

(2) Measured values reported as samples mean ± 90% confidence interval determined by the t-test.

(3) Concentrations include both dissolved and particulate metals.

TABLE 2.11

Trace Metals in Digested Primary Sludge from LACSD
Analysis by Atomic Absorption Spectrophotometry (1)

Metal	gm Me/gm wet sludge(2)	gm Me/gm Tot solids	moles/l(3)
Ag	0.83×10^{-6} $\pm .49$	3.46×10^{-5}	7.75×10^{-6}
Cd	2.12×10^{-6} $\pm .05$	8.83×10^{-5}	1.90×10^{-5}
Cr	7.09×10^{-5} $\pm .34$	2.95×10^{-3}	1.37×10^{-3}
Cu	3.19×10^{-5} $\pm .03$	1.33×10^{-3}	5.06×10^{-4}
Fe	6.86×10^{-4} $\pm .00$	2.86×10^{-2}	1.24×10^{-2}
Mn	6.39×10^{-6} $\pm .50$	2.66×10^{-4}	1.17×10^{-4}
Ni	1.37×10^{-5} $\pm .03$	5.71×10^{-4}	2.35×10^{-4}
Pb	3.13×10^{-5} $\pm .25$	1.30×10^{-3}	1.52×10^{-4}
Zn	1.29×10^{-4} $\pm .10$	5.38×10^{-3}	1.99×10^{-3}

(1) Based on complete acid digestion of ∿ 10 gm wet sludge, 2.4% TROE.

(2) Measured values reported as sample mean ± 90% confidence interval determined by the t-test.

(3) Concentrations include both dissolved and particulate metals.

trace metals (see Table 2.12) was far lower than that reported previously (see Section 2.4.1.3). This difference was attributable to one of two reasons. The first was the separation technique used in this work, which minimized contact between the sludge solids and air (oxygen) until after the majority of solids had been removed. Direct filtration provides more contact between air and the sample and thus more opportunity for oxidation of sludge solids unless filtration is done under nitrogen. The second explanation may be the difference in the sludges. The author's sample was taken during the summer and showed a sulfur concentration of 2.3 percent dry solids (see Section 2.7.5). A high sulfur content in a strongly reducing environment should tie up all the metals analyzed (except Cr and Mn) as metal sulfides (see Section 3.6.2). The author's sample was also undiluted with effluent or seawater.

2.7.4 Sludge Inorganic Ligands

Typical concentrations for sludge inorganic ligands have been presented in Section 2.4.2. For this work, NH_3-N in Hyperion sludge filtrate was checked with an ammonia-specific ion electrode; NH_3 = 1100 mg-N/l was found. This number compared well with the NH_3-N concentration of 300 mg/l reported for the Hyperion sludge outfall (SCCWRP, 1975), where the flow is one part sludge and three parts effluent. Potentiometric titrations of Hyperion sludge filtrate gave Cl^- concentrations of about 200 mg/l; for LACSD sludge filtrate, the values were about 340 mg/l. Alkalinity titrations of both Hyperion and LACSD sludge filtrates gave values of 4040 mg/l and 2570 mg/l (as $CaCO_3$), respectively.

TABLE 2.12

Dissolved and Total Trace Metals Measured in Digested Sludge (LACSD)

	Dissolved(1)	Total(1)	% Dissolved
Ag	$< 2.5 \times 10^{-7}$	8.4×10^{-4}	< 0.03
Cd	4.6×10^{-6}	2.1×10^{-3}	0.2
Cr	2.8×10^{-5}	7.1×10^{-2}	0.04
Cu	2.7×10^{-6}	3.2×10^{-2}	0.008
Fe	5.8×10^{-5}	6.9×10^{-1}	0.008
Mn	9.7×10^{-5}	6.4×10^{-3}	1.5
Ni	1.2×10^{-5}	1.4×10^{-2}	0.08
Pb	$< 8.8 \times 10^{-6}$	3.2×10^{-2}	< 0.03
Zn	2.3×10^{-5}	1.3×10^{-1}	0.02

(1) All values in gm/l

2.7.5 Sludge Elemental Analysis

Direct elemental analysis of digested sludge can provide useful inputs for digester chemical modeling and can help in measuring non-ammonia nitrogen and total sulfur. Sample drying by either heat or freeze-drying prior to analysis will result in the loss of ammonium bicarbonate and ammonium carbonate (NH_4HCO_3 and $(NH_4)_2CO_3$). Volatile organic losses also occur.

Freeze-dried LACSD digested primary sludge was run on a Perkin-Elmer Model 240 Elemental Analyzer for H, C, N, and S as part of this research. As percent dry solids the elemental concentrations found were:

H	4.6 percent
C	27.8 percent
N	2.8 percent
S	2.3 percent

(The absolute instrumental error is 0.3 percent; the variation of sample values was about 15 percent.) On a molar basis the averages give:

$$H:C:N:S = [62.6]:[31.7]:[2.78]:[1.00].$$

The value of H is probably high; the freeze-dried sludge is very hydroscopic. Handling and weighing exposed it to water vapor in the air.

If the carbon measured by elemental analysis is organic carbon, these data can be compared with the relation between organic carbon and percent volatile solids found by Mitchell and Schafer (1975). Their measurements were for volatile solids and organic carbon in sediment samples near the Hyperion sludge outfall. Sediments in the area showed a strong influence from the outfall sludge discharge. The empirical relationship is

$$\%\ \text{organic carbon} = 0.484\ (\%\ \text{VPS} - 1.86) \qquad (2.3)$$

where % VPS = percent volatile solids (correlation coefficient = 0.993). The LACSD sludge was 52 percent volatile by combustion at 550°C. The corresponding organic carbon is 24.3 percent by the above equation, very close to the 27.8 percent reported for this work.

The sulfur concentration here is of special interest, since sulfur, reduced to sulfide by anaerobic bacteria in sewage and during sludge digestion, apparently controls the chemistry of all trace metals analyzed in this research except Cr and Mn. (See section 3.6.3 for a detailed explanation of relevant chemical modeling.) Typical Los Angeles area drinking waters have SO_4^{2-} concentrations of up to 300 mg/l (∿3mM). The sludge sample recorded above had a sulfur concentration six times as great, indicating the existence of either large sulfur discharges to the sewers or of processes that tend to concentrate sulfur in the digesters.

The discharge of domestic and industrial wastes increase total sulfur in the sewage above the concentrations found in drinking water. The average sulfur concentration should remain relatively constant throughout the year but the amount of sulfur reaching the sludge digesters apparently varies greatly. The hydrogen sulfide (H_2S) content of digester gas at the Hyperion treatment plant varies by a factor of more than four with highest concentrations measured in the summer (Wade, 1976). This situation is expected since the sulfate in sewage can be reduced bacterially to sulfide. Warm temperatures and long residence times enhance this conversion. Lower total flows occur in both City and County of Los Angeles sewers during the dry warm summer months. With some trunk lines extending 50 to 100 km inland from the coastal treatment plants, sewage flow times of up to 24 hours might be expected.

The total sulfur reaching the sludge digesters is then sulfate ions at the same concentration found in the sewage, sulfur incorporated into proteinaceous solids, and metal sulfide particles. The efficiency of metal removal to the digesters might also be expected to show some seasonal variation since metal sulfides are extremely insoluble and occur as solids. The sulfide concentration in the sewage is not always necessarily sufficient to precipitate all the metals.

PART III. THE INTERACTION OF SLUDGE TRACE METALS AND SOLIDS WITH SEAWATER: SEDIMENTATION AND OXIC MIXING

The following presentation looks at two processes that collectively approximate the behavior of sludge in contact with seawater. The oxic mixing experiments, while only done at one dilution, allow for precipitation-dissolution, adsorption, and oxidation of metals in the particle system. The sedimentation experiments, done under quiescent conditions hardly like the ocean, do provide some insight into the settling and flocculation of sludge particles in seawater. The temperature used closely matches that found around the present day LACSD outfalls at Whites Point and thus allows for the comparison of the experimental results from this work with field measurements taken by Galloway (1972) and others. The final section on metal analysis of particle fractions provides a crude estimate of the metals associated with particles trapped on 8.0-μ and 1.0-μ Nuclepore membranes.

2.8 Sedimentation Experiments

Sedimentation experiments were made to observe the settling behavior after dilution in seawater of (a) sludge trace metals and (b) filterable solids. Such observations are necessary if predictive modeling is to be done for sludge disposal to the ocean; in addition, they allow the comparison of sedimentation values measured in the laboratory with the trace-metal concentrations observed in the sediments around existing sludge discharges. A properly designed experiment also provides insight into the flocculation of sludge in a high ionic strength medium (e.g. seawater) and can be used to calculate sludge particle diameters (or densities) if additional information on particle densities (or size distributions) is available.

Sedimentation experiments in this research were carried out at 10.5 ± 0.5°C in artificial seawater. (See Table A.6 for a list of the seawater constituents and their quantities.) The artificial seawater (pH ∿ 7.9) was filtered through a 0.45-micron Millipore filter to remove the background solids. Digested primary sludge (LACSD) was used for all runs. All samples were taken at a depth of 15 ± 0.3 cm with a volumetric pipette. A 2.0-liter graduated cylinder was used as a sedimentation column. Solids were separated from the solution with a 1.0-μ Nuclepore filter. Various sample volumes were chosen to keep solids loading per filter as uniform as possible. All samples were dried at 105°C and weighed to ± 0.000005 grams. Trace metal analysis was done by X-ray fluorescence (XRF) by Dan Shadoan at the Crocker Nuclear Laboratories, University of California at Davis.

The experiments were designed to follow both the solids and selected trace metals upon sedimentation. Nuclepore membranes were chosen because of their favorable properties for metal analysis by XRF and because their particle-removal efficiency for the 1.0-μ size apparently increases linearly with solids loading (see Section 2.6.4).

The technique chosen has several disadvantages which will be mentioned before experimental results are presented and discussed.

Sampling was done at only one depth by inserting a clean pipette. This method may disrupt the surrounding fluid and fails to measure the effects of flocculation as a multiple-depth sampling technique might. Multiple dilutions (500:1, 100:1, and 50:1) were used in this work to test for flocculation effects. Repetition of experiments at 50:1 dilution indicated that the sampling technique was consistent if not uniform.

Rapidly settling particles (large and/or very dense) were lost by sampling from the top only. These particles settled out before the initial samples were taken in a given run. Mass balances on the total solids and metals showed that these particles did not constitute a large fraction of the total mass or of total metals. These "fast" particles could be very important, however, in the zone immediately surrounding any sludge discharge to the ocean. They are also easily removed by centrifugation of the sludge before discharge.

Sample size was an additional limitation on these sedimentation experiments. At dilutions greater than 500:1, individual samples of 100 or 200 ml are necessary if trace-metal analysis by XRF is run and if significance is placed on the solids recovery. In a 2.0-liter graduate, a 100-ml extraction lowers the water surface by 2.0 cm, hardly a point sample. Such large volumes require a sedimentation column of 4.0-liter capacity or greater. Uniform mixing of such volumes is a documented problem (McLaughlin, 1958).

The results of four sedimentation experiments (one each at 100:1 and 500:1 dilutions and two at 50:1 dilutions) are shown in Figure 2.15 with curves fitted as third-order polynomials. Experimental data are

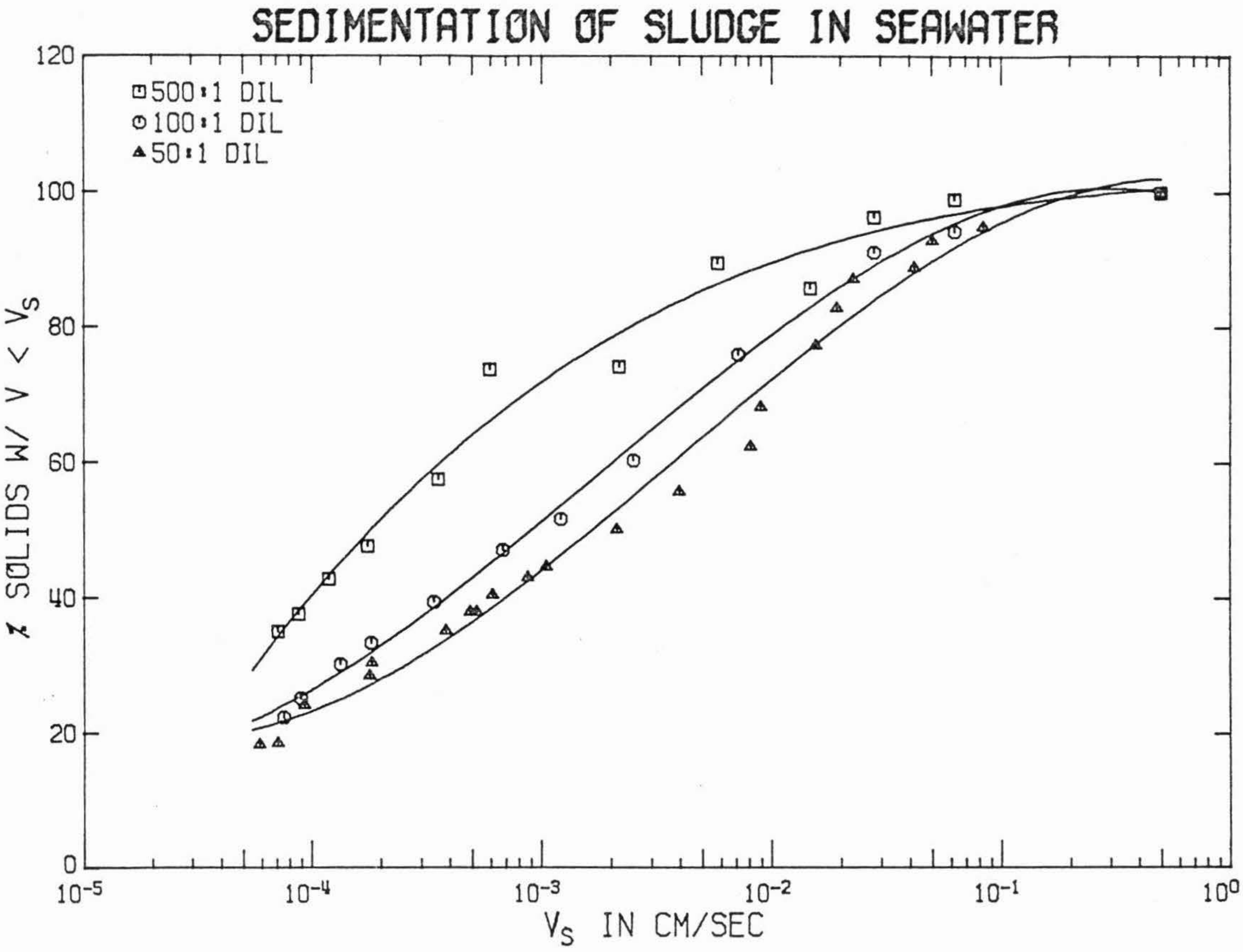


FIGURE 2.15

Summary of Sedimentation Data for LACSD Sludge-Seawater Mixture at Three Dilutions shown as points. The metal data from the same experiments for Cr, Cu, Fe, Ni, Pb, and Zn are plotted as points with the related solids curves in Figures 2.16 through 2.18.

Comparison of the sedimentation curves in Figures 2.5 and 2.15 showed that the sludge at 500:1 dilution settled more slowly than all samples but those taken by Morel, et al. (1975). The filterable solids concentration at the 500:1 dilution was ∿ 50 mg/l. Morel's 10:1 dilution of effluent/NaCl should have had a solids concentration of 25 to 30 mg/l. An experiment with a lower particle concentration would be expected to show less flocculation. (Possible effects from Morel's use of a NaCl solution have already been mentioned above.) Myers' particle separation with glassfiber filters and 1:1 dilution (final solids concentration of ∿ 150 mg/l) accounted for the relatively fast sedimentation in this system. In the case of Brooks' work (where the initial particulate concentration was ∿ 1600 mg/l) visible flocculation was observed and the rapid sedimentation measured was expected.

Increasing the dilution decreased the apparent sedimentation rate indicating that the sludge flocculated at low dilutions. This result was not surprising; higher dilutions decreased the frequency of particle-particle collisions necessary for flocculation.

Sedimentation velocities for the highest dilution were used to calculate the apparent spread of sludge after ocean discharge. In the case of the Whites Point outfalls of the LACSD, a plume-rise height of 30 meters was estimated. Ten percent of the solids as measured in this work settled with a velocity $v_s \geq 1 \times 10^{-2}$ cm/sec and 20 percent

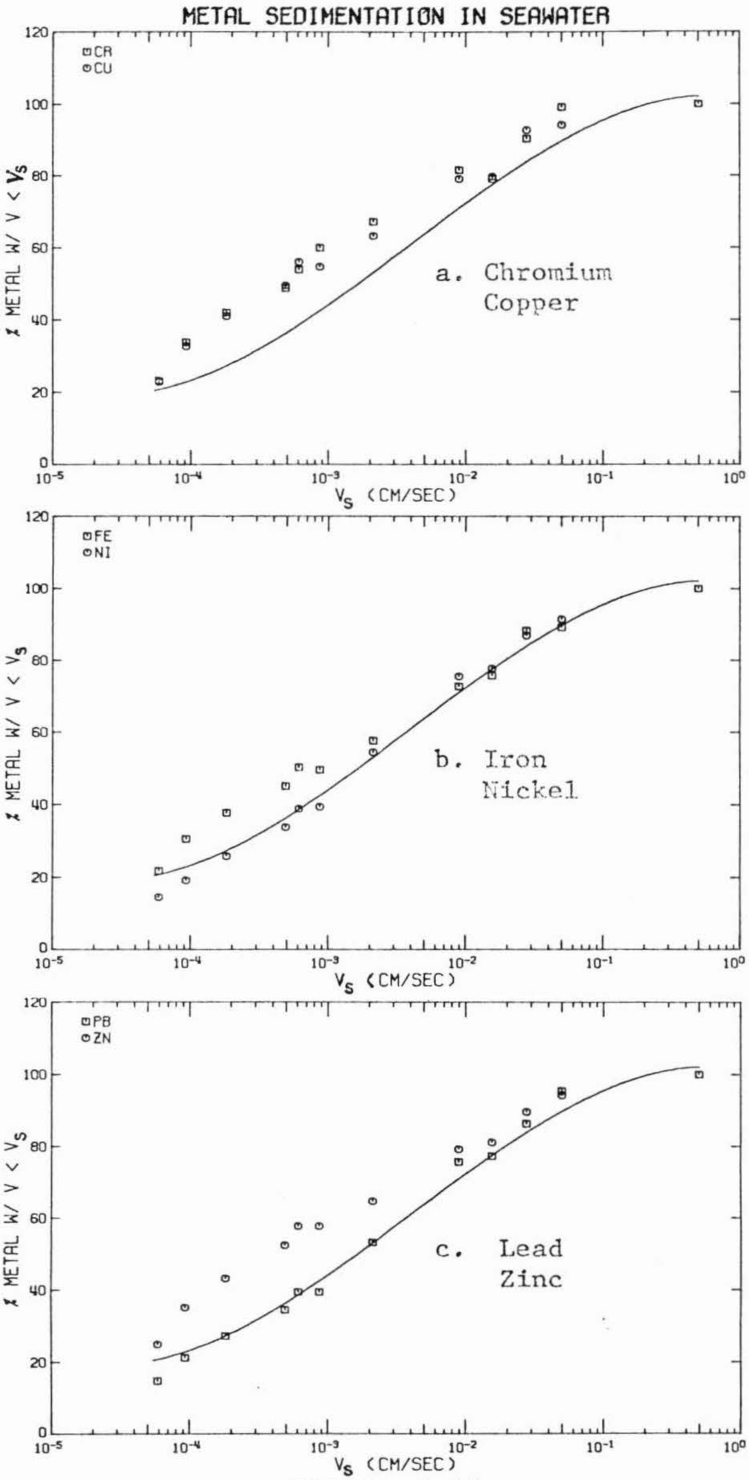


FIGURE 2.16
Behavior of Filterable Metals During Sedimentation, 50:1 Dilution
Solid Curve is Fitted from Solids Data

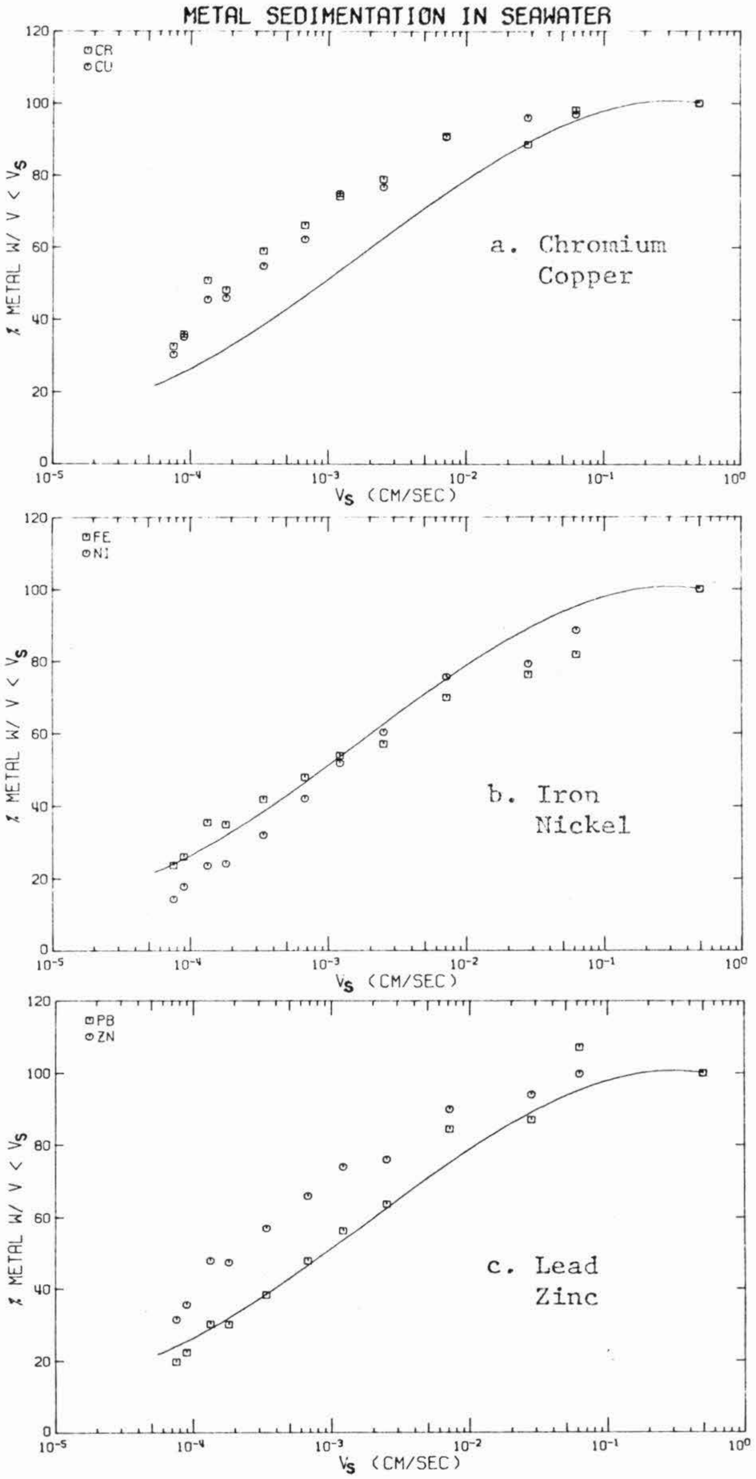


FIGURE 2.17

Behavior of Filterable Metals During Sedimentation, 100:1 Dilution
Solid Curve is Fitted from Solids Data

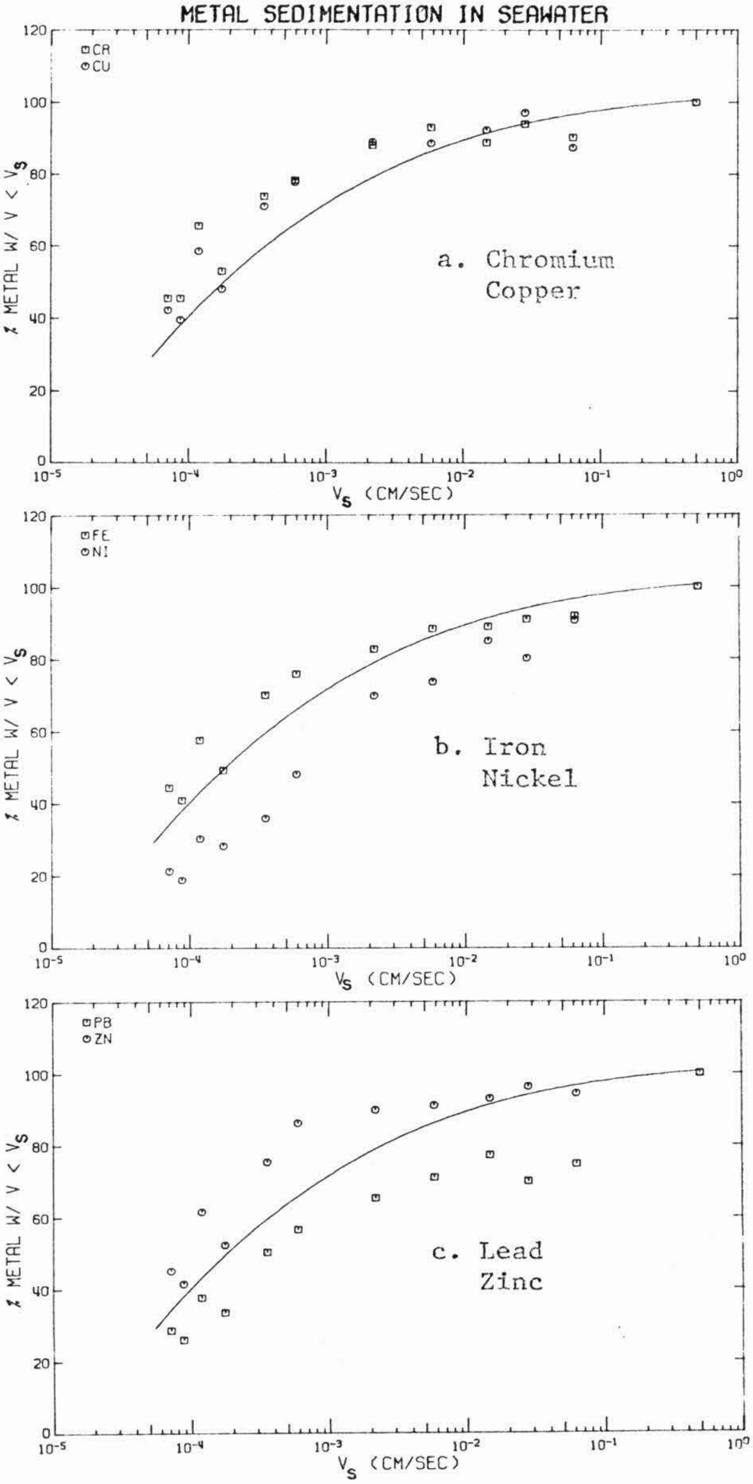


FIGURE 2.18
Behavior of Filterable Metals During Sedimentation, 500:1 Dilution.
Solid Curve is Fitted from Solids Data

with $v_s \geq 2.2 \times 10^{-3}$ cm/sec. By kinematics

$$v_s = y/t \rightarrow t = y/v_s \qquad (2.4)$$

where

v_s = settling velocity

y = plume height of rise

t = settling time,

the corresponding settling times were 3×10^5 and 1.4×10^6 seconds (about three to fifteen days). With local currents of five to ten cm/sec, the maximum travel distances for the sludge would be 15 to 30 km for 10 percent of the solids and 70 to 140 km for 20 percent of the solids.

Galloway (1972) accounted for 15 to 20 percent of the total trace metals discharged at Whites Point over the life of the system within five miles of the outfall complex. Myers (1974) found 0.5 percent of the discharged organic carbon within the same area. A recomputation of Myer's data by Hendricks (1976) gave three to six percent of the organic carbon close to the outfall.

Sedimentation data alone were not adequate to explain the concentrations of metals and organic carbon of terrestial origin. Several explanations more readily described these local phenomena. Recent work by Roberts (1975) on model buoyant plumes has shown that cross-currents tend to bend the plume over so that it contacted the bottom very close to the discharge site. This effect would bring the sludge particle field into direct contact with the bottom and less settling distance was required before the solids reached the bottom. The plume was also more evenly mixed in the water column, and the particles would have an elevation distribution as well as a sedimentation-velocity distribution. More of the solids could settle out near the outfall.

The second factor was temporal variations in local current pattern. The general flow trend for surface waters off Whites Point is north-west to south-east. Recent current measurements (Hendricks, 1976), however, showed substantial local variation that would leave the average particle over the enriched zone immediately around the outfalls for up to five days. Such residence times reduced the potential travel distance by up to 80 percent.

The third mechanism for increased solids fallout in the outfall locale was flocculation of effluent solids with natural ocean particles and with other effluent particles. An increased residence time as indicated by temporal velocity variations increased the solids content in the water column. The natural concentration of particles in ocean waters is low, but the initial 100:1 dilution of effluent at 300 mg/l of suspended solids puts the sewage and natural particles at approximately the same concentration. Flocculation is expected.

At sufficiently high dilutions, the probability of interparticle collisions, and with them flocculation, becomes very low. The solids concentration at which that point is reached is unknown but the calculation of v_s for particles of known diameter suggested appropriate bounds on v_s. Using Stokes Law with μ and ρ values for seawater at 10.5°C, an 8.0-μ sphere had a v_s range of 1.2×10^{-3} to 4.1×10^{-3} cm/sec for ρ_s in the range 1.5 to 2.65 gm/cm^3. More than 70 percent of the solids (by weight) in Figure 2.15 had $v_s < 1.0 \times 10^{-3}$ cm/sec for the 500:1 dilution. Since at least 55 percent of the solids by weight had diameters less than 8.0 μ (Figure 2.12), to a first approximation, dilutions greater than 500:1 did not significantly decrease sedimentation velocities.

The metal data from the sedimentation experiments showed some scatter but several general conclusions are drawn. The scatter was probably due to inhomogeneities in the sedimentation columns, to the sampling technique, and to the final sample used for XRF analysis. Mass balances of metals in the first sample of each run (Table 2.13) showed good agreement between expected metals via AAS analysis and those found by XRF analysis. Nickel recovery was generally the poorest, probably owing to mobilization of nickel from the solids. Mixing experiments with LACSD sludge in aerated seawater showed that Ni was mobilized up to 60 percent in 28 days (Section 2.9). Not surprisingly, Ni values throughout the experiments fell on or below the fitted solids curves. Chromium, Cu, Fe, and Zn consistently fell above the solids curve. Lead behaved more like Ni. Since Pb showed no mobilization in mixing experiments,it can be concluded that this metal was on larger and/or denser particles than Cr, Cu, Fe, and Zn, or that the differences were attributable to experimental errors. The total possible errors for metal analysis in the sedimentation experiments (estimated at ∿ 30 percent in Appendix A.7) were greater than the spread of any of the metal data from the solids curves. To a first approximation, the metals settled with the filterable solids.

TABLE 2.13a

Metal Mass Balances for Sedimentation of LACSD Digested Primary Sludge in Artificial Seawater at 10.5°C (1)

#1 50:1 Dilution - Initial solids = 502 mg/1

Metal	Total Metal Found (gm)	Total Metal (2) Expected (gm)	Metal Found/ Metal Expected (%)
Cr	3.19×10^{-5}	3.58×10^{-5}	89
Cu	1.49×10^{-5}	1.60×10^{-5}	93
Fe	3.25×10^{-4}	3.44×10^{-4}	94
Ni	4.80×10^{-6}	6.9×10^{-6}	70
Pb	1.39×10^{-5}	1.58×10^{-5}	88
Zn	6.67×10^{-5}	6.50×10^{-5}	103

#2 50:1 Dilution - Initial solids = 497 mg/1

Cr	3.46×10^{-5}	3.58×10^{-5}	97
Cu	1.54×10^{-5}	1.60×10^{-5}	96
Fe	3.34×10^{-4}	3.44×10^{-4}	97
Ni	5.51×10^{-6}	6.90×10^{-6}	80
Pb	1.46×10^{-5}	1.58×10^{-5}	93
Zn	7.24×10^{-5}	6.50×10^{-5}	111

(1) All total metals values found are for the first sample of each experiment, by XRF.

(2) Total metals expected are based on total sludge metals by AAS from Table 2.11, with the appropriate dilution factor.

TABLE 2.13b

Metal Mass Balances for Sedimentation of LACSD Digested Primary Sludge in Artificial Seawater at 10.5°C (1)

#3 100:1 Dilution - Initial solids = 254 mg/l

Metal	Total Metal Found (gm)	Total Metal(2) Expected (gm)	Metal Found/ Metal Expected (%)
Cr	1.67×10^{-5}	1.79×10^{-5}	93
Cu	7.22×10^{-6}	8.00×10^{-6}	90
Fe	1.87×10^{-4}	1.72×10^{-4}	109
Ni	2.80×10^{-6}	3.45×10^{-6}	81
Pb	7.51×10^{-6}	7.90×10^{-6}	95
Zn	3.50×10^{-5}	3.25×10^{-5}	108

#4 500:1 Dilution - Initial solids = 50.4 mg/l

Cr	3.34×10^{-6}	3.58×10^{-6}	93
Cu	1.48×10^{-6}	1.60×10^{-6}	92
Fe	2.87×10^{-5}	3.44×10^{-5}	83
Ni	5.66×10^{-7}	6.90×10^{-7}	82
Pb	1.92×10^{-6}	1.58×10^{-6}	122
Zn	6.73×10^{-6}	6.50×10^{-6}	104

(1) All total metals values found are for the first sample of each experiment, by XRF.

(2) Total metals expected are based on total sludge metals by AAS from Table 2.11, with appropriate dilution factors.

2.9 A Time History of Sludge in Oxic Seawater

As a part of this research, aerated mixtures of sludge and artificial seawater were monitored for pH, filterable solids, and trace metals with time. Both Hyperion and LACSD sludges were used. These experiments provided insight into the behavior of sludge on mixing and were also necessary for the separation of the phenomena of mobilization and sedimentation in trace-metal data from sedimentation experiments.

For the experiments in this work digested sludge was diluted 100:1 with artificial seawater, in a completely mixed aerated reactor. A four-liter acid-washed polyethylene bottle was used as a reactor. Stirring was provided with a polyethylene propeller turned by an electric motor. Compressed air, bubbled first through doubly-distilled water, was used to keep the system oxic. All experiments were done in a constant-temperature, constant-humidity room at 10.5°C ± 0.5. The artificial seawater was pre-filtered through a 0.45-micron membrane filter to remove background solids.

All samples were taken with 25-ml volumetric pipettes and the solids separated with 1.0-μ Nuclepore membranes. Before each sample was taken the reactor was capped and inverted several times to insure the complete mixing of the contents. No visible loss of solids to the reactor walls or the stirrer was detected. The pH was checked on most samples. Total filterable solids were measured by weighing after drying and metals were quantified by XRF. Duplicate samples were taken for a limited number of points and metal analysis performed on these samples for Cr, Cu, and Fe by flame AAS.

A mixture of Hyperion mesophilic sludge and seawater was run for ten days. A mixture of LACSD primary sludge with seawater was run for 28 days. The solids decrease in each experiment was less than 10 percent. Visually, initial samples taken from the reactor were black when filtered onto the Nuclepore membranes. After several days of aeration the samples were brown, indicating some physical or chemical change had taken place in the interim. The pH rose systematically from 7.9 to 8.3 or 8.4 over the course of the experiment. This pH change is difficult to explain. The dissolution of metal sulfides or the oxidation of organic nitrogen would possibly account for the pH increase. In a real ocean system, increased dilution and the natural buffering capacity of the seawater prevent such pH changes.

The trace-metal data in all cases were normalized with the filterable solids weight, to check for mobilization of metals from the particles. The solids, trace metals, and pH data appear in Table 2.14. Initial examination of the metal data showed no systematic changes in metal capture with time except for Ni. Trace metal balances were then run as

$$\overline{m} = \frac{1}{n} \sum_{i}^{n} m_i \qquad (2.5)$$

and

$$\overline{s} = \frac{\Sigma\, m_i/s_i}{n} \qquad (2.6)$$

where

$\overline{m}$ = average metal capture

m_i = grams of metal captured on the i-th filter

s_i = grams of solids on the i-th filter

$\overline{s}$ = solids specific metal capture

n = number of filters analyzed

TABLE 2.14a

Summary of Mixing Experiment Data

	Hyperion - AAS				Hyperion - XRF							
Time (min)	Solids (mg)	Metals (gm/gm) $Cr\times10^3$	$Cu\times10^3$	$Fe\times10^2$	Solids (mg)	Metals (gm/gm) $Cr\times10^3$	$Cu\times10^3$	$Fe\times10^2$	$Ni\times10^4$	$Pb\times10^4$	$Zn\times10^3$	pH
0	5.63	2.77	2.31	1.55	5.63	2.43	2.56	1.29	6.23	7.60	3.80	---
30	5.72	2.34	1.75	1.48	5.66	3.59	3.36	2.00	8.74	12.1	5.49	7.94
60	5.93	1.97	2.02	1.41	5.71	3.71	3.43	2.01	8.56	12.6	5.46	8.10
120	5.68	2.59	2.29	1.60	5.71	2.98	2.75	1.61	6.97	10.2	4.43	8.08
120	5.82	2.58	2.40	1.68	5.81	3.29	3.10	1.74	7.50	12.1	4.99	8.08
315	5.71	2.49	2.10	1.63	5.55	3.66	3.39	2.05	8.74	12.1	5.66	8.10
420	5.35	2.43	2.06	1.50	5.74	3.22	3.03	1.83	6.60	11.0	4.84	8.12
1540	5.49	2.57	2.73	1.78	5.75	2.99	2.94	1.59	5.44	9.58	4.52	8.33
1540	5.31	2.60	2.26	1.93	5.57	2.94	2.94	1.61	5.56	11.2	4.40	8.33
2940	5.85	2.12	2.82	1.84	5.58	2.47	2.13	1.11	4.01	6.09	3.39	8.37
4320	5.61	3.03	2.14	1.64	5.50	2.96	2.73	1.36	4.72	8.54	4.13	8.33
7200	5.57	3.00	2.51	1.84	5.79	3.04	2.56	1.53	5.53	8.64	4.23	8.42
14400					5.33							
AVE($\overline{s}$)		2.54	2.28	1.66		3.11	2.81	1.64	---	10.1	4.61	

TABLE 2.14b

Summary of Mixing Experiment Data

	LACSD - XRF							
Time (min)	Solids (mg)	Metals gm/gm						
		Cr×10^3	Cu×10^3	Fe×10^2	Ni×10^4	Pb×10^4	Zn×10^3	pH
0	6.76	2.18	1.03	2.05	3.36	8.8	4.28	7.86
30	6.55	2.75	1.24	2.61	7.16	10.9	5.44	8.08
60	6.72	2.62	1.19	2.60	3.55	10.7	5.40	8.11
60	6.67	2.61	1.18	2.53	3.45	11.6	5.22	8.11
120	6.74	2.90	1.35	3.02	3.73	13.4	6.03	8.13
360	6.69	2.73	1.28	2.97	3.22	12.5	5.50	8.18
1365	6.16	2.79	1.57	2.75	3.14	12.0	5.76	8.26
2910	6.11	2.91	1.36	2.81	3.02	12.5	5.85	8.28
4440	6.45	2.36	1.04	2.58	2.29	10.3	4.93	8.30
5850	6.23	2.43	1.12	2.43	2.20	9.4	5.17	8.32
8640	6.37	2.46	1.10	2.34	2.23	10.6	4.94	8.23
10200	6.28	2.62	1.24	2.70	2.65	12.0	5.27	8.32
13050	6.35	2.61	1.19	2.52	2.58	11.9	5.12	8.32
21435	6.40	2.39	1.08	2.59	2.49	11.4	4.61	---
28860	6.70	2.39	1.04	2.73	2.44	12.0	4.17	8.34
31680	6.24	3.14	1.39	3.10	2.72	14.6	5.50	8.40
40880	6.16	2.55	1.23	2.63	2.25	12.4	4.68	---
AVE($\overline{s}$)		2.78	1.29	2.81	3.28	12.3	5.49	

The $\overline{m}$'s (see Table 2.15) compared favorably for total metals based on AAS analyses, assuming no mobilization (with the exception of Ni). The high values for Cr, Cu, Pb, and Zn by XRF in the Hyperion run may be caused by sampling errors. These samples were the first prepared for the XRF analysis. A calibration error for the XRF analyses was also a possible source of error. However, the total errors were within the experimental error bounds. The $\overline{s}$ values, when compared to weight-specific metal data from the total sludge (see Tables 2.10 and 2.11), were again quite reasonable. Statistical analysis of the metal data for trends was inconclusive except for Ni. A plot of $(m_i/s_i)_{Ni}$ versus time (see Figure 2.19) showed a substantial mobilization of Ni for both sludges. The mobilization of Ni was extremely rapid, with the majority of the change complete in less than one day.

This mobilization may be caused by surface desorption with the increase in ionic strength and/or to the oxidation (or dissolution) of NiS. Other metals may in fact be released by dissolution and/or oxidation but with the abundance of surface area (at least 25 m^2/l from Coulter Counter data) they would be re-adsorbed immediately onto particles.

2.10 Metal Fractionation by Filtration

The sieving of sludge particles by vacuum filtration has already been introduced in Section 2.3.4 and 2.6.4. Even the most sieve-like membranes available tend to clog readily and thus intercept particles far smaller than the stated pore size. The same membranes used for the solids fractionation were also analyzed by XRF for Cr, Cu, Fe, Ni,

TABLE 2.15a

Metal Mass Balances on Mixing Experiments
LACSD Digested Primary Sludge

Metal	Total Metal(2) Found (gm)	Total Metal(3) Expected (gm)	Metal Found/ Metal Expected (%)
Cr(1)	1.59×10^{-5}	1.79×10^{-5}	89
Cu(1)	0.78×10^{-5}	8.0×10^{-6}	98
Fe(1)	1.7×10^{-4}	1.72×10^{-4}	99
Ni(1)	2.0×10^{-6}	3.45×10^{-6}	58
Pb(1)	7.4×10^{-6}	7.88×10^{-6}	94
Zn(1)	3.33×10^{-5}	3.25×10^{-5}	102

(1) Based on the average of 16 samples ($\overline{m}$).

(2) Total metal found by XRF.

(3) Based on AAS analysis for total sludge metals.

TABLE 2.15b

Metal Mass Balances on Mixing Experiments
Hyperion Digested Mesophilic Sludge

Metal	Total Metal Found (gm)	Total Metal(2) Expected (gm)	Metal Found/ Metal Expected (%)
Hyperion - AAS Data			
Cr(1)	1.43×10^{-5}	1.52×10^{-5}	94
Cu(1)	1.29×10^{-5}	1.38×10^{-5}	94
Fe(1)	9.34×10^{-5}	9.58×10^{-5}	98
Hyperion - XRF Data			
Cr(1)	1.76×10^{-5}	1.52×10^{-5}	116
Cu(1)	1.65×10^{-5}	1.38×10^{-5}	120
Fe(1)	9.33×10^{-5}	9.58×10^{-5}	97
Ni(1,3)	3.72×10^{-6}		
Pb(1)	5.75×10^{-6}	4.73×10^{-6}	121
Zn	2.62×10^{-5}	1.95×10^{-5}	134

(1) Based on the average value for 12 samples.

(2) Based on AAS analysis for total sludge metal content and a dilution of 1 part sludge + 99 parts artificial seawater.

(3) No total Ni analysis was done on Hyperion sludge by AAS.

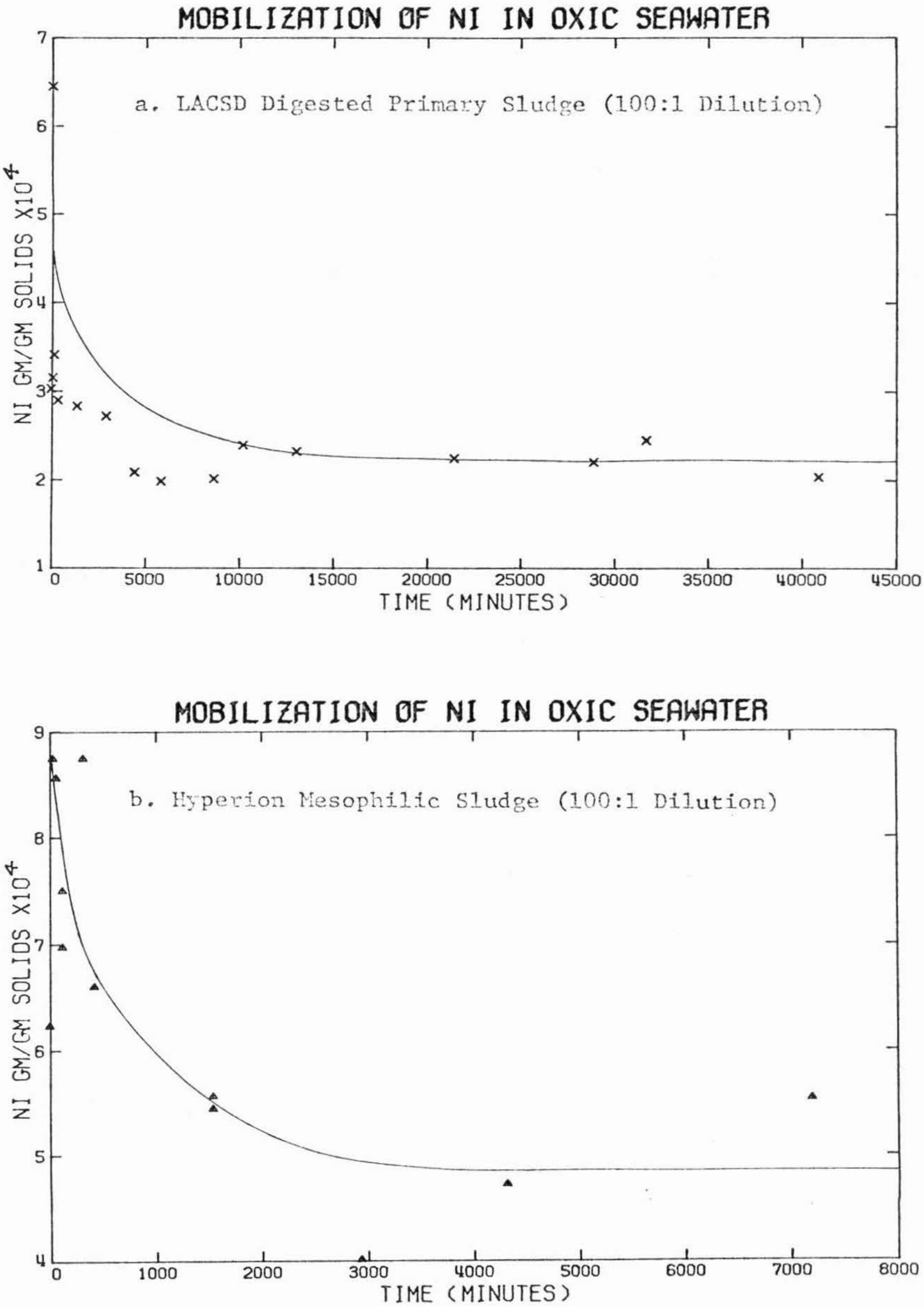


FIGURE 2.19

Mobilization of Ni Away From the Sludge Particles During Mixing in Oxic Seawater

Pb, and Zn. The Ni data were inconclusive but the behavior of the other metals followed that of the solids very closely. For the 1.0-μ Nuclepore membranes, the mass of metals captured plotted against volume loaded gave linear fits with correlation coefficients greater than 0.99 in all cases. Comparison of metals captured on the 8.0-μ membranes to those on the 1.0-μ for the lightest filter loadings were Cr (44%), Cu (49%), Fe (60%), Pb (64%), and Zn (46%). These values indicate some difference in the association of particular metals with given particle-size fractions. The order of capture agreed with the metal sedimentation data. Chromium, Cu, and Zn, which all lay above the solid sedimentation curves (see Figures 2.16 through 2.18) showed lower capture efficiencies, suggesting metal association with smaller particle sizes. Lead, whose sedimentation data fell on or below the solids curves, showed larger capture efficiencies on the 8.0-μ membranes and hence larger particle size association.

2.11 Summary

Physical, chemical, and physical-chemical properties of digested sewage sludge have been reviewed in the preceding sections and the results of this research into these areas have been presented. Particle-size distributions for two sludges over a range from one to 60 μ were measured using a Coulter Counter. By number of count, particles with diameters less than 10 μ are predominant although they make up less than 20 percent of the total volume measured. Based on Coulter Counter measurements, the surface area of the sludges is conservatively estimated to be 25 m^2/l.

Attempts at particle sizing by vacuum filtration with Nuclepore membranes showed that the capture efficiency of the 8.0-μ membrane increased rapidly with increasing loading. These membranes are thus unsuited for sizing using vacuum removal of the liquid phase. However, at the lowest loading applied, 8.0-μ membranes captured 46 percent of the weight retained by the 1.0-μ membranes.

Chemical measurements on the sludge samples included total and dissolved metals in LACSD sludge and total metals in Hyperion sludge. Ninety-nine plus (99+) percent of all metals but Mn were associated with the particulate phase. Analysis for chloride, ammonia, and total alkalinity gave values typical for digested sludges. Elemental analysis of freeze-dried sludge samples showed sulfur levels of approximately two percent by weight.

The physical-chemical interactions of digested sludge with artificial seawater were measured during both sedimentation and oxic-mixing experiments. Sedimentation experiments demonstrated that sludge flocculated in seawater and the extent of flocculation decreased with increasing dilution. Trace metal analysis by XRF for Cr, Cu, Fe, Ni, Pb, and Zn, indicated that Cr, Cu, and Zn settled more slowly than the filterable solids while Ni and Pb settled as fast or faster than the solids. The Ni behavior was attributed to either association with faster settling particles or to desorption or dissolution from the particles. To a first approximation the metals and the solids settled together. The oxic mixing of sludge in artificial seawater simulated the behavior of sludge upon discharge to actual oxic ocean waters. Of the six metals analyzed only Ni showed significant mobilization away from the particulate phase. Metal analysis from the particle sizing by vacuum membrane filtration gave results in agreement with those from the sedimentation experiments.

CHAPTER 3

A PROPOSAL FOR SLUDGE DISPOSAL TO THE SAN PEDRO AND SANTA MONICA BASINS

3.1 Introduction

Present practices of sludge disposal to the ocean, usually made in close proximity to the highly productive surface waters, are generally unacceptable because of possible adverse environmental impacts. This chapter is a proposal to make use of far-less-productive, near-coastal, deep basins for the continued ocean disposal of sludge. These geologic structures, specifically the San Pedro and Santa Monica Basins, are natural sediment traps nearly devoid of life. They are deep (over 600 meters) and close to the shore (less than 24 km). If digested sludge, which comes from an anoxic*, anaerobic environment, was deposited in these natural sinks, the economic advantages of ocean discharge could be maintained while adverse environmental impacts would be minimized.

In the presentation that follows, the coastal oceanography and geochemistry of the San Pedro and Santa Monica Basins will be summarized to show the stable local conditions in the target area for discharge. Near-coastal and basin biology will be reviewed so that environmental impacts may be assessed. The actual analysis for the

---

*Anoxic as it is used throughout this work means devoid of dissolved oxygen (D.O.) in contrast to anaerobic, which refers to the biochemical pathways utilized by certain bacteria.

disposal plan includes 1) computer modeling of the sludge discharge as a buoyant plume in the ocean; 2) chemical modeling of the behavior and effects of the chemical constituents of sludge (both on a stoichiometric and on an equilibrium basis; 3) sedimentation analysis using experimental results from Chapter 2 combined with documented data on basin sedimentation; and 4) estimates of the effects of diffusion and dispersion on the dissolved constituents and particulate matter in discharged sludge. The methods of sludge transport will be confined to pipeline discharge of sludge flows from the City of Los Angeles and LACSD Treatment Plants. A total assessment of environmental impacts of the proposed discharge will conclude this chapter.

The analysis that follows is specifically oriented toward the ocean sludge discharge possibilities for Los Angeles County. The concepts used and the modeling carried out could be easily adapted for any sludge disposal plan to the ocean.

3.2 Coastal Oceanography

If sludge is to be disposed of safely and efficiently in the ocean off southern California, careful consideration must be given to local oceanographic conditions. Target areas for sludge disposal are the Santa Monica and San Pedro Basins, indicated on Figures 3.1 and 3.2. These depressions are apparently the partially-filled remnants of successive block faulting of the late Miocene period. The depth of sediment within them is already over 3000 meters.

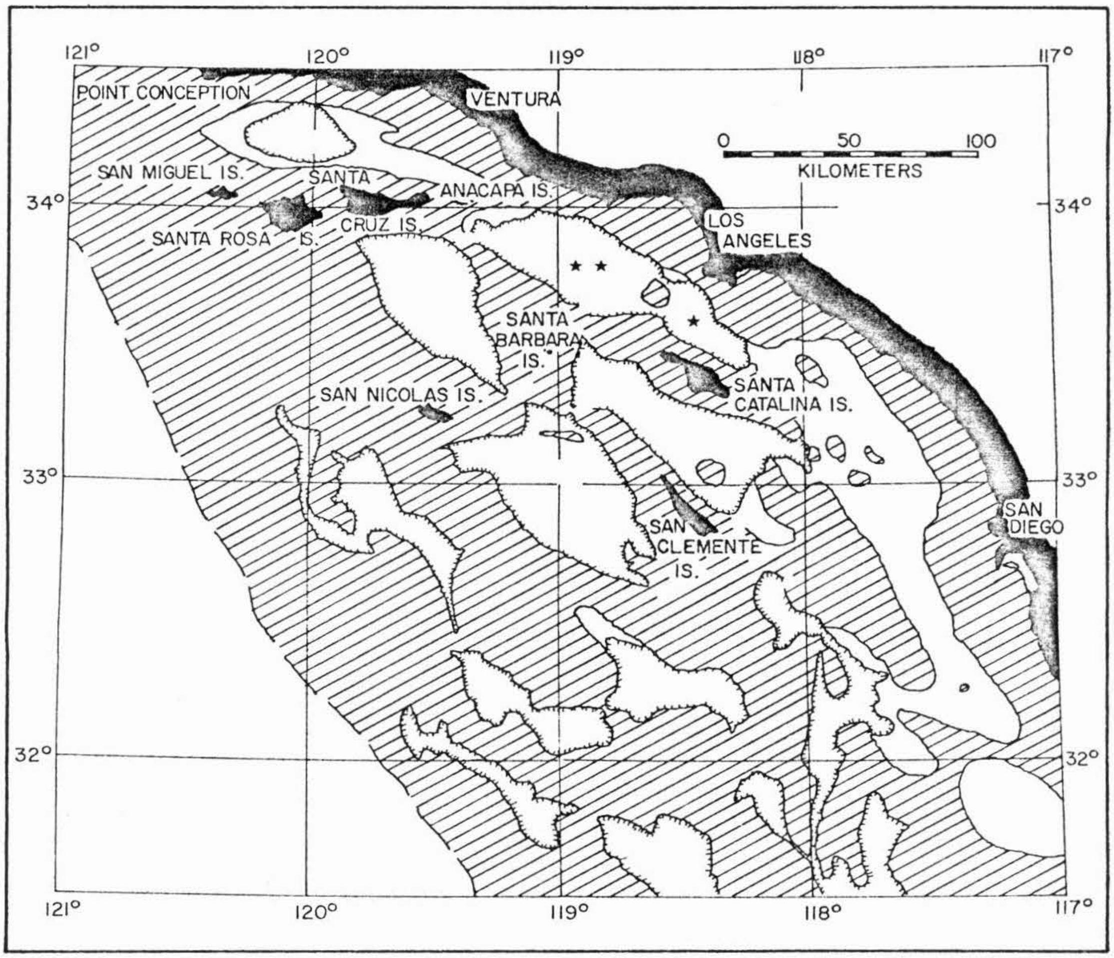


FIGURE 3.1

Marine Basins off Southern California

The hatched area denotes the Continental Shelf. The San Pedro and Santa Monica Basins are indicated by (★) and (★ ★) respectively.

Source: Emery, 1954.

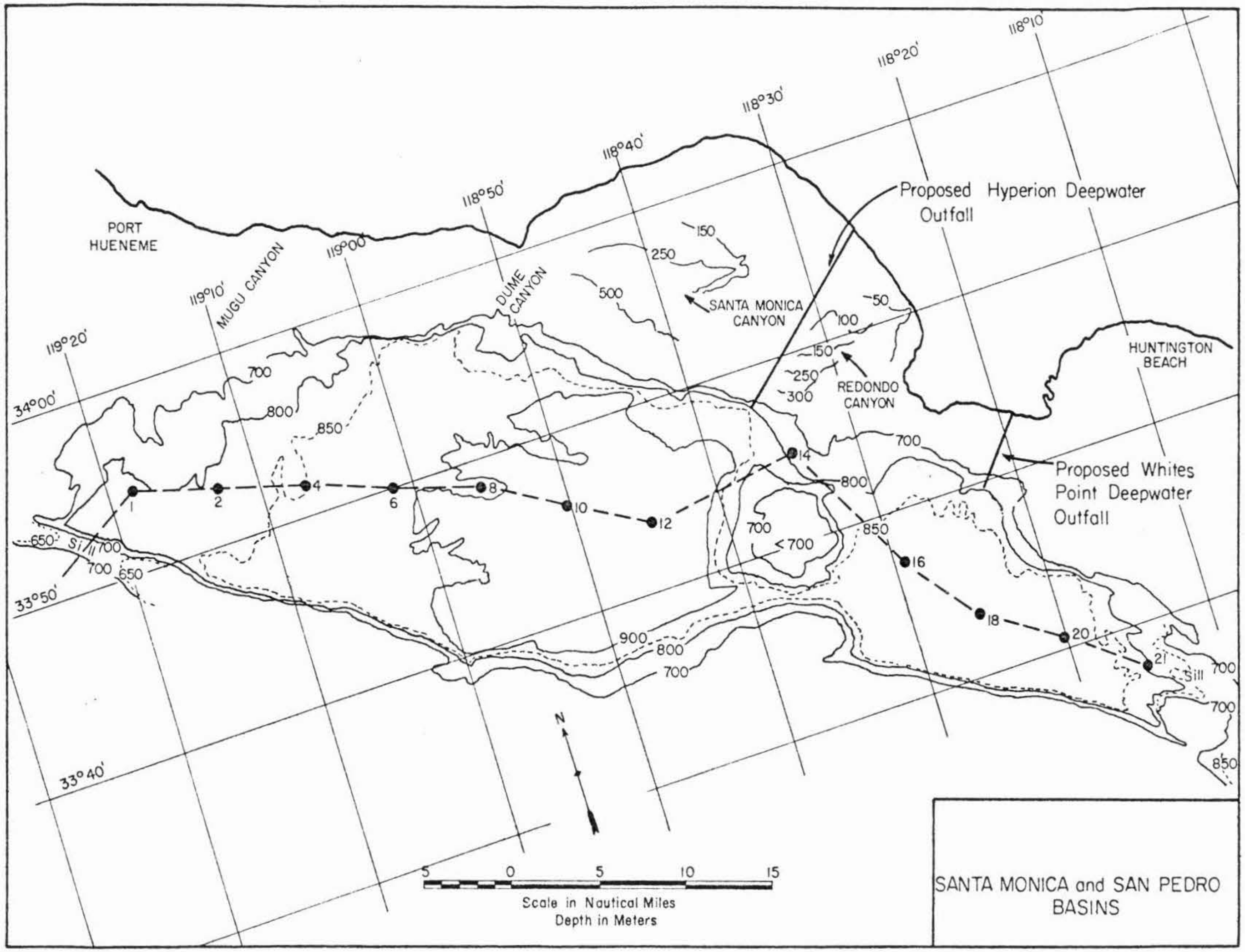


FIGURE 3.2

Santa Monica and San Pedro Basins
The dashed line and dots refer to the stations where sampling was done for the profiles in Figures 3.5 through 3.7.
Source: Minard, 1968

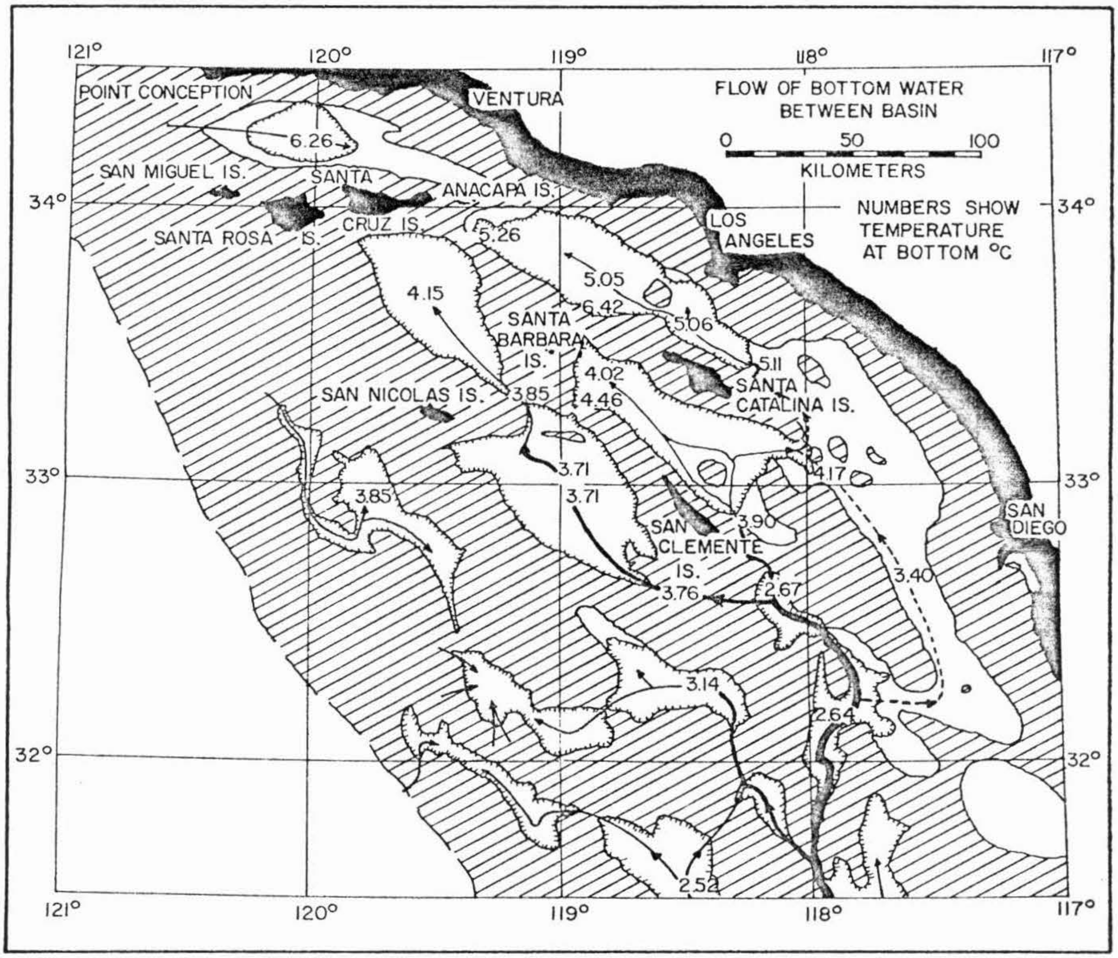


FIGURE 3.3

Water Flow Pattern in the Coastal Marine Basins

The hatched area denotes the Continental Shelf

Source: Emery, 1954.

Basin filling is a continuous process and includes detrital fallout, atmospheric fallout, diffusion of sediments from the shore, and turbidity flows from submarine canyons (Emery, 1960).

3.2.1 Basin Water Circulation

The temperature and salinity measurements over the last 40 years indicate that the waters of the Santa Monica and San Pedro Basins flow in from the southeast (Emery, 1954). The basin sill, the lowest point in the surrounding rim, allows deep-ocean water to flow into successive basins as shown in Figure 3.3. Only water from above the sill depth can enter the basins, and since ocean temperature decreases with depth, a series of basins, each shallower than the one directly "upstream" from it, will be filled with successively warmer water. Temperature, water density, and dissolved oxygen (D.O.) below the sill are nearly constant. (See Figures 3.4 through 3.7). In lateral cross section the same stability is present (see Figure 3.8). The D.O., an important biological parameter, is particularly low. In the open ocean the D.O. decreases with depth down to a minimum between 500 and 800 meters and then increases slowly with further depth. Since the sill depths of the Santa Monica and San Pedro Basins coincide with the D.O. minimum for the waters of the open ocean, these basins are nearly depleted. Average D.O. concentrations are less than 0.4 mg/1, while ocean surface waters have saturation concentrations of about 8.6 mg/1.

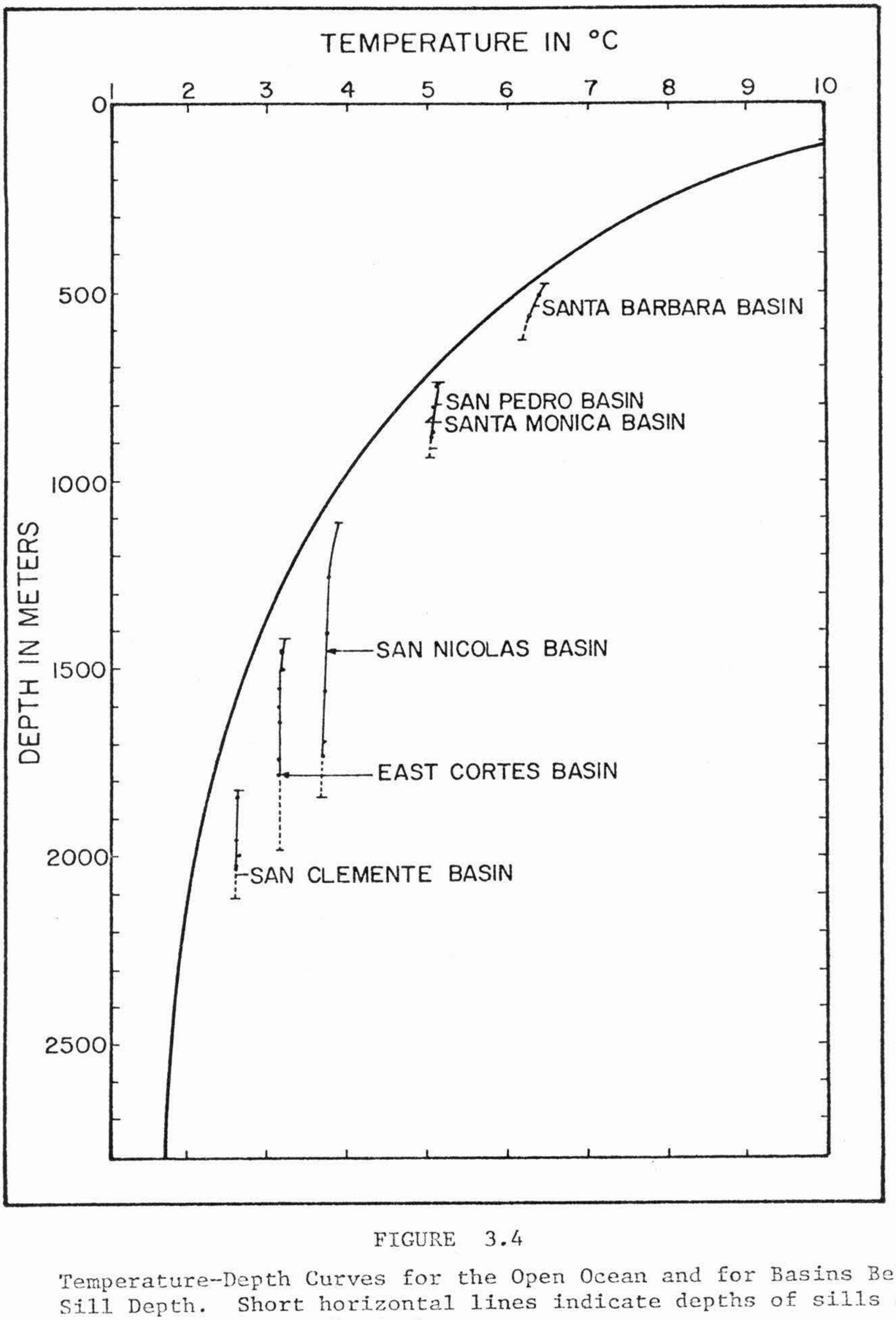


FIGURE 3.4

Temperature-Depth Curves for the Open Ocean and for Basins Below Sill Depth. Short horizontal lines indicate depths of sills and basin bottoms.

Source: Emery, 1960.

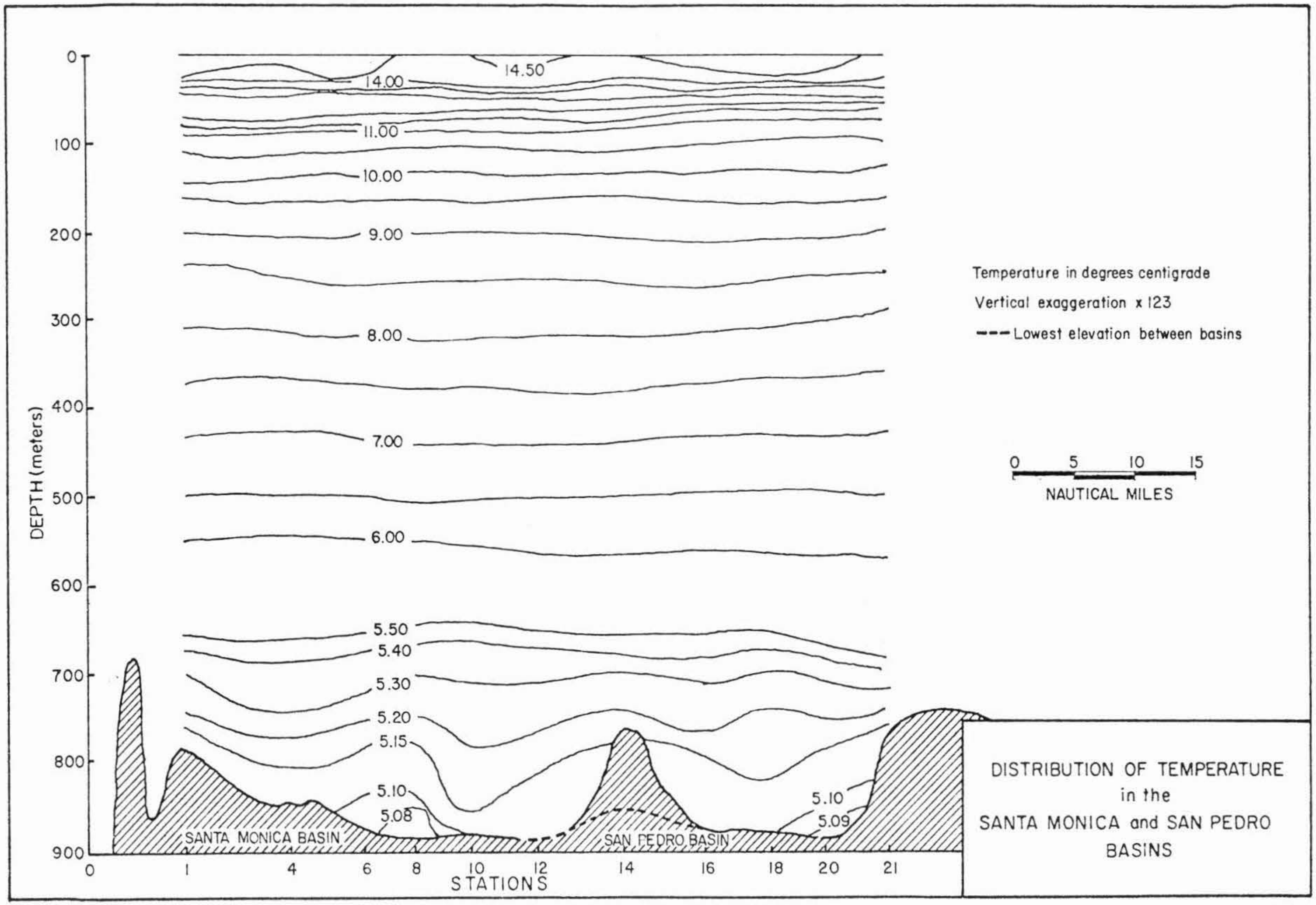
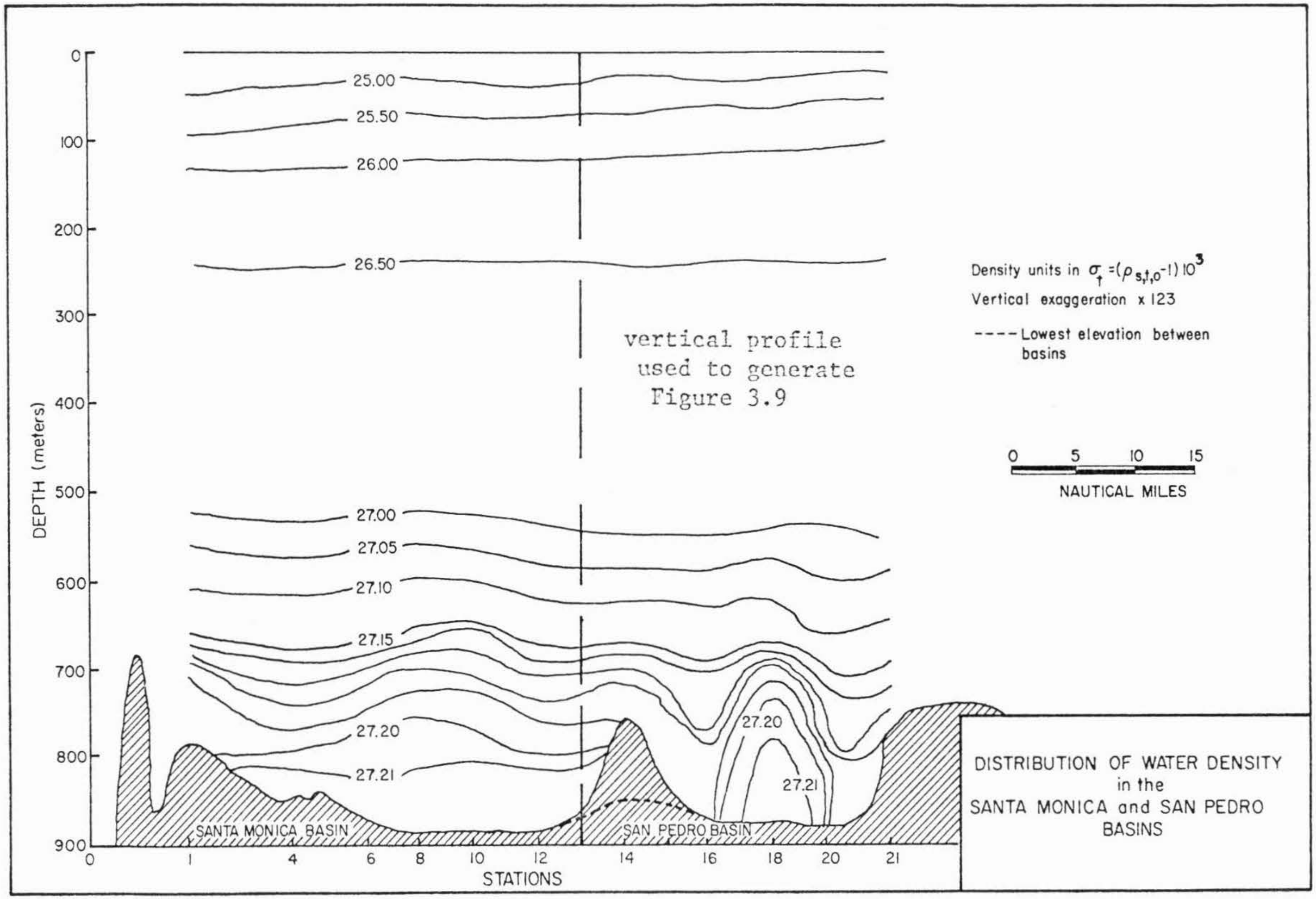


FIGURE 3.5

Temperature Profile-Santa Monica and San Pedro Basins
Station numbers refer to points of Figure 3.2

Source: Minard, 1968.



vertical profile
used to generate
Figure 3.9

FIGURE 3.6

Water Density Profile-Santa Monica and San Pedro Basins
Station numbers refer to points of Fig. 3.2

Source: Minard, 1968.

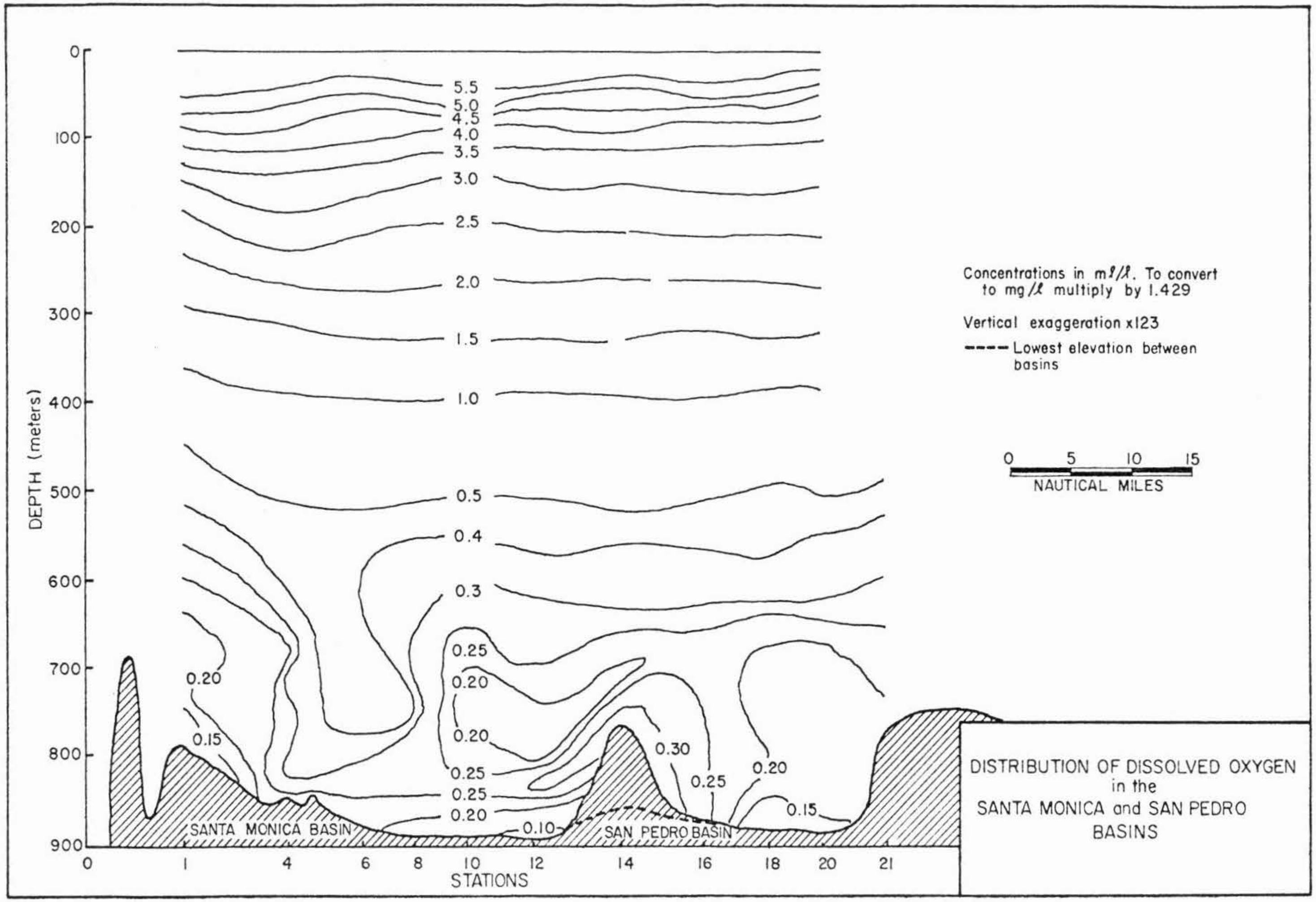


FIGURE 3.7

Dissolved Oxygen Profile - Santa Monica and San Pedro Basins
Station numbers refer to points of Fig. 3.2

Source: Minard, 1968

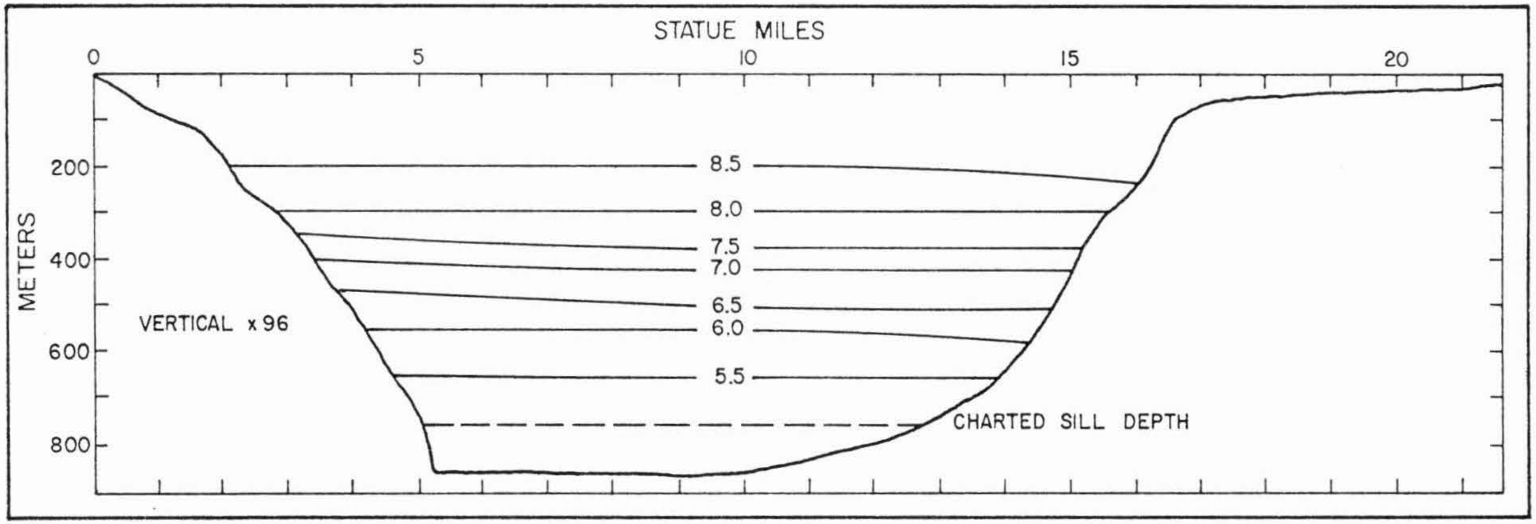


FIGURE 3.8

Temperature Stability in the San Pedro Basin

Lateral cross section between San Pedro shelf (right) and Catalina Island (left). All temperatures in °C. Isotherms shallower than 200 meters have been omitted because of seasonal variations

Source: Emery, 1954.

Biochemical data on the rate of oxygen depletion within the Santa Monica and San Pedro Basins suggest water-residence times of about two years. The principal mixing mechanism with overlying waters has been postulated to be internal waves. Upwelling of denser ocean waters and turbidity currents are other possible mixing agents that have been documented in the adjacent Santa Barbara Basin. This phenomenon will be discussed further in Section 3.3.

3.2.2 Currents in the Deep Basins

Values for basin currents are necessary in order to estimate the travel distances of sludge particles or flocs from sedimentation data. A limited number of current measurements have been made using both current meters and dye studies. Directly above the bottoms of San Pedro and Santa Monica Basins, Emery (1954) measured currents of 7 to 10 cm/sec. He suggested that bottom currents, possibly caused by deep seiches, may be more intense than those currents a short distance above the bottom. Minard (1968) reported measurements of the drift of dye clouds at the bottom of the San Pedro Basin of 0.5 to 1.0 cm/sec. In the nearby Santa Barbara Basin, Sholkovitz and Gieskes (1971) found currents of 2.6 cm/sec at a depth of 280 meters and 6.1 cm/sec at 430 meters.

An alternative approach to current measurement is to assume relative isolation of basin water below the sill depth as indicated by temperature and salinity data, and then to consider mass exchange of basin waters with time scales set by D.O. and nutrient measurements. These values show basin residence times of less than two years. The volume of the Santa Monica Basin is about 200 km^3 below 700 meters. If a further depth of 200 meters to the bottom of the basin is assumed, and if a greatest width of 24 km laterally and a residence time of one year are set, mean velocities of 0.1 to 0.2 cm/sec can be calculated. At narrower cross sections, a value five-fold greater might be reasonable, with still greater velocities expected at the basin sills. For the purposes of sedimentation analysis later in this chapter, velocity values of 0.1 to 10.0 cm/sec will be used.

3.3 Biology of Near-Coastal Basins

Possible biological effects of deep water sludge disposal measure the ultimate and most important environmental impact of this disposal plan. Two major sources of information about marine life in the San Pedro and Santa Monica Basins are available. One of these sources is direct enumeration of species in actual bottom samples. The other is indirect but more revealing in the long term, viz. an examination of box cores taken from the basin floors. Inferences can be made about the history of the basin bottoms from the latter source. An additional resource is the more complete information available from studies in the Santa Barbara Basin, another southern California marine basin with similar depth and comparable chemical behavior.

The bottoms of the San Pedro and Santa Monica Basins are described as "impoverished-to-dead" in an Allan Hancock Foundation report by Hartman and Barnard (1958). Such bottom conditions are expected because the D.O. is so low in the overlying waters. Organic debris that settles out from the more productive surface waters is incompletely oxidized as it falls. Oxygen demand then continues in the sediments and anoxic conditions unfavorable to most life forms higher than bacteria result (Davis, 1967). Actual animal specimens recovered from the San Pedro Basin floor include two polycheates (Phyllochaetoptersis, a chaetoptrial and Protis pacifica Moore, a serpulid) and also the shell of a scallop (Cyclopecter, sp. unknown). The same species were recovered from the Santa Monica Basin. These species occur in much greater numbers at sill depth and on deep slopes. It has been suggested that the samples recovered from the basin depths may be vegetative individuals from the sill depth or slope communities. Biological productivity measured in grams of biomass per meter^2 is less than 1.0 gm/m^2, at least a thousand-fold less than that for productive coastal waters (SCCWRP, 1973).

Box cores from the bottom at two stations showed varved (layered) sediments on the surface, in one case indicating an absence of bottom life for at least 50 years (Minard, 1968). Below that level, however, the sediments were well mixed with numerous evidences of worm burrowings. Similar phenomena have been observed in sediment cores from the Santa Monica Basin. Intense upwelling has also been measured in the Santa Barbara Basin. Such upwelling apparently occurs when a mass of dense water from the deep ocean, rich in oxygen and nutrients, is pushed over the basin sill, displacing the warmer oxygen-depleted water within the basin (Sholkovitz and Gieskes, 1971). Until the new oxygen supply is depleted, the bottom might support a much more active and numerous bottom fauna. Since the rate of biological degradation and physical change is apparently very slow, worm tubes, burrowing mounds, and other remnants from periods of intense activity might persist for many years. A second mechanism for oxygen replenishment in the Santa Barbara Basin is turbidity currents, apparently originating at sill depths (Sholkovitz and Soutar, 1975).

The San Pedro and Santa Monica Basins are similar to the Santa Barbara Basin in depth, distance from the shore, and bottom geochemistry, but their means of water replenishment probably differs. The Santa Barbara Basin, which receives its waters from the northwest, is separated from the open ocean by only one topographic feature. Water that reaches the San Pedro and Santa Monica Basins at depth must flow in from many kilometers to the south. On that basis, the possibility of upwelling such as that documented for Santa Barbara seems remote.

Turbidity currents are probably far more important. Several major submarine canyons empty into the Santa Monica Basin. Cores from both the Santa Monica and San Pedro Basins also show many thick layers of sand, which are strong evidence for turbidity flows.

3.4 Chemistry of Basin Sediments and Overlying Waters

Some understanding of the chemical processes of the near coastal basins is necessary in any attempt to predict the fate of sludge discharges to those regions. In the discussion below, the basin sediments and overlaying waters will be considered separately.

The sediments of the San Pedro and Santa Monica basins are described as green mud, with averages of 25.5 percent $CaCO_3$ and seven percent organic matter by weight. (The rate of sediment accumulation will be discussed in the following section.) Sediment-water content decreases with depth owing to compaction by the overburden. The Eh, a measure of the redox potential, is 0 or negative, indicating a reducing environment. The ammonia concentration increases with depth, mainly from the oxidation of organic matter. At least 90 percent of the nitrogen is found as organic nitrogen. The majority of the phosphate is inorganic, either as precipitated or adsorbed species.

The basin waters below the sill depth are nearly uniform in chemical composition; typical nitrate and phosphate concentrations are 35 μM and 3.2 μM respectively. Dissolved oxygen values range from 0.14 mg/l to 0.52 mg/l. Ammonia nitrogen is not measureable. Higher concentrations of nitrates and phosphates have been measured in waters directly above the bottom, apparently as a result of diffusion of the interstitial waters out of the sediment. These higher concentrations extend no more than 0.5m above the bottom. The pH ranges from 7.7 to 7.8, increasing slightly near the basin bottom (Rittenberg, et al, 1955).

3.5 Natural Sedimentation in the San Pedro and Santa Monica Basins

The impact of sludge discharges to near-coastal deep basins cannot be assessed without comparing the natural sedimentation rates to those increments expected from the projected sludge flows. As was mentioned earlier, the basins are natural sediment traps, slowly being filled with sand, silt, and clay from stream runoff, wind-carried dust fallout, and calcareous, siliceous, and organic detrital matter. As this material falls in the water column it can affect the surrounding water by exerting a local oxygen demand, by dissolving, or by capturing other suspended materials.

Once the material reaches the bottom, it undergoes burial by the subsequent fallout, it is decomposed aerobically or anaerobically by bacteria, or it is reworked by higher organisms. With sufficient bottom currents, resuspension may continue the mixing and movement of the materials; however, resuspension is highly unlikely. For the basin sill areas, where water flows are greater and currents faster than the basin bottoms, winnowing of the sediment has not been observed. Emery (1960) has said of the sill areas, "...it is unlikely that the currents required for the known replenishment of basin waters are sufficiently fast to still control the sediments." The varved nature of the sediments indicates little or no reworking by higher organisms.

Sedimentation rates have been measured in the San Pedro and Santa Monica Basins by dating core samples. Sediment traps have also been used in the Santa Barbara Basin. For core samples, the age is established by counting varves or by isotopic analysis for ^{14}C or ^{210}Pb. The total dry weight of sediment in a unit area column is then corrected for dissolved salt content and compaction. Total corrected weight per unit area divided by the total age gives the sedimentation rate. The results of such analysis are reported in Table 3.1. For sediment traps, the calculation is simply the total mass of sediment trapped per unit area of trap surface divided by the time the trap is left in place. The results from sediment traps must be viewed with skepticism, however, since the natural processes of resuspension and biological degradation are prevented from occurring.

Large variations in reported sedimentation rates may reflect local variations of sedimentation. Cores for the Santa Monica and San Pedro Basins showed substantial layers of sand which have been attributed to turbidity currents. Sediment contributions from turbidity currents are assumed to be half the total sediment by volume in these near-coastal basins (Emery, 1960). Improved dating techniques in the more recent work may also give a different picture than the less refined methods previously used. The reported sedimentation rates differ by no more than a factor of five. If the basin floors have an area of almost 2600 square kilometers, the range of total sediment deposition is 6.2×10^5 metric tons per year to 3.2×10^6 metric tons per year.

TABLE 3.1

Measured Sedimentation Rates for Southern California Coastal Basins

$(mg/cm^2/yr)$	METHOD	LOCATION	SOURCE
60	Mass balance on sediment supply	All coastal basins (mass average)	Revelle and Shepard, 1939
91	Mass balance on stream runoff to near coastal basins	San Pedro and Santa Monica Basins	Emery, 1960
123.2	Core sample	Santa Monica Basin	Emery, 1960
35.2	Core sample	San Pedro Basin	Emery, 1960
52.9	Core sample	San Pedro Basin	Emery, 1960
28	Core sample	San Pedro Basin	Bruland, et al., 1974
24	Core sample	Santa Monica Basin	Bruland, et al., 1974
170[1]	Sediment trap	Santa Barbara Basin	Sholhovitz and Soutar, 1975

[1] This high value is attributed to turbidity currents originating on the basins slopes at sub-sill depths.

3.6 The Disposal Plan

The disposal plan that follows includes the results from hydraulic and chemical modeling and discussions of the effects of sedimentation and diffusion on the discharged sludge. The engineering details associated with the outfall design are beyond the scope of this work, but preliminary sizing of outfalls indicates that a 60-cm (24-inch) pipe would be adequate in either case. The disposal depth of 730 m, approximately the sill depth, was chosen for modeling and would require pipelines of approximately 21 km from Hyperion and seven km from Whites Point (LACSD). Rough locations for the outfall are shown in Figure 3.2. Neither of these lines as modeled would reach the deeper central portions of the basins but they are long enough to take advantage of the density stratification and low D.O. in waters at this depth. Future economic and engineering analysis would optimize location and depth selection for the outfalls.

It should be noted that the deepest existing outfalls end near depths of 100 meters. The construction technology of deep-water pipelines is, however, advancing very rapidly, partially as a result of the need for moving oil shoreward from deep-water drilling sites. Point-to-point oil movement at depths of over 300 meters is already practiced between North Sea production platforms and the British Isles. Since the implementation of the proposed sludge outfalls is at least several years away, the technological problems of outfall placement and design should not be insurmountable.

3.6.1 Hydraulic Modeling - Buoyant Jet in a Density-Stratified Medium

The physical modeling of the sludge discharge has been done using a computer simulation of a round buoyant jet in a density-stratified medium (see Ditmars, 1969). Three different density stratifications were used, based on a density profile extracted from Figure 3.6. The actual profile is shown in Figure 3.9, and an enlarged profile at the discharge depth appears in Figure 3.10. The two constructed profiles, one lighter and one denser than the normal profile, were taken into account. They correspond to a case of greater mixing with the lighter overlying water and to an upwelling situation where denser water would come up over the sill and displace lighter waters in the bottom of the basin. These two additional cases were chosen because available density, salinity, and other relevant measurements (while taken some 30 years apart) only cover a seasonal period of approximately four months from January through April. These extreme profiles should cover variations in basin-water density.

The model flow in the program was set at 5.0 MGD (7.74 cfs or 220 l/sec) to approximate present sludge flows at Hyperion and Whites Point (both about 1.6 MGD) diluted two to one with another fluid, the treatment plant effluent. The effluent was assumed to have a density of 1.002 gm/cm^3. One discharge depth, 2400 feet (731 meters), was modeled. Five different port sizes were used in the model with each of the three density profiles, both to check the effect of the different profiles and to find the best configuration of the outfall. The extreme configurations would either maximize

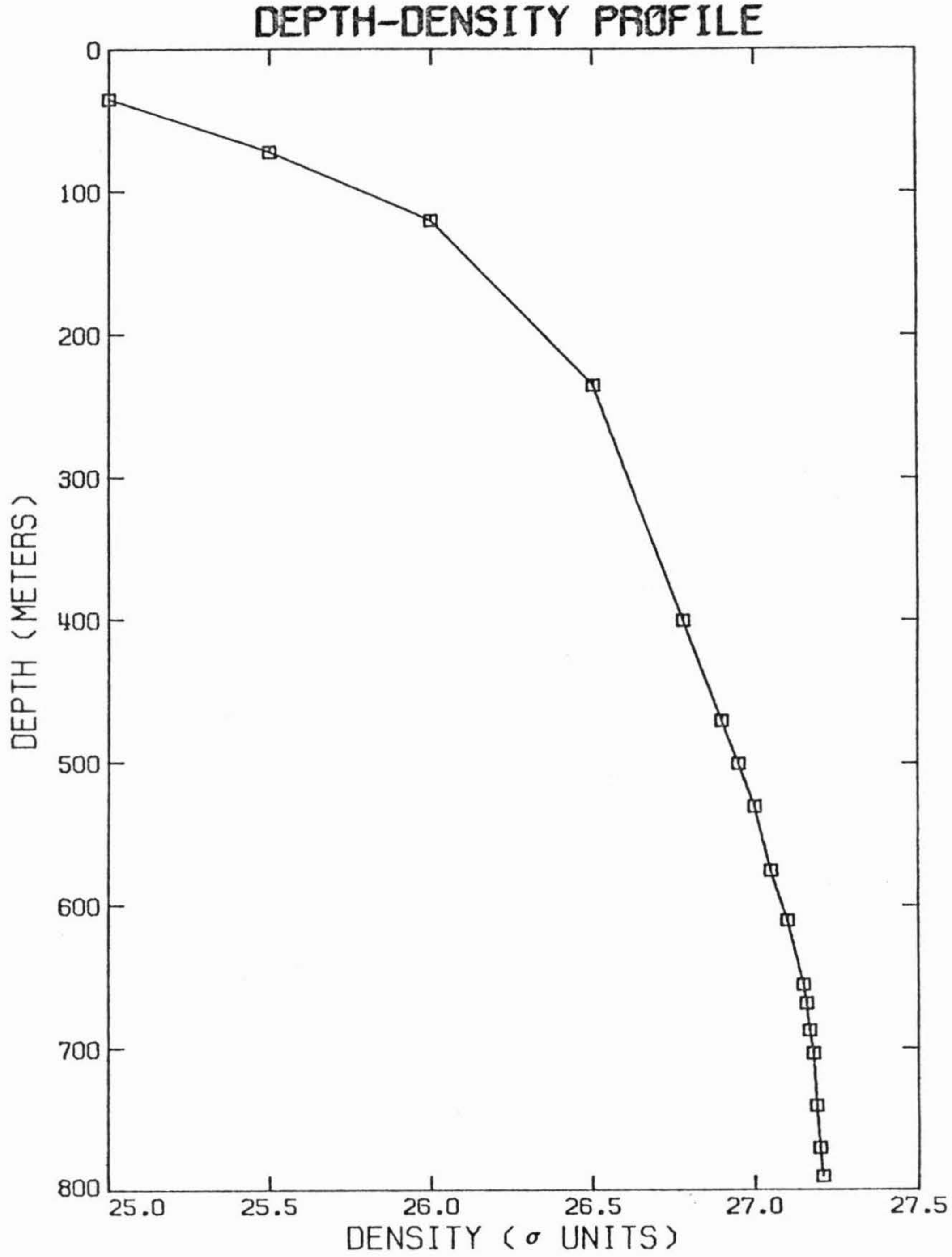


FIGURE 3.9

Actual Depth - Density Profile
The profile was extracted from the dashed vertical line on Fig. 3.6

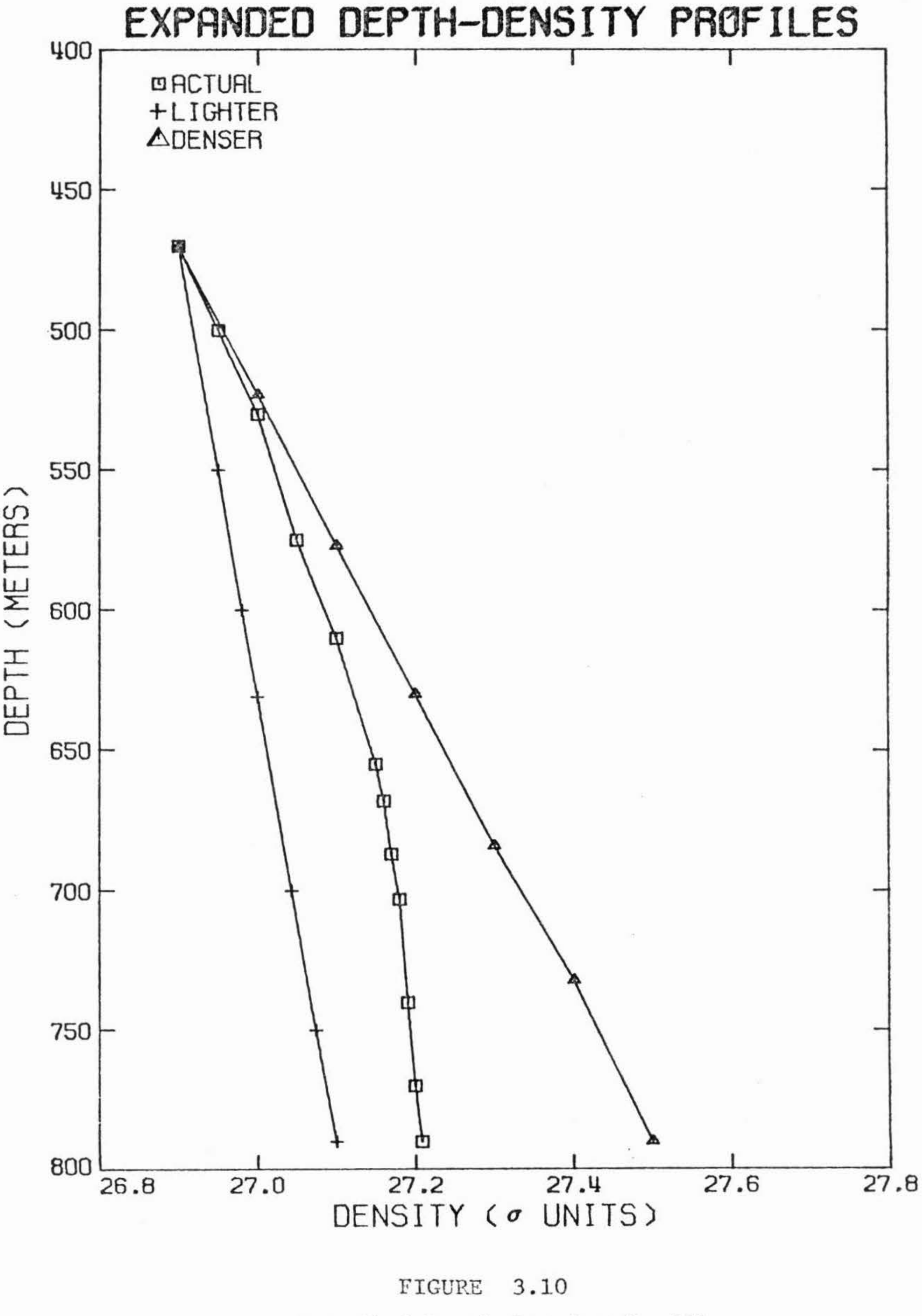


FIGURE 3.10

Detailed Depth Density Profiles

dilution or maximize height of rise. The results of the computer simulations are summarized in Figure 3.11. It should be noted that the maximum height of rise never exceeds 400 feet (120 meters) and that the computed dilution ranges are from 450-fold to 2600-fold. The different port diameters would only change the rise height by a factor of two. For the jets from the individual ports to be initially non-interfering, the diffuser length would have to be varied from 550m for 1 ft ports to 5000m for 2 in. ports. The actual dilution of the sludge-particulate matter and chemical constituents increases by a factor of three over the values reported in Figure 3.11 because of the initial dilution with sewage effluent before routing to the sludge outfall.

One additional calculation should be mentioned at this point. The projected 10 MGD flow from both outfalls equals $2.44 \times 10^8 ft^3/yr$ ($0.0069 km^3/yr$). The basin volume was crudely estimated by integrating around the contours on Figure 3.2 with a planimeter and then by multiplying the average area between adjacent contours by the depth of contour separation. The volume of the basin below 700 meters is about $280 km^3$. The total yearly discharge would then only be a small fraction of the total basin volume. No major volumetric displacement should be caused by the sludge discharge.

3.6.2 Chemical Modeling

Predictive modeling of the behavior and effects of sludge chemical constituents is necessary if an assessment of the environmental

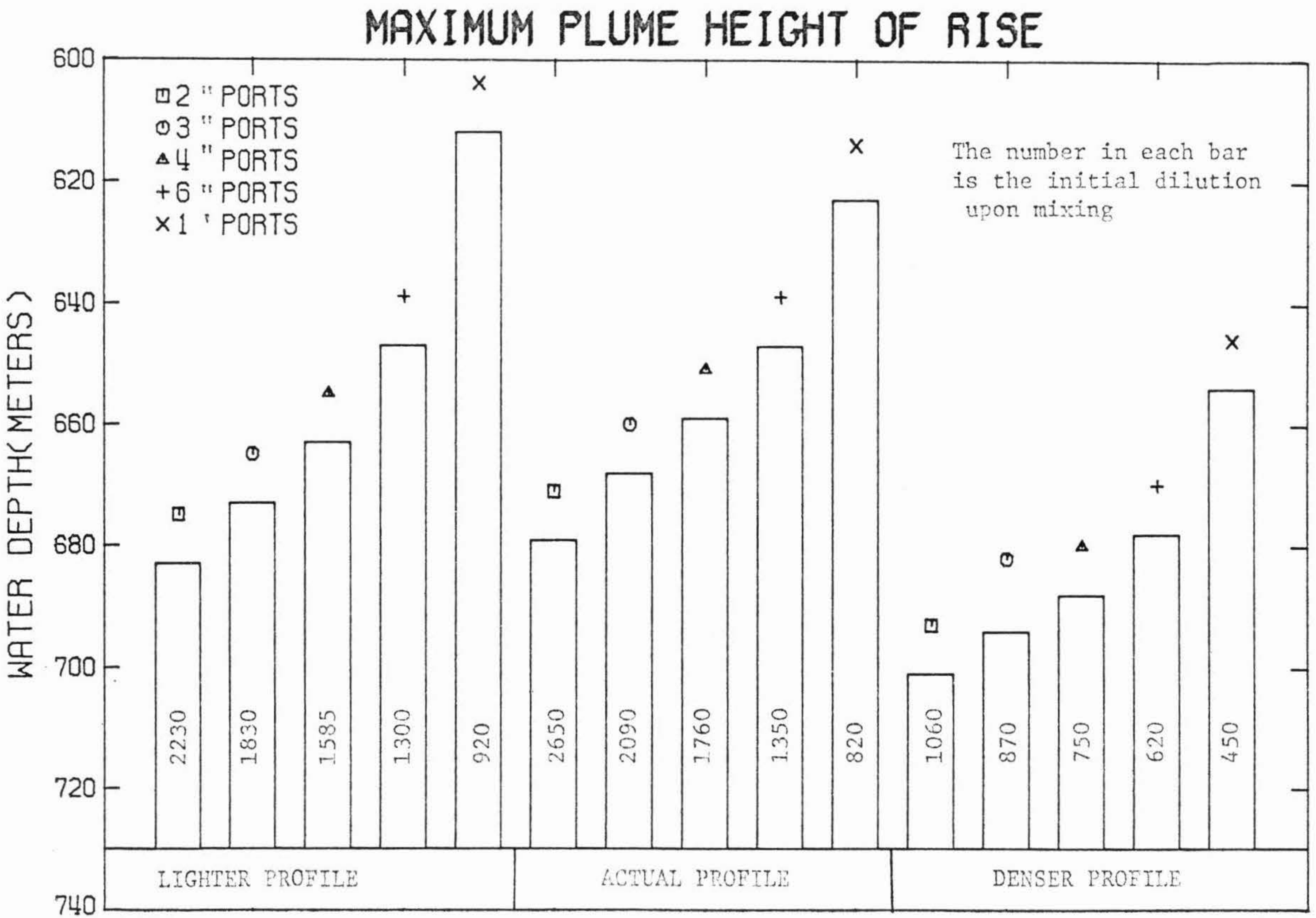


FIGURE 3.11

Plume Height of Rise Prediction
All discharges at 730 meters with nozzle diameters as indicated.

impacts of the proposed sludge discharges is to be made. Two views of basin chemistry have been taken in this work. The first approach is a stoichiometric one in which the total mass of discharged constituents is examined. The second approach uses a chemical equilibrium model to predict the behavior of individual chemical constituents. The two models are interrelated: the stoichiometric one provides an assessment of gross phenomena that in turn provides guidelines for parameter selection for the chemical equilibrium modeling.

It cannot be overemphasized that both these approaches assume that equilibrium chemistry governs the fate of chemical constituents in the discharge. In reality, the rate at which equilibrium is approached is probably as important as the final system configuration. The paucity of kinetic data for dissolution, precipitation, and redox reactions prevents the following results from being anything more than speculative, but hopefully the speculation is guided by reasonable chemical intuition.

3.6.2.1 Stoichiometric Modeling

The simplest model for the discharges of sludge to the near-coastal basins should consider only the gross effects of the total mass discharged. The chemical constituents in the buoyant jet are divided into two categories in the following work--conservative and oxidizable. Oxidizable discharges will be considered first since their effect on local geochemistry and biochemistry will be more pronounced.

3.6.2.1.1 Oxidizable Discharges

Four constituents of the sludge--ammonia-N, organic-N, organic carbon, and sulfide--can be oxidized if sufficient oxygen is available. Ammonia-N is soluble in the sludge, while the other three are mainly associated with the particulate phase. The dissolved ammonia-N will be most easily oxidized, while the breakdown of particulate matter should be expected to take place more slowly. Sedimentation may also remove particles to the anaerobic sediment environment before oxidation can occur.

The predominant reactions are assumed to produce nitrate, carbonate, and sulfate as end products. Nitrite (NO_2^-) and elemental sulfur might also be possible products, but these intermediate oxidation states will be ignored for the sake of simplicity. The detailed oxidation reactions are shown together with weight equivalents of elemental oxygen necessary for the specific oxidations, in Table 3.2. The oxidation state for ammonia-N is (-3); organic-N is shown as a secondary amine, also at (-3). Organic carbon is assumed to be at (0), and sulfide, obviously, at (-2). Biological mediation of the N and C oxidations is expected in natural systems.

With the oxidation pathways established, the mass discharges are needed to evaluate the total oxygen demand. Estimates of ammonia-N, organic-N, organic-C, and sulfide, as metric tons per year, for discharges from the projected Hyperion and LACSD sludge outfalls, are shown in Table 3.3. The specific oxygen demands from Table 3.2 were then used to calculate total oxygen demand. In the final column,

TABLE 3.2

Reactions for the Oxidation of Ammonia-N, Organic-N, Organic Carbon, and Sulfide

A. Ammonia

$1/8\ NH_4^+ + 3/8\ H_2O \rightarrow 1/8\ NO_3^- + 5/4\ H^+ + e^-$ (3.1)

$1/4\ O_2(g) + H^+ + e^- \rightarrow 1/2\ H_2O$ (3.2)

$1/4\ O_2(g) + 1/8\ NH_4^+ \rightarrow 1/8\ NO_3^- + 1/4\ H^+ + 1/8\ H_2O$ (3.3)

4 moles of 0 needed/mole of NH_3
(3.76 gm 0/gm NH_3 or 4.57 gm 0/gm N)

B. Organic Nitrogen (as a secondary amine)

$R_2NH + 3H_2O \rightarrow NO_3^- + 2R^+ + 8e^- + 7H^+$ (3.4)

$2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O$ (3.5)

$2O_2 + H^+ + R_2NH \rightarrow H_2O + NO_3^- + 2R^+$ (3.6)

4 moles of 0 needed/mole of organic nitrogen
(4.57 gm 0/gm organic N)

C. Organic Carbon

$2H_2O + C \rightarrow CO_2 + 4H^+ + 4e^-$ (3.7)

$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$ (3.8)

$C + O_2(g) \rightarrow CO_2$ (3.9)

2 moles 0 needed/mole C
(2.67 gm 0/gm organic C)

D. Sulfide

$S^{2-} + 4H_2O\ (1) \rightarrow SO_4^{2-} + 8H^+ + 8e^-$ (3.10)

$2O_2\ (g) + 8H^+ + 8e^- \rightarrow 4H_2O\ (1)$ (3.11)

$2O_2\ (g) + S^{2-} \rightarrow SO_4^{2-}$ (3.12)

4 moles 0 needed/mole S^{2-}
(1.88 gm 0/gm sulfide)

TABLE 3.3

Potential Discharges of Oxidizable Substances in LACSD and Hyperion Sludges

LACSD$^{(4)}$	DISCHARGE (metric tons/year)	OXYGEN REQUIREMENT (gm/gm)	TOTAL O REQUIRED (metric tons/year)	WATER DEPLETED$^{(3)}$ (ℓ)	km^3
Ammonia-N	8.84×10^2	4.57	4.04×10^3	9.42×10^{12}	9.42
Organic-N	2.03×10^3	4.57	9.28×10^3	21.6×10^{12}	21.6
Organic-C$^{(1)}$	1.42×10^4	2.67	3.79×10^4	88.4×10^{12}	88.4
Sulfide$^{(2)}$	7.01×10^2	1.88	1.32×10^3	3.08×10^{12}	3.08
TOTAL			5.25×10^4		

HYPERION$^{(5)}$					
Ammonia-N	1.95×10^3	4.57	8.91×10^3	20.8×10^{12}	20.8
Organic-N	1.63×10^3	4.57	7.45×10^3	17.4×10^{12}	17.4
Organic-C$^{(1)}$	1.44×10^4	2.67	3.84×10^4	89.5×10^{12}	89.5
Sulfide$^{(2)}$	7.01×10^2	1.88	1.32×10^3	3.08×10^{12}	3.08
TOTAL			5.61×10^4		

(1) Organic carbon values calculated from SCCWRP (1975) and Mitchell and Schafer (1975).

(2) The sulfide number for LACSD was calculated assuming sludge flow = 1.6 MGD with $pS_T = 2.03$. The Hyperion sulfide content was assumed to be equal to that for LACSD.

(3) The water is assumed to have a D.O. of 0.3 ml/1 (0.429 mg/1).

Source:

(4) Sanitation Districts of Los Angeles County, 1973.

(5) SCCWRP, 1975.

the equivalent volume in km^3 of seawater that would be completely depleted of D.O. by the total oxidation of the entire discharge was computed, assuming a D.O. of 0.3 ml per liter (0.429 mg/l).

Even with a high initial dilution (at least 1000:1), the ammonia-N demand should be sufficient to deplete the low D.O. of the basin waters. The slower dissolution of metal sulfides and bacterial degradation of particulate organics should maintain the anoxic conditions. (This situation will be discussed further in relation to the computer chemical modeling.)

As soon as local anoxic conditions develop, anaerobic bacteria first begin to use NO_3^- and NO_2^-, and then SO_4^{2-} as electron donors in the degradation of organic matter of both natural and sludge origin. Such degradation should be particularly pronounced at the water-sediment interface near the basin bottom. Nitrate reduction to N_2 gas would be expected, and the reduction of sulfate to sulfide should insure the incorporation of trace metals, except Cr and Mn, into the sediments as metal sulfides.

3.6.2.1.2 Conservative Discharges

The trace metals discharged from an anoxic sludge flow into the nearly anoxic waters of the San Pedro and Santa Monica Basins should not be as greatly affected as the oxidizable compounds--ammonia, sulfide, and organic-C. The trace metals may be mobilized as a result of changes taking place in the particle system to which they are attached. The comparison of the total mass discharged to total mass now reaching the basin will give a crude measure of the potential impact. Metal flux data for the basin were calculated by Bruland, et al. (1974). These data (see Table 3.4) were based on one core from each basin. For most metals, the relative contributions from natural and anthropogenic sources were separated, using geologic dating techniques. The anthropogenic sources considered included atmospheric fallout, surface runoff, and sewage effluent discharges.

Metal mass inputs from the projected sludge outfalls have been calculated (Table 3.4). The totals from the sludge are one to five times the present total metal input reaching the basin from all sources, except for Fe and Mn. Iron and Mn sludge inputs are substantially lower than those from natural sources. The existing metal inputs already includes some metal from sludge and sewage effluent sources. The proposed sludge outfalls would divert all sludge trace metals directly to the basins.

3.6.2.2 Computer Modeling

Computer simulation of the discharge of sludge to the ocean was modeled as a three-step process. First, the sludge digester was modeled to determine the chemical state of the trace metals before discharge. Second, the dilution of sludge with treatment-plant effluent was done to approximate what might happen as the sludge was

TABLE 3.4
Trace Metal Inputs to the San Pedro
and Santa Monica Basins - Existing Totals and Projected Totals from Sludge Outfalls

Metal	SAN PEDRO BASIN		SANTA MONICA BASIN		HYPERION (1974)	LACSD
	Flux(7) ($\mu g/cm^2/yr$)	Total(4)(7) (metric tons/yr)	Flux(7) ($\mu g/cm^2/yr$)	Total(4)(7) (metric tons/yr)	Total(5)	Total(6)
Ag	0.14 (64)(2)	0.91	0.12 (75)(2)	2.14	2.61	2.21
Cd (1)					8.27	3.76
Cr	5.9 (52)	38.2	4.7 (55)	83.8	98.4	164
Cu	2.6 (54)	16.8	2.1 (52)	37.4	90.5	107
Fe (3)	1260	8160	1200	21,400	513	1520
Mn (3)	13	84	8	142	1.24	14.2
Ni (3)	1.6	10.4	1.3	23.2	20.2	15
Pb	1.96 (87)	12.7	1.14 (79)	20.3	7.36	37.6
Zn	5.0 (38)	32.4	4.9 (43)	87.3	156	380

(1) Data unavailable.

(2) Number in () represents percent attributed to anthropogenic sources.

(3) Fraction from anthropogenic sources not reported.

(4) Totals calculated from fluxes and from basin areas below the sill reported by Emery, (1960). San Pedro Basin area = 253 mi^2 = 648 km^2; Santa Monica Basin area = 696 mi^2 = 1782 km^2 ($1\ \mu g/cm^2/yr$) = (1×10^{-2} metric tons/km^2/yr).

(5) Based on data reported by SCCWRP (1975).

(6) Based on average sludge centrate values for LACSD digested primary sludge except Fe and Mn values were calculated from Table 2.8 above.

(7) Data from Bruland, et al. , 1974.

mixed with effluent prior to pumping through a sludge outfall. Third, a series of dilutions of the sludge/effluent mixture with seawater simulated the sludge plume rising and spreading in the ocean.

3.6.2.2.1 Model Description and Inputs

The REDEQL2 computer model, originally described by Morel and Morgan (1972), considers precipitation-dissolution, complexation, oxidation-reduction, and adsorption reactions at 25°C in its present form. The use of REDEQL2 in this work follows the hierarchial structure of Morel, et al. (1975) and Morgan and Sibley (1975). These authors have modeled the discharge of a sewage effluent into oxic coastal waters.

The modeling sequence was first to pose a system of metals and inorganic ligands, then to expand it with the addition of an organic, acetic acid, and finally to consider two adsorbing surfaces. The addition of acetate to the digester computations showed no significant complexation of the trace metals. Organics such as cysteine and EDTA (ethylenediaminetetraacetic acid), which are known to have much stronger affinities for trace metals than acetate, would be more realistic. In the absence of any concentration data for such compounds, no other organics were included in subsequent computations. Model metal and ligands inputs, expressed as $p[X] = -\log$ [molar concentration of X], are summarized in Table 3.5. The trace metal concentrations are those measured for LACSD sludge as a part of this research and reported in Table 2.8. Concentrations of Na, K, Mg, and Ca are those typical for Los Angeles area drinking waters. The carbonate concentration was taken from alkalinity titrations of sludge filtrate

(Section 2.7.4) corrected for ammonia concentration. The phosphate and cyanide values were those reported for LACSD sludge centrate. Total sulfur was varied from a high value equal to that measured for this work by elemental analysis (Section 2.7.5) to a low value of 1/8th the high total. The effect of assumed seasonal variations of total S within the digester have thus also been checked. For the effluent/sludge and sludge/seawater mixtures, an intermediate level of ~10mM ($pS_{TOT} = 2.03$) in the undiluted sludge was used.

The system ionic strength for the digester was determined by summing the appropriate metal and ligand concentrations. For sludge/seawater dilutions, the seawater was assumed to have an ionic strength $I = 0.66$ and appropriate corrections were made for the relative mixtures of sludge and seawater.

Before any conclusions are drawn from the REDEQL2 modeling, the model limitations should be discussed in some detail. The equilibrium constants for the precipitation and complexation reactions of the REDEQL2 program are those for chemical systems of 25°C. An actual mesophilic digester operates at 35 to 37°C. Primary effluent averages 15 to 20°C, and seawater in deep marine basins, 5 to 6°C. The effects of these temperature differences should be small compared to the gross chemical picture sought with the model.

The chemical combinations, that is, complexes and solids considered in the calculations by REDEQL2, are limited by equilibrium constants available in literature and by the accuracy of those constants. This limitation of the calculations should be kept in mind when

TABLE 3.5

Chemical Computer Model Inputs(1)
(pH = 7.9)

Constituent	Sludge(3) I = 0.15(2)	Seawater(4) I = 0.65(2)
(Metals)		
Ca	2.60	1.98
Mg	2.21	1.27
K	2.60	1.98
Na	2.11	0.32
Fe	1.90	2.17
Mn	3.93	7.44
Cr	3.30	7.33
Cd	4.72	9.35
Zn	2.70	7.12
Ni	3.63	7.47
Pb	3.82	9.84
Ag	5.11	9.43
Cu	2.86	9.02
(Ligands)		
CO_3	1.60	2.63
SO_4	1.73	1.54
Cl	2.38	0.25
NH_3	1.63	6.50
PO_4	2.42	5.65
Si	3.78	-
CN	5.41	-
F		4.13

(1) Concentrations listed as -log (molar concentrations)

(2) I (Ionic Strength) = $1/2 \Sigma C_i Z_i^2$ (3.13)
Ci = the molar concentration of the i-th constituent
Z_i = the charge of the i-th constituent

Source:

(3) Table 2.8; Sanitation Districts of Los Angeles County, 1973; SCCWRP, 1973.

(4) Sibley and Morgan, 1975.

examining the actual results, complexes, free metals, solids, and corresponding quantities predicted by the program. Species that are important in the real systems may not appear as program outputs if appropriate thermodynamic measurements are unavailable or have not been included as program inputs.

The pH, a measure of hydrogen ion activity in chemical systems, is one of the REDEQL2 input parameters that can be extremely important to trace-metal chemistry. The model pH was set at 7.9 for all cases, typical for both stable sludge digesters and Santa Monica Basin waters below the sill. The constant pH values were selected after preliminary calculations showed no strong dependence on pH for chemical speciation over the possible pH range for these systems.

The final significant parameter that must be selected for computer computations is $p\varepsilon$, an indication of the oxidizing or reducing tendency of the chemical system.

$$p\varepsilon = -\log \{e\} \qquad (3.14)$$

where, $\{e\}$ = relative electron activity

Low $p\varepsilon$'s (e.g., −4.0) are typical of reducing environments; high $p\varepsilon$'s (10 to 12) are found in oxidizing environments. The $p\varepsilon$ is calculated for measured values of the constituents of a redox reaction. For an unambiguous determination of $p\varepsilon$, equilibrium must exist and the activities of the constituents, e.g.,

$$\{SO_4^{2-}\} \text{ and } \{S^{2-}\}$$

or

$$\{Fe^{3+}\} \text{ and } \{Fe^{2+}\}$$

must be measured. (The concept of pε is well summarized in Stumm and Morgan, Ch. 7, 1970.)

At a practical level, the problem is somewhat more complicated. Breck (1974) summarized the work of Sillén and others on this problem. In the case of the sludge digester the production of methane would indicate a $p\varepsilon = -6.1$; the reduction of all nitrogen to ammonia, a $p\varepsilon < -5.5$. The sulfate/sulfide couple would give a $p\varepsilon < -4.0$. An unambiguous choice of the digester pε, where all three of these processes occur, is difficult.

When sludge is diluted with effluent and then seawater, the problem becomes far more difficult. Kinetic processes--metal sulfide solid (MeS(s)) dissolution and sulfide and ammonia oxidation--probably are far more important. In a surface-water situation such as that modeled by Morel, et al. (1975), it is safe to assume that the local waters are nearly oxygen saturated and the pε may be set at an oxidizing (positive) level. The question of pε for oxic waters has been discussed recently by Stumm (1975). He examined possible pε determining reactions and concluded that "oxygen obviously is the atmospheric oxidant that is most influential in regulating, with its redox partner, water, the redox level of aerobic waters." Stumm also stated,"Since many other redox processes are slow to come to equilibrium, it is possible to have several different redox levels in the same locale."

The proposed sludge discharge described here would be to the nearly anoxic and relative stable (slowly mixed) basin waters. It was pointed out previously that the oxidizable components within that discharge should easily deplete the available D.O. and wholly anoxic, anaerobic conditions should result. To select a system pε upon dilution with seawater, the SO_4^{2-} $-S^{2-}$ redox reaction was removed from the REDEQL2 computations and that redox reaction

$$SO_4^{2-} + 8H^+ + 8e^- \rightarrow S^{2-} + 4H_2O\ (1) \qquad (3.15)$$

was considered separately.

The pε relation for any redox reaction is

$$ox + ne^- = K^*\ red \qquad (3.16)$$

where

n = number of electrons

K^* = equilibrium constant of the reduction reaction

$$p\varepsilon = 1/n \log K^* + 1/n \log (\{ox\}/\{red\}). \qquad (3.17)$$

For seawater, $pSO_4 = 1.54$. If pH = 7.9 HS^- is the predominate sulfide species, the couple SO_4^{2-}/HS^- has $K^* = 10^{34}$ and

$$p\varepsilon = 1/8 \log K^* + 1/8 \log ([SO_4^{2-}]/[HS^-]) - 9/8\ pH$$

$$= -4.44 - 1/8 \log [HS^-]. \qquad (3.18)$$

Now $[HS^-]$ must be evaluated based upon the total sulfide in the system as affected by the formation of metal sulfide complexes and precipitates and by pH.

$$\text{Total sulfide} = \sum_{k,j} [Me_kS_j]_{complexes} + \sum_{k,l} [Me_kS_l]_{solids} + [H_2S(aq)]$$

$$+ [HS^-] + [S^{2-}]. \qquad (3.19)$$

Metal sulfide complexes are assumed to have negligible importance and $[HS^-] >> [H_2S(aq)] + [S^{2-}]$ at pH = 7.9. Then

$$[HS^-] \cong (\text{Total sulfide} - \sum_{k,l} [Me_kS_l])\alpha_1 \qquad (3.20)$$

where

$$\alpha_1 = \frac{[HS^-]}{[H_2S]+[HS^-]+[S^{2-}]} \cong \frac{K_{a,1}}{[H^+]+K_{a,1}} \qquad (3.21)$$

and $K_{a,1}$ is the dissociation constant for the removal of the first H^+ from H_2S. For seawater ionic strengths, $K_{a,1} = 10^{-6.96}$ was calculated with the REDEQL2 program and α_1 is thus 0.90.

The metal sulfide solids of potential importance on a total mass basis are those formed with Fe, Cu, and Zn. Iron sulfide will only affect the system if the pε is sufficiently negative and FeS(s) forms rather than Fe_3O_4(s). For a 3000-fold dilution of sludge (two to one with effluent and 1000 to one with seawater) pFe = 5.38, pCu = 6.77, and pZn = 6.18, and

$$\sum_{k,l} [Me_kS_l] = 10^{-5.30} \qquad (3.22a)$$

If total sulfide is $10^{-5.21}$, $p\varepsilon = -3.70$. If Fe is present as Fe_3O_4 (more realistic if $p\varepsilon \sim -3.70$ as will be seen in Section 3.6.2.2.2.)

$$\sum_{k,l} [Me_kS_l] = 10^{-6.08} \text{ and } p\varepsilon = -3.78. \qquad (3.22b)$$

At a lower total sulfide (pS = 5.51), $p\varepsilon = -3.73$. Based on these calculations, pε's of -3.00, -3.50, and -4.00 were set for the sludge/seawater models.

Surfaces were incorporated into the digester and outfall system models for this work by using an electrostatic model developed by James and Healy (1972a,b,c,). In the model the free energy of adsorption, ΔG_{ads}, is treated as a sum of coulombic, solvation, and chemical free energies: $\Delta G_{ads} = \Delta G_{coul} + \Delta G_{solv} + \Delta G_{chem}$ (3.23)

The constant of adsorption

$$K_{ads} = \exp(-\Delta G_{ads}/RT) \tag{3.24}$$

where

R = gas constant

T = absolute temperature

This model has been used extensively by Vuceta (1976) and is thoroughly developed and discussed in her thesis.

Two types of surfaces were modeled, namely SiO_2 and ferric oxide. The ΔG_{chem}'s of adsorption of metals onto SiO_2 were set according to Vuceta. Ferric oxide surfaces are less well defined; values used for the pH_{pzc} (pH of zero surface charge) were 6.5, 7.5, and 8.5 and the ΔG_{chem}'s or adsorption were set at -4.0, -6.5, and -8.5.

3.6.2.2.2 Chemical Modeling Results

For the digester model in this work, the strong dependence of trace-metal solubility on sulfide concentrations led the author to examine the dissolved versus suspended fractions of Ni in LACSD sludge samples (Section 2.4.1.4). Preliminary calculations showed that substantial portions of the Ni would appear as inorganic complexes and thus be soluble at pε's lower than that necessary for NiS(s) precipitation. At pε's lower than that necessary for NiS(s) precipitation, some Ni would remain in solution as Ni(CN) complexes but the fraction of the total nickel, Ni_T in solution would be very small.

With the pS_T = 2.03, simulations were run with pε's ranging from 0.0 to -0.6. The effect of pε variation on the speciation of Ni in the model system is shown in Figure 3.12. The fraction of dissolved Ni approximately equal to 0.1 percent of the Ni_T measured in this research was found at pε = -4.4 and this level was assumed to be that of the digester. Production of CH_4 and NH_3, which would indicate still lower pε's, probably is dependent on biological mediation, and does not necessarily represent the digester as a whole. Changes in the total sulfur concentration, S_T, had no marked effect on Ni solubility.

The change in speciation of the other trace metals with pε and pS_T variations may be likened to a titration where electrons or sulfur is added. At a constant sulfur concentration, Ag is converted from AgCl(s) and Ag-NH_3 complexes to Ag_2S(s) at a pε approximately equal to -1.5. Copper is converted from Cu^o (metallic copper) to Cu_2S(s) at pε = -2.7, Pb from $PbCO_3$(s) to PbS(s) at -3.4 , Cd from $CdCO_3$(s) to CdS(s) at -3.5, Zn from $ZnCO_3$(s) and $ZnSiO_3$(s) to ZnS(s) at -3.8, and Fe from Fe_3O_4(s) to FeS(s) at -4.2. Copper also changes oxidation states from +1 to +2 (Cu_2S(s) to CuS(s)) at -3.9. The converse of this ordering represents oxidation of the MeS(s) present in the sludge.

The total sulfur is important on a stoichiometric basis. The most stable metal sulfides precipitate first, removing sulfur

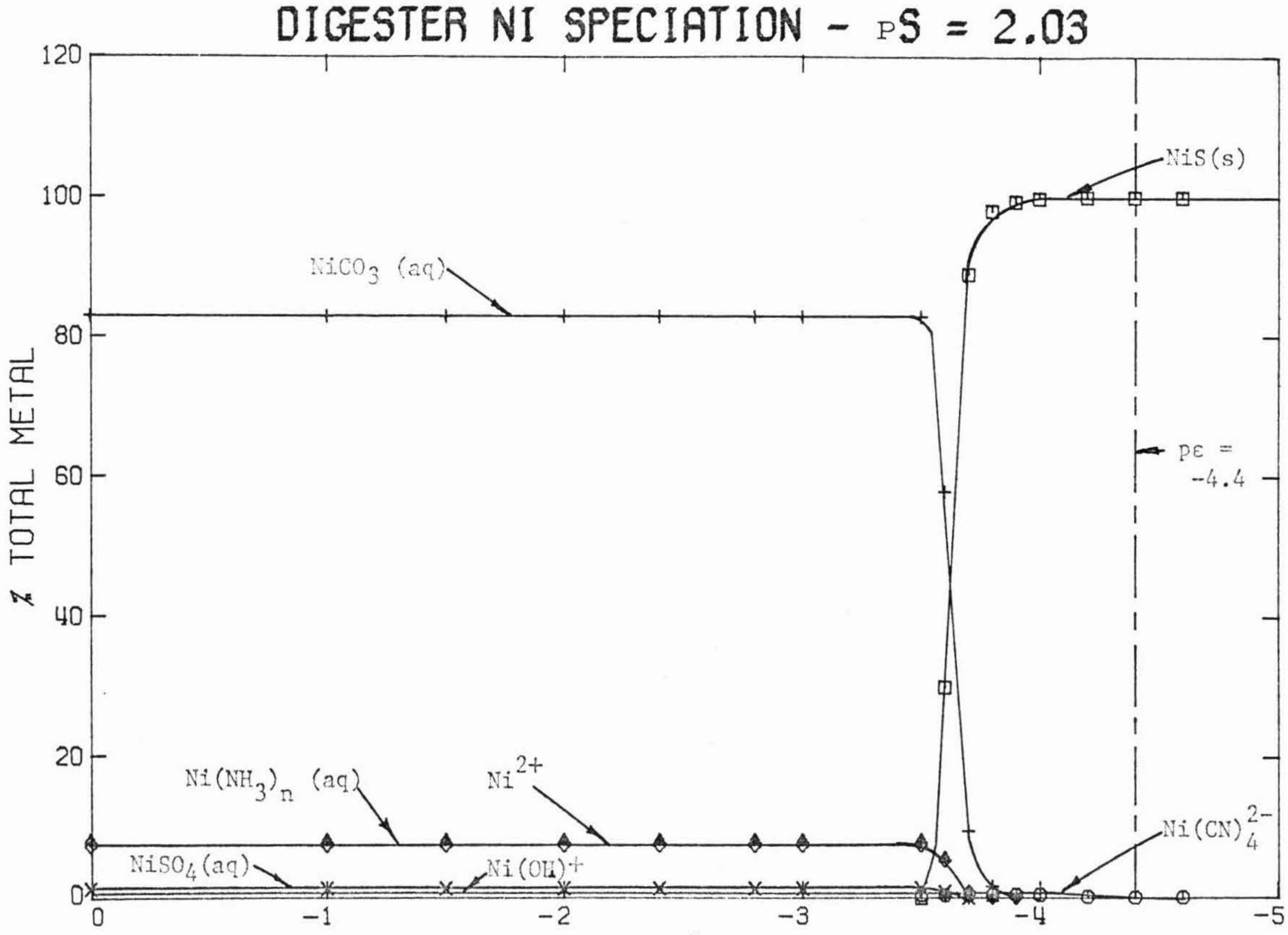


FIGURE 3.12

Nickel Speciation in a Sludge Digester as a Function of pε
(pH = 7.9)

from the reaction system. If the total metals Me_T present, considered on an equivalent molar basis, exceed the S_T necessary for the metal precipitation, i.e. $Me_T > S_T$, the metals remaining in solution will be present as free metal ions or metal-ligand complexes. With the lowest pS_T (2.33) checked in this work, at $p\varepsilon = -4.4$, both FeS(s) and Fe_3O_4(s) were present. If excess sulfur is present, HS^- and H_2S (g) should form and the digester might be upset by sulfide toxicity.

The higher solubilities of Cd and Mn in Table 2.11 need further explanation. The speciation of Mn in the digester is $p\varepsilon$ independent since Mn is either precipitated with or bound to carbonate over the entire $p\varepsilon$ range modeled. Cadmium, on the other hand, does form complexes with sulfide and other ligands for the $p\varepsilon$ range modeled. The input thermodynamic data in its present form may overlook complexation reactions which would account for the 0.2 percent dissolved Cd found, or this measurable solubility may be an experimental artifact.

The complete chemical makeup of the model digester at $p\varepsilon = -4.4$, is summarized in Table 3.6. The predominance of sulfide and hydroxide solids for trace metal speciation should be particularly noted. The dissolved fraction for any trace metal rarely approaches one percent of the total metal. Most of the concentrations of dissolved species are too low even to consider for laboratory measurement, but their inclusion in the tables emphasizes their consideration in the computer computations. Where several complexes occurred, the total of all metal complexes with any given ligand is reported.

TABLE 3.6

Equilibrium Speciation
in a Sludge Digester Inorganic Model (1)
$p\varepsilon = -4.40$, pH = 7.9

metals	total conc	free conc	COMPLEXES (2)									SOLIDS	
		ligands →	CO_3	SO_4	Cl	NH_3	S	PO_4	SiO_3	CN	OH		
	total conc →		1.60	---	2.38	1.63	2.03	2.42	3.78	5.40	---		
		free conc →	3.47	2.94	2.38	2.82	11.0	8.34	10.0	6.78	5.91		
Ca	2.60	4.41	5.08	6.02	---	7.33	---	7.78	---	---	9.03	$Ca_3(PO_4)_2$	3.31
Mg	2.21	2.64	3.26	4.14	---	5.36	---	5.50	---	---	6.25	$Mg_3(PO_4)_2$	2.98
K	2.60	2.60	---	4.95	---	---	---	---	---	---	---		
Na	2.11	2.11	4.90	4.86	---	---	---	---	---	---	---		
Fe^{3+}	1.90	23.7	---	24.0	25.4	---	---	21.5	19.4	21.8	15.0	Fe_3O_4	2.63
Fe^{2+}	---	6.93	---	8.59	8.92	8.44	---	3.38	---	11.7	7.94	FeS	2.28
Mn	3.93	5.90	6.14	7.56	7.70	8.02	---	8.27	---	---	8.42	$MnCO_3$	3.94
Cu^{2+}	3.30	26.2	23.9	27.5	26.2	23.9	---	28.2	---	---	26.6	CuS	3.30
Cu^{1+}	---	19.6	---	---	19.2	14.4	---	---	---	9.4	---		
Cd	4.72	16.8	15.8	18.0	17.4	17.1	12.9	22.7	---	17.9	19.1	CdS	4.72
Zn	2.70	10.6	9.75	11.8	11.9	11.0	---	13.3	---	20.9	11.7	ZnS	2.70
Ni	3.63	10.8	9.85	12.1	13.2	11.0	---	13.9	---	6.59	12.0	NiS	2.63
Pb	3.82	16.8	13.7	17.7	17.9	---	---	---	---	33.8	17.0	PbS	3.82
Ag	5.11	19.8	---	21.9	19.2	18.2	14.2	---	---	12.3	24.0	Ag_2S	5.41
Cr	2.86	10.8	---	12.5	13.1	---	---	7.71	---	---	3.66	$Cr(OH)_3$	2.94
H^+	---	7.90	1.62	9.09	---	1.66	5.75	4.44	3.79	5.36	---		

(1) All values as p[X] = -log(molar concentration of X).

(2) Concentrations of complexes are sums of all complexes of a given metal Me with a given ligand L. $\sum_{k,j}[Me_kL_j]$ where k,j are the stoichiometric coefficients.

The addition of acetate as an organic ligand had no major effect on the model (Table 3.7). Two different surfaces, quartz (SiO_2) and ferric oxide, also caused little change when modeled with surface areas of 100 m^2/l (Tables 3.8 and 3.9). The ferric oxide surface results of Table 3.9 are those with $pH_{pzc} = 8.5$ and ΔG_{chem} of adsorption = -8.5. These parameter settings showed the largest adsorption effect for any ferric oxide surface computation. Three to 10 percent of the Cr was adsorbed. Sodium and K were also adsorbed. The high stability of MeS(s) solids, $MnCO_3(s)$, and $Cr(OH)_3(s)$ clearly dominates trace metal chemistry in digester environment.

The inorganic models of sludge mixed with effluent at pε's of -4.0 to -4.4 showed no major changes in metal speciation except for Mn and Cr. Approximately 10 percent of the Mn was in a dissolved form either as the metal ion or bound with carbonate; 43 percent of the Cr was bound with hydroxide.

Successively greater dilutions of the sludge/effluent mixture with seawater at pε's from -3.0 to -4.0 left all MeS(s) except FeS(s) intact. The FeS(s) was progressively converted to $Fe_3O_4(s)$. Manganese and Cr dissolved completely with Mn present as free ions and chloride and sulfate complexes. Chromium was completely bound to OH^-. The speciation for a combination of one part sludge/effluent and 999 parts seawater is summarized in Table 3.10. The trace metal concentrations were still above background seawater concentrations (Table 3.5).

At this point an oxic model (pε = 10.0) with 0.1 m^2/l of ferric oxide surface was run to examine the effects of oxidation on

TABLE 3.7

Equilibrium Speciation in a Sludge Digester Organic Model(1)
$p\varepsilon = -4.40$, pH = 7.9

metals	total conc	free conc	COMPLEXES(2)										SOLIDS	
		ligands →	CO_3	SO_4	Cl	NH_3	S	PO_4	SiO_3	CN	AC	OH		
	total conc →		1.60	---	2.38	1.63	2.03	2.42	3.78	3.81	1.78	---		
		free conc →	3.48	2.93	2.38	2.82	11.4	8.40	10.0	6.23	1.78	5.91		
Ca	2.60	4.38	5.04	6.04	---	7.30	---	7.80	---	---	5.67	8.99	$Ca_3(PO_4)_2$	3.31
Mg	2.21	2.59	3.22	4.15	---	5.31	---	5.52	---	---	3.79	6.20	$Mg_2(PO_4)_2$	3.03
K	2.60	2.60	---	4.95	---	---	---	---	---	---	---	---		
Na	2.11	2.11	4.90	4.86	---	---	---	---	---	---	---	---		
Fe^{3+}	1.90	23.7	---	24.1	25.4	---	---	21.5	19.4	18.8	20.1	15.0	Fe_3O_4	2.63
Fe^{2+}	---	6.93	---	8.59	8.92	8.45	---	3.36	---	8.71	5.52	7.94	FeS	2.28
Mn	3.93	5.90	6.14	7.56	7.69	8.02	---	8.33	---	---	7.05	8.41	$MnCO_3$	3.94
Cu^{2+}	3.30	25.8	23.4	27.5	25.8	23.5	---	27.9	---	---	25.8	26.1	CuS	3.30
Cu^{1+}	---	19.2	---	---	18.7	14.0	---	---	---	8.13	---	---		
Cd	4.72	16.3	15.4	18.0	17.0	16.6	12.9	22.4	---	17.1	16.0	18.7	CdS	4.72
Zn	2.70	10.1	9.33	11.8	11.2	10.6	---	13.0	---	18.7	10.6	11.5	Zn	2.70
Ni	3.36	10.4	9.40	12.1	12.8	10.5	---	13.6	---	4.44	11.5	11.5	NiS	3.70
Pb	3.82	16.4	13.3	17.7	17.6	---	---	---	---	31.6	16.2	16.5	PbS	3.82
Ag	5.11	19.6	---	21.9	19.0	---	14.2	---	---	11.2	21.0	23.8	Ag_2S	5.41
Cr	2.86	10.8	---	12.5	13.1	---	---	7.78	---	---	---	3.66	$Cr(OH)_3$	2.94
H^+	---	7.9	1.63	9.09	---	1.66	5.75	4.46	3.79	5.12	4.88	---		

(1) All values as p[X] = -log (molar concentration of X).

(2) Concentrations of complexes are sums of all complexes of a given Metal Me, with a given ligand L. $\sum_{k,j} [Me_k L_j]$ where k,j are the stoichiometric coefficients.

TABLE 3.8

Equilibrium Speciation
in a Sludge Digester with SiO_2 Surface(1)
$p\varepsilon = -4.50$, pH = 7.9, surface area = 100 m^2/l

			COMPLEXES(2)										SOLIDS	
		ligands→	CO_3	SO_4	Cl	NH_3	S	PO_4	SiO_3	CN	SiO_2 (SUR)	OH		
	total conc →		1.60	---	2.38	1.63	2.03	2.42	3.78	3.81	2.00	---		
metals ↓	↓	free conc → ↓	3.48	3.80	2.38	2.82	11.5	8.45	10.0	6.34	2.34	5.91		
Ca	2.60	4.35	5.01	6.87	---	7.27	---	7.82	---	---	7.43	8.96	$Ca_3(PO_4)_2$	3.31
Mg	2.21	2.56	3.19	4.98	---	5.20	---	5.53	---	---	5.28	6.17	$Mg_3(PO_4)_2$	3.04
K	2.60	2.60	---	5.82	---	---	---	---	---	---	4.73	---		
Na	2.11	2.11	4.90	5.73	---	---	---	---	---	---	4.25	---		
Fe^{3+}	1.90	23.7	---	25.0	25.5	---	---	21.6	19.4	18.9	13.1	15.0	Fe_3O_4	2.71
Fe^{2+}	---	6.87	---	9.39	8.86	8.39	---	3.34	---	8.74	7.41	7.88	FeS	2.20
Mn	3.93	5.90	6.14	8.43	7.69	8.02	---	8.38	---	---	6.86	8.41	$MnCO_3$	3.94
Cu^{2+}	3.30	25.8	23.4	28.3	25.7	23.5	---	27.8	---	---	24.5	26.1	CuS	3.30
Cu^{1+}	---	---	---	---	18.6	13.8	---	---	---	8.00	21.2	---		
Cd	4.72	16.3	15.3	18.8	17.0	16.5	---	22.4	---	17.0	18.2	18.7	CdS	4.72
Zn	2.70	10.1	9.3	12.6	11.4	10.6	---	12.9	---	18.7	10.4	11.4	ZnS	2.70
Ni	3.63	10.4	9.32	12.9	12.8	10.4	---	13.5	---	4.43	11.0	11.5	NiS	3.70
Pb	3.82	16.4	11.4	18.5	17.4	---	---	---	---	31.6	16.0	16.5	PbS	3.82
Ag	5.11	19.6	---	22.8	19.0	18.0	14.3	---	---	11.2	21.7	23.7	Ag_2S	5.41
Cr	2.86	10.8	---	13.4	13.1	---	---	7.82	---	---	3.81	3.71	$Cr(OH)_3$	3.00
H^+	---	7.90	1.63	9.95	---	1.66	5.81	4.50	3.79	5.14	---	---		

(1) Values as p [X] = -log (molar concentration of X), except SiO_2(sur) which is -log (hectare/liter).

(2) Concentrations of complexes are sums of all complexes of a given metal Me with a given ligand L. $\sum_{k,j} [Me_kL_j]$ where k,j are the stoichiometric coefficients.

TABLE 3.9
Equilibrium Speciation
in a Sludge Digester with Ferric Oxide Surface(1)
pε = -4.40, pH = 7.9, surface area = 100 $m^2/1$

			COMPLEXES(2)										SOLIDS	
ligands →			CO_3	SO_4	Cl	NH_3	S	PO_4	SiO_3	CN	Fe (SUR)	OH		
total conc →			1.60	---	2.38	1.63	2.03	2.42	3.78	5.41	2.00	---		
free conc →			3.48	2.94	2.38	2.82	11.4	8.43	10.0	6.83	5.48	5.91		
metals ↓	total conc ↓	free conc ↓												
Ca	2.60	4.63	5.03	6.02	---	7.28	---	7.81	---	---	7.60	8.97	$Ca_3(PO_4)_2$	3.31
Mg	2.21	2.58	3.20	4.14	---	5.30	---	5.53	---	---	5.95	6.19	$Mg_3(PO_4)_2$	3.03
K	2.60	2.61	---	4.96	---	---	---	---	---	---	4.10	---		
Na	2.11	2.12	4.91	4.87	---	---	---	---	---	---	3.59	---		
Fe^{3+}	1.90	23.9	---	24.1	25.4	---	---	21.5	19.4	21.8	16.2	15.0	Fe_3O_4	2.64
Fe^{2+}	---	6.93	---	8.59	8.92	8.45	---	3.38	---	11.8	9.33	7.94	FeS	2.28
Mn	3.93	5.90	6.14	7.56	7.69	8.02	---	8.35	---	---	9.14	8.41	$MnCO_3$	3.94
Cu^{2+}	---	25.8	23.4	27.5	25.8	23.5	---	27.9	---	---	27.5	26.1	CuS	3.30
Cu^{1+}	3.30	19.2	---	---	18.7	14.0	---	---	---	9.13	20.9	---		
Cd	4.72	16.3	15.4	18.0	17.0	16.6	---	22.4	---	17.6	19.5	18.7	CdS	4.72
Zn	2.70	10.1	9.33	11.8	11.5	10.6	---	13.0	---	20.8	12.1	11.5	ZnS	2.70
Ni	3.63	10.4	9.40	12.1	12.8	10.5	---	13.6	---	6.46	12.9	11.5	NiS	3.70
Pb	3.82	16.4	13.3	17.7	17.5	---	---	---	---	33.7	17.9	16.5	PbS	3.82
Ag	5.11	19.6	---	21.9	19.0	18.0	14.2	---	---	12.2	21.1	23.8	Ag_2S	5.41
Cr	2.86	10.8	---	12.5	13.1	---	---	7.80	---	---	4.37	3.66	$Cr(OH)_3$	2.95
H^+	---	7.9	1.63	9.09	---	1.66	5.75	4.50	3.79	5.63	---	---		

(1) Values as p[X] = -log (molar concentration of X), except Fe(sur) which is -log (hectare/liter).

(2) Concentrations of complexes are sums of all complexes of a given metal Me with a given ligand L. $\sum_{k,j} [Me_k L_j]$ where k,j are the stoichiometric coefficients.

TABLE 3.10

Equilibrium Speciation:
Sludge-Effluent Mixture Diluted with Anoxic Seawater (1)
pε = -3.50, pH = 7.9

metals	total conc	free conc	COMPLEXES (2)										SOLIDS	
ligands →			CO_3	SO_4	Cl	F	Br	NH_3	S	PO_4	CN	OH		
total conc →			2.63	1.54	0.25	4.13	3.07	5.11	5.51	5.81	8.41	---		
free conc →			4.91	1.89	0.25	4.35	3.07	6.32	11.3	11.7	9.59	5.86		
Ca	1.98	2.10	4.45	2.98	---	6.00	---	8.52	---	9.25	---	6.80	$CaCO_3$ 2.85	$Ca_3(PO_4)_2$ 6.30
Mg	1.27	1.34	3.66	2.12	---	4.54	---	7.56	---	7.99	---	5.04		
K	1.98	2.00	---	3.43	---	---	---	---	---	---	---	---		
Na	0.32	0.33	4.69	2.16	---	---	---	---	---	---	---	---		
Fe^{3+}	5.38	23.1	---	22.8	22.7	22.7	26.3	---	---	24.8	38.0	14.6	Fe_3O_4	5.87
Fe^{2+}	---	7.44	---	8.32	7.44	---	---	12.5	---	7.59	28.6	8.54		
Mn	7.37	7.88	9.80	8.76	7.56	---	10.7	13.5	---	14.0	---	10.5		
Cu^{2+}	6.77	25.7	25.24	26.6	23.7	29.4	28.4	28.0	---	31.5	---	26.1	CuS	6.74
Cu^{1+}	---	20.1	---	---	15.0	---	20.7	20.6	---	---	15.6	---		
Cd	8.20	16.2	17.0	17.1	14.6	20.2	17.9	20.1	12.9	26.0	20.4	18.8	CdS	8.20
Zn	6.18	10.0	10.9	10.9	9.26	13.8	12.9	14.2	---	16.6	31.9	11.5	ZnS	6.18
Ni	6.93	10.3	11.0	11.2	10.3	14.2	13.5	14.0	---	17.2	17.6	11.6	NiS	6.98
Pb	7.30	16.3	15.1	16.8	14.8	---	18.2	---	---	---	44.8	16.5	PbS	7.30
Ag	8.28	19.6	---	21.0	14.7	23.9	18.4	22.7	14.2	---	17.8	23.8	AgS	8.58
Cr	6.34	13.2	---	14.4	13.6	13.9	19.2	---	---	14.1	---	6.34		
H^+	---	7.90	3.18	8.16	---	9.50	---	5.14	5.68	7.93	8.44	---		

(1) All values as p[X] = -log (molar concentration of X).

(2) Concentrations of complexes are sums of all complexes of a given metal Me with a given ligand L. $\sum_{k,j} [Me_k L_j]$ where k,j are the stoichiometric coefficients.

speciation. All solids but $Fe_3O_4(s)$, $CaCO_3(s)$, and $Ca_3(PO_4)_2(s)$ dissolved and the trace metals were found as chloride complexes or free ions. (Table 3.11).

For the anoxic systems with an additional tenfold dilution, FeS(s) dissolved completely, NiS(s) and ZnS(s) began to dissolve. A further tenfold dilution completed the dissolution of Ni and Zn and began the dissolution of PbS(s). Ferric oxide also disappeared completely.

3.6.3 Sedimentation

One evaluation of the effect of sludge discharges to the deep basins is a comparison of solids, organic carbon, and metal input from the outfalls with that from naturally occurring fallout. The total solids input from natural sources to the basins is 6.0×10^5 to 3.0×10^6 metric tons per year (Section 3.5). If five to 10 percent of the sediment consists of organic material, organic carbon inputs would conservatively be 3.0×10^4 to 3.0×10^5 metric tons/year. The sludge inputs of total solids would be about 1.0×10^5 metric tons/year, with organic carbon (Table 3.3) at 7.5×10^4 metric tons/year. The sludge solids would then represnt three to 17 percent of the natural solids total and the organic-C, a 25 to 150 percent increase over natural inputs.

The comparison of mass inputs fails to give a complete picture, however, because the outfalls, even if designed with diffusers, are essentially point sources when viewing the basin on a macroscopic

TABLE 3.11

Equilibrium Speciation:
Sludge-Effluent Mixture Diluted with Oxic Seawater(1)
surface area = 0.1 $m^2/1$, pε = 10.0, pH = 7.9

			COMPLEXES(2)											SOLIDS
	ligands →		CO_3	SO_4	Cl	F	Br	NH_3	S	PO_4	CN	Fe(SUR)	OH	
	total conc →		2.63	1.54	0.25	4.13	3.07	5.11	5.51	5.81	8.41	4.00	---	
metals ↓	↓	free conc →	4.91	1.89	0.25	4.35	3.07	6.32	---	11.7	9.59	9.25	5.86	
Ca	1.98	2.10	4.45	2.98	---	6.00	---	8.52	---	9.25	---	8.81	6.80	$CaCO_3$ 2.86 $Ca_3(PO_4)_2$ 6.29
Mg	1.27	1.34	3.66	2.12	---	4.54	---	7.56	---	7.99	---	8.19	5.04	
K	1.98	2.00	---	3.43	---	---	---	---	---	---	---	7.11	---	
Na	0.32	0.33	4.69	2.16	---	---	---	---	---	---	---	5.43	---	
Fe^{3+}	5.38	18.6	---	18.3	18.2	18.2	21.7	---	---	20.3	33.5	15.1	10.1	Fe_3O_4 5.86
Fe^{2+}	---	16.4	---	17.3	16.4	---	---	21.5	---	16.6	37.6	22.5	17.5	
Mn	7.37	7.88	9.80	8.76	7.58	---	10.7	13.5	---	14.0	---	14.6	10.5	
Cu^{2+}	6.77	8.84	8.34	9.72	6.76	12.5	11.5	11.1	---	14.6	---	14.2	9.24	
Cu^{1+}	---	16.7	---	---	11.6	---	17.3	17.2	---	---	12.2	21.8	---	
Cd	8.20	9.84	10.6	10.7	8.21	13.7	11.5	13.7	---	19.6	14.0	16.5	12.3	
Zn	6.18	7.06	7.91	7.93	6.30	10.8	9.88	11.2	---	13.6	28.9	12.9	8.50	
Ni	6.93	7.33	8.00	8.21	7.30	11.2	10.4	11.0	---	14.2	14.5	13.5	8.53	
Pb	7.30	9.03	7.84	9.52	7.54	---	10.9	---	---	---	37.4	14.3	9.24	
Ag	8.28	13.2	---	14.6	8.33	17.5	12.0	16.3	---	---	11.4	18.3	17.4	
Cr	6.34	13.2	---	14.4	13.6	13.9	19.2	---	---	14.1	---	11.0	6.34	
H^+	---	7.9	3.18	8.16	---	9.50	---	5.14	---	7.96	8.44	---	---	

(1) Values as p[X] = -log (molar concentration of X), expect for Fe(sur) which is -log (hectare/liter).

(2) Concentrations of complexes are sums of all complexes of a given metal Me with a given ligand L. $\sum_{k,j} [Me_k L_j]$ where k,j are the stoichiometric coefficients.

level. Measurements with sediment traps around the existing Hyperion sludge outfall (Mitchell and Schafer, 1975) and the resulting mass balance calculations run on the organics and metals indicate that 30 percent of the organics and 70 percent of the trace metals (Cd, Cr, Cu, Hg, Ni, Pb, and Zn) discharged during the entire history of the outfall are still in the sediments within 3 to 4 km of the outfall.

The plume height of rise from the proposed outfalls should be about the same as the maximum for the existing Hyperion sludge outfall. The local currents at the proposed sites are probably somewhat less. A zone of major influence immediately around the outfall would be expected. An extension of the sedimentation analysis of Section 2.5.2 for a maximum plume rise of 100 meters gives settling times of 1×10^6 to 5×10^6 seconds (10 to 50 days) for the fastest 10 percent and 20 percent of the solids. With local currents of 0.1 to 10 cm/sec, travel distances of 1 km to 500 km are predicted.

An additional correction must be made for the water temperature difference between the sedimentation experiments (10°C) and the basin bottoms (5 to 6°C). For Stokes Law settling $v_s \propto 1/\mu$ and thus

$$\frac{v_{s,1}}{v_{s,2}} = \frac{\mu_2}{\mu_1} \qquad (3.25)$$

For the temperatures in question,

$$\mu^*_{10.5} = 0.0137 \text{ cm}^2/\text{sec}$$
$$\mu_{5.5} = 0.0163 \text{ cm}^2/\text{sec}$$

---

[*] See Figures A.2 and A.3 for μ and ρ as functions of percent salinity and water temperature

and the settling velocities at the lower temperature should decrease by approximately 20 percent. (This change is equivalent to shifting the sedimentation curves about 1/10 cycle to the left on Figures 2.15 through 2.18).

3.6.4 Dispersion and Diffusion after Discharge

One final consideration in the behavior of sludge discharges is the effect that diffusion will have on both the suspended and dissolved components after initial mixing. If flocculation is ignored, the sludge/seawater mixture is assumed to be carried in a constant velocity field with gravitational forces acting on the particles and eddy diffusion influencing the entire discharge. The governing differential equation for the particles is

$$\frac{\partial \eta}{\partial t} + \vec{V} \cdot \nabla n = D\nabla^2 \eta - \nabla \cdot \vec{v}_s \eta \tag{3.26a}$$

where, $\vec{v}_s$ = the particle terminal settling velocity
η = the number concentration of particles
$\vec{V}$ = the velocity field
D = the diffusion coefficient

For dissolved constituents

$$\frac{\partial c}{\partial t} + \vec{V} \cdot \nabla c = D\nabla^2 c \tag{3.26b}$$

with

c = the chemical concentration

The coordinate axes have positive y toward the water surface and x perpendicular to the diffuser, positive downcurrent. For steady flow

$$\frac{\partial}{\partial t} = 0, \quad \vec{V} \cdot \nabla \eta = V \frac{\partial \eta}{\partial x} \tag{3.27}$$

$$\overline{V} \cdot \nabla c = V \frac{\partial c}{\partial x} \tag{3.28}$$

$$\nabla \cdot \eta \overline{v}_s = \nabla \eta \cdot \overline{v}_s + \eta \nabla \cdot \overline{v}_s = v_s \frac{\partial \eta}{\partial y} + \eta \frac{\partial v_s}{\partial y}, \tag{3.29}$$

where v_s is negative for falling particles. Hence

$$V \frac{\partial \eta}{\partial x} = D_x \frac{\partial^2 \eta}{\partial x^2} + D_y \frac{\partial^2 \eta}{\partial y^2} + D_z \frac{\partial^2 \eta}{\partial z^2} - \left(v_s \frac{\partial \eta}{\partial y} + \eta \frac{\partial v_s}{\partial y} \right) \tag{3.30}$$

and

$$V \frac{\partial c}{\partial x} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} \tag{3.31}$$

In its complete form, the equation including sedimentation has no simple solution and must be approached numerically with the computer. Such analysis is beyond the scope of the present work, but the case for dissolved constituents has been solved by Brooks (1960) with some simplifying assumptions.

For sludge discharges to the strongly stratified environment of the deep basins, $D_y << D_x$. An extensive compilation of vertical diffusion coefficients and discussion about their determination can be found in Koh and Fan (1969). Sholkovitz and Gieskes (1971) report values for D_y of 3 to 6 cm^2/sec for the Santa Barbara Basin. The persistently low D.O. values for the basin waters below sill depth confirm the assumption of low D_y.

The lateral spread of any constituent will be assumed to be governed only by downstream distance or travel time from the diffuser with longitudinal diffusion (x-direction) neglected compared to differential advective transport and lateral mixing (z-direction). Therefore,

$$V \frac{\partial c}{\partial x} = D_z \frac{\partial^2 c}{\partial z^2} . \tag{3.32}$$

The "4/3-Law" for the lateral diffusion coefficient implies

$$D_z = \alpha P^{4/3} \tag{3.33}$$

where

α = a coefficient

P = the width of the plume at a distance x downcurrent

With additional manipulation, the solution for the plume width is

$$P = b[1 + (2/3)\beta\ x/b]^{3/2} \tag{3.34}$$

with

$$\beta = \frac{12\ D_{z,o}}{Vb},\ b = \text{the diffuser length},\ D_{z,o} = \alpha b^{4/3}$$

The centerline concentration, c_{max}, at a distance x downcurrent is given as

$$\frac{c_{max}}{c_o} = \text{erf}\left\{\left[\frac{1.5}{(1 + \frac{2}{3}\frac{\beta x}{b})^3 - 1}\right]^{1/2}\right\} \tag{3.35}$$

with c_o = the initial concentration. In the x direction, c_{max} can be expressed as a function of downcurrent travel time.

$$\frac{c_{max}}{c_o} = \text{erf}\left\{\left[\frac{1.5}{(1+8\alpha\frac{t}{b^{2/3}})^3 - 1}\right]^{1/2}\right\} \tag{3.36}$$

Values of c_{max} as a function of α, b, and t, have been tabulated by Koh (1976). For a diffuser length of 1000 meters (15-cm ports and an initial dilution of 1350) the corresponding plume width and centerline dilutions are summarized in Table 3.12. These values are independent of velocity. The current will only effect distance downcurrent where these values are found. Away from the centerline of

TABLE 3.12

Plume Width and Centerline Dilutions

Time (hours)	0.25	0.5	1.0	2.0	3.0	4.0	5.0	6.0	8.0	10.0	12.0	15.0
Plume Width (meters)	1050	1100	1200	1420	1660	1880	2120	2380	2920	3503	4110	5090
Centerline (1) Concentration c_{max}/c_o	1.000	1.000	.991	.916	.817	.724	.645	.578	.473	.395	.337	.272

(1) Source: Koh, 1976.

the plume a Gaussian distribution of concentrations is assumed. After 15 hours, the dilution by diffusion is only a factor of four greater than that caused by the initial mixing. Similar tabulation easily can be made for other diffuser lengths.

The lateral spread of the particles in the sludge discharges cannot be predicted explicitly as was mentioned earlier. Qualitatively, turbulent diffusion should spread the particle field as it moves downcurrent. The width of spread should be no greater than that for the dissolved constituents.

3.7 Evaluation of Potential Environmental Impacts

Based on upper-bound estimates of the major constituents in the proposed sludge discharges, the input of total solids to the San Pedro and Santa Monica Basins would be increased by no more than 15 percent over the natural fallout. Organic carbon inputs would rise by no more than 100 percent, nitrogen by no more than five percent and trace metals (Ag,Cr,Cu, Ni,Pb, and Zn) by no more than a factor of five. The local effects near the proposed sludge outfall would be somewhat larger, inasmuch as most of the sludge solids and metals would probably reach the sediments less than 10 km downcurrent from the discharges. The higher natural sedimentation rates should bury the sludge and its constituents, effectively trapping them in the sediments. Heavy metals may be mobilized from the sediments by bacterially mediated alkylation. Mercury methylation has been shown to take place in a variety of sediments containing inorganic Hg and organic matter. Data for the alkylation of other heavy metals are scarce or nonexistent. This form of mobilization was not investigated further for this work. Local water should be converted from nearly anoxic to totally anoxic.

The effect on waters above the sill depths should be minimal because of the apparent low rates of exchanges for the basin waters.

Any effects on biota in the two basins should be minimal, since anaerobic bacteria are apparently the only continuous inhabitants of the bottom. Discharge of sludge to the basins would also remove these inputs of solids and metals from the more productive surface waters (less than 100 meters) where the majority of the present discharge now occurs. Any potential adverse impacts of land-disposal schemes for the sludge would also be eliminated.

3.8 Summary and Conclusions

A plan for the disposal of digested sludge to the San Pedro and Santa Monica Basins has been presented and modeled in the previous sections. Sludge flows from the City of Los Angeles Hyperion facility and from the Los Angeles County Sanitation District Carson facility were included. A review of available oceanographic, biological, geochemical data indicates that the basin waters below sill depth have long residence times (up to two years) and low D.O. (less than 0.4 mg/l). They are stable vertically, longitudinally, and laterally. The underlying bottom sediments are nearly devoid of life with anaerobic bacteria the only permanent inhabitants.

Hydraulic modeling of the sludge discharges by multi-port diffusers at depths of 730 meters (2400 feet) showed that plume rise heights should be less than 120 meters and a dilution factor of 450 to 2600 should be expected. Dispersion and diffusion for periods of up to 15 hours following the initial turbulent mixing should increase dilution by a factor of four. Simple calculations showed that no major volumetric displacement of waters below the sill depth should occur. Chemical modeling using the stoichiometric or box model and mass balances on the total sludge discharges showed that the inputs of oxidizable substances such as ammonia-N and organic carbon should be sufficient to deplete the basin water D.O., especially near the diffuser. Computer modeling of the chemical constituents in the digester and upon discharge demonstrated that the predominant metal sulfide solids control all trace metals but Cr and Mn. Chromium appeared as a hydroxide solid and Mn as a carbonate solid. At dilutions of up to 3000-fold the metal sulfides continue as solids while Cr and Mn solids dissolve, leaving Cr completely bound as hydroxide complexes and Mn as a free ion or in chloride or sulfate complexes. As further dilution occurs the metal sulfides begin to dissolve.

Mass balances on total solids, organic carbon, and trace metal discharges result in a solids increment to the basins of less than 17 percent of the natural fallout, a 25 to 150 percent increase in organic carbon discharge, and two-to five-fold increase in trace metal inputs.

An examination of sedimentation data and observations of the behavior of solids and metals around the existing Hyperion sludge outfall strongly suggest that the metals which are already associated with particulate matter in the digester should stay with the solids and reach the nearly lifeless basin bottoms.

The adverse environmental impacts should be minimal. The transfer of sludge solids and metals from the present shallow water discharge sites should indeed be considered as an environmental improvement.

CHAPTER 4

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS FOR FUTURE WORK

4.1 Summary

Some physical, chemical, and physical-chemical properties of two digested sludges have been measured in this work. Experiments were conducted to characterize and delineate particle sizes in digested sludge and their relationship to trace metals. The particle-size distribution for two sludges was measured with a Coulter Counter. Vacuum filtration techniques for particle sizing were also applied. Total metals in Hyperion and LACSD sludges and dissolved trace metals in LACSD sludge were quantified. Standard analytical techniques were also used for the determination of chlorides, ammonia, and total alkalinity in the sludge samples. Sedimentation and oxic-mixing experiments were designed and carried out to determine the behavior of sludge in seawater, thus simulating ocean disposal conditions. Finally the results from the laboratory work were combined with information from the literature as shown in Figure 4.1, to propose and model the discharge of digested sludge to the San Pedro and Santa Monica Basins off coastal southern California.

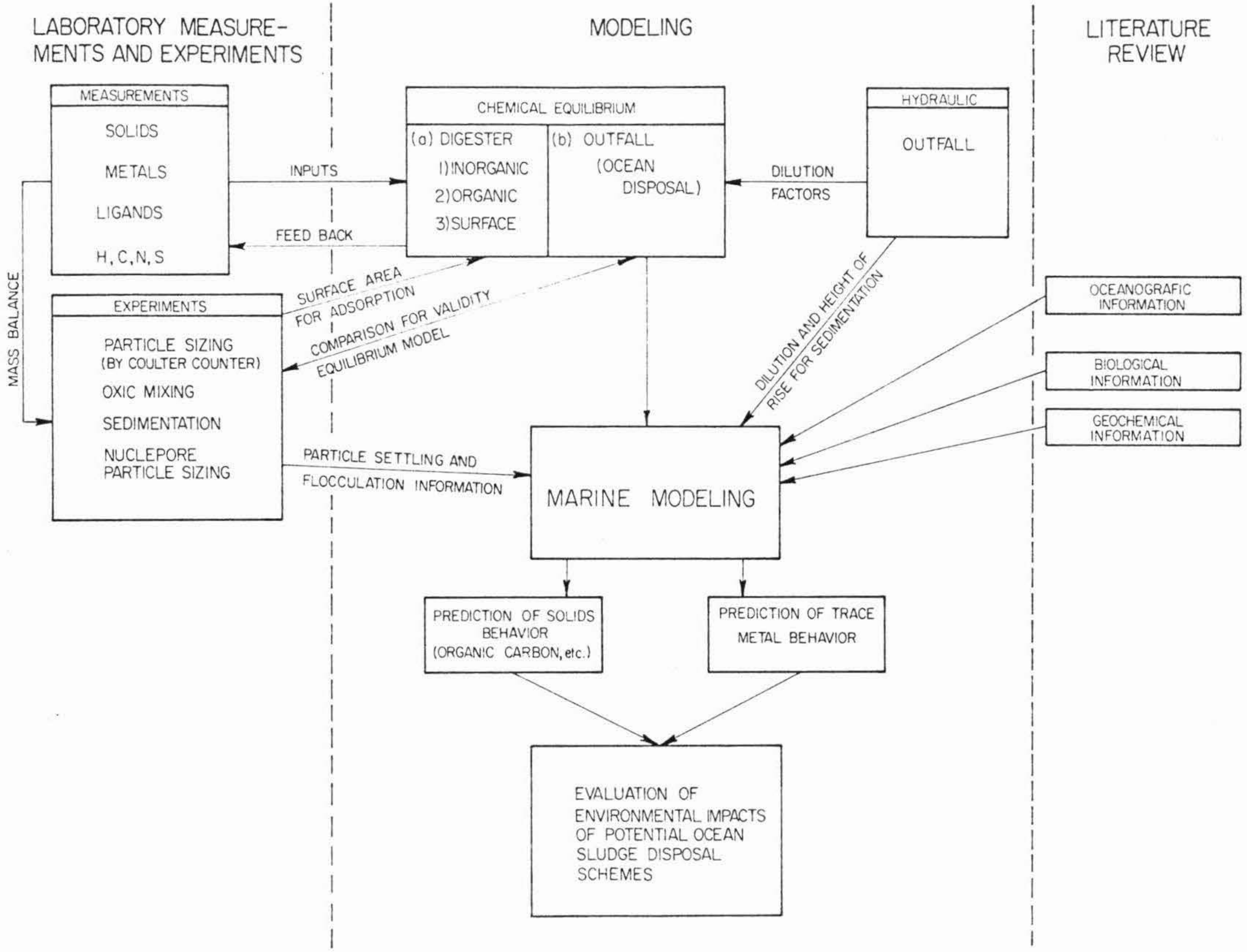


FIGURE 4.1

Scheme for the Evaluation of Sludge Discharge to the Ocean

The modeling and calculations were specific to the aforementioned basins but the general approach should be appropriate for any sludge disposal scheme to the ocean where deep, nearly anoxic basins are close to shore. Modeling efforts included the use of a hydraulic model for sludge discharge to a density stratified medium and both simple-box and computer-equilibrium-speciation chemical modeling for the prediction of gross and fine-scale chemical efforts. Calculations were also performed to estimate the spread of suspended and dissolved constituents after the initial jet mixing of the discharge. Based on this information, a preliminary assessment of environmental effects from the proposed discharges was then made.

4.2 Conclusions

4.2.1 Conclusions: Analytical and Experimental Techniques

The trace-metal analysis of this research showed good agreement between Atomic Absorption Spectrophotometry (AAS) and energy dispersive X-ray fluorescence (XRF) analytical techniques. No direct cross-calibration runs were made but the correspondence of mass balances was better than 20 percent in almost all cases and within five to 10 percent for most experiments. Since the reported total instrumental errors on the XRF data were in the range of 11 to 20 percent, the agreement of data was very good. The advantage of XRF was speed and low cost for multi-element analysis on filter-mounted samples. The

XRF technique was sensitive enough to detect trends in the behavior of trace metals in the sludge-particle system.

The sedimentation analysis based on single-depth sampling was constrained because flocculation effects were undetected when the experiments were run at only one dilution. When particle concentrations were varied, however, flocculation was detected, at least qualitatively. A tenfold increase in the dilution of sludge/seawater mixtures in this research decreased settling velocities by an order of magnitude. Nuclepore membrane filters were apparently ideal for solid-liquid separation in sedimentation experiments because 1) they were not measurably hydroscopic; 2) they did not retain significant amounts of dissolved solids such as sea salts; 3) their low initial weight allowed for the accurate detection of small solids increments; and 4) they were well suited for metal measurement of the captured solids, either by direct XRF analysis or by AAS after acid digestion.

Particle sizing by vacuum filtration using Nuclepore membranes (8.0-μ and 1.0-μ pore sizes) was attempted and found to be unsatisfactory for sludge. The efficiency of solids capture for the 8.0-μ membranes increased rapidly with increased solids loading because pore clogging decreased the effective pore size.

4.2.2 Conclusions: The Nature of Sludge and the Behavior of Sludge in Seawater

Particle-size measurements for two sewage sludges showed that the majority of particles by number count have diameters of less than 10 μ. This size fraction is selectively chosen by many filter feeders in the ocean. It also disrupts the penetration of light in the water column if it is in suspension. Actual number counts for the digested sludges were in excess of 10^{12} particles/l. Such small particles settle more slowly than particles of larger diameter and thus will be carried much greater distances if discharged into the ocean. The crude particle sizing performed by filtration also showed that more than 50 percent of the particles by weight passed the 8.0-μ pores of the Nuclepore membranes during vacuum filtration. Owing to pore clogging of the membrane, the weight fraction passing the 8.0-μ pores but captured by the 1.0-μ pores may be substantially smaller than the fraction that actually has diameters less than 8.0 μ.

Analysis for dissolved trace metals (Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in LACSD sludge showed that only Mn had a soluble fraction greater than one percent.

During the oxic mixing of Hyperion and LACSD sludges (1 part) in seawater (99 parts) for periods of up to 28 days, less than 10 percent of the solids were oxidized or solubilized. Substantial metal mobilization away from the particle phase occurred only for Ni.

Sedimentation experiments for LACSD sludge diluted 50:1, 100:1, and 500:1 with artificial seawater revealed that the sedimentation velocities decreased with increasing dilutions. For trace metals (Cr, Cu, Fe, Ni, Pb, and Zn) measured by XRF, Cr, Cu, and Zn settled more slowly than the filterable solids in all cases whereas Ni and Pb settled with or faster than the solids. Nickel may have been mobilized away from the particle phase. Lead is possibly associated with larger or faster settling particles than Cr, Cu, and Zn. Metal analysis of the size fractions separated by Nuclepore filtration showed the same trend. Approximately 60 percent of the lead was captured by the 8.0-μ membrane (where capture by the 1.0-μ membrane = 100 percent). Less than 50 percent of the Cr, Cu, and Zn were caught in the same solids fraction.

4.2.3 Conclusions: Modeling and the Sludge Disposal Scheme

The hydraulic modeling of sludge discharges in San Pedro and Santa Monica Basins indicated that the maximum rise heights for the sludge plume would be less than 120 m. All discharges were assumed to be made at a depth 730 m and three different density profiles were used to cover any conceivable density stratification. Five different port sizes were also tried. Larger ports, which correspond to shorter diffusers for non-interfering jets, gave larger rise heights and lower initial dilutions. Initial jet mixing gave dilution factors of 450 to 2600. Analysis for the dispersion and diffusion of dissolved constituents after initial jet mixing indicated that in a time period of 15 hours, an additional dilution by a factor of four would occur.

Stoichiometric chemical modeling of the sludge constituents predicted that the nearly anoxic waters of the deep basins should become wholly depleted of D.O. as a result of the discharge. Assuming such anoxic conditions, chemical equilibrium modeling of the discharged sludge showed that the metal sulfide solids, which predominate trace-metal chemistry in the digester, remain stable for dilution factors of up to 3000. Manganese and Cr were exceptions to this pattern, existing as carbonate and hydroxide solids respectively in the digester. These solids dissolved much more readily than metal sulfide solids upon dilution with seawater.

Existing information from the Hyperion sludge outfall and calculations based on sedimentation experiments in this work combined with current velocity data showed that the majority of the sludge solids should reach the anoxic, anaerobic sediments at the basin bottoms. Published biological information showed that the basin bottoms have been anaerobic for long periods of time and biological productivity there was virtually nil. Well designed and conceived sludge-disposal schemes to these waters should cause no major adverse environmental impacts.

4.3 Recommendations for Future Investigation

The direction chosen for future work depends entirely on the aspect of sludge characterization and/or sludge disposal in which the researcher is interested. Analytically, sludge-particle sizing should be done on samples of digested sludge from other systems to see if the curve shapes, particle number counts, and surface areas found in this work are characteristic of other digested sludges. Coulter Counter experiments should be conducted with lower ionic-strength solutions to check for flocculation of the sludge particles. Other particle-sizing apparatus such as that manufactured by Hiac (see

Appendix B), should be tested to see if particle sizing may be done more rapidly.

If ocean disposal is considered further as a viable disposal alternative, particle-size measurements of samples taken during sedimentation experiments should give direct insight into the flocculation of sludge in seawater. Multi-depth sampling would also serve the same purpose as would larger sedimentation columns which would allow larger sample sizes and reasonable weight recovery for metal analysis while using higher dilution ratios. The sludges considered for ocean disposal should be tested in this manner.

Oxic and anoxic mixing experiments with analysis for other metals, e.g. Cd, Ag, Hg, should also be run at a variety of dilutions for ocean disposal plans. The addition of a chelating agent specific for ferric iron may prevent the possible re-adsorption of released metal ions onto ferric oxide surfaces. Such an experiment might allow for the separation of the effects of dissolution and oxidation from those of adsorption. The fractionation of sludge particles by size for trace metal analysis may be accomplished using Nuclepore-type membranes with apparatus that allows for pressure filtration and backwash cycles to alleviate the problems of membrane pore clogging. Several such cells have recently become available.

If any plan for ocean sludge disposal in deep waters is pursued, additional hydraulic modeling will be necessary along with a comprehensive ocean-monitoring effort. In the particular case of the San Pedro and Santa Monica Basins, year-round measurements of density stratification, D.O., and current velocities would be a first step. Extensive bottom sampling should be conducted to establish the true state of the biota there and the actual rates of sedimentation for solids, trace metals, and organic carbon.

APPENDIX A

SAMPLING AND ANALYTICAL TECHNIQUES

A.1 Sludge Samples

Grab-samples of sludge were taken both at the Hyperion Treatment Plant of the City of Los Angeles (flow = 340 MGD) and at the Joint Water Pollution Control Facility of Los Angeles County Sanitation Districts (flow = 370 MGD). The Hyperion samples for metal analysis were all taken from digester 5C, a mesophilic digester; the samples used for particle-size analyses were taken from digester 3C, also a mesophilic digester. The LACSD sludge samples for metal analyses and for use in the sedimentation and mixing experiments were taken from the sludge recirculation seeding line in the sludge wetwell. Samples used for particle sizing were taken from the sludge line going into (that is, before) the sludge centrifuges.

Sludge-sample sizes ranged from four to 16 liters and were taken in acid-washed wide-mouth polyethylene jars. All sludge samples were sieved through 0.5 mm polyethylene mesh to remove seeds and other large particles that clogged the pipettes during volumetric transfers of sludge. The reproducibility in a given sample was checked by running replicates of both TROE and total metals. The results of such duplicate analysis showed no variation at a 90 percent confidence level as determined with the Student t-test. The measured TROE values are shown in Table A.1.

TABLE A.1

Summary of Digested Sludge Solids Analysis(1)

Source	Hyperion Digester 5C	LACSD Primary(2)	LACSD Primary(2)	LACSD Primary(3)	Hyperion Digester 3C(3)
TROE	.02374 ± .00008	.02429 ± .00013	.02528 ± .00007	.02880 ± .00010	.02402 ± .00017
VROE	.01356 ± .00007	.01260 ± .00013	.01323 ± .00006	.01578 ± .00006	.01397 ± .00011
FROE	.01018 ± .00003	.01169 ± .00013	.01205 ± .00002	.01302 ± .00005	.01005 ± .00004
% Volatile	57.1	51.9	52.3	54.8	58.2

(1) All results expressed as gms solids/gm wet sludge

TROE = total residue on evaporation
VROE = volatile residue on evaporation
FROE = fixed residue on evaporation.

(2) Used for metals analysis, mixing, and sedimentation experiments.

(3) Used for particle sizing by Coulter Counter.

A.2 Sample Capture with Nuclepore Filters

Nuclepore polycarbonate membranes were used for all solids capture in this experimental work. They were chosen because of their suitability for XRF analysis, and because of their apparent sieve-like properties for particle separation. All samples were drawn through the filters by vacuum (up to 74 cm of mercury). The 10-to 15-micron thick membranes were difficult to use with a standard Millipore filter head and funnel, hence a teflon funnel was designed and built by the author. (See Figure A.1.) The membrane was also placed on top of a 55-cm diameter Whatman GF/C glassfiber filter to insure a good seal. Teflon funnels were boiled in concentrated nitric acid and rinsed with doubly-distilled water (D^2H_2O) between experiments.

A.3 Chemical Analysis Techniques

The analysis done in this work was based on standard analytical methods. Reagent-grade chemicals were used at all stages. All glassware was soaked in NOCROMIX, rinsed with tap water, soaked in strong detergent, rinsed with tap water again, rinsed with tap-distilled water, rinsed four times with 4 N nitric acid (Baker grade) and finally rinsed four times with D^2H_2O.

Pipettes were washed with ALCONOX and tap-distilled water, rinsed with tap-distilled water, soaked for 20 minutes in ethanol saturated with potassium hydroxide (KOH), rinsed repeatedly with tap-distilled water, soaked in 1 N nitric acid, and finally rinsed with doubly-distilled water.

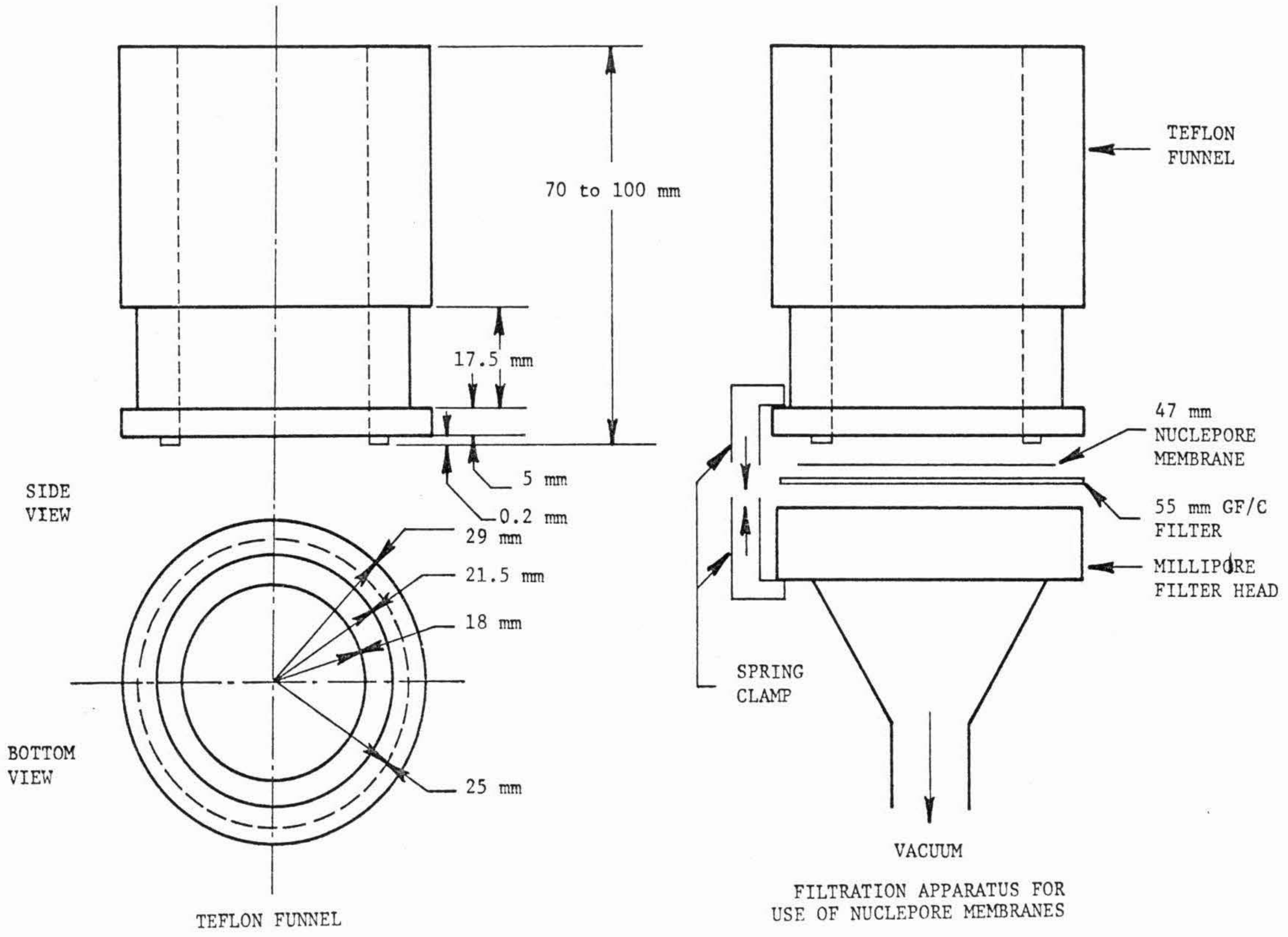


FIGURE A.1

Teflon Funnel Details and Use of Nuclepore Membranes

Polyethylene or polypropylene bottles were used for storage of all raw samples, treated samples, and metal standards. New bottles were soaked for 48 hours in 1 N HNO_3 and rinsed repeatedly with D^2H_2O. Used bottles were soaked for at least 48 hours in concentrated HNO_3 and then washed with D^2H_2O. Teflon bottles were used for sample preparation and storage in the dissolved trace metals in sludge. All Teflon containers were degreased with detergent, boiled in concentrated G. Fredrick Smith (GFS) grade redistilled HNO_3, and finally rinsed with D^2H_2O.

A.4 Sludge Metal Extractions

Total metal concentrations in sludge were measured by flame Atomic Absorption Spectrophotometry (AAS) following an acid digestion of sludge. Approximately 10 ml of wet sludge (250 mg dry solids) were pipetted into a weighed 100-ml round-bottom flask and the exact quantity of sludge determined by an additional weighing. Twenty ml of concentrated HNO_3 (GFS grade) were added, the flask was attached to a Friedricks condenser and placed in a heating mantle. The sludge/acid mixture was then maintained at a 110 to 120°C for at least 24 hours. After cooling, the mixture was washed into a 100-ml beaker and the flask washed repeatedly with 4 N HNO_3 to insure the transfer of all flask contents to the beaker. The beaker was placed on a hot plate, covered with a watch glass, and the mixture evaporated to a volume of about five ml. Thirty percent hydrogen peroxide (H_2O_2) was then added (about 20 ml) until the remaining solution was clear. The volume was again reduced by heating and the contents transferred to a 50-ml volumetric flask with 1 N HNO_3. About one ml of 50 percent hydrofluoric acid (HF) was added to the beaker to dissolve any particulate matter remaining after the peroxide treatment. Contents of the volumetric flask were then put into a clean,60-ml polyethelyne bottle.

Metals were determined by flame AAS using the machine setting shown in Table A.2. Metal standards were made from commercially available 1000 mg/l standards or by dissolving reagent grade metal or metal salts in the nitric acid. The acid concentration of all standards was 1 N. Non-atomic absorption was checked on all samples using a hydrogen-continuum lamp separately or with a continuous background corrector (Varian Techtron Model BC-6) that became available in the last year of this research. The available hydrogen lamp had a nickel cathode so that background corrections for nickel analysis was not done.

The efficiency of acid digestion was checked for chromium, copper, iron, manganese, and lead using National Bureau of Standards (NBS) Orchard Leaves Standard Reference Material #1571. The metal values measured in this research and those reported by the NBS appear in Table A.3. A blank was run in conjunction with all NBS and sludge digestions. The blank was D^2H_2O which received nitric acid, peroxide, and hydrofluoric acid additions in the same sequence and quantity as the sample. The upper limits of metal blanks are shown in Table A.4. The metal level of some of the blanks was below the detection limits of flame AAS. Atomic absorption analysis with a carbon rod (Varian Techtron Model 63) was used for the metals with concentrations below flame detection limits.

TABLE A.2

AAS Analysis - Metals and Wavelengths Used(1)

Metal	Wavelength (ηm)
Ag	328.07
Cd	228.80
Cr	357.87
Cu	324.75
Fe	248.33
Mn	279.48
Ni	232.00
Pb	217.00
Zn	213.86

(1) Air-acetylene flame used in all cases.

TABLE A.3

Trace Metal Analysis of NBS Orchard Leaves Standard Reference Material #1571 (1)

Metal	Set 1(2)	Set 2(2)	NBS (3)
Cr	4.3 ± 0.3	5.0 ± 1.0	(2.3)
Cu	13.3 ± 0.2	15.8 ± 1.7	12 ± 1
Fe	311 ± 7	304 ± 4	300 ± 20
Mn	96 ± 2	89 ± 1	91 ± 4
Pb	44 ± 2	41 ± 1	45 ± 3

(1) All values expressed as (mg/g) on a dry weight basis.

(2) Measured values reported as sample mean ± 90% confidence interval determined by t-test.

(3) NBS values reported as mean ± 95% confidence interval or 2 standard deviations, whichever is larger . No NBS uncertainty was reported for Cr.

TABLE A.4

Trace Metal Blanks

Metal	Weight(1)	Metal	Weight(1)
Ag	5.0×10^{-8}	Mn	1.6×10^{-7}
Cd	4.0×10^{-8}	Ni(2)	$<1.2 \times 10^{-6}$
Cr	8.4×10^{-7}	Pb	1.6×10^{-6}
Cu	3.5×10^{-7}	Zn	1.4×10^{-6}
Fe(2)	$<1.2 \times 10^{-5}$		

(1) Expressed as grams metal in a 50-ml blank. All measurements by carbon rod AAS (Varian Techtron Model 63) unless otherwise indicated.

(2) Measured by flame AAS (Varian Techtron Model AA-5).

The recovery for all metals was also checked by running blanks spiked with all nine metals analyzed for this research. These samples were treated as sludge or NBS samples except that the metals were added from nitric acid standards. The results of the spiked blank recoveries are shown in Table A.5.

A.5 Sludge Separation Procedure

In order to analyze for dissolved constituents in the sludge, the solids and the surrounding liquid phase first had to be separated. A combination of filtration and low-speed and high-speed centrifugation was used to accomplish this goal. Sludge samples that passed a 0.5 mm polyethylene mesh were transferred to 500-ml bottles and spun at 2100 rpm for two hours. The top fraction in each bottle (∿ 400 ml) was then placed in 250-ml bottles and spun for one hour at 3000 rpm. The centrate was then filtered successively through 14-μ and 8.0-μ Millipore filters and the filtrate spun in 30 ml bottles for one hour at 20,000 rpm in a Beckman Model L-2 centrifuge (5°C). The centrate was finally filtered through 0.45-μ Millipore filters and stored at 4°C.

A.6 Dissolved Trace Metal Analysis

One hundred ml of the final filtrate from the sludge separation procedure (see Section A.5) were pipetted into a 150-ml beaker, covered with a watch glass, and reduced to a volume of 10 ml over low heat. Five ml of concentrated HNO_3 (GFS grade) were then added and the

TABLE A.5

Metal Recovery from Spiked Blanks

Metal	% Recovered	Metal	% Recovered
Ag	91.3	Mn	100.0
Cd	100.0	Ni	102.5
Cr	107.0	Pb	100.5
Cu	99.0	Zn	99.2
Fe	100.5		

TABLE A.6

Composition of Artificial Seawater

NaCl	gm	23.477
$MgCl_2$		4.981
Na_2SO_4		3.917
$CaCl_2$		1.102
KCl		0.664
$NaHCO_3$		0.192
KBr		0.096
H_3BO_3		0.026
$SrCl_2$		0.024
NaF		0.003

Water to 1 Kg

Source: Riley and Skirrow, ed., 1975.

mixture boiled slowly for one hour. Ten ml of 30 percent hydrogen peroxide were then added, the mixture boiled, and the remaining solution transferred to a 50-ml volumetric flask and brought to volume with 1 N NHO_3. This procedure was run in triplicate on the sludge filtrate. A blank of 100 ml of D^2H_2O was run concurrently. The measured dissolved trace metals in the digested sludge are reported in Table 2.12.

A.7 Trace Metal Analysis by X-ray Fluorescence

Energy dispersive X-ray fluorescence (XRF) is a recently developed technique for simultaneous multiple-element analysis of solid samples. An X-ray beam is impinged upon a sample surface and the characteristic X-rays generated by this process are sensed by a semiconductor detector. The resulting signals are sorted electronically and eventually processed by a computer to yield concentrations per area of sample. The system is calibrated with thin metal foils and has a sensitivity of approximately one ppm. A complete description of XRF theory and operation can be found in Giauque, et al. (1973).

XRF analysis for this research was done by Dan Shadoan at the Crocker Nuclear Laboratory, University of California at Davis. All samples were deposited on 1.0-μ Nuclepore membranes. Typical errors reported for metal analysis were approximately 11 to 20 percent with filter loadings of $\sim$0.1 to $\sim$1.5 mg/cm^2 of total solids. When considering metal data from sludge samples it should be remembered the beam impinges only on a one cm^2 area in the center of a target; the total area of the target is approximately 10 cm^2. The implicit assumption is that the sample is spread uniformly over the surface of the membrane; however, with samples from the mixing experiments (Section 2.5.3) and the first samples from the sedimentation columns (Section 2.5.2) discrete particles were often seen. A 100-μ diameter particle with a density of 1 gm/cm^3 would weigh approximately 0.5 μgm or 500 nanograms. Very few of these particles, if their metal content was large, would radically change the reported metal concentration. Several larger particles, say 400-μ diameter of mineral density (2.65 $grams/cm^3$), would have a significant effect on the total weight capture. The total errors in the XRF then probably exceed the 11 to 20 percent reported on the metal values only; a total error of approximately 30 percent is probably more reasonable.

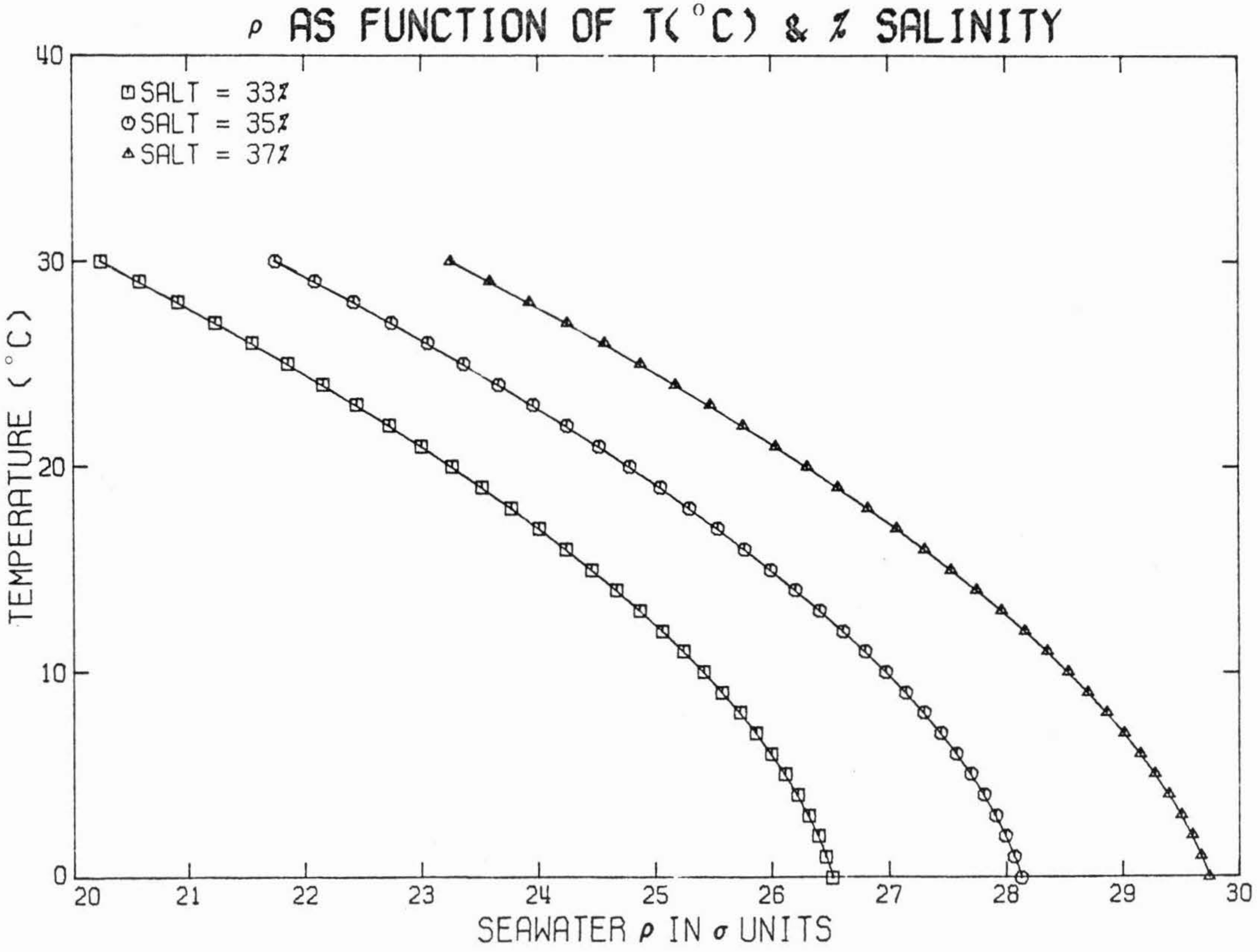


FIGURE A.2
Seawater Density as a Function of Temperature and Salinity

Source: U. S. Navy Hydrographic Office, 1952.

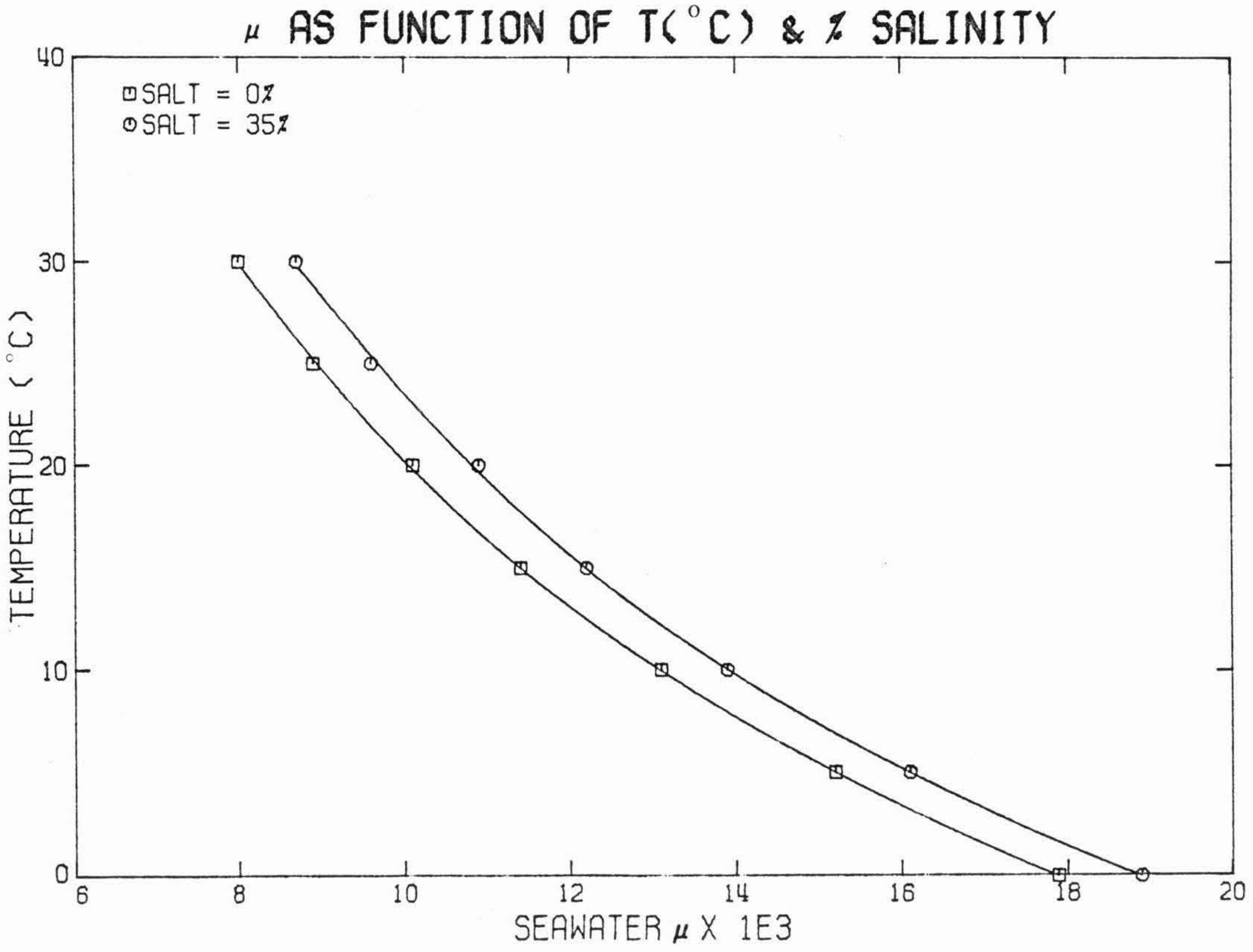


FIGURE A.3
Seawater Viscosity as a Function of Temperature and Salinity

Source: Sverdrup, et al. (1942)

APPENDIX B

CALIBRATION OF THE COULTER COUNTER

B.1 Experimental Conditions

The electronic sizing of the sludge particles was done with a Model B Coulter Counter interfaced with a Nuclear Data Model 555 Pulse Height Analyzer (PHA) and Multichannel Analyzer (MCA). Four apertures, 30μ, 70μ, 140μ, and 280μ, were selected to cover a size spectrum from approximately one to 60 microns. The salt solution for sludge dilutions was 1 M NaCl for the 30-, 70-, and 140-μ apertures and 0.1 M for the 280_{μ}. These solutions of reagent-grade NaCl were prefiltered three times through pairs of 0.22-μ Millipore membrane filters and then once through a 0.1-μ membrane overlaid with a 0.22-μ filter.

B.2 Coulter Counter Calibration

Two types of instrumental calibration were necessary with the Coulter Counter and the associated electronics. First, the log base of the PHA had to be established and related to a known particle diameter; second, the accuracy of the number of counts had to be verified. The log base calibration was done with a voltage pulse generator. This test confirmed both the constancy of the log base over the 128-channel spectrum of the MCA and also gave a numerical value for the log base.

The relationship between voltage pulse, log base, and channel number

$$\log (V_j/V_i) = (C_j - C_i) \log f \qquad (B.1)$$

where V_i and V_j are the voltage pulses necessary to produce a PHA/MCA response in channels C_i and C_j, and f = log base, was assumed to hold. The pulse generator had a maximum output of 20 volts so that the higher channel numbers with large apertures could not be checked. In such cases, linearity and constancy of the log base were assumed to hold over the entire 128-channel scale. It should be noted that although the MCA has 128 channels, the entire channel range could not be used. The lower 20 channels were generally excluded because of electronic noise that appeared there. Ten to 20 channels at the upper end of the spectrum were generally excluded by signal pileup or because the PHA did not fill them.

An alternative calibration technique using several standard particles with known diameters was not applicable because, at the salt concentrations chosen and with the available particles, it was not possible to get the complete spectrum from two different calibration particles on the 128 channel spectrum at one time. For the 5.7 PSL spheres, however, the diameter standard deviation was broad enough to allow for statistical manipulation of the MCA particle counts. These particles had previously been sized optically with a Patterson-graticle-equipped microscope. That sizing showed the particles to be normally distributed with mean diameter of 5.44 microns, very close to the 5.7 micron diameter reported by Dow, the manufacturer.

The diameter of these spheres was also checked with a Hiac Criterion Particle Size Analyzer, Model PC-320, and found to be normally distributed with a mean particle diameter of approximately 5.6 microns. The Hiac operates on a light blockage principal. A particle suspension is forced between a light source and a photodetector cell. Interruptions of the light signal produce voltage pulses which are amplified and sorted according to particle size based on a calibrated scale. The maximum particle area perpendicular to the light source is measured.

The relation between particle diameter and channel number for the Coulter Counter is assumed to be

$$d_j = d_i \, f^{(C_j - C_i)/3} \qquad \text{(B.2)}$$

where, d_i, d_j = diameters of the i, j particle whose signals are sorted into channels C_i and C_j respectively. A probability plot of the Coulter Counter-MCA channel response to the 5.7-μ spheres was then made. (See Figure B.1). Using the standard deviation of 1.5 μ reported for the 5.7-μ spheres, the log base f was calculated and was found to be indistinguishable from that determined with the voltage pulse generator. This result held for both 30-μ and 70-μ apertures.

Number counts of the 5.7-μ spheres were checked by weight concentration, by optical counting with a bright line hemacytometer, and by number counts on known volumes with the Coulter Counter and with the Hiac Particle Analyzer. Dilution of the particle suspensions was necessary for all counting techniques except evaporation and weighing. The particle counts were

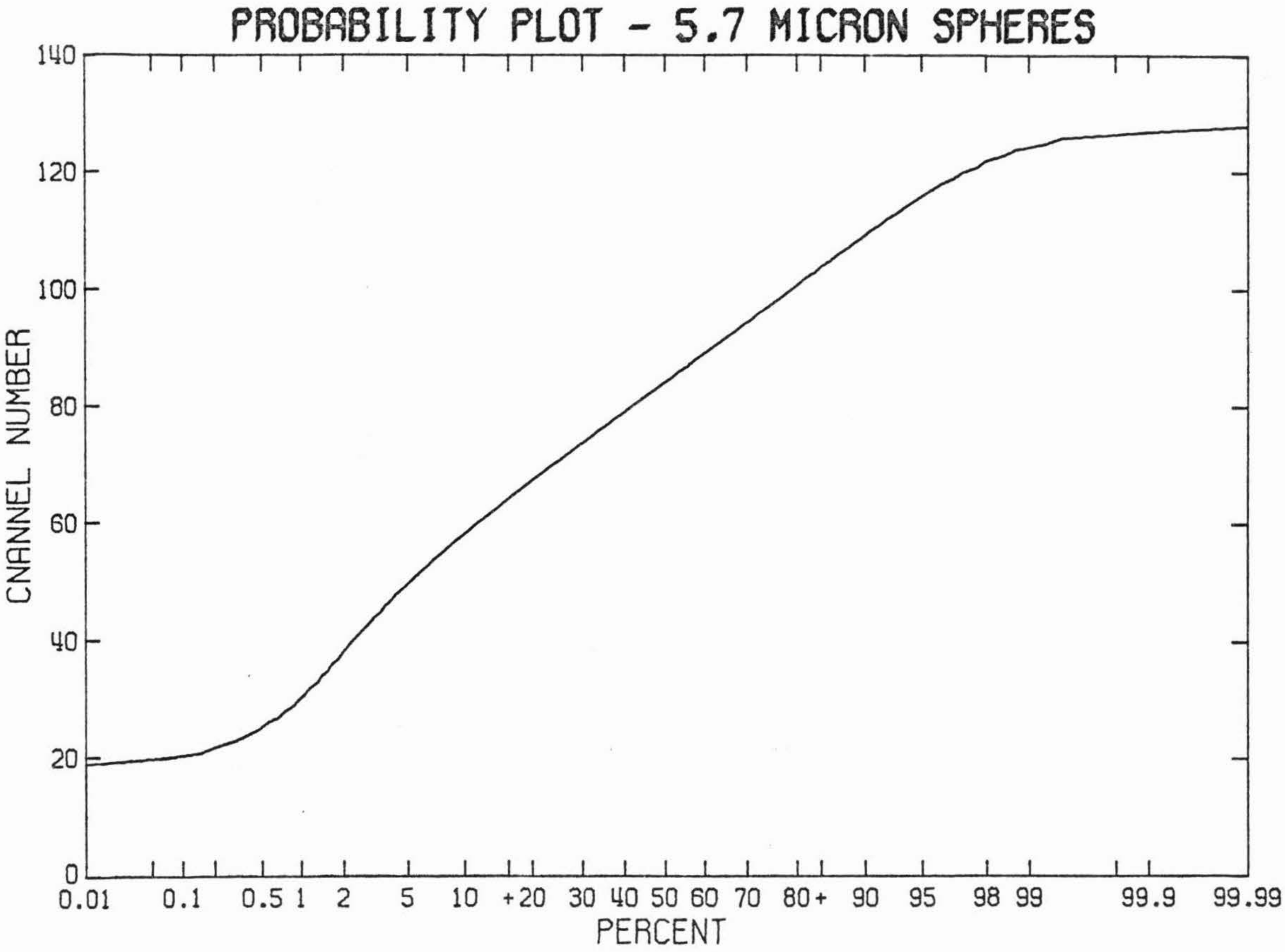


FIGURE B.1
Probability Plot of Coulter Counter Data for 5.7μ PSL Spheres

Coulter Counter - $1.71 \times 10^{10}/l$ (± 3.0%)
Hiac - $1.97 \times 10^{10}/l$ (± 2.6%)
Hemacytometer - $2.05 \times 10^{10}/l$ (± 9.0%)
By evaporation - $2.8 \times 10^{10}/l$ (± 1.0%)

The hemacytometer, Coulter Counter, and Hiac Particle Analyzer data agreed closely. The weight concentration information was high by a factor of 50 percent. The Coulter Counter data was at the low end of the particle count range, probably because the Coulter Counter sizing "window" in the spectrum was small and both larger and smaller particles were excluded. With the Hiac Particle Analyzer these counts appeared in the first and last channels of measurement with proper instrument settings, thus contributing to the total numbers for the spectrum. The hemacytometer values were higher than those found with either electronic means and also show a larger standard deviation. The high counts and the large standard deviation were due to dilution problems, uneven particle distributions in the counting chamber, and counting errors by the analyst. Particle counts by evaporation were calculated from the particles per ml suspension reported by Dow, the particle manufacturer; this result was the highest and probably least credible of the total counts because sample drying measured all particles in solution, regardless of size, and also included any dissolved constituents present.

The calibration information for the Coulter Counter operation with all apertures is summarized in Table B.1. The log base information that appears there was determined with a voltage pulse generator.

TABLE B.1

Coulter Counter Calibration Information

Aperture(1) Diameter	Calibration(2) Particle	Log Bias Setting	Amplification	Current	Log/Base
30	2.02(3)	.06	2	1/8	1.0458
70	5.7 (3)	.50	4	1/8	1.0480
70	9.8 (4)	.50	16	1/8	1.0480
140	9.8 (4)	2.00	4	1/8	1.0514
140	18.1 (4)	2.00	16	1/8	1.0491
280	40.0 (4)	2.00	32	1/8	1.0514

(1) Diameters in microns

(2) Calibration particle diameters in microns

(3) Calibration particles manufactured by Dow Diagnostics

(4) Calibration particles marketed by Duke Standards

REFERENCES

Anderson, D. W. and Hickey, J. J. (1970), "Oological Data on Eggs and Breeding Characteristics of Brown Pelican", Wilson Bulletin, Vol. 82, No. 1.

Anderson, M. S. (1956), "Comparative Analyses of Sewage Sludges", Sewage and Industrial Wastes, Vol. 28, No. 2.

Bargman, R. D. and Garber, W. F. (1972), "The Control and Removal of Materials of Ecological Importance from Wastewaters in Los Angeles, California, U.S.A.", Inter. Ass'n. on Water Pollution Research.

Breck, W. G. (1974), "Redox Levels in the Sea", Chapter 4, The Sea, Vol. 5, ed. by E. D. Goldberg, John Wiley & Sons, New York.

Brooks, N. H. (1960), "Diffusion of Sewage Effluent in an Ocean-Current", Waste Disposal in the Marine Environment, Pergamon Press.

Bruland, K. W., Bertine, K., Koide, M. and Goldberg, E. D., (1974), "History of Metal Pollution in Southern California Coastal Zone", Environmental Science and Technology, Vol. 8, No. 5.

Camp, Dresser, and McKee (1975), Phase 1 Report of Technical Alternatives to Ocean Disposal of Sludge in the New York City-New Jersey Metropolitan Area, prepared for Interstate Sanitation Commission.

CDM Inc., Environmental Engineers, (1972), Sludge Disposal in the Marine Environment, A Report to SCCWRP, Pasadena, California.

Chen, K. Y., Young, C. S., Jan, T. K., and Rohatgi, N., (1974), "Trace Metals in Wastewater Effluents", Jour. Water Poll. Cont. Fed., Vol. 49, No. 12.

Cranston, R. E and Buckley, D. E. (1972), "The Application and Performance of Microfilters in Analyses of Suspended Particulate Matter", Unpublished Manuscript, Bedford Institute of Oceanography, Dartmouth, Nova Scotia, Canada, BI-R-72-7.

Davis, J. A. III, and Jacknow, J. (1975), "Heavy Metals in Wastewaters in Three Urban Areas", Jour. Water Poll. Cont. Fed., Vol. 47, No. 9.

Davis, J. B. (1967), Petroleum Microbiology, Elsevier Publishing Co., New York.

Ditmars, J. D. (1969), Computer Program for Round Buoyant Jets into Stratified Ambient Environments, TM 69-1, W. M. Keck Laboratories, California Institute of Technology, Pasadena, California.

East Bay Municipal Utilities District (1975), Project Report for the East Bay Municipal Utility District Sewage Sludge Management Project, Oakland, California.

REFERENCES (continued)

Emery, K. O. (1954), "Source of Water in Basins Off Southern California", Jour. Marine Research, Vol. 13, No. 1.

Emery, K. O. (1960), The Sea Off Southern California, John Wiley & Sons, Inc., New York.

Finney, C. D., and Evans, R. S., II (1975), "Anaerobic Digestion: The Rate-Limiting Process and the Nature of Inhibition", Science, Vol. 190.

Galloway, J. N. (1972), Man's Alteration of the Natural Geochemical Cycle of Selected Trace Metals, Ph.D. Thesis, University of California at San Diego.

Garber, W. F. and Ohara, G. T., (1972), "Operation and Maintenance Experience in Screening Digested Sludge", Jour. Water Poll. Cont. Fed., Vol. 44, No. 8.

Garber, W. F., Ohara, G. T., Colbaugh, J. E., and Rakit, S. K., (1975), "Thermophilic Digestion at the Hyperion Treatment Plant", Jour. Water Poll. Cont. Fed., Vol. 47, No. 5.

Giauque, R. D., Goulding, F. S., Jaklevic, J. M., and Pehl, P. H., (1973), "Trace Element Determination with Semiconductor Detector X-Ray Spectrometers", Analytical Chemistry, Vol. 45, No. 4.

Goldberg, E. D., ed. (1974), The Sea, Vol. 5, "Marine Chemistry", Wiley-Interscience, New York.

Grigg, R. W. and Kiwala, R. S. (1970), "Some Ecological Effects of Discharged Wastes on Marine Life", California Fish and Game Quart., Vol. 56, pp. 145-155.

Hartman, O. and Barnard, J. L. (1958), "The Benthic Fauna of the Deep Basins Off Southern California", Allan Hancock Pacific Expeditions Vol. 22, No. 1, Univ. of So. Calif. Press, Los Angeles, California.

Hendricks, T. (1976), Personal Communication.

Haven, D. S. and Morales-Alamo, R. (1970), "Filtration of Particles from Suspension by the American Oyster Crassostrea Virginica", Biol. Bull. Vol. 139, p. 248-264.

Hill, M. N., ed. (1963), The Sea, Vol. 2, "The Composition of Sea-Water Comparative and Descriptive Oceanography", Interscience Publishers, New York.

REFERENCES (continued)

Hickey, J. J. and Anderson, D. W. (1968), "Chlorinated Hydrocarbons and Eggshell Change in Raptorial and Fish-Eating Birds", Science, Vol. 162.

James, R. O. and Healy, T. W. (1972a), "Adsorption of Hydrolyzable Metal Ions at the Oxide-Water Interface—I. Co (II) Adsorption on SiO_2 and TiO_2 as Model Systems", J. Colloid-Interface Sci., 40:42.

James, R. O. and Healy, T. W. (1972b), "Adsorption of Hydrolyzable Metal Ions at the Oxide-Water Interface—II. Charge Reversal of SiO_2 and TiO_2 Colloids by Adsorbed Co (II), La (III), and Th (IV) as Model Systems", J. Colloid-Interface Sci. 40:53.

James, R. O. and Healy, T. W. (1972c), "Adsorption of Hydrolyzable Metal Ions at the Oxide-Water Interface—III. A Thermodynamic Model of Adsorption", J. Colloid Interface Sci., 40:65.

Jørgensen, C. B., and Goldberg, E. D. (1953), "Particle Filtration in Some Ascidians and Lamellibranchs", Biol. Bull., Vol. 105, p. 477-489.

Kaplovsky, A. J. (1952), "Volatile Acid Productin of Several Industrial Wastes", Sewage and Industrial Wastes, Vol. 24, No. 2.

Klein, L. A., Lang, M., Nash, N., and Kirschner, S. L., (1974), "Sources of Metals in New York City Wastewater", Jour. Water Poll. Cont. Fed., Vol. 46, No. 12.

Koh, R. C. Y. (1976), Unpublished calculations.

Koh, R. C. Y., and Fan, L. N. (1969), "Further Studies on the Prediction of the Radioactive Debris Distribution Subsequent to a Deep Underwater Nuclear Explosion", Tetra Tech., Inc., Pasadena, California.

Kubitschek, H. E. (1960), "Electronic Measurement of Particle Size", Research (London), Vol. 13, pp. 128-135.

McCarty, P. L. (1964a), "Anaerobic Waste Treatment Fundamentals -- Chemistry and Microbiology", Public Works, Vol. 95, p. 107-112.

McCarty, P. L. (1964b), "Anaerobic Waste Treatment Fundamentals -- Environmental Requirements and Control", Public Works, Vol. 95, p.123-126.

McCarty, P. L. (1964c), "Anaerobic Waste Treatment Fundamentals -- Toxic Materials and Their Control", Public Works, Vol. 95, p. 91-94.

McCarty, P. L. (1964d), "Anaerobic Waste Treatment Fundamentals -- Process Design", Public Works, Vol. 95, p. 95-99.

REFERENCES (continued)

McLaughlin, R. T. (1958), On the Mechanics of Sedimentation in Artificial Basins, Ph.D. Thesis, California Institute of Technology, Pasadena, California.

McLaughlin, R. T. (1959), "The Settling Properties of Suspensions", J. Hydraulics Division, Proc. ASCE, Vol. 85, HY12.

Metcalf and Eddy, Inc., (1972), Wastewater Engineering, McGraw-Hill Book Co., Inc., New York.

Minard, R. D. (1968), Water Quality in Submarine Basins Off Southern California, U.S. Department of the Interior, Federal Water Quality Administration.

Mitchell, F. K. (1974), "Evaluating the Impact of Sludge Discharge to Santa Monica Bay, California", Rutgers/EPA Symposium, New Brunswick, New Jersey, EPA-902/9-74-002.

Mitchell, F. K. and H. A. Schafer (1975), "Effects of Ocean Sludge Disposal", Coastal Water Research Project Annual Report, El Segundo, California.

Morel, F. M. M. and Morgan, J. J. (1972), "A Numerical Method for Computing Equilibria in Aqueous Chemical Systems", Environmental Science and Technology, Vol. 6, No. 1.

Morel, F. M. M., Westall, J. C., O'Melia, C. R., and Morgan, J. J.,(1975), "Fate of Trace Metals in Los Angeles County Wastewater Discharge", Enviornmental Science and Technology, Vol. 9, No. 8.

Morgan, J. J. and Sibley, T. H., (1975), "Chemical Models for Metals in Coastal Environments", ASCE Coastal Engin. Conf., Dover, Delaware.

Mueller, H. F., Buswell, A. M., and Larson, T. E., (1956), "Chromatographic Determination of Volatile Acids", Sewage and Industrial Wastes, Vol. 28, No. 3.

Myers, E. P. (1974), The Concentration and Isotopic Composition of Carbon in Marine Sediments Affected by a Sewage Discharge, Ph.D. Thesis, California Institute of Technology, Pasadena, California.

North, W. J. (1972), "Effects of Wastewaters on Marine Biota", Proceedings of the 13th Coastal Engineering Conference of the ASCE.

Orange County Flood Control District (1974), Unpublished Data.

Page, A. L. (1974),"Fate and Effects of Trace Elements in Sewage Sludge When Applied to Agricultural Lands--A Literature Review Study," EPA-670/2-74-005.

REFERENCES (continued)

Peterson, L. L. (1974), The Propagation of Sunlight and the Size Distribution of Suspended Particles in a Municipally Polluted Ocean Water, Ph.D. Thesis, California Institute of Technology, Pasadena, California.

Revelle, R. and Shepard, F. P. (1939), "Sediments Off the California Coast", Recent Marine Sediments, Amer. Assoc. Petrol. Geologists, Tulsa, p. 245-282.

Riley, J. P. and Skirrow, G., ed., (1975), Chemical Oceanography, Vol. 1 and 2, 2ed., Academic Press, London.

Rittenberg, S. C., Emery, K. O., and Orr, W. L., (1955), "Regeneration of Nutrients in Sediments of Marine Basins", Deep-Sea Research, Vol. 3, pp. 23-45.

Roberts, P. J. W., (1975), The Diffusion of Buoyant Effluent from Outfall Diffusers of Finite Length--Progress Report, Tech. Memo 75-1, W. M. Keck Laboratory, California Institute of Technology, Pasadena, California.

Rohatgi, N. and Chen, K. Y. (1975), "Transport of Trace Metals by Suspended Particulates on Mixing with Seawater", Jour. Water Poll. Cont. Fed., Vol. 47, No. 9.

Rowe, D. R. (1971), "Anaerobic Sludge Digestion, Mesophilic-Thermophilic", Water and Sewage Works, Vol. 118, p. 74-76.

Rudolfs, W. and Balmat, J. L. (1952), "Colloids in Sewage", Sewage and Industrial Wastes, Vol. 24, No. 3.

Sanitation Districts of Los Angeles County (1973), Technical Report--Waste Discharge to the Ocean, Vol. I.

Sheldon, R. W. (1972), "Size Separation of Marine Seston by Membrane and Glass-Fiber Filters", Limnol. Ocean, Vol. 17, p. 494-498.

Sheldon, R. W. and Sutcliffe, R. (1969), "Retention of Marine Particles by Screens and Filters", Limnol. Ocean, Vol. 14, p. 441-444.

Shipp, R. F. and Baker, D. E. (1975), "Pennsylvania's Sewage Sludge Research and Extension Program", Compost Science, March-April, p. 6-8.

Sholkovitz, E. R. and Gieskes, J. M. (1971), "A Physical-Chemical Study of the Flushing of the Santa Barbara Basin", Limno. Ocean. Vol. 16, No. 3.

REFERENCES (continued)

Sholkovitz, E. R. and Soutar, A. (1975), "Changes in the Composition of the Bottom Water of the Santa Barbara Basin: Effect of Turbidity Currents", Deep-Sea Research, Vol. 22, p. 13-21.

Sibley, T. H., and Morgan, J. J. (1975), "Equilibrium Speciation of Trace Metals in Freshwater:Seawater Mixtures", Submitted for publication; Inter. Conf. on Heavy Metals in the Environment, Toronto, Canada.

Southern California Coastal Water Research Project (SCCWRP) (1973), The Ecology of the Southern California Bight: Implications for Water Quality Management, (T.R. 104), El Segundo, California.

Southern California Coastal Water Research Project (1974), Annual Report, El Segundo, California.

Southern California Coastal Water Research Project (1975), Annual Report, El Segundo, California.

Standard Methods, 13th ed. (1971), Prepared and published jointly by: American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, D.C.

Strickland, J. D. H. and Parsons, T. R. (1968), A Practical Handbook of Seawater Analysis, Bulletin 167, Fisheries Research Board of Canada, Ottawa.

Stumm, W. and Morgan, J. J. (1970), Aquatic Chemistry, Wiley-Interscience, New York.

Stumm, W. (1975), "Redox Processes in the Sea", Inter. Union Geology and Geophysics, Grenoble Symposium.

Sverdrup, H. U., Johnson, M. W., and Fleming, R. H., (1942), The Oceans, Prentice-Hall, Inc., Englewood Cliffs, N. J.

Treweek, G. P. (1975), The Flocculation of E. coli with Polyethyleneimine, Ph.D. Thesis, California Institute of Technology, Pasadena, California.

U.S. Environmental Protection Agency and Sanitation Districts of Los Angeles County (1976), Draft Environmental Impact Statement and Environmental Impact Report for the Joint Outfall System Facilities Plan, C-06-1051-010. SCH-740-506-05.

U.S. Navy Hydrographic Office (1952), Tables for Sea Water Density, Publication No. 615.

REFERENCES (continued)

Van Loon, J. C. and Lichwa, J. (1973), "A Study of the Atomic Absorption Determination of Some Important Heavy Metals in Fertilizers and Domestic Sewage Plant Sludge", Environmental Letters, Vol. 4, No. 1.

Van Loon, J. C., Lichwa, J., Ruttan, D. and Kinrade, J., (1973), "The Determination of Heavy Metals in Domestic Sewage Treatment Plant Wastes", Water, Air and Soil Pollution, Vol. 2, p. 473-482.

Vos, J. G., Koeman, J. H., van der Maas, H. L., ten Noever de Brauw, M.C., and de Vos, R. H., (1970), "Identification and Toxilogical Evaluation of Chlorinated Dibenzofuran and Chlorinated Naphthalene in Two Commercial Polychlorinated Byphenyls", Fd. Cosmet. Toxicol. Vol. 8, p. 625-633.

Vuceta, Jasenka (1976), "Adsorption of Pb (II) and Ca (II) on x-Quartz from Aqueous Solutions: Influence of pH Ionic Strength, and Complexing Ligands", Ph.D. Thesis, California Institute of Technology, Pasadena, California.

Wachtel, R. E. and LaMer V. K. (1962), "The Preparation and Size Distribution of Some Monodisperse Emulsions", J. of Colloid Science, Vol. 17, p. 531-564.

Wada, F. F. (1976), Personal Communication.