THE CONCENTRATION AND ISOTOPIC COMPOSITION OF CARBON IN MARINE SEDIMENTS AFFECTED BY A SEWAGE DISCHARGE

Thesis by

Edward Payson Myers

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ABSTRACT

The impact of the discharge of primary treated effluent of a high suspended solids concentration on the sedimentary environment of the Palos Verdes Shelf was investigated. Analyses of the carbon content and the isotopic composition of sedimentary organic material with depth in the sediments and the areal distribution of these properties relative to the location of the Los Angeles County Sanitation Districts' ocean outfalls indicate that the outfalls are extremely important in determining the chemical and physical properties of sediments on the Palos Verdes Shelf. The analyses of various sedimentary cores specifically indicate that sludge-like matter has accumulated to depths of as great as twenty centimeters during the past 38 years.

Calculation of the accumulation rates of organic carbon suggests that the present outfall-induced sedimentation rate for organic carbon in the immediate vicinity of the discharge is as much as about 260 times that of the natural sedimentation of organic carbon for the Palos Verdes Shelf. One result of this rapid input of organic carbon is the occurrence of a relatively large area of surface anaerobic sediments. The relationship between the mass accumulation rates of organic carbon and the areal extent of surface anaerobic conditions is further discussed as related to the suspended solids concentration of discharged effluent.

The uppermost outfall-influenced sediments are shown to be of high water content and to have a total organic carbon concentration as high as 12 percent which has a δC^{13} value of about -24.5o/oo. Particulate organic carbon discharged from the outfall has narrow-ranged δC^{13} values of about -23.5 o/oo, thus indicating that the sedimentary carbon has incurred a diagenetic change resulting in the preferential decay of a higher δC^{13} fraction, or that there has been a preferential deposition near the outfall of particulates with a more negative δC^{13} value. Other possibilities are also discussed.

The lower pre-outfall natural sediments on the Palos Verdes Shelf have organic carbon concentrations of about one percent. The δC^{13} values for these natural sediments are about -22.5 to -23.0o/oo which is typical of other data reported in the literature for sediments of marine basins offshore of southern California.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF FIGURES (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

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I. INTRODUCTORY MATERIAL AND PERTINENT LITERATURE REVIEW

I-1 Introduction

The relationship between man and the oceans and fresh waters of the world has been accentuated by the threatening exponential rise in human population. Ketchum (1972) notes that more than fifty per cent of the United States' population lives in the counties bordering the Great Lakes and the oceans, and that the percentage is increasing. By the year 2000, an estimated 200 million people may live in the coastal zones of the United States. The increase in human density, with the corresponding increased demand upon resources associated with such areas, pose a threat to both the recreational and living resources provided by the nearby waters. A proper and rational concern is needed for taking the correct measures to preserve these resources for present and future generations of the world.

One such action is the "Water Quality Control Plan for Ocean Waters of California" (California, State of; 1972), which was adopted and became effective July 6, 1972. This plan has the objective of enhancing and preserving the quality of its coastal waters by setting limits on various pertinent water quality parameters relating to both discharged wastewaters and receiving waters. These include limits on bacteriological, physical, chemical, biological, toxicological, and radioactive characteristics.

This action was prompted by concern over the large flow of municipal and industrial wastes discharged to the marine waters of Southern California. The Southern California Coastal Water Research

Project (SCCWRP, 1973) reports the following such discharges to these waters:

Source	Approximate Flow (1972)
treated municipal wastewaters	1,000 MGD (million gallons/day)
discrete industrial wastes	180 MGD
returned cooling waters	5,600 MGD

Four discrete treatment plants are responsible for about 93 per cent of the above noted municipal wastewater flow. These are

(1) The Joint Water Pollution Control Plant (JWPCP) of the Los Angeles County Sanitation Districts (LACSD) which discharges approximately 371 MGD of primary treated wastewater to the waters offshore of Palos Verdes;

(2) The Hyperion Sewage Treatment Plant operated by the City of Los Angeles, which discharges approximately 235 MGD of primary treated and 100 MGD of secondary treated wastewater through a 5-mile outfall in Santa Monica Bay, and approximately 5 MGD of sewage sludge through a separate 7-mile sludge outfall in Santa Monica Bay;

(3) The Orange County Sanitation Districts treatment plant which discharges approximately 120 MGD of primary treated and 10 MGD of secondary treated wastewater from a location offshore of the Santa Ana River;

(4) and the Point Loma Sewage Treatment Plant, which discharges about 90 MGD of primary treated wastewaters to the waters offshore of Point Loma in San Diego.

The location of points of discharge for these four plants is shown in

Figure I-1.

The research described in this thesis deals with the discharge of municipal wastes to the waters offshore of the Palos Verdes coastal area. It is therefore relevant to elaborate on the general characteristics of this particular waste. The characteristics of the other wastewaters are discussed by both SCCWRP (1973) and CDM, Inc. (1972).

The chemical and physical characteristics of the LACSD discharge from Whites Point are shown in Table I-1. Due to the high industrial contribution to this waste and the return of digested sludge centrate to its final effluent (Figure III-1), the JWPCP final effluent has the highest concentration of almost all commonly monitored contaminants when compared to the other major discharges (SCCWRP, 1973). Of particular interest to this thesis is the concentration of total suspended solids in the final effluent, which is about 300 milligrams per liter. For a flow of about 360 MGD (Table I-1), this concentration therefore represents a yearly flux of suspended solids to the marine environment of approximately $1.5(10^8)$ kilograms. The settling velocities of these particulates (Figure III-4) are such that a certain fraction of these particles is estimated to settle in the local area (Hendricks, 1973) and form accumulations which cause important ecological disturbances.

In 1969, Grigg and Kiwala (1970) reported such ecological changes in the benthos offshore of Whites Point to cover about six miles of the local coastline. Their study indicated a decrease in the number of benthic species to occur in a high sludge environment

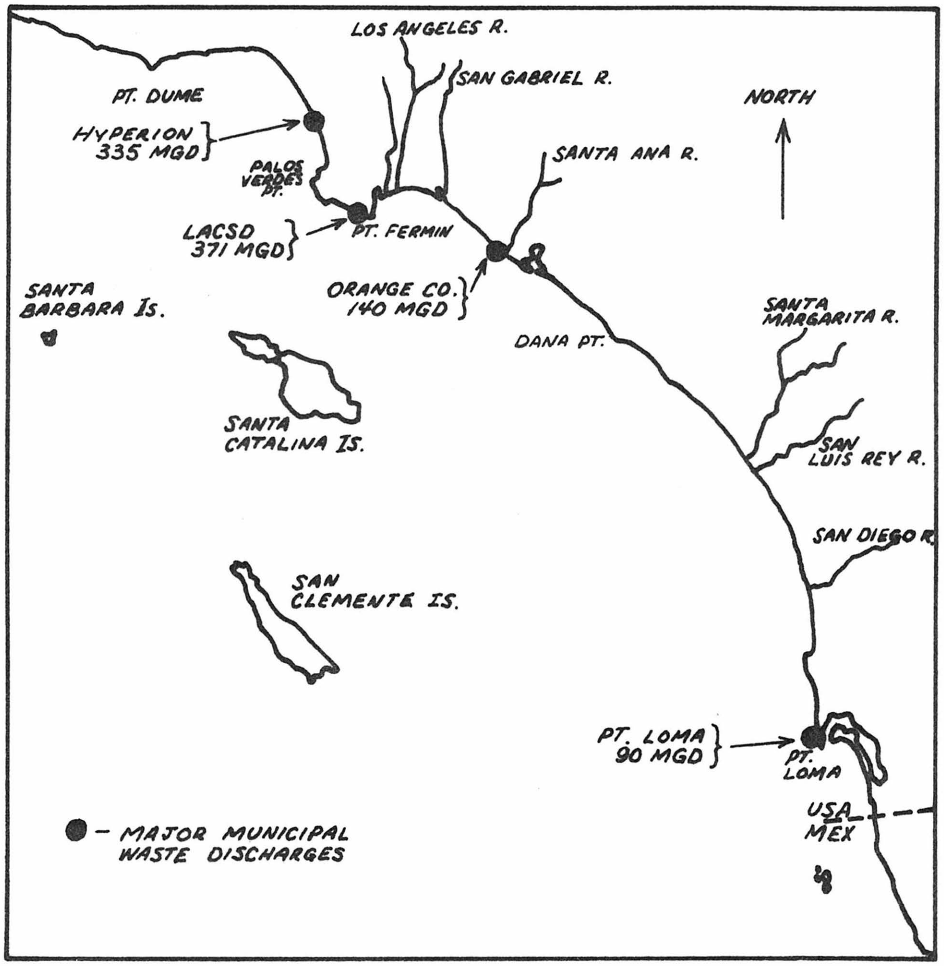

Figure I-1. The locations of major municipal waste discharges to the marine waters of southern California.

Table I-1. Final Effluent Quality for the Joint Water Pollution Control Plant Operated by Los Angeles County Sanitation Districts (data for October 1971 - September 1972).

Parameter	Units	Number of Analyses	Lowest Value	Mean Value	Highest Value
Flow(1)	MGD	366	257	357	439
Grease & Oil	mg/l	154	37.8	70.5	166
Floating Part(2)	mg/l	25	.10	.63	2.1
Susp. Solids	mg/l	359	97	293	634
Sett. Solids	ml.l	360	.5	3.1	9.0
Turbidity	JTU	359	38	72	100
pH	-	360	7.00	7.61	8.65
Arsenic	mg/l	12	<.01	<.01	.03
Cadmium	mg/l	12	.011	.021	.031
Total Chromium	mg/l	12	.61	.79	1.04
Copper	mg/l	12	.31	.57	.94
Lead	mg/l	7	.19	.28	.36
Mercury	mg/l	12	.0005	.0010	.0019
Nickel	mg/l	12	.15	.27	.51
Silver	mg/l	12	.010	.016	.022
Zinc	mg/l	12	1.43	2.02	3.02
Cyanide	mg/l	12	<.01	.21	.57
Phenolic cmpds.	mg/l	12	.30	2.43	4.65
Ammonia nitrogen	mg/l	12	31.9	53.0	108
TICH	mg/l	12	.0066	.0182	.0328
Toxicity	TU	5	1.70	2.11	2.70
Radioactivity	pCi/l	39	9.0	60.3	379

Table I-1. Final Effluent Quality for the Joint Water Pollution Control Plant Operated by Los Angeles County Sanitation Districts (data for October 1971 - September 1972).(Continued)

Parameter	Units	Number of Analyses	Lowest Value	Mean Value	Highest Value
Temperature	^{o}C	728	21.6	27.2	31.4
BOD_5	mg/l	359	113	269	1060.
Total Phosphate	mg/l	12	47.0	53.9	68.0
Total Nitrogen	mg/l	12	47.0	75.7	134.0

NOTES: (1) Average daily flow including days with rain.
(2) Floating particulate data collected during November, 1972.

when compared to a low sludge environment. Similar ecological changes had been reported by Limbaugh (1954) to cover a distance of only two miles, indicating an increase in the extent of ecological disturbances with time.

North (1964) has been studying factors causing the disappearance of the giant kelp Macrocystis pyrifera from the local Palos Verdes coastline. He strongly suspects the intermittent accumulation of outfall solids on rocky substrates in shallow waters to be one of the factors that interfere with the healthful propagation of this kelp species.

Due to the high industrial input to the JWPCP waste, the discharged effluent (Table I-1) is seen to have high concentrations of trace metals. Galloway (1972) investigated the accumulation of certain trace metals in the sediments surrounding the four major outfalls. The sediments surrounding the LACSD's discharge at Whites Point were shown to contain the highest concentration of these contaminants. Trace metal concentrations many times those of background for zinc, copper, lead, cadmium, and chromium gave elliptical contours which centered on an area slightly northwest of the Whites Point discharge. Based on trace metal concentrations in sedimentary cores, Galloway estimated a sedimentation rate near the point of discharge of approximately 0.22 $gr/cm^2/yr$ (0.72 cm/yr) as compared to a "natural" sedimentation rate reported by Emery (1960) of approximately 0.009 $gr/cm^2/yr$. In addition, Galloway reported that most of these trace metals are in the particulate state and not in solution.

A much more lengthy and detailed summary of investigations into the biological, chemical, and physical properties of these sediments is given in reports by SCCWRP (1973) and the LACSD (1973). From these reports it can be concluded quite confidently that the near-outfall benthos is markedly disturbed with respect to these properties.

This thesis will present the data, analysis, and conclusions on the fate of particulate matter discharged from the Whites Point outfall system, based on its carbon content. This approach is based upon an intensive investigation of organic and inorganic carbon associated with particulate sedimentary matter, and includes measurements of the percentage of total organic carbon and its respective carbon isotopic content (C^{13}/C^{12} ratio) in the local sediments.

The investigation of a new independent variable related to such a complex problem as the effect of effluent on the ocean sediments is desirable. However, the C^{13}/C^{12} ratio and carbon concentration of the sediments (both organic and inorganic) and of particulate matter in the ocean waters is also of particular relevance to the very important carbon cycle in the oceans.

I-2 Terminology

This thesis will present a large number of carbon isotopic data on sedimentary organic and carbonate carbon associated with the San Pedro Shelf sediments in the vicinity of Whites Point. The carbon isotopic measurements were determined on a double-collecting sixty-degree deflection mass spectrometer of the Nier (1947) type with the modifications of McKinney, et al. (1950). Basically, this instrument measures the ratio of C^{13}/C^{12} in a sample (R_s), which is introduced to the mass spectrometer in the form of gaseous carbon dioxide, to the C^{13}/C^{12} ratio of a standard CO_2 (R_o). The desired R is therefore the ratio of the abundance of ions of mass 45 ($C^{13}O^{16}O^{16}$) to the abundance of ions of mass 44 ($C^{12}O^{16}O^{16}$). However, R, as measured on the mass spectrometer, is actually the ratio of ($C^{13}O^{16}O^{16}$ + $C^{12}O^{16}O^{17}$) to $C^{12}O^{16}O^{16}$. Therefore, a correction factor must be applied to account for the abundance of O^{17}. This correction factor, and a correction factor which accounts for machine background and mixing of sample and standard gases, was applied to all isotopic data to be presented. A detailed account of these correction factors and their application to measured isotopic data is provided by Craig (1957) and Deines (1970).

Isotopic data of this type are typically reported as δ-values, where

$$\delta\,(o/oo) = \frac{(R_s - R_o)\,1000}{R_o} = \left(\frac{R_s}{R_o} - 1\right)1000 \quad . \qquad (1.1)$$

Therefore, carbon samples depleted in carbon of mass 13 relative to the standard will have negative δ-values, and samples enriched in carbon-13 will have positive δ-values. As an example, a sample with a $\delta\ (C^{13}/C^{12}) = -20.0$ o/oo indicates that the sample is depleted in C^{13} relative to the standard, such that the C^{13}/C^{12} ratio differs by 20 o/oo, or 2 per cent. Such mass spectrometric measurements are reproducible to ± 0.1 o/oo (±0.01 per cent). All isotopic data in this thesis are reported relative to the standard (R_o) of CO_2 prepared from a Cretaceous belemnite, Belemnitella americana, from the Peedee formation of South Carolina. This is the common reference used in most isotopic work of this kind.

I-3 Theoretical Considerations in Isotope Effects

Differences exhibited by isotopic molecules between coexisting phases are primarily due to either:

(1) kinetic differences between isotopic molecules resulting in differences in such properties as diffusional rates, or

(2) purely chemical differences due primarily to differences in the vibrational frequencies of isotopic molecules.

Urey (1947) points out that the isotopic species of hydrogen differ in many ways, including heats of fusion, vaporization, molar volumes, and heats of solution.

Differences in the kinetic energy of isotopic molecules result in different diffusional velocities and rates of vaporization. Graham's law predicts the ratio of the diffusional fluxes of two molecular species to be inversely proportional to the square root of the ratios of the masses. For example, for $C^{12}O_2$ and $C^{13}O_2$, the ratio of diffusional fluxes would be predicted by

$$\frac{D_{44}}{D_{45}} = \left(\frac{45}{44}\right)^{\frac{1}{2}} = 1.011 \quad .$$

Wahl and Urey (1935) showed that the vapor pressures of the isotopic species of water varied such that at a temperature of 23°C the vapor pressures of the species H_2O^{16}, D_2O^{16}, HDO^{16}, and H_2O^{18} were 21.0, 18.25, 19.51, and 20.82 mm Hg, respectively.

It is not in the domain of this thesis to delve deeply into the rigorous theoretical considerations, which are based upon statistical mechanics, relating to the chemical equilibrium properties of isotopic exchange reactions. A comprehensive account of the formulations is given by Urey (1947). It is pertinent, however, to briefly mention some of the basic considerations.

A typical exchange reaction expressing the distribution of two isotopic species between two coexisting phases is represented by the isotopic exchange of gaseous carbon dioxide with aqueous bicarbonate:

$$C^{13}O_2\ (\text{gas}) + HC^{12}O_3^-\ (\text{aq.}) \rightleftharpoons C^{12}O_2\ (\text{gas}) + HC^{13}O_3^-\ (\text{aq.})\ . \tag{1.2}$$

Such a reaction can be generalized as

$$aA_1 + bB_2 \rightleftharpoons aA_2 + bB_1\ , \tag{1.3}$$

where A and B are different molecules, both of which contain a common element existing in the light isotopic form (denoted by subscript 1) and the heavy isotopic form (subscript 2).

A fractionation factor, α, between two molecular species A and B is defined for the case of carbon as:

$$\alpha = \frac{(C^{13}/C^{12})A}{(C^{13}/C^{12})B}\ . \tag{1.4}$$

The fractionation factor is directly related to the thermodynamic equilibrium constant K which, for reaction (1.2), is given by

$$K = \frac{[C^{12}O_2(g)]\,[HC^{13}O_3^-(aq)]}{[C^{13}O_2(g)]\,[HC^{12}O_3^-(aq)]}\ , \tag{1.5}$$

where the brackets denote molar concentrations. For this reaction it is seen that $\alpha = K$. In general, for an isotopic equilibrium reaction such as (1.3), the fractionation factor is related to the equilibrium constant by the following expression:

$$\alpha = K^{\frac{1}{ab}} . \tag{1.6}$$

The equilibrium constant K for an isotopic exchange reaction can furthermore be calculated from the ratios of the statistical mechanic partition functions which, for the representative reaction (1. 3) is shown (Urey, 1947) to be equal to

$$K = \frac{(Q_{A2}/Q_{A1})^a}{(Q_{B2}/Q_{B1})^b} , \tag{1.7}$$

where Q_{ij} = statistical mechanical partition function for species ij. At ordinary temperatures and above, it is further shown that

$$\frac{Q_{i2}}{Q_{i1}} = \frac{\sigma_1}{\sigma_2} \frac{u_2}{u_1} \frac{e^{-u_2/2}}{1-e^{-u_2}} \frac{1-e^{-u_1}}{e^{-u_1/2}} \text{ for a diatomic molecule} \tag{1.8a}$$

$$\frac{Q_{i2}}{Q_{i1}} = \frac{\sigma_1}{\sigma_2} \prod_j \frac{u_{2i}}{u_{1j}} \frac{e^{-u_{2j}/2}}{1-e^{-u_{2j}}} \frac{1-e^{-u_{1j}}}{e^{-u_{1j}/2}} \text{ for polyatomic molecules} \tag{1.8b}$$

The parameters σ_1 and σ_2 are the symmetry numbers of the two molecules, which are identical for this type of isotopic exchange, and

$$u_j = \frac{h\nu_j}{kT} , \tag{1.9}$$

where ν_j denote the various vibrational frequencies of a polyatomic molecule, h equals Planck's constant, and k equals Boltzmann's constant. Therefore, it is seen that the equilibrium constants for isotopic exchange reactions are dependent upon the vibrational frequency shifts produced upon isotopic substitution and can be calculated solely from a knowledge of the fundamental frequencies of the isotopic species (Urey, 1947). It is further shown by Urey that for small u's (i.e., either low frequencies or high temperature), the ratio of the Q's approaches unity, and therefore differences in chemical properties will cease.

An example of the effect of isotopic mass differences on the vibrational frequency and partition functions of molecular species is provided by data from Urey (1947) on the diatomic molecules, H_2, D_2 and $C^{12}O^{16}$, $C^{13}O^{16}$ which are as follows.

Table I-2. Vibrational Frequencies and Partition Functions for the Molecules H_2, D_2 and $C^{12}O^{16}$, $C^{13}O^{16}$ (from Urey, 1947).

Molecule	Vibrational Frequency
H_2	4405.3 sec^{-1}
D_2	3118.8
$C^{12}O^{16}$	2167.4
$C^{13}O^{16}$	2119.2

	Ratio of Partition Function at a Temperature of				
Molecular Pair	273.1°K	298.1°K	400°K	500°K	600°K
$(D_2/H_2)^{\frac{1}{2}}$	4.2803	3.7346	2.5570	2.0462	1.7650
$(C^{13}O/C^{12}O)$	1.1086	1.0970	1.0659	1.0479	1.0360

These data also show the increase in isotopic effects for elements of smaller mass as well as the decrease in isotopic differences with increasing temperature.

The effects of isotopic substitution on chemical reaction rates is discussed by Bigeleisen (1949) and a comprehensive review is given by Melander (1960). In general, molecular species containing the lighter isotope will react slightly more quickly as compared to the heavier molecular species. This is primarily due to the fact that the zero point energy of the lighter species is greater (due to a greater vibration frequency for the smaller mass) than that for the heavier species, and therefore, there is a smaller free energy barrier to overcome for the reacting light species.

I-4. Carbon Isotopic Variations in Nature -- a Review of the Pertinent Literature

To provide a better understanding of the work to be presented in this thesis, it is important to discuss the carbon isotopic variations found in nature and some of the processes involved.

Utilizing a mass spectrometer of relatively high sensitivity, Nier and Gulbransen (1939) made the first measurements of the relative abundances of the two stable isotopes of carbon in various natural carbon reservoirs. Their basic findings showed the heavy isotope to be generally more abundant in limestones and the lighter isotope more abundant in plant forms. Wickman (1952) extended this work by determining the C^{13}/C^{12} ratios of 105 plants, representing all the major systematic groups. Although Wickman found no major systematic differences between the various plant forms, his work did show differences to occur between some of the major biotypes. Of particular interest to this thesis, Wickman's data revealed a distinct difference between marine plants and terrestrial plants, with marine plants being more enriched in C^{13}.

Craig (1953) performed a most extensive investigation into the isotopic variation of a wide variety of both inorganic and organic carbon forms using the mass spectrometer of the Chicago group (McKinney, et al., 1950). Craig's data showed that, in general, oxidized carbon compounds tend to be more enriched in C^{13} and reduced carbon compounds more depleted in C^{13}. An enrichment of C^{13} in marine plants and invertebrates of some 5 to 18 o/oo relative to terrestrial organic material was also quite evident. Craig (1954) was of the opinion that this consistent difference between marine and terrestrial organic carbon was primarily due to the partial or total utilization of dissolved CO_2 derived from adjusting bicarbonate equilibria when local dissolved CO_2 is diminished.

Park and Epstein (1960) experimentally determined what is undoubtedly the most important fractionation associated with biological systems and which results in the major difference between the isotopic composition of organic and inorganic forms of carbon. This is the photosynthetic fixation of carbon (in the form of dissolved CO_2 within the plant) via the carboxylation of ribulose-1, 5 diphosphate to yield two 3-phosphoglyceric acid molecules, the reaction being enzyme catalyzed. The fractionation factor associated with this step was experimentally determined to be about 1.017, i.e., an approximate 17 o/oo depletion of C^{13} fixed within the plant.

Degens (1969) presents a comprehensive review, based on more than 5000 isotopic data primarily from the existing literature, of the carbon isotopic variations in nature. Based on these data, he constructs a schematic of the natural carbon cycle with included isotopic ranges (Figure I-2). The following reservoirs and their respective average isotopic compositions are worthy of special notice.

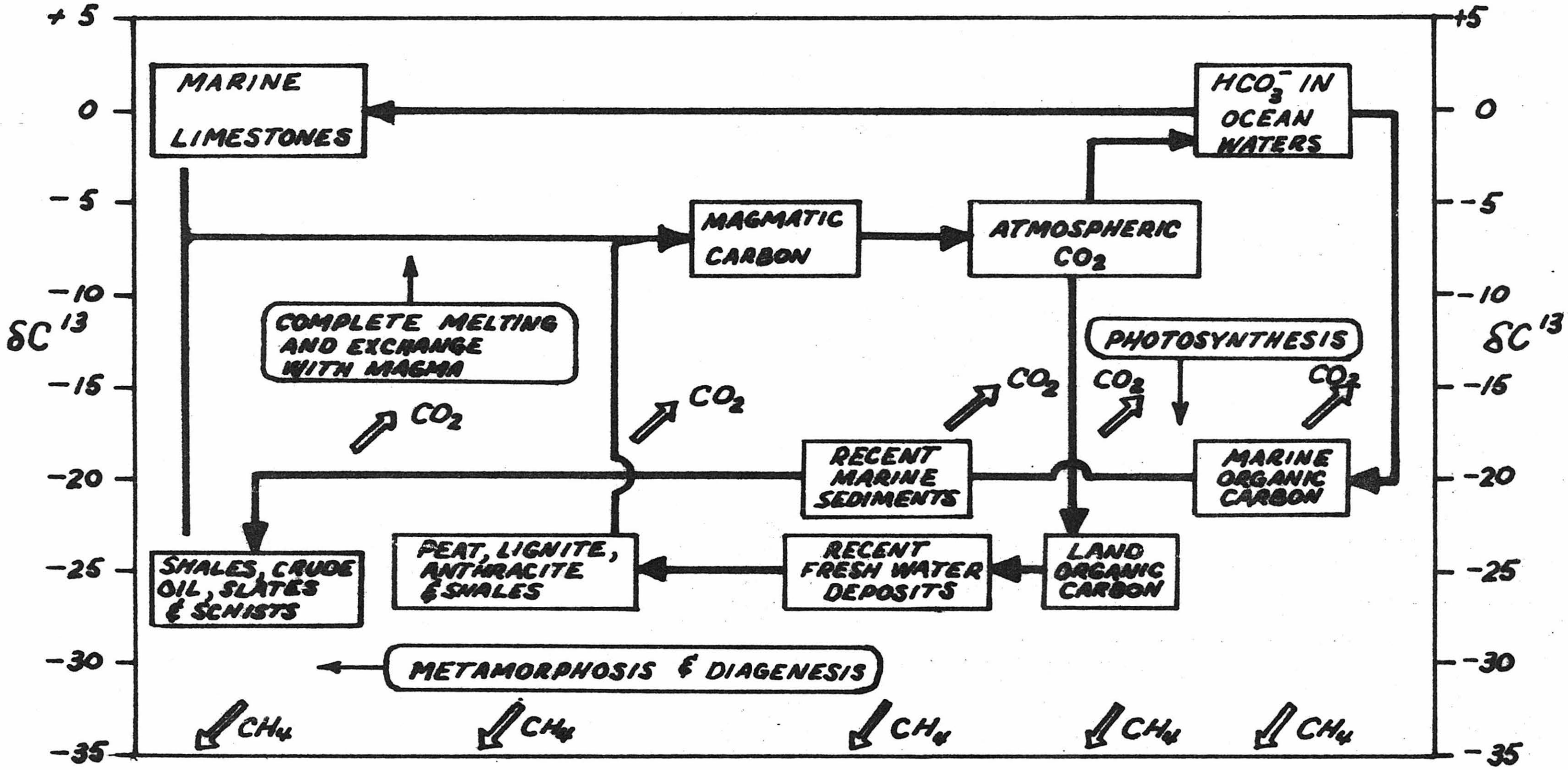

Figure I-2 . The carbon isotopic cycle in nature (from Degens, 1969).

Table I-3. Typical δC^{13} Values of Some Major Carbon Reservoirs.

Carbon Reservoir	Approximate $\delta(C^{13}/C^{12})$
Marine Limestones	0 o/oo
Bicarbonate in Sea Water	0
Atmospheric CO_2	-7
Marine Organic Carbon	-20
Recent Marine Sediments	-20
Land Organic Carbon	-25
Recent Fresh Water Deposits	-25

In regard to these data, it is quite evident that the organic carbon of recent fresh water and marine sediments have an isotopic composition which reflects their source material.

Since this thesis is involved with the marine system, it is especially important to discuss the variations in the isotopic composition of marine carbon sources. However, since such sources are intimately linked with the detailed carbon cycle of nature, it is also important to briefly discuss some of the other major reservoirs of Figure II-2 in order to impart an overall understanding.

I-4a. Atmospheric Carbon Dioxide. Based on a number of analyses of Chicago air, Craig (1953) accepted a tentative value of -7 o/oo for the carbon isotopic composition of uncontaminated atmospheric CO_2. More recently, Friedman and Irsa (1967) showed that an even greater depletion of C^{13} can result from the combustion of C^{13}-depleted petroleum products (Silverman and Epstein, 1958). Friedman and Irsa showed such a shift to occur in New York City, and this is undoubtedly a possibility in other highly industrialized metropolitan areas.

Keeling (1961) investigated a variety of rural air samples in different locations and observed a range in isotopic composition of approximately -7 o/oo to -11 o/oo, and a corresponding concentration of CO_2 of 0.031 to 0.040 volume per cent. Keeling explained the variation and correlation by assuming an initial concentration for atmospheric CO_2 of 0.031 volume per cent with an isotopic composition of -7 o/oo to which is added carbon dioxide due to plant respiration with an isotopic composition of about -23 o/oo.

Since coals and limestones of all geologic ages show a relatively constant isotopic composition, Park and Epstein (1960) reason that the δC^{13} ratio of atmospheric CO_2 has probably remained constant over geologic time.

I-4b. The Dissolved CO_2 and Bicarbonate-Carbonate System. In a series of controlled laboratory experiments, Degens, et al. (1968a) studied the fractionation of carbon associated with atmospheric CO_2 in isotopic, and therefore chemical, equilibrium with aqueous bicarbonate. The fractionation was shown to be temperature dependent with an enrichment of C^{13} in bicarbonate of 9.2 ± 0.4 o/oo at $0^\circ C$ to 6.8 ± 0.4 o/oo at $25^\circ C$. Thode, et al. (1965) further demonstrated that this fractionation is dependent upon added metal ions and the pH of the equilibrium mixture. The above fractionation between gaseous CO_2 and aqueous HCO_3^- was seen to increase upon the addition of magnesium ions, whereas increasing the pH in the range of 7 - 11 resulted in a further depletion of C^{13} in the gas phase.

Epstein (1968) reports that there is little fractionation between bicarbonate and carbonate, perhaps 1 or 2 o/oo.

Based on a study of the carbon isotopic composition of dissolved inorganic carbon at six stations in the North and South Atlantic oceans, Deuser and Hunt (1969) concluded that a value of about +0.5 o/oo is probably characteristic of inorganic carbon of the deep sea.

I-4c. Precipitated Carbonates. In general, isotopic data on precipitated carbonates reflect the isotopic composition of the bicarbonate ions in the waters from which they were precipitated. Keith and Parker (1965) investigated the carbon and oxygen isotopic composition of mollusk shells in a marginal marine environment. Samples were taken to reflect the changing environmental conditions as progression is made from terrestrial-influenced waters (Mobile Bay, Alabama) to open marine waters (Gulf of Mexico). A summary of their carbon isotopic data is shown in Table I-4 and clearly reflects an increase in δC^{13} values as progression is made toward the open marine environment, thus indicating a decreasing accessibility of continental carbon.

Epstein and Lowenstam (1953) give a variety of carbon and oxygen isotope data for the carbonate shell material of Recent and Interglacial Pleistocene shoal-water biota (primarily mollusks) in Bermuda. The carbon isotopic data show a very narrow range of -0.7 o/oo to -2.7 o/oo for seventy-seven samples.

Carbonates precipitated and/or altered during diagenetic (i.e., post-depositional) conditions have been shown to deviate widely from the δC^{13} range reported for carbonates precipitated in open waters [Clayton and Degens (1959), Hathaway and Degens (1968), Hodgson (1966), Murata, et al. (1967), Nissenbaum, et al. (1972), Presley and Kaplan (1968), Thode, et al. (1954)]. Thode, et al. (1954) utilized sulfur and carbon isotopic data to investigate the origin of sulfur in sulfur well cores and adjacent formations in the Texas and Louisiana salt domes. Both the free sulfur and the carbon of co-existing calcite were found to be depleted in their respective heavier isotope (i. e., S^{34} and C^{13}), supporting their conclusion that the large sulfur deposits of the southwestern United States were formed by sulfate-reducing bacteria. The calcite in these sulfur well cores was shown to be depleted in C^{13} by some 33 to 55 o/oo when compared to standard limestone. The authors concluded that this calcite was

Table I-4. Summary of Carbon Isotopic Data for Mollusk Shells Collected from a Marginal Marine Environment (from Keith and Parker, 1965).

Environment	Mean δC^{13}	Approximate Mean Salinity (o/oo)
Estuary	-6.51	8
Delta	-3.62	14
Sound (Mississippi)	-3.19	18
Marginal Bays	-1.03	-
Aransas	-1.26	34
Laguna Madre	-1.14	47
Copano and St. Charles	-0.70	34
Littoral Zone (open gulf)	-0.53	36
Shelf Area (open gulf)	+0.53	36

formed by the precipitation of CO_2 derived from the oxidation of organic material during the reduction of sulfate to free sulfur. It was felt that the lack of uniformity of the carbon isotopic composition of calcite from different cores further indicated a localized production of calcite.

Presley and Kaplan (1968) report such processes to be taking place in Recent sediments in basins offshore of southern California. Their data on a core from the San Pedro Basin and one from the Santa Catalina Basin showed that as the sulfate concentration became depleted with core depth there was a corresponding increase in the concentration of total dissolved CO_2 carbon with a corresponding decrease in its δC^{13} value, thus indicating a microbiological production of this carbon from the oxidation of organic material. Their work and data are further discussed in Chapter IV.

The effect of the anaerobic microbiological oxidation of organic material on the δC^{13} value of newly-formed dissolved inorganic carbon is, however, not a simple matter. This is indicated by the data of Nissenbaum, et al. (1972). They reported data (Table I-5) for both the sediment and the interstitial water from four cores taken from a reducing fjord (Saanich Inlet, British Columbia). Chemical data reported on these cores (Brown, et al, 1972) showed core 1 to represent the most oxidizing situation and core 4 the most reducing. Furthermore, a decrease of sulfate with core depth for all of these cores and a corresponding increase of dissolved organic matter and total dissolved CO_2 carbon within the interstitial water indicated all cores to be undergoing diagenesis. However, in this

Table I-5. Carbon Content and δC^{13} of Sediment and Interstitial Water in Four Cores from Saanich Inlet, British Columbia (taken from Nissenbaum, et al.,1972).

Core and Depth (cm)	$CaCO_3$		Organic C		I.W.* mg/l	Organic C δC^{13} o/oo	Total I.W.* mg/l	CO_2 δC^{13} o/oo
	%	δC^{13} o/oo	%	δC^{13} o/oo				
No. 1								
0-15	0.55	+0.3	1.23	-21.4	60	-21.4	33	-11.2
40-50	0.47	-0.8	1.05	-21.3	58	-	163	-37.1
85-100	0.55	-0.4	0.95	-21.1	78	-	285	-11.3
135-150	1.10	-8.8	1.07	-21.1	116	-	357	+ 3.3
175-185	1.75	-8.2	1.13	-21.5	120	-21.7	435	+ 9.4
No. 2								
0-15	0.89	0.0	2.74	-20.1	104	-23.9	488	+12.0
75-85	0.98	+0.9	2.56	-20.6	148	-20.9	590	+16.4
150-160	0.89	+1.2	2.53	-20.7	98	-	-	-
225-235	0.90	+0.9	2.42	-20.6	104	-21.1	615	+16.7
No. 3								
0-10	1.50	+0.9	3.87	-20.2	70	-21.3	362	- 6.6
50-60	1.37	+0.7	3.58	-20.1	68	-	490	- 0.1
100-110	1.42	+0.6	3.52	-20.3	72	-	-	-
145-160	1.16	+0.7	3.49	-20.3	73	-	435	+ 5.6
190-200	-	-	-	-	68	-20.5	470	+12.7
No. 3B								
790-820	0.67	+0.1	3.57	-20.6	72	-21.5	595	+10.3
1710-1740	1.42	-0.6	2.82	-21.6	92	-21.0	794	+17.8
2620-2650	5.66	-1.5	2.96	-21.7	146	-21.7	635	+15.1
3450-3480	3.67	-5.6	2.53	-22.5	148	-21.9	536	+13.3

Table I-5. Carbon Content and δC^{13} of Sediment and Interstitial Water in Four Cores from Saanich Inlet, British Columbia (taken from Nissenbaum, et al., 1972). (Continued)

Core and Depth (cm)	$CaCO_3$		Organic C		I.W.*	Organic C	Total CO_2 I.W.*	
	%	δC^{13} o/oo	%	δC^{13} o/oo	mg/l	δC^{13} o/oo	mg/l	δC^{13} o/oo
No. 4								
0-15	1.96	+0.1	4.75	-20.9	42	-21.5	390	-0.7
50-65	1.66	+0.1	4.56	-20.2	48	-20.8	415	+1.5
100-110	1.19	-11.2	1.33	-21.7	50	-23.0	440	+4.0
150-160	1.68	+0.1	3.77	-20.8	52	-21.2	477	+4.7
200-210	1.82	+0.6	5.05	-20.4	52	-20.9	510	+5.3
240-250	1.62	+0.3	4.72	-20.2	52	-20.6	482	+5.6
Soil			15.40	-26.6				
Plankton			16.54	-19.2				

* = Interstitial water.

study, the δC^{13} value of total dissolved CO_2 carbon became more positive with depth and is thus in contrast to the data of Presley and Kaplan (1968) and suggests that the δC^{13} value of microbiologically-formed dissolved CO_2 cannot be assumed _a priori_ or that the δC^{13} is diagnostic of bacterial alteration. This particular increase of δC^{13} for total dissolved inorganic carbon with core depth was assumed to be due to methane production by hydrogenation of carbon dioxide resulting in a C^{13}-depleted methane and therefore a C^{13}-enriched residual CO_2.

Using anaerobic bacteria cultured from a Pacific Ocean mud, Rosenfeld and Silverman (1959) showed that the anaerobic bacterial fermentation of methanol can result in a large isotopic fractionation between evolved methane and carbon dioxide, causing a C^{13}-enriched CO_2. Such C^{13} fractionation was also observed by Nakai (1960), who investigated the carbon isotopic composition of coexisting methane and dissolved carbonate and organic material in connate waters of natural gas fields in Japan. Methane was found to be depleted in C^{13}, whereas dissolved CO_2 carbon was enriched in C^{13} relative to the source organic material. Values reported for methane were approximately -70 o/oo, whereas total dissolved carbon varied from +2.6 o/oo to - 8.1 o/oo.

The complexity of the isotopic record in sediments is further indicated by data of Hathaway and Degens (1968) who reported a number of extremely light Pleistocene carbonates (-30 to -60 o/oo) associated with sandstones dredged from five localities on the continental margin of the northeastern United States. They attributed this large depletion of C^{13} as due to a source of carbon derived from either the chemical or microbiological oxidation of isotopically light methane.

I-4d. Biogenic Organic Matter.

The isotopic composition of biogenic organic matter is primarily due to the fractionation associated with the photosynthetic fixation of carbon into plant matter. This fractionation was mentioned earlier and was shown by Park and Epstein (1960) to be comprised of two steps. The first step involves the preferential uptake of C^{12} from the atmosphere; the second step involves the preferential conversion of C^{12}-enriched dissolved CO_2 to phosphoglyceric acid, which is known to be the first product of photosynthesis. Park and Epstein (1961) also showed that the subsequent metabolism of photosynthetic products may also be accompanied by isotopic fractionation, but that these fractionations are relatively small. Based on the analyses of chemical fractions from different plant phyla, they also showed that the δC^{13} of carbon in the lipid fraction is consistently depleted in C^{13} relative to the isotopic composition of the whole plant.

Abelson and Hoering (1961) performed isotopic analyses of amino acids in both photosynthetic and nonphotosynthetic organisms. Although isotopic differences were found at the amino acid level, the data generally supported the above model, i.e., that the major fractionation in photosynthesis does occur in the carbohydrate-forming process and specifically at the ribulose diphosphate step. Data on both types of organisms showed a depletion of C^{13} of approximately 7 o/oo in the lipid fraction. This was in agreement with the lipid data of Park and Epstein (1961) and gave further support to the fact that a carbon isotopic fractionation is involved in the biosynthesis of lipids. Since lipids are generally less degradable during diagenesis than some of the other biogenic fractions (Bordovsky, 1965), the isotopic composition of lipids is particularly relevant to the carbon isotopic record of sedimentary material.

Carbon isotopic data on marine plankton have been summarized by Degens (1969) and show a range of -16 to -25 o/oo with a mean of about -20 o/oo for plankton from waters with a temperature of about 22°C. Plankton from colder waters are shown to be more depleted in C^{13}.

Sackett, et al. (1965) also found the carbon isotopic composition of marine plankton to reflect a temperature dependence. The average isotopic composition of nine plankton samples taken from 25°C water was -21.7 o/oo, whereas twelve samples from 0°C waters gave -27.9 o/oo. It was felt that the observed trend was due to an increased photosynthetic fractionation occurring at the lower temperature or to some other unknown factor. Such a temperature-dependent trend is also supported by the data of Eadie and Jeffrey (1973) who performed carbon isotopic analyses on particulate organic matter from both cold polar waters and from semi-tropical waters. The δC^{13} for particulate organic matter from cold polar waters was found to be lighter (-24.7 to -26.0 o/oo) than that for such matter in the semi-tropical waters (-19.8 to -22.3 o/oo).

Experimental culture work by Degens, et al. (1968a) on the diatoms <u>Skelotonema</u> <u>costatum</u> and <u>Cyclotella</u> <u>nana</u> for varying conditions of temperature and CO_2 supply led these authors to a different interpretation of such apparently temperature-dependent data. They observed a relatively constant fractionation between the dissolved CO_2 species and cell carbon with varying temperature and with otherwise the same environmental conditions. However, the depletion of C^{13} in the cell relative to the bicarbonate system was seen to vary with temperature under conditions of reduced CO_2 availability. The variation, which amounted to a reduced fractionation with increasing temperature, was related to the changing isotopic equilibria between bicarbonate ionic species and dissolved CO_2. The fractionation between cell carbon and dissolved CO_2 and/or HCO_3^- was further seen to be quite dependent on the CO_2 supply, with the highest fractionation observed when CO_2 was most abundant, and vice versa. These authors concluded that carbon isotopic differences for marine plankton are due to environmental differences in temperature, pH, and carbon availability.

Some isotopic data have been taken to investigate the possibility of successive fractionations associated with succeeding levels of a food chain. The small amount of work which has been done indicates that the isotopic composition of consumers varies little, if at all, from that of their average diet. Carbon isotopic data on a number of plankton samples reported by Sackett, et al. (1965) showed that the isotopic composition was not significantly dependent on the relative amounts of phytoplankton and zooplankton, indicating that zooplankton do not perform any significant overall carbon fractionations on their ingested diet. This observation was also confirmed by the data of Degens, et al. (1968b). Isotopic data determined by Smith and Epstein (1970) on animals and plants in an open coastal environment and in a salt marsh generally indicated that carbon fractionations are not involved in food chain steps. Parker (1964) performed an intensive investigation of the carbon isotopic compositions of various plants and animal species within Redfish Bay, a shallow marine estuary near Port Aransas, Texas. The data on plants and animals showed about the same range for each, indicating that there was no evidence of successive fractionations associated with the food chain.

I-4e. Sedimentary Organic Carbon. The δC^{13} of sedimentary organic matter is generally a reflection of the organic matter supplied by the local biomass. However, secondary sources carried by turbidity currents (Sackett, 1964) and transport by currents and turbulent diffusion may also affect a sedimentary situation. Coupled with this, consideration must also be given to any possible diagenetic changes.

Eckelmann, et al. (1962) report carbon isotopic data for a number of marine sedimentary core samples taken from the Southeastern Pacific, South Atlantic, Equatorial Atlantic, Caribbean Sea, and the Mediterranean Sea. These data are summarized in Table I-6. The one Equatorial Atlantic sample was taken from the Mid-Atlantic Ridge and was given an approximate age of 80,000 years. Based on its large distance from any given land mass, the δC^{13} value of -19.3 o/oo reflected a source consisting only of marine plant and animal remains. With reference to the Caribbean core (V 12-97), it was taken at a location where present anaerobic conditions prevail. This anaerobic condition extends into the core to a depth of 470 cm beneath the sediment-water interface. It is likely that the change in

Table I-6. δC^{13} Analyses of Marine Sediments in Cores from the Southeastern Pacific, South Atlantic, Equatorial Atlantic, Caribbean Sea, and Mediterranean Sea (from Eckelmann, et al., 1962).

Core No.	Latitude	Longitude	Water Depth Meters	Depth in Core cm.	δC^{13}
		Southeastern Pacific Ocean			
V 15-32	03°15'S	82°30'W	2,800	701	-22.3
		South Atlantic			
V 12-64	22°23'S	14°12'E	73	70	-20.8
				110	-21.0
				140	-20.2
				200	-20.3
				230	-20.3
				380	-20.3
		Equatorial Atlantic			
A 180-72	00°35'N	21°47'W	3,840	320	-19.3
		Caribbean Sea (Cariaco Trench)			
V 12-97	10°35'N	65°04'W	460	100	-20.1
				200	-20.3
				300	-20.3
				400	-20.6
				460	-20.4
				480	-22.1
				601	-23.2
				701	-22.7
		Mediterranean Sea			
V 10-57	32°21'N	28°25'E	2,816	136	-22.1
V 10-56	24°01'N	30°08'E	2,816	80	-20.5
				595	-22.9
				785	-23.0

the δC^{13} of this core at this level reflects a change in sedimentary conditions in the past. Eckelmann, et al. also report δC^{13} data for a core taken from the Pedernales area northeast of Venezuela, an area of rapid sedimentation of primarily terrestrial organic material. These data are presented in Table I-7 and isotopically reflect a terrestrial low δC^{13} carbon.

Table I-7. δC^{13} Data from Pedernales Core (from Eckelmann, et al., 1967).

Core Depth, cm	δC^{13}
0-31.8	-26.7
31.8 - 67.3	-26.9
67.3 - 92.7	-26.1

Parker's (1964) carbon isotope investigation of the various carbonaceous reservoirs of organic carbon in a marine bay near Port Aransas, Texas, showed that the isotopic composition of the sediments fell within a range which reflected a composition dependent upon the relative contributions of the various species of biomass.

Oana and Deevey (1960) describe the interactions of the carbonaceous reservoirs in some dimictic lakes in Connecticut. The carbon isotopic data from one such lake (Linsley Pond) showed that the isotopic composition of bottom mud (-30 o/oo) reflected the determined δC^{13} for net plankton (-30 o/oo). The already mentioned C^{12} depletion for a terrestrial system is also quite evident.

Degens (1969) summarized the majority of the then-existing carbon isotope data for recent sediments. These data are summarized in Figure I-3.

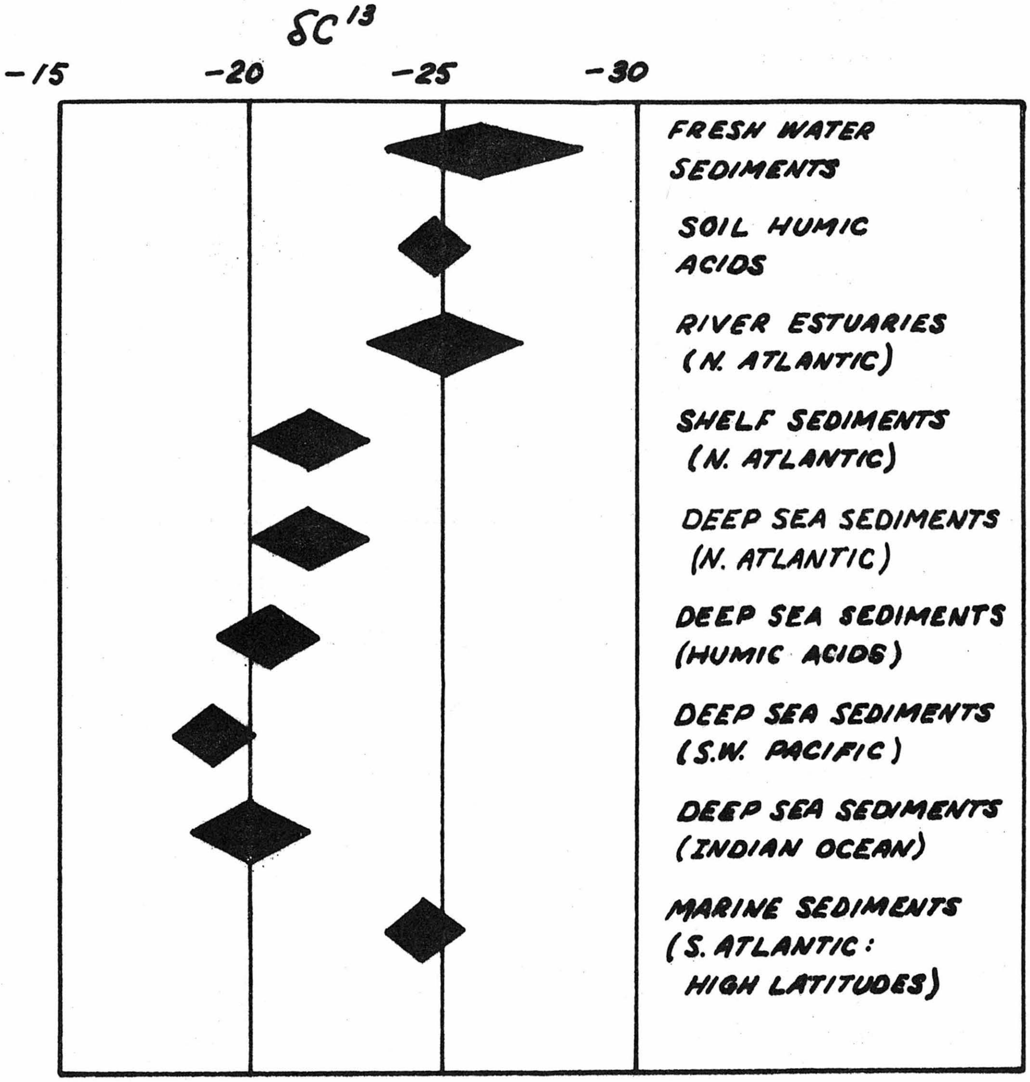

Figure I-3 . Isotopic composition of organic carbon in recent sediments (from Degens (1969) and based on unpublished data of J. M. Hunt and K. O. Emery).

Sackett and Thompson (1963) report δC^{13} values for organic carbon of sediments which represent a gradient in sediment types from the terrestrial-influenced Eastern Gulf Coast to the open ocean waters of the Upper Gulf of Mexico. These isotopic data are summarized in Figure I-4 and reflect the expected δC^{13} gradient from a terrestrial-derived organic carbon of -26 to -28 o/oo to a marine-derived organic carbon δC^{13} of -20 o/oo .

Sackett and Thompson (1963) also report δC^{13} data for a number of plankton trawls collected from the Mississippi Sound area and the Gulf of Mexico. In addition, they obtained δC^{13} data for the sediments in this area, thus allowing a comparison between the δC^{13} of the sediments and the δC^{13} of the source organic matter. These data are given in Table I-8. Although the data generally indicate that the sedimentary organic matter is principally derived from the local biomass, there is an indication that the sediments reflect a slight depletion of C^{13} relative to the source organic matter. A depletion of C^{13} in organic matter of modern marine sediments representing progressive stages of diagenesis is also indicated in carbon isotopic data reported by Emery (1960) for various southern California basin sediments (Table IV-4).

The decrease in the δC^{13} of sedimentary organic matter in sediments may be due in part to the preferential retention of C^{13}-depleted lipid-type compounds in the sediments (Degens, 1969; Epstein, 1968; Epstein and Silverman, 1958; and Sackett and Thompson, 1963). Another possibility is suggested by the results of Abelson and Hoering (1961) in which they showed the carboxyl groups of amino

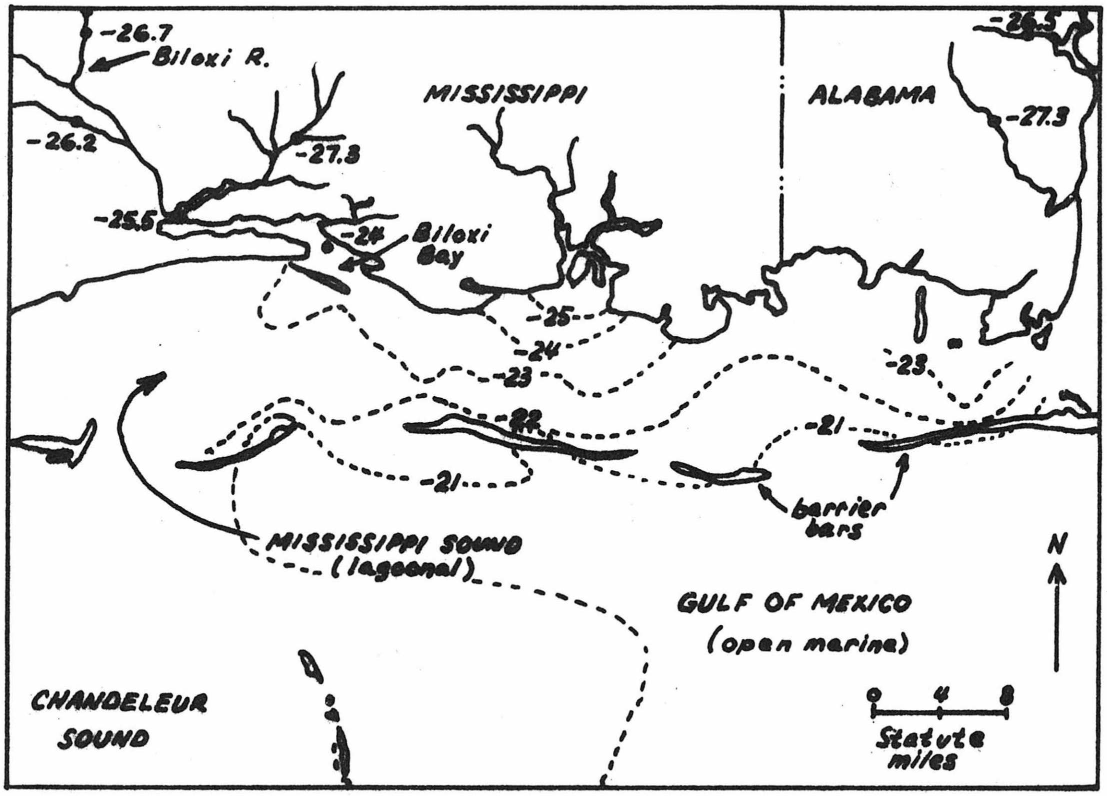

Figure I-4 . The isotopic composition of organic carbon in recent Eastern Gulf Coast sediments (from Sackett and Thompson, 1963).

Table I-8. δC^{13} Analyses of Plankton and Sediments of the Mississippi Sound Area and the Gulf of Mexico (from Sackett and Thompson, 1963).

Location	Description*	$\delta C^{13}/C^{12}$ of Organic Material: Collected in Tow	$\delta C^{13}/C^{12}$ of Organic Material: in Sediments below Tow
Mississippi Sound			
(1) $30^{\circ}16'X88^{\circ}57'$	Diatoms, some land-derived plant fragments and pollen	-21.0	-21.7
(2) $30^{\circ}13'X89^{\circ}00'$	Diatoms, dinoflagellates, copepods, tintinnids	-23.3	--
(3) $30^{\circ}17'x89^{\circ}10'$	Diatoms, tintinnids, copepods	-23.3	--
(4) $30^{\circ}17'X88^{\circ}4'$	Diatoms, dinoflagellates, some pine pollen	-22.5	-22.6
(5) $30^{\circ}15'X88^{\circ}34'$	Diatoms, dinoflagellates, copepods	-19.6	-22.6
(6) $30^{\circ}14'X88^{\circ}36'$	Diatoms, dinoflagellates, copepods	-21.0	-22.6
Gulf of Mexico			
(1) $24^{\circ}29'X92^{\circ}05'$	About 20% near-shore marine plant forms	-16.8	-19 to -22**
(2) $25^{\circ}17'X92^{\circ}21'$	About 50% near-shore marine plant forms	-12.8	-19 to -22**
Gulf Stream Atlantic	Phytoplankton (Craig, 1953)	-12.9	-19 to -22**

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*By Palynological Group of Pan American Petroleum Corporation

**Range of values reported in literature acids to be more enriched in C^{13} than the rest of the amino acid. Decarboxylation of proteins is a common enzymatic reaction catalyzed by bacteria which may result in a depletion of C^{13} in organic material undergoing bacterial decomposition (Sackett and Thompson, 1963).

On the other hand, Sackett (1964) points out that there is considerable evidence to contradict the hypothesis that diagenesis results in a C^{12}- depleted organic matter. He cites the uniformity of δC^{13} with core depth for two marine cores as such evidence and also notes that the data of Eckelmann, et al. (1962) do not indicate any systematic change with the depth.

A very comprehensive study of the chemical and isotopic changes accompanying early diagenesis in a sediment under reducing conditions in a fjord (Saanich Inlet, British Columbia) is reported by Nissenbaum, et al. (1972), and Brown, et al. (1972). These data were mentioned earlier in this section (precipitated carbonates) and are further discussed in Chapter IV, and also presented in Table I-5. The chemical data reported on these cores (Brown, et al., 1972) indicated that all cores were undergoing diagenesis. Although a diagenetic isotopic effect is seen in the δC^{13} for total dissolved inorganic carbon, no significant effect is noticed with depth, and therefore time, for total organic carbon. However, it may well be that such an effect has taken place quite early in the core. This is suggested by the isotopic value reported by the authors for plankton which is 1 to 2 o/oo heavier than δC^{13} values reported within the cores.

In summary, it appears that the effect of diagenesis on the isotopic composition of total organic carbon within sediments is not only a complex process but most likely depends greatly on the specific diagenetic environment and on the source material. This thesis will present some additional data relating to such processes in Chapter III.

II. SAMPLE COLLECTION AND ANALYTICAL TECHNIQUES

II-1. Sample Collection

Several sampling devices were utilized for obtaining samples of sediment. The majority of the core samples were provided by the Southern California Coastal Water Research Project (SCCWRP) and were obtained with either a Phleger gravity piston corer or a box coring device. It was felt that the box coring device had the least potential for disturbing the core and also penetrated deeper to provide a longer core (SCCWRP, 1973). The available samples of the Phleger cores were provided in the frozen state and kept that way until time of analysis. The box cores were frozen in glass or polyethylene containers on board ship upon collection and were dried at 110°C and water contents determined at a later date. Subsamples of these cores were therefore provided in the dry state. The most extensively studied core was the Phleger core P6C which was provided by the Los Angeles County Sanitation Districts (LACSD). The history of this core was such that it was maintained frozen until time of analysis, at which time it was semi-thawed and extruded. The extruded sediment was divided into segments and the outer surface of these segments was removed in order to minimize any homogenization and contamination due to the interaction of the core liner with the sediment.

A majority of the surface samples were also supplied by the Los Angeles County Sanitation Districts and were obtained by means of a Shipek sampler. Some of the nearshore surface samples were taken by the author by means of a small piston coring device for which just the top centimeter of sediment was removed. All surface cores were frozen at the time of collection and kept frozen until time of analysis.

Water samples were obtained by using a 2-liter Van Dorn water sampler. The water samples were stored in clean brown-glass bottles to which several milligrams of $HgCl_2$ had been added to inhibit bacterial activity. Upon return to the laboratory these samples were either filtered immediately or refrigerated over night and filtered the following day.

II-2. The Determination of Total Organic Carbon

Sample preparation for total organic carbon determinations consisted of the following.

(1) Samples, usually in the wet state, were washed with triple-distilled water over Whatman GF-C (4.5 cm) glass fiber filters. Washed samples and glass fiber filters were then dried at 50°C for periods of at least fifteen hours. Prior to filtration, the glass fiber filters had been washed with triple-distilled water, dried, and pre-combusted at 400°C for several hours. Williams (1968) used these same filters to discriminate between dissolved organic matter and particulate organic matter. He reported a pore size of 1 to 2 microns.

(2) The dried glass fiber filters with included samples were cut into strips and placed in pre-combusted (900°C) quartz boats. Approximately 1-milliliter (or more, if needed) of one normal hydrochloric acid was then added to the boats to acidify and remove any solid carbonates. The samples were then re-

dried at 50°C. Several tests were conducted to insure that there were no adverse fractionations associated with acidification followed by drying and combustion (Table II-1). The three tests are self-explanatory and indicate no significant detectable fractionation effects associated with this procedure.

The conversion of a sample to gaseous carbon dioxide employed the same basic technique as presented by Craig (1953). Samples were combusted in the presence of copper oxide and within an oxygen atmosphere at temperatures of about 950°C. The details of the combustion line are schematicized in Figure II-1. Periodic blanks were combusted and indicated no detectable CO_2 associated with the pre-combusted glass fiber filters.

The sample was loaded by removing end-cap (1) and placing the sample as shown with clean metal tweezers. The end-cap was then replaced with fresh high-vacuum grease and the total system pumped down to a high vacuum. Furnace B was heated to an approximate 950°C, whereas furnace A was heated only slightly (about 300°C). Pure oxygen was liquified at liquid nitrogen temperature in trap (2). When the line had attained a high vacuum, as detected by the thermocouple vacuum gauge, then oxygen was bled into the system such that the total pressure was about 1 cm Hg as measured by manometer (3). A Dewar containing liquid nitrogen was placed over trap (4) to sublime any passing carbon dioxide, and a Dewar containing an organic solvent - dry ice mixture was placed over trap (5) to sublime any passing water vapor. The mercury Toepler pump (6) was then

Table II-1. Percentage Organic Carbon and Corresponding Carbon Isotopic Data for Acidification Tests.

TEST	Percent Organic Carbon	δC^{13}
I) Wood Sample:		
a) Sample only	53.0	-19.8
b) Sample acidified with IN HCl and dried at 50°C	49.4	-19.7
c) Sample only (Previously run by J. Young on a different line)	49.5	-19.8
II) 24-Hour Composite Effluent Sample		
a) Sample filtered onto Whatman GF-C glass fiber filters and washed with triple distilled water	Not determined	-23.0
b) Same as (a), but acidified with IN HCl	"	-23.1
c) Same as (a), but effluent solution was brought to a 35°/oo NaCl concentration and let stand for one-half hour before filtering (to check for any possible flocculation effect at high ionic strength)	"	-23.0
III) Raw Sludge Solids		
a) Raw sludge solids alone	37.3	-23.4
b) Same as (a), but acidified with IN HCl and dried at 50°C	36.9	-23.4
c) 3 gr. $CaCO_3$ added to raw sludge sample and then acidified and dried at 50°C	36.4	-23.6

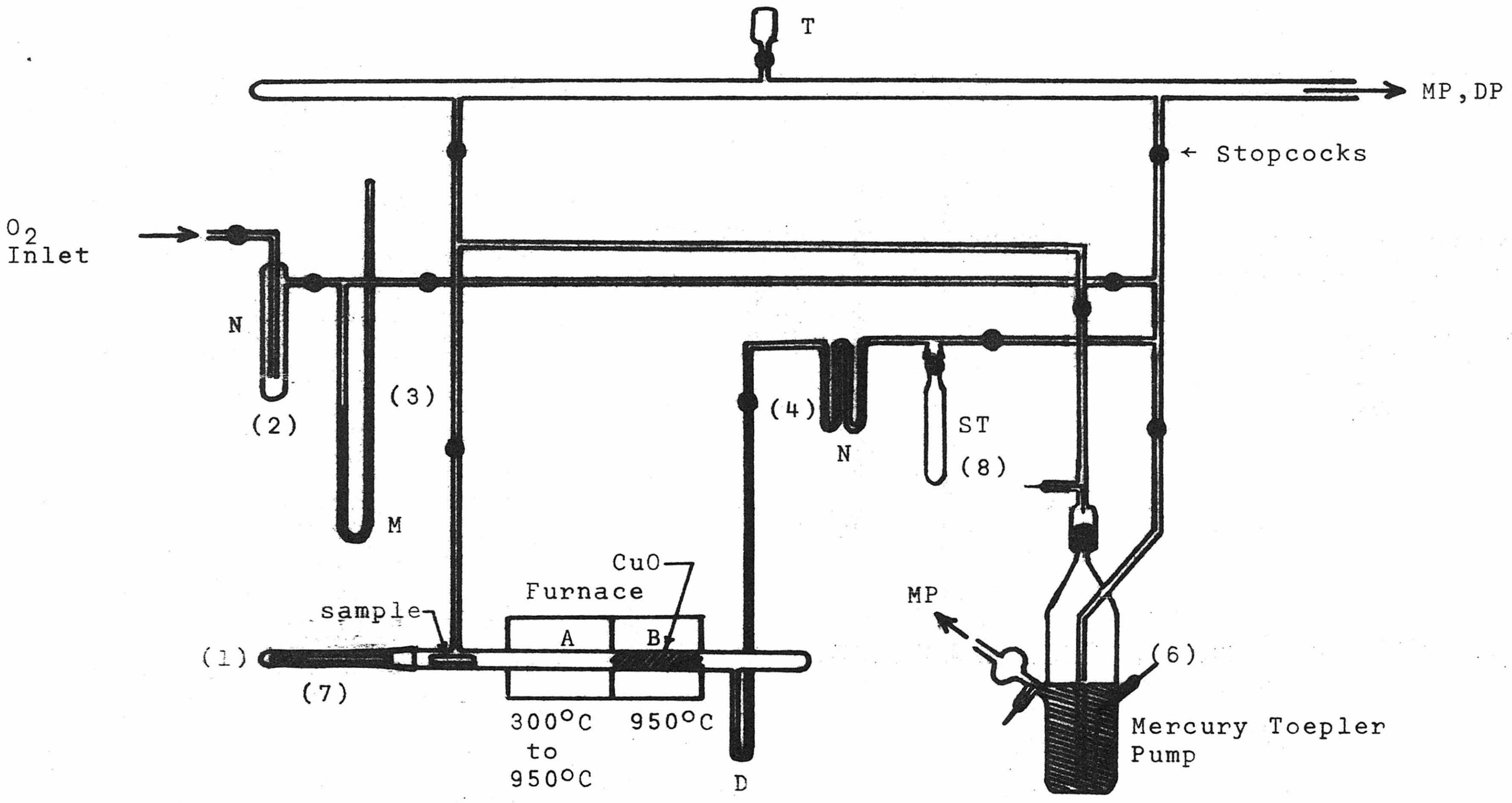

Figure II-1. High vacuum carbon combustion line. Legend: A-furnace for which temperature is raised from 300°C to 950°C during combustion; B-furnace maintained at 950°C; D-dry ice-organic solvent trap; DP-diffusion (Hg) pump; M-manometer; MP-mechanical pump; N-liquid nitrogen traps; ST-sample tube; T-high vacuum thermocouple gauge.

switched on to cycle oxygen through the combustion furnace. The sample was then slid, by using a glass push-rod with an enclosed end-magnet (7), into furnace A and the temperature of A was then allowed to increase to 950°C. The oxidation of the sample was monitored by watching the loss of oxygen as detected by the manometer, and additional oxygen added as needed. The total combustion process took about forty-five minutes. When combustion was complete, the system was again pumped down to a high vacuum and the collected carbon dioxide sample sublimed to sample tube (8) for subsequent purification (Section II-5), manometric measurement of yield, and mass spectrometric measurement of the carbon isotopic ratio. Yields of carbon were reported as percentages based on dry-weight.

II-3. Analysis for Carbonate Carbon

Sediments and other particulate material for which carbonate-carbon data are reported were washed with triple-distilled water and centrifiged at 2000 rpm followed by withdrawal of the supernatant. This process was repeated four times, and then the samples were dried at 50°C for several days and homogenized with pestle and mortar. An appropriate aliquot was then taken and acidified with 1-normal hydrochloric acid utilizing the conventional extraction technique (McCrea, 1950). The evolved carbon dioxide was collected in a liquid nitrogen trap and then purified (Section II-5), followed by the measurement of yield. Measurements of carbonate carbon are also reported as dry-weight percentages.

II-4. Lipid Extractions

The term lipid, also referred to as bitumen, typically refers to fats and oils. Bordovsky (1965) points out that the term is somewhat indefinite due to the varying nature of the molecular units which fall within this classification. Bordovsky notes that both the yield of lipid matter and its composition are affected by the use of solvents of different types and of different extraction techniques. Carbon isotopic data for lipids usually refer to the chloroform-soluble substances. Reference to lipids within this thesis will therefore pertain to fatty substances extracted with and soluble in chloroform.

The method of extraction followed that set forth by Bligh and Dyer (1959) in which the extraction is carried out with a miscible solution of methanol:chloroform:water in the volumetric proportions of 2:1:0.8 . After extraction, methanol and water are added to the extracted solution to bring the volumetric proportions to 2:2:1.8 which results in an immiscible biphasic solution. A period of time is then allowed for complete separation of the phases and the overlying methanol-water layer is then removed by aspiration leaving behind a chloroform layer containing purified lipid. The exact steps followed consisted of the following.

(1) A sample which had been previously washed and dried according to Section II-3 was homogenized with pestle and mortar and placed within a 40-ml conical centrifuge tube.

(2) Approximately 20 ml of the methanol-chloroform-water (2:1:0.8) solution was added and allowed to sit for approximately one hour.

(3) The tube with included sample and solvent was centrifuged at 2000 rpm, followed by decanting of the solvent with extracted

lipids to a graduated cylinder.

(4) The extraction was repeated an additional three to four times until the supernatant appeared quite clear.

(5) The collected supernatant solution was brought to a 2:2:1.8 solution and allowed to separate and clarify overnight.

(6) The volume of the chloroform layer was noted and then the methanol-water layer was aspirated off along with a thin layer of the lower chloroform portion. The remaining volume was noted and then filtered through Whatman GF-C glass fiber filters to insure removal of any fine particulates which may have been transferred in steps (3) and (4). The solution was then evaporated to dryness at 50°C over night, followed by quantitative weighing of the lipid yield.

(7) The residue was resolubilized in a small amount of chloroform and pipetted to a precombusted and weighed quartz combustion boat. This solution was then evaporated at 50°C (over night) followed by weighing and combustion as outlined in Section II-2.

The methanol and chloroform were of reagent grade purity and were redistilled prior to use. The water was of triple-distilled quality. Non-detectable yields were obtained on blank samples which followed steps (1)-(7), with the exception of no sample.

II-5. Purification of Carbon Dioxide Samples and Measurement of Yield.

Since contaminants consisting of oxides of sulfur and nitrogen can interfere with mass spectrometric determinations, it is desirable to purify CO_2 samples obtained from the combustion of complex organics, as found in sediments, from such impurities (Sackett and Thompson, 1963; Degens, 1969). Sackett and Thompson suggested passing such samples over hot (about 450°C) copper metal and manganese dioxide which reduced oxides of nitrogen to nitrogen gas and combined with oxides of sulfur, respectively. The purification high-vacuum line used in the present work is shown in Figure II-2. This line also includes a facility for measuring yields as well as for handling the carbonate extractions. In summary, samples of CO_2 were therefore sublimed from the sample tube 1 to 2 , to 3 , to 2 , to 4 , and back to 2 . The yield was then determined manometrically and the sample sublimed back to tube 1 . This procedure resulted in repeated passes through the dry ice - organic solvent trap which insured maximum removal of any water vapor.

The U-tubes containing the MnO_2 and Cu were both heated at 470°C. Several tests were made to insure the removal efficiency for oxides of nitrogen and sulfur and to check for any possible associated fractionation. One test consisted of the addition of a known amount of SO_2 to a known CO_2 sample, and the other consisted of the addition of a quantity of NO_2 to a known CO_2 sample. Both tests showed total removal of the added impurities with no consequent detectable change in the δC^{13} of the CO_2. In another test designed to check whether any fractionation is associated with the passage of CO_2 over either or both furnaces, CO_2 obtained from the acidification of Baker reagent-grade $CaCO_3$ was passed over the MnO_2 and Cu furnaces. The results of this test are reported in Table II-2 and indicate no consequent frac-

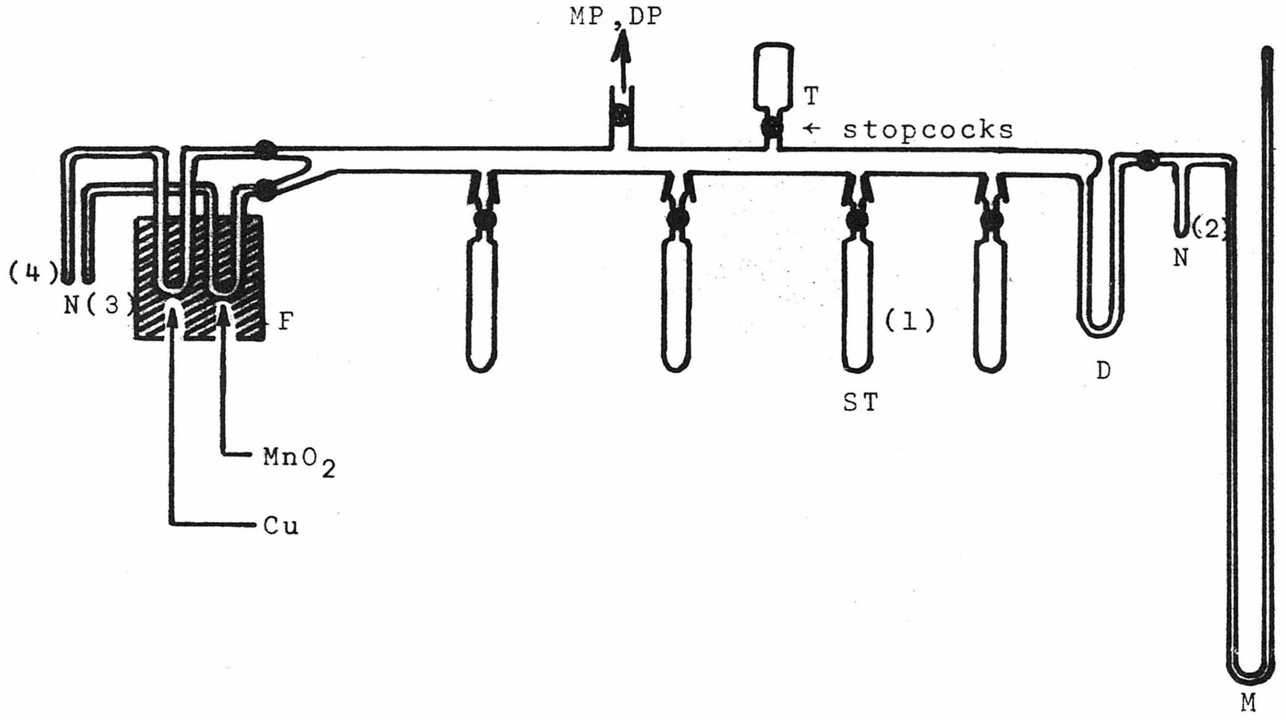

Figure II-2. Carbonate extraction and CO_2-purification apparatus, Legend; D-dry ice-organic solvent trap; DP-diffusion (Hg) pump; F-furnace maintained at 470°C; M-manometer; MP-mechanical pump; N-liquid nitrogen traps; T-high vacuum thermocouple gauge; ST-sample tube.

tionations.

Table II-2. Test of CO_2 Purification Technique

Sample	δC^{13} before passing	over	δC^{13} (after)
a	-13.21	MnO_2	-13.23
b	-13.16	Cu	-13.17

III. THE CHARACTER OF DISCHARGED WASTES AND THE RECEIVING OCEAN WATERS

III-1. The Character of Discharged Wastewaters

In order to study the effect of discharged wastes on the ocean sediments, it is first necessary to understand the nature of the discharged wastes and the receiving waters.

III-1a. Treatment of the Wastes and the Discharge System.

The Joint Outfall System operated by the County Sanitation Districts of Los Angeles County (LACSD) presently disposes of approximately 370 MGD of primary treated wastewater, which is generated by a population of 3.7 million and the industry contained within an area of about 750 square miles (LACSD, 1973). The treatment flow steps are outlined in Figure III-1 (LACSD, 1973). Essentially, this treatment results in the removal and anaerobic digestion for 13 days of the settleable and floatable solids to produce what is referred to as digested sludge. The digested sludge is centrifuged, after which the supernatant (centrate) is reunited with the primary effluent, whereas the more solid residue (cake) is transferred to drying beds. A portion of the dried cake is sold to a fertilizer company and a portion is used as landfill material. The combined primary effluent and sludge centrate will hereafter be referred to as the effluent. This effluent receives intermittent chlorination for disinfection and then is discharged to the ocean about two miles offshore of Whites Point at a depth of 200 feet.

The outfall system operated by the LACSD presently consists of two simultaneously operating multiport diffuser ocean outfalls

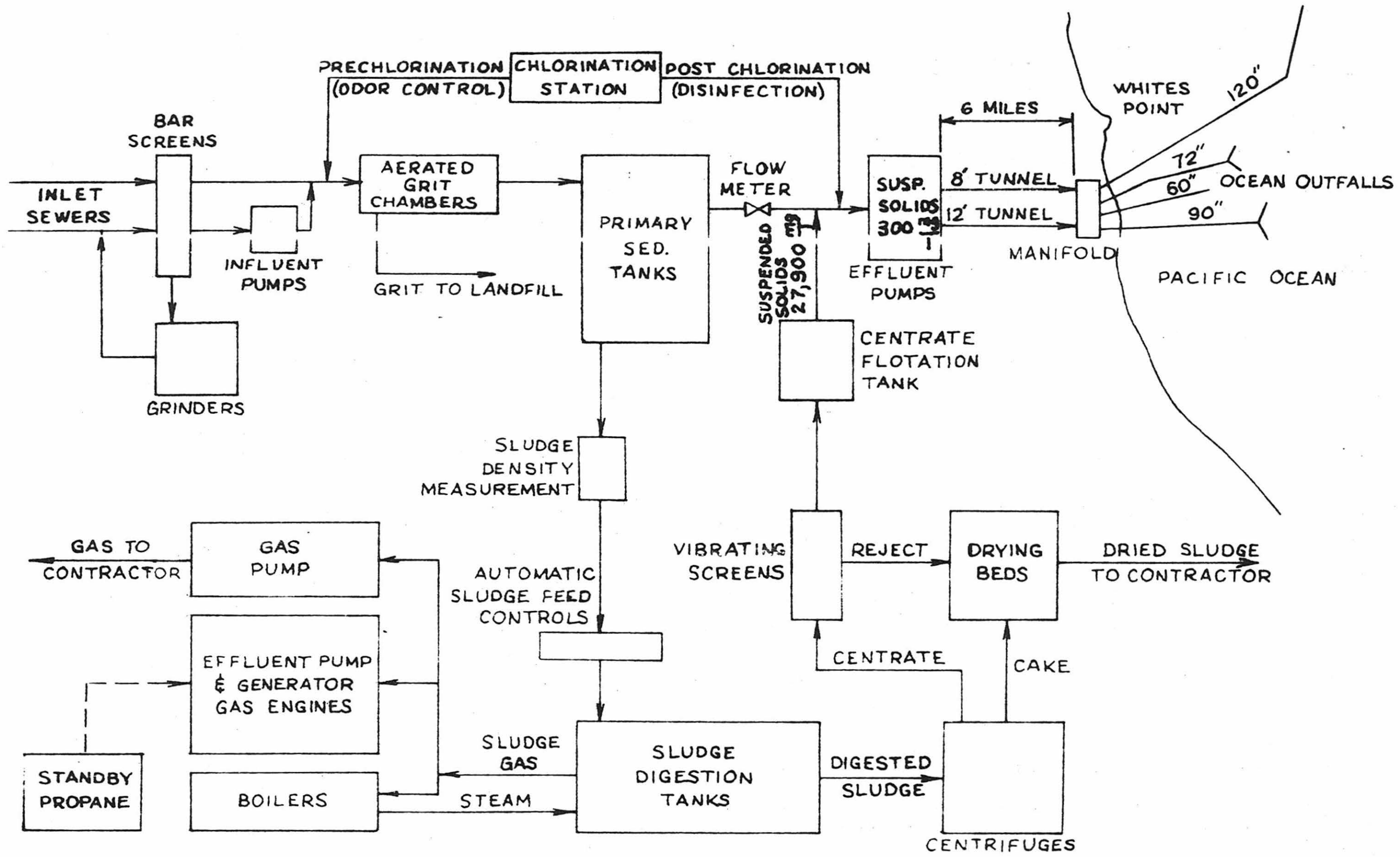

Figure III-1. Schematic of primary treatment flow steps at the Los Angeles County Sanitation Districts JWPCP Treatment Plant (from LACSD, 1973).

(Figure III-2); a 90-inch diameter outfall completed in 1956, and a 120-inch diameter outfall completed in 1965. The history of the LACSD's discharge to the ocean via ocean outfalls actually dates back to 1937 (CDM, Inc., 1973), when wastewater was discharged through a 60-inch diameter outfall, terminating in an open pipe about one mile offshore in 110 feet of water. This outfall was modified in 1954, resulting in a multiport diffuser end section. A 72-inch diameter outfall was constructed in 1947 and extended in 1953 to 6800 feet offshore. The 1953 extension resulted in a "Y"-multiport diffuser section with ports on all three legs. This outfall is presently maintained for emergency purposes. The rate of flow history for total discharge to the ocean is presented in Figure III-3, which is based upon flow data provided by D. Hotchkiss (1973) of the LACSD. The flow history reveals two different linear periods of growth with a transition at about 1945. The suspended solids concentration over this time period has not been accurately recorded. However, data collected during the past few years indicate that the suspended solids concentration has remained relatively constant at a value of about 300 mg/l .

III-1b. Settling Velocities of Discharged Particulates. The fate of effluent particulates discharged to the ocean is intimately related to the settling velocities of these particulates. Settling velocity analyses were therefore performed on several 24-hour composite effluent samples obtained from the LACSD. A 2-liter graduated cylinder was used as a settling column, and samples of specified volume were pipetted from a defined depth for various time periods after

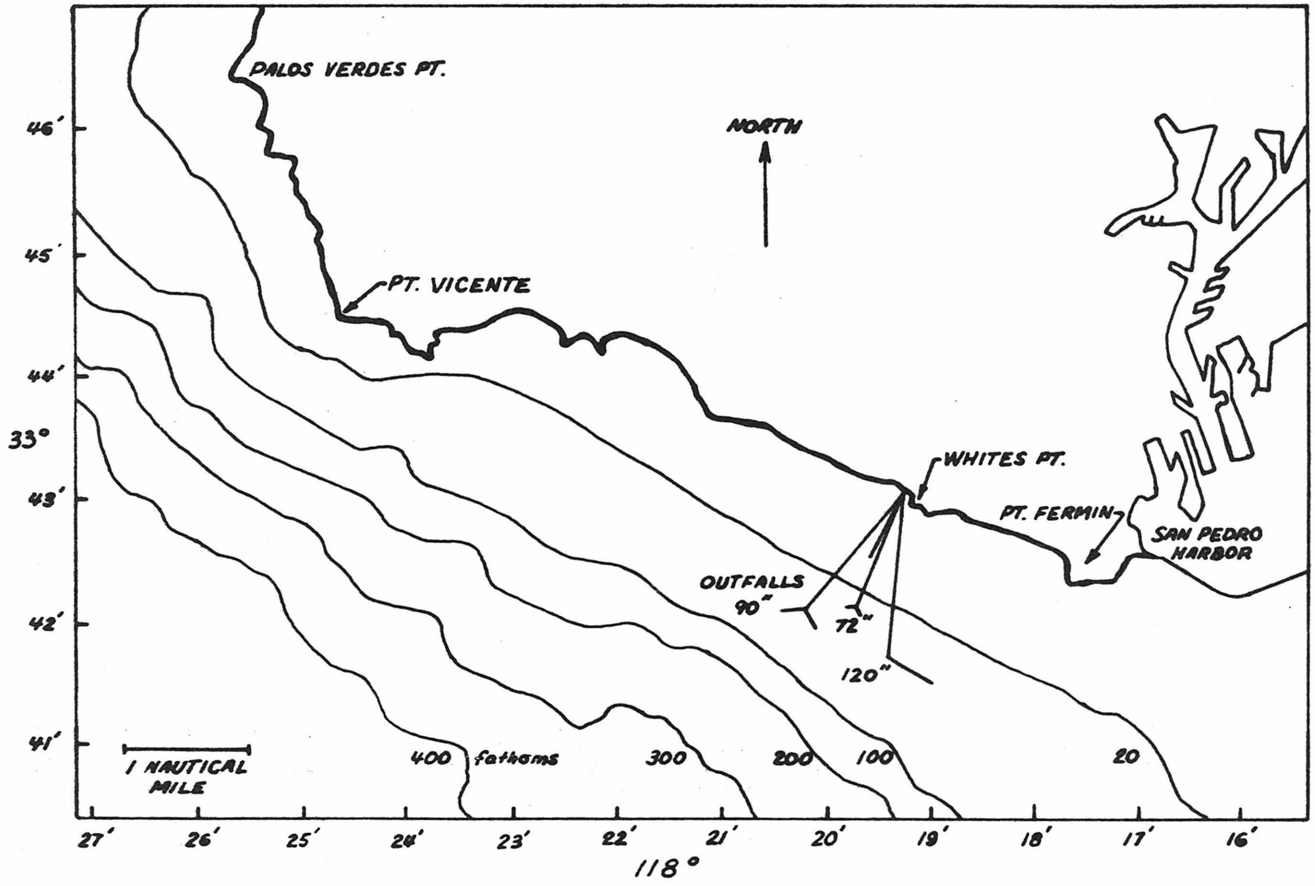

Figure III-2 . The location of the LACSD ocean outfall system on the Palos Verdes Coast.

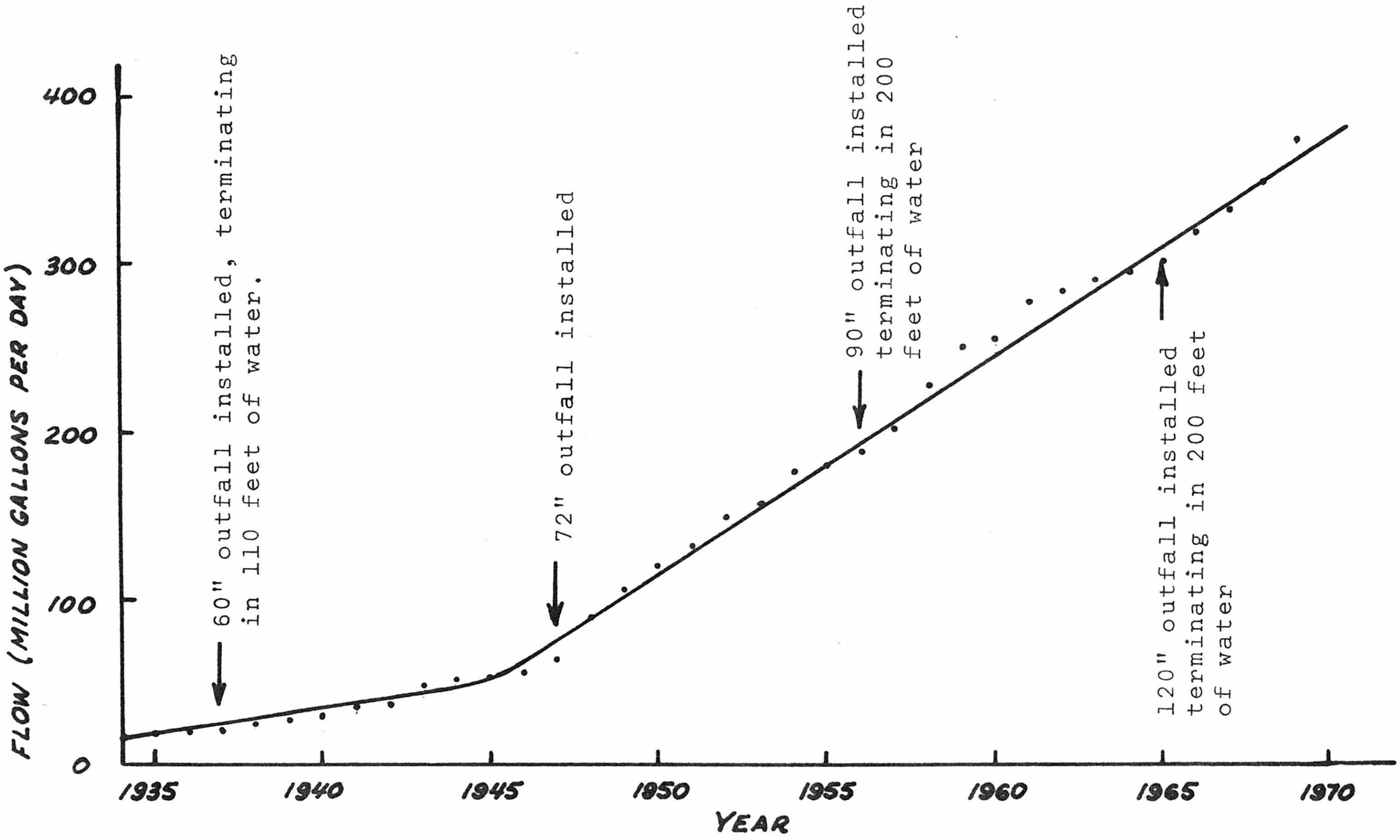

Figure III-3 . Flow history of effluent discharge from the Whites Point ocean outfall system (based on data provided by D. Hotchkiss, 1973).

initial mixing. The samples were filtered over Whatman GF-C glass fiber filters and therefore account only for those particulates larger than about 1 micron. The method of analysis essentially follows that referred to as the pipette method in Krumbein and Pettijohn (1938). In such an experiment, there are present certain inherent problems such as the adherence of particulates to the walls of the graduated cylinder. Nevertheless, the data as presented in Figure III-4 indicate that the majority of effluent particulates have a settling velocity between 10^{-2} and 10^{-3} cm/sec and that these settling velocities are slower in the more dense media of a saline environment.

III-1c. The Relative Amounts and the Isotopic Composition of Total Organic Carbon, Lipid Carbon, and Carbonate Carbon in the Effluent. Total organic carbon, lipid carbon, and carbonate carbon, and their respective stable carbon isotopic compositions have been determined for the particulates in a number of effluent samples and are listed in Table III-1. Since the centrate represents a concentrated solution of the particulates found in the effluent (Figure III-1), it was therefore used as material for analysis of lipid and carbonate fractions.

A unique carbon content of the waste is difficult to obtain because of its heterogeneous nature. Nevertheless, the data for the percentage of total organic carbon for effluent particulates give a mean of 34 per cent with a rather small variance of 3 per cent. The corresponding isotopic composition is seen to fall within a quite narrow range of -22.7 o/oo to -24.5 o/oo with a mean of -23.5 o/oo and a variance of only 0.5 o/oo.

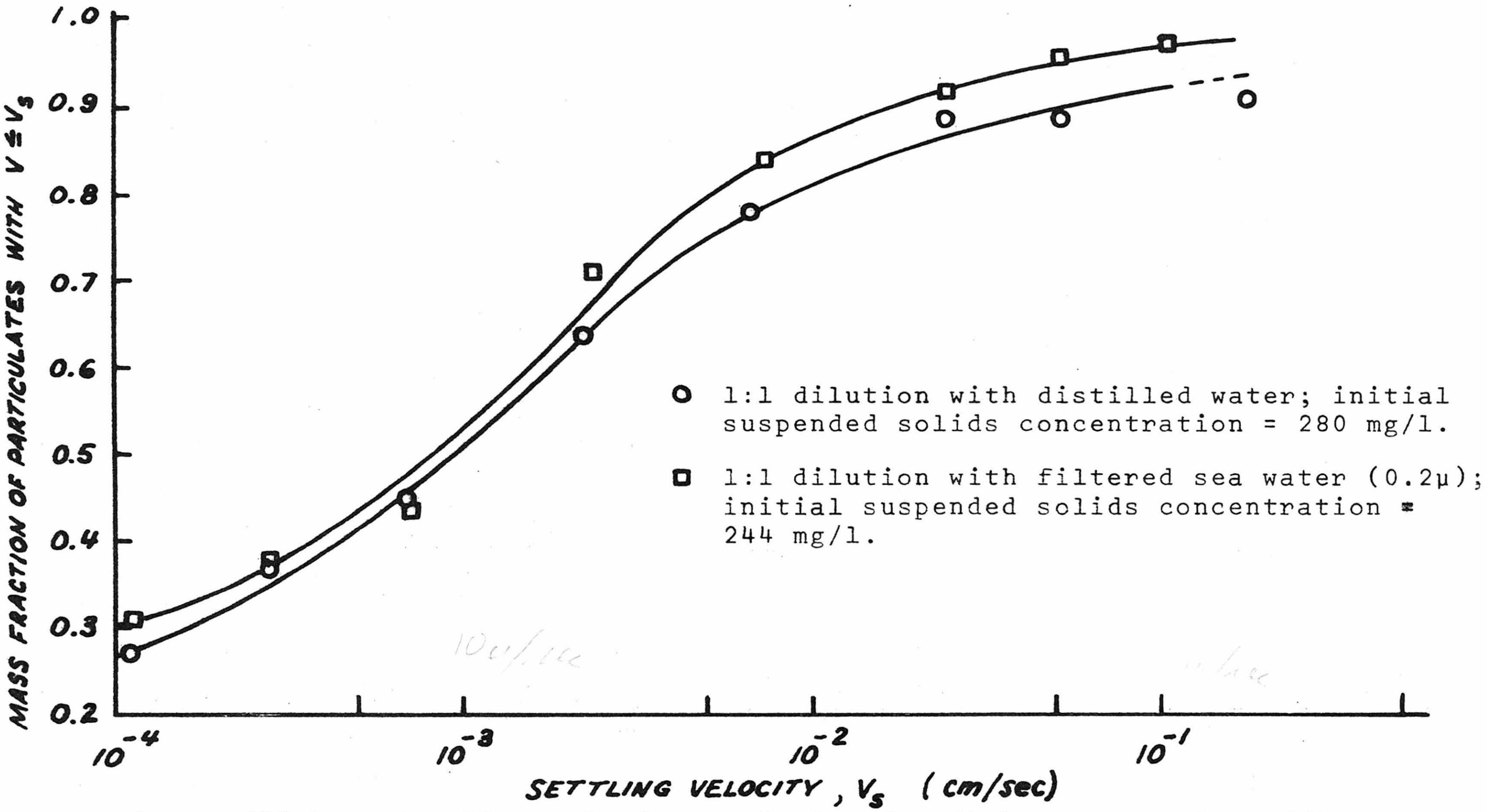

Figure III-4 . Settling velocity analysis of a 24-hour composite effluent sample obtained 2/1/73 from the Los Angeles County Sanitation Districts.

Table III-1a. Carbon Characterization of Discharged Effluent Particulates

Sample		Percent Organic Carbon	δC^{13} (org.)	Percent Lipid Matter	Percent Carbon in Lipid	δC^{13} (Lipid)	Percent Carbonate Carbon	δC^{13} (Carb.)
Composite	(a)		-23.0					
12/4/72	(b)		-23.0					
	(c)		-23.1					
Composite	(a)		-22.9					
12/15/72	(b)		-23.3					
Raw sludge	(a)			15.4	67	-24.6		
9/20/72	(b)	37	-23.5					
	(c)	37	-23.5					
	(d)	36	-23.7					
Composite	(a)	36	-22.7					
1/11/73	(b)			20.0	64	-25.3		
Composite	(a)	38	-23.4					
2/1/73	(b)	36	-23.3					
Composite	(a)	36	-22.9					
5/12/73	(b)	36	-23.0					
Composite	(a)	35	-23.9					
6/8/73	(b)	28	-23.5					
	(c)	32	-23.5					
	(d)	33	-23.1					
Composite	(a)	33	-24.0					
6/29/73	(b)	33	-23.4					
	(c)	31	-23.9					
	(d)	28	-23.6					
	(e)	36	-23.6					

Table III-1a (Cont'd)Carbon Characterization of Discharged Effluent Particulates

Sample	Percent Organic Carbon	δC^{13} (org.)	Percent Lipid Matter	Percent Carbon in Lipid	δC^{13} (Lipid)	Percent Carbonate Carbon	δC^{13} (Carb.)
Composite 7/6/73	34	-24.5					
Composite 7/12/73	34	-23.8					
Composite 7/18/73	41	-24.3					
Composite 7/25/73	40	-24.0					
Composite 8/29/73 (a)	36	-24.0					
(b)	34	-23.8					
(c)	35	-24.3					
Centrate 6/29/73			11	61	-25.8	.33	-7.8
Centrate 7/5/73			10	66	-26.3	.28	-4.6
Centrate 7/18/73			14	68	-25.6	.31	-5.6

Table III-1b. The Organic Carbon Concentration and δC^{13} Value of Effluent Dissolved Organic Matter*

Sample	ppm Dissolved Organic Carbon	δC^{13}
Composite 7/18/73	36	-31.9 o/oo
Composite 7/25/73	41	-32.0
Composite 8/29/73 (a)	32	-25.1
(b)**	41	-28.1

* As used here, dissolved organic matter refers to that organic carbon which passed through a Whatman GF-C glass fiber filter and was left as a residue when the filtered solution was evaporated at 50°C.

**After filtering through a glass fiber filter, this sample was further passed through an 0.05-micron Millipore filter.

Table III-1 also indicates that effluent solids have a mean of about 14 per cent for chloroform-extractable lipid matter, 65 per cent of which is carbon. This suggests that about one-fourth of the discharged carbon is in lipid form which is of greater biochemical stability than most other biogenic matter (Bordovsky, 1965). This is consistent with data reported by Maier (1973) on the carbon composition of a primary effluent from the Minneapolis - St. Paul Sewage Treatment Plant. For this particular waste, Maier found that lipid-related compounds accounted for more than 45 per cent of the total organic carbon, with the remainder being principally in the form of bound amino acids and carbohydrates. The above data are also consistent with the data of Bordovsky (1965), who indicated that lipids of planktonic diatoms contain about 66 per cent carbon and the lipids of sediments contain about 73 per cent carbon.

Table III-1 also shows that the isotopic composition of the effluent lipid carbon is depleted in C^{13} relative to the composition of total organic carbon. Four different samples of the centrate gave a mean composition of -25.6 o/oo. This depletion of C^{13} in the lipid carbon as compared to total organic carbon is of the same trend as for lipid data reported in the literature.

Several analyses were also made on organic matter which passed through a Whatman GF-C glass fiber filter. This organic matter, which will be referred to as dissolved, is a mixture of particulates smaller than about a micron as well as truly dissolved organic matter. A 10 cc aliquot of this solution was evaporated in a quartz combustion boat. The residue was acidified to eliminate carbonates, re-evaporated, and then combusted in the same manner as total organic carbon. The results reported in Table III-1b give a valueof about 40 mg carbon/liter of this "solution," but this concentration does not include any material which may have been volatilized during the evaporation procedure and the high-vacuum pumping prior to combustion.

The δC^{13} values of the "dissolved" matter combusted in the quartz boats is variable and indicates a large depletion of C^{13}. Two samples (7-18-73 and 7-25-73) have a δC^{13} value of about -32 o/oo. Although not as light, the sample of 8-29-73 is also depleted in C^{13} (-25.1 o/oo) relative to the mean δC^{13} value of the particulate fraction, and indicates a greater depletion with smaller particle sizes. This particular sample (8-29-73) was further passed through a millipore 0.05-micron filter, and the residue from the evaporated eluant gave an isotopic value of -28.1 o/oo.

This relatively large depletion of C^{13} in the "dissolved" fraction is probably due to the high input of industrial wastes to the LACSD's effluent. Calder and Parker (1968) have discussed the utilization of carbon isotopic compositions as indices of petrochemical pollution in the Houston ship channel. They reported a range of about -24 to -32 o/oo for the isotopic composition of various products produced within a petrochemical plant, whereas the raw waste discharged to a stabilization pond gave a very negative value of about -40 o/oo for dissolved organic material and -32 o/oo for particulate organic carbon.

A variable settling velocity distribution for wastewater particulate (Figure III-4) implies a variable fate for such matter in the ocean.

For example, it would be expected that sediments down-current from the discharge source would contain more of the slower settling particulates as compared to those near the source. Also, if the very small particles which pass through the filter have low δC^{13} values, then it is interesting to check for any consistent trends in δC^{13} values of different settling fractions of effluent particulates. δC^{13} and carbon content analyses were performed on three different settling fractions of several 24-hour composite effluent samples: (1) total; (2) quick settleables, which settled in 2 to 3 minutes; and (3) non-settleables, which were particulates which would not settle out when centrifuged at 2000 rpm for 5 minutes. There was no definite obvious trend observed for this qualitative experiment (Figure III-5). It is possible that trends of a statistical significance would become evident in a longer term study than represented here.

III-2. Discharge of Effluent to the Ocean

It is of interest to determine the δC^{13} values of particulate matter suspended in the water column above the effluent discharge location in order to determine whether the distribution of the δC^{13} data for particulate matter conforms with the expected distribution of effluent.

The theory and design criteria pertaining to ocean outfalls has been discussed in detail by Brooks (1960, 1972). The utilization of a large number of relatively small discharge ports is incorporated to maximize dilution and to also take maximum advantage of any vertical density stratification in the ocean. The principle behind this is that if a rising buoyant turbulent plume (consisting of sewage wastewaters of

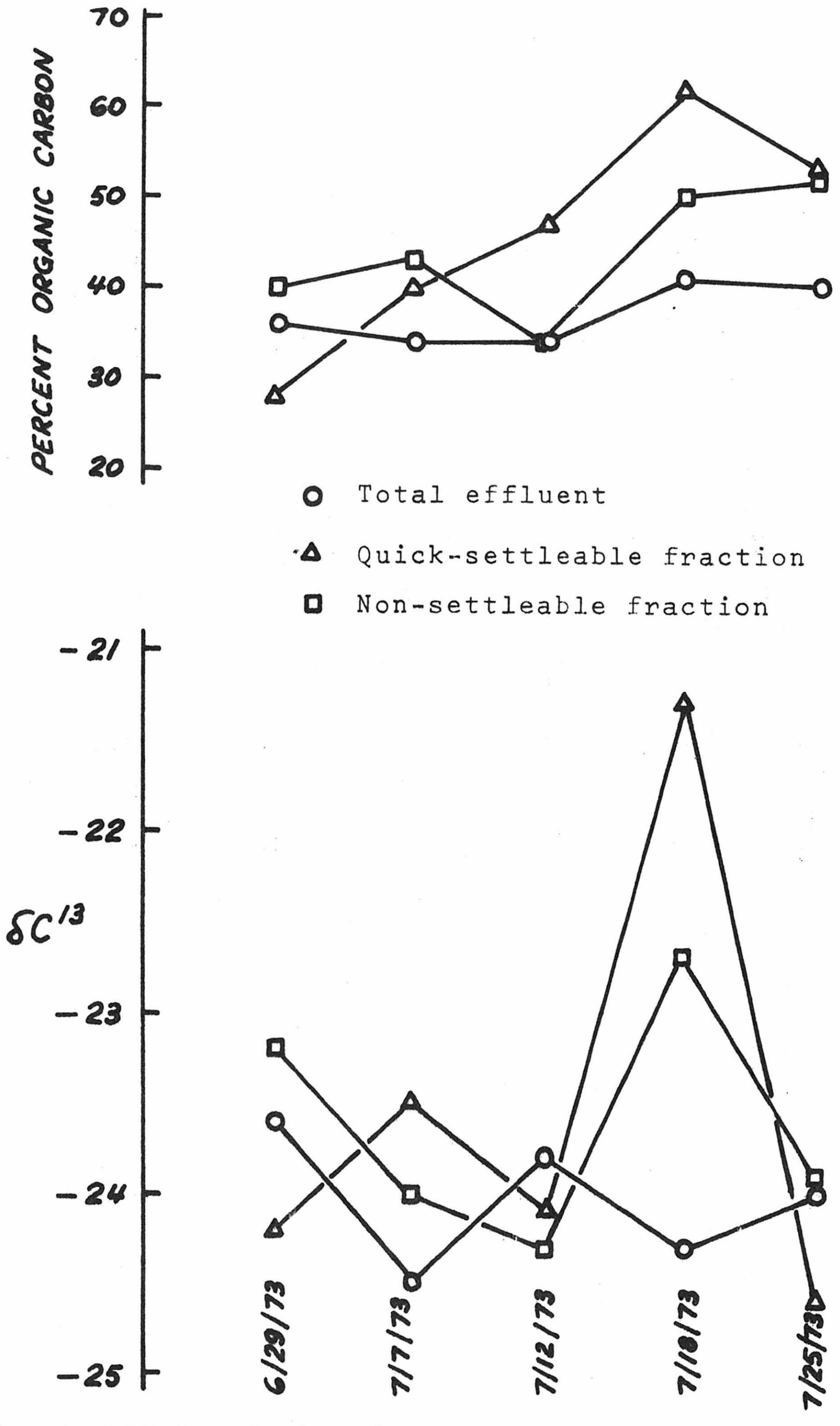

Figure III-5. Carbon isotope analyses on particulates with different settling velocities for five different 24-hour composite effluent samples.

a lower density than the surrounding sea water) becomes sufficiently diluted before reaching the ocean surface, due to the ensuing entrainment of ambient ocean water, then the waste plume will stratify into a waste field beneath the surface. The further combined effect of advective transport and eddy dispersion will enhance the dilution and transport of the waste field from the point of discharge. The fact that, in practice, the waste field is generally held beneath the surface, excepting some days during the winter when thermal stratification is nonexistent, provides both aesthetic and public health advantages.

The vertical distribution of waste material is evident in Figures III-6 and III-7 which present related data taken from a station over the 90-inch "Y" diffuser and also from a station about 3 miles south of the Y diffuser. As the data in Figures III-6 and III-7 indicate, the sewage field, as defined both by the percentage of light transmission (broad band visible spectral sensitivity) over a 1-meter path length and by the concentration (mg/l) of filtered particulates, is held beneath the thermocline. The δC^{13} data for total organic carbon also follow these trends. Both stations reflect a shift towards a higher δC^{13} composition in the surface waters. The higher δC^{13} values are undoubtedly due to the preponderant presence of marine planktonic material. The percentage organic carbon and its δC^{13} values within the waste field are somewhat unusual for this particular day. The heavier value of -22.0 o/oo and the low percentage organic carbon, as compared to the data in Table III-1, indicate that either the waste differed from what was usually present or that some complex processes were taking place within the plume. The carbon content and δC^{13} values for suspended particulates at

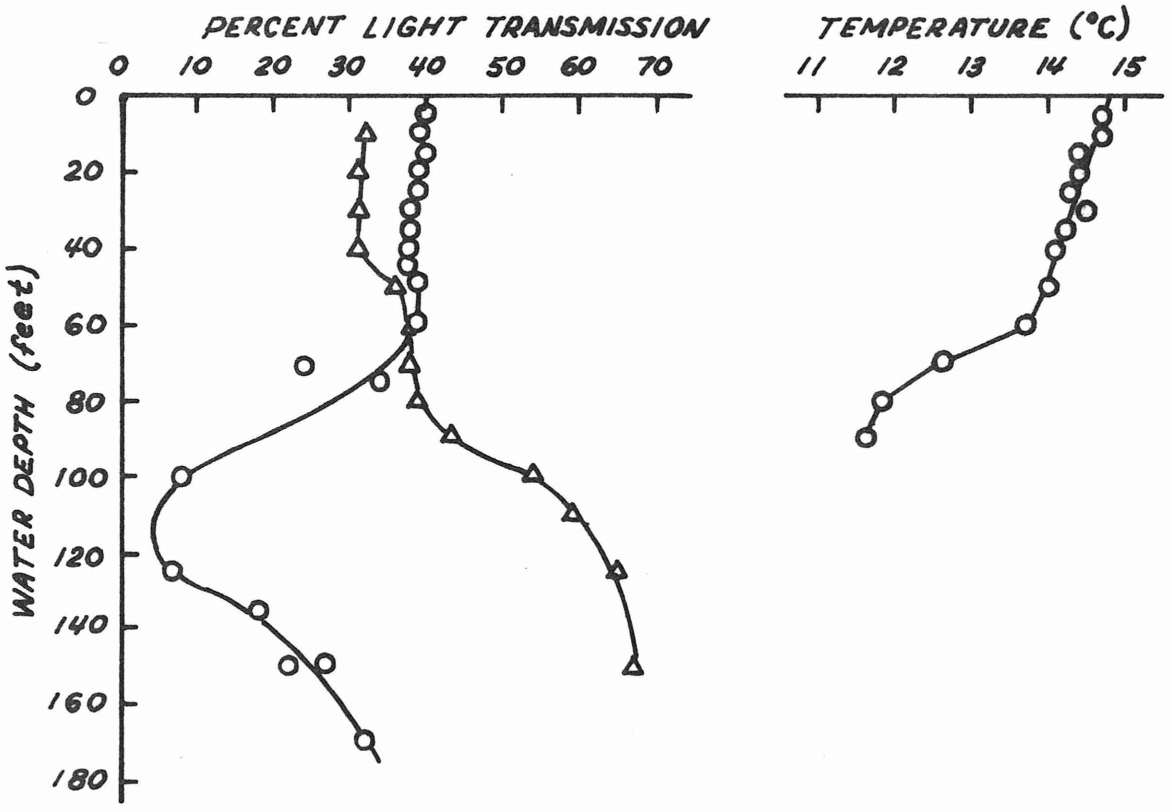

Figure III-6. Light transmission (broad band visible spectral sensitivity) and temperature in the water column at a station over the 90-inch "Y" diffuser (0) and at a station several miles offshore of this station (Δ) on 4/12/73 (Data taken by Peterson, 1974).

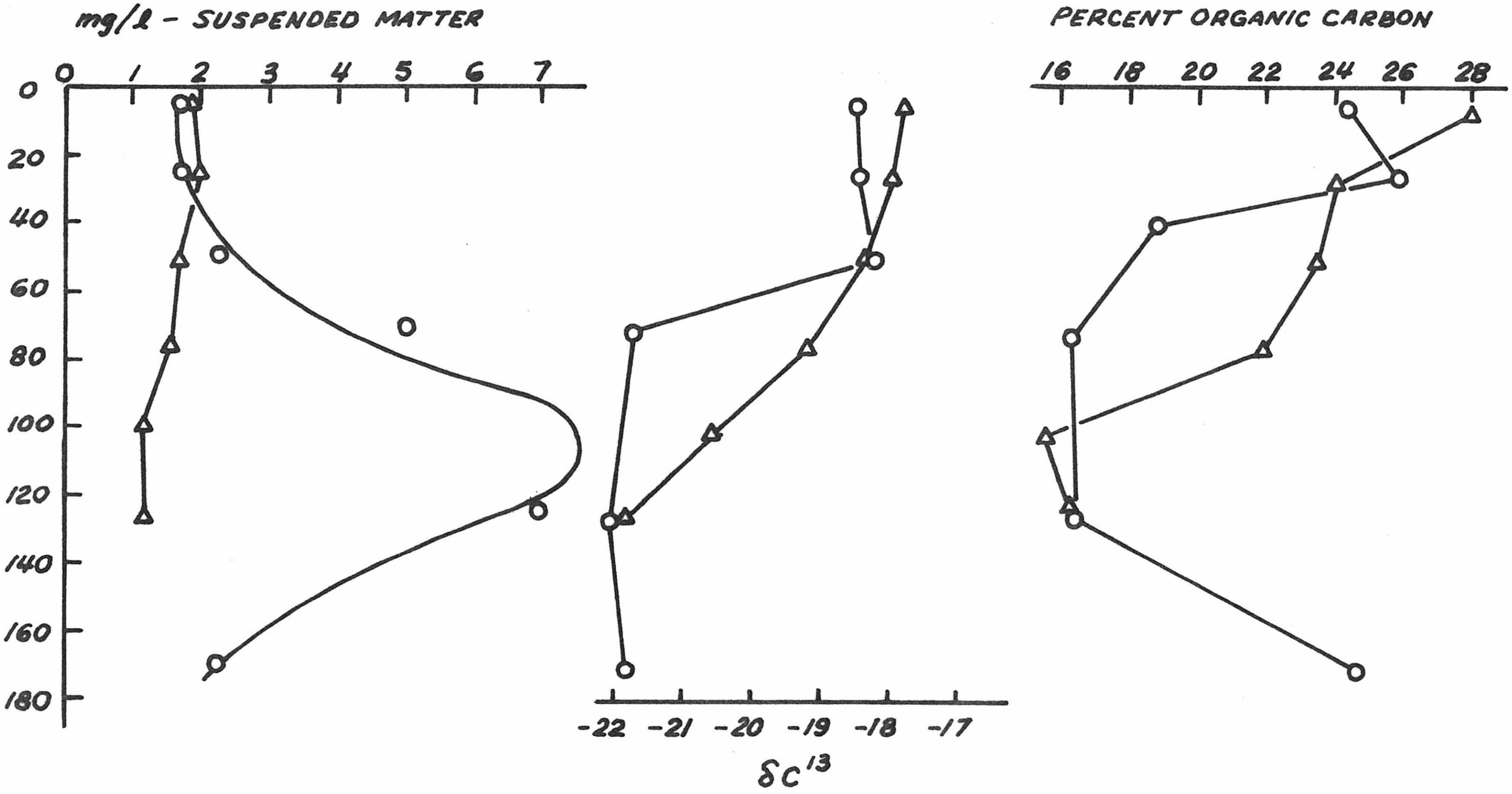

Figure III-7. The concentration of particulate matter and the isotopic composition and concentration of associated organic carbon in the water column at a station over the 90-inch "Y" diffuser (O) and at a station several miles offshore of this station (Δ) on 4/12/73.

the station south of the diffuser reflect a contribution of particulates of outfall source at the lower depths despite the low concentration of particulates. Based upon the particle size distribution of these same samples, Peterson (1974) reached the same conclusion regarding the source of the particulates in the lower portion of the water column at the southern offshore station.

III-3. Biochemical Stability of Effluent Particulates

The fate of the effluent particulates in the ocean waters and sediments is affected by the presence of bacteria. Indeed, the ultimate fate of all organic matter in the ocean is dependent upon its resistance to the decay action of aerobic and anaerobic bacteria. Deuser (1971) defined an organic carbon budget for the Black Sea and estimated that between 85 per cent and 95 per cent of the organic carbon input is recycled aerobically in the top 200 meters of the sea. Vertical profile data for both particulate and dissolved organic carbon in the tropical Pacific and Atlantic Oceans have been shown by Menzel (1967) to possess a uniformity in their concentrations below a depth of about 100 - 300 meters. Menzel concluded that surface organic matter must either enter solution or be remineralized within a short distance of the surface. Based upon decomposition experiments, Menzel and Goering (1966) further postulated that these deep-water particulates are uniformly resistant to degradation and therefore represent refractory detritus. Skopintsev (1950) estimates the decomposition of unstable planktonic organic material to take place between 5 to 9 and 112 days (Bordovsky, 1965). The presence of suitable bacterial populations within the marine environment is therefore seen to result in an efficient decomposition of labile organic material.

In considering the fate of waste discharged particulate organic material associated with the discharged effluent, it is a necessity to account for the degradability of this material within the oceanic environment. Several decomposition experiments were therefore performed in an attempt to characterize the potential for decay of these particulates. The first experiment was based upon the decomposition technique used by Menzel and Goering (1966), and consisted of filtering the particulates from 25-ml subsamples of a 24-hour composite non-chlorinated effluent sample over Whatman GF-C precombusted glass fiber filters. The filters were then placed in sterile plastic petri dishes along with an approximate 10 ml of 0.2-micron filtered sea water and allowed to sit in darkness to decompose for various periods of time at three different constant temperatures ($2^{o}C$, $17^{o}C$, and $35^{o}C$). These three different temperatures were utilized to determine the effect of temperature on the rate of decomposition. The experiment was carried out for 78 days. The results are presented in Table III-2 and Figure III-8.

Although there is considerable scatter in the data, a temperature dependent decay is indicated. The data for these two effluent samples indicate that about 35 per cent of the initial organic carbon is easily decomposed. There is a small trend towards C^{13} depletion as decay progresses, indicating that carbon-13 enriched compounds may be preferentially degraded.

The second decomposition experiment consisted of using aero-

Table III-2 . Decay of Particulate Organic Carbon from 24-hour Composite Effluent Sample. Samples were Filtered onto Whatman GF/C Glass Fiber Filters and Allowed to Decay Utilizing the Technique of Menzel and Goering (1966).

Temperature	Time	Percent Organic Carbon	f(t)*	δC^{13}
35°C	0 days	35.7	1.00	-22.7
	7	23.3	.65	-23.3
	16	22.9	.64	-23.4
	42	23.3	.65	-23.6
	78	25.1	.70	-24.1
17°C	0	35.7	1.00	-22.7
	7	27.9	.78	-22.9
	16	25.8	.72	-23.2
	42	22.6	.63	-23.4
	78	23.7	.66	-23.9
4°C	0	35.7	1.00	-22.7
	7	31.9	0.89	-22.9
	16	32.2	0.90	-23.1
	42	29.6	0.84	-23.3
	78	27.3	0.77	-23.3

$$^{*}f(t) = \frac{\text{\% organic carbon at time } t}{\text{\% organic carbon at time } 0}$$

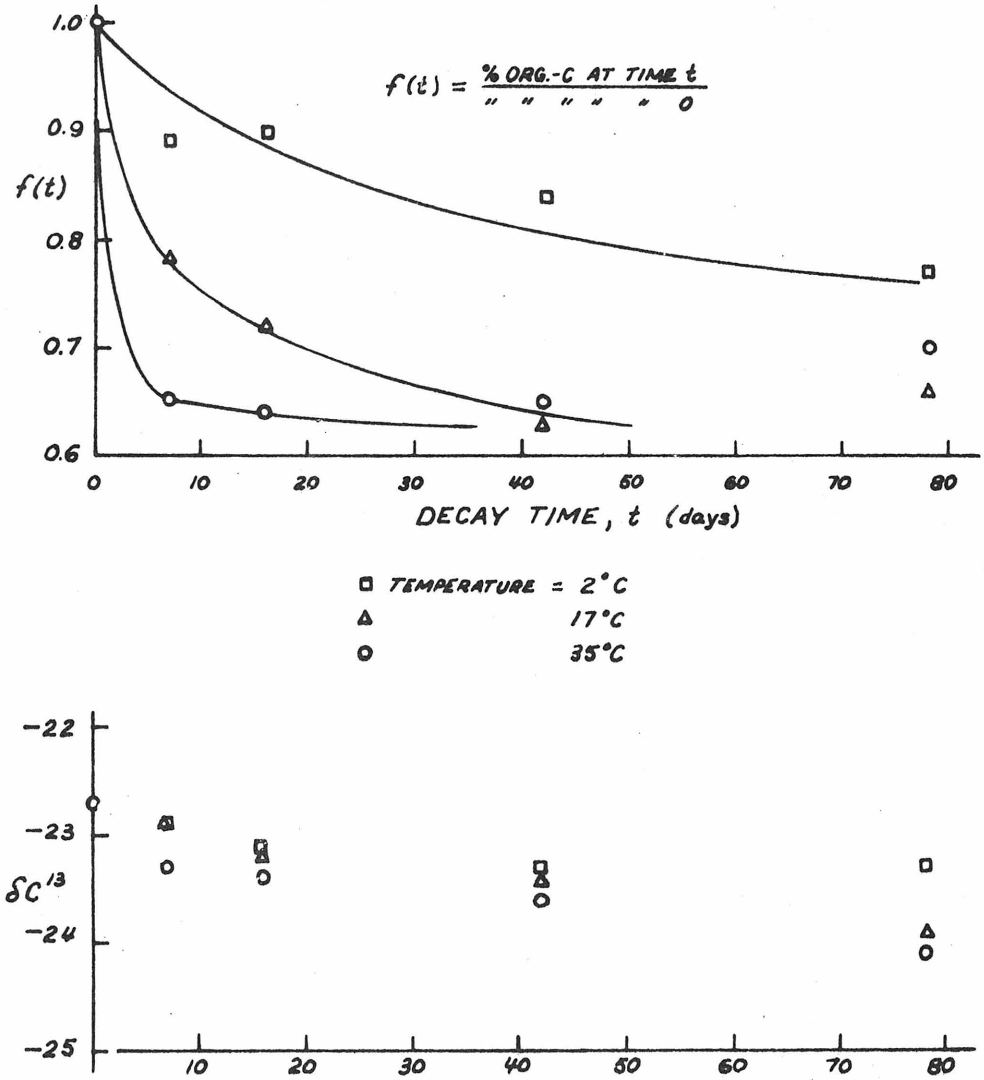

Figure III-8. Decay of particulate organic carbon from a 24-hour composite effluent sample. Samples were filtered onto Whatman GF/C glass fiber filters and allowed to decay utilizing the technique of Menzel and Goering (1966).

bic and anaerobic digestion bottles (4 liter capacity), both of which were thoroughly taped with black electrical tape and kept in a darkened constant-temperature room at 17°C. The usual procedures of passing cleansed water-saturated air through a solution were used with the aerobic digestion bottle. The anaerobic digester bottle was simply sealed off to prevent the entrance of oxygen and allowed to proceed to anaerobic conditions by using up what little oxygen was present. Both bottles had sample draw-off tubes at their base. To each digester was added 2000 ml of a 24-hour composite effluent sample and 2000 ml of unfiltered sea water obtained from the shoreline of Whites Point. Due to the availability of a limited amount of effluent, two different 24-hour composite non-chlorinated effluent samples were used in the two digesters. The data for the starting materials of sea water and effluent are as follows.

Sample	mg/l	% Organic Carbon	δC^{13}
sea water	4.5	9.4	-20.6
effluent (for aerobic experiment)	328	36, 36	-23.0, -22.9
effluent (for anaerobic experiment)	324	33, 28	-23.7, -23.5

The decay data and corresponding isotopic compositions are presented in Table III-3 and Figure III-9. The data indicate that decay of the residual effluent for the anaerobic case is negligible for a 14-day time period. The aerobic decay data are similar to those of the first decomposition experiment and indicate a relatively quick loss of labile organic material with time. It appears that approximately 30 to 40 per cent of the particulate organic carbon in this effluent sample is

Table III-3 . Decay of Particulate Organic Carbon from a 24-hour Composite Effluent Sample. Two Different Effluent Samples were Used, as Noted by the δC^{13} at Time Zero, and were Diluted 1:1 with Unfiltered Sea Water and Placed in an Aerobic Digester and in an Anaerobic Digester at a Temperature of 17°C.

AEROBIC CONDITIONS

Temperature	Time	Percent Organic Carbon	f(t)*	δC^{13}
17°C	0 days	35.8,36.0	1.00	-22.9,-23.0
	2	32.2	0.90	-23.4
	4	30.3	0.83	-23.0
	6	26.3	0.73	-23.7
	9	24.2	0.67	-23.7
	11	27.1	0.75	-23.3
	14	26.7	0.74	-23.2
	20	25.8	0.72	-23.5

ANAEROBIC CONDITIONS

Temperature	Time	Percent Organic Carbon	f(t)*	δC^{13}
17°C	0	32.8	1.00	-23.7,-23.5
	1	27.7	0.84	-23.5
	3	34.2	1.04	-23.9
	5	34.4	1.04	-23.1
	8	34.4	1.04	-23.4
	14	34.8	1.05	-24.2

$$^{*}f(t) = \frac{\%\text{ organic carbon at time } t}{\%\text{ organic carbon at time } 0}$$

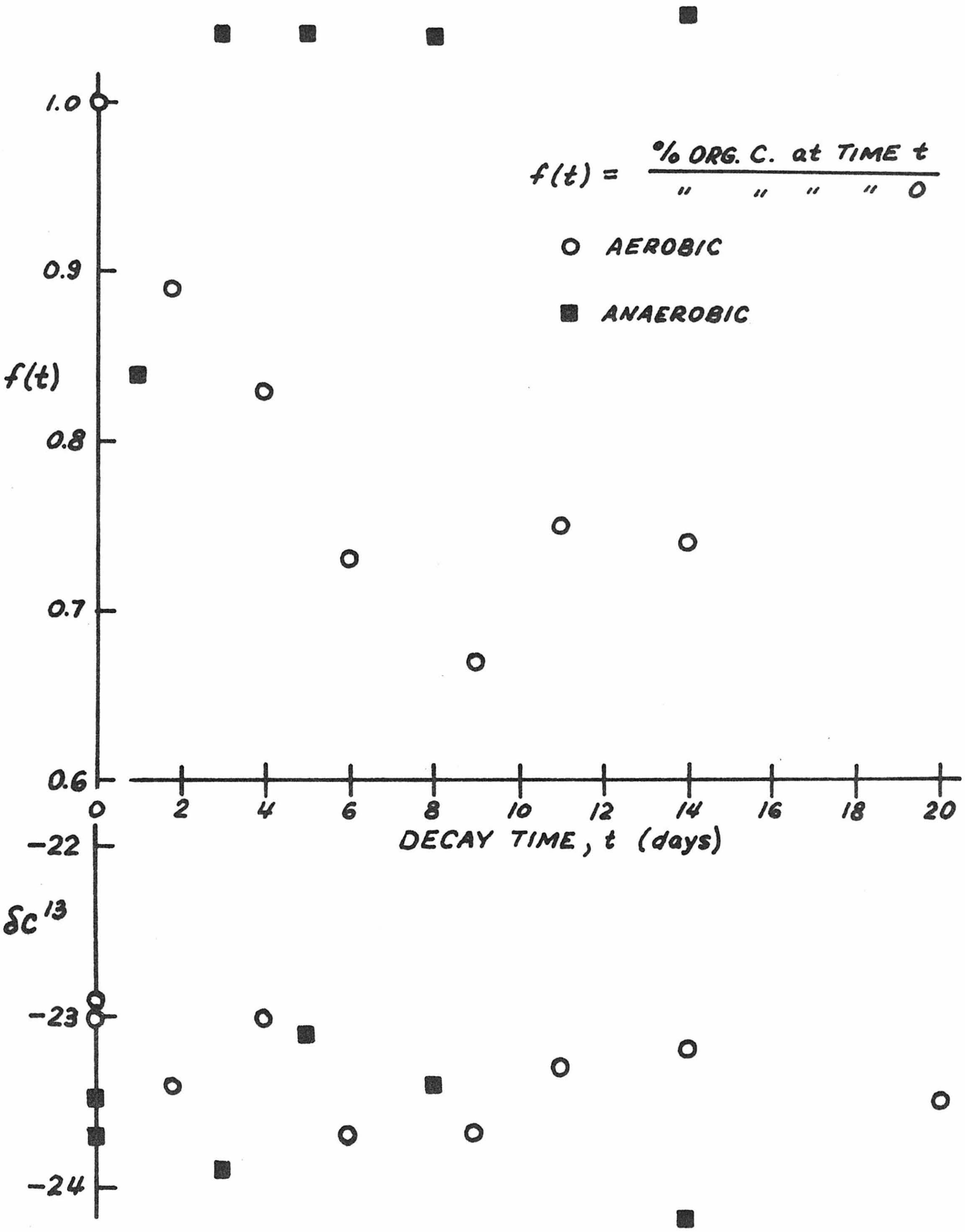

Figure III-9. Decay of particulate organic carbon from a 24-hour composite effluent sample. Two different effluent samples were used, as noted by δC^{13} at time zero, and were diluted 1:1 with unfiltered sea water and placed in an aerobic digester and in an anaerobic digester at a temperature of 17°C.

readily decomposed. Although there appears to be a lowering in the δC^{13} with loss of organic material, the isotopic data are too few and scattered to be certain of any definite trends.

The third decomposition experiment was similar to the previous one and consisted of mixing 2 liters of effluent with 2 liters of rough-filtered (sintered glass) sea water. This time, seventy grams of NaCl were added to bring the salinity of the total solution to approximately 30 o/oo. Initial carbon concentrations and δC^{13} analyses were not performed on the sea water due to the obviously dominant presence of the effluent solids. Carbon yields and the corresponding isotopic data are given in Table III-4 and Figure III-10. The particulate organic carbon data for the aerobic case indicate an approximate loss of 22 per cent of the initial carbon within 74 days. The decay of effluent particulate organic carbon for the anaerobic case shows only a slight decay over the total period of 74 days. The isotopic data show a shift towards a carbon-13 depletion at about five days in both cases. The fact that anaerobic conditions result in a very slow decay further suggests that the C^{13} depletion within several days is not due solely to a decay effect. Since the dissolved organic carbon is more depleted in C^{13} than the particulate material (Table III-1), it is suggested that such a C^{13} depletion as indicated in the decay data may be due to an interaction between particulate and dissolved organic matter such as surface adsorption or the flocculation of very fine particulates at a higher ionic strength (represented by a saline environment) than exists in the discharged effluent. A discussion of such processes can be found in the works of Postma (1967a, 1967b). However, the pos-

Table III-4 . Decay of Particulate Organic Carbon from a 24-hour Composite Effluent Sample. Effluent was Diluted 1:1 with Sinter-glass Filtered Sea Water and the Salinity Adjusted to 35% by the Addition of NaCl. Portions of this Solution were then Placed in an Aerobic and an Anaerobic Digester at a Temperature of 17°C.

AEROBIC CONDITIONS

Temperature	Time	Percent Organic Carbon	f(t)*	δC^{13}
17°C	0 days	32.5, 32.5	1.0	-24.0,-23.4
	3	30.9, 32.2		-23.6,-23.8
	7	30.2, 30.7		-24.2,-24.1
	17	27.7, 27.1		-23.9,-24.0
	34	16.1, 27.2		-24.5,-24.2
	74	26.2, 25.0		-24.8,-24.4

ANAEROBIC CONDITIONS

Temperature	Time	Percent Organic Carbon	f(t)*	δC^{13}
17°C	0	30.9, 27.5		-23.9,-23.6
	3	35.3, 32.1		-23.9,-24.5
	7	32.9, 32.0		-24.5,-24.5
	17	23.6, 28.7		-24.1,-24.5
	34	32.9, 32.9		-24.4,-24.6
	74	30.4, 28.4		-24.5,-24.5

$$^{*}f(t) = \frac{\%\text{ organic carbon at time } t}{\%\text{ organic carbon at time } 0}$$

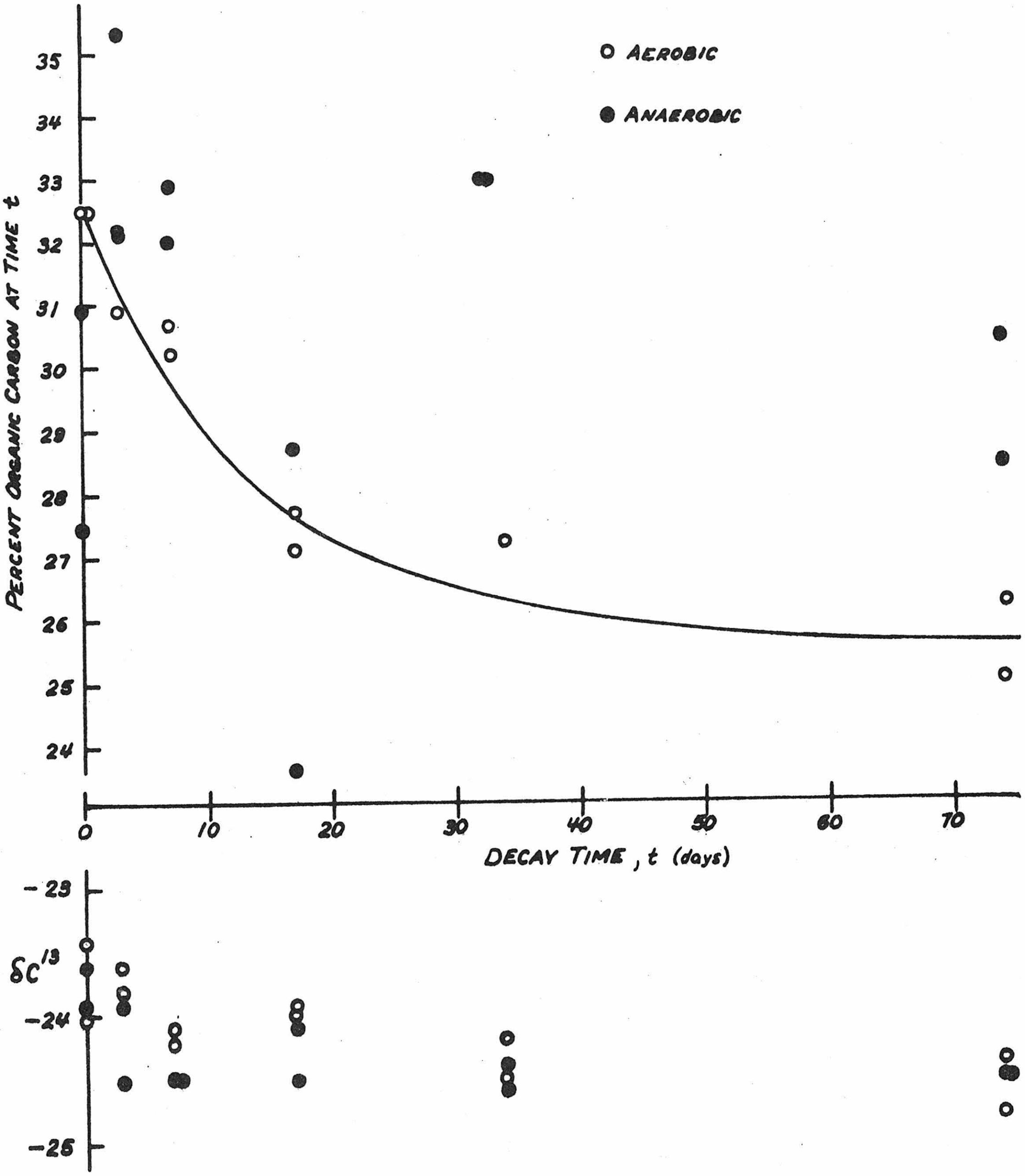

Figure III-10. Decay of particulate organic carbon from a 24-hour composite effluent sample. Effluent was diluted 1:1 with sinter-glass-filtered sea water and the salinity was adjusted to 35% by addition of NaCl. Portions of this solution were then placed in an aerobic and in an anaerobic digester at a temperature of 17°C.

sible role of such processes in lowering the δC^{13} of particulate organic carbon does not rule out a fractionation due to the decay process itself as suggested by the first decay experiment.

In an attempt to simulate natural oceanic conditions as near as possible, a fourth decomposition experiment was performed within the marine environment. Subsamples of a 24-hour non-chlorinated effluent sample were pipetted to Pyrex containers of a special design shown in Figure III-11. These thick-walled containers had both an open and a closed end. Two precombusted and washed Whatman GF-C glass fiber filters were placed over the open end and held in place by an open end-piece which was secured snugly with monofilament nylon line. The outer surface of these containers was then covered with black vinyl plastic electrical tape to prevent the possibility of photosynthesis within the vials. The vials, along with blanks containing triple-distilled water, were placed within a nylon mesh bag and suspended approximately five feet above the ocean bottom at a water depth of 30 feet offshore of Corona del Mar, California. The water temperature was approximately 17°C. The containers were then retrieved at various time periods. The rationale behind this design was that the glass fiber filters would contain the particulates while allowing the diffusive transport of dissolved constituents. The data for this experiment are given in Table III-5 and shown in Figure III-12. As the data show, initial samples which were quite enriched in particulate organic carbon (41.2 per cent organic carbon) show a relatively rapid decay of this carbon within the marine environment. The blanks were analyzed to check if there was any fine marine par-

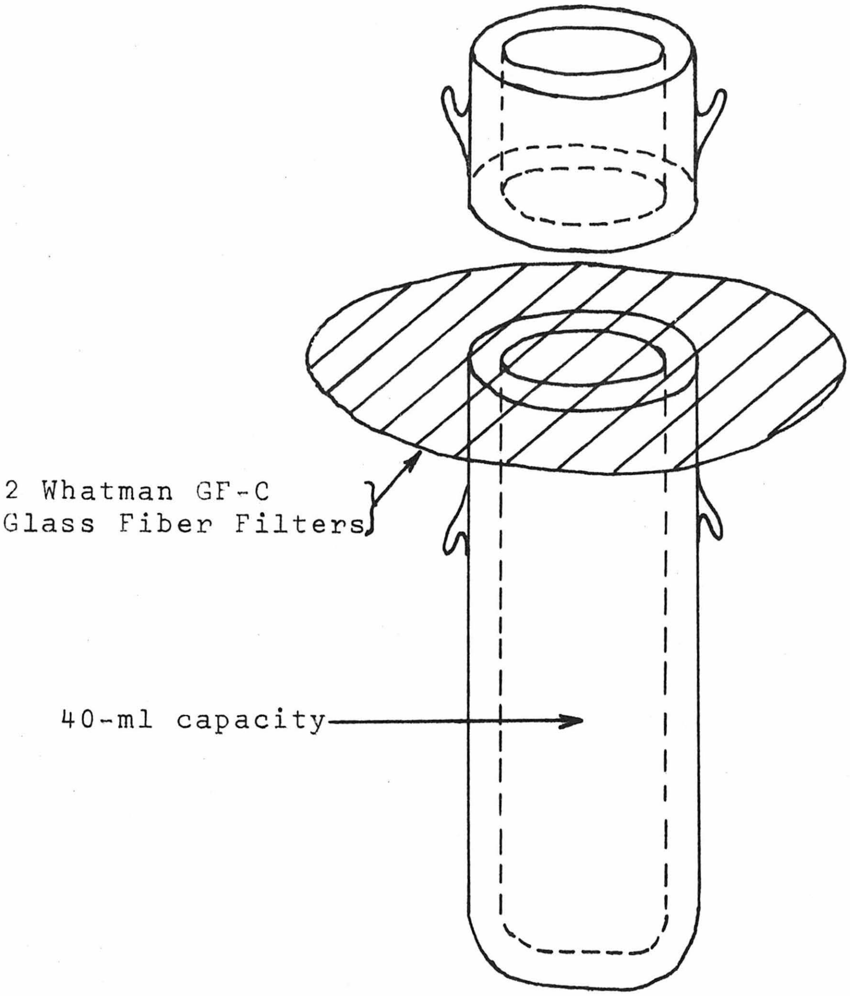

Figure III-11. Illustration of Pyrex decay vials used in a 42-day ocean decay experiment of effluent particulate organic carbon.

Table III-5 . Decay of Particulate Organic Carbon from a 24-hour Composite Effluent Sample in an Ocean Environment at a Temperature of 17°C.

Temperature	Time	Percent Organic Carbon	f(t)*	δC^{13}
17°C	0 days	41.2	1.00	-24.3
	14	36.0	.88	-24.7
	28	34.1	.83	-24.8
	42	30.9	.75	-25.7

$$^{*}f(t) = \frac{\text{\% organic carbon at time } t}{\text{\% organic carbon at time } 0}$$

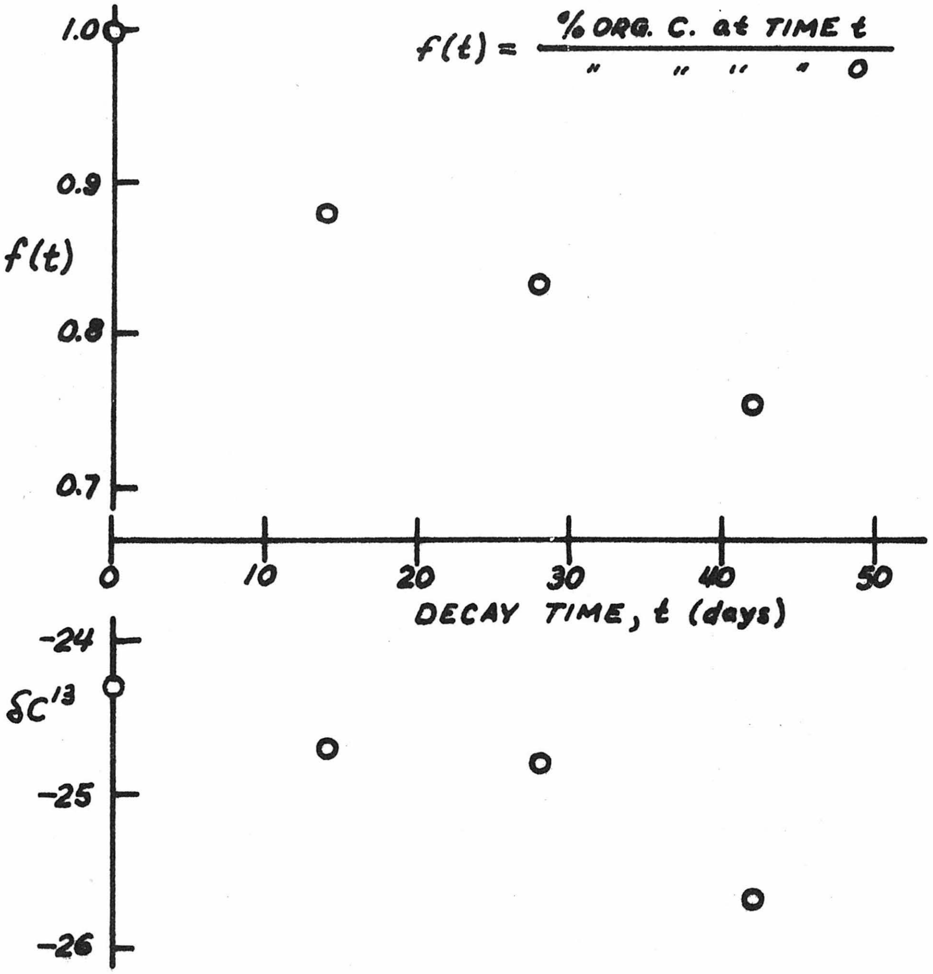

Figure III-12 . Decay of particulate organic carbon in an ocean environment at a temperature of 17°C.

ticulate carbon managing to pass through the containing filters which could later be filtered by a fresh filter of the same type. All blanks indicated non-detectable yields. In regard to this ocean experiment, the shift in the isotopic composition with time is in the same direction (depletion of C^{13}) as noted in the previous experiments.

Effluent sample solutions, such as the ones used in the previous experiments, are typically turbid even after sitting for a long period of time. It was therefore interesting to observe that all of the retrieved containers of the latter experiment contained a flocculent mass at the bottom of the container with a clear supernatant. It appeared that the diffusion of ocean salts into the containers resulted in the flocculation of effluent particulates. Since such a process can result in the further inclusion of dissolved organic matter (of a more negative δC^{13}) with the particulate state, it is difficult to separate the relative role of such processes in producing a more negative δC^{13} from those due to decay effects alone.

To summarize the decay experiments, these data indicate that effluent particulates are undoubtedly subject to further decay within aerobic marine waters. The bacterial decay processes in the foregoing experiments indicated a reduction in the initial percentage of organic carbon content from a typical value of 30 to 35 per cent to a value of about 20 to 25 per cent. An accompanying C^{13} depletion of the residual carbon is also indicated and can be explained in at least two ways: (1) flocculation and adsorption of dissolved organic matter more depleted in C^{12}, and (2) preferential decay of C^{13}-enriched fractions. A depletion in the C^{13} content of waste particulates discharged to the ocean is also observed in the sedimentary data to be presented in Chapter IV. It is for this reason that the above decay experiments are particularly relevant.

It is desirable to quantify the effluent particulate organic carbon decay rates which have been presented in order to account for the fate of such material upon discharge to the ocean. Olsen (1963) has treated a similar system by describing the balance between the amount of organic material entering an ecological system and the amount retained as governed by a first-order decay rate for losses from the system. Skopintsev (1966) has used the same approach to determine the age of deep-water organic material. Through laboratory experiments designed to simulate natural conditions, Foree and McCarty (1970) investigated the rates and mechanisms for the anaerobic decomposition of algae. The degree of degradation was evaluated on the basis of chemical oxygen demand. The majority of cultures used in this latter experiment showed the rate of decay of particulate algal matter could be accurately represented in terms of first-order decay kinetics, as follows:

$$M = (M_o - fM_o)e^{-kt} + fM_o \qquad (3.1)$$

where M = particulate chemical oxygen demand concentration,

M_o = M at time $t = 0$,

f = refractory organic fraction,

t = time (days),

k = first-order decay constant (day^{-1}) .

The experimental decay data for 16 cultures showed a mean k of .022/day and a range of .011 - .032/day at 25°C. Jewell and

McCarty (1968) found a similar range of 0.01 - 0.06/day for the aerobic decomposition of algae.

If the decay of sewage particulate carbon can be described by first-order kinetics, then we can represent the decay as

$$f(t) = f_R + (1-f_R)e^{-kt} \qquad (3.2)$$

where $f(t)$ = fraction of organic carbon remaining at time t,

f_R = refractory fraction of organic carbon,

k = first-order decay constant

or

$$\frac{df(t)}{dt} = -(1-f_R)ke^{-kt} \qquad (3.3)$$

and

$$\left.\frac{df(t)}{dt}\right|_{t=0} = -(1-f_R)k \ . \qquad (3.4)$$

Despite the scatter, the aerobic decay data presented in Figure III-10 appear to follow an approximate first-order decay rate when plotted as shown in Figure III-13. This is a plot of $(f(t)-f_R)/(1-f_R)$ versus time which was computed for these data assuming f_R to be 0.77.

The aerobic decay data (at 17°C) shown in Figures III-8, 9, 10, and 12 have been summarized in Figure III-14 in order to indicate a probable range of decay rates for effluent particulate organic carbon. These data reveal a variable susceptibility towards decay from sample to sample. Those samples which indicated a faster decay rate also tended to be of a lower refractory fraction, f_R. Based on these experiments, upper and lower limits of decay have been indicated and the derivative of these two limits at time zero has also been approxi-

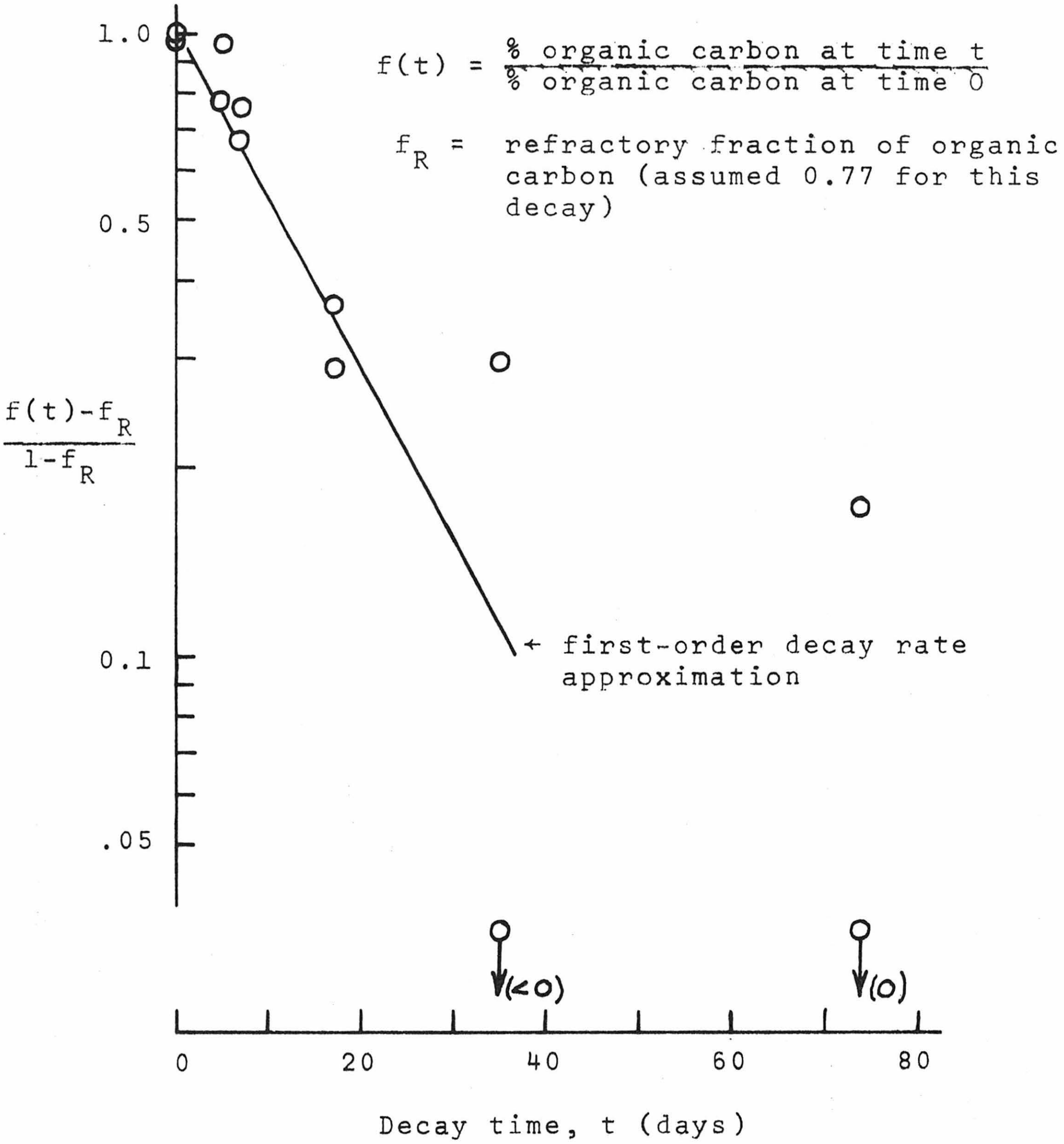

Figure III-13. First order decay rate approximation to the data of Table III-4 and Figure III-10. Temperature = 17°C.

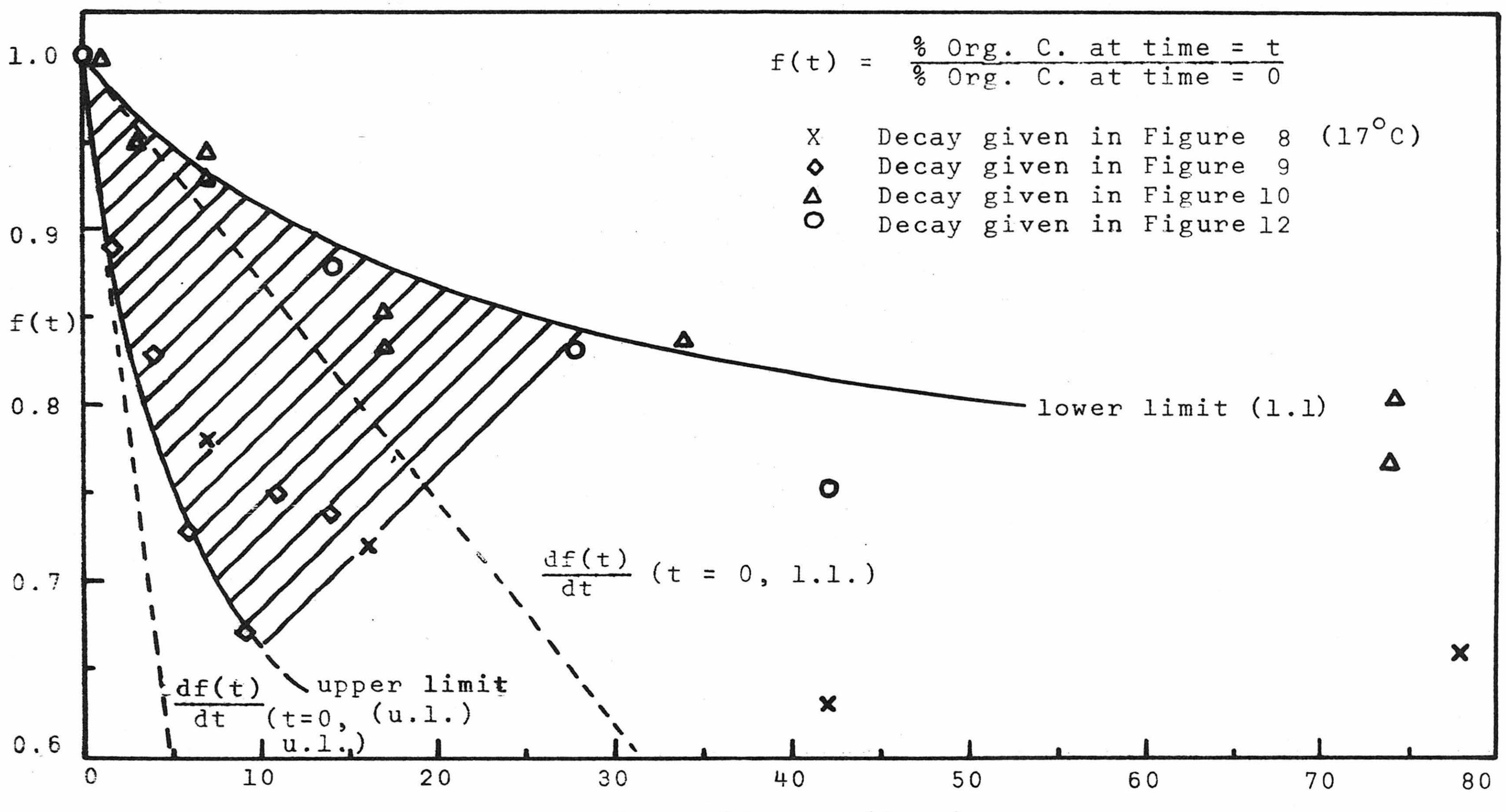

Figure III-14. A summary of the decay data presented in Figures 8 , 9 , 10 , and 12 for a temperature of 17°C. Approximate upper and lower limits of decay and the corresponding $df(t)/dt$ at $t = 0$ are indicated.

mated to indicate a probable range for the term $(1-f_R)k$. By further assuming refractory carbon values, an estimated decay rate (k) range can be calculated (Equation 3.4). For the two limits indicated in Figure III-14, the results of these calculations are as follows.

Decay Limit	Approximate $\frac{df(t)}{dt}$ (t=0)	Approximate f_R	Estimated k
upper	-0.088/day	0.60	0.22/day
lower	-0.013/day	0.75	0.05/day

The data therefore suggest an approximate decay constant of 0.05 to 0.22 per day.

Water Resources Engineers (1965) also used such a first-order decay rate to predict the fate of sludge discharge offshore of Point Loma in San Diego. Although they gave no justification for the selection of a k value of about 0.01 per day, they did feel that a probable range was 0.005 to 0.05 per day. The lower limit k value (estimated above) is seen to be consistent with this; however, the upper limit value suggests that some particulate organic carbon may be more quickly decayed.

It is of interest to compute an upper limit for the time needed to stabilize 95 per cent of the particulate carbon discharged to the ocean. Assuming a k = 0.05 per day, such a calculation (Equation 3.2) gives $t_{95} = 60$ days. Therefore, a relatively short time period is suggested for the stabilization of particulate organic carbon discharged to the marine environment.

III-4. Marine Sources of Organic Matter

Since the purpose of this thesis is to understand the extent of the input of effluent particulate matter to the ocean sediments offshore of Whites Point, as determined by carbon isotopic and total concentration measurements, it is then also important to describe the carbon content of inputs due to various marine sources.

A number of plankton trawls were made over a period of time at several different locations in order to define the range in isotopic composition of the most productive source of organic material (Emery, 1960) in shallow oceanic waters. These data are presented in Table III-6. Based on the samples analyzed, the δC^{13} of plankton is represented by a narrow range of -19.9 o/oo to -22.6 o/oo.

Isotopic data were also determined on the particulates within a number of ocean water samples, in addition to those presented in Figure III-7. These data are presented in Table III-7 and are somewhat variable. The low δC^{13} values of the particulates collected offshore of Dana Point (see Figure I-1) most likely reflect a source of organic material entrained by nearshore turbulence from the sediments. Sediments along a transect extending offshore from Dana Point were also sampled and gave the results also tabulated in Table III-7. For these Dana Point samples, it is evident that particulates in the lower part of the water column reflect an isotopic composition similar to the bottom sediments. The depletion of C^{13} in these sediments reflects a terrestrial source of organic material which is undoubtedly due to the presence of the nearby San Juan Creek, which handles the drainage from a large watershed. It should also be noted

Table III-6. Carbon Isotopic Data for Various Plankton Trawls Made in Southern California Ocean Waters

Location-Plankton Trawl Made Off-shore of:	Date	Percent Organic Carbon		δC^{13}
Point Vicente	12/19/72	Not determined		-21.9
Point Fermin	12/19/72	Not determined		-20.0 (-24.6 lipid)
Point Fermin	2/20/73	(a)	45	-19.9
		(b)	41	-20.1
		(d)	40	-20.1
Whites Point (far offshore)	3/11/73	(a)	49	-20.4
		(b)	49	-20.6
Whites Point (far offshore)	3/29/73	(a)	55	-21.2
		(b)	54	-20.7
Dana Point	5/15/73		43	-21.6
Santa Barbara Isl. (over bank north of)	7/5/73		30	-22.6
Corona Del Mar	8/4/73		34	-21.4,-21.6 (filter divided)
Summary	Mean		44	- 20.9
	Variance		8	0.8

Table III-7. δC^{13} Values for Particulate Organic Carbon in Various Ocean Water Samples.

Sample location	Date	mg/l	Percent Organic Carbon	δC^{13}
Shoreline of Whites Point	5/11/73	4.5	9	-20.6
Offshore of Dana Point* at a water depth	5/15/73			
= 5 feet		1.9	8	-21.9
= 25 "		2.1	7	-23.3
= 50 "		1.7	13	-22.7
= 75 "		1.5	--	--
= 100 "		1.7	6	-25.5
= 125 "		0.8	9	-23.1
= 140 "		2.0	5	-24.0
Shoreline of Cypress Point	6/11/73	1.5	8	-19.8
Shoreline of Whalers Cove		7.4	2	-19.7
Shoreline at San Simeon		15.7	8	-19.6
Over bank north of Santa Barbara Island	7/5/73	1.0	8	-23.1

* Organic carbon concentrations and δC^{13} values for sediments offshore of Dana Point are as follows:

Water Depth, ft.	Percent Organic Carbon	δC^{13}
75	0.3	-23.2
100	0.5	-24.4
150	0.7	-24.3
200	1.1	-24.5
250	1.1	-25.1
300	0.9	-25.4

that an observed extreme clarity of the water column offshore of Dana Point on this particular day and the low percentage of particulate organic carbon indicated very little biological activity.

The particulates from the surface water sample taken over the bank just north of Santa Barbara Island were somewhat lighter (-23.1 o/oo) than one might expect. However, the plankton sample collected at this station (Table III-6) was also somewhat lighter than was usually encountered. In connection with this, it should also be mentioned that concentrations of DDT in the soft tissue of the mussel Mytilus californianus (SCCWRP, 1973) indicate that long-term transport of the waste field may be in the direction of Santa Barbara Island. If such is the case, this could have an effect on the isotopic composition of particles in these waters.

The data reported for particulates in the upper part of the water column at Whites Point, the data from the Whites Point shoreline, and those data from shorelines north of Los Angeles (Cypress Point, Whalers Cove, and San Simeon) tend to indicate that a typical marine value for filtered particulates from nearshore oceanic waters would be about -19 o/oo to -20 o/oo. This is quite consistent with the data reported for plankton.

Since attached benthic plants probably account for the second largest source of marine organic material in nearshore areas (Emery, 1960), a number of samples of benthic algae from several locations were analyzed for their isotopic composition (Table III-8). Several points of interest are noteworthy regarding these data. First of all, it is seen that the range in isotopic compositions of benthic algae is quite

Table III-8. δC^{13} for Benthic Algae Collected from Shallow Southern California Ocean Waters.

Species*	Location	Percent Organic Carbon	δC^{13}
Cystoseira osmundacea (P)	Abalone Cove (Palos Verdes)	30	-17.4
Dictyota flabellata (P)	" "	28	-20.9
Macrocystis pyrifera (P)	" "	24	-14.2
Dictyota flabellata (P)	Corona Del Mar	30	-20.8
Eisenia arborea (P)	" " "	30	-19.4
Egregia laevigata (P)	" " "	28	-18.9
Hesperophycus harveyanus(P)	" " "	35	-22.8
Macrocystis pyrifera (P)	" " "	30	-15.0
Rhodymenia californica (R)	" " "	25	-22.0
Colpomenia (C)	Catalina Is.	26	-12.6
Cystoseira osmundacea (P)	"	--	-16.3
Gelidium sp. (R)	"	37	-17.6
Plocamium pacificum (R)-a	"	29	-32.4
Plocamium pacificum (R)-b	"	31	-32.4
Sargassum sp. (C)	"	27	-16.4

*Parentheses denote phylum; C = Chlorophyta, P = Phaeophyta, R = Rhodophyta variable. Secondly, δC^{13} values for the same species from different localities are approximately the same; and thirdly, the isotopic composition for the major species found along the local coast has a significantly higher δC^{13} value than the δC^{13} value of sewage effluent particulate organic carbon. A low δC^{13} value of particulates in the vicinity of Whites Point should therefore characterize them as having been discharged from the sewage outfall.

IV. SEDIMENTARY CHARACTERISTICS OF THE PALOS VERDES SHELF AS ALTERED BY THE WHITES POINT SEWAGE DISCHARGE

In order to discuss the effects of waste discharge on the sedimentary characteristics of the Palos Verdes Shelf, it is relevant to briefly mention the physiographic and hydrodynamic characteristics of this area. It is reasonable to assume that these characteristics, among others, will affect the sedimentary distribution of particulate organic matter discharged from the outfall.

IV-1 The Palos Verdes Shelf

The Palos Verdes coastline and sample locations for which data are reported are shown in Figure IV-1. Also shown in this figure is the present-day spatial occurrence of anaerobic sediments as estimated by the Southern California Coastal Water Research Project (SCCWRP, 1972). The Palos Verdes Shelf is an eroded rock platform lying about 220 to 290 feet below sea level which is unconformably overlain by about 50 feet of layered sediments, which in turn are covered by about 40 feet of unbedded homogeneous deposits (Uchupi and Gaal, 1963). The shelf is of a variable width ranging from one mile in width offshore of Pt. Vicente to five miles offshore of Palos Verdes Point. In general, the shelf has a slope of about $1^{o}42'$. The break in the shelf occurs at a water depth of 350 to 300 feet, where the slope steepens to about 14^{o}. The presence of raised, marine terraces on the Palos Verdes peninsula provides evidence to the fact that this area is an emerging one, i. e., has emerged from the ocean over geologic time.

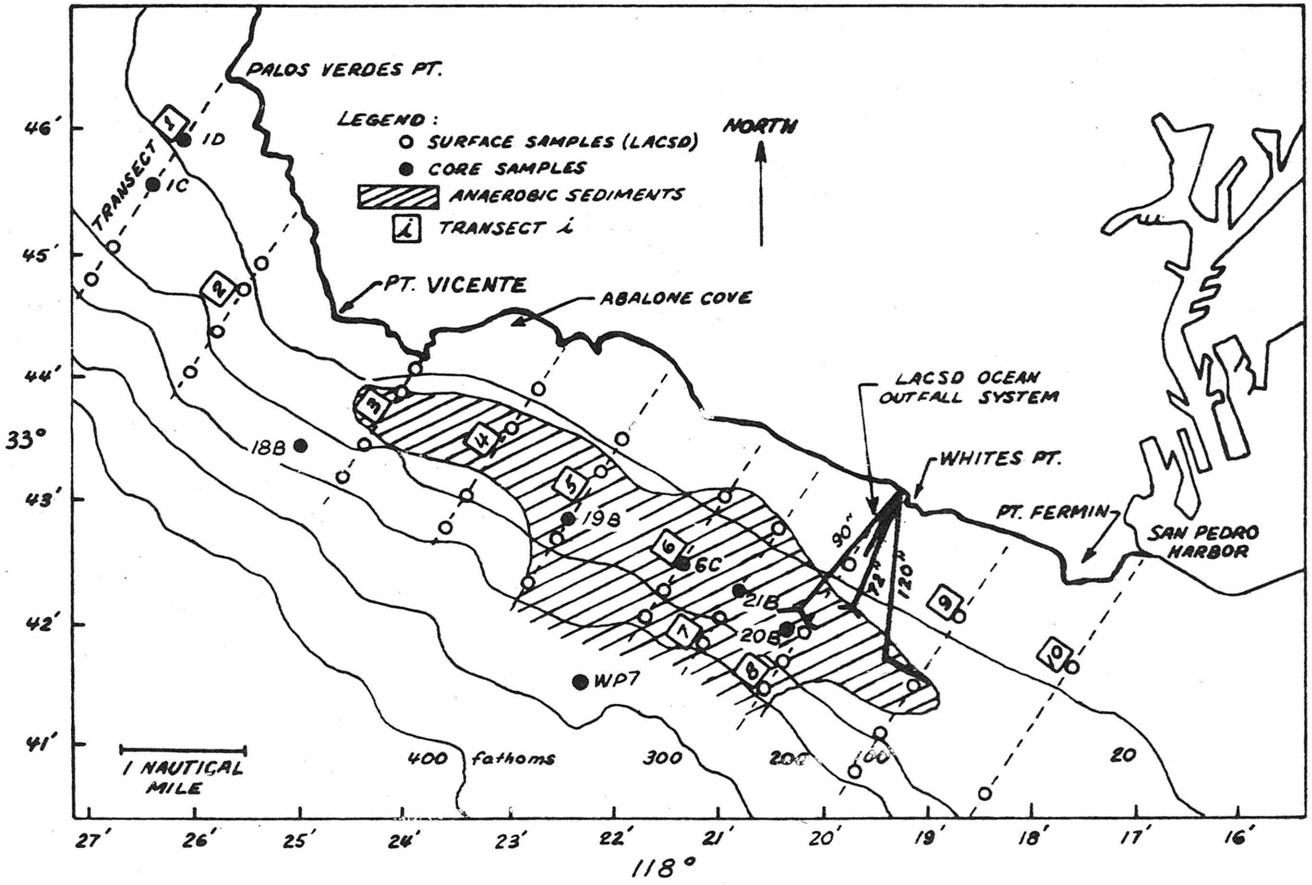

Figure IV-1 . The Palos Verdes Coastline and sample locations for which carbon data are reported.

The shelf is bounded to the north by Redondo Canyon and to the south by the San Pedro Sea Valley. This topographical arrangement is an important factor which affects the erosional-depositional processes of this area. Emery (1960) and Inman and Frautschy (1966) describe sedimentation patterns along the southern California coastline to take place in several well-defined cells which are confined by topographic boundaries (Figure IV-2). Each cell contains a complete cycle of littoral transportation and sedimentation. After introduction of suspended matter to the coast via rivers, the littoral transport is energized by wave action, which in turn transports the material downcoast until the transport is intercepted by a submarine canyon which acts as a sink for the suspended matter. The eventual destination of this matter is the deeper basins and depressions (Inman and Brush, 1973).

The relationship of the Palos Verdes Shelf to this overall process is somewhat unique. Since the movement of littoral drift is generally downcoast (Emery, 1960), the presence of Redondo Canyon acts as a trap for sediment transport from the Santa Monica Bay area. The Palos Verdes coastline is consequently an erosional area which is evidenced by the absence of any sandy beaches.

The magnitudes and directions of currents offshore of Palos Verdes have been described by SCCWRP (1973). The existing data indicate that the speed and direction of the currents is quite complex and varies both with season and with depth. SCCWRP's summary of current data taken over a four year period by the Los Angeles County Sanitation Districts showed the general characteristics outlined in

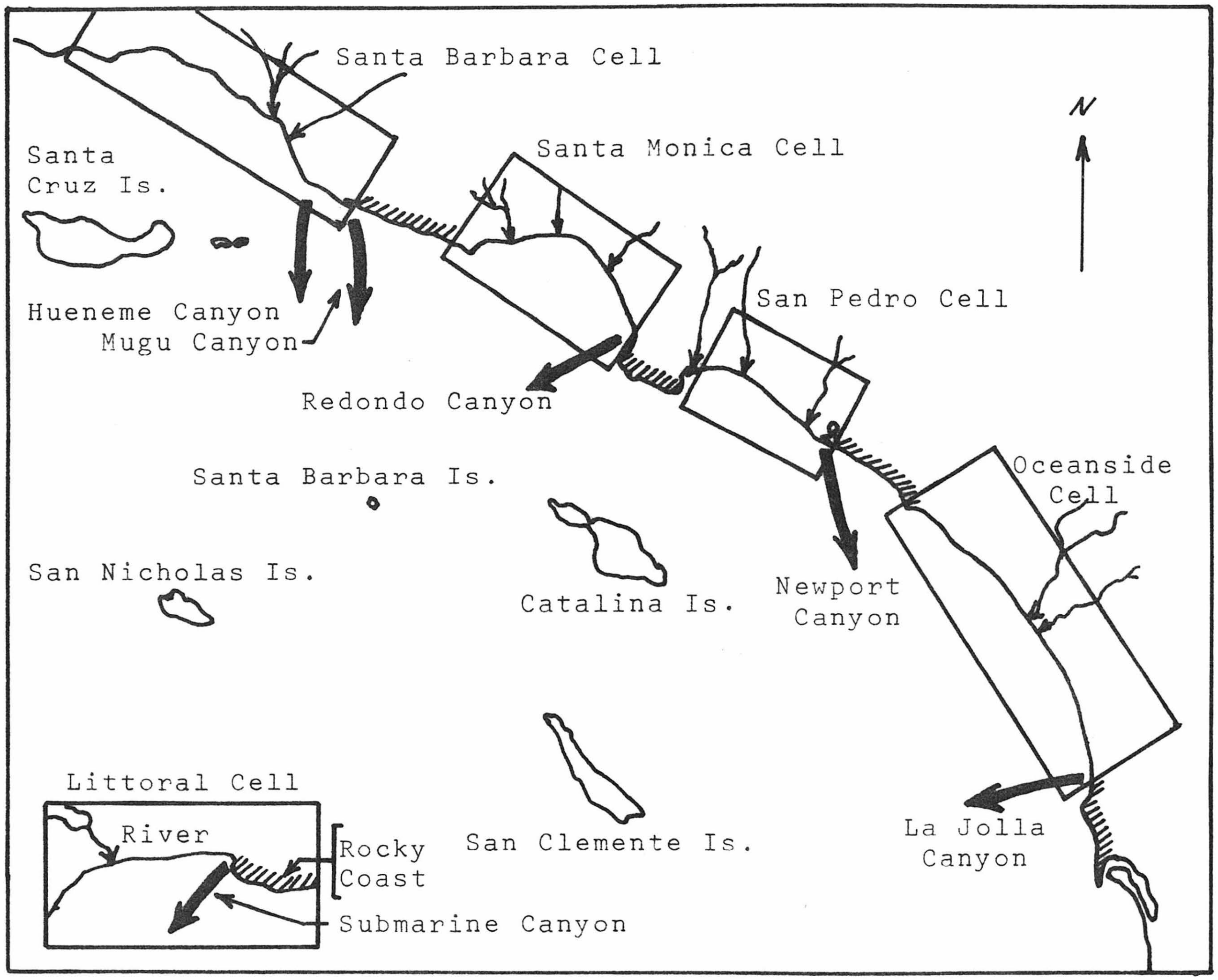

Figure IV-2. Schematic representation of littoral sedimentation cells along the southern California coast. Each cell contains a complete sedimentation cycle: Sand is brought to the coast by streams, carried along the coast by waves and currents, and lost into deep submarine basins through submarine canyons (from Inman and Frautschy, 1966).

Table IV-1. Since the sewage field can be found at a variable depth (Section III-2), the interaction of both the field and the included particulates with the current system is going to be complex. However, as Galloway's (1972) trace metal data showed, and as the data to be presented in this thesis will also show, the bottom currents play a major role in regard to the fate of sewage particulates in the local sediments.

Table IV-1. Characteristic Directions Towards Which Winds and Currents are Flowing Offshore of Palos Verdes (from SCCWRP, 1973)

Season	Prevailing Wind	Current Direction at a Depth of: 1 Meter	30 Meters	60 Meters
Winter	SW	Bimodal NW, SE	Bimodal NW (dominant)	NW to SW
Spring	E-SE	Bimodal SE (dominant), NW	Bimodal SE (domi- (nant), NW	Bimodal E-SE (domimant), W-NW
Summer	E-SE	E-SE	Primarily W-NW	Primarily NW
Autumn	E-SE	Bimodal E-SE (dominant), W-NW	Primarily NW	Primarily W-NW

Note: mean current speeds range from 0.10 to 0.25 meters/second with the higher speeds occurring more frequently in the surface waters (15 meters or less).

The physiographic situation of the Palos Verdes Shelf and the fact that it represents an erosional area to which a new source of organic material has been introduced provide a convenient system for the application of carbon isotope analysis. Since there are no natural streams discharging a suspended load of organic and inorganic material to this area, the ocean-outfall input of terrestrial waste organic matter and any ensuing deposition of particulate matter would be expected to be evident in the carbon isotopic record of the local sediments.

IV-2 Sedimentary Core Data

The locations of the various cores for which data are reported are shown in Figure IV-1. This particular selection of cores adequately represents the sedimentation record as affected by the Whites Point sewage discharge and provides for an examination of predischarge sedimentary conditions. The principal consideration in choosing these particular cores (with the exception of P6C) was the existence of chemical data on these cores. The intact core P6C was provided by the Los Angeles County Sanitation Districts.

Relatively large aliquots were sampled from P6C, whereas the other core material was available in smaller amounts. The initial letter (B or P) of each core number designates whether the core was a box core (B) or a Phleger core (P), and the additional notation defines the core location as given on Figure IV-1.

IV-2a. Core P6C. Core P6C was studied in the greatest detail because of the greater availability of core material. The various data obtained for this core are presented in Table IV-2 and summarized in Figures IV-3 and IV-4. These data include water content, wet density (defined as the mass of dry solids per unit wet volume), percentage organic carbon, percentage carbonate carbon, precentage lipid matter, and the corresponding carbon isotopic compositions of these various forms of carbon. With the exception of water content, all per-

Table IV-2. Sedimentary characteristics of core P6C

Core depth, cm	Percent water	Wet density d_w, gr/cm^3	Percent organic carbon	δC^{13}(org)	Percent lipid matter	δC^{13} (lipid)	Percent carbonate carbon	δC^{13} (carbonate)
Surface			8.3	-23.8				
0-2	83(3)	0.21	11.4,11.2	-24.5,-24.5	3.6	-26.4	0.4	- 9.1
4-5	79(3)	0.25	10.9,11.4	-24.5,-24.5	4.4	-26.1		
5-6							0.3	-10.9
6-7	73(3)	0.28	10.3,11.0	-24.4,-24.4	3.2			
8-9	69(3)	0.35	8.2,8.5	-24.2,-24.3	2.2		0.3	-10.7
10-11	66(3)	0.44	7.3,7.8	-24.3,-24.5	2.1			
12-13	55(1)	0.58			1.0		0.4	-11.6
14-15	44(3)	0.87	2.5,2.2	-23.7,-23.6	0.5	-25.5	0.5	-12.2
15-16							0.4	-12.1
16-17	34(1)	1.24			0.2			
17-18							0.7	-11.1
18-19	33(3)	1.17	0.9,0.9	-23.0,-23.3	0.1	-24.4	0.7	-10.8
20-21	30(1)	1.23						
22-23							0.7	-11.0
24-25	30(2)		0.6,0.7	-23.2,-23.0				
26-27							0.6	-10.9
28-29	31(2)		0.6,0.7	-22.8,-23.2		-24.4		

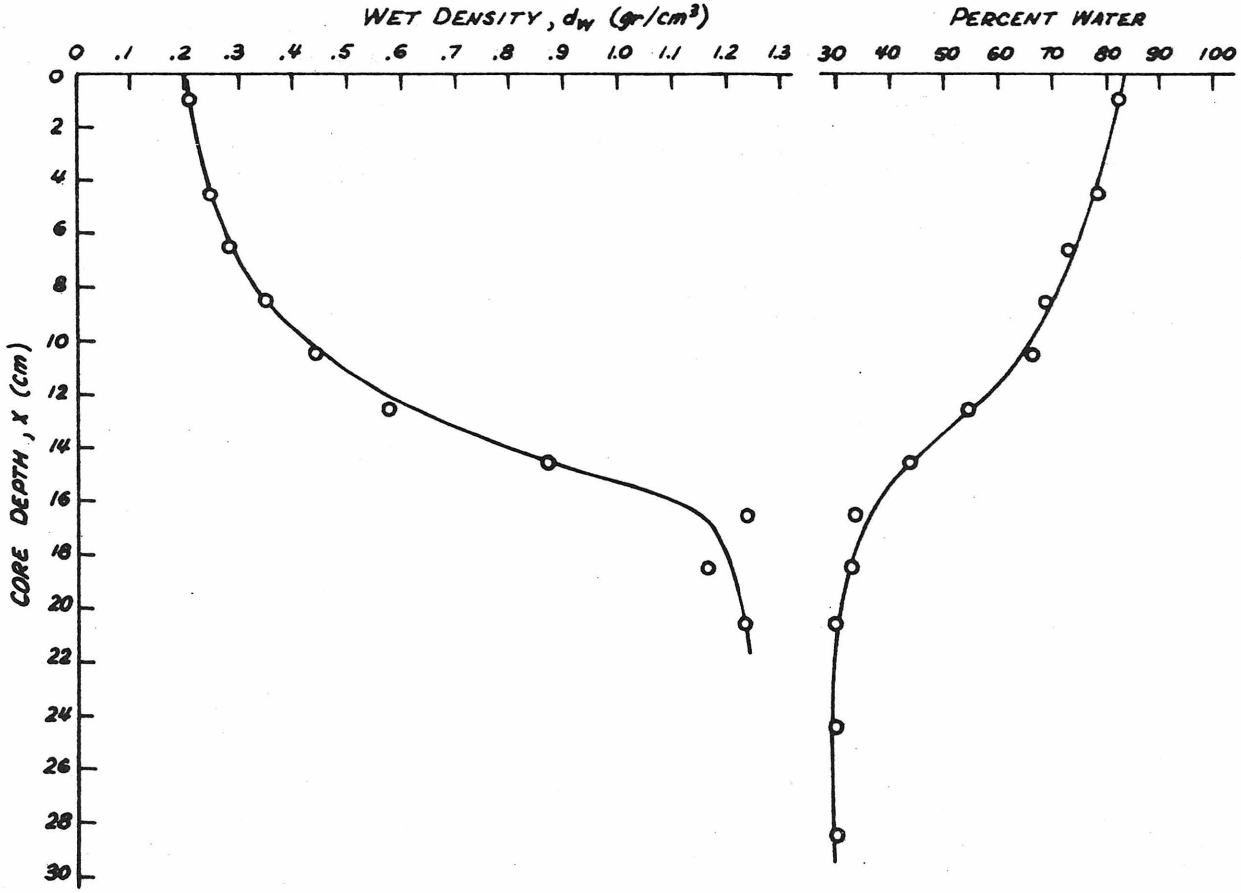

Figure IV-3. Wet density and water content of Phleger core P6C.

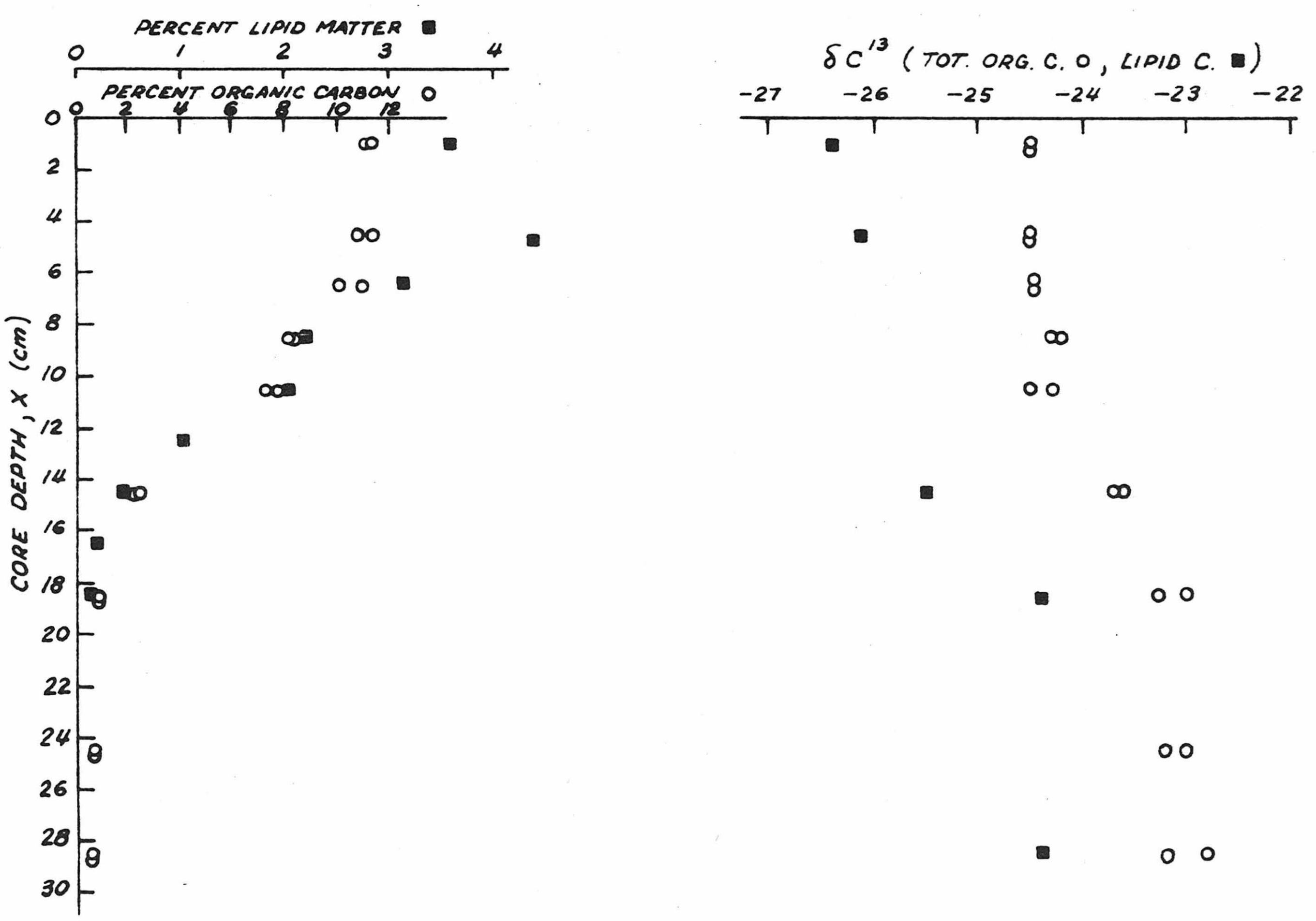

Figure IV-4. Concentration and isotopic composition of lipid and organic carbon in Phleger core P6C.

centages are relative to dry weight. The water content is reported as a percentage of the initial total wet weight. The importance of the wet density (d_w) will become evident later. The wet density was measured by filling brass rings (1 cm length, 11.81 mm inner diameter) with samples of the wet sediment. The samples of specified wet volume were then washed into 40-ml conical centrifuge tubes and washed with distilled water, centrifuged and decanted three separate times, after which the solids were allowed to dry and were then weighed.

All of the measured data for this particular core provide evidence for a change in the physical and chemical properties of the sedimentary material at a core depth of about 16 - 18 centimeters. In contrast to the sediment below this depth, the surface material is high in total organic and lipid carbon as well as of high water content with a corresponding low wet density. The carbon isotopic data reveal a definite change in the nature of the source of organic material from a non-sewage sediment enriched in carbon-13 to the present-day sewage influenced sediment more depleted in carbon-13. This is evident in the δC^{13} data for both the total organic and the lipid fractions. The data for this core indicate that a sludge blanket of outfall origin has covered the immediate area adjacent to the sewage discharge.

The pre-outfall background δC^{13} value of about -23.0 o/oo for total organic carbon within this core is slightly lighter than δC^{13} data reported by others for basin sediments farther offshore of southern California. Nissenbaum and Kaplan (1972) reported δC^{13} data for humic and fulvic substances in the various basins offshore of southern

California. Their data are presented in Table IV-3.

Table IV-3. The Isotopic Composition of Humic and Fulvic Acids in the Sediments of Marine Basins Offshore of Southern California (Nissenbaum and Kaplan, 1972)

Basin	C^{13}, Humic	C^{13}, Fulvic
San Pedro Basin	-22.7 o/oo	-21.7 o/oo
Santa Cruz Basin	-21.8	-20.7
Santa Barbara Basin	-22.5	-19.1
Tanner Basin	-22.0	-20.3
Long Basin	-22.3	-20.3

Since marine sediments may contain as much as 70 per cent of their total organic carbon in the humic and fulvic acid fraction (Nissenbaum and Kaplan, 1972), the isotopic composition of these substances should be quite similar to that of total organic carbon. Accordingly, Emery (1960) has reported a similar range of isotopic data for total organic carbon in the sediments of these offshore marine basins (Table IV-4).

Although the carbon δC^{13} data for pre-outfall sediments of core P6C (about -23.0 o/oo) are in general agreement with the above data reported by Nissenbaum and Kaplan (1972) and Emery (1960), δC^{13} data for pre-outfall sediments further upcoast and offshore of Palos Verdes Point are about -22.0 to -22.5 o/oo (Table IV-6). These latter data are more consistent with the offshore marine basin data of Emery and suggest that the local Los Angeles and San Gabriel Rivers (located to the east of Palos Verdes) may provide a low δC^{13} terrestrial contribution which diminishes in the upcoast direction (northwest).

The difference in δC^{13} of the deeper pre-outfall sediments and

Table IV-4. δC^{13} values for marine basin sediments offshore of southern California (from Emery, 1960).

Basin	Core	Depth cm	Carbonate	Organic carbon	Total Extract	Paraffin-Naphthenes	Aromatics
Santa Barbara	4701	0- 19	+0.3	-20.4			
	4701	228-241		-21.2			
	4701	406-419	-0.7	-21.6			
	3503	102-162				-23.3	
	2622C	31- 41			-23.3		
	2622C	183-193			-23.3		
	2622C	386-396			-23.3		
Santa Monica	4647	386-396	-1.9				
San Pedro	4679	300-310		-22.0			
	4690	5- 25		-21.0			
	4690	330-348		-23.3			
San Diego	4667	343-356	+0.2	-21.5			
Santa Cruz	4700	343-356		-22.7			
Santa Catalina	4703	267-279		-21.7			
	4704	3- 13	+0.5	-20.8			
	4704	13- 25	+0.9	-21.7			
	4704	406-419	-0.7	-22.6			
San Clemente	4670	305-318	-0.9	-23.1			
	4672	267-279		-24.8			
San Nicolas	4693	0- 5		-20.6			
	4693	330-343	+0.4	-21.0			
East Cortes	4671	441-454	+0.7	-19.9			
No Name	4673	401-414		-21.2			
Tanner	4696	2- 38				-27.9	-26.3
	4696	330-343		-20.5			
West Cortes	4674	3- 13		-21.3			
	4674	419-432		-21.5			
Long	4699	343-354		-23.3			

Table IV-4. (Cont'd.). δC^{13} values for marine basin sediments offshore of southern California (from Emery, 1960).

Basin	Core	Depth cm	Carbonate	Organic carbon	Total Extract	Paraffin-Naphthenes	Aromatics
Continental slope	4697	381-396		-20.6			
Deep sea	4698	102-112	-9.9				
Average			-0.1	-21.7			

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[1] Values for carbonate and organic carbon by T. A. Rafter, New Zealand Department of Scientific and Industrial Research, Lower Hutt; other values by Silverman and Epstein (1958) and Silverman (personal communication).

the upper outfall-influenced organic-rich sediments is consistent with the δC^{13} composition of their respective source materials, i.e., the recent addition of sewage particulate carbon of a lower δC^{13}. In addition, the upper sediments of core P6C reflect a δC^{13} value of -24.5 $^o/oo$ which is about 1 o/oo depleted in C^{13} relative to the outfall source organic matter (-23.5 o/oo). This isotopic shift may reflect a diagenetic change due to both the aerobic and anaerobic decomposition of sedimentary carbon which can result in a lower δC^{13} refractory organic carbon. The effect of the decay of organic carbon on its δC^{13} is discussed in detail in Section III-3.

The difference in δC^{13} between predischarged effluent particulate carbon and that found in the sediments may also be due to the preferential loss of C^{13}-rich and perhaps finer materials to the deeper parts of the ocean. Although the δC^{13} analyses on different settling fractions of effluent particulates (Figure III-5) indicated no statistically significant trend, such considerations should not be disregarded until more detailed work is done.

Data reported by Presley and Kaplan (1968) for dissolved bicarbonate in the interstitial waters of sediments of marine basins offshore of southern California bear particular relevance to the carbonate data of core P6C. These data are presented in Table IV-5. They discussed the origin of bicarbonate due to anaerobic metabolic activity involved in the oxidation of organic matter according to the reaction:

$$2(CH_2O) + SO_4^{-2} \rightleftharpoons 2HCO_3^- + HS^- + H^+ \qquad (4.1)$$

Table IV-5 . pH, sulfate, calcium and total dissolved carbon dioxide in interstitial water, percent of calcium carbonate in the sediment and C^{13}/C^{12} content ΣCO_2 and carbonate in San Pedro and Santa Catalina Basins (from Presley and Kaplan, 1968).

Sample (cm)	pH	$mMSO_4^{2-}$	*$mM\Sigma CO_2$	*δC^{13} of Σ CO_2 wt of water	% $CaCO_3$ in sediment	δC^{13} of CO_3 in sediment	ppm Ca^{2+} in water	mM Ca^{2+} in water
San Pedro Basin								
0- 50	7.5	6.0	5.14	- 1.01	7.6	-0.55	415	10.4
100-125	7.6	3.6	12.5	-15.40	8.6	-1.91	334	8.4
200-225	7.6	2.9	17.4	-18.62	8.6	-2.87	342	8.5
300-325	7.6	2.6	24.4	-19.43	8.1	-2.12	236	5.9
400-425	7.7	0.5	29.6	-20.43	5.8	-3.00	183	4.6
500-525	7.7	0.1	34.4	-21.17	7.7	-2.95	148	3.7
Catalina Basin								
0- 20	7.7	6.9	3.22	- 5.95	16.0	+0.95	380	9.5
60- 80		11.	3.22	- 8.07	16.2	+0.74		
100-120	7.7	12.	3.61	- 8.53	18.0	+1.45	365	9.1
140-160		5.8	3.84	- 8.99	8.5	-0.65		
180-200	7.9	8.6	4.19	- 9.63	8.9	-0.81	380	9.5
220-240		8.6	5.26	-12.72	14.5	+0.07		
260-280		8.6	6.25	-14.17	7.1	-0.71		
300-320	8.0	7.1	7.15	-18.25	11.5	-0.41	365	9.1
320-340		9.6	8.25	-16.27	9.2	-0.88		
400-420	8.0	11.4	9.42	-17.62	10.6	-0.33	365	8.9
460-480		9.3	11.2	-18.37	9.6	-0.27		
500-520	8.0	5.9	12.3	-19.31	9.7	-0.51	435	10.9

*Surface water off Santa Cruz Island (Avg. of 3 Measurements): 1.7 + 0.96.

Evidence that such a process takes place in marine sediments is provided by the data of Table IV-5 on dissolved sulfate, calcium, and carbonate in the interstitial water of such sediments. Eh measurements on the San Pedro core of Table IV-5 indicate an oxidizing environment throughout the core, whereas the Catalina core was shown to be in an anaerobic environment below a core depth of 2 meters. The low δC^{13} values for total dissolved CO_2 (HCO_3^-) indicate that the increase in dissolved bicarbonate with depth is due to an addition of metabolic CO_2 and is not derived from the solution of sedimentary carbonate (Presley and Kaplan, 1968). The decrease of δC^{13} values of solid carbonate with core depth also suggests a metabolic contribution of carbon to the solid carbonate. According to Presley and Kaplan (1968), this latter trend is due to either the exchange of metabolically derived bicarbonate with solid carbonate matter and/or the possible deposition of authigenic calcium carbonate due to supersaturation at depth.

The carbonate data of core P6C (summarized in Figure IV-5) behave similar to the carbonate data of Presley and Kaplan. The greater depletion of C^{13} with depth down to 15 cm suggests that active diagenesis is taking place within this anaerobic core, resulting in a δC^{13} depleted bicarbonate which is either exchanging with existing solid carbonates or precipitating as fresh carbonate. According to Presley and Kaplan (1968), the isotopic composition of metabolic bicarbonate should be similar to that of the source organic material which is being degraded. If it is assumed that the isotopic composition of metabolically-derived bicarbonate due to the bacterial break-

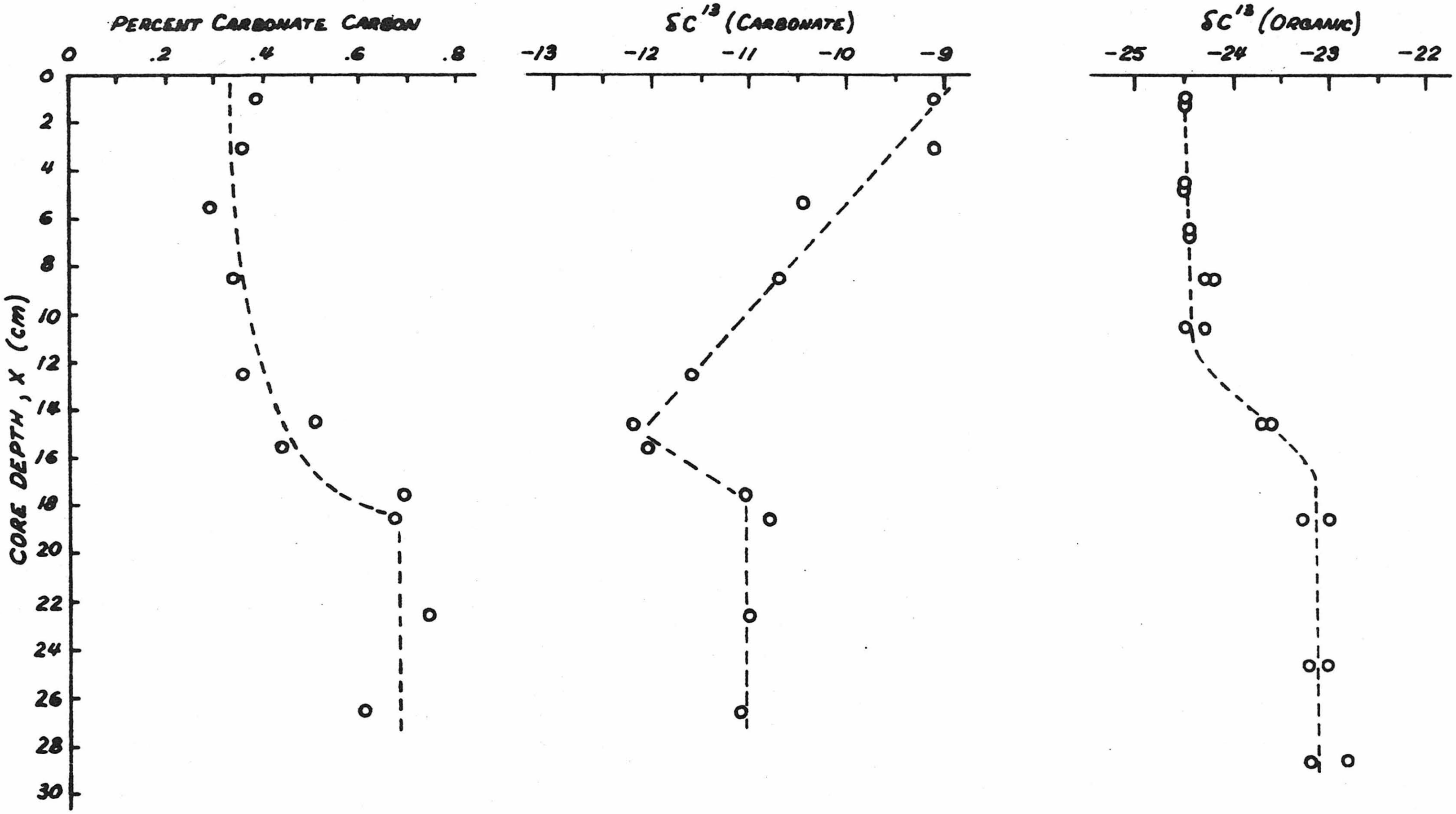

Figure IV-5 . The distribution of carbonate carbon and its isotopic composition within Phleger core P6C. The isotopic composition of total organic carbon is presented for comparison.

down of effluent particulate material has a similar composition to that of its source material (i. e., about -24.5 o/oo), then only a small quantity of this bicarbonate would be needed to change the δC^{13} of the total carbonate carbon from -11 to -12 o/oo at the 15 cm depth of core P6C. The complexity of the carbonate δC^{13} profile is undoubtedly due to a combination of several processes, including the sedimentation of carbonate matter from both the outfall and natural sources, the entrainment (mixing) of pre-discharge sedimentary carbonates into the upper part of the core, and the precipitation and/or exchange of metabolically-derived carbonate. The potential role of the entrainment of background sediments into the upper part of a core such as P6C is further discussed in Chapter V.

The δC^{13} value of carbonate carbon in the lower pre-discharge sediments of core P6C (-11 o/oo) is very light when compared to the normal range for marine carbonates of about -1 to +1 o/oo. The low δC^{13} carbonates of the pre-discharge sediments may be due to the addition of fossil carbonate from the Palos Verdes Hills. Murata, et al. (1967) showed that carbonate material from the Miocene strata of the Palos Verdes Hills were lighter than the normal range of δC^{13} for marine carbonates (Section I-4c). Samples taken from two different bed types of the Palos Verdes Hills gave δC^{13} values of -5.6 and -12.1 o/oo, respectively. Since the Palos Verdes coastal area represents an erosional area, the δC^{13} values of background sedimentary carbonates may reflect the contribution of erosional material from the cliffs and shoreline of Palos Verdes.

IV-2b. Other Sedimentary Core Data. The information obtained from core P6C specifically showed that the sewage discharge from Whites Point has affected the benthic sedimentary environment at one location. On the basis of these results it was obviously worthwhile extending this investigation to a wider geographic area. A number of additional sedimentary cores were analyzed in order to accurately describe the sedimentary record near Whites Point and the variation with distance from the outfall source of particulates. The concentration and δC^{13} of organic carbon in Phleger cores P1D, P1C, P18B, P19B, P20B, and P21B are presented in Table IV-6 and summarized in Figure IV-6. Data for the box cores B18B, B20B, and B21B are presented in Table IV-7 and summarized in Figure IV-7.

The concentration of total organic carbon data in the above cores reveals that the depth of accumulation of an organic-rich sludge deposit generally varies inversely with distance from the outfall source, a relationship which is not unexpected. Furthermore, there is a similarity in the various profiles of all the cores (i. e., per cent organic carbon and water, and the δC^{13} values for total organic carbon), although the extent of the total accumulation varies. This similarity can best be observed by plotting the data for the various cores relative to the depth of accumulation above pre-discharge sediments. Such a plot is presented in Figure IV-8, which was plotted on the basis that pre-discharge conditions are defined by a sedimentary organic carbon composition of 1 per cent or less. This figure summarizes all of the data from both the Phleger and the box cores. When plotted in this manner, the organic carbon concentration and

Table IV-6 . Water content and the concentration and isotopic composition of total organic carbon in various Phleger cores obtained offshore of Palos Verdes

Core	Core Depth,cm	Percent water	Percent organic carbon	δC^{13}
P1C	0		5.8	-23.2
	2		3.4	-22.9
	4		2.8	-22.6
	6		1.2	-22.5
	8		1.0	-22.6
	10		0.7	-22.5
	12		1.0	-22.0
P1D	0		1.0	-22.3
	2		0.6	-22.4
	4		1.2	-22.7
	6		0.7	-22.1
P18B	0		2.9	-23.3
	4	37	1.8	-23.5
	8	31	0.9	-23.6
	12	32	0.8	-23.0
	16	29	0.7	-22.5
P19B	0		9.6	-24.0
	2	82	10.8	-24.2
	6	47	8.1	-23.7
	10	53	3.4	-23.8
	14	34	1.1	-23.2
	18		1.2	-23.6
	22	33	0.8	-22.6
	26		0.8	-23.0
P20B	0		9.4	-24.0
	2	72	8.4	-24.5
	4	63	6.0	-24.1
	6	55	3.5	-24.2
	8	45	2.4	-23.4
	10	38	1.6	-23.3
	12	43	1.2	-23.7
	14		0.9	-23.5
	16		0.7	-23.1
	18	29	0.7	-23.0
P21B	6		11.7	-24.7
	10		9.7	-24.6
	14		8.2	-24.6
	16		7.6	-24.5
	18		3.9	-24.2
	20		2.3	-24.1
	22		1.0	-24.0
	24		0.9	-23.3
	28		0.8	-23.5

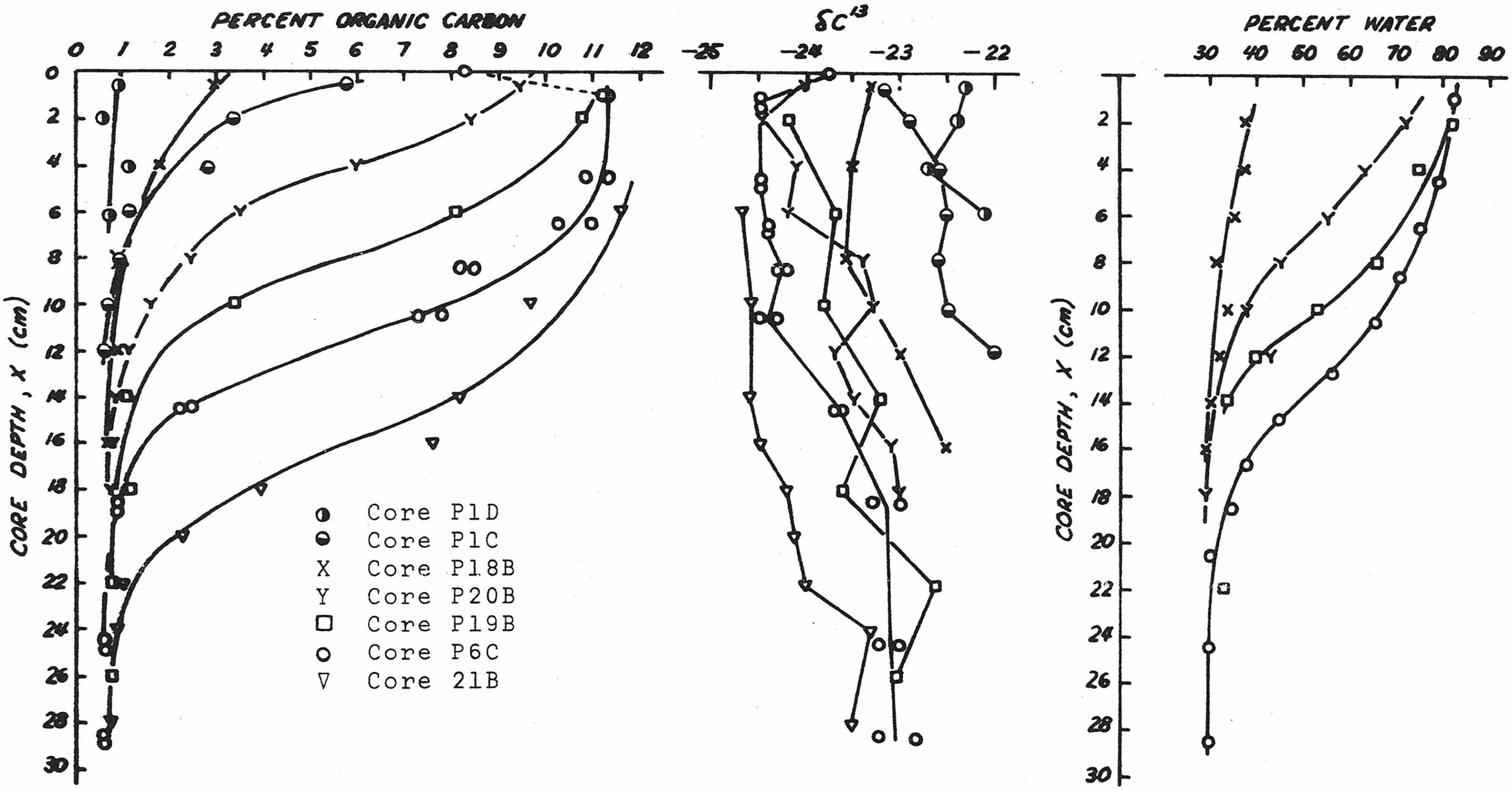

Figure IV-6. The distribution of organic carbon, δC^{13} (organic) and water content within the various Phleger cores.

Table IV-7. Water content and the concentration and isotopic composition of total organic carbon in various box cores obtained offshore of Palos Verdes

Core	Core Depth, cm	Percent water	Percent organic carbon	δC^{13}
B18B	0	51	2.0	-23.4
	2	47	1.8	-23.3
	4	41	1.2	-23.3
	6	41	1.0	-23.0
	8	40	0.7	-23.1
	10	39	0.9	-23.2
	12	39	0.7	-22.8
	14	36	0.8	-22.7
B20B	0	83	12.2	-24.6
	2	76	10.0	-24.5
	4	77	11.5	-24.7
	6	70	9.0	-24.6
	8	69	8.5	-24.5
	10	64	5.4	-24.5
	12	53	--	-24.0
	14	46	1.7	-23.8
	16	43	1.7	-23.7
	18	36	1.0	-23.4
	20	37	0.9	-23.0
B21B	0	76	9.9	-24.3
	4	78	11.0	-24.3
	8	73	7.5	-23.8
	12	71	7.5	-24.0
	16	51	2.3	-24.3
	20	37	1.1	-24.3
	28	37	1.0	-23.5
	32	35	0.9	-23.7
	36	36	0.8	-23.2

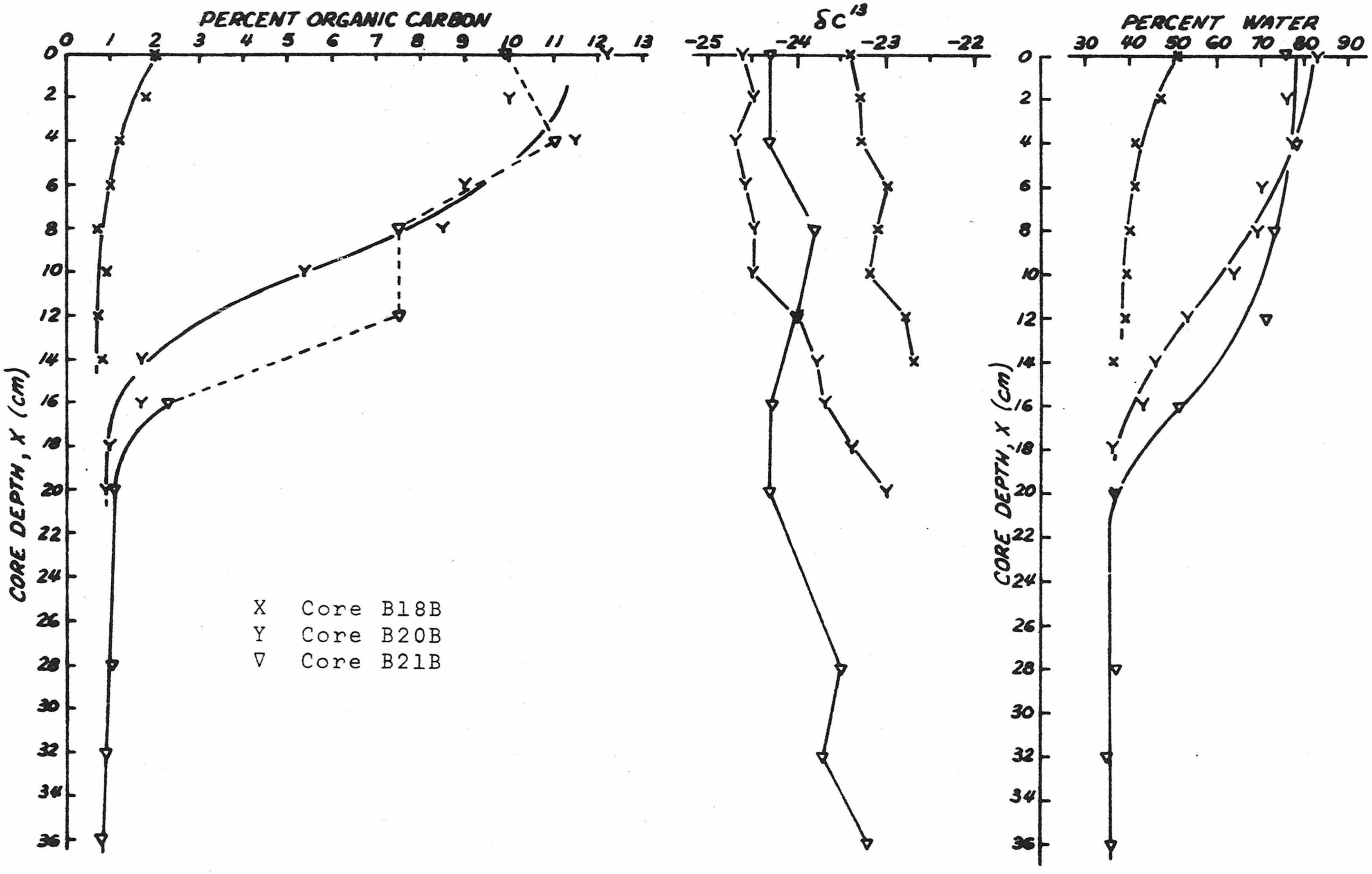

Figure IV -7 . The distribution of organic carbon, δC^{13} (organic), and water content within the box cores.

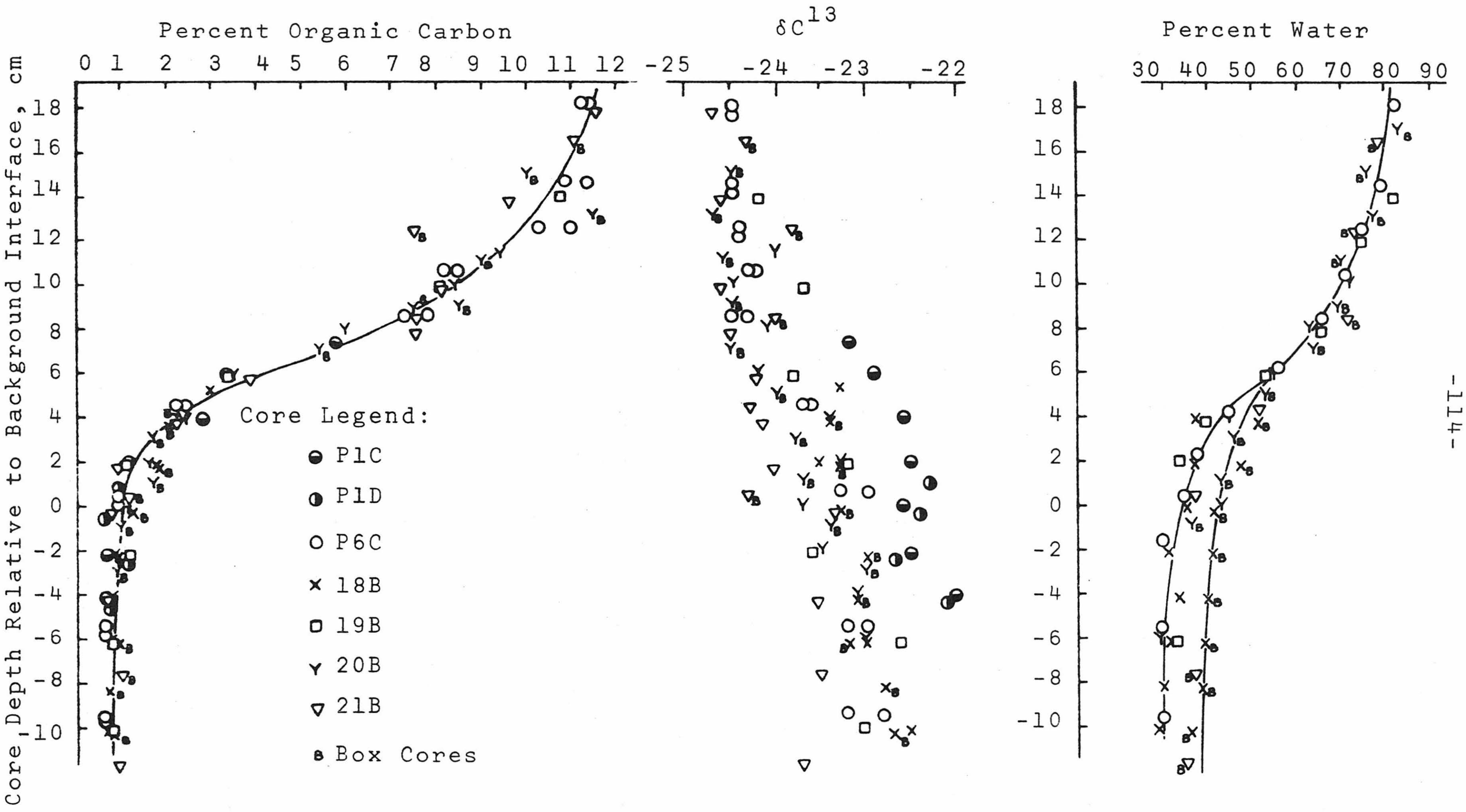

Figure IV-8. Sedimentary core data of the Palos Verdes Shelf expressed as a function of sediment depth (X) above background sediments.

water content data essentially describe remarkably similar relationships with depth. These curves will be referred to as "characteristic" profiles and will be used in Chapter V concerning the total accumulation of outfall carbon on the San Pedro Shelf.

Although there is also a general characteristic trend with depth of the δC^{13} data determined on the Phleger and box cores, the curves are slightly different for each core. This difference is particularly evident in the data of cores P1C and P1D, where the curves are displaced toward a heavier isotopic composition for a specific carbon concentration. These particular cores happen to be located farthest from the outfall. There is also an indication of a distance-dependent trend in the other core δC^{13} data. For any given organic carbon concentration, those cores nearest the outfall tend to have a lower δC^{13} value. Such a trend is probably due to the relative importance of the contribution of natural marine organic matter to the sediment. Further discussion of the relative contribution of carbon from different sources to the sediments will be discussed in Section V-2.

There is one other important relationship indicated by the data plotted in Figure IV-8. A comparison between the water contents of the Phleger cores with that of the box cores reveals that a compaction of the lower portion of the Phleger cores has occurred during sampling. However, such compaction is absent in the organic-rich upper portions of these cores.

The Phleger and box core data indicate a δC^{13} value of about -23.0 o/oo for pre-discharge sediments near the outfall. However, the Phleger cores obtained farther west of the outfall, and offshore of Palos Verdes Point, reveal a more positive δC^{13} value of about -22.0 to -22.5 o/oo for pre-discharge sediments. The cause of the lower δC^{13} values for pre-discharge sediments offshore of Whites Point may be due to a greater contribution of terrestrial carbon from the Los Angeles and San Gabriel Rivers to the east of Whites Point. The data would then indicate such a contribution to diminish with distance in the upcoast direction.

Two additional box cores (BWP7 and BSP) were analyzed in order to obtain a better idea of the distribution of the δC^{13} for total organic carbon which was deposited prior to effluent discharge. One core (BWP7) was taken in 270 fathoms of water several miles offshore of Whites Point (see Figure IV-1) in 1972 by SCCWRP. The other core (BSP) was obtained from the San Pedro Basin by the Scripps Institute of Oceanography*. Lead data for the latter core were reported by Chow, et al. (1973). The carbon and isotopic data for these cores are given in Table IV-8.

The δC^{13} data for core BWP7 suggest an input of effluent organic carbon to a core depth of about 18 cm. Such a suggestion is supported by unpublished mercury analyses performed on this same core by SCCWRP, which indicated higher concentrations of mercury in the upper 18 cm of sediments as compared to values below this level. The fact that the organic carbon concentrations are lower in the upper part of this core, as compared to the upper sediments from

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*Subsamples of core BSP were kindly provided by Ken Bruland of the Scripps Institute of Oceanography.

cores on the shelf and nearer the outfall, suggests that there is a greater input of inorganic matter to the location where this core was sampled. The pre-outfall carbon in core BWP7 has a lower δC^{13} value than such carbon in cores P1C and P1D, which also implies a greater transport of non-outfall terrestrial carbon to location WP7 as compared to 1C and 1D.

Table IV-8. Carbon Isotopic Data for Total Organic Carbon in Two Cores Located in Deeper Waters Offshore of Palos Verdes.

Core	Core Depth cm	Percent Organic Carbon	δC^{13}
BWP 7	0	3.6	-25.1
	6	2.7	-24.6
	10	2.1	-24.4
	18	1.7	-24.3
	36	1.7	-23.3
	80	1.5	-23.1
BSP (San Pedro Basin)	1-2	4.2	-22.8
	2-3	4.1	-23.1
	4-5	3.4	-23.8
	8-9	4.1	-22.6
	14-15	3.8	-22.5
	20-22	3.9	-23.1
	28-30	3.5	-23.0

The lower δC^{13} value for pre-outfall carbon is also evident in the San Pedro Basin core, which has a δC^{13} value of about -23.0 o/oo. Chow, et al. (1973) have reported increased concentrations of lead in the upper 4 cm of this core which they attribute to any of four sources: (a) river transport, (b) storm runoff, (c) sewage discharge, and (d) atmospheric fallout. If this increased concentration is associated with a relatively new source of terrestrial material such as a sewage input, then it appears that such a contribution is diluted enough with marine organic material such that carbon δC^{13} data are insensitive to it. It may also be that this lead is associated with particulate terrestrial matter which has constituted a continuous input during the recent history of the basin and merely reflects the increase in the industrial usage of lead.

Cores BWP7 and BSP also reveal that the concentration of organic carbon in natural sediments offshore of the southern California coast tends to increase with distance from shore. This merely indicates that the relative rate of input of organic carbon to that of inorganic matter tends to increase farther from shore.

IV-3 Surface Core Data

The analysis of organic carbon and its δC^{13} values in the surface sediments of the Palos Verdes Shelf was undertaken in order to provide a rather complete surface mapping of these two variables. Organic carbon concentrations and δC^{13} values for surface sediments sampled along the transects noted in Figure IV-1 are presented in Table IV-9. Those samples taken at 100, 200, 500 and 1000 foot depths were provided by the Los Angeles County Sanitation Districts and were taken with a Shipek sampler in August, 1972. Those samples taken from depths other than those noted above were taken by the author with a small piston coring device for which only the top centi-

Table IV-9 . Water content and the concentration and isotopic composition of total organic carbon in the surface sediments offshore of Palos Verdes

Transect	Water Depth, ft.	Percent water	Percent organic carbon	δC^{13}
1	100	34	0.6	-22.8
	128	46	1.7	-22.9
	170	50	2.7	-23.0
	200	66	5.7	-23.1
	500	45	1.9	-23.5
	1000	51	2.2	-23.0
2	45	51	1.3	-23.4
	100	33	1.4	-21.9
	200	66	6.2	-23.9
	500	45	2.3	-24.1
	1000	51	2.2	-24.8
3	70	45	1.6	-22.2
	100	44	2.3	-23.0
	115	46	2.0	-22.9
	155	63	4.5	-22.9
	200	69	8.2	-23.8
	500	53	3.8	-23.9
	1000	49	2.4	-23.1
4	200		9.0	-24.4
5	70	42	1.1	-23.6
	100	48	2.7	-23.9
	115	52	2.6	-23.7
	155	76	8.4	-24.8
	200	70	9.8	-24.0
	500	61	5.7	-23.8
	1000	52	2.9	-23.6
6	200		9.9	-24.5
7	200		10.7	
8	70	35	1.2	-23.8
	100	46	2.2	-23.9
	115	59	3.7	-24.3
	155	70	8.9	-24.5
	200	73	12.8	-24.5
	500	59	9.9	-24.3
	1000	48	3.3	-24.1
9	200		8.7	-24.5

Table IV-9 . (Cont'd.) Water content and the concentration and isotopic composition of total organic carbon in the surface sediments offshore of Palos Verdes

Transect	Water Depth, ft.	Percent water	Percent organic carbon	δC^{13}
10	25	31	0.6	-22.8
	50	40	2.4	-22.6
	70	35	0.6	-22.5
	100	53	3.3	-23.0
	115	40	0.9	--
	155	52	2.4	-23.6
	200	53	3.9	-23.7
	500	47	2.7	-23.8
	1000	48	2.8	-23.4

meter was removed. These latter samples were taken in March, 1973.

The data presented in Table IV-9 have been summarized in Figures IV-9, 10, and 11. Figure IV-9 presents the spatial distribution of organic carbon on the shelf and clearly indicates the dominant input from the ocean outfall offshore of Whites Point. Although there is some transport of settleable particulates in the downcoast direction, the main transport is seen to be in the upcoast direction. Such a distribution is consistent with the earlier mentioned current distributions in this area and indicates that the bottom currents play a major role in the transport of this material.

Figure IV-10 summarizes the distribution of organic carbon and the respective δC^{13} values along the 200-foot depth contour, which is the approximate depth at which peak concentrations occur. Also shown on this figure is the background (pre-discharge) distribution of δC^{13} as measured on cores 1C, 1D, 18B, 19B, 20B, and 21B. The earlier noted trend in background δC^{13} values is more evident in this representation of the data. A more quantitative interpretation of these surface data, as related to relative mass flux rates of organic carbon of different sources, is saved for Chapter V.

Figure IV-11 presents surface δC^{13} values from transect 8 (located through the discharge area) and from the boundary transects: transect 1 to the northwest, and transect 10 to the southeast. The other data of Table IV-9 would plot somewhere in between these data. These data show a distinctive trend. Of particular interest is the observation that the δC^{13} value becomes more positive in the shallow

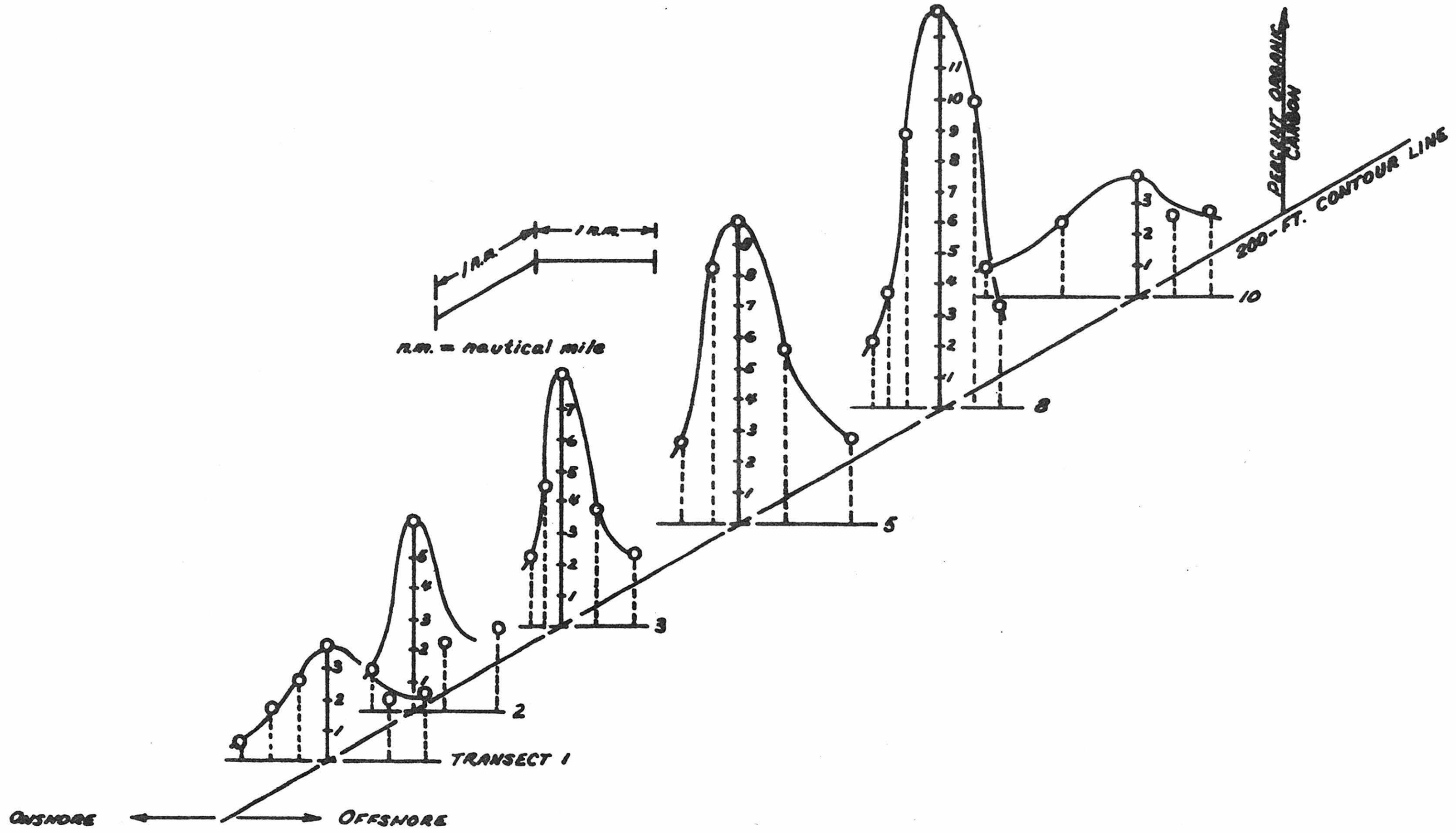


Figure IV-9. The spatial distribution of organic carbon in the Palos Verdes Shelf surface sediments.

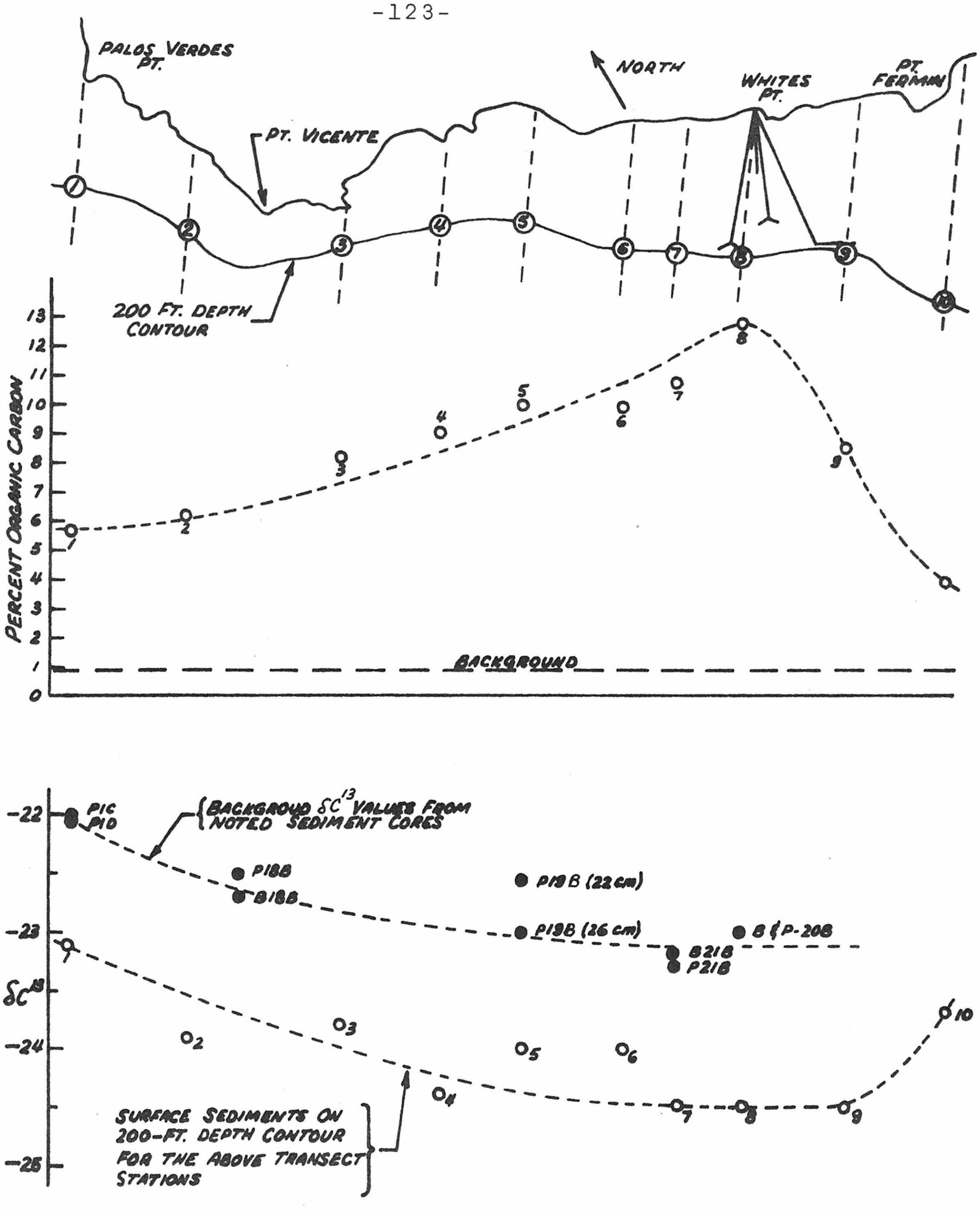


Figure IV-10. The distribution of organic carbon and its isotopic composition in surface sediments on the 200-foot depth contour of the Palos Verdes Shelf.

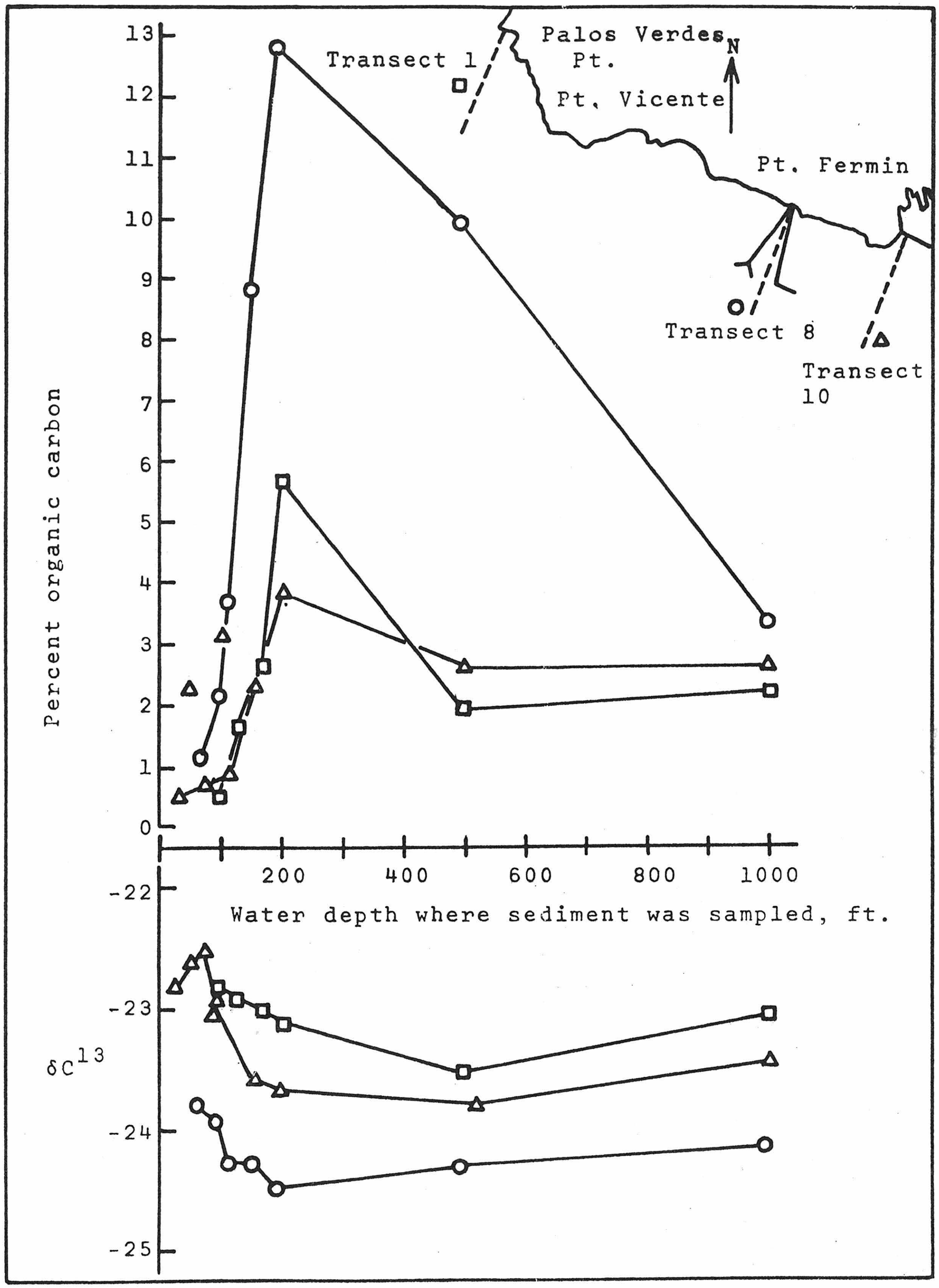


Figure IV-11. Total organic carbon and its isotopic composition in surface sediments of the San Pedro Shelf.

waters near Palos Verdes Point to the northwest and near Point Fermin to the southeast. These data most likely indicate that the relative mass flux rate for natural particulate organic carbon is higher for both locations as compared to locations nearer the discharge. This could be effected by either, or a combination, of two processes:

(1) the sewage field, as reflected by settled particulates, is diverted from the shoreline in the vicinity of these two points, and/or

(2) a relatively larger input of organic carbon of a more positive δC^{13} value (such as marine planktonic matter) is indicated in the vicinity of these two points.

That it is most likely a combination of these two processes is suggested by the below-noted coliform work of Rittenberg, et al. (1958) and by considerations to be presented in Chapter V.

Figure IV-11 indicates that the shallow water sediments between Point Fermin and Point Vicente reflect a residual component of outfall carbon although the total percentage of organic carbon is relatively low. Support for such a conclusion is provided by an investigation of the density of coliform bacteria in surface sediments of the San Pedro Shelf in 1958 (Rittenberg, et al., 1958). This latter investigation showed the concentration of coliform bacteria to be less than one in the vicinity of both Point Fermin and Point Vicente. Nearshore sediments between these two points and sediments farther offshore had coliform concentrations which were orders of magnitude greater. Values greater than 10,000 per cubic centimeter were reported near the point of discharge. The authors concluded that the coliform bacteria were associated with settleable particulate matter from the Whites Point outfall, and that the distribution indicated the general movement of the sewage field.

It was mentioned in the Introduction that North (1964) strongly suspects that the possible intermittent accumulation of outfall solids on rocky substrates in shallow waters may be one of the factors which has interfered with the healthful propagation of the giant kelp <u>Macrocystis</u> <u>pyrifera</u>. In regard to this, the nearshore data from transect 2 do suggest such an intermittent accumulation. The sample from the 45-foot depth was taken by the author on a different date (noted earlier) than the other samples provided by the LACSD. The 45-foot sample was both of a different nature (very black) and of a lighter isotopic composition (-23.4 o/oo) than that from the 100-foot depth. This was in contrast to the trends in δC^{13} data from other transects and suggests that such matter at such a shallow depth is probably of a transient nature and is scoured away with time and the periodic occurrence of larger swells.

North (personal communication) and Hotchkiss (1973) have noticed the occurrence of flocculent accumulations in relatively shallow Palos Verdes waters. North collected two samples of such material from the shallow waters of Abalone Cove (Figure IV-1) and provided them for carbon isotopic analysis to determine whether this material was of sewage origin or of marine origin. The isotopic results on the organic carbon of these samples are indicated in Table IV-10. The δC^{13} values of these samples are compatible with a non-outfall source of this matter, and a source which is likely to be dead planktonic matter (See Chapter II). The intermittent accumulation of such material may be a common phenomenon or it may also be due to an increased productivity in these waters due to an increase in nutrients supplied by the outfall.

Table IV-10. δC^{13} Values for Flocculent Matter Collected from the Sediments of Abalone Cove

Sample		% Organic C	δC^{13}
Abalone Cove - 20 ft	(a)	3.2	-20.6
	(b)	2.6	-20.9
Abalone Cove - 40 ft	(a)	1.9	-21.7
	(b)	1.8	-21.8

V. MATERIAL BALANCE CONSIDERATIONS

The data presented in the previous chapter indicated that the sewer outfall discharge of particulates to the marine waters offshore of Palos Verdes has significantly affected the chemical and physical characteristics of the Palos Verdes Shelf sediments. In particular, the carbon isotopic data on sedimentary particulate carbon identify the large accumulations of organic-rich matter to be of sewage outfall origin. In order to gain further insight into the accumulation process, a more quantitative treatment of the data is attempted in this chapter. Specifically, an attempt will be made to account for the relative rates of input of organic matter due to the sewage source and to the natural input of the local marine biomass.

V-1. Total Mass Accumulations

In order to estimate the rate of sedimentation of outfall particulate matter to the Palos Verdes Shelf, it is desirable to consider the accumulation of the mass of organic carbon within sedimentary cores from this area. To calculate the mass accumulation of organic carbon within a sedimentary core, a knowledge of the depth distribution of both the wet density (d_w) and the percentage of organic carbon (f_c) is needed. Since core P6C was the only core for which wet density was measured, the calculation of the accumulation of the total mass of organic carbon can be performed on this core alone. A generalization of the calculation on core P6C will then be extended to the other cores.

V-1a. The accumulation of organic carbon in core P6C.

The wet densities of core P6C were specifically determined for the purpose of calculating total mass accumulations of total organic carbon. From some reference point (x_o) in a sedimentary core, the total accumulation of mass of a substance, p, per unit area is given by:

$$\bar{M}_p = \int_{x_o}^{x} f_p(x) d_w(x) dx \qquad (5.1)$$

where

$\bar{M}_p$ = the total mass of substance p per unit area accumulated between some reference point x_o and some upper point x ,

$f_p(x)$ = the fractional abundance on a dry weight basis of substance p at x (i.e., $\%p \times 10^{-2}$) ,

$d_w(x)$ = the wet density (grams of dry solids per cubic centimeter of wet sediment) at x .

Based on the percentage organic carbon distribution of core P6C (Figure IV-4) and the wet density distribution (Figure IV-3), the accumulation of organic carbon has been calculated and is presented in Figure V-1, which shows that the accumulation of total organic carbon varies linearly with depth in the lower portion of the core followed by a change in the rate of accumulation at about a 16 - 18 cm depth. Thereafter, organic carbon accumulated at a greater rate. This shift in the rate of accumulation of organic carbon is consistent with the δC^{13} shifts in total organic, lipid, and carbonate matter at this same core depth (Figures IV-4 and IV-5).

The mass accumulation of organic carbon data shown in Figure V-1 allows for a comparison between the input of organic carbon due to outfall particulate matter and that due to a natural sedimentation for

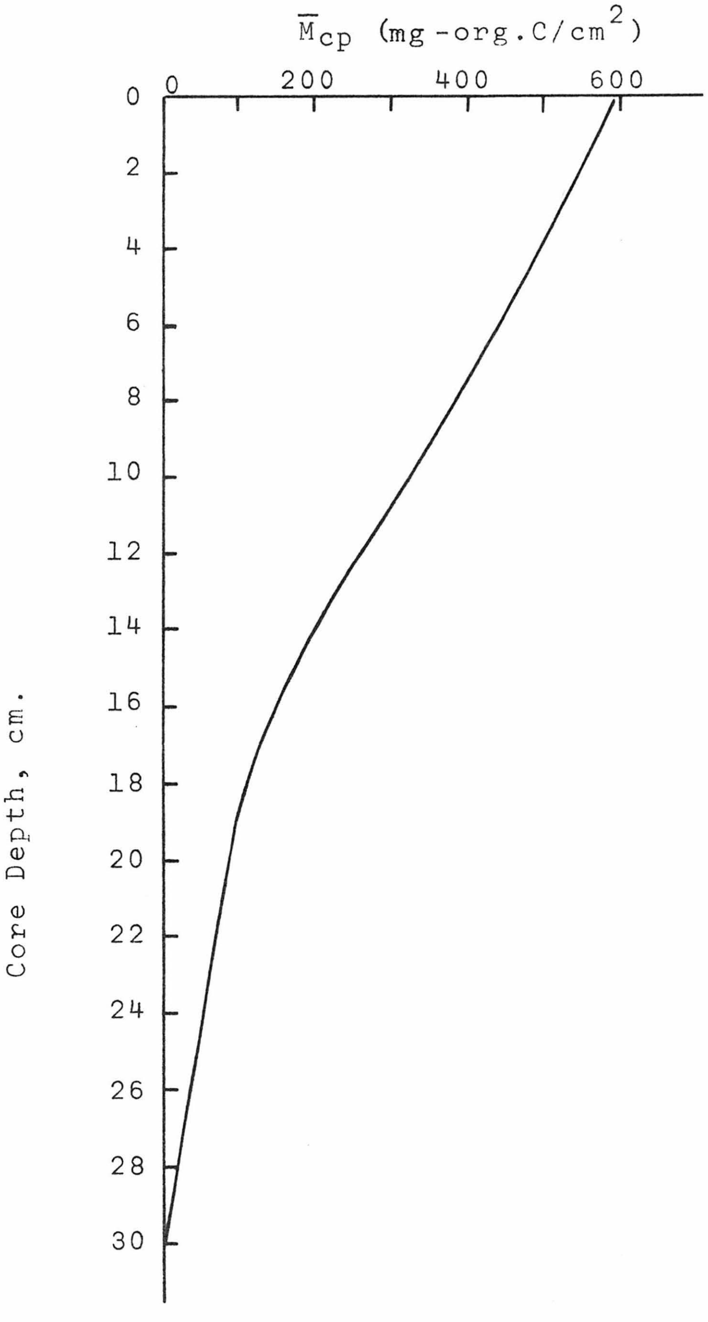


Figure V-1. The mass accumulation of total organic carbon per unit area ($\overline{M}_{cp}$) in core P6C as a function of the depth of accumulation above the 30-cm depth.

core P6C. A natural sedimentation rate of about 9 mg/cm^2/yr for total solids was reported by Emery (1960) for the Palos Verdes Shelf area. Emery also reported the sedimentation rate of organic carbon to this location to be about 0.1 mg/cm^2/yr. The carbon data of Figure V-1 indicate a total accumulation for organic carbon (from the 18-cm depth to the surface) of about 500 mg/cm^2. The time span of discharge from the Whites Point outfall can be ascertained from Figure III-3 and suggests that this accumulation has taken place during a time span of about 38 years (i. e., 1934 to 1972). The total accumulation of effluent organic carbon (500 mg/cm^2) in core P6C would therefore imply a mean sedimentation rate for organic carbon of about 13 mg/cm^2/yr. If it is further assumed that the outfall-induced rate of accumulation of total solids varies, and that this variation can be approximated by a linear dependence with respect to time, such as

$$\frac{d\bar{M}^i_{sp}}{dt} = \alpha^i t \,, \qquad (5.2)$$

where

$d\bar{M}^i_{sp}/dt$ = the mass flux of outfall solids into the sediments at some location i,

α^i = a constant, characteristic of location i , and

t = time, relative to the initiation of the outfall source,

then the present organic carbon mass flux rate for this particular core would attain a value of about 26 mg/cm^2/yr. A linear time dependence is suggested if it is assumed that the mass flux rate at any particular station is proportional to the flux of particulate matter from the outfall and that this flow rate can be approximated by a linear time dependence as the discharge flow data suggest (Figure III-3).

Also, if it is assumed that the settleable outfall particulate matter contains about 20 per cent refractory organic carbon fraction, as suggested by the effluent decay data of Section III-3, a flux of 130 mg/cm^2/yr for total solids due to the outfall is implied. This is about 14 times that noted by Emery for pre-outfall sedimentation of total solids, and the estimated present input of total organic carbon (26 mg/cm^2/yr) is about 260 times the reported natural sedimentation of organic carbon.

In order to convert the above mass flux rates to actual depth accumulation rates, it is necessary to know the wet density of the deposited material to account for the presence of water in the sediments. Three wet density analyses were performed on centrate solids in order to estimate the wet density of "deposited" effluent particulate material (d_{wp}). These analyses consisted of washing and centrifuging centrate solids at 2000 rpm. Densities were then determined on the "centrifuged" solids as outlined in Section IV-2a. The results are given in Table V-1.

Table V-1. Water Contents and Wet Densities of Centrifuged Effluent Particulate Matter

Sample	d_{wp}	% Water
24-hr composite effluent (6/29/73)	0.12 gr/cm^3	88
centrate (7/18/73)	0.11	89
centrate (7/18/73)	0.11	84

If a wet density of 0.11 gr/cm^3 is assumed for "deposited" particulate material from the outfall, then the above estimated present mass flux rate of total dry solids due to the outfall (130 $mg/cm^2/yr$ for core P6C) implies a sedimentation rate of about 1.2 cm/yr. As in the derivation of the present mass flux rate, if it is assumed that the sedimentation rate has increased linearly with time, then a total depth of accumulation over a 38-year time period of about 22 cm is inferred. Such a calculation is in general agreement with the measured accumulation for core P6C of about 18 cm.

The estimated present sedimentation rate of about 1.2 cm/yr can further be compared with an expected natural sedimentation rate by using a wet density for natural deposited matter of about 0.98 gr/cm^3. This wet density is estimated from the water content of pre-outfall sediments in the box cores and from a relationship between water content and wet density shown in Figure V-2. Using this wet density, Emery's mass flux rate of 9 $mg/cm^2/yr$ implies a natural sedimentation rate of about $9(10^{-3})$ cm/yr. The present sedimentation rate is therefore estimated to be totally dominated by the sewage input of particulate matter.

V-1b. The Estimated Total Accumulation of Effluent Organic Carbon on the Palos Verdes Shelf. It is highly desirable to extend the above type of calculation performed on core P6C to the rest of the Palos Verdes Shelf. The fact that a "characteristic" profile was suggested for organic carbon concentrations and water contents in the various cores analyzed (Figure IV-8) would allow for a reasonable extension of the above calculations to the sediments of the whole shelf if a characteristic wet-density profile could also be shown. It seemed quite reasonable to expect the wet density of sediments to be highly dependent on the water content for those sediments of high water content (i. e., conditions for which individual grain sizes and shapes would not be a limiting factor). The wet densities of a number of different sediment samples were therefore determined and the results have been expressed as a function of water content in Figure V-2. For the type of sediments under consideration, the data reveal that there is a strong relationship between the two variables, water content and wet density. The characteristic water content profile of Figure IV-8 therefore suggests a characteristic wet density profile.

Since the wet densities and organic carbon concentrations of the shelf sediments are relatively well defined by characteristic depth profiles, then it is implied that the integration of these two variables with depth (equation 5. 1) essentially defines a characteristic trend for the total accumulation of organic carbon, where only the extent of accumulation may vary from one core to another. In other words, the total mass accumulation of organic carbon for various cores on the shelf would follow a similar trend as shown in Figure V-1 for core P6C. To make further use of such a generalization of the organic carbon data, the mass accumulation of organic carbon at some depth x (as shown in Figure V-1) has been plotted as a function of the percentage organic carbon (at that same depth) in Figure V-3. This representation is for those sediments affected by an outfall input of organic matter and assumes that pre-outfall sediments are characterized by an organic carbon concentration of 1 per cent or less.

In an attempt to estimate the total accumulation of outfall carbon on the Palos Verdes Shelf, the relationship which was derived

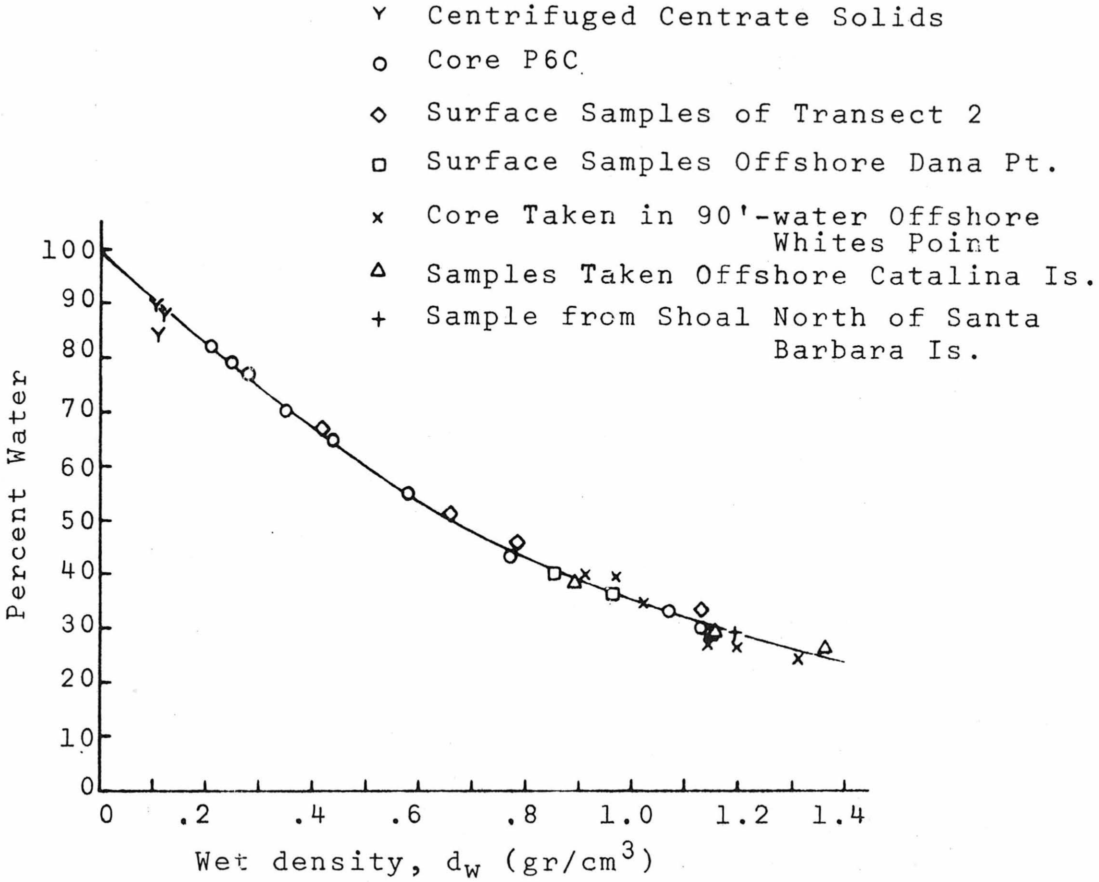


Figure V-2. The relationship between water content and wet density for various sediment samples.

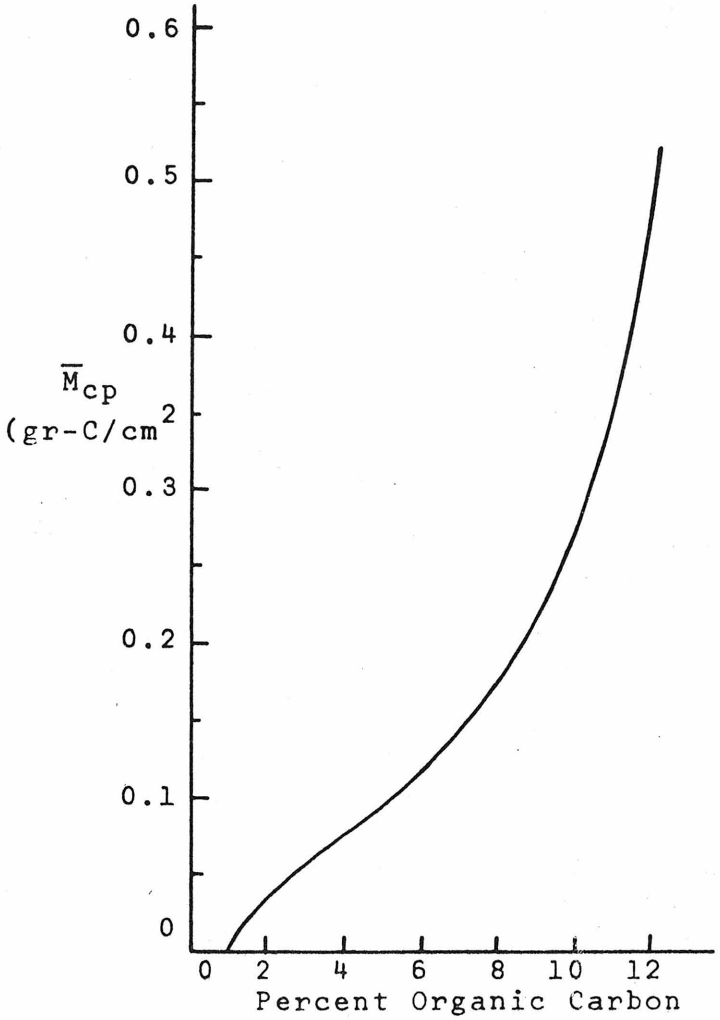


Figure V-3. The outfall-induced total mass accumulation of organic carbon per unit area ($\overline{M}_{cp}$) within a sedimentary core as a function of the organic carbon concentration at the surface of that core (based on data from core P6C).

from the Phleger core P6C and which is shown in Figure V-3 and the distribution of outfall organic carbon in the shelf's surface sediments (Figure IV-9) have been used. The estimated geographical distribution of the total accumulation of outfall particulate organic carbon is shown in Figure V-4. This distribution is based upon the assumption that the organic carbon and water content, and therefore the wet density distributions, are similar over the shelf.

An estimate of the total contribution of organic carbon from the outfall to the local shelf sediments was made by integrating the spatial distribution of the estimated accumulations of organic carbon shown in Figure V-4. The integration was performed in an approximate manner by determining the area under the individual transect distributions and then assuming a stepped distribution between transects. This approximate calculation indicated that the total mass of outfall organic carbon which has accumulated within the area of the shelf under consideration was about $1.4(10^{10})$ grams. In order to compare this value with the total discharge of organic carbon from the outfall, the effluent flow distribution shown in Figure III-3 was also integrated and expressed in terms of total discharge of particulate organic carbon by assuming an effluent suspended solids concentration of 300 mg/l and a particulate organic carbon concentration of 34 per cent (Table III-1a). Based on these assumptions, the value for total particulate organic carbon discharged from the outfall was estimated to be $9(10^{11})$ grams. A comparison between the estimated total accumulation and the total discharge of this carbon thus indicated that about one per cent of the total discharged particulate organic

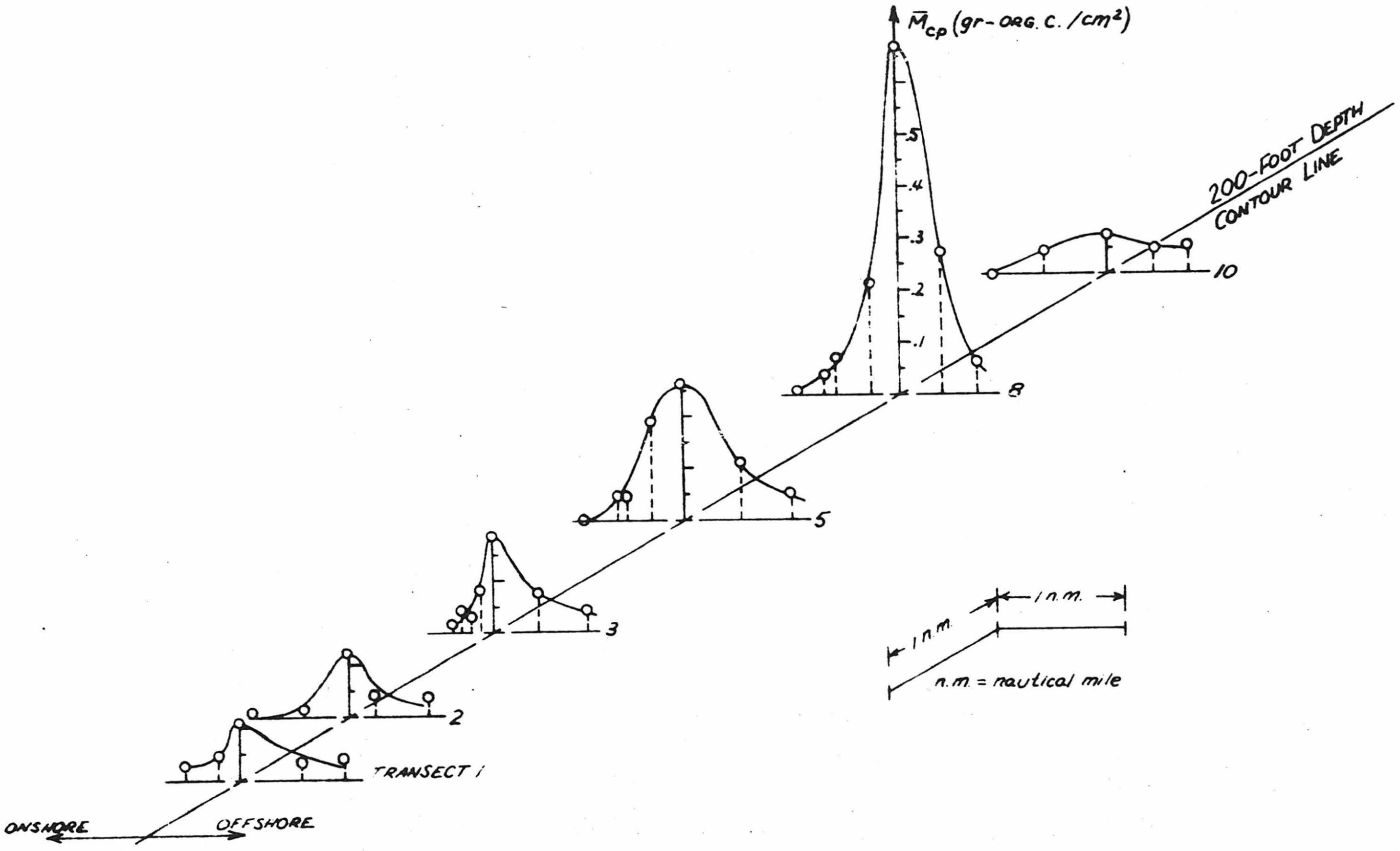


Figure V-4. The estimated distribution of the total mass of effluent particulate organic carbon per unit area ($\overline{M}_{cp}$) deposited on the San Pedro Shelf.

organic carbon has been retained on the shelf. However, although the total accumulation of mass is relatively small, the depth of the accumulation is relatively large due to the high water content (low wet density) of this matter.

V-2. Isotopic Considerations

The source of total organic carbon in the sediments offshore of Whites Point has been shown to be primarily due to a sewage input via a submerged sewer outfall system and a natural marine input due to the local biomass. The fractional abundance of organic carbon within a particular sedimentary sample may accordingly be defined as

$$f_{cs} = \frac{\bar{M}_{cp} + \bar{M}_{cn}}{\bar{M}_s} , \qquad (5.3)$$

where $\bar{M}_{cp}$ and $\bar{M}_{cn}$ are the mass of organic carbon per unit area due to the pollutant (subscript p) and natural (subscript n) sources, respectively, and $\bar{M}_s$ is the mass of total solids (both organic and inorganic) per unit area. Defining r_{sp} (r_{sn}) as the ratio of total solids of the pollutant (natural) source to the total solids due to all sources (p and n) within a sample of sediment, and f_{cp} (f_{cn}) as the refractory fractional abundance of organic carbon in the source material p (n), then

$$f_{cs} = r_{sp}f_{cp} + r_{sn}f_{cn} \qquad (5.4)$$

where $r_{sp}+r_{sn} = 1.0$. Therefore,

$$r_{sp} = \frac{f_{cs}-f_{cn}}{f_{cp}-f_{cn}} \qquad \text{and} \qquad r_{sn} = \frac{f_{cp}-f_{cs}}{f_{cp}-f_{cn}} , \qquad (5.5)$$

and the ratio of the two mass sources (R_s) is defined and expressed as:

$$R_s = \frac{r_{sp}}{r_{sn}} = \frac{f_{cs} - f_{cn}}{f_{cp} - f_{cs}} \quad . \qquad (5.6)$$

Similarly, if the δC^{13} values of the two sources within the sediments can be taken as constants, then the ratios of the mass input of carbon (R_c) can be expressed as:

$$R_c = \frac{r_{cp}}{r_{cn}} = \frac{\delta_n - \delta_s}{\delta_s - \delta_p} \quad , \qquad (5.7)$$

where r_{cp} (r_{cn}) is defined as the ratio of the mass of organic carbon of source p (n) to the total mass of organic carbon within a sediment sample, and δ_p (δ_n) is the δC^{13} value of refractory organic carbon from source p (n). R_c can also be expressed as

$$R_c = \frac{f_{cp}}{f_{cn}} R_s = F_c R_s \qquad (5.8)$$

where $F_c = f_{cp}/f_{cn}$. Combining equations (5.5) and (5.6) then gives the following relation for the δC^{13} within such a sedimentary sample (δ_s):

$$\delta_s = \frac{F_c R_s \delta_p + \delta_n}{F_c R_s + 1} \quad . \qquad (5.9)$$

Equation (5.9) is the result of a mass balance on the organic carbon and describes the δC^{13} shift within such a sedimentary core (i.e., two sources of organic matter with δC^{13} values δ_p and δ_n) to be solely governed by $F_c R_s$. In other words, the distribution of f_{cs} within a particular core is assumed to result from the contribution of two sources: (a) f_{cp}, which is in the range of 0.20 to 0.25 (Section III-3); and (b) f_{cn}, which is about 0.01; and that the relative contributions of the two sources of carbon describe the δC^{13} variation.

Figure V-5 presents the results of computations based on

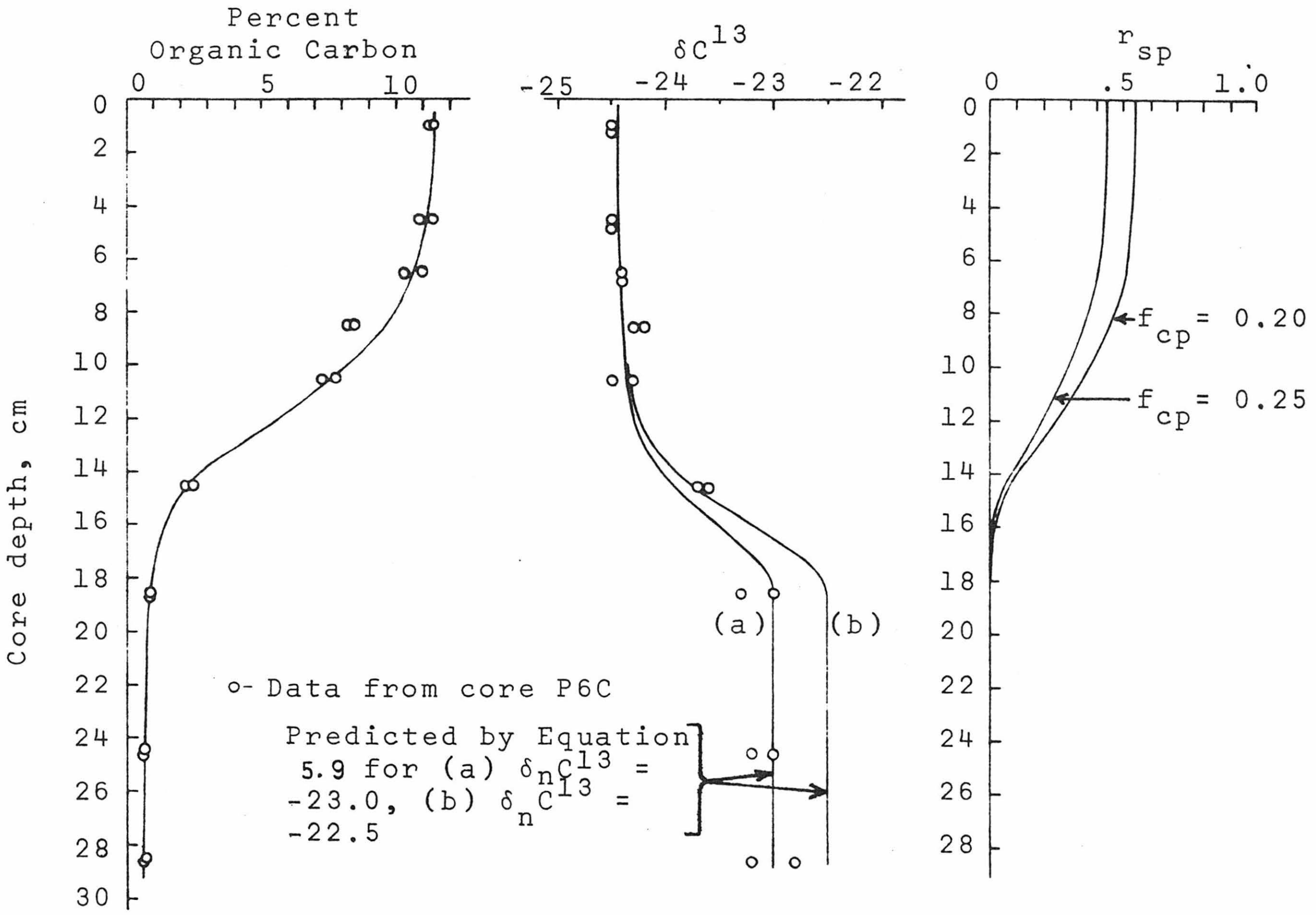


Figure V-5. Predicted δC^{13} profiles assuming f_{cs} represents a mixing of two sources of organic matter (f_{cp}, $\delta_p C^{13}$ and f_{cn}, $\delta_n C^{13}$).

equation (5.9) for two different background δC^{13} values (δ_n). The f_{cs} data (for differing core depths) which were used in equation (5.9) were taken from core P6C and are therefore also shown. The measured isotopic data for core P6C are presented for comparison. Although δC^{13} as given by equation (5.9) is insensitive to a varying value of f_{cp}, the observed trend in δC^{13} values is generally consistent with that predicted by a mixing of two different sources of organic matter where the relative contributions are defined by the organic carbon concentration (f_{cs}) variation with depth.

Data are also presented in Figure V-5 for the corresponding ratio of pollutional solids per unit area to total solids per unit area (r_{sp}) as given by equation (5.5). This parameter is dependent upon the value of f_{cp}.

The data on the rate of decay of effluent particulate organic carbon of Section III-3 indicated that such matter discharged from the Whites Point outfall possessed a potential for decay which could result in a refractory percentage organic carbon of only 20 to 25 per cent (i.e., $f_{cp} = 0.20$ to 0.25). The change with depth of the fractional mass abundance of total pollutant solids (r_{sp}) predicted by equation (5.5) and shown in Figure V-5 is based on these two refractory carbon (f_{cp}) values. As Figure V-5 indicates, there is no important difference in the predicted r_{sp} values for the indicated range of f_{cp}. The calculation for r_{sp} suggests that about 50 per cent of the total mass of surface material of core P6C is due to the outfall source; i.e., the ratio of the mass of outfall solids to the mass of natural solids (R_s) in the surface sediments of core P6C is about 1.

Based on the estimated high refractory organic carbon content (20 to 25 per cent) for sediments of outfall origin, the ratio of outfall carbon to natural carbon (R_c) is estimated to be in the range of 20 to 25. These estimated values of R_s and R_c are of an order of magnitude less than the approximations based strictly on the comparison of total carbon mass accumulations in core P6C in the last 38 years as compared to the value given by Emery for a pre-outfall sedimentation rate (Section V-1a). The latter estimates suggested values for R_s and R_c of 14 and 260, respectively.

The discrepancy in these two different estimates of R_c and R_s would indicate that a dilution of deposited outfall matter with natural marine material of a more inorganic nature has occurred. A similar dilution was also noticed in trace metal determinations on these same sediments by Galloway (1972), and could be due to several factors. It could be caused by a much greater natural sedimentation rate than that of 9 $mg/cm^2/yr$ reported by Emery (1960). A second possibility is that the organic-rich deposits derived from the outfall may act somewhat as a "sink" for fine-grained natural sediments which are normally transient on the shelf and for particulates associated with a suspended load of the overlying bottom waters. In other words, the presence of effluent sludge deposits may have induced an increased sedimentation rate of non-outfall matter. It would be important to determine if there exist such effects on the sedimentation of non-outfall matter in the sediments near the effluent discharge.

The third possible process which may affect the composition of the sediment is the possible role of biophysical mixing processes acting at the changing sedimentary interface. Such a process could result in an upwards entrainment of some pre-outfall sediments and thereby produce a lower relative abundance of pollutant solids (r_{sp}) in the surface sediments than that predicted on the basis of total carbon accumulations. The potential role of such a process and also the possibility of a greater sedimentation rate for non-outfall matter will be further discussed in Section V-3.

It is of interest to examine the δC^{13} data determined for sedimentary total organic carbon on the San Pedro Shelf to determine if the data could assist in a further evaluation of the relative contribution of different sources of carbon. The δC^{13} data on cores P6C, P1C, and P1D and the δC^{13} data from transects 1, 8, and 10 (see Tables IV-2, 6, and 9) have been plotted in Figure V-6 as a function of the corresponding percentage organic carbon. The mixing relationship, equation (5.9), expressing δC^{13} as a function of the percentage organic carbon in a sediment core, for given δC^{13} and organic carbon concentration properties of two source materials, is also shown in Figure V-6 for comparison. The data for core P6C and transect 8 follow the predicted "mixing" relationship reasonably well; however, it is seen that the carbon data taken offshore of Rocky Point (cores 1C and 1D, and transect 1) and some of the nearshore data from transect 10 deviate from the predicted relationship. This deviation is the opposite of that which would be suggested by decay processes (the loss of carbon and a corresponding lowering of the δC^{13} value), and in a direction which could be caused by a relatively

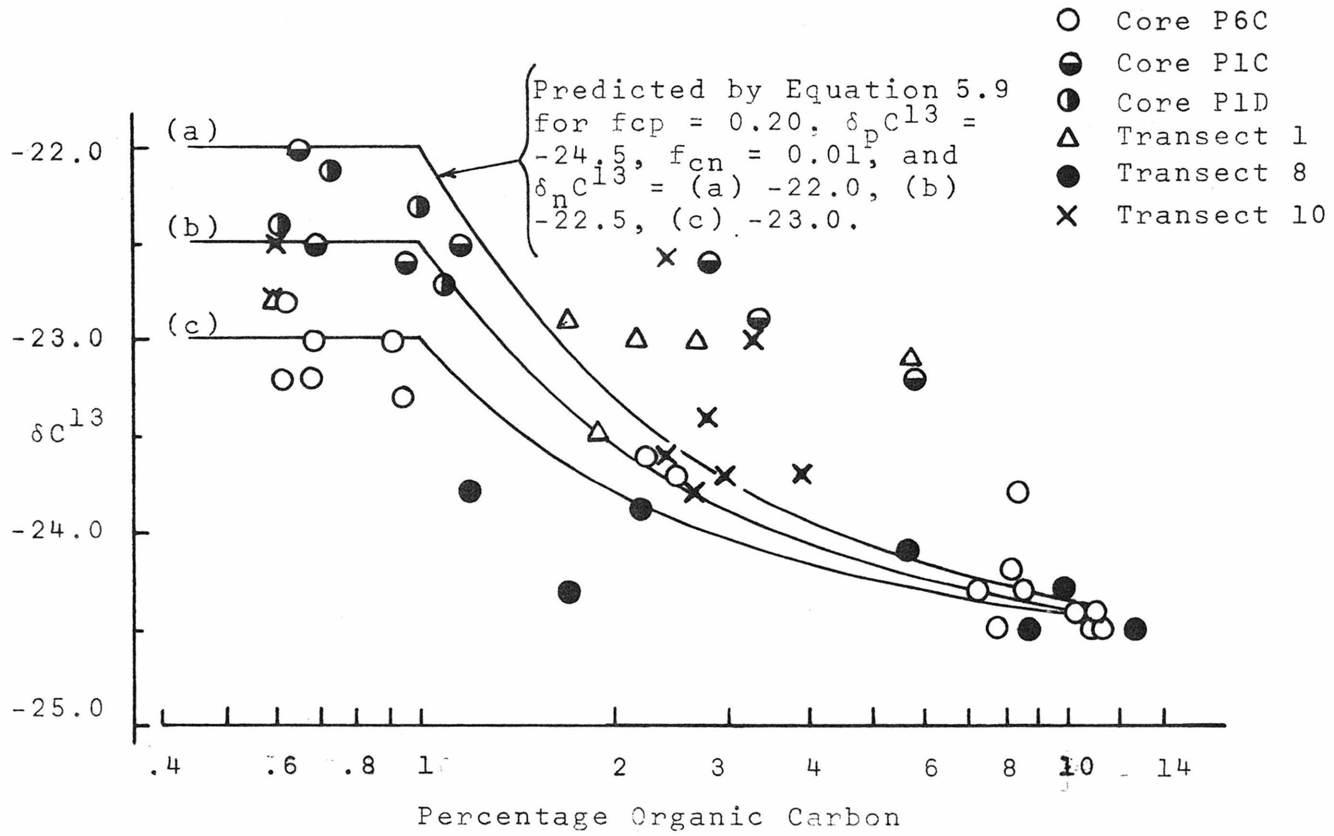


Figure V-6. δC^{13} values for total organic carbon plotted as a function of percentage organic carbon.

greater fractional contribution of marine organic carbon. Such a trend in the data could be caused by a greater primary productivity of these local waters due to nutrients from the sewage discharge.

The possibility of an increased productivity being reflected in the δC^{13} values of sedimentary organic carbon is generally supported by the work of Reid (1972) and SCCWRP (1973). Reid (1972) reports an increase in phytoplankton near southern California coastal sewage outfalls, including a station near the Whites Point discharge. This increase in productivity was reported to be similar to those found in areas of upwelling. Studies by SCCWRP (1973) also indicate a modest enhancement of productivity within a few kilometers of an outfall. Comparison of chlorophyll levels in various marine waters offshore of southern California indicated a general enhancement in the area offshore of Whites Point.

The nearshore δC^{13} data for transect 10 indicate that the shallow waters offshore of Point Fermin tend to be productive in plankton. This is in agreement with observations of Hotchkiss (1973).

The fact that a higher productivity appears to be indicated in the sediments along transects 1 and 10 does not negate the possibility that such an input of marine organic carbon is present in the other sediments of the area under study. In fact, such an input was suggested by the δC^{13} data shown in Figure IV-8 and discussed in Section IV-2b. However, in this latter case the δC^{13} data for the surface sediments indicated that the input of particulate organic carbon from the outfall was the dominant source of carbon near the location of effluent discharge.

V-3. Quantitative Considerations of Mass Flux Rates as Related to the Distribution of Organic Carbon in the Palos Verdes Shelf Sediments

It is of interest to consider the accumulation of organic carbon on the Palos Verdes Shelf in terms of mathematical modeling in order to gain a further understanding of the sedimentary distribution patterns for carbon. Such considerations will also allow for a further examination of the possible roles of either a biophysical mixing process or an increased natural sedimentation rate in affecting the depth distribution of organic carbon in the sediments.

V-3a. The Mass Accumulation of Organic Carbon. For some station j , the rate of accumulation of substance i per unit area may be described as

$$\frac{d\bar{M}_i^j(x,t)}{dt} = \left.\frac{\partial \bar{M}_i^j(x,t)}{\partial x}\right|_t \frac{dx}{dt} + \left.\frac{\partial \bar{M}_i^j}{\partial t}\right|_x = \left.\frac{\partial \bar{M}_i^j(x,t)}{\partial x}\right|_t \omega^j(t) + \left.\frac{\partial \bar{M}_i^j}{\partial t}\right|_x \qquad (5.10)$$

where

$\bar{M}_i^j(x,t)$ = mass per unit area of substance i at station j (a function of x and t),

x = vertical distance in sediment (taken as positive in the upwards direction from some reference level) ,

t = time , and

$\omega^j(t)$ = the rate of sediment depth accumulation at station j .

Berner (1971) refers to eq. (5.10) as the general diagenetic equation. With x taken as positive in the upwards direction, $\partial\bar{M}_i^j/\partial t|_x$ accounts for all diagenetic (post-depositional) changes in $\bar{M}_i^j$, and $\partial\bar{M}_i^j/\partial x|_t\,\omega(t)$ accounts for changes in $\bar{M}_i^j$ due to the deposition of substance i .

The rate of decay data on effluent organic carbon discussed in Section III-3 indicated that the decay of labile particulate organic carbon should be relatively rapid in an aerobic marine environment and extremely slow in an anaerobic environment. Based on the decay data, an upper time limit for the time needed to aerobically stabilize 90 per cent of the labile particulate carbon was estimated to be 60 days. Such a stabilization rate suggests that the major decay of deposited effluent particulate carbon would probably occur at the sediment - water interface. When considering the accumulation of effluent particulate organic carbon on the Palos Verdes Shelf, it is therefore reasonable to assume the diagenetic term in eq. (5.10) to be of minor importance compared with the accumulatory term. For the case of the accumulation of effluent particulate organic carbon on the Palos Verdes Shelf, equation (5.10) may then be approximated as:

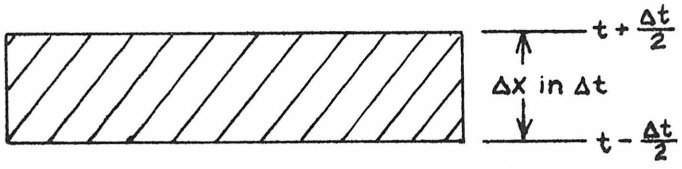
$$\frac{d\bar{M}^{j}_{cp}}{dt} = \left.\frac{\partial \bar{M}^{j}_{cp}}{\partial x}\right|_{t} \omega^{j}(t)$$

or (5.11)

$$\left.\frac{\partial \bar{M}^{j}_{cp}}{\partial x}\right|_{t} = \frac{1}{\omega^{j}(t)} \frac{d\bar{M}^{j}_{cp}}{dx} \quad ,$$

where $\bar{M}^{j}_{cp}$ is the mass of organic carbon per unit area at station j.

If we now consider a layer of sediment (Δx) which has accumulated in a time interval Δt ,



Accumulated Layer of Sediment

then it can be shown (Berner, 1971) that the rate of sediment depth accumulation at station j is given by

$$\omega^j(t) = \frac{d\bar{M}_s^j/dt}{d_s(t)(1-\phi(t)} \tag{5.12}$$

where

$\frac{d\bar{M}_s^j}{dt}$ = the rate of accumulation of total solids at station j ,

$d_s(t)$ = average density of dry sediment particles at time t ,

and $\phi(t)$ = the porosity of this layer at time t.

The average density of the sedimentary particulates is defined as

$$d_s(t) = \frac{M_s(t)}{V_s(t)} \tag{5.13}$$

where M_s = the dry mass of sedimentary particles, and V_s = the dry volume of the mass M_s.

The sedimentary property previously described (Section IV-2) as the wet density (d_w) is defined as:

$$d_w(t) = \frac{M_s(t)}{V_s(t)+V_w(t)} = \text{the mass of dry solids per unit total wet volume,} \tag{5.14}$$

where V_w = the volume of water associated with the mass of sediment M_s. Combining (5.12) and (5.14) gives

$$d_w(t) = (1 - \phi(t))d_s(t) \ . \tag{5.15}$$

Equation (5.12) can now be expressed as

$$\omega(t) = \frac{1}{d_w(t)} \frac{d\bar{M}_s}{dt} \ , \tag{5.16}$$

and (5.11) can be expressed as

$$\left.\frac{\partial\bar{M}_{cp}^j}{\partial x}\right|_t = \frac{d_w^j(t)}{[d\bar{M}_s^j/dt](t)} \cdot \frac{d\bar{M}_{cp}^j}{dt}(t) \ . \tag{5.17}$$

The total mass accumulation considerations of Section V-1 indicated that, on the Palos Verdes Shelf, the rate of sediment depth accumulation is totally dominated by the input of particulate matter from the outfall. For this situation, the rate of depth accumulation may be expressed as

$$\omega^j(t) = \frac{1}{d_{wp}} \frac{d\overline{M}^j_{sp}}{dt} \tag{5.18}$$

where $\overline{M}^j_{sp}$ = the mass of total dry effluent solids per unit area at station j , and d_{wp} = the wet density of these deposited solids. Letting $d\overline{M}^j_{cp}/dt = f_{cp}\,(d\overline{M}_{sp}/dt)$, where f_{cp} is the fractional mass abundance of organic carbon in the deposited effluent particulates, allows (5. 17) to be described by:

$$\left.\frac{\partial \overline{M}^j_{cp}}{\partial x}\right|_t = f_{cp} d_{wp} \; . \tag{5.19}$$

We can estimate what $f_{cp} d_{wp}$ should be if we assume an average wet density of 0.11 gr/cm^3 (Table V-1) for deposited effluent particulates which have a refractory organic carbon concentration of about 20 to 25 per cent ($f_{cp} d_{wp} = 0.11 \times (0.20 \text{ to } 0.25)$). This results in a range for the term $f_{cp} d_{wp}$ of 0. 022 to 0. 028 gr carbon/cm^3. This range is in general agreement with the slope ($\partial \overline{M}_c/\partial x$) of the organic carbon accumulation curve shown in Figure V-1 for core P6C. The slope in the upper portion (outfall-influenced) of this core is somewhat variable but is approaching a value of about 0. 025 gr-carbon/cm^3. The agreement of this value with that suggested by (5. 19) indicates that the rate of accumulation of organic carbon on the shelf, expressed as $\partial \overline{M}_c/\partial x$, is primarily defined by the term $f_{cp} d_{wp}$.

The result of the above formulations may appear somewhat obvious. However, the formulations are needed in order to discuss the possible role of a biophysical mixing process in these sediments.

V-3b. The Biophysical Mixing of Sediments. A comparison of the rates of accumulation of total mass in core P6C with a natural rate of sedimentation reported by Emery (1960) for the Palos Verdes Shelf area indicates that the Whites Point outfall has been the dominant source of sedimentary matter to the local shelf sediments during the operational history of the outfall (see Section V-1). However, the mass balance considerations of Section V-2 indicate that there is a greater amount of matter of a more inorganic nature in the surface sediments than is expected from the dominant contribution of the outfall carbon-rich material. Such a dilution of outfall sedimentary matter with a more inorganic-like natural sediment has resulted in a less marked depth transition from pre-outfall sedimentary conditions for such properties as water content, wet density, and the percentage organic carbon.

Jackson (1973) suggested that this relatively slow change with depth in these properties could be due to a biophysical mixing of the uppermost sediments to a depth of some centimeters. Such processes of mixing near the sediment - water interface are due to the burrowing activities of certain biota as well as to physical forces caused by swells and turbulence in shallow marine waters. In their discussion of the sediment textural patterns on the San Pedro Shelf, Gorsline and Grant (1972) report that the infauna undoubtedly work over the upper few tens of centimeters of sediments over the entire shelf area. It is possible by simple mass balance considerations to derive an expression relating the extent of biophysical mixing with the nature of the transition of the various properties of the sediments from pre-outfall time to the present.

Defining a biophysical mixing depth D as a vertical interval of sediment at the sediment - water interface within which the sediments are well mixed by biophysical processes, the time rate of change of the mass of organic carbon per unit area within this interval may be described as

$$\frac{d\bar{M}_c^V}{dt} = \frac{d}{dt}(f_{cs} d_{ws} D) = \frac{d\bar{M}_{cp}}{dt} + \frac{d\bar{M}_{cn}}{dt} - \omega(t) f_{cs} d_{ws} \qquad (5.20)$$

where

$\bar{M}_c^V$ = mass of organic carbon per unit area (A) within an element of sedimentary volume V ($V = A \times D$) ,

f_{cs} = fractional abundance of organic carbon in the sediment within V ,

d_{ws} = wet density of sediment within V ,

D = vertical interval of complete mixing,

$\bar{M}_{cp}$ = mass of outfall carbon per unit area within V ,

$\bar{M}_{cn}$ = mass of natural carbon per unit area within V ,

ω = sedimentation rate, and

t = time.

The last term in this equation represents the flux of organic carbon through the base of the element of volume due to the fact that the interval progresses upwards with time (i. e., sedimentation). Since $d\bar{M}_{cp}/dt$ has been shown to be much greater than $d\bar{M}_{cn}/dt$, we can approximate (5.20) by:

$$\frac{d}{dt}(f_{cs}d_{ws}D) = \frac{d\overline{M}_{cp}}{dt} - \omega(t)f_{cs}d_{ws}$$

or (see eq. (5.11))

$$\frac{\partial}{\partial x}(f_{cs}d_{ws}D) = \frac{1}{\omega(t)}\frac{d\overline{M}_{cp}}{dt} - f_{cs}d_{ws} = f_{cp}d_{wp} - f_{cs}d_{ws} \quad . \qquad (5.21)$$

Although D is unknown, if we assume it to be a constant, then an estimate of the possible contribution of a mixing process can be made. Imposing the following boundary conditions,

$$f_{cs}d_{ws} = f_{cp}d_{wp} \quad \text{at } x = \infty$$

$$f_{cs}d_{ws} = f_{cn}d_{wn} \quad \text{at } x = -D$$

results in the following solution,

$$(f_{cs}d_{ws} - f_{cp}d_{wp}) = (f_{cn}d_{wn} - f_{cp}d_{wp})\,e^{-(1+\frac{x}{D})} \quad . \qquad (5.22)$$

Similarly, repeating such a balance on the accumulation of total solids within this sedimentary interval leads to:

$$(d_{ws} - d_{wp}) = (d_{wn} - d_{wp})\,e^{-(1+\frac{x}{D})} \quad . \qquad (5.23)$$

Using different assumed values of D , eqs. (5.22) and (5.23) were used to calculate profiles of the variation of the percentage organic carbon with depth for different intervals of mixing and for the following boundary conditions.

boundary conditions for equation (5.22):

$f_{cs}d_{ws} = f_{cp}d_{wp} = (0.20)(.11) = 0.022$ gr-carbon/cm^3 at $x = \infty$

$f_{cs}d_{ws} = f_{cn}d_{wn} = (.01)(.97) = 0.097$ gr-carbon/cm^3 at $x = -D$

boundary conditions for equation (5.23):

$d_{ws} = d_{wp} = 0.11$ gr-solids/cm^3 at $x = \infty$

$$d_{ws} = d_{wn} = 0.97 \text{ gr-solids/cm}^3 \text{ at } x = -D$$

The first boundary conditions (at $x = \infty$) assume that the input matter from the outfall is defined by a refractory organic carbon concentration of 20 per cent and a wet density of 0.11 gr/cm^3. The other boundary conditions (at $x = -D$) are based on data from the lower portions of the box cores and thus represent pre-outfall sediment values.

The results of the calculations using equations (5.22) and (5.23) are presented in Figure V-6. Also shown in Figure V-6 for the purpose of comparison is the "characteristic" profile of the percentage organic carbon (see Section IV-2b) for the sediment cores from the Palos Verdes Shelf. The relationship between the calculated and measured variation of organic carbon concentrations with depth suggests that a mixing of surface sediments takes place, resulting in a gradual transition from the initial sediments to those more characteristic of the outfall source in spite of a relatively sudden change in the type of input material. However, a difference in the shape of the calculated and observed curves exists. It is particularly significant that the distribution of the organic carbon appears to be such that an asymptotic value of about 12 per cent is approached rather than the expected 20 to 25 per cent. Such a discrepancy could be due to the assumptions upon which the mixing model was based.

Thus, the discrepancy between the observed and calculated profiles of the variation of the percentage organic carbon with depth is most likely related to either a lower value for the refractory fraction of effluent organic carbon (f_{cp}) and/or the possibility of a relatively greater contribution of natural sedimentation. A convenient

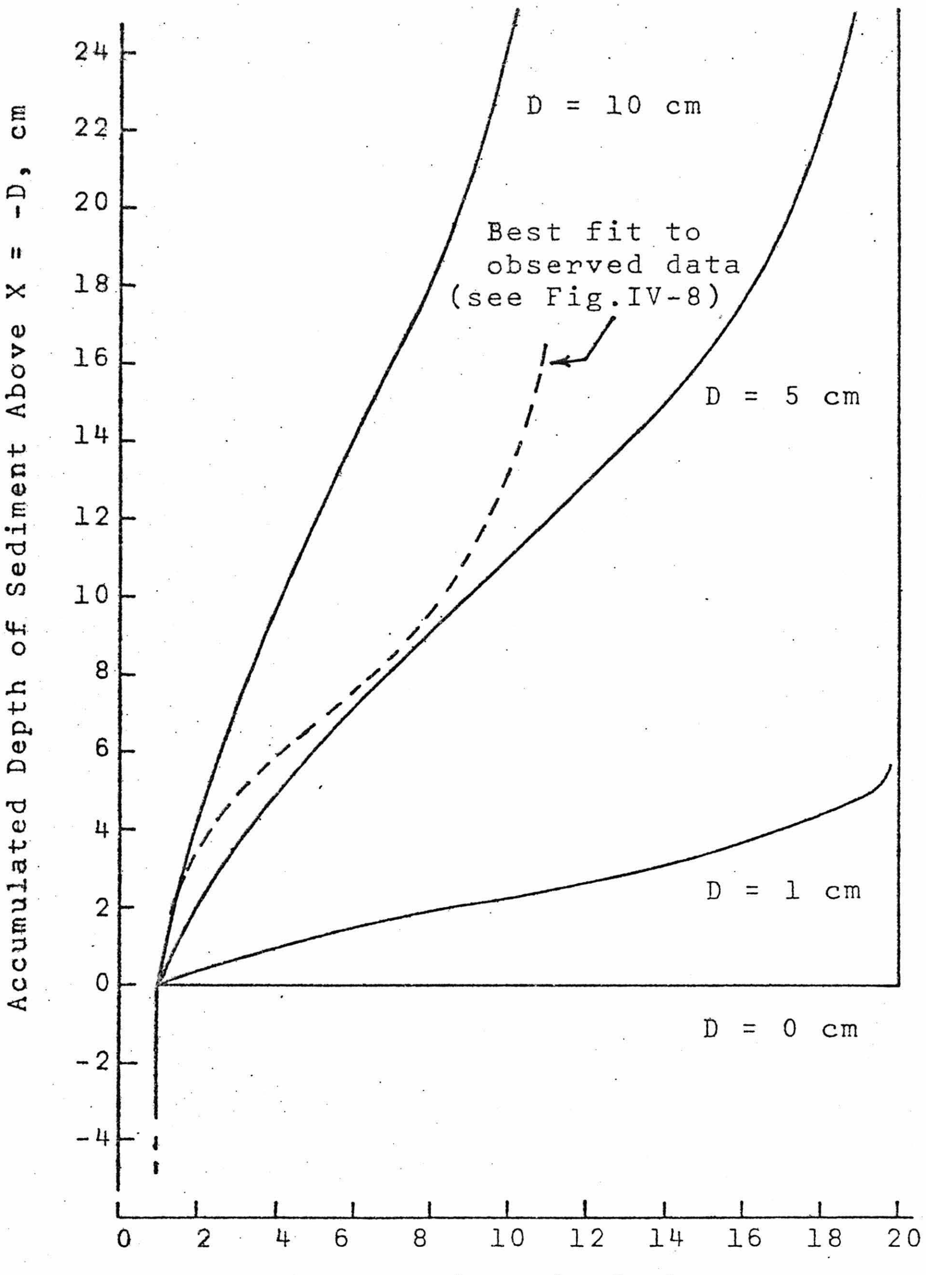


Figure V-6. The predicted depth distribution of the percentage organic carbon as a function of an assumed surface interval of complete mixing (D) (for conditions where f_{cs} dws = 0.022 gr-C/cm^3 and dws = 0.11 gr/cm^3 at X = ∞)

method of estimating the effect of a change in either of these variables on the calculated curves is to merely change the boundary conditions imposed on equations (5.22) and (5.23) to be compatible with values of percentage organic carbon and wet density measured in surface sediments of the Palos Verdes Shelf. Figure IV-8 showed that the percentage organic carbon and the percentage water of surface sediments near the outfall approach values of about 12 per cent and 80 per cent, respectively. The 80 per cent water content is analogous with a wet density of 0.20 gr/cm^3 (Figure V-2).

Using the 12 per cent organic carbon value and a wet density of 0.20 gr/cm^3, the following upper boundary conditions for equations (5.22) and (5.23) are respectively suggested:

$$f_{cs} d_{ws} = (0.12)(0.20) = 0.024 \text{ gr-carbon/cm}^3 \quad \text{at } x = \infty \ ,$$

$$d_{ws} = 0.20 \text{ gr-solids/cm}^3 \quad \text{at } x = \infty \ .$$

With these new boundary conditions, equations (5.22) and (5.23) give results for the variation of percentage organic carbon with depth for different assumed intervals of mixing, as shown in Figure V-7. Again, the characteristic profile of the variation of percentage organic carbon with depth (Figure IV-8) is shown for comparison. It appears that the above changed boundary conditions result in a better fit between the observed data and calculated curves, indicating that either the refractory organic carbon value for effluent matter is less than the 20 per cent previously estimated and/or that the natural sedimentation rate is greater than Emery's value of 9 mg/cm^2/yr.

It is possible that a better fit could be obtained between the calculated and observed distributions of the carbon content in the

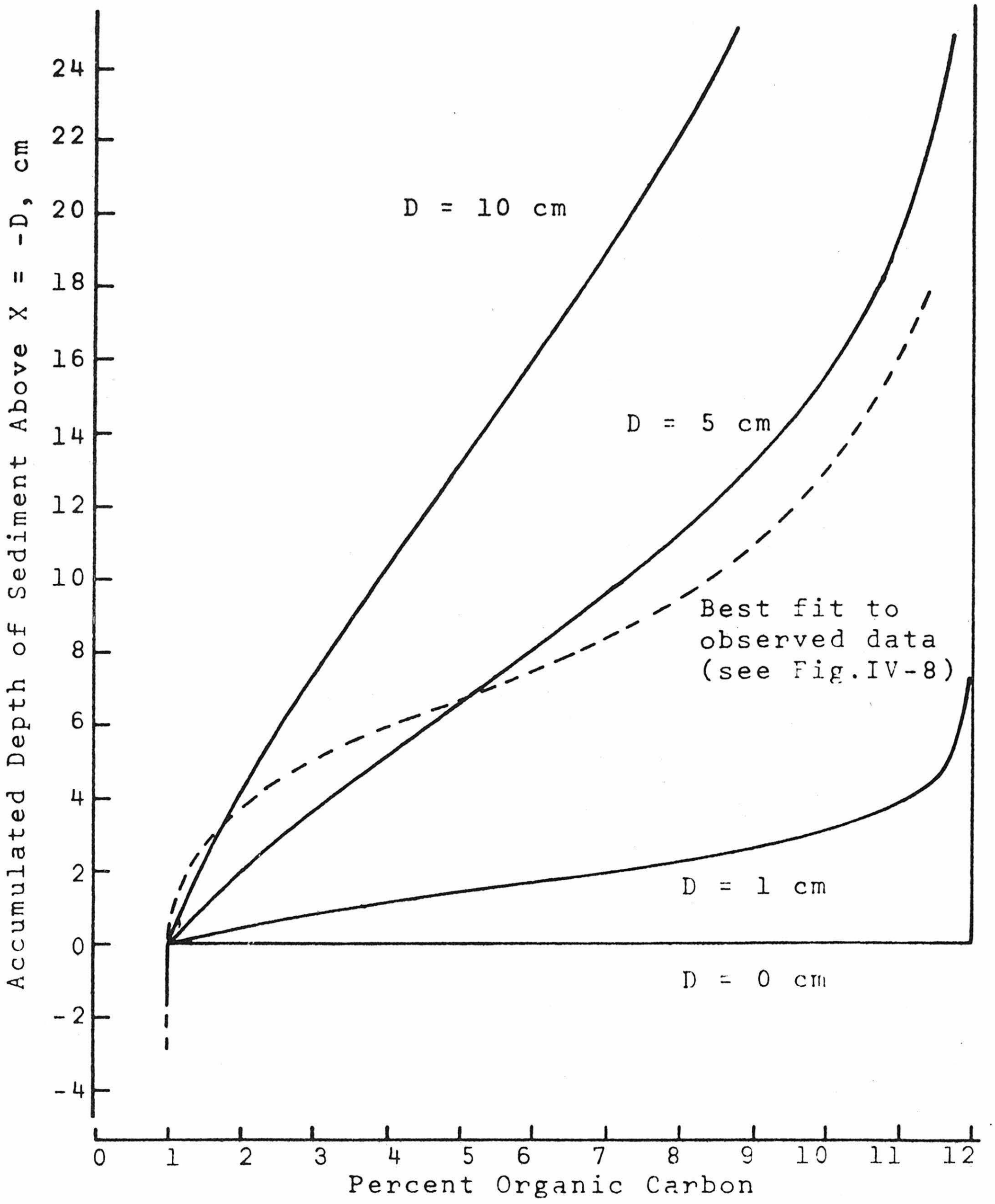


Figure V-7. The predicted depth distribution of the percentage organic carbon as a function of an assumed surface interval of complete sediment mixing (D) (for conditions where f_{cs} dws = 0.024 gr-C/cm^3 and dws = 0.20 gr/cm^3 at X = ∞; f_{cs} dws = 0.0097 gr-C/cm^3 and dws = 0.97 gr/cm^3 at X = -D) sediments as related to the degree of biophysical mixing. However, at the present time an additional effort is not warranted without first obtaining more information on sedimentation rates and processes such as mixing in the sediments. This might be done at a later time.

VI. THE EFFECT OF THE PROPOSED CHANGES IN THE CONCENTRATION OF SUSPENDED SOLIDS IN THE DISCHARGED EFFLUENT ON THE PALOS VERDES SHELF SEDIMENTS

The accumulations of organic-rich material in the sediments of the Palos Verdes Shelf have been shown to be directly attributable to the discharge of sewage effluent to the marine waters offshore of Whites Point. This primary treated effluent has a present suspended solids concentration of about 300 milligrams per liter and is currently discharged at a rate of about 3. 8(10^8) gallons per day. The Water Quality Control Plan for Ocean Waters of California (California, State of, 1972) calls for a decrease in the allowable concentration of particulate matter in discharge effluent to a value of 50 mg/liter. Since the organic-rich sediment accumulations are due to the fact that a certain fraction of these particulates settle to the bottom of the shelf, it might be useful to comment on the effect of these changes in the suspended solids concentration on the sedimentary environment. The results in this thesis may provide some insight into the degree of improvement in the environment for benthic biota which may be achieved by more stringent water quality standards.

VI-1. The Total Accumulation of Organic Carbon as Related to the Occurrence of Anaerobic Sediments on the Palos Verdes Shelf

It is difficult to show the importance of merely the physical addition of effluent particulate matter to the sediments on the changes in the distribution of the benthic biota. The difficulty is due to the association with the particulates of trace concentrations of toxic organic compounds and metals which may have important inhibitory effects on the biological regime. Benthic biological changes due to the mere physical presence of these particles may furthermore be due to several factors such as the sedimentation rate, the particle size distribution, or the presence of anaerobic versus aerobic conditions due to the oxidation of such matter.

The deterioration of an aerobic sedimentary environment to an anaerobic environment can be directly attributable to the rapid sedimentation of oxidizable organic matter. After the oxygen concentration is markedly reduced, dissolved sulfate is utilized as an electron acceptor in the oxidation of organic matter resulting in a buildup of dissolved sulfides. The Los Angeles County Sanitation Districts (LACSD, 1973) estimate the area near Whites Point which is influenced by dissolved sulfides to be about five square miles. Hydrogen sulfide is toxic and may have a direct inhibitory effect on sensitive benthic biota. It is therefore relevant to compare the extent of the anaerobic region with the total accumulation of organic carbon in the same area.

The spatial extent of anaerobic surface sediments estimated by SCCWRP (1973) was presented in Figure IV-1, and the estimated mass accumulation of effluent organic carbon on the Palos Verdes Shelf was shown in Figure V-4. A comparison of the extent of anaerobic sediments along the 200-foot depth contour with the accumulation of organic carbon for the same 200-foot depth contour is presented in Figure VI-1. This figure shows that the occurrence of surface anaerobic conditions is only present if an accumulation of organic carbon from

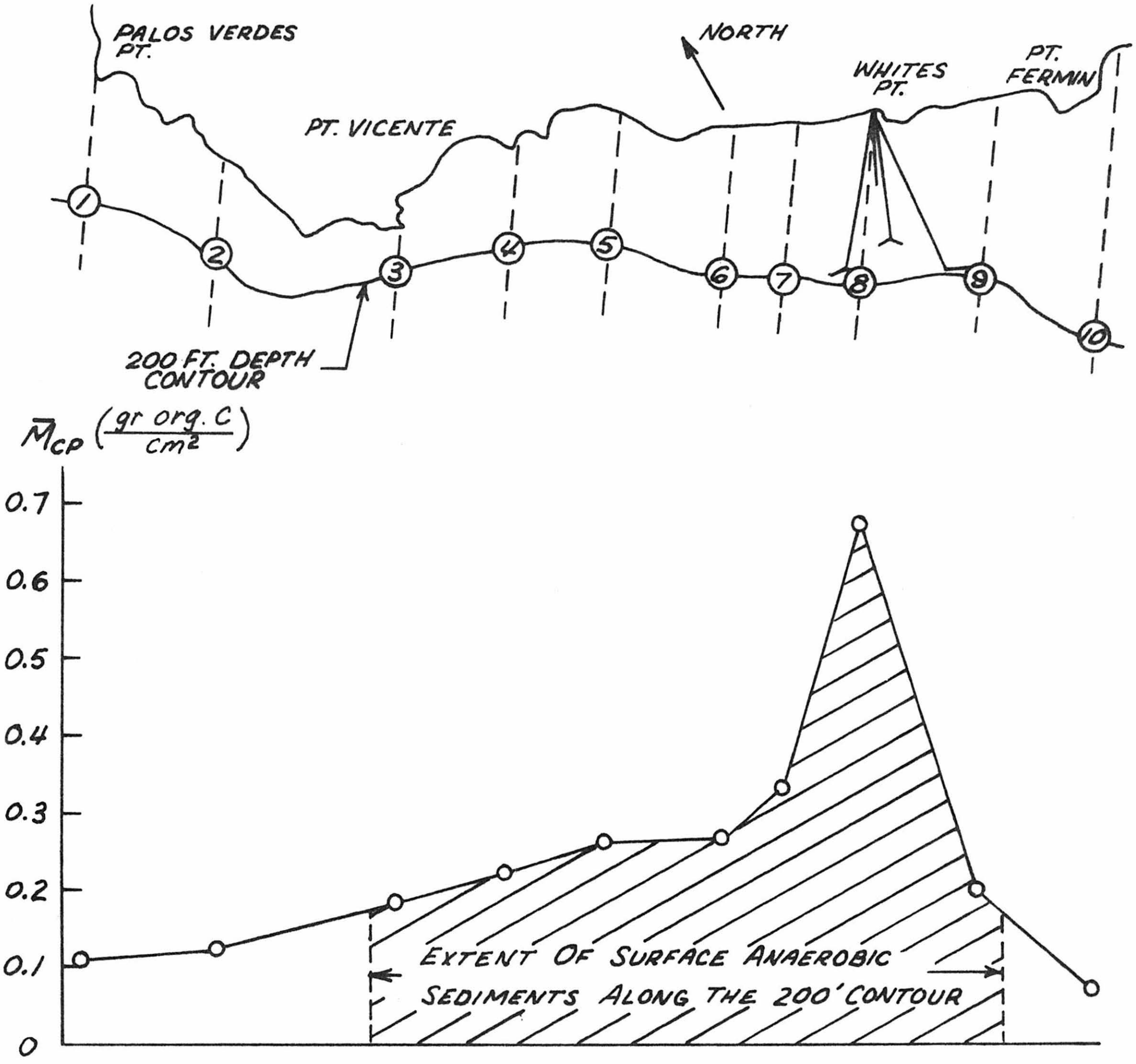


Figure VI-1. A comparison of the accumulation of mass of organic carbon due to the Whites Pt. outfall with the occurrence of anaerobic sediments on the 200-foot depth contour of the Palos Verdes Shelf.

this particular outfall is more than about 0.15 gr/cm^2. Thus, to maintain an aerobic environment, it would have been necessary for an area to have received less than 0.15 gr/cm^2 in the past 38 years. However, it should be noted that the validity of this statement rests upon the assumption that the balance between the input of organic carbon and its oxidation is presently at a steady state. In other words, it is assumed that if the present rate of discharge of effluent particulate matter continued, the transition zone between aerobic surface sediments and anaerobic sediments would remain in the approximate same location. This may or may not be the case.

VI-2. Sedimentary Conditions of the Future

Assuming that the accumulation of effluent organic carbon at any particular station is proportional to the emission of total solids and its associated organic carbon from the sewage outfall to the ocean, an estimate of the relationship between suspended solids concentration in the effluent and the accumulation of such matter in the local sediments may be made if an extrapolation of the presented accumulation data is made. The accumulation of organic carbon at a 200-foot depth along transect 8 is about 0.68 gr/cm^2. Therefore, if the sediments at this particular station were to be aerobic, the above reasoning indicates that the flow of organic carbon would have to be about one-fourth (0.15/0.68) that of the present flow. For the same flow of total effluent (380 MGD), this would require that the concentration of suspended solids be about one-fourth of the present value (300 mg/l) or about 75 mg/l .

Such an extrapolation assumes that there will exist a similarity in the areal distribution pattern of settled effluent particulates in the future (reflected in total accumulation patterns), i. e., that the settling velocity distribution would remain the same. Also, any relationship between the rate of scour of this material from the shelf to the rate of sedimentation has not been taken into account. Although the method of estimating the 75 mg/ l concentration is a highly simplified one, it does allow for some rough guidelines in considering future changes in the suspended solids concentration.

VI-3. Future Changes in Effluent Characteristics

In order to meet water quality requirements of both the Environmental Protection Agency and the State Water Resources Control Board (SWRCB), the board of directors of the Sanitation Districts has passed a resolution calling for compliance and a plan of implementation for improvements in the quality of discharged effluent. In addition to the implementation of a strict source control program on the quality of wastes which will be accepted from industrial plants, the time schedule for compliance calls for the completion of a new sludge dewatering facility by March, 1975 and the completion of a secondary treatment facility by July, 1977. The degree of water quality improvement which is expected to be achieved by these steps is indicated in Table VI-1.

Based on considerations of the rates of accumulation of effluent particulate organic carbon in Section VI-2, the anticipated lowering of the suspended solids concentration should result in more aerobic sedimentary conditions as well as meet the requirements of the SWRCB (California, State of, 1973) which calls for a reduction in the sus-

Table VI-1. Anticipated Future Effluent Characteristics as Related to the California Ocean Plan Requirements (from LACSD, 1973).

Parameter	Ocean Plan Requirements 50% of time	Ocean Plan Requirements 10% of time	1972 JWPCP Median Values	Anticipated JWPCP Median Values(1975)	Anticipated JWPCP Median Values(1977)
Table A					
Grease and Oil, mg/l	10	15	66	50	<10
Floating Part., mg/l	1.0	2.0	0.40	< 0.4	< 0.4
Suspended Solids, mg/l	50	75	286	150 - 175	<50
Settleable Solids, ml/l	0.1	0.2	3.0	1.0	< 0.1
Turbidity, JTU	50	75	71	60 to 70	30 to 50
pH	6 to 9	6 to 9	7.6	7 to 8	7 to 8
Table B					
Arsenic, mg/l	0.01	0.02	< 0.01	< 0.01	< 0.015
Cadmium, mg/l	0.02	0.03	0.019	0.015	0.005
Total Chromium, mg/l	0.005	0.01	0.77	0.35	0.010
Copper, mg/l	0.2	0.3	0.55	0.35	0.10
Lead, mg/l	0.1	0.2	0.29	0.15	0.05
Mercury, mg/l	0.001	0.002	0.001	0.0005	0.0002
Nickel, mg/l	0.1	0.2	0.26	0.20	0.075
Silver, mg/l	0.02	0.04	0.015	0.01	0.005
Zinc, mg/l	0.3	0.5	1.85	1.0	< 0.3
Cyanide, mg/l	0.1	0.2	0.20	0.20	< 0.1
Phenolic Compounds,mg/l	0.5	1.0	2.00	2.00	< 0.1
Total Chlorine Residual, mg/l	1.0	2.0	0	0	0
Ammonia - N, mg/l	40.0	60.	70	40 to 50	30 to 40
TICH, mg/l	0.002	0.004	0.018	0.004	< 0.002
Toxicity Conc., (Toxicity Units)	1.5	2.0	1.8	1.5 to 1.8	< 1.5
Radioactivity, (picocuries/liter) (Gross Beta)	<30 above water supply	-	27.8	<30 above water supply	

pended solids concentration to 50 mg/l.

The effluent suspended solids concentration of 75 mg/l referred to above was obtained using a number of assumptions, and thus should be viewed with caution. In particular, a similarity between settling velocity distributions of the present effluent and that of the future was assumed. The proposed changes in waste treatment will undoubtedly alter the settling velocity distribution, and the effect of this change requires some consideration. For instance, the sludge processing treatment step planned for 1975 is expected to remove the larger and more quickly settling particulates (Hotchkiss, 1973). Thus, it may be that a larger suspended solids concentration than the suggested 75 mg/l could be allowed for maintaining aerobic sediments. On the other hand, a subtle change in the settling characteristics might merely result in an extension of the anaerobic area, although total rates of sedimentation near the outfall might be somewhat less. In other words, the outfall particulates which settle to the sediments might just be spread over a much wider area at such a rate to still cause anaerobic conditions.

The sedimentary δC^{13} data for total organic carbon which were presented in Chapter IV and further discussed in Chapter V indicate that there may also presently be a greater sedimentation of planktonic matter due to the input to the ocean of various nutrients from the outfall. Since the decomposition of planktonic organic matter could also result in a high demand on the available oxygen to bottom sediments, it would be important to assess the effect of future proposed changes in waste treatment on planktonic productivity and any resultant sedimentation of this matter.

It is therefore suggested that a continuous monitoring of inputs to the sediments be made. Such a program would allow for an overall evaluation of how the sedimentary environment will react to improved methods of waste treatment in the future and also give a better idea of the tolerance of the sedimentary environment to additional effluent.

VII. SUMMARY AND CONCLUSIONS

Marine waters of the world are presently being used as dumping grounds for the various waste materials created by a large human population. It has been a misconception that the oceans could provide an infinite sink for such disposal, and it has been only recently realized that the environment of the ocean can be significantly altered by man's wastes. A more extensive knowledge of the chemical and physical interaction of receiving waters with waste material discharge to the ocean is needed such that guidelines for man's ability to deal with such problems are available for the future.

The impact of the discharge of about $3.8(10^8)$ gallons per day of primary treated wastewaters to the marine waters offshore of Palos Verdes was evaluated on the basis of the accumulation of organic carbon on the Palos Verdes Shelf. The method of analysis employed the use of stable carbon isotopic techniques to relate sedimentary organic carbon to its source of origin.

The findings of this investigation are not only of interest to the environmental engineer but also of interest to the sedimentary geochemist since the response of a sedimentary environment to a relatively well-defined input of matter was possible.

VII-1. Principal Findings

1) δC^{13} values of potential sources of sedimentary organic carbon on the Palos Verdes Shelf indicated that there exists a difference in δC^{13} values of the primary potential sources. Planktonic matter, which is the greatest contributor of organic carbon to most ocean sediments, had a small range of δC^{13} values with a mean of

about -20 o/oo. Particulate organic carbon discharged from the sewage outfall offshore of Whites Point also had a narrow δC^{13} range with a mean of about -23.5 o/oo and an organic carbon concentration of about 34 per cent.

2) Investigations of the biochemical stability of effluent particulate matter suggested that the labile organic carbon in this matter is readily decomposed in aerobic conditions and very slowly decomposed in anaerobic conditions. Decay experiments indicated approximate first order decay rates of about 0.05 to 0.22 per day. An upper limit for the time needed to stabilize 95 per cent of the labile organic carbon was estimated at 60 days. The decay experiments also indicated that refractory matter would have an organic carbon concentration of about 20 to 25 per cent. In all decay experiments, there was evidence for a preferential decay of a C^{13}-enriched fraction of the particulate organic carbon.

3) Measured δC^{13} data of total and lipid sedimentary organic carbon show that the large accumulations of organic-rich matter on the Palos Verdes Shelf are due to the outfall. δC^{13} values for organic carbon in the uppermost sediments near the outfall are about -24.5 o/oo, and thus of about a 1 o/oo lower δC^{13} value than measured on the source effluent particulate matter. The lower δC^{13} of the sedimentary matter suggest either a preferential deposition of a particulate fraction of a lower δC^{13} value or, most likely, the preferential decay of a C^{13}-enriched organic carbon fraction. The decay experiments supported this latter possibility.

4) δC^{13} values of carbonate carbon in cores on the Palos

Verdes Shelf suggest that diagenesis of the organic-rich sediments is occurring and that a small fraction of the resultant metabolic CO_2 is either exchanging with or precipitating as solid carbonate matter.

5) δC^{13} data on total organic, lipid, and carbonate carbon indicate that, during the operating history of the outfall, sediment accumulations as great as 20 cm have occurred. The organic carbon data on one of the cores near the outfall suggested that the present rate of deposition of organic carbon may be as much as 26 $mg/cm^2/yr$. If it is assumed that the total particulate matter associated with this carbon has a refractory organic carbon composition of about 20 per cent (as suggested by the decay data), then the 26 $mg/cm^2/yr$ for effluent organic carbon sedimentation suggests that the accumulation of total outfall solids for core P6C may be about 130 $mg/cm^2/yr$. The total accumulation of effluent particulate total organic carbon on the Palos Verdes Shelf between transects 1 and 10 (see Figure IV-1) was estimated to be about $1.4(10^{10})$ grams. The area of the shelf between these transects is about $4(10^{11})$ square centimeters and the time period for operation of the outfall is about 38 years. Therefore, the time-averaged accumulation rate of effluent particulate organic carbon on the total shelf area being considered is about 0.9 $mg/cm^2/yr$. This accumulation rate of total organic carbon would suggest an average accumulation rate for total effluent solids of about 4.5 $mg/cm^2/yr$ if a refractory organic carbon content of 20 per cent is assumed. These sedimentation rates for organic carbon and total solids compare with reported natural sedimentation rates for these materials of 0.1 $mg/cm^2/yr$ and 9 $mg/cm^2/yr$, respectively (Emery, 1960). Due

to the high water content of the effluent particulate matter, the actual depth accumulation of this matter is quite large.

6) The actual distribution of effluent organic carbon within cores indicates that a greater sedimentary dilution of this matter has occurred than is expected from a comparison of the relative inputs from the different sources. It is shown that this may be due to sedimentary mixing processes acting in the upper several centimeters of surface sediments which can cause an upwards entrainment of lower pre-outfall sediments of a more inorganic nature. This may also be combined with the effect of a greater sedimentation of natural matter than that reported by Emery (1960). The apparent dilution of surface sediments near the outfall with material of a more inorganic composition may also be due to the actual refractory fraction of this matter being less than estimated by the decay experiments.

7) A comparison of the areal extent of anaerobic surface sediment with the accumulation of effluent particulate organic carbon was made in an attempt to extrapolate the findings of this thesis to provide some rough guidelines on water quality standards as related to the content of suspended solids in discharged effluent. For the present rate of discharge of effluent from the Whites Point outfall, and assuming a similarity in the physical properties of the suspended solids, a suspended solids concentration of 75 mg/l was arrived at as a value which might result in a notable reduction in the areal distribution of anaerobic surface sediments. This value was further discussed in Chapter VI as to how it related to future proposed changes in the suspended solids concentration.

VII-2. Conclusions

The discharge of primary treated wastewaters to the marine waters offshore of Whites Point on the Palos Verdes Shelf has significantly altered the physical and chemical properties of surface sediments. It is suggested that further and more extensive monitoring of the outfall area be maintained so that the response of the altered sedimentary environment to future improvements in the quality of the wastewaters may be observed. Such monitoring of the reaction of a sedimentary environment would allow for future guidelines in deciding the quality of discharges to be allowed into the oceans.

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