AN ABSTRACT OF THE THESIS OF

William Paul Muellenhoff   for the degree of Doctor of Philosophy

in Civil Engineering   presented on   December 20, 1976

Title: EFFECTS OF PRESSURE AND DEPOSIT THICKNESS ON THE

STABILIZATION RATE OF BENTHIC MARINE SLUDGE DEPOSITS

Abstract approved Redacted for Privacy

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The biochemical degradation of domestic sludge deposits exposed
to benthic marine conditions was investigated using a laboratory Deep
Sea Simulator. The rate and extent of deposit stabilization were
determined for select hydrostatic pressures and hydrogen acceptor con-
ditions by monitoring depletion of particulate organic carbon in 2.0
and 3.0 centimeter deposits. The extent of aerobic and anaerobic-exog-
enous zones in a 33 centimeter deep deposit was determined by measuring
dissolved oxygen, sulfate and hydrogen sulfide concentrations as a
function of distance from the deposit surface. Marine deposit stabili-
zation processes and a set of mathematical expressions for temporal
particulate organic carbon changes were formulated based on studies of
fresh water organic matter stabilization and characteristics of the
benthic marine environment.

Aerobic depletion of particulate organic carbon amounted to
between 14 and 19 percent in 20 days. After 120 days, depletion
reached 30.6 percent (k_{avg} = 0.042 day^{-1}) and the remaining refractory
component was 0.21 mg-C/mg solid. Thereafter, degradation proceeded
slowly. Comparable anaerobic decreases were 2.5 to 4.0 percent in 20
days and 7.0 percent in 130 days (k_{avg} = 0.024 day^{-1}). Calculated
anaerobic particulate organic carbon residuals ranged from 0.25 to 0.28
mg-C/mg solid. Differences in the aerobic and anaerobic biochemical

depletion rates resulted in a 30 percent higher particulate organic carbon concentration in the anaerobic zone than in the near-surface aerobic zone in 120 days. Variance analyses confirmed the significance of degradation rate differences as a function of hydrogen acceptor zone, but indicated that differences were not significant for hydrostatic pressures of one and 34 atmospheres. Interactive hydrostatic pressure/hydrogen-acceptor-type effects were also found to be insignificant.

The sludge deposit aerobic zone extended from the sea water/ sludge interface to approximately two millimeters. The anaerobic-exogenous zone (defined by a ten-fold reduction in the surface dissolved sulfate concentration) extended from the dissolved oxygen diffusion limit to approximately 16 centimeters deep in a 33 centimeter deposit, 180 days after deposit formation. Hydrogen sulfide concentrations in excess of 500 mg/l were measured at the 16 centimeter depth in the 33 centimeter deposit, whereas the maximum hydrogen sulfide concentration measured in 2.0 and 3.0 centimeter deposits was 20 mg/l.

Although aerobic particulate organic carbon degradation rates were larger than anaerobic rates, overall depletion of particulate organic carbon occurred principally in the anaerobic zone which was 15 times greater than the aerobic zone in a 3.0 centimeter deposit. Study findings indicate that the formation of marine sludge deposits which are greater than a few millimeters in depth enhances material preservation. When deposits become deeper than a few centimeters, dissolved hydrogen sulfide may accumulate to levels known to be toxic to marine organisms.

EFFECTS OF PRESSURE AND DEPOSIT THICKNESS ON THE
STABILIZATION RATE OF BENTHIC MARINE SLUDGE DEPOSITS

by

William Paul Muellenhoff

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Doctor of Philosophy

Completed December 20, 1976

Commencement June 1977

APPROVED:

Redacted for Privacy

Professor of Civil Engineering

Redacted for Privacy

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Date thesis is presented December 20, 1976

Typed by Patricia Muellenhoff for William Paul Muellenhoff

ACKNOWLEDGEMENT

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INTRODUCTION

Approximately 7.9 million cubic meters (2.1 billion gallons) of sewage sludge are being dumped from ocean-going barges or discharged from submarine outfalls to U.S. coastal waters each year (Anderson, 1976; Muir, 1976; Garber, 1976). In addition to an estimated five percent annual increase in sludge production, the 1972 Federal requirement to upgrade existing wastewater treatment plants to secondary by 1977 is expected to triple sewage sludge production, with comparable increases in the amounts requiring disposal at sea (Dendy, 1974; Dewling, 1974).

The continued coastal disposal of domestic sludges is now being critically reviewed amid controversial claims regarding the impacts of this procedure. Following a half century of unregulated marine sludge disposal, it has become apparent that the marine ecology in some disposal areas has been severely stressed (Buelow, 1968; Buelow et al., 1968; Ketchum, 1970; Sandy Hook Marine Laboratory, 1972; NOAA, 1975) while in others the effects have been minimal (SCCWRP, 1974, 1975). The U.S. Environmental Protection Agency (EPA) now controls the amounts of sludge disposed at sea by issuing short-term permits, by limiting the period in which some cities must find alternative disposal methods, and by requiring others to prepare for future extended transport to new offshore dumping grounds. The EPA has set as a goal the phasing out of all ocean dumping by 1981 (Environmental Reporter, 1975).

The relatively rapid reversal in the national marine sludge disposal policy is being challenged on the grounds that controlled disposal of preconditioned sludges could be environmentally acceptable, if properly implemented. Arguments are predicated on the hypothesis that the ocean has a limited assimilative capacity which, if not exceeded, allows for the unharmful disposal of significant quantities of waste materials (Bascom, 1974).

Studies to define optimal disposal procedures have been limited to date. Research efforts have primarily been devoted to the definition of impacted areas and descriptions of observed effects. Only recently have efforts turned to the identification and understanding of processes which control the assimilation of released sludges. Although general ecological models which include assimilation rate terms exist, these models cannot be effectively utilized to design optimal disposal programs due to a lack of required quantitative input data. Virtually no information exists on the biochemical utilization rate of marine sludge deposit organics or on the long term stability of such deposits as a function of disposal site conditions or sludge bed configuration. The need for basic data on the rates and mechanisms of marine sludge stabilization has been repeatedly emphasized by the National Academy of Sciences (NAS), the National Academy of Engineering (NAE) and the Council on Environmental Quality (CEQ) (NAS/NAE, 1970, 1972; NAS, 1971; CEQ, 1970). Without such information, it will continue to be impossible to predict the safety and acceptability of marine sludge disposal, and to implement optimal disposal plans.

Research Objectives and Approach

The research program has had as an overall objective the advancement of the understanding of marine sludge deposit biochemical stabilization processes. The approach included an extensive literature review of non-marine organic matter stabilization processes and of the nature of the marine receiving environment. Based on these reviews, the probable mechanisms of marine organic deposit stabilization were hypothesized and a mathematical model of the benthic stabilization process was adopted.

Preliminary experiments were performed to gain some insight into changing conditions within marine sludge deposits, and to establish the approximate magnitude and order of the stabilization rates. Data generated from the initial experiments became the basis for hypotheses of the effects of elevated pressure and location within the

deposit (i.e. type of hydrogen acceptor zone) on deposit stabilization rates. A final series of experiments was performed to statistically test the significance of measured degradation rate differences as a function of these two parameters. Data generated in the final experiment series allowed conclusions to be drawn regarding the effects of selected parameters, and provided quantitative input data for the detailed marine sludge deposit model formulated herein as well as for more general models developed by others (Chen et al., 1975).

To enhance text continuity, supplemental information gained as a result of the laboratory experiments (e.g. oxygen, sulfate and sulfide concentrations, and microbial observations) has been relegated to the Appendix C.

II. PREVIOUS INVESTIGATIONS

Organic River Deposit Stabilization

Early efforts to determine stabilization rates of organic deposits were directed toward river-bed studies due to concerns for oxygen depletion zones downstream of major population centers. Surveys of 32 Connecticut River sludge deposits showed that their five day, $20^\circ C$ biochemical oxygen demand (BOD) decreased rapidly within a few kilometers of the primary source, but more slowly thereafter for several kilometers downstream. Rudolfs (1932) concluded that the deposited material consisted of both a readily oxidized fraction and a more resistant residue which exerted a reduced oxygen demand on overlying waters for much longer periods of time.

Theriault and McNamee (1931) found, in laboratory streamflow experiments, that aerobic oxidation of sewage sludge occurred at a rate comparable to that measured for suspended river water particulates ($k = 0.10$ day^{-1} at $20^\circ C$).[1] They also observed that anaerobic decomposition products in deeper portions of the sludge deposit exerted an "immediate" oxygen demand upon contact with overlying waters at 16 times the aerobic biochemical rate.

Experiments by Fair and Moore (1932) on the rates of anaerobic sewage sludge digestion in laboratory fresh water tanks indicated that decomposition in the absence of molecular oxygen proceeded at approximately one-half the aerobic biochemical oxidation rate (i.e. $k = 0.05$ day^{-1} at $20^\circ C$). The results of Fair and Moore and the findings of

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1. $dy/dt = K(L-y)$, $y = L(1-e^{-Kt}) = L(1-10^{-kt})$
   y = the biochemical oxygen demand exerted at time t (mg/l)
   L = the total carbonaceous biochemical oxygen demand (mg/l)
   K, k = the oxidation rate constant, base e and base 10, respectively (day^{-1}).

Rudolfs suggested that decomposition of deeper organic river deposits proceeded more slowly than for relatively thin deposits through which oxygen could continually diffuse.

By 1935, the total (aerobic and anaerobic) benthal oxidation rates of river sludge deposits could not yet be reliably predicted (Streeter, 1935). Equations describing the cumulative BOD of a growing deposit suggested that in time, for a constant input of organic material, a deposit would approach a limiting volume. This equilibrium would occur when the total deposit oxidation rate equaled the BOD addition rate. This equivalence was predicted to occur in as little as 15 days ($k = 0.10$ day^{-1}) or to take much more than 100 days ($k = 0.01$ day^{-1}) depending on the then undetermined benthal stabilization rates of a river deposit. Streeter discussed the need to determine the biochemical rate constants, or series of constants, which would define the benthal stabilization rates as a function of deposit depth and stream temperature.

In 36-day laboratory experiments using carboys, Baity (1938) measured the oxygen consumption rates of thin (0.089 to 4.0 centimeters) raw sewage sludge deposits for selected temperatures, supernatant water dissolved oxygen concentrations and selected light conditions. Although most of his efforts were devoted to fresh water experiments, the effects of synthetic (10,000 mg Cl/l) and filtered natural sea water (19,000 mg Cl/l) on stabilization rates were also examined. Baity found no correlation between oxygen consumption rates and oxygen concentrations in supernatant water; that for increasingly deeper sludge beds the consumption rate of oxygen did not go up proportionately; and for increased salinities, the amount of oxygen consumed was significantly reduced (e.g. for 19,000 mg Cl/l water, the deposit consumed 40 percent less oxygen than a bed of same thickness exposed to fresh water). The disappearance within 24 hours of all protozoan life in saline water carboys was cited as a possible cause for the lower oxygen uptake rate. Baity concluded that sludge deposits would accumulate more rapidly and become deeper in a marine environment.

Baity's assumption that deposit oxygen demand was essentially satisfied after 36 days was critically reviewed by Mohlman (1938) who found that, after as much as 700 days, the BOD per gram of volatile solid in sludge deposits remained as high as 25 percent of the original 380 mg/g value.

In 400 day static open-carboy experiments, Rudolfs (1938) measured an 81 percent BOD reduction for a sludge which had an initial BOD of 540 mg/g of volatile solid. The sludge consisted of settled fresh sewage solids which had been comminuted, diluted with sewage and allowed to ferment for a week prior to beginning the experiment.

The findings of a very comprehensive research program on the natural purification of river muds and polluted sediments were published in 1941 (Fair et al.). Following a procedure similar to Baity's (whereby sludge deposits in carboys were exposed to a controlled flow of continuously renewed supernatant water at selected temperatures), the difference in the dissolved oxygen of entering and leaving water was measured. In fitting a retardant unimolecular equation[2] to their cumulative oxygen consumption data, the authors found decomposition rate coefficients (k) of 0.0033 and 0.0027 day^{-1} for 1.4 and 10.2 cm deep deposits respectively. A fit of a simple unimolecular curve[3] gave corresponding rate constants of 0.0044 and 0.0029 day^{-1}. In terms of the amount of time required to stabilize a given fraction of the original deposit organic material, these rates indicated that stabilization would be 50 percent complete in four months, 90 percent complete in one and a half years, and 99 percent complete in approximately five to six years.

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2. $dy/dt = [K/(1 + at)] (L - y), y = L [1 - (1 + at)^{-k/a}]$
   a = the retardation coefficient

3. Same differential equation with a = 0.

For comparison to recorded carbon changes in polluted Mersey
River muds stored in darkness under static sea water for six to
twelve months (Calvert et al., 1938), Fair et al. exposed unseeded
sludge-clay mixtures to similar fresh water conditions for 140 days.
Where sludge samples had an original organic carbon content of less
than 2.5 percent (dry weight), the organic carbon increased over time
by as much as 12 percent (Figure 1). For all mixtures having organic
carbon concentrations greater than 2.5 percent, the organic carbon
content decreased non-linearly in relation to original content.
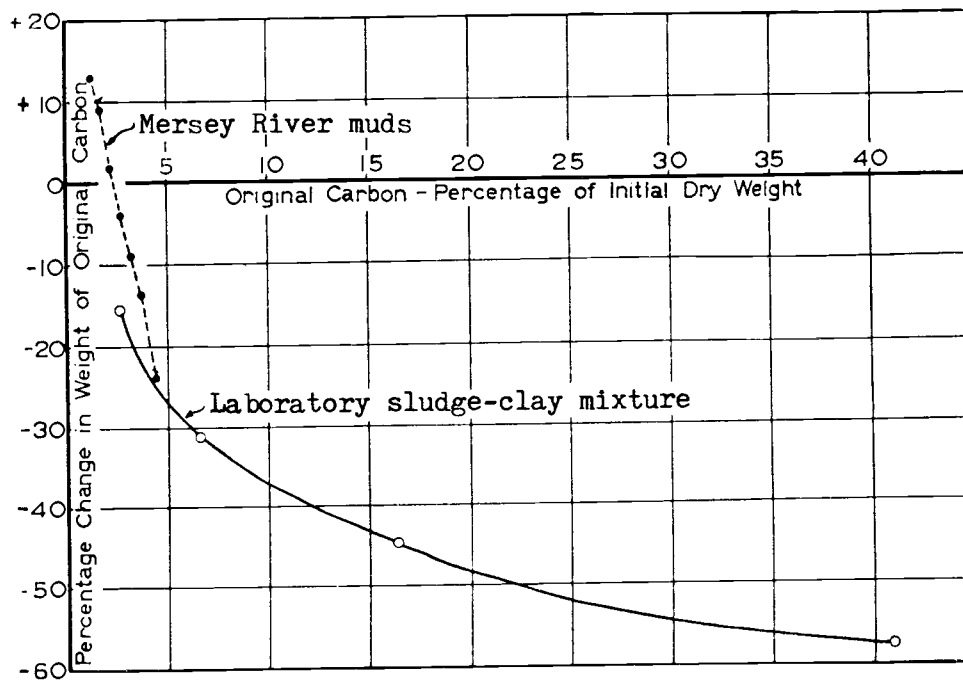
Figure 1. Percentage change in the organic carbon content of Mersey
River muds and artificial sludge-clay mixtures during
anaerobic decomposition (from Fair et al., 1941)

Fair et al. concluded that the rate of organic carbon loss would be greatest in benthal deposits containing large amounts of organic carbon compounds. Also, as the original carbon concentration decreased, the loss rate would decline until an organic carbon level of approximately two percent was reached. Thereafter changes in the organic content would be very slow, requiring more than a year to be significant.

It is noteworthy that the benthal oxidation rates as measured by Fair et al. on the basis of oxygen consumption in supernatant waters were lower than those measured by earlier experimenters who ran a series of five-day BOD tests on deposit samples. Rate constants (day^{-1}) for Mohlman's (1938) experiments were 0.0079 for the retardant formulation of Fair et al., and 0.0053 for a simple unimolecular fit. Corresponding rate constants for Rudolfs' (1932) work were 0.0055 and 0.0046 day^{-1} respectively. Fair et al. concluded that rates associated with decreases in the deposit BOD were necessarily higher than dissolved oxygen depletion rates in overlying waters since they represented both aerobic and anaerobic stabilization. A portion of the anaerobically stabilized BOD might not be exerted on overlying waters. Measuring oxygen consumption rates of supernatant water would therefore not necessarily give a true indication of the rate or extent of deposit stabilization. This would be particularly true for deeper deposits in which a major portion of the stabilization would proceed anaerobically.

Heukelekian (1941) studied the self-purification rate of sewage by measuring the BOD of sewage stored quiescently in open battery jars. The original 150 mg/l BOD of medium strength sewage was reduced 37 percent in 96 hours. For stronger sewage with an original BOD of 500 mg/l, the reduction was more rapid, decreasing 38 percent in 72 hours. Using closed jars to insure anaerobic conditions, Heukelekian found a 20 percent BOD reduction in 72 hours. To examine the effect of deposit depth on the BOD reduction rate, sewage having an original 250 mg/l BOD was placed in open containers to depths of 2.5 and 19.0 centimeters. The

BOD of the shallow deposit decreased 74 percent in 72 hours, whereas for the deeper deposit, overall BOD reduction was 48 percent for the same storage period. These experiments confirmed that BOD reduction of quiescent fresh water deposits proceeded rapidly and extensively in open vessels with shallow deposits.

Balmat (1957) measured the biochemical oxidation rate of settleable (greater than 100 microns), supracolloidal (1.0 to 100 microns), colloidal (0.08 to 1.0 microns) and soluble (below 0.08 microns) domestic sewage fractions suspended in BOD dilution water with a one percent sewage seed. The BOD rate constant generally increased with smaller particle size. For settleable and supracolloidal fractions, rate constants (k) were 0.08 and 0.09 day^{-1} respectively. For soluble organic matter, which presumably requires little or no physical modification prior to microbial decomposition, the rate constant was 0.39 day^{-1}. Balmat concluded that the rate at which sewage solids undergo decomposition may be limited by the relatively slow rate of biochemical hydrolysis.

Marine Stabilization Rate of Organic Matter

After the preliminary work of Baity, research efforts to determine the stabilization rates of sea water sludge deposits were not pursued for over 30 years. Hanes and White (1968) decided to rectify an apparent conflict between Baity's work (which indicated a reduced stabilization rate of organic materials exposed to sea water) and the reported effective aerobic biological treatment of shipboard wastes using highly saline water (Stewart et al., 1962).

The measurement of oxygen depletion rates in fresh water, 50 percent natural sea water, and 100 percent natural sea water covering 0.3 cm deep sludge deposits revealed slight increases in oxygen uptake rates for increased salinities. Compared to fresh water, the oxygen consumption rate of 50 percent sea water was 11.1 percent higher and a 38.4 percent increase was measured for undiluted sea water. Without nutrient addition, the dissolved oxygen in supernatant waters

approached zero in 20 to 25 hours whereas with nutrient addition, depletion occurred in 10 to 14 hours. Nutrient addition had a larger effect than salinity changes, increasing the oxygen consumption rate 137 percent for fresh water and 100 percent in natural sea water. Oxygen consumption rates were found to be constant after an initial six to eight hour lag period during which biota apparently adapted to the saline conditions. The authors generally concluded that, contrary to Baity's findings, sea water did not reduce oxygen consumption by sludge deposits. Lower rates measured by Baity were attributed to his use of artificial and aged-filtered sea water, each of which might have had toxic properties different than natural sea water.

During an investigation of the isotopic composition of carbon in marine sediments affected by sewage discharges, Meyers (1974) performed a series of static laboratory tests and an in situ exposure experiment to characterize the decay potential of particulate organics under marine conditions. Filtered effluent particulates (25 milliliter subsamples of a 24 hour composite non-chlorinated sample) were placed in sterile petri dishes with 10 milliliters of 0.2 micron filtered sea water and stored in darkness for 78 days at $2^{\circ}C$, $17^{\circ}C$ and $35^{\circ}C$. The data (Figure 2) indicated a temperature dependence, the decay rate being considerably slower at $2^{\circ}C$. Approximately 35 percent of the sample initial particulate organic carbon was rapidly decomposed at $17^{\circ}C$ and $35^{\circ}C$.

Using sealed four-liter bottles containing two liters of 24-hour composite effluent sample and two liters of unfiltered sea water (stored in darkness at $17^{\circ}C$), Meyers found that anaerobic decay of particulate matter was negligible in 14 days. For aerobic conditions, the particulate organic carbon loss in the same period of time was 26 percent. A similar experiment was performed in which sodium chloride was added to a mixture of equal volumes of composite effluent and rough-filtered (sintered glass) sea water to bring the mixture salinity up to approximately 30 parts per thousand. Aerobically, effluent particulate organic carbon was reduced 22 percent, whereas for anaerobic conditions the carbon loss was only slight in 74 days.

$$f(t) = \frac{\% \, ORG.-C \; AT \; TIME \; t}{\text{"} \quad \text{"} \quad \text{"} \quad \text{"} \quad \text{"} \quad 0}$$
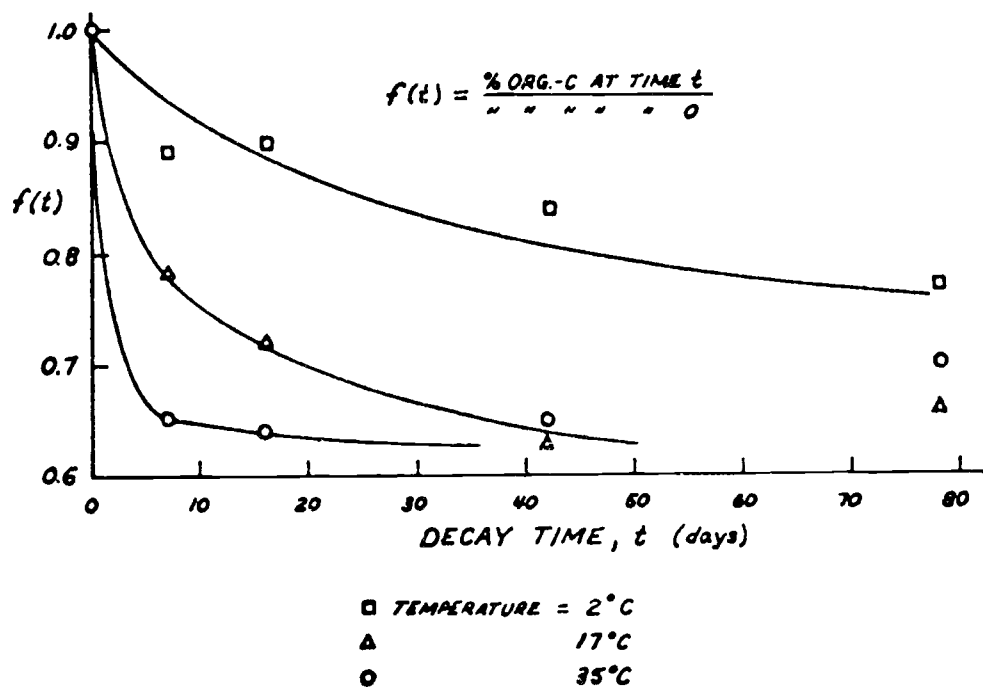
Figure 2.   Decay of particulate organic carbon from a 24 hour composite
sample (from Meyers, 1974)

Meyers also performed an in-situ experiment by placing opaque 40
milliliter vials containing 24-hour non-chlorinated effluent samples
at 7.6 meters deep (1.5 meters above the seafloor) in $17^{\circ}C$ water. The
open end of each vial was covered with precombusted and washed Whatman
GF-C glass fiber filters. Periodically, the vials were retrieved and
the contents analyzed for particulate organic carbon. The initial 41.2
percent organic carbon content of effluent particulates was reduced to
30.9 percent in 40 days, representing a decrease of 25 percent.

Meyers generally concluded that effluent particulates released
(via outfall) to aerobic marine waters would be subjected to further
decay which would reduce particulate organic carbon by 20 to 35 per-
cent. Upper and lower limits for a decay rate constant (converted to
base 10) were estimated to be 0.096 and 0.022 day^{-1}, respectively.

An extensive literature review failed to reveal documented efforts to measure biochemical stabilization rates of organic sludge deposits exposed to flowing sea water. Of the two flowing sea water experiments reported, neither included the monitoring of deposit organic content, and only one was for a domestic sludge (Barber and Kirby-Smith, 1973; Pratt et al., 1973).

Sewage and Marine Bacteria

Chemoheterotrophic bacteria are ubiquitous in raw and digested sludges, recent marine sediments and in the sea water through which ocean disposed sludges must settle.

Large numbers of chemoheterotrophs are present in sludge as evidenced by large coliform MPNs. Analyses of domestic sludges stored for New York Bight disposal produced total coliform MPN values of between 4.3×10^4 and 2.4×10^7 per milliliter, and fecal coliform MPN values of 4.3×10^3 to 2.4×10^7 per milliliter (Buelow, 1968). Sewage sludge stored for disposal off Delaware Bay produced a total coliform MPN of 7×10^4 and fecal coliform MPN of 7.9×10^3 per milliliter.

Bacteriological surveys of marine sediments have produced viable counts of aerobic heterotrophic bacteria ranging from a few to 10^8 bacteria per milliliter or gram of wet sediment. Mid-latitude continental shelf and slope sediments have approximately 10^4 bacteria per gram of wet sediment (Wiebe and Liston, 1972). Surveys of Oregon and Washington coast sediments produced viable counts of aerobic nonexacting heterotrophs of 2.0×10^4 bacteria per milliliter of mud/water slurry. This and other surveys have confirmed the predominance of gram-negative rods, particularly of the genera Pseudomonas, Achromobacter and Vibrio in sea water and marine sediments (Quigly and Colwell, 1968). Anaerobes (esp. sulfate reducers) are found in all marine bottom deposit samples and in some sea water samples (Zobell, 1946; Zobell and Rittenberg, 1948).

Sampling of sediments in the sludge disposal areas of the New York and California Bights has confirmed the presence of both marine

and fresh water bacteria capable of utilizing domestic sludges as an energy source. Total and fecal coliform MPN values in the New York Bight dumping ground have been reported at approximately 9.2×10^3 and 4.6×10^2 per milliliter, respectively, with little seasonal variation (Pararas-Carayannis, 1973). Sediment samples near Santa Monica Bay outfalls have contained bacteria from the genera Vibrio, Aeromonas, Pseudomonas and Streptococcus, as well as coliforms (SCCWRP, 1974, 1975). Benthal concentrations of fresh water aerobes and anaerobes have been found to be generally higher than their marine counterparts near two California Bight outfalls (Table I).

TABLE I. CONCENTRATIONS (CELLS/ML) OF TOTAL MARINE AND FRESH WATER AEROBIC AND ANAEROBIC BACTERIA IN WATER AND SEDIMENT SAMPLES FROM DANA POINT, SANTA MONICA BASIN AND SANTA MONICA BAY (from SCCWRP, 1975)

	Dana Point	Santa Monica Basin	5- and 7-Mile Outfall Area, Santa Monica Bay
Surface Water			
Marine aerobes	770	773	360
Freshwater aerobes	390	390	328
Midwater			
Marine aerobes	130	—	423
Freshwater aerobes	10	—	760
Sediment			
Marine aerobes	50,000	7,200	13,266
Freshwater aerobes	12,600	72,000	49,000
Marine anaerobes	20,800	8,800	2,475
Freshwater anaerobes	2,100	2,800	6,850

Thus, bacteriological surveys of sea water, marine sediments, and coastal sludge disposal sites have confirmed the presence of large numbers of marine and fresh water, aerobic and anaerobic heterotrophs capable of utilizing settled organic particulates.

III. BENTHAL DECOMPOSITION PROCESSES

Organic Characteristics of Domestic Sludge

The organic characteristics of domestic sludges depend on the
nature of the wastewater from which they are derived, the point in
the wastewater treatment process at which they are collected and the
type and extent of the predisposal treatment which they receive
(Table II). Eighty-one percent of the sludge being disposed of in
the ocean is anaerobically digested while the remaining 19 percent
receives only partial or no treatment upon withdrawal from the var-
ious stages of a wastewater treatment plant. The quantity of ocean
disposed sludges subjected to aerobic digestion is insignificant.

Even though the chemical characteristics of sludges are quite
variable, major constituent concentrations fall within some broad
ranges (Table III). Sludge solids concentrations range from two to
ten percent but are often diluted with treated effluent or water to
facilitate pumping onto ocean-going barges or through submarine out-
falls. Volatile solids account for as much as 85 percent of the
total solids (dry weight basis) in raw sludges and 60 percent in di-
gested sludges. Associated total carbon content can be as high as
50 and 36 percent of the total solids, respectively.

Undigested sludge solids consist of approximately 34 percent
carbohydrates, 29 percent proteins and 28 percent lipids (Table IV).
Anaerobic digestion modifies this distribution due to the varying
degradability of these three organic compound classes (Table V).
Digestion reportedly decreases lipids by the greatest amount (76%),
followed by proteins (36%) and then carbohydrates (13%). Digested
sludges are therefore more likely to be high in carbohydrates and low
in lipids, with intermediate concentrations of proteins.

Sludges dumped in the New York Bight have an average organic
matter content of 55 percent (dry weight basis) with a range of from

TABLE II. GENERAL CHARACTERISTICS OF SLUDGES FOR SELECT
TREATMENTS*

SOURCE	DESCRIPTION
Primary Sedimentation Tanks	Yellow-grey, slimy, extremely offensive odor, small and large pieces of fecal matter, matchsticks, paper, waste vegetable residues from kitchens, and other particulate matter, readily digested under suitable conditions.
Chemical Precipitation Tanks	Black, possibly odorous, slimy but gelatinous, decomposes in tank but at a slower rate than primary sludge, gives off large quantities of gas.
Activated Sludge	Brown, flocculant, inoffensive characteristic odor, becomes dark and offensively odorous when septic, digests readily alone or with fresh sewage solids.
Trickling Filter Humus	Brownish, flocculant, inoffensive when fresh, decomposes more slowly than other undigested sludges but readily digested.
Digested Sludge	Dark brown to black (due to iron sulfide), homogenous, lower moisture content, contains large quantities of gas (e.g. CH_4, CO_2, H_2S), inoffensive odor when thoroughly digested (tar-like, burnt rubber, sealing wax), lower organic content than undigested sludges, humus like and lignin like material, organic acids.

* Adapted from Metcalf and Eddy, 1972.

TABLE III. CHEMICAL CONSTITUENTS OF RAW AND DIGESTED SLUDGES

CONSTITUENT	RAW PRIMARY SLUDGE		DIGESTED SLUDGE	
	RANGE	TYPICAL	RANGE	TYPICAL
Total dry solids (% by weight)	2.0 - 7.0	4.0	5.0 - 10.0	8.0
Volatile solids (% TS)	60 - 85	65	30 - 60	45
Grease & fats (% TS)	6.0 - 30	-	5.0 - 20	-
Cellulose (% TS)	3.0 - 15	10.0	8.0 - 15	10.0
Protein (% TS)	20 - 30	25	15 - 20	18
Nitrogen (N, % TS)	0.8 - 6.0	2.5	1.5 - 6.0	3.0
Phosphorus (P_2O_5, % TS)	0.8 - 4.0	1.6	0.9 - 5.0	2.5
Potash (K_2O, % TS)	0 - 1.0	0.4	0 - 3.0	1.0
Iron	2.0 - 4.0	2.5	3.0 - 8.0	4.0
Silica (SiO_2, % TS)	15 - 20	-	8.5 - 20	-
pH	5.0 - 8.0	6.0	6.5 - 8.0	7.0
Alkalinity (mg/l as $CaCO_3$)	500 - 1500	600	2500 - 3500	3000
Organic Acids (mg/l as HAc)	200 - 2000	500	100 - 600	200
Carbon (% TS)	40 - 50	-	22 - 36	-
Bulk Specific Gravity	1.00 - 1.03	-	1.002 - 1.100	-
Solids Specific Gravity, dry	-	1.40	1.35 - 1.60	-
BOD (5 day, 20°C, mg/l)	-	-	2000 - 3000	-

OTHER CONSTITUENTS

Aluminum	Cadmium	Chlorinated	Cobalt	Lead	Mercury	Phenols	Silver	Zinc
Arsenic	Calcium	Hydrocarbons	Chromium	Magnesium	Molybdenum	Potassium	Sodium	
Boron	Chloride	Copper	Cyanide	Manganese	Nickel	Selenium	Sulfate	

TABLE IV.   COMPOSITION OF RAW SLUDGE*

| REF. | PERCENT VOLATILE SOLIDS | | | | PERCENT TOTAL SOLIDS |
	CARBOHYDRATE	PROTEIN	LIPID	TOTAL	VOLATILE SOLIDS
1	30.2	32.3	24.5	87.0	78.0
2	17.7	31.8	41.4	90.9	60.9
3	16.9	35.7	45.3	97.9	75.9
4	30.2	30.8	23.5	84.5	65.0
5	43.5	19.4	18.4	80.9	81.0
6	62.4	29.2	21.5	113.1	65.1
7	-	21.6	23.4	-	79.6
AVG.	33.5	28.5	28.2	90.1	72.2

*From Chynoweth and Mah, 1971.

TABLE V.   PERCENT REDUCTION DURING ANAEROBIC DIGESTION*

REF.	CARBOHYDRATE	PROTEIN	LIPID	VOLATILE SOLIDS
1	9.3	35.5	72.6	35.2
2	17.6	27.4	76.2	42.0
3	-	17.0	65.2	-
4	-	63.5	90.3	-
5	-	-	75-89	-
6	-	-	70-80	-
7	-	-	71	-
8	-	38	-	-
AVG.	13.5	36.3	76.0	38.6

*From Chynoweth and Mah, 1971.

46 to 80 percent.[4] A fraction of sludge organic matter consists of water soluble acids (e.g. glutaric, glycolic, lactic, citric and benzoic) and soluble sugars (e.g. glucose, sucrose and lactose) which will be dispersed upon release to marine waters. A larger fraction, however, is relatively insoluble and will either remain suspended in the form of small particulates or become part of the bottom sediments upon settling. The insoluble material can include proteins, carbohydrates, fats, esters and unidentified particulate organic components (Walter, 1961). The inorganic material (approximately 45 percent) consists primarily of aluminosilicate, chemically similar to shale. The total carbon content of New York Bight sludges ranges from 25 to 40 percent (dry weight basis) averaging 32 percent. Of the carbon present, an average of 65 percent is inorganically oxidizable.[5]

The chemical characteristics of the sludge/effluent mixture pumped from the Los Angeles Hyperion outfall are presented in Table VI. In 1973 and 1974, Hyperion's sludge-effluent mixture had a volatile suspended solids concentration which accounted for 61 percent of the total suspended solids. Analysis of sludge particulates collected in benthic sediment traps showed a post-discharge range of volatile particulate solids of from 14 to 50 percent, and organic carbon contents of from four to 24 percent (SCCWRP, 1975).[6] In examining the particulate organic carbon of 24 hour composite effluent samples, Meyers (1974) found that about 35 percent of the initial organic carbon content (originally 35.7 percent) was readily decomposed in 78 days.

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4. Organic content was measured by loss-on-ignition at $550^{\circ}C$ for several hours (Gross, 1970).

5. Wet combustion with 0.4 N $K_2Cr_2O_7$ in H_3PO_4 at $160^{\circ}C$.

6. The results of all chemical analyses were expressed on a dry-weight basis, with appropriate corrections for the sea-salt content of the dried solids.

TABLE VI.   AVERAGE CONSTITUENT CONCENTRATIONS IN THE FINAL
EFFLUENT OF THE HYPERION SLUDGE OUTFALL[7, 8]

CONSTITUENT	1971	1973	1974
Flow (mgd)	5.0	4.82	4.72
General Constituents (mg/l)			
Total Suspended Solids	3,000	7,500	8,400
Volatile Suspended Solids	1,600	4,620	5,100
Biochemical Oxygen Demand	-	-	1,400
Chemical Oxygen Demand	-	-	7,700
Oil and Grease	760	922	900
Total Nitrogen	590	-	550
Ammonia Nitrogen	160	-	300
Organic Nitrogen	430	-	200
Total Phosphate	-	-	221
Cyanide	-	0.11	0.53
Phenols		-	-
Trace Metals (mg/l)			
Silver	0.03	0.80	0.40
Arsenic	-	0.27	0.18
Cadmium	0.23	0.98	1.27
Chromium	2.1	18.2	15.1
Copper	12.2	13.6	13.9
Iron	47.0	76.8	78.7
Mercury	0.10	0.14	0.15
Manganese	1.6	0.37	0.19
Nickel	2.6	3.57	3.1
Lead	0.51	1.57	1.13
Selenium	-	0.45	0.4
Zinc	16.5	27.0	23.9
Cobalt	0.03	-	-
Chlorinated Hydrocarbons (µg/l)			
Total DDT	2.07	4.03	2.59
Total PCB	28.7	25.4	3.30
Dieldrin	1.3	0.49	0.17
Total Identifiable	39.0	-	-

7.   Outfall effluent consists of sludge and treated wastewater. In 1974, 2.3 mgd of sludge were mixed with 2.4 mgd of effluent for a total outfall volume of 4.7 mgd.

8.   Data presented in this Table are from the 1970-1972, 1973, and 1974 Annual Reports of the Southern California Coastal Waters Research Project (SCCWRP, 1973, 1974).

Although digestion reduces the concentration of organics and alters the ratios of major organic compounds, digested sludges still contain significant amounts of potentially biodegradable material. Carbon is the most abundant element of sewage sludges, and sludge carbonaceous compound concentrations change significantly during wastewater treatment plant digestion and marine decomposition.

Organic Content of Ocean Waters and Sediments

The concentration of total organic carbon in the open seas varies from 0.2 to 2.7 mg/l, averaging about 1.0 mg/l (Provasoli, 1966). Of this, the majority is in dissolved form, with particulate organic carbon representing only 0.75 to 1.5 percent of the total (Gordon, 1971; Sharp, 1973a). Organic carbon is generally highest in surface waters, decreases with depth until approximately 300 meters, and is relatively constant in deeper waters.

Menzel and Ryther (1968) reported dissolved organic carbon concentrations for southwest Atlantic Ocean surface water of from 0.65 to 1.1 mg/l. At 400 meters, dissolved organic carbon concentrations decreased to between 0.3 and 0.55 mg/l. Associated particulate organic carbon concentrations for the surface and 400 meters deep water ranged from 0.014 to 0.1 mg/l, and 0.002 to 0.009 mg/l, respectively. Sharp (1973b) reported somewhat higher total organic carbon concentrations for surface central western North Atlantic Ocean waters of 1.1 to 1.6 mg/l. Corresponding values at 500 meters were 0.8 to 1.5 mg/l. Using high-temperature combustion rather than persulfate oxidation, Sharp found total organic carbon concentrations to be 28 percent higher on the average and much more variable in deeper waters.

Carbon concentrations of coastal waters are apt to be somewhat higher and more variable due to higher phytoplankton productivity and an influx of organic material from rivers, storm water runoff, wastewater outfalls and shipping activities. Meyers (1974) measured particulate organic carbon concentrations in California Bight coastal

waters (Dana Point) of from 0.8 to 2.1 mg/l. Relatively high parti-
culate organic carbon concentrations were measured in shallow waters
near Whites Point (4.5 mg/l), Whalers Cove (7.4 mg/l) and near San
Simeon (15.7 mg/l).

Pelagic sediment of the deep ocean contains approximately one
percent organic matter. Sediment in the Atlantic contains 0.3 to 1.5
percent, in the South Pacific 0.4 to 1.0 percent and in the North
Pacific 1.0 to 1.5 percent (Trask, 1939). The carbon fraction of or-
ganic matter in deep marine sediment ranges from 50 to 60 percent,
with an average of 58 percent. Most of the organic material produced
photosynthetically in near-surface ocean waters is mineralized long
before reaching the seafloor. The material which does settle to the
seafloor consists of plant and animal residues which are relatively
stable and resistant to further biodegradation.

Continental slope and outer continental shelf sediments of the
Northeast Pacific Ocean typically have organic carbon contents
ranging from 1.0 to 2.0 percent with concentrations reaching in ex-
cess of 2.5 percent in isolated areas (Gross et al., 1972). Near-
shore sediment organic content varies widely throughout the world,
ranging from as low as 1.0 percent to as high as 10.0 percent, aver-
aging 2.5 percent (Sverdrup et al., 1942). The relatively high and
variable concentrations of organic matter in nearshore sediments are
due to accumulations from highly productive overlying waters, and from
a number of discrete natural and antropogenic inputs. Final organic
matter distributions are a function of local deposition rates, turbu-
lent resuspension and bottom water transport, reworking by organisms,
and destruction due to chemical processes or marine organisms.

Sludge dumping in the New York Bight has significantly in-
creased the organic content of sediments in the disposal area. Vola-
tile matter concentrations have been measured as high as 13.8 percent,
averaging six percent (Gross et al., 1971). Comparative volatile

matter concentrations of sediments 11 kilometers from the disposal
site are 1.2 percent (0.2 percent total carbon). The area covered with
sediments having more than 2.0 percent total carbon (10 times back-
ground) or five percent volatile matter was approximately 50 square
kilometers in 1971. The 1.0 percent total carbon isoconcentration
contour enclosed a 100 square kilometer area.

Organic carbon concentrations of California Bight sediments off
the Palos Verdes shelf (along the 61 meter contour) clearly indicate
accumulations of organic matter due to input from the Whites Point
wastewater outfall and other wastewater sources (Meyers, 1974). Total
organic carbon concentrations in surface sediments directly offshore
from the outfall are as high as 12.8 percent. For comparison, two
deeper water cores taken prior to the discharge of this effluent were
analyzed. One core taken in 494 meters of water 3.7 kilometers off-
shore had a total organic carbon concentration of 3.6 percent at the
surface, decreasing to 1.5 percent at 80 centimeters deep. The
second core in San Pedro Basin showed a relatively constant carbon
concentration as a function of depth, being 4.2 percent at the surface
and decreasing to 3.5 percent at a depth of 30 centimeters.

Released sludges represent highly enriched organic inputs to
the marine environment, particularly when disposed to restricted
areas. Although the discharged material contains a significant biode-
gradable fraction, anomalously high concentrations of organics have
occurred in disposal areas.

Marine Benthic Deposit Formation

Upon discharge to sea water, the colloidal organic suspensions
of sludges are destabilized (i.e. net interparticle forces become
attractive), thereby permitting the formation of agglomerations called
flocs, whose size and settling velocities can be much greater than
that of individual particles (Edzwald et al., 1974; Kranck, 1973;
Cohen and Hannah, 1971). Due to flocculation, and to a lesser degree

settling of larger particulates, a large fraction of discharged sludge particulates may reach the seafloor in the vicinity of coastal disposal areas. Approximately 70 percent of particulate matter discharged from the Hyperion sludge outfall can be accounted for in nearby sediments (SCCWRP, 1974).

Additional material can be chemically precipitated when domestic wastes with cations (e.g. calcium, iron, lead, aluminum, magnesium, copper, mercury, potassium, nickel and zinc) are added to slightly soluble halides, carbonates, oxides or hydroxides, and sulfates in ocean waters (Richards, 1969). The settling of this material to the seafloor is dependent on the size and density of the precipitated fraction, and the density and dynamics of the receiving waters.

Upon release to the sea, the dissolved fraction of the disposed waste is diluted and advected from the release point by ocean currents. A recently formed deposit therefore consists of elutriated organic and inorganic particulates with an interstitial water having characteristics similar to the overlying sea water.[9] In shallow coastal areas, the sludge macro-particulate organic content remains relatively constant during transit due to rapid deposition (Mitchell and Shafer, 1975). In deeper waters over the Continental Slopes or Ocean Basins, however, the organic content could significantly decrease depending on the suspension period and rates of biochemical conversion.[10]

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9. Pre-experiment settling of domestic sludges through a 1.2 meter sea water column (sea water/sludge dilution ratio of 10:1) confirmed the replacement of nonsaline sludge interstitial water with sea water of much higher dissolved solids. The ratio of total volatile solids to total solids decreased 47 percent due to sea water entrapment during deposit formation

10. A review of the literature failed to reveal quantitative data on the degradation rates of dilute organic mixtures suspended in ocean waters for long periods of time.

As the settled sludge forms a thin deposit, biochemical decomposition proceeds aerobically. Organic and reduced inorganic compounds are metabolically oxidized by aerobic bacteria through the process of aerobic respiration. Molecular oxygen diffusing downward into the deposit serves as the terminal hydrogen acceptor, thereby enabling regeneration of coenzymes reduced during the oxidation of organic matter.

When sludge particulates are deposited at a rate greater than the rates of microbial hydrolysis and resuspension/transport, material accumulates causing the deposit depth to increase. Aerobic respiration continues throughout the deposit until the deposit depth exceeds the limiting oxygen diffusion depth. Beyond this depth, oxygen is depleted within a matter of hours and microbial stabilization proceeds anaerobically. In highly organic deposits, the limiting oxygen diffusion depth is a few millimeters at most. This is due to rapid microbial utilization, chemical oxidation of reduced organics and a limited oxygen supply from supernatant waters (Pratt et al., 1973; Sanders et al., 1970).

As organic material continues to accumulate, stabilization proceeds by anaerobic respiration in all but the shallow aerobic surface layer. This energy-yielding metabolic process involves the oxidation of organic and reduced inorganic compounds through the reduction of exogenous hydrogen acceptors other than molecular oxygen (e.g. nitrates and sulfates).[11]

Dissolved nitrate concentrations in anaerobic regions of newly formed deposits are low due to the initial 0-2.0 mg/l interstitial water concentration (as a result of settling through the sea water column). The amount of nitrate produced by nitrification while the

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11. Exogenous hydrogen acceptors exist outside the cell, whereas endogenous acceptors must be internally generated.

deposit remains aerobic is estimated to be small, and would be
rapidly depleted in the absence of oxygen as a hydrogen acceptor.

Following depletion of nitrates, organic matter continues to be
oxidized by sulfate reducing bacteria. The dissolved sulfate concen-
tration in the deposit is initially high due to the 2730 mg/l (1470
mg/l free-ion) in sea water. As this sulfate is utilized, a relatively
large gradient may be created, causing further diffusion from the over-
lying sea water.[12] Limiting dissolved sulfate diffusion depths are
predicted to be as great as five centimeters, and measurements by Bella
(1975) confirm significant sulfate diffusion approximately ten centi-
meters in highly organic deposits.

As a deposit deepens beyond the maximum sulfate diffusion depth,
microbial conversion of organic matter continues by fermentation, an
energy-yielding metabolic process in which organic compounds serve as
both the hydrogen donors and acceptors. Endogenously generated hydro-
gen acceptors known to be used in the process include pyruvate, acetal-
dehyde, lactate, glycerol, acetoin and carbon dioxide (Schroeder and
Busch, 1966).

The ecological succession of deposit microbial species depends
in part on the types and concentrations of available hydrogen accept-
ors, and the free energies derivable from their use. Tables VII and
VIII list biologically-mediated reactions involving the conversion of
organic matter, and other chemical reactions expected in the aerobic
and anaerobic portions of a benthic deposit. Also listed are the free
energy changes associated with each reaction and the bacteria known to
be instrumental in mediating these reactions.

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12. A large dissolved sulfate gradient is expected, for
example, when the deposited material is high in organics or when the
sulfate reduction rate is high.

TABLE VII.   AEROBIC CHEMICAL REACTIONS, MEDIATING BACTERIA AND FREE ENERGY CHANGES (kcal mole^{-1} of electrons)

CHEMICAL REACTION	REPRESENTATIVE BACTERIA	ΔF^0
Aerobic Respiration $1/4\ CH_2O + 1/4\ H_2O = 1/4\ CO_2(g) + H^+ + e^-$ $1/4\ O_2(g) + H^+ + e^- = 1/2\ H_2O$ ───── $1/4\ CH_2O + 1/4\ O_2(g) = 1/4\ CO_2(g) + 1/4\ H_2O$	Aerobic heterotrophs	-29.9
Sulfide Oxidation $1/8\ HS^- + 1/2\ H_2O = 1/8\ SO_4^= + 9/8\ H^+ + e^-$ $1/4\ O_2(g) + H^+ + e^- = 1/2\ H_2O$ ───── $1/8\ HS^- + 1/4\ O_2(g) = 1/8\ SO_4^= + 1/8\ H^+$	Beggiatoa Thiobacillus Thiothrix	-23.8
Ferrous Oxidation $FeCO_3(s) + 2H_2O = FeOOH(s) + HCO_3^- + 2H^+ + e^-$ $1/4\ O_2(g) + H^+ + e^- = 1/2\ H_2O$ ───── $FeCO_3(s) + 1/4\ O_2(g) + 3/2\ H_2O = FeOOH(s) + HCO_3^- + H^+$	Iron Bacteria Thiobacillus ferrooxidans	-21.0
Methane Oxidation $1/4\ CH_4(g) + 1/2\ H_2O = 1/2\ CH_3OH + H^+ + e^-$ $1/4\ O_2(g) + H^+ + e^- = 1/2\ H_2O$ ───── $1/4\ CH_4(g) + 1/4\ O_2(g) = 1/2\ CH_3OH$	Methanomonas	-14.8
Nitrification $1/8\ NH_4^+ + 3/8\ H_2O = 1/8\ NO_3^- + 5/4\ H^+ + e^-$ $1/4\ O_2(g) + H^+ + e^- = 1/2\ H_2O$ ───── $1/8\ NH_4^+ + 1/4\ O_2(g) = 1/8\ NO_3^- + 1/4\ H^+ + 1/8\ H_2O$	$(NH_4^+ \longrightarrow NO_2^-)$ Nitrosomonas Nitrosocystis Nitrosouva $(NO_2^- \longrightarrow NO_3^-)$ Nitrobacter Nitrococcus	-10.3
Manganese Oxidation $1/2\ MnCO_3(s) + 3/8\ H_2O = 1/2\ MnO_2(s) + 1/2\ HCO_3^- + 3/2\ H^+ + e^-$ $1/4\ O_2(g) + H^+ + e^- = 1/2\ H_2O$ ───── $1/2\ MnCO_3(s) + 1/4\ O_2(g) = 1/2\ MnO_2(s) + 1/2\ HCO_3^- + 1/2\ H^+ + 1/8\ H_2O$		- 7.2

TABLE VIII.   ANAEROBIC CHEMICAL REACTIONS, MEDIATING BACTERIA
AND FREE ENERGY CHANGES (kcal mole^{-1} of electrons)

CHEMICAL REACTION	REPRESENTATIVE BACTERIA	ΔF^o
Denitrification $1/4\ CH_2O+1/4\ H_2O=1/4\ CO_2(g)+H^++e^-$ $1/5\ NO_3^-+6/5\ H^++e^-=1/10\ N_2(g)+3/5\ H_2O$ $1/4\ CH_2O+1/5\ NO_3^-+1/5\ H^+=1/4\ CO_2(g)+1/10\ N_2(g)+7/20\ H_2O$	_Bacillus_ _Thiobacillus_	-28.4
Nitrate Reduction $1/4\ CH_2O+1/4\ H_2O=1/4CO_2(g)+H^++e^-$ $1/8\ NO_3^-+5/4\ H^++e^-=1/8\ NH_4^++3/8\ H_2O$ $1/4CH_2O+1/8NO_3^-+1/4\ H^+=1/4CO_2(g)+1/8NH_4^++1/8\ H_2O$	Nitrate reducers	-19.6
Fermentation $1/2\ CH_2O+1/2\ H_2O=1/2\ HCOO^-+3/2\ H^++e^-$ $1/2\ CH_2O+H^++e^-=1/2CH_3OH$ $CH_2O+1/2H_2O=1/2\ HCOO^-+1/2\ CH_3OH+1/2\ H^+$	Acid forming bacteria	- 6.4
Sulfate Reduction $1/4\ CH_2O+1/4\ H_2O=1/4\ CO_2(g)+H^++e^-$ $1/8\ SO_4^=+9/8\ H^++e^-=1/8\ HS^-+1/2\ H_2O$ $1/4\ CH_2O+1/8\ SO_4^=+1/8\ H^+=1/4\ CO_2(g)+1/8\ HS^-+1/4\ H_2O$	_Desulfovibrio_ _Clostridium_	- 5.9
Methane Fermentation $1/4\ CH_2O+1/4\ H_2O=1/4\ CO_2(g)+H^++e^-$ $1/8\ CO_2(g)+H^++e^-=1/8\ CH_4(g)+1/4\ H_2O$ $1/4\ CH_2O=1/8\ CH_4(g)+1/8\ CO_2(g)$	Methanobacterium Methanosacini Methanococcus	- 5.6
Nitrogen Fixation $1/4\ CH_2O+1/4\ H_2O=1/4\ CO_2(g)+H^++e^-$ $1/6\ N_2+4/3\ H^++e^-=1/3\ NH_4^+$ $1/4\ CH_2O+1/6\ N_2+1/4\ H_2O+1/3\ H^+=1/4\ CO_2(g)+1/3\ NH_4^+$	Nitrogen fixing bacteria	- 4.8

Stumm and Morgan (1970) indicate that molecular oxygen, if available, is always utilized in preference to other exogenous hydrogen acceptors and provides the greatest amount of free energy. Thereafter, denitrification and nitrate reduction, also having relatively high free energy changes, would proceed.[13] Relatively low energy yields are available through alcoholic fermentation, sulfate reduction, or methane fermentation. Although sulfate reduction and methane fermentation through the reduction of carbon dioxide can reportedly occur almost simultaneously (Stumm and Morgan, 1970), there is experimental evidence that methane fermentation proceeds only in the absence of dissolved sulfate. The known coexistence of dissolved sulfate and methane in upper portions of anaerobic marine sediments is apparently due to the upward diffusion of methane fermented in deeper sulfate-free zones (Martens and Berner, 1974).

In summary, organic deposit formation can be described as an accumulation of particulates at a rate greater than removal and biochemical conversion. Sufficiently thin deposits (e.g. 0-3 mm) are subjected to aerobic stabilization, while intermediate ocean deposits (3 mm - 10 cm) will experience aerobic stabilization in the surface layer, and anaerobic stabilization (predominantly by sulfate reducing bacteria) in the remainder of the deposit. Deposits deeper than ten centimeters will have a fermentation zone in addition to the aerobic and sulfate reducing zones above it.

The extent of aerobic, anaerobic-exogenous, and anaerobic-endogenous (fermentation) zones, as well as the rates of organic matter conversion in these zones will control the overall stabilization rate of the deposit. Aerobic metabolism is reportedly very rapid, but results in a greater production of microbial biomass. Anaerobic

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13. The difference between denitrification and nitrate reduction as listed in Table IX relates to the reduction of nitrate as a source of cell nitrogen in the latter case. Although initial reduction of nitrate to nitrite is the same in both cases, different enzymes are involved.

stabilization, although reported to be slower and much more sensitive to changing environmental conditions, can result in the more complete stabilization of organic matter if it proceeds beyond the intermediate acid-forming stage to the final production of methane gas.[14]

As pointed out by Stumm and Morgan (1970), the reported association of organic matter preservation with the occurrence of anaerobic conditions is not fully understood, and may be due to the coincidence of anaerobic conditions wherever accumulations of organic matter are found. The inability of multicellular organisms to exist anaerobically, and the higher probability of toxic conditions (e.g. due to high ammonia and hydrogen sulfide levels) in anaerobic deposits could be responsible for retarded stabilization and resultant accumulation.

Organic Compound Metabolism

Microbial utilization of particulate organic matter begins with hydrolysis. Bacteria excrete extracellular enzymes which convert complex insoluble organic compounds into simple dissolved compounds which can then be transported across the cell membrane. Carbohydrates are reduced from polysaccharide (e.g. starch and cellulose) and disaccharide (e.g. sucrose and lactose) forms to simple sugars, primarily glucose with some fructose and galactose (Figure 3). Proteins are broken down to α-amino acids (Figure 4) and lipids are hydrolyzed to glycerol and organic fatty acids (Figure 5).

Carbohydrate metabolism proceeds by glycolysis, a process by which monosaccharides are converted to pyruvic acid. Under aerobic conditions, the pyruvic acid is further converted to acetyl coenzyme-A.

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14. Anaerobic digestion at wastewater treatment plants permits stabilization of 80 to 90 percent of the biodegradable material, in contrast to aerobic systems in which stabilization is only about 50 percent complete (McCarty, 1964).
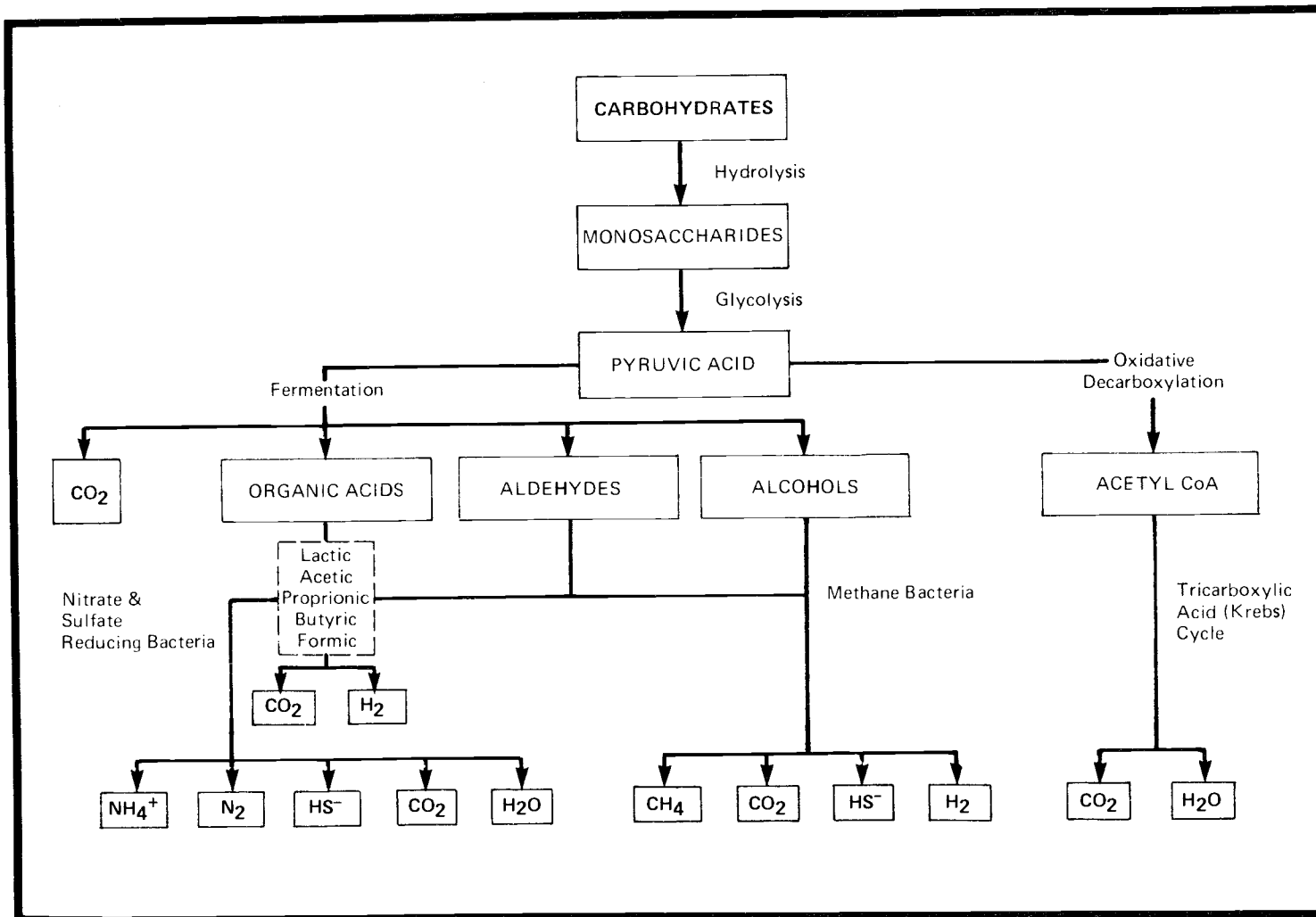
Figure 3. Carbohydrate Metabolism
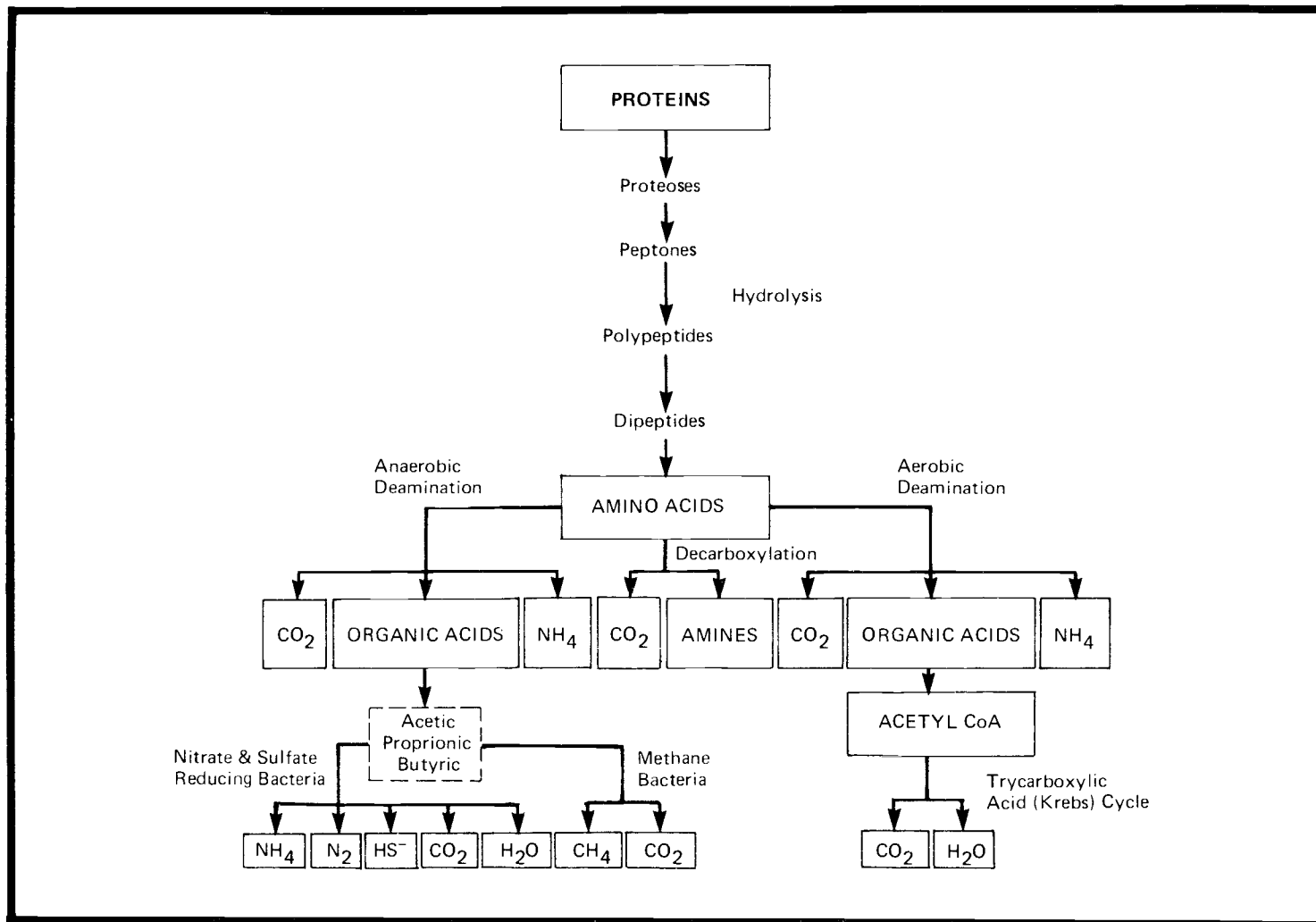
Figure 4.   Protein Metabolism
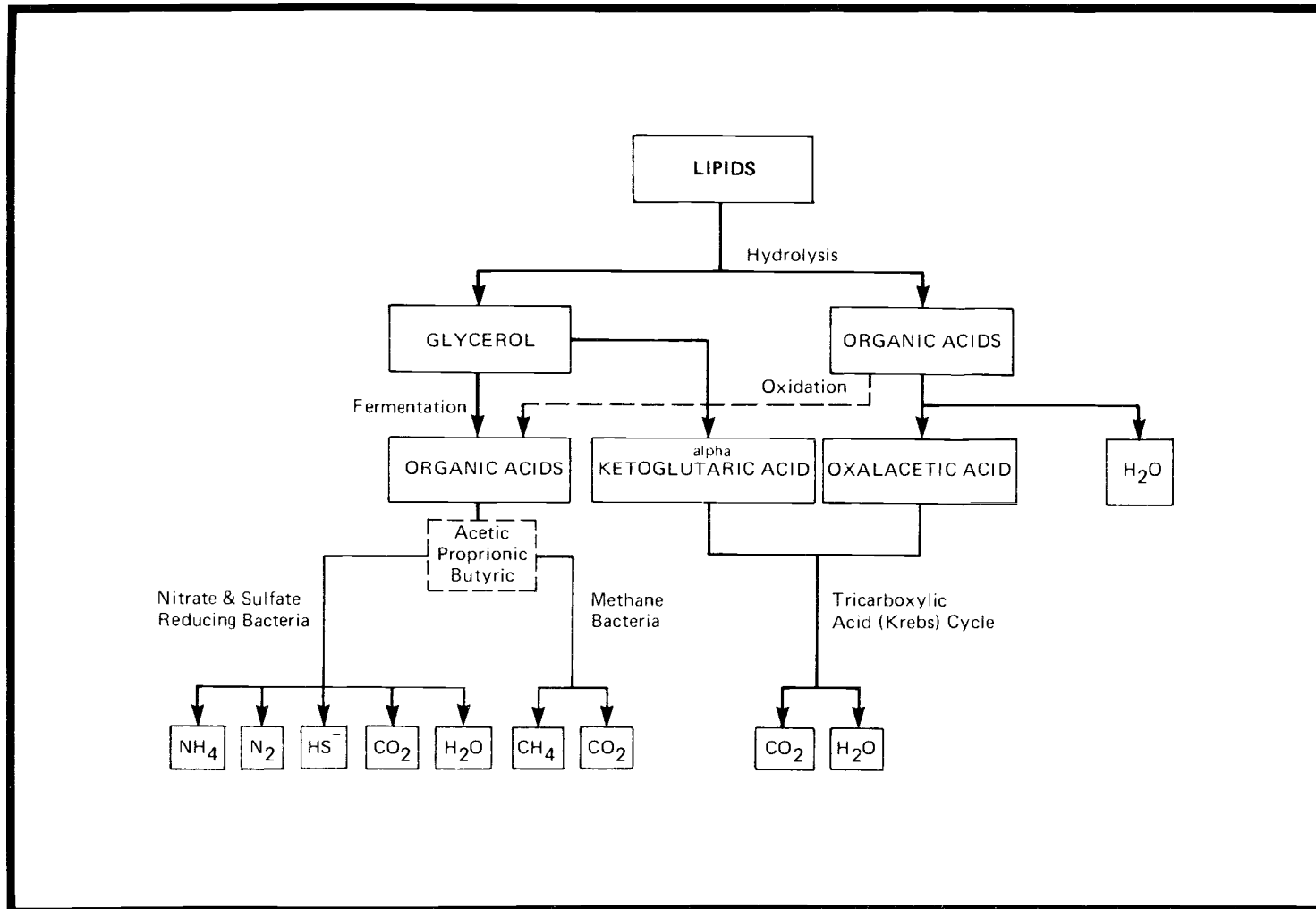
Figure 5.   Lipid Metabolism

This permits entry into the tricarboxylic acid (Krebs) cycle and complete oxidation to carbon dioxide and water. Under anaerobic conditions, fermentation produces organic acids, alcohols and ketones. The organic acids are utilized by nitrate and sulfate reducing bacteria resulting in end-products of ammonia, molecular nitrogen, hydrogen sulfide, carbon dioxide and water. In the absence of nitrates and sulfates, methane bacteria convert the organic acids to methane and carbon dioxide.

Breakdown of protein derived α-amino acids proceeds by aerobic and anaerobic deamination. Aerobically, saturated acids with one less carbon atom, or hydroxy acids with the same number of carbon atoms, are produced in addition to ammonia and carbon dioxide. The acids are thereafter completely oxidized to carbon dioxide and water. Anaerobic deamination proceeds with or without reduction to form saturated or unsaturated acids and ammonia. Thereafter the acids are utilized by nitrate and sulfate reducers, or in their absence, by methane bacteria, producing final end-products of ammonia, nitrogen, hydrogen sulfide, carbon dioxide and water.

Lipid hydrolysis produces organic acids which are further subjected to β-oxidation involving enzymatic removal of hydrogen and the addition of water. As a result of the β-oxidation process, oxalacetic acid is produced allowing further complete oxidation to carbon dioxide and water via the Krebs cycle. Under anaerobic conditions, the organic acids are further utilized by nitrate and sulfate reducers, or methane bacteria. The second hydrolytic product of lipids, glycerol, is aerobically converted to α-ketoglutaric acid, thereby permitting further conversion to carbon dioxide and water by way of the Krebs cycle. Anaerobically, glycerol can be fermented to organic acids, with resultant end-products of ammonia, nitrogen, sulfide, carbon dioxide and water.

Relative to sludge deposit stabilization, it is noteworthy that aerobic conversion of carbohydrates, lipids and proteins results in the production of carbon dioxide which will readily diffuse to supernatant waters due to the shallow nature of the aerobic zone. However,

in deeper anaerobic portions of the deposit, conversion of organic material results in a number of organic or inorganic end-products, the latter of which include sulfide and ammonia. Accumulation of these products due to retardation of interstitial water diffusion or entrapment of bubbles could result in concentrations toxic to deposit microorganisms.

It should be pointed out that breakdown of proteins, carbohydrates and lipids does not occur independently. Many bacteria cannot form the extracellular enzymes required to hydrolyze protein in the absence of an energy supply such as glucose, a product of carbohydrate degradation. Some bacteria require small initial supplies of ammonia-nitrogen and amino acids for synthesis of extracellular enzymes. Anaerobic digestion studies have shown that methane bacteria are dependent on the production of organic acids. Under adverse environmental conditions, the methane bacteria are unable to utilize the accumulating acids, resulting in a pH depression and even further inhibition of the stabilization process.

Controlling Factors

Many chemical factors are known to influence the metabolic efficiency of microorganisms. The presence or absence of molecular oxygen controls the mode of metabolic conversion and can therefore affect the rate of deposit stabilization. Aerobic stabilization is considered more rapid due to the greater availability of energy. Bacteria can grow more rapidly and be more responsive to changing environmental conditions. Per unit of material converted, however, a greater amount of microbial cell mass is created aerobically than anaerobically.[15] The extent of aerobic stabilization is found to be

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15. The low solids production anaerobically is attributed to the higher substrate energy content of methane than carbon dioxide created during aerobic respiration.

approximately 50 percent, whereas anaerobically, over much greater periods of time, the waste can be 80 to 90 percent stabilized. This slower anaerobic conversion is more complete due to the ultimate creation of relatively insoluble methane which, upon loss from the deposit, represents a reduction in organic content. A disadvantage of fermentation is its limit due to the production of equal amounts of oxidized and reduced organic products.

The effect of exogenous hydrogen acceptors other than oxygen was examined by Schroeder and Busch (1966). Their data on anaerobic nitrate systems indicated that the time for completion of biologically mediated reactions was of the same order as comparable aerobic systems.

Other factors which can control sludge deposit stabilization rates include temperature, pH, buffering capacity, nutrients, salinity, toxic substances, oxidation/reduction potential, and hydrostatic presure.

Temperature

Biochemical reaction rates generally increase with increased temperatures due to higher enzyme production rates, up to approximately $35^{\circ}C$. Above this temperature denaturing of enzymes causes a reduction in reaction rates. According to Streeter and Phelps (1925), the temperature dependence of a biochemical reaction rate can be approximated by the Arrhenius Equation (ref. Appendix A) which applies to many chemical reactions, i.e.

$$\frac{K_2}{K_1} = \theta^{(T_2 - T_1)} \tag{1}$$

where K_1, K_2 = the reaction rate constants at temperatures T_2 and T_1

θ = the temperature coefficient

T_1, T_2 = temperatures in degrees Kelvin

Although θ is expected to be relatively constant, it is found to vary even over small temperature ranges. Between $30^{\circ}C$ and $9^{\circ}C$, $\theta = 1.047$ provides relatively good agreement with observed reaction rates (Phelps, 1944). At lower temperatures under aerobic conditions, Moore (1941) found sewage particulate stabilization was described by

θ = 1.065 between $20^{\circ}C$ and $5^{\circ}C$ (K_{20} = 0.311) and 1.145 between $5^{\circ}C$ and $0.5^{\circ}C$ (K_5 = 0.108). Data on anaerobic reaction rates are limited to temperatures generally above the $4^{\circ}C$ to $10^{\circ}C$ expected on the sea-floor. Sawyer and McCarty (1967) report θ for anaerobic sludges between $20^{\circ}C$ and $10^{\circ}C$ to be 1.0526. This translates to a reaction rate constant at $10^{\circ}C$ which is approximately 60 percent as high as at $20^{\circ}C$.

These data indicate that, upon formation of a sludge deposit in relatively cold ocean waters, decomposition would be expected to proceed more slowly than at the ambient wastewater treatment plant temperatures or at the elevated temperatures of anaerobic digestion tanks. In addition to affecting the biochemical activities, the lower temperatures will increase the viscosity and density of interstitial waters, and the solubility of gases produced during decomposition, while decreasing molecular diffusion. These conditions would tend to decrease the depth of the aerobic and sulfate reducing zones.

Buffering Capacity and pH

Enzyme activities are very pH specific, i.e. there are narrow ranges of pH over which they can effectively operate. Enzymes are typically most effective in neutral solutions and the presence of buffers can enhance the maintenance of neutral conditions during the decomposition process. Methane bacteria, for example, require a pH of between six and nine. The breakdown of proteins and urea releases ammonia which can buffer pH decreases associated with the accumulation of organic acids. For anaerobic treatment of sludges a pH range of from 6.6 to 7.6 has been found acceptable, with 7.0 to 7.2 being optimum. Since the pH of surface ocean waters averages 8.2 and in the deep sea is approximately 7.9, the pH of a newly formed seafloor deposit (95-99 percent sea water) will be above that considered ideal for anaerobic digestion by fresh water bacteria. The effectiveness of marine bacteria under such conditions has not been well documented.

Nutrients

Nitrogen, phosphorus and trace materials required by bacteria degrading an organic deposit are abundant in municipal wastes. Therefore, these materials provide an ideal environment for growth, and nutrients should not be limiting in seafloor sludge deposits.

Salinity

McCarty (1964, 1968) reports that the cation portion of salts (e.g. sodium, potassium, calcium and magnesium) can, in sufficiently high concentrations, decrease the efficiency of anaerobic sludge treatment. As cation concentration increases, an initial stimulatory effect is followed by a mild inhibition and finally by the creation of highly toxic conditions. Table IX lists the stimulatory and inhibitory concentrations of four cations and their average concentrations in sea water. Initial sodium concentrations in seafloor sludge deposit interstitial waters will be inhibitory to the fresh water bacteria carried to the seafloor in particulate organic matter. Baity's work (1938) with raw sewage sludge deposits exposed to sea water indicated reduced biochemical activity (40 percent of the fresh water rate) as measured by oxygen consumption. However, this author was unable to locate other data on the stabilization rates of marine bacteria operating on domestic sewage sludges. Therefore, conclusions

TABLE IX.   CATION CONCENTRATIONS (MG/L) AFFECTING ANAEROBIC TREATMENT OF SLUDGES, AND CORRESPONDING SEA WATER CONCENTRATIONS

CATION	STIMULATORY RANGE	INHIBITORY RANGE	TOXIC RANGE	OCEAN WATERS
Sodium	100-200	3500-5500	8000	10805 (0.47M)
Potassium	200-400	2500-4500	12000	391 (0.01M)
Calcium	100-200	2500-4500	8000	409 (0.01M)
Magnesium	75-150	1000-1500	3000	1303 (0.05M)

cannot be drawn regarding the overall effect of increased salinities on marine deposit stabilization since it may be mediated by either fresh water or marine bacteria, or both.

Toxic Substances

During the anaerobic degradation of wastes containing proteins or urea, ammonia is commonly formed. At a pH of below 7.2, ammonia exists primarily in the form of ammonium ion (NH_4^+). Above 7.2, the primary form is ammonia gas (NH_3) which exhibits a toxic effect at much lower concentrations than ammonium ions. Ammonia-nitrogen experiments (which did not distinguish between NH_4^+ and NH_3) with anaerobically digesting sludges showed that concentrations of 50-200 mg/l stimulate biodegradation, 200-1000 mg/l are non-effective, and 1500-3000 mg/l are inhibitory at a pH higher than 7.4. Ammonia concentrations above 3000 mg/l are toxic at all pH levels (McCarty, 1964).

Sulfide can be produced due to sulfate reduction and the breakdown of sulfur-containing amino acids. Soluble sulfide concentrations of from 50 to 100 mg/l are apparently not harmful in anaerobic sludge treatment, whereas levels approaching 200 mg/l are considered marginal and above 200 mg/l can be toxic to functioning microorganisms. Due to the limited solubility of hydrogen sulfide, some may exist in gaseous form and diffuse upward through the deposit. Metals (e.g. copper, nickel and iron) form insoluble precipitates which are non-toxic. Approximately 0.5 mg/l of sulfide will precipitate approximately 1.0 mg/l of the heavy metals mentioned.

Reported sulfide concentrations of as much as 130 mg/l in highly organic estuarine sediments (Bella, 1975) suggest that sulfide accumulation in the deeper portions of a marine sludge deposit could create inhibitory or toxic conditions. The normal metabolic activities of methanogenic bacteria may also be inhibited by the product gases, carbon dioxide and methane (Finny and Evans, 1975).

Hydrostatic Pressure

Pressure, like temperature, influences enzyme stabilities and

chemical reaction rates. Most terrestrial microorganisms and marine microorganisms from the upper few hundred meters in the ocean are unable to grow at hydrostatic pressures of greater than 400 to 500 atmospheres. Some growth retardation has been observed as low as 50 atmospheres (Zobell, 1970; Zobell and Kim, 1972). Marine bacteria isolated from deeper ocean waters grow more rapidly at lower pressures, indicating their normal existance at other than optimal conditions.

The relatively constant organic carbon concentrations as a function of depth in the ocean suggested to some researchers that little or no microbial activity persisted in the deep sea (Menzel and Ryther, 1968). But high pressure and low temperature microbial exper-iments indicated that such activity might be considerable if suitable nutrients and energy sources were available (Zobell, 1968).

In an effort to verify the viability of deep ocean microbial activity, Jannasch incubated laboratory cultures and mixed populations of surface-born bacteria at 5000 meters in the deep sea at 3 to 4°C. After two to five months exposure he found that microbial conversion of a number of organic substrates occurred from 0.15 to 12 percent as fast as laboratory controls held at the same temperature. To determine if microbial flora of the deep water or sediments would respond differ-ently, Jannasch directly innoculated nutrient solutions on the seafloor at 1830 meters (4°C). After a year of exposure, he found that the deep water microbial population had converted substrates at rates of between 0.8 and 5.7 percent that of laboratory controls held at 4°C (Jannasch and Wirsen, 1973). The fact that not only surface-form bacteria but resident deep sea bacteria exhibited extremely slow metabolic rates was interpreted by Jannasch to indicate that either (1) a relative retarda-tion of metabolic processes due to high pressure or (2) the nonexist-ence of active adapted microflora in deep-sea sediments.

Due to concern for the isolated nature of both the substrates exposed by Jannasch and the well preserved lunchbox contents recovered from the submersible Alvin, Sieberth and Dietz (1974) exposed food materials in perforated and triple enclosed containers at two meters, 1500 meters and 5200 meters deep in the ocean (1 to 3°C). After ten

weeks they found that the materials in containers allowing free access of marine organisms were consumed or decayed, whereas the enclosed material remained in a well preserved state. Sieberth and Dietz concluded that labile foodstuffs held near the ocean floor may readily undergo deterioration, and that even though metabolism of deep sea scavengers and microorganisms is apparently greatly reduced, cumulative activities might not be as slow as indicated by Jannasch's observations. Conditions which enclose organic matter or lead to the accumulation of deposits, would, in their assessment, be conducive to storage rather than mineralization of organic matter.

Paul and Morita (1971) found that high pressure and low temperature inhibited amino acid uptake in a facultatively psychrophilic marine bacterium. Reduced uptake of ^{14}C - glutamic acid was evident at relatively low elevated pressures, amounting to between 8.0 and 20 percent at 50 atmospheres. Because respiratory enzymes necessary for amino acid metabolism after transport were not affected to any great extent, the retarded uptake was attributed to a reduction in the organism's nutrient supply. The authors proposed that this reduction was caused by inhibited membrane transport. Specific substrates would, under such conditions, be prevented from reaching the internal metabolic components of the cell. Others have reported that decreased metabolic rates at elevated pressures were due to the inability of cells to assimilate dissolved amino acids (Baross et al., 1974; Albright and Hardon, 1974). Reductions in metabolic activities have also been attributed to inactivation of dehydrogenases of the tricarboxylic acid cycle (Hill and Morita, 1964), general retardation of enzymatic reactions (Zobell and Kim, 1972), and blockage in the synthesis of macromolecules such as ribonucleic acid and proteins (Schwartz et al., 1974).

It is generally conceded that sufficiently high pressure in conjunction with low temperature causes a slowdown in metabolic rates of most bacteria. There are marine bacteria (e.g. Vibrio marinus) for which this rule may not apply, however (Morita and Albright, 1965). A large variety of microbial enzymes are known to be produced and

active at all known depths in the ocean. Complex polymers such as agars, cellulose, starch, chitin and various proteins undergo enzymatic hydrolysis at deep sea temperatures and pressures, although sometimes at reduced rates. Nitrate reduction is also known to proceed at pressures of up to 1000 atmospheres, although the rate relative to that at one atmosphere is decreased by as much as 80 percent (Zobell and Budge, 1965). Information regarding the effects of pressure on anaerobic bacteria (e.g. acid fermenters and methane formers) was not found during the literature review.

Since metabolic rate reductions are generally reported at sufficiently high pressures (at a single temperature), it may be appropriate to describe such rate reductions, within limited pressure ranges, with an equation of the following form:

$$\frac{K_{2P}}{K_{1P}} = \theta_p^{(P_2-P_1)} \qquad (2)$$

where θ_p = the empirically derived pressure coefficient

P_2, P_1 = the hydrostatic pressure levels

This procedure follows that previously discussed for describing biochemical rate temperature dependence over limited ranges, at a single pressure.

Sludge Deposit Conceptual Model

The discussions of marine benthic deposit formation and organic compound metabolism can be summarized in the form of a Marine Sludge Deposit Conceptual Model (Figure 6). The principal components of the model are particulate and dissolved organic carbon, chemoheterotrophic and chemoautotrophic bacteria, and their metabolic products. To depict the presence or absence of oxygen, nitrate or sulfate, three distinct hydrogen acceptor zones are shown; aerobic (dissolved oxygen present),
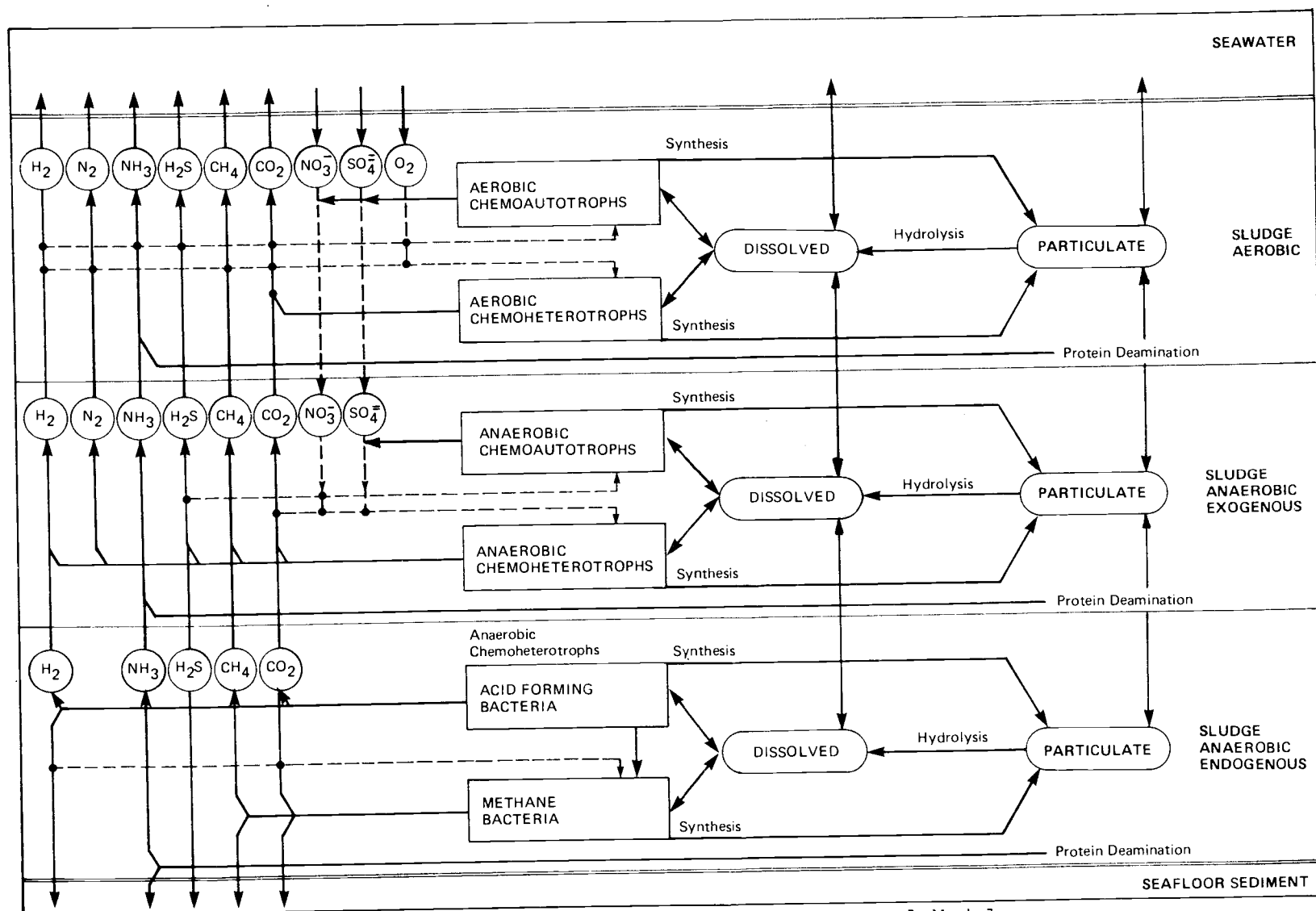
Figure 6.   Marine Sludge Deposit Conceptual Model

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anaerobic-exogenous (no dissolved oxygen, nitrate or sulfate present) and anaerobic-endogenous (no dissolved oxygen, sulfate or nitrate).

The bi-directional exchange of particulate organics represents inputs due to settling and losses due to resuspension and transport. Dissolved organic carbon exchange represents advective pore-water transfer and diffusional transfers due to concentration gradients. Dissolved oxygen, nitrate and sulfate are shown diffusively entering the deposit as a result of gradients caused by their utilization, whereas metabolic products produced (e.g. carbon dioxide, methane, ammonia and sulfide are shown leaving the deposit.

Hydrolysis of particulates is followed by heterotrophic utilization and the production of metabolic products. Cell synthesis is shown as a means of increasing the particulates. The production of soluble organics due to fermentation and due to cell lysing is represented as a return from bacteria to the dissolved organic component.

This conceptual model serves as a basis for a following development of mathematical expressions to describe the temporal decrease of particulate organic carbon (POC) within a stabilizing sludge deposit as a function of location within the deposit.

IV. THEORETICAL CONSIDERATIONS

Diagenesis of Marine Deposit Particulate Organic Carbon

The changes which take place in marine deposits can generally be described with one-dimensional models because vertical gradients are typically much greater than lateral variations (Berner, 1971, 1972, 1974). Variation in the particulate organic carbon concentration of a marine sludge deposit can therefore be described as a function of depth (z) beneath the deposit surface.

$$dC = (\frac{\partial C}{\partial z})_t \, dz + (\frac{\partial C}{\partial t})_z \, dt \qquad (3)$$

where

$(\frac{\partial C}{\partial z})_t$ = the variation in particulate organic carbon with depth at any time t

$(\frac{\partial C}{\partial t})_z$ = the variation in particulate organic carbon with time at any depth z

Rewriting according to the Chain Rule (Thomas, 1962),

$$\frac{dC}{dt} = (\frac{\partial C}{\partial z})_t v + (\frac{\partial C}{\partial t})_z \qquad (4)$$

where

v = the net rate of material deposition (deposition rate minus rate of compaction)

Particulate Organic Carbon Changes in a Continuous Deposit

A significant fraction of sludge and wastewater particulates from a submarine outfall settles in the proximity of the release point,

continuously contributing particulate organic carbon to localized marine sediments over long periods of time. Where the particulate organic carbon content of the material arriving at the seafloor is constant ($\partial C/\partial t = 0$ at $z = 0$), and if all particulates experience the same diagenetic processes (e.g. biochemical degradation and compaction) in becoming buried to a given deposit depth, the vertical particulate organic carbon profile is constant in time (Steady State Diagenesis). The applicable form of equation (4) is

$$\frac{dC}{dt} = \left(\frac{\partial C}{\partial z}\right)_t v \tag{5}$$

Where the only diagenetic process operating is biochemical degradation as described by first-order kinetics, equation (5) becomes

$$-KC = \frac{dC}{dz} v \tag{6}$$

or

$$v\frac{dC}{dz} + KC = 0 \tag{7}$$

Integrating and solving for C with boundary conditions of $C = C_0$ at $z = 0$ and $C = 0$ at $z = \infty$ gives

$$C(z) = C_0 e^{-\frac{K}{v} z} \tag{8}$$

Where compaction and biochemical degradation are occurring, equation (8) must be modified to read

$$C(z) = C_0 \left(\frac{h_0}{h_z}\right) e^{-\left(\frac{K}{v}\right)z} \tag{9}$$

where h_0/h_z is equal to the ratio of the near surface thickness of a deposit layer to the decreased thickness of the same layer upon burial

to some deposit depth z.[16]

Figure 7 presents steady state particulate organic carbon pro-
files where (a) a single biochemical reaction rate constant is appli-
cable and (b) where multiple biochemical reaction rate constants are
applicable as a result of zonal differences in degradation rates (com-
pactive effects assumed equal in both cases).
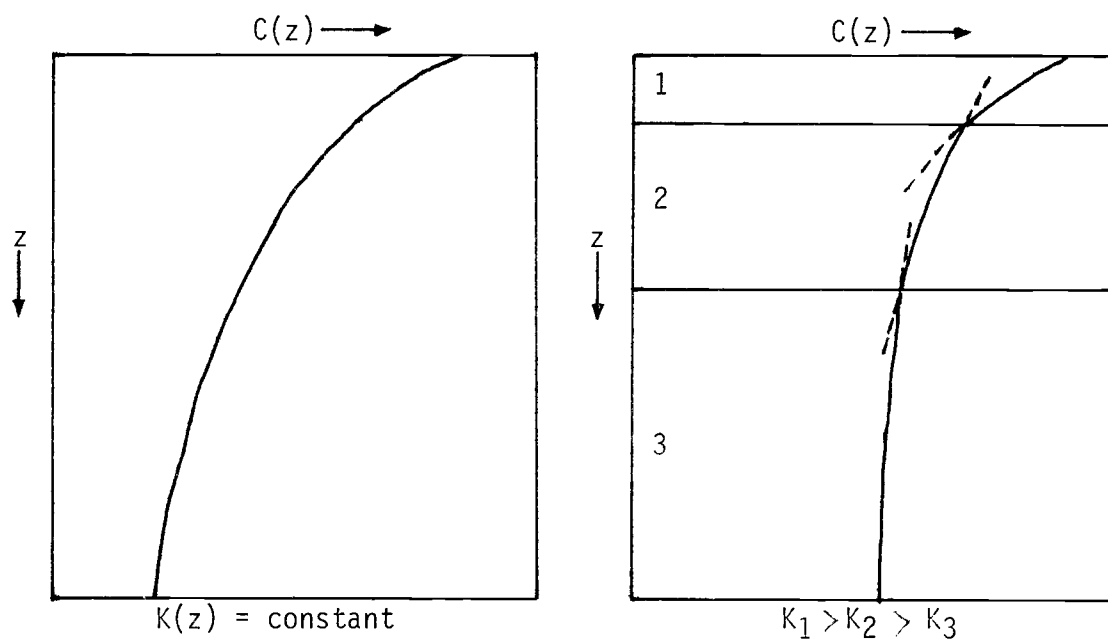
Figure 7. Steady State Particulate Organic Carbon Profiles

Particulate organic carbon profiles based on steady state
diagenesis are idealized since settling particulates are assumed to
have a constant organic carbon content when deposited. Nevertheless,
steady state diagenesis is a useful concept for examining those changes

16. $C_z \equiv \dfrac{M}{V_z} = \dfrac{M}{A} \dfrac{1}{h_z} \quad \therefore \dfrac{C}{C_o} = \dfrac{M}{Ah_z} \bullet \dfrac{Ah_o}{M} = \dfrac{h_o}{h_z}$

where
M = the deposit layer particulate organic carbon mass
V_z = the volume of a deposit layer at a depth z
h_o, h_z = the deposit layer thickness at the surface and depth z, respectively
A = the deposit horizontal area

due to diagenetic processes alone (e.g. biochemical degradation). Although the discussion neglects the effects of bioturbation and periodic erosion, the models developed may apply to relatively quiet bottom areas (e.g. deeper coastal basins) where the activity of burrowing organisms is low (Berner, 1974). Such a low activity might be expected in the hydrogen sulfide permeated regions of a sludge deposit because of the reported extreme toxicity of hydrogen sulfide for marine benthos (Caldwell, 1975).

Particulate Organic Carbon in an Instantaneous Deposit

When sludge is released from a barge in relatively shallow waters, the settled material can be considered as an instantaneously formed deposit. Assuming further sludge is not added to the localized deposit, the operative factors controlling the subsequent particulate organic carbon concentration are compaction and biochemical degradation (again neglecting periodic erosion and bioturbation).

The laboratory use of an instantaneously formed deposit was motivated by its similarity to sludge deposits formed by barge releases, and because it permitted an evaluation of biochemical degradation rate constants applicable to deposited material, regardless of whether such deposition was continuous or instantaneous.

In the absence of continuous material input, and where the material deposited has an initially uniform particulate organic carbon content ($\partial C/\partial z = 0$ at $t = 0$) and changes in the particulate organic carbon content at any deposit depth z can be described by

$$(\frac{\partial C}{\partial t})_z = (\frac{dC}{dt})_{compactive\ and\ biochemical} \tag{10}$$

To isolate biochemical decreases in particulate organic carbon from compactive increases, the particulate organic carbon concentration (mass particulate organic carbon per volume sample) must be normalized

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with respect to the particulate solids content (mass particulate solids per volume of sample).[17] Thus, where the units of C are mass particulate organic carbon/mass particulate solids, equation (10) becomes

$$\left(\frac{\partial C}{\partial t}\right)_z = \left(\frac{dC}{dt}\right)_{biochemical} \tag{11}$$

The total particulate organic carbon at any deposit location can be expressed in terms of biodegradable and refractory components.

$$C = C_d + C_r \tag{12}$$

where

C = the total POC concentration (mass-C/mass solid)

C_d = the biodegradable POC concentration (mass-C/mass solid)

C_r = the constant refractory POC concentration (mass C/mass solid)

Where depletion of the biodegradable particulate organic carbon follows first-order kinetics, differentiating equation (12) gives

$$\frac{dC}{dt} = \frac{dC_d}{dt} = -KC_d \tag{13}$$

which integrates to

$$\ln \frac{C_d}{C_0} = -Kt \quad \text{or} \quad \log \frac{C_d}{C_0} = -kt \tag{14}$$

where   K, k = the first-order particulate organic carbon removal rate constants, natural and common logarithms, respectively

C_0 = the value of C_d at t = 0.

---

17. A compactive increase in the particulate organic carbon mass is accompanied by an equivalent relative increase in particulate solids mass, thus causing the mass ratio of particulate carbon to particulate solids to remain constant.

Solving for C_d and substituting into (12) gives

$$C = C_0 e^{-Kt} + C_r = C_0 10^{-kt} + C_r \qquad (15)$$

This equation is graphically presented in Figure 8.
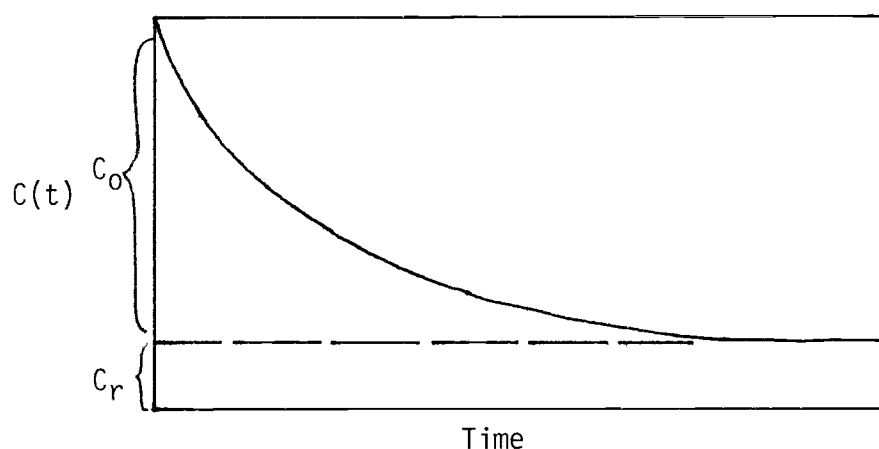
Figure 8.   Sludge Deposit Particulate Organic Carbon
             Concentration vs. Time

The assumption of first-order kinetics in describing biochem-
ical degradation of sludge is based on experimental findings of others
with single and mixed substrates. Tischler and Eckenfelder (1969)
showed that simultaneous linear removal of mixed substrates by a mixed
culture can be the same as the sum of removals by mixed cultures in the
presence of each substrate. As shown in Figure 9, the summation of a
series of overlapping zero-order reactions can produce a result which
has an effect that is similar to first-order, i.e. approximates a
first-order reaction. This is only one of many explanations offered
for the first-order appearance of BOD removal curves. Gaudy et al.
(1962) and Stumm-Zollinger (1966) confirmed that catabolic repression
in heterogeneous bacterial populations can cause sequential substrate
removal, which may lead to an overall decreasing removal rate. Mea-
surements of organic river-bed decomposition rates also indicate that
the overall effect of complex degradation processes can be represented
by first-order kinetics (Rudolfs, 1938; Mohlman, 1938; Fair et al.,

1941).
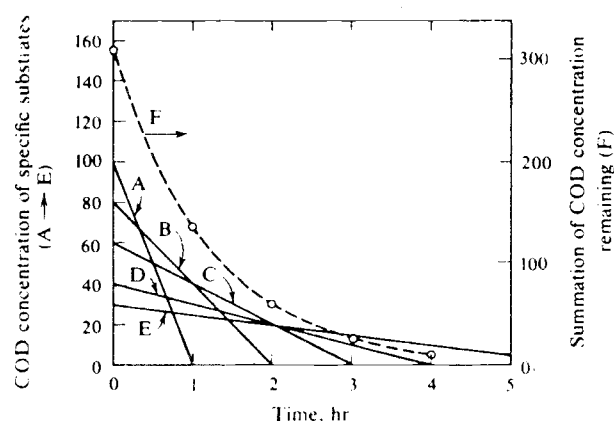
Figure 9.   Graphical Explanation of the Zero-Order Removal
            Concept (Tischler and Eckenfelder, 1969)

Hydrogen Acceptor Zone Dependence

    Although it is generally believed that preservation of organic
material is greater in anaerobic than aerobic environments, the reasons
for such preservation are not well understood (Stumm and Morgan, 1970).
There is some evidence that mixed system anaerobic biochemical reaction
rates can be comparable to aerobic rates, provided an appropriate ex-
ogenous hydrogen acceptor (e.g. nitrate) is present (Schroeder and
Busch, 1966). Endogenous methane fermentation is slower than aerobic
oxidation because it is coupled with much slower cell synthesis
(McCarty, 1964, 1965). Retarded anaerobic degradation is also attri-
buted to the increased sensitivity of anaerobes to fluctuating environ-
mental conditions, and the accumulation of hydrogen sulfide to toxic
levels in the anaerobic portions of highly organic deposits.

The general form of equation (13) can be refined to allow for variability in POC depletion rates within unique hydrogen acceptor zones (Figure 10). The uppermost zone is defined by the deposit surface and depth d_1, at which dissolved molecular oxygen becomes depleted. A deeper zone extends from d_1 to depth d_2, where hydrogen acceptors other than oxygen (e.g. nitrate and sulfate) become depleted. Depths beyond d_2 form a third zone in which hydrogen acceptors are endogenously (within the bacterial cell) generated.

Assumptions

1. One dimensional model with vertical variations only.

2. Uniform particulate organic carbon concentration within each hydrogen acceptor zone at any time t.

3. Uniform particulate organic carbon concentration in the sea water above and sediment below the sludge deposit.

According to equation (15), the particulate organic carbon concentration in compartments 1 , 2 and 3 can be described by[18]

$$C_1 = C_{01} \; 10^{-k_1 t} + C_{r1} \tag{16}$$

$$C_2 = C_{02} \; 10^{-k_2 t} + C_{r2} \tag{17}$$

$$C_3 = C_{03} \; 10^{-k_3 t} + C_{r3} \tag{18}$$

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18. Fair et al. (1941) found a correlation between lower overall first-order k-values and increased anaerobic portions of fresh water deposits. This finding suggests that increased anaerobic zone effects on the overall stabilization rate of the deposit can be described by changes in the first-order reaction rate constant.
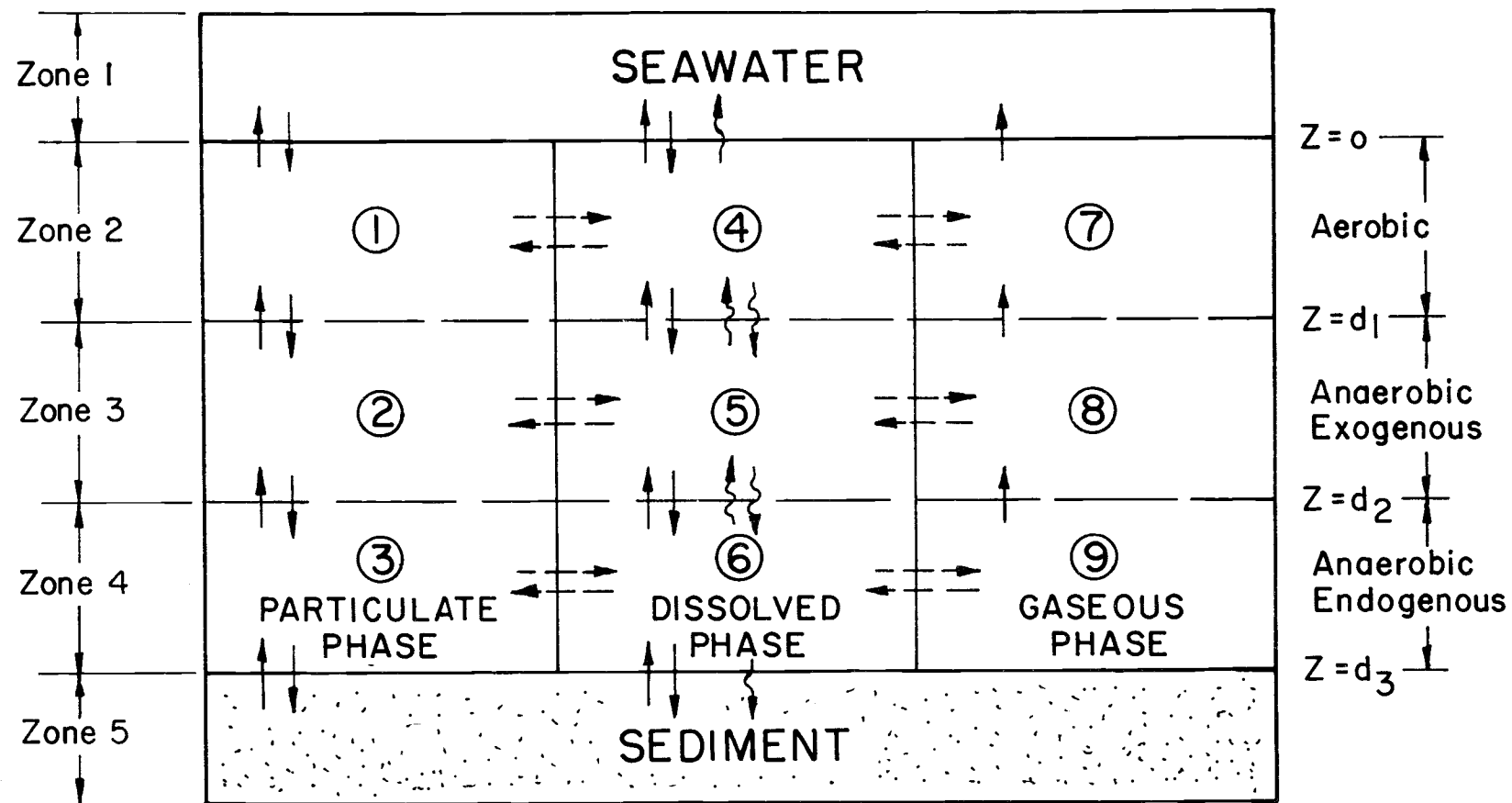
Figure 10. Zoned Fractional Organic Carbon Model

The overall deposit particulate organic carbon concentration (C_T) at any time t can be determined by summing the instantaneous particulate organic carbon mass in each hydrogen acceptor zone and dividing by the deposit's total volume.

$$C_T = M_T/V_T = \left[\sum_{i=1}^{3} (C_{oi}10^{-k_i t} + C_{ri})(S_i V_i) \right] /V_T \tag{19}$$

where

M_T = the total instantaneous mass of particulate organic carbon in the benthic deposit (mass-C)

V_T = the total deposit volume at time t (volume)

C_{oi} = the initial biodegradable particulate organic carbon concentration in each zone (mass-C/ mass particulate solid)

S_i = the particulate solids concentration in each hydrogen acceptor zone (mass particulate solid/volume)

V_i = the hydrogen acceptor zone volume (volume)

Temporal variations in C_T give the particulate organic carbon depletion rate for the overall deposit. Determination of C_T requires a knowledge of C_i, the instantaneous particulate organic carbon concentration in each zone (or the factors required to calculate C_i, i.e. k_i, C_{oi} and C_r). In addition, the particulate solids concentration within each zone (S_i) and the volume of each zone (V_i) are also required.

Elevated Hydrostatic Pressure Dependence

A literature review failed to provide information on the degradation rates of marine deposits at elevated hydrostatic pressures. Although retardation in aerobic microbial metabolic rates is known to

occur at high (100 to 1000 atmospheres) hydrostatic pressures,[19] the understanding of even single substrate metabolism by one bacterial species remains limited (Albright and Hardon, 1974). In addition, the author was unable to find reported research for hyperbaric effects on anaerobic microbial metabolism. It would therefore be pretentious to hypothesize the pressure dependence of a mixed microbial community operating on a complex substrate such as domestic sludge. However, recent studies suggest that an overall first-order approximation may be appropriate for the small (1-100 atmospheres) hydrostatic pressure increases expected at coastal disposal sites.

Paul and Morita (1971) found amino acid uptake by a facultatively psychrophilic marine bacterium (MP-38) to be linear with time (five hours) and substrate concentration (to 200 μg/l). At elevated pressure, ^{14}C-glutamic acid uptake, though depressed relative to one atmosphere uptake, remained linear in time at both 5°C and 20°C. A first-order approximation of the overall POC depletion rate at limited increased pressures is therefore proposed because:

1. First-order overall substrate removal rates at one atmosphere occur with mixtures of simple compounds which are known to be linearly removed on an individual basis.

2. Linear removal of isolated substrates is also known to occur at elevated hydrostatic pressures.

3. Changes in the one-atmosphere microbial utilization rates for individual substrates at hydrostatic pressures typical of continental shelf disposal sites are small (Paul and Morita, 1971).

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19. Many mechanisms have been proposed including volume changes and associated reduced enzyme reaction rates; loss of microorganism ability to synthesize macromolecules (e.g. DNA, RNA and proteins); inhibited amino acid uptake; enzyme and protein denaturation; decreased membrane permeability; metabolite leakage; decreased cell division; and blockage of cell wall synthesis (Zobell and Kim, 1972; Albright and Hardon, 1974).

Where deposit particulate organic carbon depletion rates at hydrostatic pressures above one atmosphere can be approximated by overall first-order reaction kinetics, the equations describing such depletions take the form

$$C_{ij} = C_{oij}10^{-k_{ij}t} + C_{rij}$$ (20)

where i = the hydrostatic pressure level
j = the hydrogen acceptor zone

Applicable equations for an experiment involving two hydrostatic pressures and three hydrogen acceptor zones would include those listed in Table X.

TABLE X. COMPONENTS OF AN EXPERIMENT AT TWO HYDROSTATIC PRESSURES WITH THREE HYDROGEN ACCEPTOR ZONES

PRESSURE ZONE	P_1	P_2
1	$C_{11} = C_{011}10^{-k_{11}t} + C_{r11}$	$C_{21} = C_{021}10^{-k_{21}} + C_{r21}$
2	$C_{12} = C_{012}10^{-k_{12}t} + C_{r12}$	$C_{22} = C_{022}10^{-k_{22}} + C_{r22}$
3	$C_{13} = C_{012}10^{-k_{13}t} + C_{r13}$	$C_{23} = C_{023}10^{-k_{23}} + C_{r23}$

The presence of hydrostatic pressure or hydrogen acceptor zone effects on POC depletion rates may be apparent when comparing C_{ij} data based on a series of samples at each of two pressures and from each hydrogen acceptor zone. Apparent effects could be statistically confirmed through a variance analysis of k-values calculated on the basis of temporal variations in C_{ij} values.

EXPERIMENTAL PROGRAM

Preliminary Laboratory Experiments

In the absence of data from earlier investigations of stabilizing marine sludge deposits, a set of preliminary experiments was designed to determine:

1. The order of the rate equations which describe the depletion data

2. The magnitude of temporal particulate organic carbon decreases

3. The magnitude of the refractory organic component and the time required to experimentally observe this value (i.e. when $\frac{dC_d}{dt}$ becomes small)

4. Whether an initial lag period would occur

5. The acceptibility of proposed analytical methods

6. The extent of distinguishable hydrogen acceptor zones

In addition, the experiments allowed for the testing of newly constructed one-atmosphere and high-pressure sludge reactors and the Deep Sea Simulator.[20]

The preliminary organic carbon degradation experiment consisted of the six-month exposure of a 2.0 centimeter deep sludge deposit to flowing (approximately 1.5 cm/sec) natural sea water at a hydrostatic pressure of 34 atmospheres.[21] This pressure, which occurs at an ocean depth of 345 meters, typifies the pressure at a continental slope disposal site such as those which have been considered for future

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20. A summary of the design characteristics of the Deep Sea Simulator is presented in Appendix B.
21. An ancillary experiment with a 33 centimeter deep sludge deposit was simultaneously performed to determine the extent of distinguishable hydrogen acceptor zones. A description of this experiment and related findings are presented in Appendix C.

releases.[22] A higher pressure was not considered appropriate for initial experiments since seafloor sludge accumulation beyond a few hundred meters is questionable due to the highly dispersive nature of the open ocean environment.

All experiments reported herein were performed in darkness (except when sampling) at $23^{\circ}C$ to prevent photosynthetic and temperature dependent effects. Although many seafloor environments have lower temperatures, it was considered logistically desirable to maintain $23^{\circ}C$ to avoid any reduction in an expected slow reaction rate. This temperature also coincided with that of an in-situ experiment, permitting a comparison of respirometric measurements made under both conditions (to be published separately).

Materials

Anaerobically digested sludge used in the laboratory experiments was obtained from holding tanks at the Bay Park Water Pollution Control Plant, East Rockaway, New York.[23] Upon arrival from New York and until used, the 18.9 liter cubitainers of sludge were stored in a cold room at $4^{\circ}C$. The characteristics of the Bay Park sludge are presented in Table XI.

Pre-experiment sludge conditioning consisted of settling through a sea water column to simulate particulate elutriation which occurs upon barge release or outfall discharge. The sea water column was approximately one meter in height, 60 centimeters in diameter, and provided a 10:1 dilution ratio. Changes in the carbon and solids characteristics of the settled sludge and dilution water are listed in Table XII.

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22. Although all ocean disposal of U.S. domestic sludges now occurs at continental shelf sites (i.e. less than 200 meters) associated problems have led to proposals for the use of deeper sites farther from shore.

23. From these tanks, the sludge is pumped to marine tankers and transported offshore for dumping.

TABLE XI. CHARACTERISTICS OF DIGESTED SLUDGE FROM THE BAY
PARK WATER POLLUTION CONTROL PLANT

PARAMETER	AVERAGE	RANGE
NITROGEN (mg/1)[a]		
Ammonia	747	549 - 834
Nitrate	3.0	2.6 - 3.8
Nitrite	0.05	0.02 - 0.08
Organic	156	73 - 259
Total	905	686 - 1075
PHOSPHORUS (mg/1)		
Total	155	88 - 355
CHLORIDES (mg/1)	125	100 - 160
pH	7.2	6.7 - 7.4
GREASE AND OILS(mg/1)	3,238	2,121 - 4,730
COLIFORM (MPN)		
Total	12.3×10^6	$0.43 \times 10^6 - 240 \times 10^6$
Fecal	2.6×10^6	$0.08 \times 10^6 - 110 \times 10^6$
ALKALINITY (mg/1)	3,673	2,680 - 4,900
BOD (mg/1)	2,323	1,840 - 4,160
TOTAL SOLIDS (%)	1.67	0.99 - 3.64
VOLATILE SOLIDS (%TS)	65.2	52 - 74
METALS (mg/kg-wet)[b]		
Mercury	0.075	0.0003 - 0.151
Cadmium	0.686	0.305 - 1.95

a. As reported in "Summary of Analysis of Bay Park Sewage
Sludge", County of Nassau, Department of Public Works, Mineola, New
York.

b. As reported in "Report of Tests", New York Testing Labor-
atories, Westbury L.I., New York, Lab. No. 73-43204.

TABLE XII.   CARBON AND SOLIDS CONTENT OF SLUDGE USED IN
PRELIMINARY LABORATORY EXPERIMENTS

PARAMETER	AS RECEIVED	AFTER SEA WATER SETTLING
TOTAL SOLIDS (mg/1) (% by wt.)	13050-16700 1.2-1.6	38590-51400 3.7-5.0
VOLATILE SOLIDS (mg/1) (% TS)	7770-10760 63-64	10860-17380 28-34
TOTAL CARBON (mg/1) (% TS)	4030-5180 26-39	1900-3970 4.9-7.9
ORGANIC CARBON (mg/1) (% TC)	3517-4657 85-90	1049-3888 89-98
BULK DENSITY (g-dry/ml)	1.000-1.009	1.017-1.029
SOLIDS DENSITY (g-dry/ml)	1.5-1.6	-

The characteristics of Oregon coastal sea water used for the experiments are presented in Table XIII. Sea water taken through the Depoe Bay Aquarium ocean inlet was trucked to an Oregon State University underground storage tank. It was subsequently transferred to two 1900 liter epoxy lined steel tanks at the EPA Environmental Research Center. As required, the sea water was drawn through polyvinylchloride piping to glass holding tanks in the environmental chamber.

Sludge Reactor

Pressure experiments were conducted in a Deep Sea Simulator designed and built for this research (Figure 11). The Simulator consists

TABLE XIII.   CARBON AND SOLIDS CONTENT OF SEA WATER USED IN
               LABORATORY EXPERIMENTS

PARAMETER	NATURAL SEA WATER DEPOE BAY, OREGON
TOTAL SOLIDS (mg/1) (% by wt)	34500-41290 3.3-4.0
VOLATILE SOLIDS (mg/1) (% TS)	6620-11280 18-27
TOTAL CARBON (mg/1) (% TS)	19-28 0.06-0.08
ORGANIC CARBON (mg/1) (% TC)	0-1.0 0-3.1
DENSITY (g/ml)	1.015-1.023
SALINITY (ppt)	29.8-32.4

of a converted surplus U.S. Navy Mark 13, Mod. 2 High Capacity, 406
millimeter projectile. A covered transparent acrylic sludge reactor
(Figure 12), which contained a sludge deposit over a sand substrate,
was placed inside the pressure vessel and attached to an inlet port.
Natural sea water was pumped by air-hydraulic pump (100:1 pressure
amplification) from the 95 liter reservoir to the sludge reactor within
the Simulator, and back to the reservoir. Reactor plug flow was in-
sured by a series of baffles at inlet and exit ports. An accumulator
between the pump and pressure vessel reduced the pressure pulse to less
than 0.07 atmospheres. Sea water flow rate and hydrostatic pressure
were controlled by air pressure regulation and exit valve settings.
Reservoir dissolved oxygen levels were maintained at six to seven mil-
ligrams per liter by bubbling in dried and carbon-dioxide-scrubbed air.
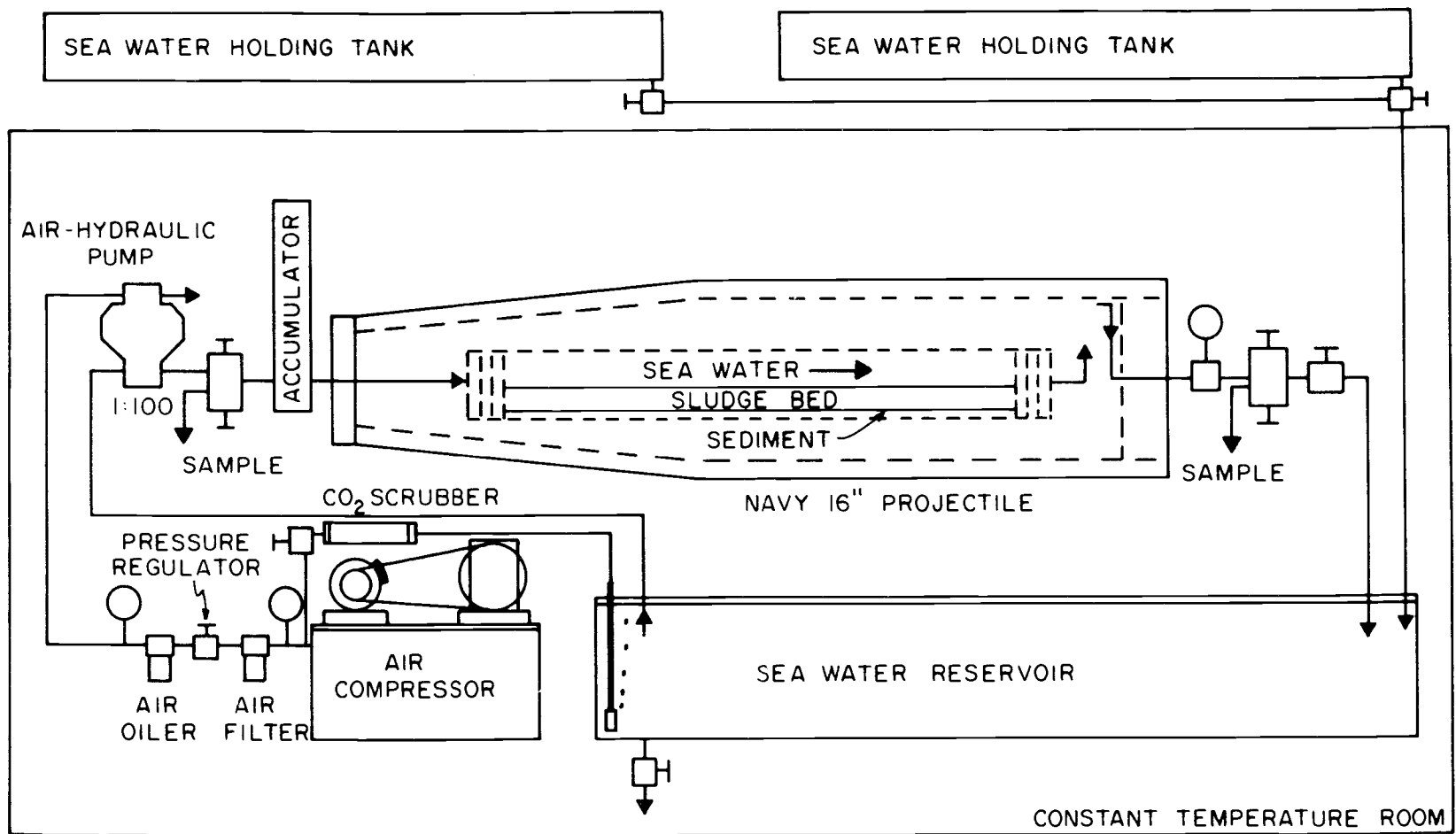
Figure 11   Deep Sea Simulator
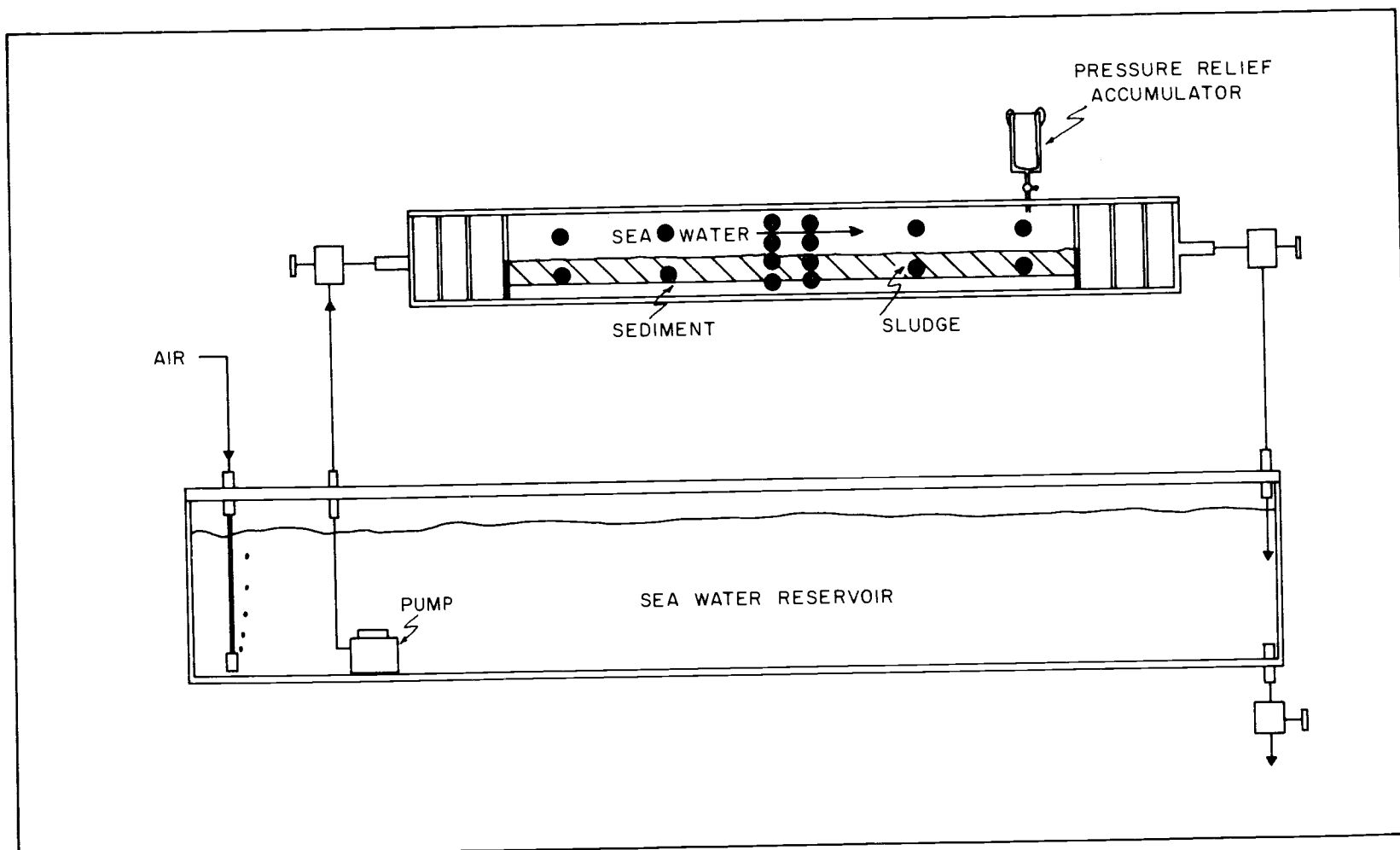
Figure 12.   One Atmosphere Laboratory Sludge Reactor for Final Experiments

Initial efforts to directly withdraw sludge samples from the pressurized vessel were not successful and limited the selectivity of sample location in the deposit. Due to reports that controlled decompression and recompression rates can minimize or negate adverse microbial effects (Zobell, 1970), sampling was performed by slowly decompressing the system (typically over 30 minutes) and removing the sludge reactor. In addition to permitting selective sampling at variable deposit depths, this procedure allowed photography of the deposit at regular sampling intervals. Sludge samples were taken both by direct sampling with the reactor cover removed (surface samples) and from side mounted septums (deeper samples). To continue the experiment, the sludge reactor was covered and returned to the Simulator, which was then sealed, filled with sea water and slowly brought back to operating pressure.

Selection of Analytical Procedures

The dependent variable selected to determine the effects of hydrostatic pressure and hydrogen acceptor type on biochemical degradation rates was particulate organic carbon. Measurement of organic carbon provides a direct, accurate and rapid method of assessing the organic content of sludges (Maier and McConnell, 1974; Arin, 1974). Carbon analyses require relatively small samples, ensuring minimal deposit disturbance and avoidance of material depletion.

Since the instantaneous magnitude of particulate organic carbon (mass-C/volume sample) is a function of both biochemical degradation and compaction, isolated monitoring of biochemically caused changes requires normalization relative to solids concentration. A compactive increase in the particulate organic carbon concentration is accompanied by a corresponding increase in the particulate solids concentration. Thus, the ratio of particulate carbon to particulate solids concentrations remains constant. The ratio is, however, dependent on microbial utilization because of selective hydrolysis of organic particulates by chemoheterotrophs.

To distinguish between particulate and dissolved concentrations of carbon, portions of extracted sludge samples were centrifuged at a relative centrifugal force (RCF) of 16,300 for one hour.[24] The decanted supernatant was filtered through Whatman GF-C (4.5 cm) glass fiber filters which had been washed with double distilled water and pre-combusted at 400°C for two hours.[25] The filtered supernatant was then analyzed for solids and carbon content. The difference between the solids and carbon content of the centrifuged/filtered supernatant and the unfiltered portion of the sample was considered to be the particulate fraction of the sample.

During the 12 to 24 hours between extraction and analysis of the samples, they were stored at 4°C. Unfiltered samples were homogenized with a high speed blender[26] and diluted with double distilled water prior to syringe injection into the total carbon analyzer.

Solids Determinations

Solids analyses of sludge samples were performed according to the recommended residue procedure in Standard Methods for the Examination of Water and Wastewater, section 208A (APHA-AWWA-WPCF, 1976). Ten milliliter aliquots of blended sludge were evaporated to dryness on a steam bath and then oven dried to a constant weight (48 hours) at 103 to 105°C.[27] A calibrated ten milliliter glass syringe (B-D No. 13

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24. Sorvall RC2-B Automatic Superspeed Refrigerated Centrifuge, RCF = $4\pi^2 rn^2/32.2$ where r = 0.479 ft., n = 166.6 revolutions per second.

25. Williams (1968), who used these filters to distinguish between particulate and dissolved organic matter reported average pore diameters ranging from one to two microns. In final experiments, 0.8 micron MF - Millipore filters were used to distinguish dissolved organic carbon.

26. Willems Polytron Type PT-10 20 3500, Nr. 4280.

27. Repetitive weighings indicated incomplete water removal in 24 hours. By 48 hours, however, weight changes became less than 0.1 percent.

needle with an internal diameter of 1.778 mm) was used to measure aliquot volumes.

Repetitive analyses (n = 12) of a digested sludge sample which had been settled through sea water gave a standard deviation of 258 mg/1 at an average concentration of 52537 mg/1 (coefficient of variation = 0.005). Analyses (n = 7) of a sludge sample filtrate (0.8 micron) gave a 124 mg/1 standard deviation at an average concentration of 33745 mg/1 (c.v. = 0.004). There is no satisfactory method of determining the solids procedure accuracy, since the true solids concentration of a sludge sample is unknown and there is no universal standard of comparison (APHA-AWWA-WPCF, 1976).

Carbon Determinations

The relatively high total carbon contents of homogenized sludge samples and filtered deposit interstitial water samples were analyzed with an Oceanography International Corporation Direct Injection Module (Model 0524-HR) in combination with an Ampoule Analyzing Unit (Model 0524B) and a non-dispersive infrared (IR) gas analyzer (MSA LIRA Model 300). A sludge sample was introduced by a 100 microliter syringe (internal needle diameter = 0.1524 mm) through a combustion tube septum onto an asbestos filled sample filament.[28] In the presence of purified oxygen, the sample filament temperature was automatically raised in two steps. The first low-temperature step allowed the sample water and volatile carbon forms to slowly vaporize without spattering. Carbon containing compounds which left the coil without oxidation were swept into a high-temperature internal combustion furnace where quantitative conversion to carbon dioxide occurred. The subsequent high-temperature step (to approximately $1000^\circ C$) insured that

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28. Sampling bias tests with internal needle diameters from 0.1143 to 0.3048 mm indicated that particulate exclusion of blended sludge did not occur for internal diameters above 0.1270 mm.

the carbon remaining on the coil was converted to carbon dioxide. After drying, the carbon dioxide gas entered the IR analyzer. The analyzer output drove both a strip chart recorder (qualitative monitoring) and an electronic disc integrator. The output from the integrator, which was proportional to the sample carbon concentration, was printed on a teletype.

Repetitive total carbon analyses (n = 20) of a digested domestic sludge diluted to an average concentration of 114 mg/l gave a standard deviation of 2.2 mg/l (c.v. = 0.019). The Manual of Methods (EPA, 1974) lists the accuracy of the total organic carbon determination as a +1.01 percent bias for samples having 107 mg/l carbon. Analyses (n = 15) of the 0.8 micron filtrate gave a standard deviation of 1.9 mg/l at an average concentration of 40.1 mg/l (c.v. = 0.047).

Inorganic carbon determinations were made by injecting a 0.1 milliliter sample aliquot into a glass ampoule containing two milliliters of 0.1 normal sulfuric acid in the presence of a nitrogen carrier gas. The released carbon dioxide was quantitatively measured using the same IR analyzer and electronic print-out equipment used for the total carbon determinations. Organic carbon was calculated as the difference between the total and inorganic carbon determinations.

Repetitive total inorganic carbon analyses (n = 21) at an average sample concentration of 16.9 mg/l indicated a sample standard deviation of 0.8 mg/l (c.v. = 0.049). Filtrate (0.8 micron) analyses (n = 11) gave a 0.2 mg/l standard deviation at an average concentration of 5.8 mg/l (c.v. = 0.034).

The carbon analyzer was calibrated before, during and after the running of a sample set. This insured the comparability of analyses over the six month analytical period, and minimized the effect of instrument drift during any one analytical session (six to twelve hours). The instrument was calibrated by introducing equal volumes of potassium acid phthalate (KHP), diluted to a range of concentrations, and recording the response of the IR analyzer. A cross-check of carbon standards indicated equivalent instrument response to amounts of carbon

ranging from 1.5 to 25 micrograms carbon in the form of KHP, nicotinic acid, sodium oxalate and nicotinamide.

Estimated Standard Deviation of the Carbon/Solids Ratio

The estimated standard deviation (s) in the particulate organic carbon to particulate solids ratio was evaluated by determining the estimated standard deviation in each component of the ratio, and then calculating the estimated standard deviation of the ratio itself by standard formula.

Applying the experimentally determined coefficients of variation to measured carbon and solids concentrations of a sludge sample gives an estimate of the standard deviation associated with each determination (Table XIV).

TABLE XIV.   ESTIMATED VARIANCE VALUES FOR CARBON AND SOLIDS
MEASUREMENTS

PARAMETER	CONCENTRATION (mg/l)	COEFFICIENT OF VARIATION	s	s^2
Total Carbon (TC)	7265	0.019	138	19054
Dissolved Carbon (DC)	182.0	0.047	8.6	73.2
Total Inorganic Carbon (TIC)	89.9	0.049	4.4	19.4
Dissolved Inorganic Carbon (DIC)	72.6	0.034	2.5	6.1
Total Solids (TS)	52531	0.005	262.7	68988
Dissolved Solids (DS)	33764	0.004	135.1	18240

The variance in particulate carbon determination (s_{PC}^2) can be estimated by

$$s_{PC}^2 = s_{TC}^2 + s_{DC}^2 = 19127 \qquad (21)$$

Similarly for particulate inorganic carbon and particulate solids

$$s_{PIC}^2 = s_{TIC}^2 + s_{DIC}^2 = 25.5 \qquad (22)$$

$$s_{PS}^2 = s_{TS}^2 + s_{DS}^2 = 87228 \qquad (23)$$

The variance in particulate organic carbon determination (s_{POC}^2) can be estimated by

$$s_{POC}^2 = s_{PC}^2 + s_{PIC}^2 = 19153 \qquad (24)$$

The standard deviation of the particulate organic carbon to particulate solids can be estimated by (Wilson, 1952)

$$s_{RATIO} = \left[\frac{s_{POC}^2}{(\overline{PS})^2} + \frac{s_{PS}^2}{(\overline{PS})^4} (\overline{POC})^2 \right]^{\frac{1}{2}} \qquad (25)$$

where $\overline{PS}$ = the sample average particulate solids concentration (mg/1)

   $\overline{POC}$ = the sample average particulate organic carbon concentration (mg/1)

Substituting into equation (25) gives s_{RATIO} = 0.0095.

Preliminary Experiment Findings

   Measured decreases in the particulate organic carbon-solids ratio at 34 atmospheres in aerobic and anaerobic-exogenous zones of a

2.0 centimeter sludge deposit are presented in Figure 13.[29] The curves and associated equations were determined using equation (15) and the Tsivoglou method of curve fitting (Appendix D).

Data from the preliminary experiment at 34 atmospheres indicate:

1. The first-order form of the degradation rate equation describing zonal organic carbon depletion appears justified at 34 atmospheres.

2. Particulate organic carbon decreases in 130 days amounted to 30.6 and 7.0 percent in aerobic and anaerobic zones, respectively.

3. The surface zone residual particulate organic carbon content (C_r) was 0.213 mg-C/mg solid. This concentration represents 70 percent of the original organic carbon content of the deposited sludge. The residual component in the anaerobic zone appeared to be considerably higher, although specification of an exact value is difficult due to continuing slow degradation at the experiment conclusion in six months. The calculated anaerobic particulate organic carbon residual was 0.277 mg-C/mg solid.

4. An initial lag in microbial utilization of the highly organic substrate was not apparent.

5. Proposed analytical methods proved to be acceptable, both procedurally and in terms of precision needed to distinguish temporal variations in deposit particulate organic carbon. In addition, the Deep Sea Simulator performed consistently, maintaining required pressures throughout the experiment and otherwise proving to be reliable.

6. Dissolved oxygen and sulfate measurements in the ancillary 33 centimeter deposit (Appendix C) indicated that the surface aerobic zone extended to a maximum of three millimeters into the deposit. The anaerobic exogenous zone extended from this depth to approximately 16 centimeters deep at the conclusion of the six month experiment.

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29. Some deep samples were invalidated due to withdrawal of sand from beneath the deposit when sampling. This problem was corrected in final experiments by enclosing screened sand (particles remaining were greater than 90 microns) in a 60 micron mesh (45% open space).
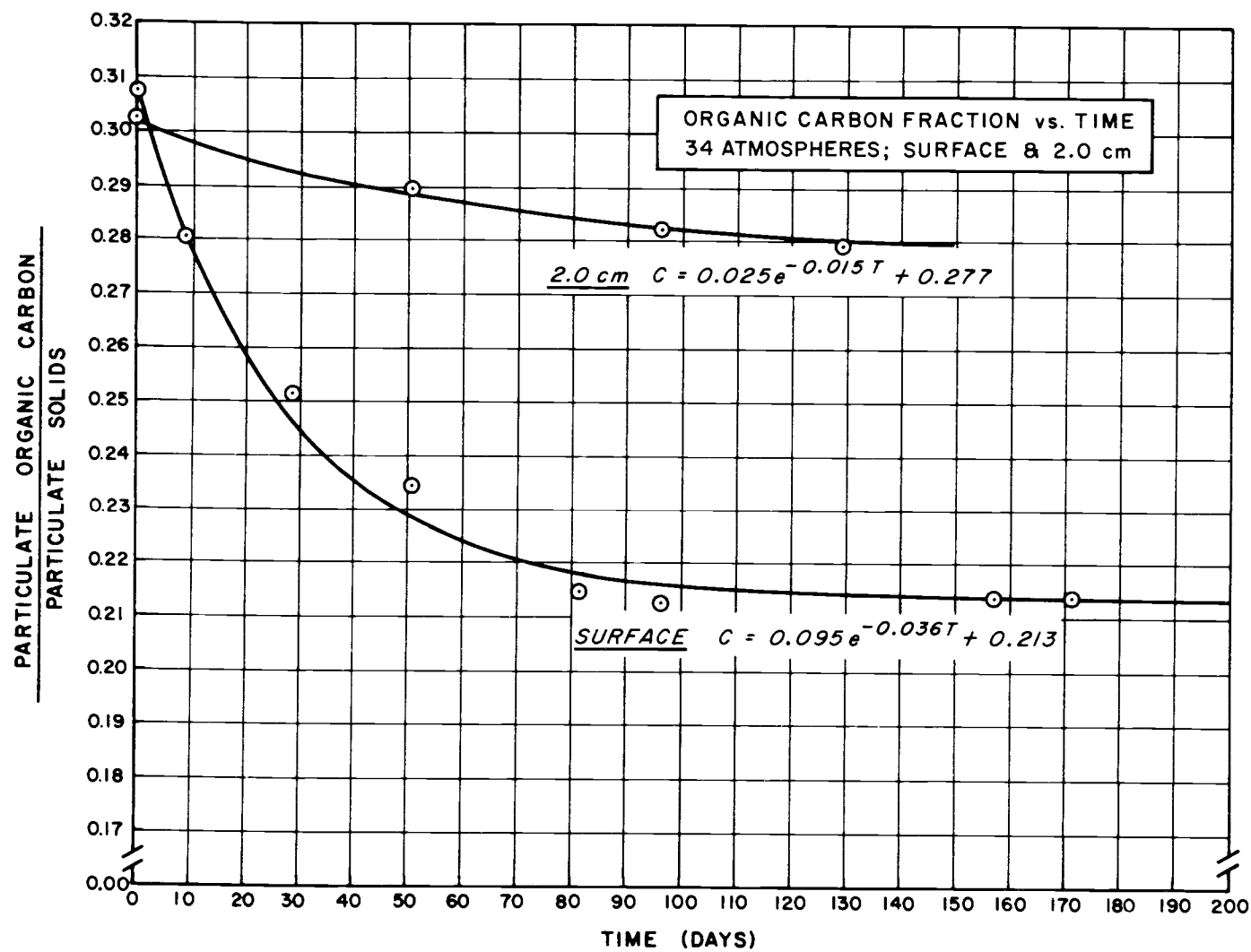
Figure 13. Preliminary Experiment Organic Carbon Concentration
Changes at 34 Atmospheres

Experimental Design

A randomized-block 2x2 factorial experiment was designed to statistically determine whether the biochemical stabilization rate of a 3.0 cm deep marine sludge deposit differed at one and 34 atmospheres, or for aerobic and anaerobic exogenous conditions. Two null hypotheses were considered:

H1: $\mu_{1 \text{ atmosphere}} = \mu_{34 \text{ atmospheres}}$ (Factor A)

H2: $\mu_{\text{aerobic}} = \mu_{\text{anaerobic-exogenous}}$ (Factor B)

Data components for the final experiment are listed in Table XV. Randomized block conditions were insured by dividing uniformly mixed sludge into ten cubitainers, three of which were randomly selected for replicate experiments. Sludge from each cubitainer was subjected to the same four treatments. Cubitainer contents were thoroughly mixed prior to filling sludge reactors to avoid preferential assignment to treatment conditions. Deposit samples were randomly withdrawn from equal sized vertical deposit zones in each reactor.

TABLE XV.   FINAL EXPERIMENT DATA COMPONENTS

B \ A	1 Atmosphere	34 Atmospheres	Block
	k_1	k_4	1
aerobic	k_2	k_5	2
	k_3	k_6	3
	k_7	k_{10}	1
anaerobic exogenous	k_8	k_{11}	2
	k_9	k_{12}	3

The sampling program was designed to insure, with some degree of certainty, that the null hypotheses would be rejected if the sampled k-values were from populations whose mean k-values (μ_i) differed by more than a designated value (δ). The following procedure (Li, 1964) was followed in determining the appropriate number of replicate experiments to perform.

1. Set an appropriate value for $\delta = \mu_2 - \mu_1$, the required detectable difference between two population mean values.

   The k-values determined in the preliminary 34-atmosphere experiment were $k_{surface} = 0.0156$ day^{-1} and $k_{2.0\ cm} = 0.0065$ day^{-1}. To distinguish populations whose mean k-values differ by 30 percent of the lower of the two k-values requires $\delta = (0.30)(0.0065) = 0.0020$.

2. Define s_1, an available sample standard deviation and its degrees of freedom ν_1.

   A value for s_1 can be estimated from previously measured k-values (i.e. for river sludge deposits).

McGowan (1913)	Fair et al. (1941)
$k_1 = 0.0019$	$k_1 = 0.0044$
$k_2 = 0.0017$	$k_2 = 0.0035$
$k_3 = 0\ 0012$	$k_3 = 0.0045$
$k_4 = 0.0007$	$k_4 = 0.0044$
$k_5 = 0.0023$	$k_5 = 0.0029$
$s_a = 0.00062$	$s_b = 0.00071$

$$s_1^2 = \frac{s_a^2 + s_b^2}{2} = (4.455)(10^{-7}) \tag{26}$$

$$\nu_1 = 2(n-1) = 8 \tag{27}$$

3. Define ν_2, the degrees of freedom associated with the error sum-of-squares of the proposed experiment.

For the proposed randomized block 2x2 factorial experiment, the error sum-of-squares degrees of freedom is ν_2 = (ab-1)(n-1), where a=2 (hydrostatic pressures), b=2 (hydrogen acceptor conditions). Hence ν_2 = 3(n-1), where n = the number of replicate experiments, yet to be selected.

4. Determine the sample size n, sufficiently large to insure that the null hypothesis $\mu_1 = \mu_2$ will be rejected at the five percent significance level (α = .05). Since rejection of the null hypothesis cannot be absolutely guaranteed, the desired probability (P') of obtaining a significant result if the true difference is δ must also be specified (Snedecor and Cochran, 1967; Li, 1964).[30]

For n replications, the detectable difference is given by

$$\delta = E \left[\frac{2(\nu_2 + 1)(s_1)^2}{n} \right]^{\frac{1}{2}} \tag{28}$$

where E is a Table 13a or 13b entry (Li, 1964) corresponding to ν_1 and ν_2. Calculated values of δ for n = 1 to 5, and P' = 0.80 and 0.95 are presented in Table XVI.

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30. The observed mean difference $\bar{D} = \bar{k}_1 - \bar{k}_2$ is normally distributed about $\delta = \mu_1 - \mu_2$ with a standard deviation $\sigma_D/\sqrt{n}$, where σ_D is the standard deviation of the paired differences. P' is the probability that $\bar{D}$ exceeds $Z_\alpha \sigma_D/\sqrt{n}$, if the true difference in population means is δ, where Z_α is the normal deviate corresponding to the two tailed significance level α.

TABLE XVI. δ VALUES AS A FUNCTION OF REPLICATES (α=.05)

Replicates	ν_2 (3)(n-1)	δ P' = .95	P' = .80
1	0	–	–
2	3	0.0037	0.0025
3	6	0.0025	0.0017
4	9	0.0021	0.0014
5	12	0.0018	0.0014
6	15	0.0016	0.0012
7	18	0.0015	0.0010

Table XVI values indicate that:

1. The hypothesis $\mu_1 = \mu_2$ will be rejected 80 percent of the time if δ is 0.0017, provided n=3.

2. The hypothesis $\mu_1 = \mu_2$ will be rejected 95 percent of the time if δ is 0.0025, provided n=3.

Thus the performance of three replicate experiments satisfies the criterion that populations having mean k-value differences of 0.002 be detected. The selection of three replicates insures that if the true difference is δ = 0.002, the null hypotheses will be rejected approximately 86 percent of the time (linear interpolation of Table XVI). Selection of n=3 also ensures that 16 percent differences (δ =0.0025) in populations with mean k-values near 0.0156 ($k_{surface}$, preliminary experiment) will be detected 95 percent of the time.

Final Laboratory Experiments

The final laboratory experiments consisted of a series of three short-term experiments[31] using sludge which was again obtained from the Bay Park Water Pollution Control Plant. Due to temporary inoperation of the marine barge holding tanks, however, the sludge was withdrawn directly from an anaerobic digester. Although the percent total solids was comparable to the sludge used in the preliminary experiments, the total and organic carbon contents were somewhat higher (Table XVII). After sea water settling, organic carbon represented 98 to 99 percent of the carbon present. Sea water with a salinity of 33.36 parts per thousand was obtained from the same Depoe Bay ocean inlet and directly stored in tanks at the EPA Environmental Research Laboratory.

For each of the three replicate experiments, two acrylic reactors were filled to form 3.0 centimeter deep sludge deposits. One reactor was placed into the Deep Sea Simulator, which then was filled and pressurized. Aerated sea water from isolated tanks was pumped over the deposits at approximately 1.5 cm/sec. Sampling intervals were initially two days but were increased to between three and four days by the experiment conclusion. This schedule resulted in approximately eight sampling events during each experiment. When flows were interrupted to facilitate sampling, each sea water reservoir was drained and refilled.

To insure repeated sampling at preselected deposit depths, a slotted plastic guide was used which allowed vertical insertion of a

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31. Tsivoglou Method of curve fitting (Appendix D) permits the determination of k-values without prior knowledge of the initial biodegradable (C_0) or residual (C_r) particulate organic carbon concentrations. In the absence of such a procedure, the series of experiments would necessarily have been six to twelve months each, to determine C_r and thus be able to calculate the associated k according to equation (15).

TABLE XVII.   CARBON AND SOLIDS CONTENT OF SLUDGE USED
IN FINAL LABORATORY EXPERIMENTS

PARAMETER	AS RECEIVED	AFTER SEA WATER SETTLING
TOTAL SOLIDS (mg/l) (% by wt.)	16570-18160 1.6-1.7	47655-52530 4.6-5.1
VOLATILE SOLIDS (mg/l) (% TS)	10525-11380 63-64	14570-17880 31-34
TOTAL CARBON (mg/l) (% TS)	no data	6255-7265 13-14
ORGANIC CARBON (mg/l) (% TC)	no data	6133-7175 98-99
BULK DENSITY (g/ml)	1.007-1.011	1.029-1.030

syringe to the required depth, and horizontal movement over a predefined horizontal area. Each deposit was divided into ten equal randomly numbered segments by scribing vertical lines on the front and rear reactor walls. Each deposit segment was sampled no more than once at the surface and at 3.0 centimeters deep during any one of the 21-day experiments.

The only other deviation from preliminary experiment procedures was to sift particles smaller than 90 microns in diameter from the sand placed beneath the deposited sludge. A one-centimeter bed of sand was enclosed in a 60 micron Nitex monofiliment nylon screen,

selected for its relatively high (45%) open area.[32] This procedure permitted withdrawal of sludge samples in the proximity of the sand/ sludge interface, without simultaneous withdrawal of sand particles.

All replicate experiments were performed at $23^{\circ}C$ to isolate temperature dependent effects and to permit correlation with the previously completed long-term experiments.

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32. TETKO Inc. Cat. No. HC-3-60, New York, N.Y.

RESULTS AND DATA ANALYSIS

Surface and 3.0 Centimeter Organic Carbon Changes

The particulate organic carbon decreases which occurred at the sludge deposit surfaces and at 3.0 centimeters in the three replicate experiments are presented in Figures 14, 15 and 16 for the one atmosphere condition and in Figures 17, 18 and 19 for a hydrostatic pressure of 34 atmospheres.

Table XVII summarizes the degradation rate constants (K) and residual particulate organic carbon concentrations (C_r) calculated using the Tsivoglou Method (Appendix D).

Indicated in the plots and in Table XVIII is an _apparent_ retardation of the organic carbon depletion for anaerobic conditions. Not readily apparent are effects due to elevated pressure or interacting pressure/hydrogen-acceptor zone effects. The following variance analysis of sampled K-values was performed to statistically establish the significance of zonal effects, pressure effects, or interactive effects due to both factors.

Variance Analysis of Sampled K-Values

The tested hypotheses are:

H1: $\mu_{1\text{-atmosphere}} = \mu_{34 \text{ atmosphere}}$ (Factor A)

H2: $\mu_{\text{aerobic}} = \mu_{\text{anaerobic-exogenous}}$ (Factor B)

Assumptions made in testing the hypotheses include:
1. The K-values are based on random sampling
2. The sampled populations have the same variance
3. The sampled populations are normal
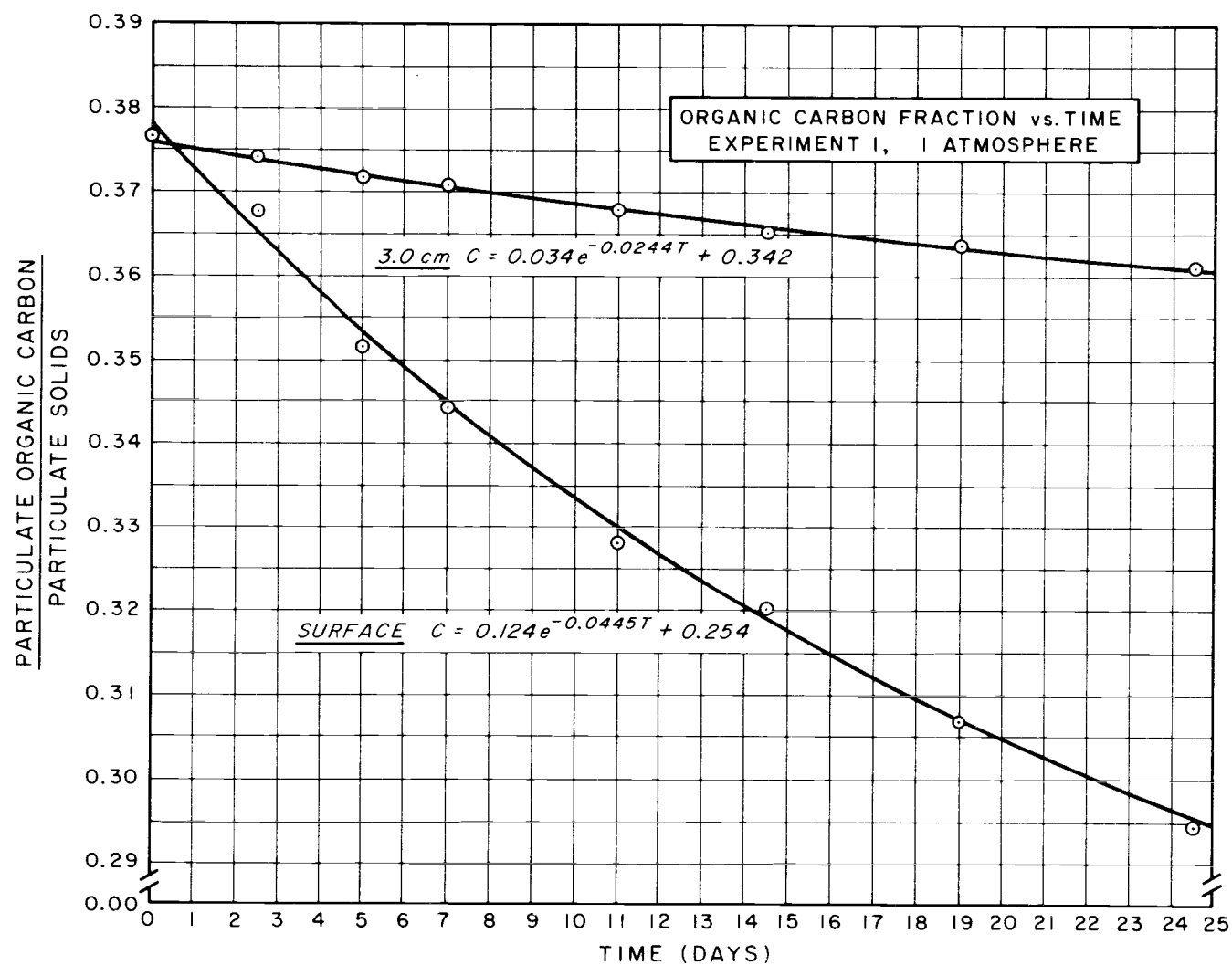
Figure 14.   Particulate Organic Carbon, Experiment 1, 1 Atmosphere
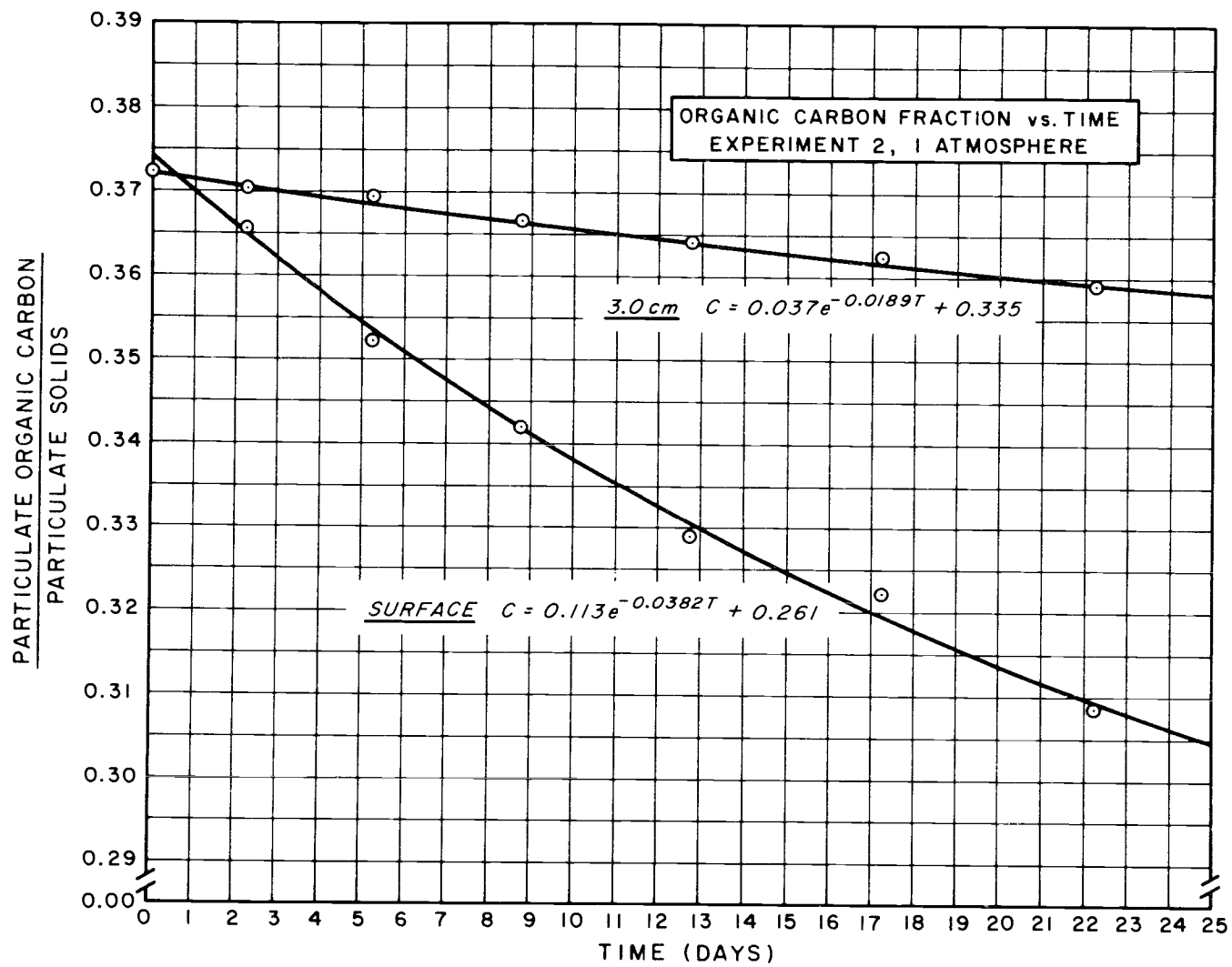
Figure 15.   Particulate Organic Carbon, Experiment 2, 1 Atmosphere
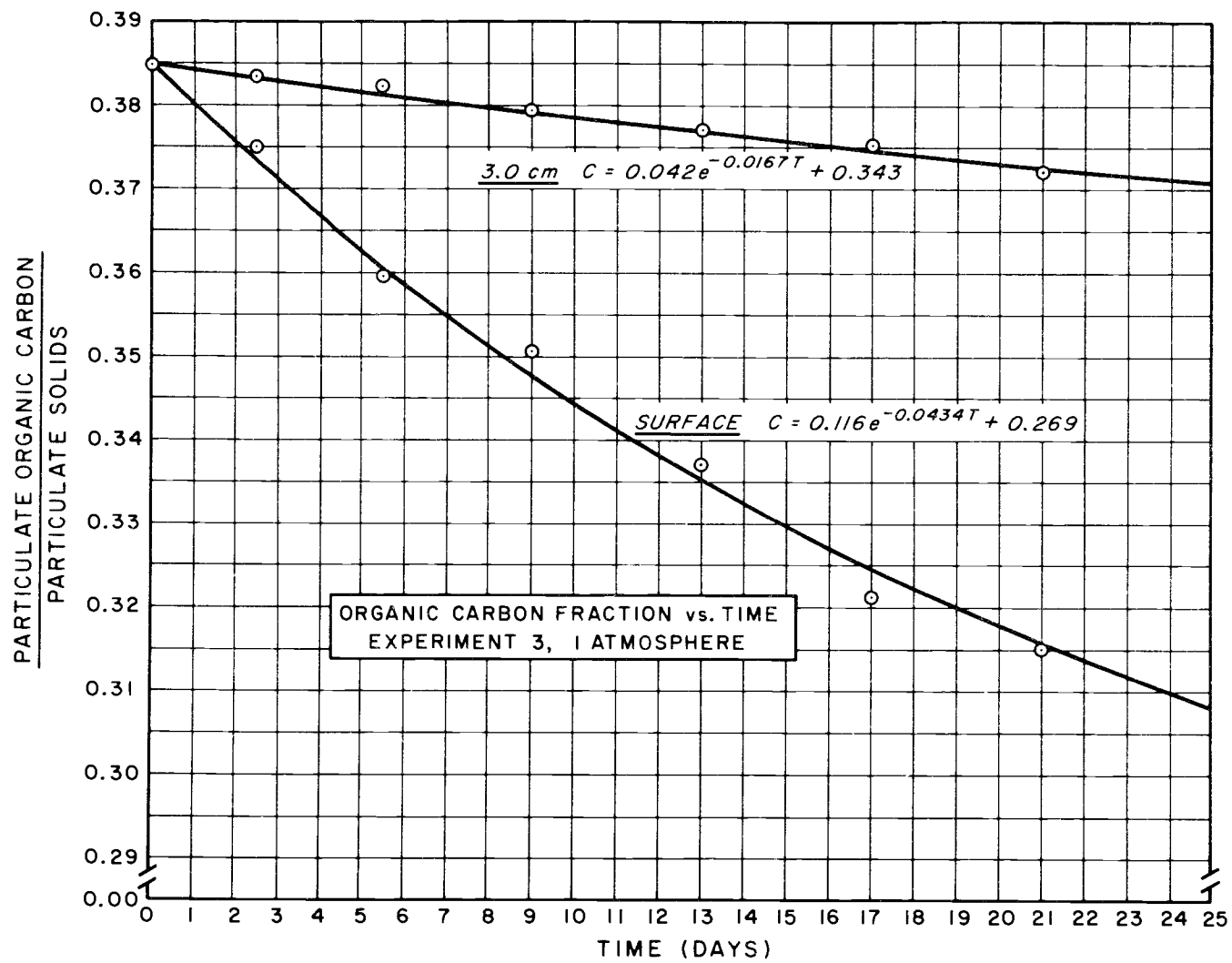
Figure 16.   Particulate Organic Carbon, Experiment 3, 1 Atmosphere
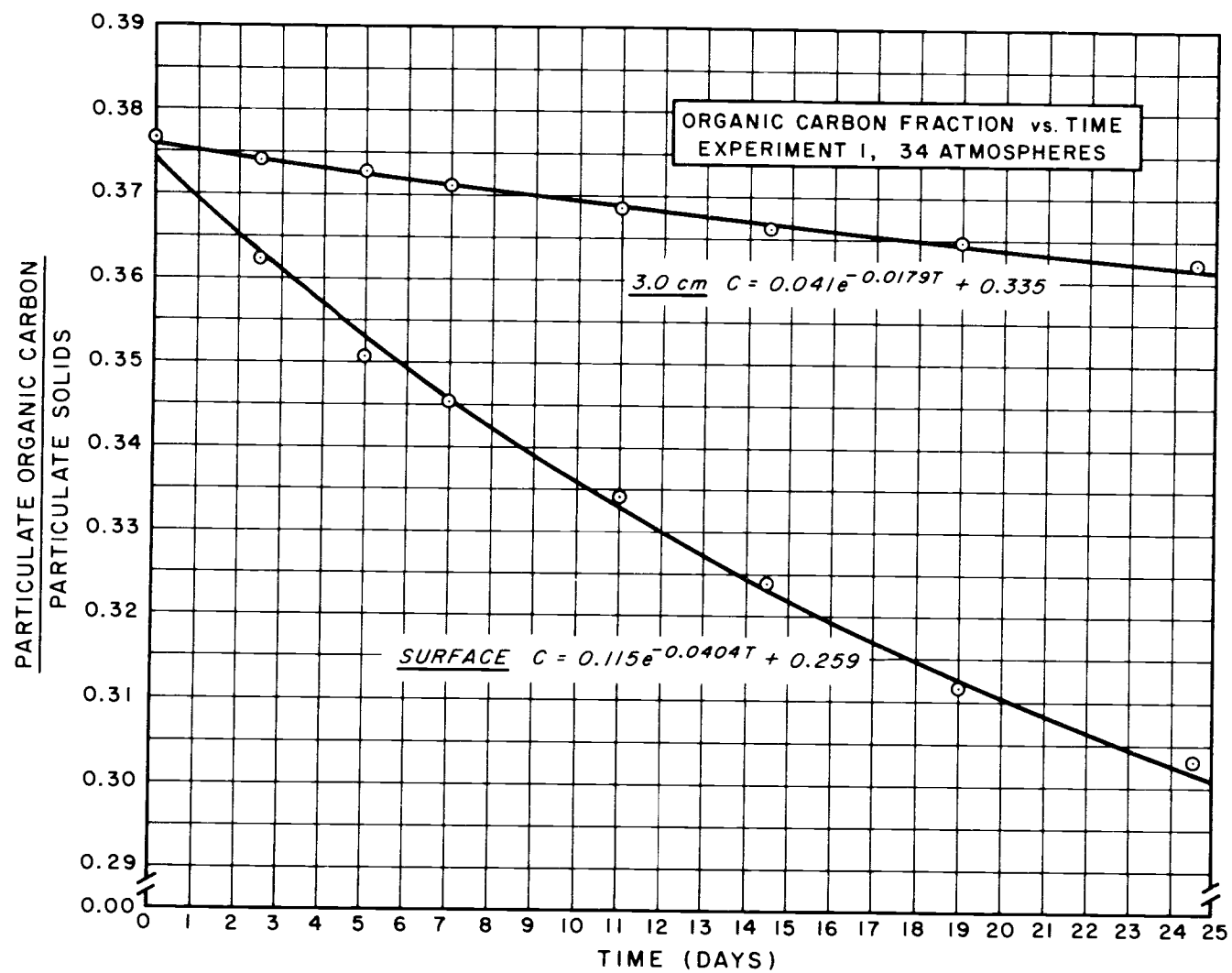
Figure 17.   Particulate Organic Carbon, Experiment 1, 34 Atmospheres
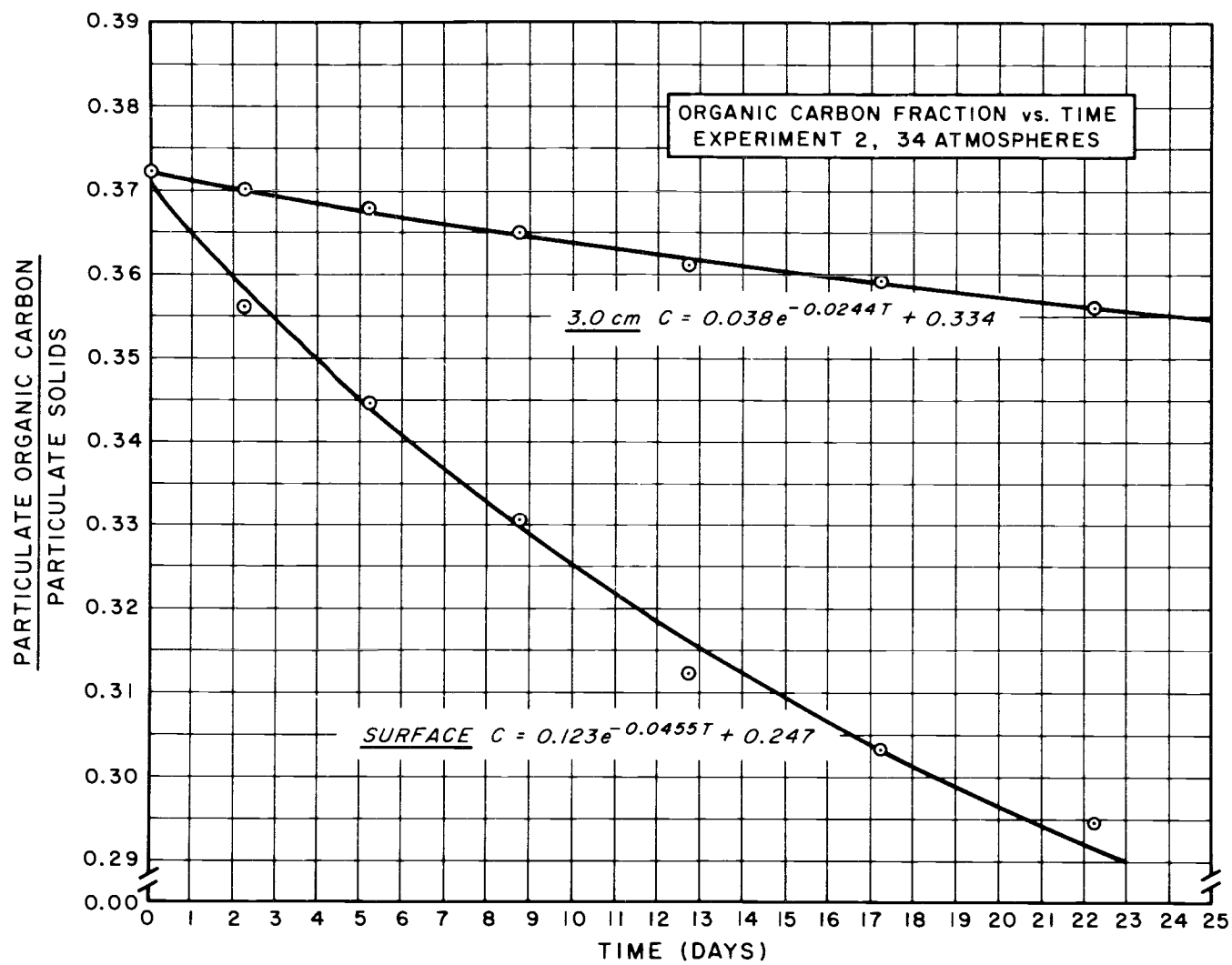
Figure 18. Particulate Organic Carbon, Experiment 2, 34 Atmospheres
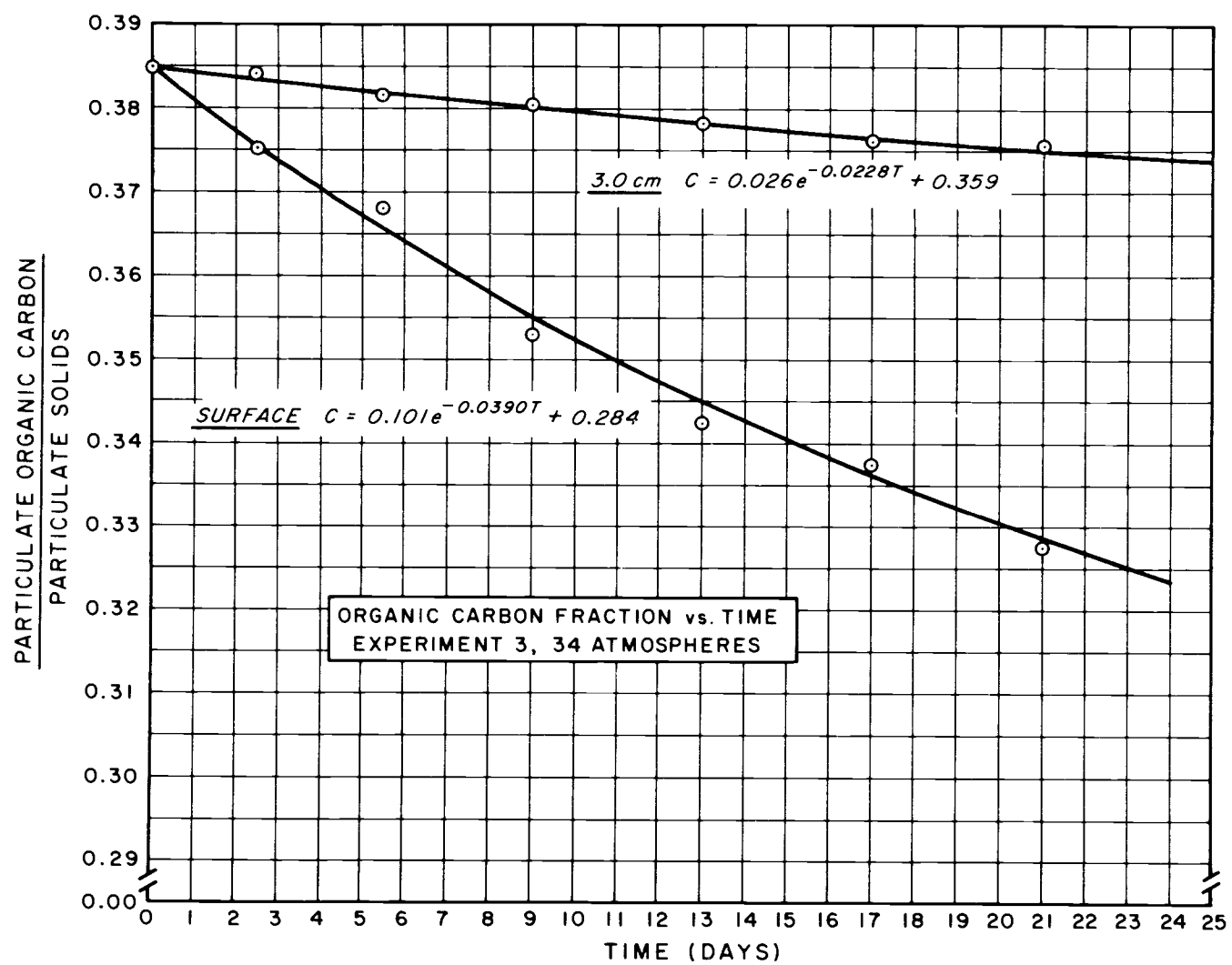
Figure 19.   Particulate Organic Carbon, Experiment 3, 34 Atmospheres

TABLE XVIII.   EQUATION CONSTANTS FOR ORGANIC
CARBON FRACTION VS. TIME

Condition	C_o mg-C/mg-S	C_r mg-C/mg-S	K day^{-1}
One Atmosphere Surface	0.124 0.113 0.116	0.254 0.261 0.269	-0.0445 -0.0382 -0.0434
One Atmosphere 3.0 cm	0.034 0.037 0.042	0.342 0.335 0.343	-0.0244 -0.0189 -0.0167
34 Atmospheres Surface	0.115 0.123 0.101	0.259 0.247 0.284	-0.0404 -0.0455 -0.0390
34 Atmospheres 3.0 cm	0.041 0.038 0.026	0.335 0.334 0.359	-0.0179 -0.0244 -0.0228

The initial step in the analysis is to compute factor A (hydro-static pressure), factor B (hydrogen acceptor), treatment and replicate totals (Table XIX).

TABLE XIX.   TOTALS FOR A RANDOMIZED BLOCK 2X2
FACTORIAL EXPERIMENT

PRESSURE A ZONE B	1 ATMOSPHERE	34 ATMOSPHERE	TOTAL
AEROBIC	-0.0445 -0.0382 -0.0434 $\overline{-0.1261}$ = T_{t1}	-0.0404 -0.0455 -0.0390 $\overline{-0.1249}$ = T_{t2}	-0.2510 = T_{b1}
ANAEROBIC EXOGENOUS	-0.0244 -0.0189 -0.0167 $\overline{-0.0600}$ = T_{t3}	-0.0179 -0.0244 -0.0228 $\overline{-0.0651}$ = T_{t4}	-0.1251 = T_{b2}
TOTAL	-0.1861 = T_{a1}	-0.1900 = T_{a2}	-0.3761 = G

where T_a = the total of nb observations belonging to treatment level A.

T_b = the total of na observations belonging to treatment level B.

T_t = the total of n observations belonging to a particular treat-ment combination.

G = the grand total of all twelve observations.

a = two hydrostatic pressures.

b = two hydrogen acceptor zones.

In addition, the replicate totals (T_r) are required, i.e. the totals of ab observations belonging to each replicate experiment. These are:

T_{r1} = -0.1272

T_{r2} = -0.1270

T_{r3} = -0.1219

Table XX presents the general computational method for analysis of variance of a randomized block factorial experiment, indicating the method of calculating F-values for Factors A, B and AB interaction. Table XXI presents the actual preliminary calculations and analysis of variance.

TABLE XX. COMPUTING METHOD FOR ANALYSIS OF VARIANCE
OF A RANDOMIZED-BLOCK FACTORIAL EXPERIMENT

PRELIMINARY CALCULATIONS				
(1)	(2)	(3)	(4)	(5)
Type of Total	Total of Squares	No. of Items Squared	Observations Per Squared Item	Total of Squares Per Observation
Grand	G^2	1	nab	I
Replication	T_r^2	n	ab	II
Factor A	T_a^2	a	nb	III
Factor B	T_b^2	b	na	IV
Treatment	T_t^2	ab	n	V
Observation	y^2	nab	1	VI

ANALYSIS OF VARIANCE				
(6)	(7)	(8)	(9)	(10)
Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square (7)÷(8)	F (9)÷Error Mean Square
Replication	II-I	n-1		
Factor A	III-I	a-1		
Factor B	IV-I	b-1		
AB Interaction	I-III-IV+V	(a-1)(b-1)		
Error	VI-V	(ab-1)(n-1)		
Total	VI-V	nab-1		

TABLE XXI.   PRELIMINARY CALCULATIONS AND VARIANCE ANALYSIS

PRELIMINARY CALCULATIONS				
Type of Total	Total of Squares	No. of Items Squared	Observations Per Squared Item	Totals of Squares Per Observation (2) ÷ (4)
Grand	0.1414500	1	12	0.0117875
Replication	0.0471684	3	4	0.0117921
Factor A	0.0707332	2	6	0.0117889
Factor B	0.0786510	2	6	0.0131085
Treatment	0.0393392	4	3	0.0131131
Observation	0.0132135	12	1	0.0132135

ANALYSIS OF VARIANCE				
Source of Variation	Sum of Squares	Degree of Freedom	Mean Square	F
Replication	0.0000046	2	0.0000023	
Factor A	0.0000014	1	0.0000014	0.08383
Factor B	0.0013210	1	0.0013210	7.91020
AB Interaction	0.0000032	1	0.0000032	0.19162
Error	0.0001004	6	0.0000167	
Total	0.0014260	11		

The critical region for one and six degrees of freedom at the five percent significance level is where F > 5.9874. Since the F-value for Factor A (0.08) is not within the critical region, H1 is accepted as true, i.e. the biochemical degradation rate at 34-atmospheres is not significantly different than at one atmosphere. The Factor B F-value (7.91) does fall within the critical region, causing rejection of H2, i.e. there is a significant effect of hydrogen-acceptor type on the biochemical degradation rate. Interactive effects were insignificant as evidenced by an F-interaction (0.19) which is not in the critical region.

DISCUSSION OF FINDINGS

Data from laboratory experiments with domestic sludge deposits exposed to benthic marine conditions indicate a retardation in the bio-chemical degradation rate for anaerobic conditions, but no significant effect due to 34 atmospheres hydrostatic pressure.

Aerobic depletion of particulate organic carbon (Figure 20) was relatively rapid, amounting to between 14 and 19 percent in 20 days. The 20-day depletion in a preliminary long-term experiment was 15.8 percent. At 120 days, the aerobic biochemical degradation rate had slowed considerably, and depletion amounted to 30.6 percent of the original particulate organic carbon. The refractory particulate or-ganic carbon concentration was 0.21 mg-C/mg-solid.

Anaerobic decreases in particulate organic carbon (Figure 21) were much smaller, amounting to between 2.5 and 4.0 percent in 20 days. The maximum anaerobic degradation measured was 7.0 percent in 130 days. Due to continuing anaerobic breakdown after long periods of time, the magnitude of the refractory component could not be experimentally determined. Residuals estimated by curve fitting ranged from 0.25 to 0.28 mg-C/mg-solid.

The 11.5 to 15 percent greater depletion of particulate organic carbon in the aerobic zone than in the anaerobic zone (Figures 22 and 23) is statistically significant. Aerobic particulate organic carbon depletions were 5.9 to 7.8 times as large as the estimated standard de-viation in organic carbon-solids ratio for 20 days of exposure, and ten times as large for 170 days of exposure. Anaerobic depletion values for 20 days were 1.0 to 1.6 times the estimated carbon-solids ratio standard deviation. The similarity in the 20-day anaerobic depletions of the short-term and long-term experiments and a long-term anaerobic depletion greater than two estimated standard deviations increase the confidence in the anaerobic data.

Repetitive curve fitting to each set of data points according to the Tsivoglou method indicated that calculating errors in k, C_o and
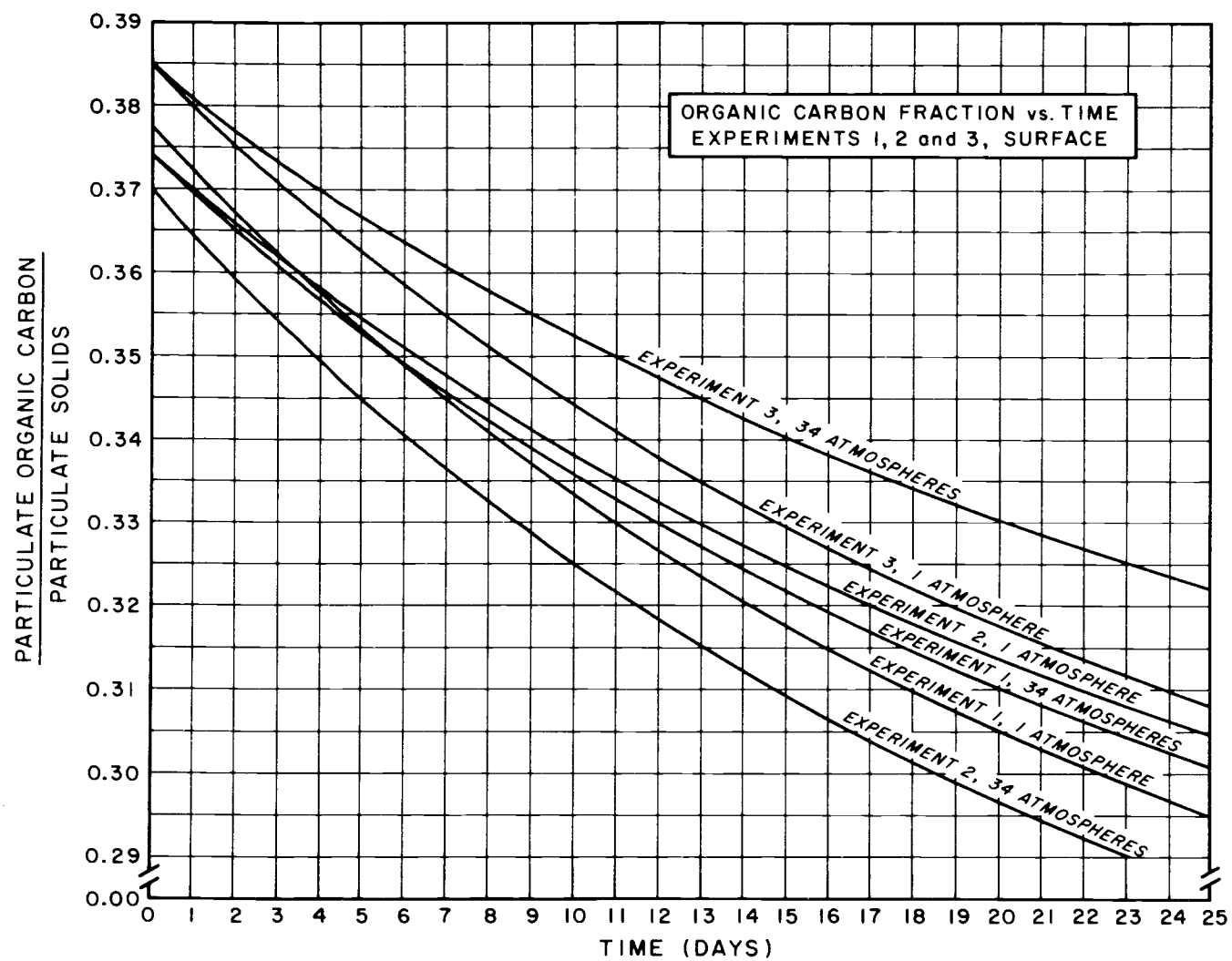
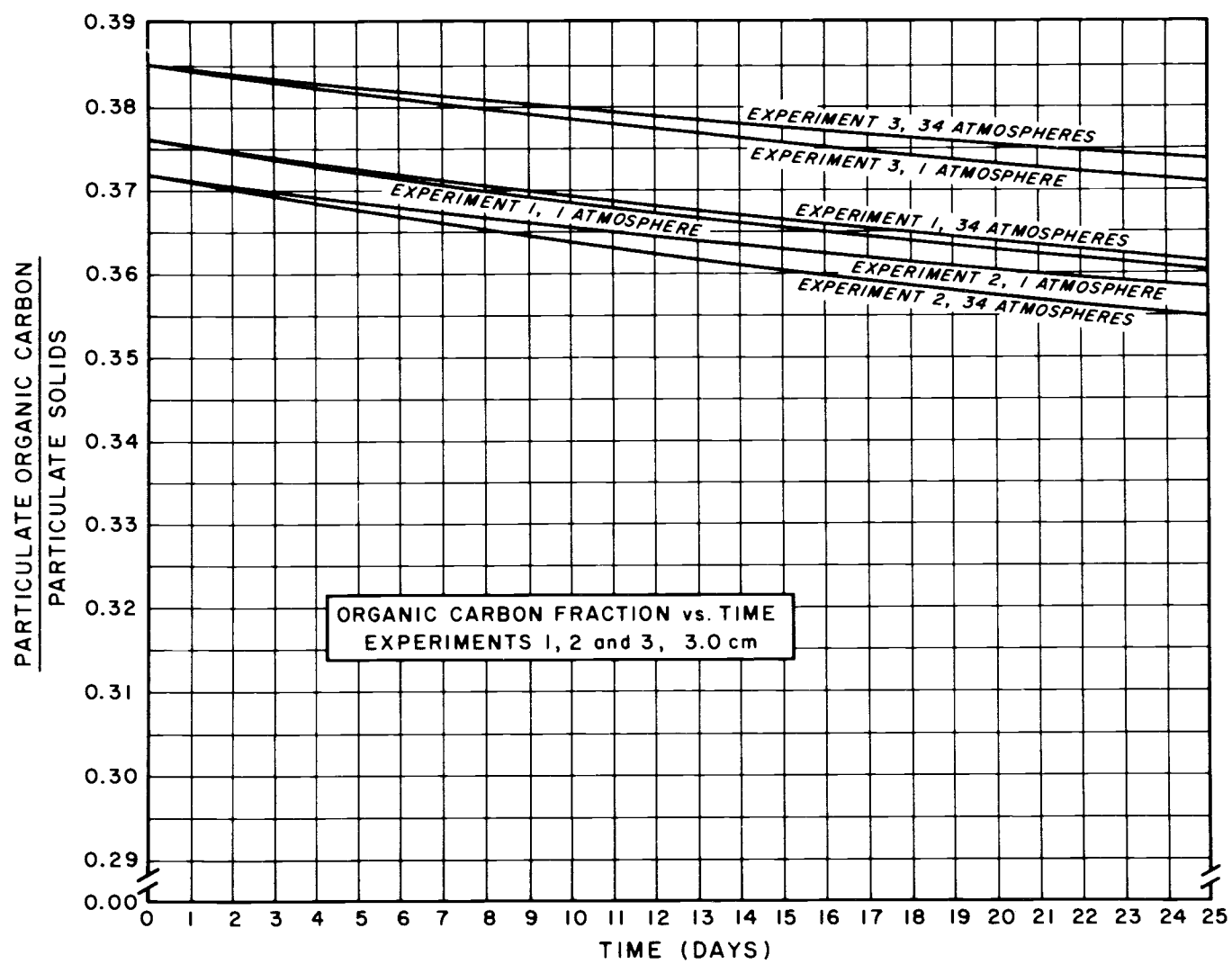Figure 20.   Aerobic Zone Particulate Organic Carbon Concentrations

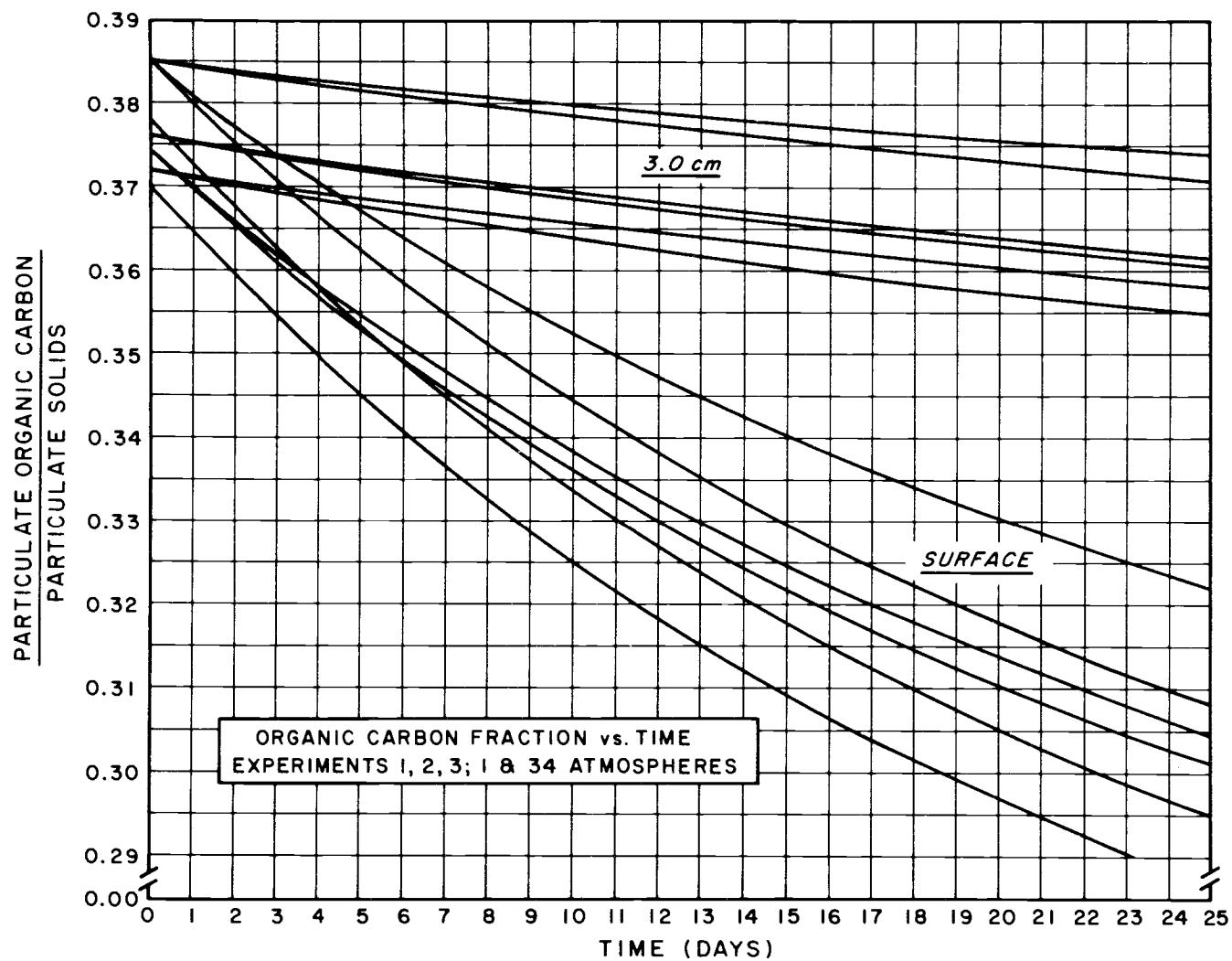Figure 21. Anaerobic-Exogenous Zone Particulate Organic Carbon Concentrations

Figure 22. Particulate Organic Carbon Concentrations in Aerobic and Anaerobic-Exogenous Zones
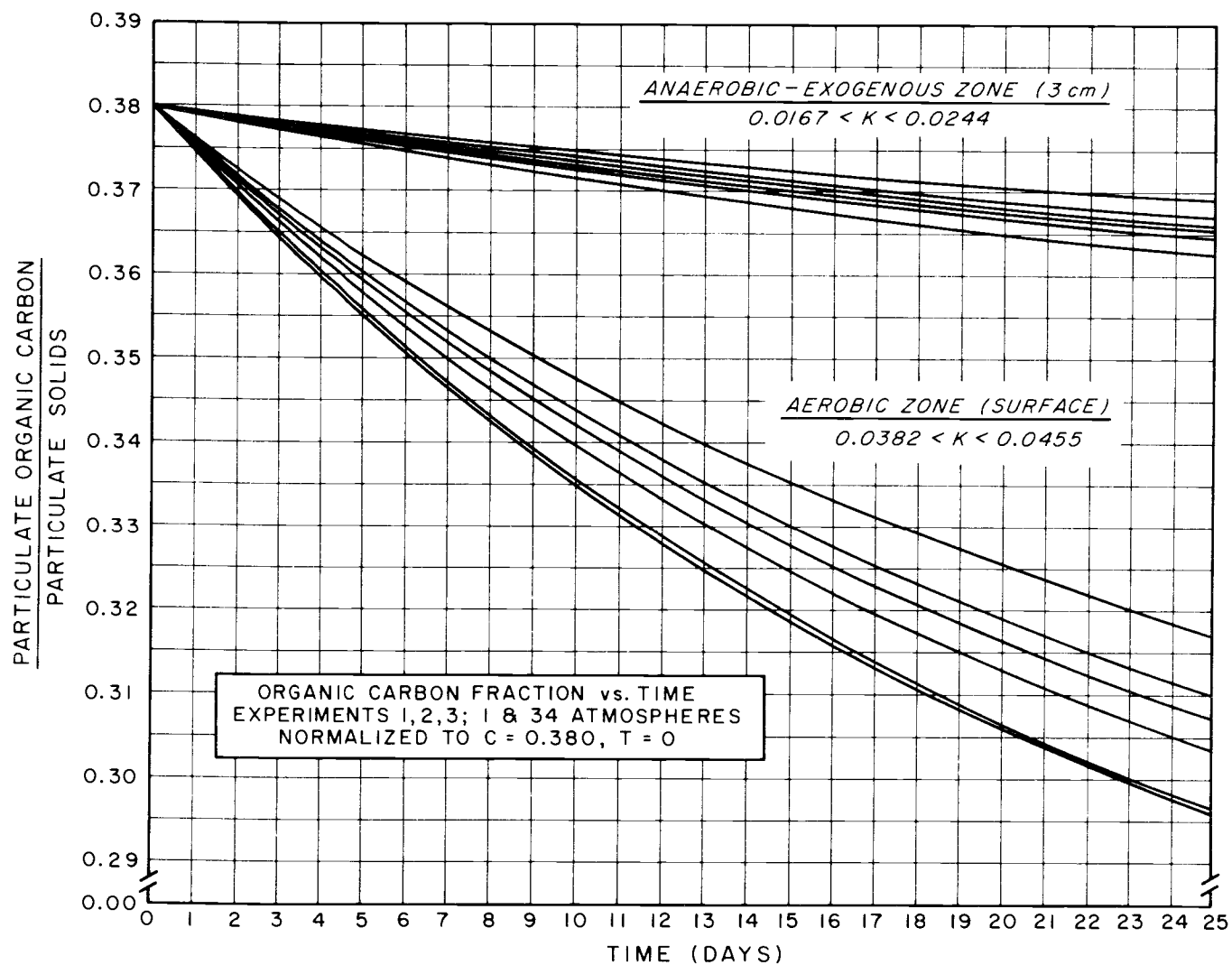
Figure 23.   Normalized Particulate Organic Carbon Concentrations
in Aerobic and Anaerobic-Exogenous Zones

C_r were insignificantly small. The major sources of error are considered to be due to analytical procedures. Since measured changes in the particulate organic carbon-solids ratio (relative to the estimated standard deviation in this ratio) were large, the author concludes that the data realistically depict both the extent of deposit stabilization, and the difference in aerobic and anaerobic rates.

The effects of 34 atmospheres of hydrostatic pressure are neither graphically evident (Figures 20 and 21) nor statistically significant. The variance analysis also shows that interactive hydrostatic pressure/hydrogen-acceptor-type effects are not significant.

Degradation rate constants presented by previous investigations (Table XXII) for sludge-clay mixtures (Fair et al., 1941) and for river muds (McGowan et al., 1913) are smaller than those reported herein. However, reported rate constants for settled sludges (Rudolfs, 1938; Mohlman, 1938) approach the anaerobic rate constants determined in this investigation. Also, the lower limit of an aerobic oxidation rate constant for thin layers of wastewater particulates (Myers, 1974) approaches the aerobic rate constants determined in this research.

TABLE XXII. DEGRADATION RATE CONSTANTS ASSOCIATED WITH DOMESTIC SLUDGES, SEWAGE PARTICULATES AND RIVER MUDS

MARINE	K^a (day^{-1})	k^b (day^{-1})	$\frac{Cr}{Co+Cr}$ %	T (days)	°C
MUELLENHOFF (1976) Sludge Deposit					
Aerobic					
1 Atmosphere	0.0420	0.0182	68.9	20	23
34 Atmospheres	0.0416	0.0180	69.9	20	23
34 Atmospheres	0.0360	0.0156	69.2	170	23
Anaerobic					
1 Atmosphere	0.0200	0.0087	89.9	20	23
34 Atmospheres	0.0217	0.0094	90.7	20	23
34 Atmospheres	0.0150	0.0065	91.7	130	23
MEYERS (1974) Filter Pads					
Upper Limit, all experiments	0.2200	0.0955	60.0	78	17
Lower Limit, all experiments	0.0500	0.0217	70.0	78	17
Note: k values calculated on the basis of T=0 slope of dC/dt for an assumed C_r = 0.77					
NON-MARINE					
BALMAT (1957)					
Aerobic biochemical Raw	0.5000	0.2200	–	5	20
oxidation of sewage Settleable	0.1840	0.0800	–	5	20
particulate fractions Soluble	0.8980	0.3900	–	5	20
(mixed) Colloidal	0.5060	0.2200	–	5	20
Supracolloidal	0.2070	0.0900	–	5	20
FAIR et al. (1941) Sludge-clay					
D = 1.42 cm Mixture	0.0102	0.0044	45.7	450	20-25
D = 1.42 cm Deposit	0.0087	0.0038	46.3	450	20-25
D = 2.55 cm	0.0103	0.0045	49.1	450	20-25
D = 4.75 cm	0.0101	0.0044	53.6	450	20-25
D = 10.2 cm	0.0067	0.0029	63.6	450	20-25
RUDOLFS (1938) Settled Sludge					
Calculated by Fair et al.	0.0105	0.0046	19.8	401	20
MOHLMAN (1938) Settled Sludge					
Calculated by Fair et al.	0.0122	0.0053	25.3	700	20
MCGOWAN et al. (1913)					
English river muds D = 0.5 cm	0.0043	0.0019	–	700	18
D = 0.7 cm	0.0040	0.0017	–	700	18
D = 1.2 cm	0.0027	0.0012	–	700	18
D = 1.4 cm	0.0015	0.0007	–	700	18
D = 1.7 cm	0.0053	0.0023	–	700	18

a = base e
b = base 10

Because the aerobic zone of a highly organic sludge deposit is limited to a few millimeters in depth, the anaerobic biochemical degradation rate will have the most pronounced effect on the overall deposit stabilization rate in all but very shallow deposits. This can be demonstrated using a form of equation (19).

$$\Delta M_{aerobic} = C_{01} S_{01} V_{01} - C_{01} 10^{-k_1 t} S_{11} V_{11} \qquad (29)$$

$$\Delta M_{anaerobic} = C_{02} S_{02} V_{02} - C_{02} 10^{-k_2 t} S_{12} V_{12} \qquad (30)$$

where ΔM = the change in the zonal particulate organic carbon mass due to biochemical degradation (mg)

C_{01}, C_{02} = the initial particulate organic carbon concentrations in the aerobic and anaerobic zones (mg-C/mg-solid)

S_{01}, S_{02} = the initial particulate solids concentrations in the aerobic and anaerobic zones (mg-solid/volume)

S_{11}, S_{12} = the particulate solids concentrations in the aerobic and anaerobic zones at time t (mg-solid/volume)

V_{01}, V_{02} = the initial aerobic and anaerobic zone volumes (volume)

V_{11}, V_{12} = the aerobic and anaerobic volumes at time t (volume)

k_1, k_2 = the aerobic and anaerobic particulate organic carbon degradation rate constants (day^{-1})

Substituting into equations (29) and (30) gives

$$\Delta M_{aerobic} = 271.6 \text{ mg} \qquad (31)$$

$$\Delta M_{anaerobic} = 1072.6 \text{ mg} \qquad (32)$$

where (data from one of the laboratory experiments)

$$C_{01} = 0.124 \text{ mg-C/mg-solid}$$

$$C_{02} = 0.034 \text{ mg-C/mg-solid}$$

$$k_1 = 0.0445 \text{ day}^{-1}$$

$$k_2 = 0.0244 \text{ day}^{-1}$$

$$S_{01}, S_{02} = 18767 \text{ mg/l}$$

$$S_{11} = 7747 \text{ mg/l}$$

$$S_{12} = 32837 \text{ mg/l}$$

$$V_{01}, V_{11} = 0.186 \text{ liters}$$

$$V_{02} = 3.16 \text{ liters}$$

$$V_{12} = 2.60 \text{ liters}$$

Thus, the extent of particulate organic carbon mass depletion in the anaerobic zone was approximately four times as great as in the aerobic zone even though the aerobic degradation rate constant was almost double the anaerobic degradation rate constant. The difference is primarily due to an anaerobic zone which was 15 times as great as the aerobic zone in the 3.0 centimeter deep deposit.

CONCLUSIONS

1. Anaerobic biochemical depletion of particulate organic carbon occurred at significantly slower rates than aerobic depletion in laboratory marine sludge deposits at hydrostatic pressures of 1 and 34 atmospheres. Zonal differences in biochemical degradation rates caused the 120-day particulate organic carbon concentration of a 34 atmosphere sludge deposit to be 30 percent higher in the anaerobic zone than the concentration in the aerobic zone.

2. The extent of aerobic depletion of particulate organic carbon was 14 to 19 percent of the original concentration in 20 days and 30.6 percent in 120 days. By 120 days, aerobic biochemical degradation had slowed considerably indicating a 0.21 mg-C/mg-solid refractory particulate organic carbon concentration. The average aerobic biochemical degradation rate constant for all experiments is 0.042 day^{-1} (base e).

3. Anaerobic decreases in particulate organic carbon amounted to between 2.5 and 4.0 percent in 20 days and 7.0 percent in 130 days. Although graphical determination of the anaerobic residual was not possible because of continuing degradation at 130 days, calculated anaerobic residuals ranged from 0.25 to 0.28 mg-C/mg-solid. The average anaerobic biochemical degradation rate constant for all experiments is 0.024 day^{-1} (base e).

4. The effects of 34 atmospheres of hydrostatic pressure on aerobic and anaerobic stabilization rates were neither graphically evident nor statistically significant. Also, interactive hydrostatic-pressure/hydrogen-acceptor-type effects were not significant.

5. The extent of the aerobic zone in a highly organic marine sludge deposit was one to two millimeters. The anaerobic-exogenous

zone (dissolved sulfate hydrogen acceptor) extended from a few milli-
meters to approximately 16 centimeters in a 33 centimeter deep deposit
(at one atmosphere) where the concentration was ten percent (225 mg/1)
of the surface concentration. Concentrations of dissolved sulfate de-
creased to 3.8 percent (80 mg/1) of the surface concentration at -31.5
centimeters. Hydrogen sulfide concentrations reached over 500 mg/1 at
the 16 centimeter depth in the 33 centimeter deep deposit in 180 days.
Dissolved sulfide did not accumulate in deposits of 2.0 to 3.0 centi-
meters, reaching a maximum concentration of 20 mg/1.

6. Although the aerobic degradation rate constants were lar-
ger than anaerobic rate constants, deposit particulate organic carbon
mass depletion was primarily due to depletion in the anaerobic zone
since this zone was typically 15 times as large as the aerobic zone
in a 3.0 centimeter deep deposit.

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APPENDICES

APPENDIX A

Arrhenius Equation

The equation relating a temperature dependence of a chemical reaction rate constant as proposed by Arrhenius in 1889 is:

$$\frac{d(\ln K)}{dt} = \frac{E_a}{RT^2} \tag{33}$$

where
K = the chemical reaction rate constant
E_a = the reaction activation energy
R = the universal gas constant
T = the temperature (degrees Kelvin)

Integrating gives

$$\ln K_2 - \ln K_1 = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{34}$$

or, rewriting

$$\ln K_2 - \ln K_1 = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \tag{35}$$

Since the term $T_1 T_2$ is very large, it is essentially constant over small temperature ranges. Thus, collecting constants gives

$$\ln \frac{K_2}{K_1} = \left(\frac{E_a}{RT_1 T_2}\right)(T_2 - T_1) \tag{36}$$

$$\frac{K_2}{K_1} = e^{A(T_2 - T_1)} = \theta^{(T_2 - T_1)} \tag{37}$$

$$A = E_a/RT_1 T_2, \quad \theta = e^A \tag{38}$$

Since $\Delta T(^oC) = \Delta T(^oK)$, many authors use Celcius temperatures when calculating relative chemical reaction rate constants. Implicit in θ, however, is the multiplication of T_1 and T_2 in degrees Kelvin.

APPENDIX B

Deep Sea Simulator Design Characteristics

A U.S. Navy 406 millimeter high capacity MK-13 MOD2 projectile was converted to provide the pressure vessel. The projectile is made of a chromium-nickel-molybdenum alloy steel with a tensile strength of 105,000 psi, proof stress of 78,000 psi and ductility of 18%. After removal of the copper rotating band near the base end, the 861 kilo- gram projectile was mounted in a lathe for surfacing of the base plug seat and removal of the tapered surface at the nose end. A redesigned stainless steel nose plug was fitted into the tapered end of the pro- jectile after O-ring grooves were cut into the base plug flange. Three threaded holes in the base plug were sealed with stainless steel (flanged O-ring groove) fittings to permit sea water entrance and exit, mounting of a thermocouple, and to allow for a sludge sampling port. The penetrators thread into the base plug from the interior.

To avoid any weakening of the 7.6 centimeter walls of the pres- sure vessel, a collar was heat shrunk into the shell body. Two bearing shafts were welded to the collar and the unit was mounted on a strengthened electronics rack. The vessel can be rotated to permit horizontal or vertical operation (e.g. static equipment tests or flowing water experiments as described). The problem of maneuvering the 46.7 kilogram base plug during closure of the vessel was solved by connecting an identical base plug to the first as a counterweight and lifting the assembly at a balance point. The hoist shackle was attached to a bearing on the connecting shaft to permit threading of the base plug into the pressure vessel.

To prevent rusting, the vessel interior was coated with Carbo- mastic 14 followed by Carboline 191 (Carboline Corp., St. Louis, Mis- souri). No deterioration of this coating has occurred on the interior walls in three years. The inside of the base plug has had some flaking, probably due to improper application of the coating in the large number of crevices and accumulation of corrosion products. An

attempt to coat the base plug threads proved unsuccessful because of chipping and lack of sufficient clearance between threads on the plug and vessel. Heavy coating of the threads with silicone grease and routine cleaning have eliminated rusting and seizure.

An SC Hydraulic Engineering (MOD 10-500-8) pump was obtained at a state surplus facility and returned to the manufacturer for replacement of the bronze barrel and piston with stainless steel components. The pump has operated continuously requiring only the daily addition of a high grade silicone oil to the incoming air oiler. The synflex high pressure hoses (Samuel Moore and Co., Mantua, Ohio), made to order, have shown no deterioration. All high pressure valves (Autoclave Engineers, Anaheim, California, and High Pressure Equipment Company, Erie, Pennsylvania) are rated to 30,000 psi. Previous tests on 406 millimeter projectiles (Civil Engineering Laboratory, Port Hueneme) have been successfully performed to 20,000 psi. The stated maximum operating pressure vessel for the Deep Sea Simulator is 10,000 psi. To minimize the pressure pulse caused by the piston pump, a polyvinyl-chloride pipe was sealed at both ends, equipped with inlet and exit ports, and placed between the pump and pressure vessel. The accumulator air cushion decreased the pulse fluctuation from 10 psi to less than 1 psi.

Information on availability of surplus 406 millimeter projectiles for research purposes can be obtained from

> Commanding Officer
> Navy Ships Parts Control Center
> (7321)
> Mechanicsburg, PA   17055
> ATTN: Mr. O. Waggoner

APPENDIX C

Preliminary Experiment Supplemental Findings

To determine the extent of aerobic, anaerobic-exogenous and anaerobic zones in a benthic marine deposit, a deep sludge reactor was constructed of transparent acrylic (Figure 24). The 50 centimeter reactor depth was selected to be much greater than known dissolved sulfate diffusion depths in estuarine sediments (Bella, 1975).

Aerobic Zone

Dissolved oxygen analyses[33] of the sea water, microbial slime layer and underlying deposit material confirmed the findings of Sanders et al. (1970) that the aerobic zone of highly organic material is limited to less than a few millimeters.

Anaerobic-Exogenous Zone

Dissolved sulfate concentrations[34] at 180 days into the experiment (Figure 25) indicated depletion by a factor of ten (re. sea water concentration) at a depth of 16 centimeters in the central portion of the deposit. At a depth of 30 centimeters, concentrations of less than 100 mg/l were typical. The depletion of dissolved sulfate and confirmed (gas chromatograph) production of methane gas indicated that deeper stabilization proceeded by fermentation

The dissolved hydrogen sulfide content[35] of the 33 centimeter deposit indicated significant accumulation in deeper portions of the deposit at 180 days (Figure 26). Maximum concentrations measured were

33. International Biophysics Corporation Mini Dissolved Oxygen Meter.
34. Turbidimetric Method 427C, Standard Methods for the Examination of Water and Wastewater, 14 Edition, p.334 (1976).
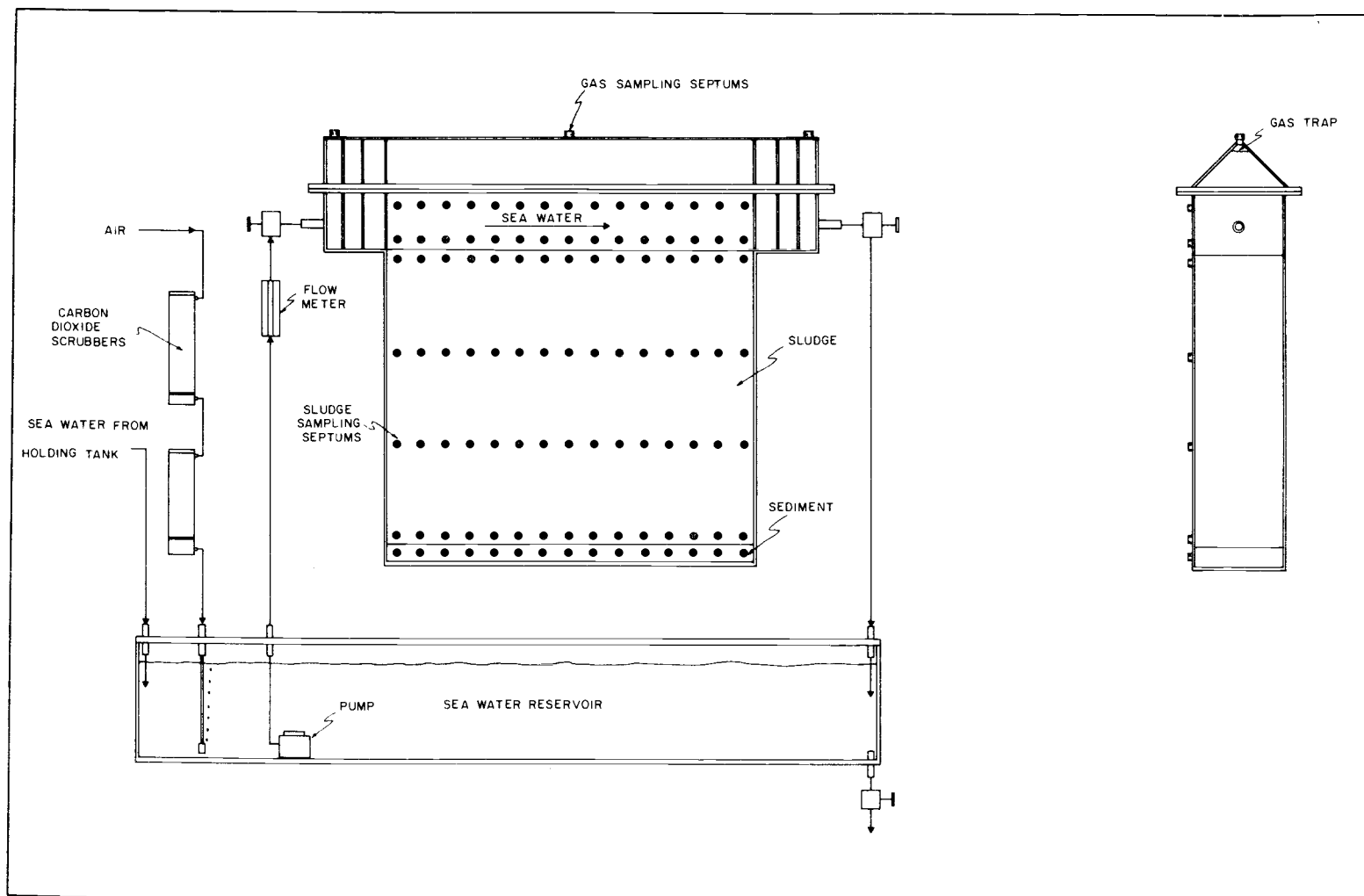35. "Titration Technique", Bella et al., 1974.

Figure 24.   One Atmosphere Laboratory Sludge Reactor for Deep Deposits
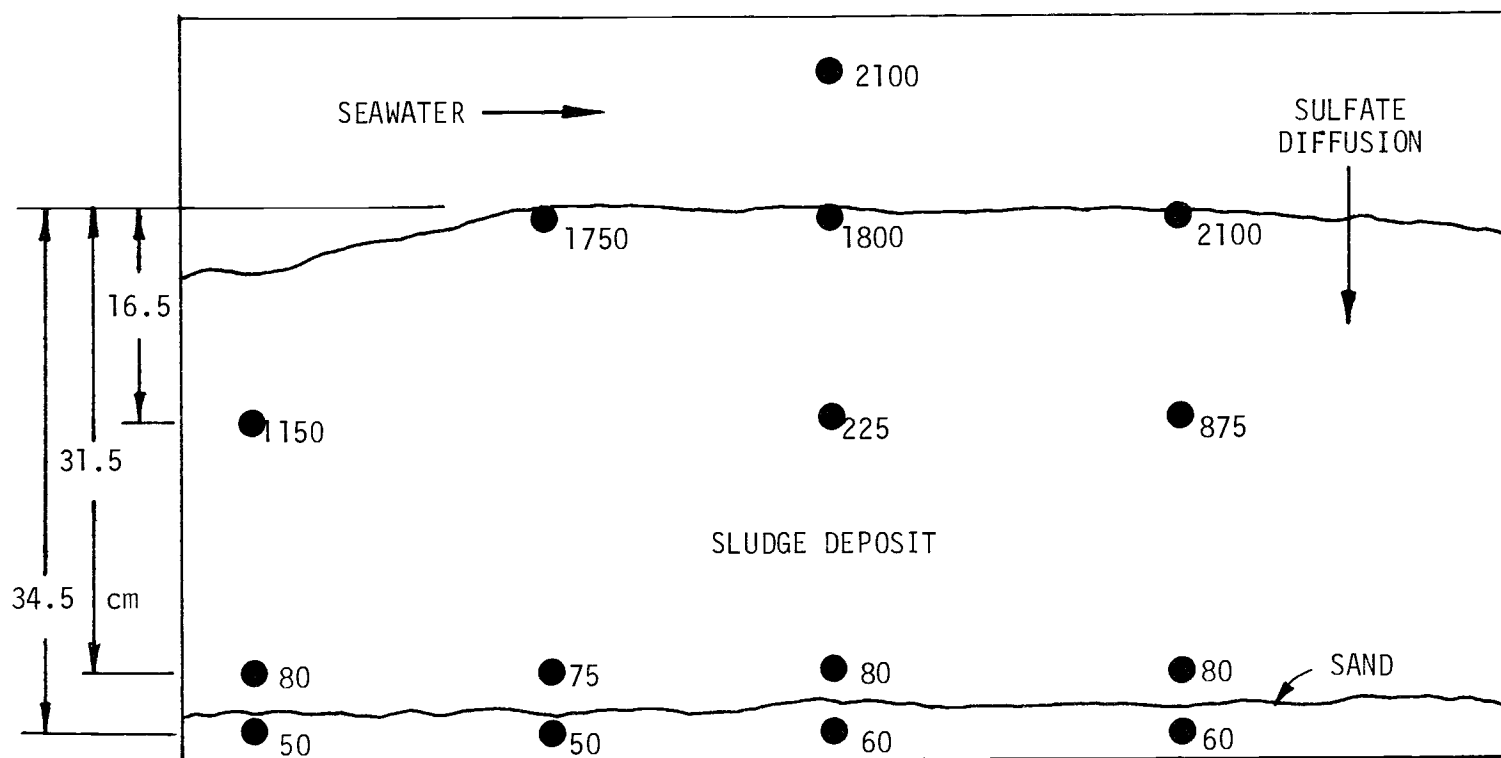
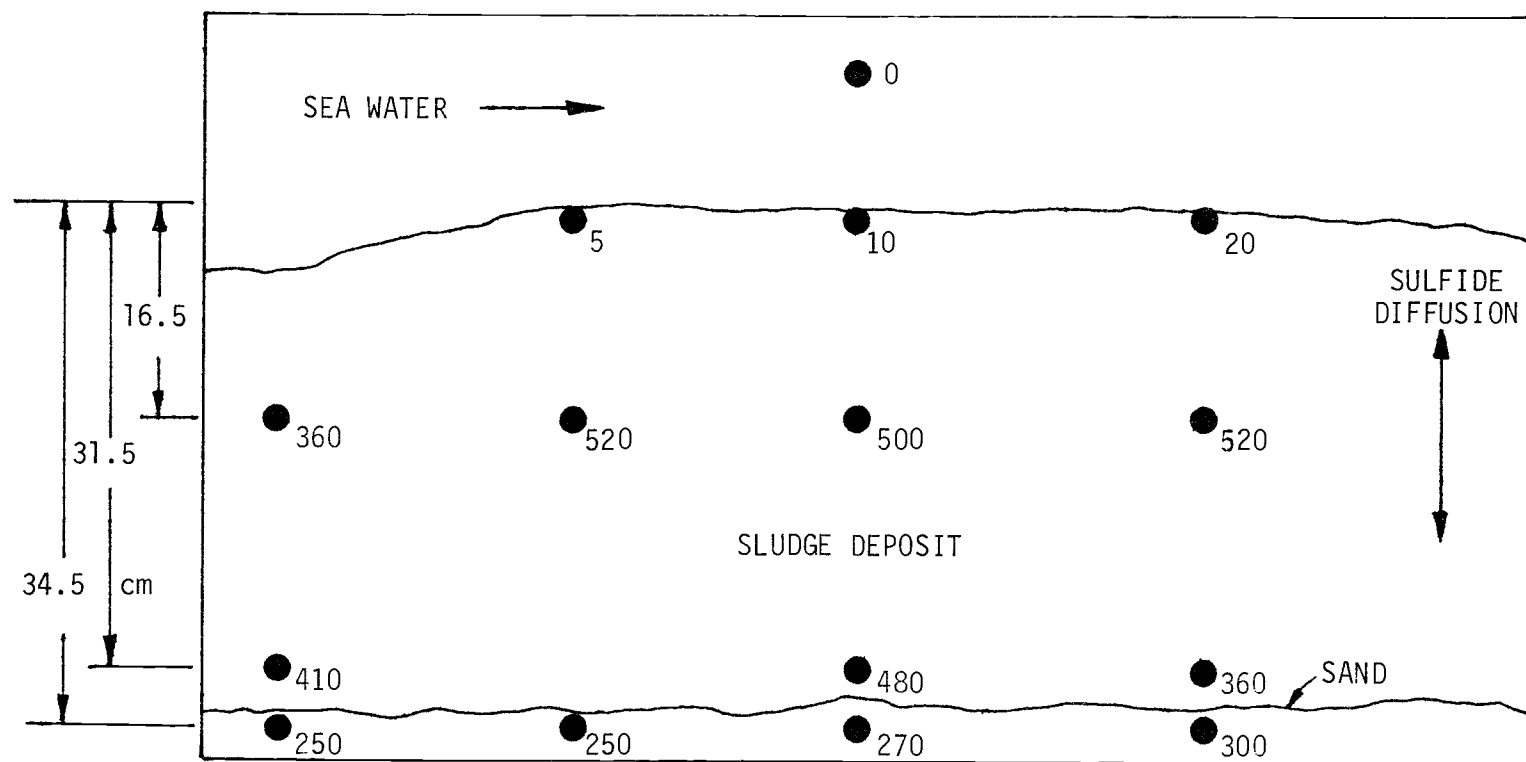Figure 25.   Dissolved Sulfate Distribution at 180 Days (mg/l)

Figure 26.   Dissolved Sulfide Distribution at 180 Days (mg/l)

approximately 500 mg/l in the deposit, and 300 mg/l in the underlying
sand. Such an accumulation did not occur in 2.0 and 3.0 centimeter
deposits in which the maximum dissolved hydrogen sulfide concentration
level was 20 mg/l. The diffusion rate of hydrogen sulfide into the
underlying sand was 1.4 mm/day for the first 30 days (as evidenced by
the movement of the characteristically black iron-sulfide boundary).
Thereafter, the diffusion rate slowed considerably.

Gas Production

Gas production as evidenced by bubble formation began within
nine days of deposit formation. Migration to the deposit surface and
rupture of the slime layer did not occur until approximately 30 days.
The methane content of released gas ranged from 71 to 86 percent,
averaging 80 percent. Carbon dioxide content ranged from 10 to 13 per-
cent, ranging from 0.29 to 0.40 percent. Hydrogen gas was not de-
tected.[36]

Microbial Observations

At the sea water sludge interface in monitored experiments,
a dense microbial population (approximately 10^9 bacteria/ml) developed
within ten days.[37] The deposits became covered with a white to cream
colored slime having a thickness of between one and two millimeters.
Initial microbial communities consisted principally of highly motile
curved rods, 0.5 microns in diameter and two to three microns long.
Many pairs appeared united in an S shape, and rapid rotational as well
as transverse movements were observed (Figure 27). Spherical coccus

36. Carle Model 100 gas chromatograph equipped with a thermal
conductivity detector cell; analytical column 4.0 meters long, 0.31
centimeters in diameter; 80 to 100 mesh Porapak-Q polymer beads; oper-
ating temperature 17.9°C; helium carrier gas at 50 ml/minute; "Disc"
Model 610 Automatic Printer; Westronics dual pen strip chart recorder
also equipped with a disc type integrator.
37. Observations and photography with a 1400X phase contrast
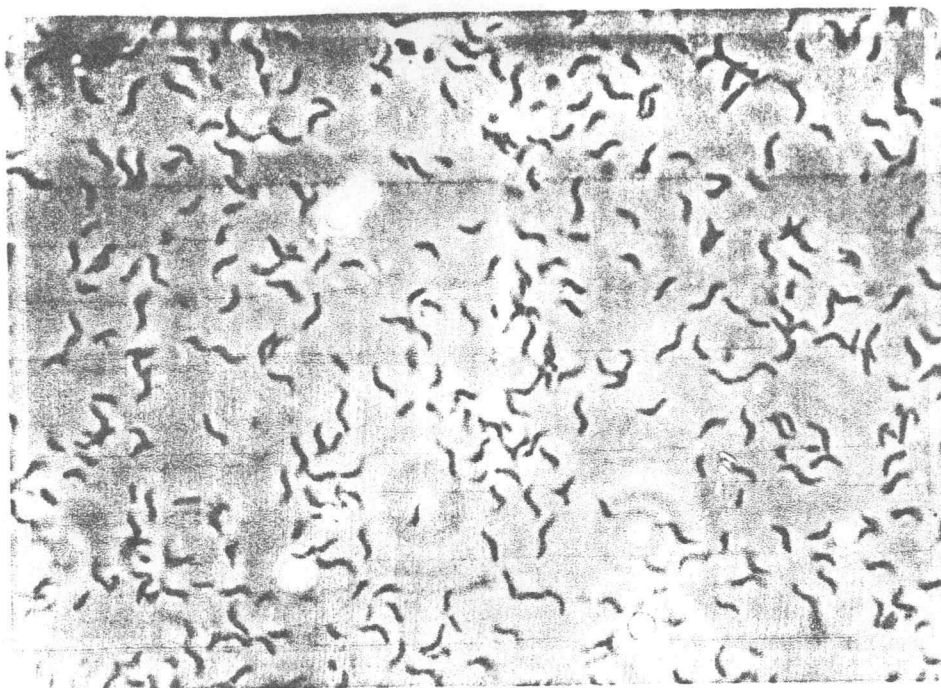microscope equipped with a 35 mm camera.

Figure 27.   Predominant Bacteria Observed in the Surface
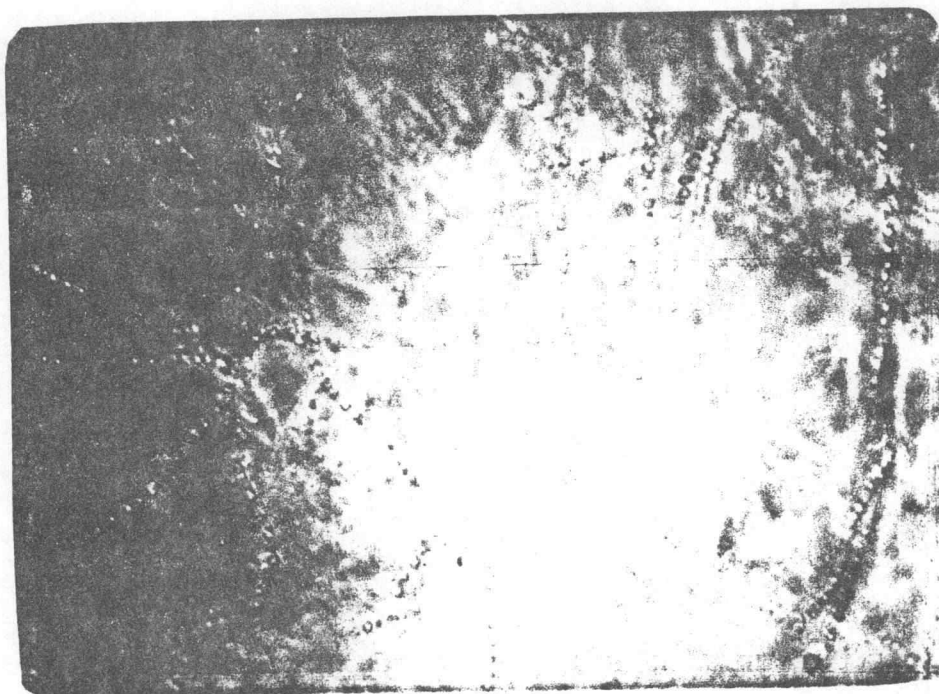Slime of the One-Atmosphere Flowing Sea Water
Experiment After 11 Days

Figure 28.   Predominant Bacteria in the Surface Slime Layer
of the One-Atmosphere Flowing Sea Water Experiment
After 19 Days

types of bacteria were not observed in the surface slime layer.

The initial community predominated by vibrio-like rods was succeeded by a dense population of trichome producing bacteria, approximately 20 days after deposit formation (Figure 28). In the presence of high hydrogen sulfide levels, it is probable that the 0.5 micron inclusions were sulfur granules. Genera noted for such inclusions include Beggiatoa and Thiothrix. Because filament motion was not observed and because trichome diameters were 1.0 microns in diameter, the predominent slime layer bacteria were tentatively identified as Thiothrix marina (Buchanan and Gibbons, 1974).

Filamentous bacteria also predominated the surface slime of the 2.0 centimeter deep 34 atmosphere deposit. However, long chains of encased granules were not apparent. Instead, shorter segments of two and three granules were most common, with four being the largest number of joined segments observed (Figure 29). Granule diameters were approximately 0.5 microns. Whether this morphological form represents a pressure adaptation (Zobell and Oppenheimer, 1950) or a change caused by decompression is not known. A predominance of morphologically similar bacterial species was not observed except at the deposit surfaces.

Erosional Velocities

The water velocity required to erode laboratory sludge deposits was found to be dependent on deposit compaction and to a lesser extent on the presence of a surface slime layer. At the onset of an experiment, velocities of between 0.25 and 0.50 cm/sec were capable of washing material from the reactor. After an initial compaction phase of a few days, however, the water velocity could be increased to between 3.5 to 5.0 cm/sec before erosion began. In this velocity range, microbial slime layers formed thereby raising the erosional threshold further. Once the slime layer covered the deposit, water velocities in excess of 5.0 cm/sec were required to lift the slime mat and erode the less cohesive underlying materials.
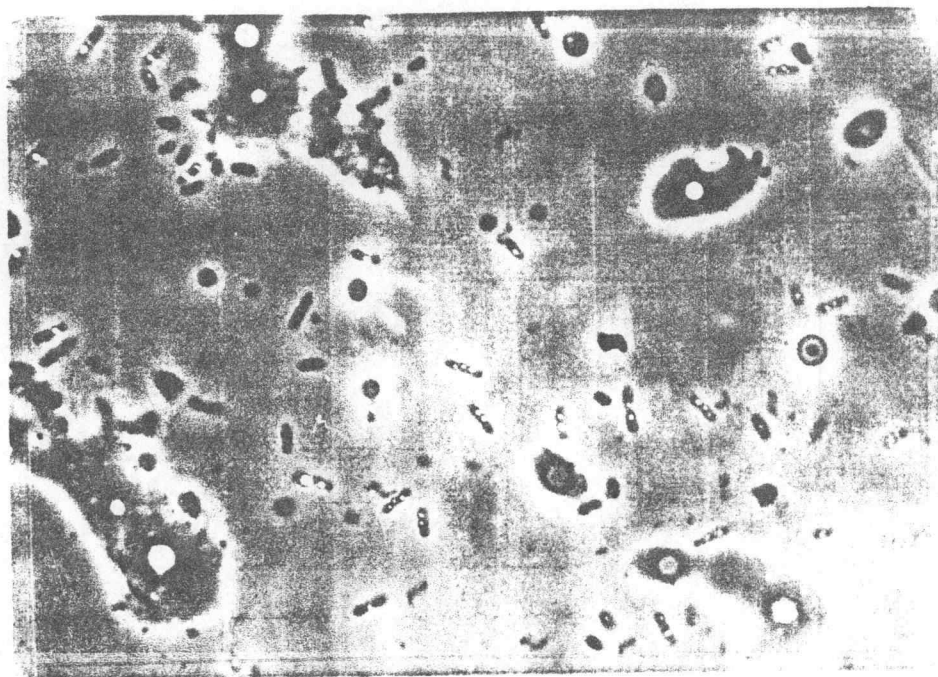
Figure 29.   Predominant Bacteria Observed in the Surface
             Slime of the 34-Atmosphere Flowing Sea Water
             Experiment After 20 Days

APPENDIX D

Tsivoglou Curve Fitting Method

Consider deposit particulate organic carbon concentrations at time t_1 and t_2. According to equation (15)

$$C_1 = C_0 e^{-Kt_1} + C_r \tag{39}$$

$$C_2 = C_0 e^{-Kt_2} + C_r \tag{40}$$

Taking the difference and assuming $t_2 = t_1 + \Delta t$ gives

$$\Delta C = C_0 \left[e^{-Kt_1} - e^{-K(t_1 + \Delta t)} \right] \tag{41}$$

$$\Delta C = C_0 e^{-Kt_1} \left[1 - e^{-K\Delta t} \right] \tag{42}$$

$$\ln \Delta C = \ln C_0 - Kt_1 + \ln(1 - e^{-K\Delta t}) \tag{43}$$

$$\ln \Delta C = -Kt_1 + \left[\ln C_0 + \ln(1 - e^{-K\Delta t}) \right] \tag{44}$$

$$\ln \Delta C = -Kt_1 + A \tag{45}$$

where $\quad A = $ a constant if $\Delta t = $ a constant.

Thus

$$\frac{d(\ln \Delta C)}{dt} = -K \approx \frac{\Delta(\ln \Delta C)}{\Delta t} \tag{46}$$

or

$$K = \frac{(\ln \Delta C)_{t_1} - (\ln \Delta C)_{t_2}}{t_2 - t_1} \tag{47}$$

Procedure:

1. Hand fit a curve to a set of data points.
2. Calculate K from ΔC and Δt curve values.
3. Calculate C_0 with equation (43).
4. Calculate C_r from equation (39) or (40).

This procedure permits a determination of K without a knowledge of C_r, the remaining refractory particulate organic carbon content after long periods of time (i.e. months). Thus, K values can be determined on the basis of short term experiments.