DEVELOPMENT OF NEW SAMPLING STRATEGIES FOR ASSESSING BENTHIC OXYGEN DEMAND IN RESPONSE TO ORGANIC MATTER LOADING IN BUZZARDS BAY SEDIMENTS

by

John J. Molongoski
and
Brian L. Howes
Department of Biology
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Final Report
Submitted to
U.S. Environmental Protection Agency
Buzzards Bay Project

September 1991

Introduction:

The cycling of organic carbon in the marine environment involves both aerobic and anaerobic metabolic processes. Aerobic reactions take place in well oxygenated sediments or at the sediment-water interface. They include the degradation of organic matter by heterotrophic bacteria into inorganic compounds, with oxygen being used as the hydrogen acceptor. Under anaerobic conditions, however, microorganisms utilize both organic and inorganic compounds (sulfate, nitrate, and carbon dioxide) as hydrogen acceptors leading to the production of either simple organic compounds (e.g., fatty acids and alcohols) or reduced inorganic compounds (e.g., methane, ammonia and hydrogen sulfide). Organic enrichment of bottom sediments may lead to an alteration of the balance between aerobic and anaerobic processes and lead to localized anoxia or hypoxia.

Increasing eutrophication in coastal marine waters results in accelerated deposition of labile organic matter to the sediments. Increased deposition of organic matter, in turn, results in greater benthic metabolism (oxygen demand) and the release of dissolved nutrients to the water column (Figure 1). In severe cases, this results in sediment and water column anoxia, the death of benthic infauna, and diminished shellfish resources. Such eutrophication and the resulting hypoxia/anoxia have been recognized as critical environmental problems along the northeastern coast of the United States, particularly in shallow regions of the continental shelf and in coastal embayments such as Buzzards Bay (National Research Council, 1984; U.S. Congress, Office of Technology Assessment, 1987; Science Applications International Corp., 1987). Because most anoxic events result from increased sediment oxygen demand, it is important to be able to monitor and predict potential or incipient anoxic events before they occur. At present, no

"HEALTHY"
COASTAL MARINE SEDIMENT

DETRIMENTAL EUTROPHICATION
RESULTS OF INCREASED
ORGANIC MATTER LOADING

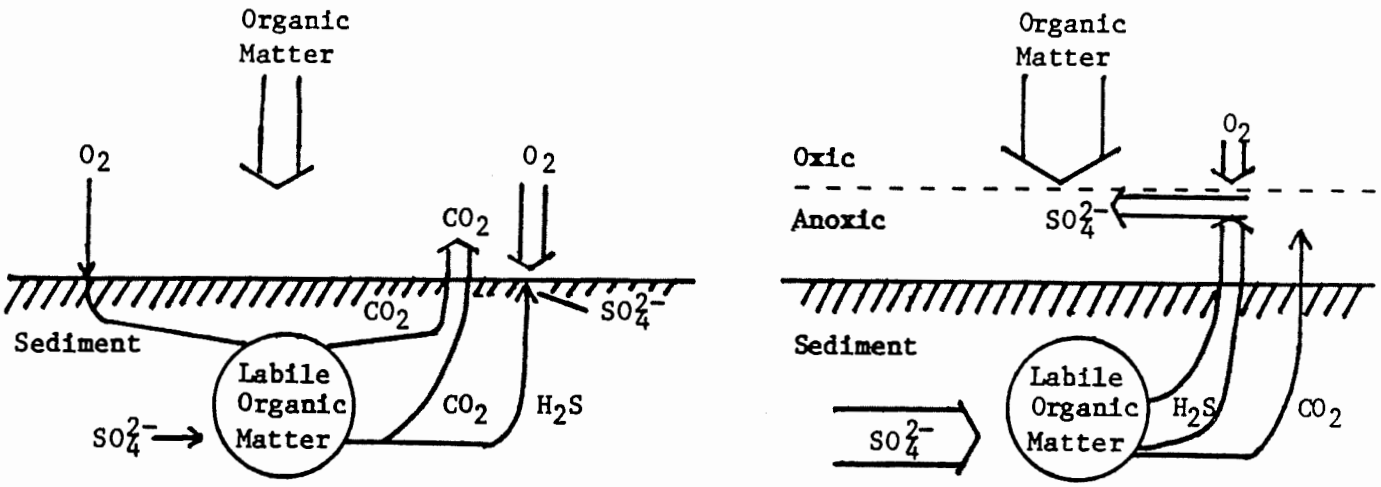

Figure 1 - Sediment oxygen consumption in coastal marine sediments is controlled by the amount of labile organic matter available. As the input of organic matter (from phytoplankton production, sewage outfalls, nutrient loading, etc.) increases, sediment oxygen demand also increases. At some level of organic loading, the rate of oxygen uptake within the surface sediments exceeds the rate of oxygen input and the sediments become anoxic. This may also result in hypoxia/anoxia in overlying bottom waters.

technique exists which will yield such predictive data and which can be employed in survey efforts.

Current water quality standards of the Commonwealth of Massachusetts for dissolved oxygen in coastal marine waters (i.e., vertically averaged water column means) are inadequate for predicting the early stages of hypoxic/anoxic events because the highest rates of oxygen consumption in shallow coastal systems occur in the sediments, not the water column. Thus, early stages of eutrophication may have little or no manifestation in water column oxygen conditions. Organic loading may occur over an extended period of time without any increasing oxygen demand occurring in the overlying water (SAIC, 1987). Moreover, water column dissolved oxygen measurements are frequently difficult to interpret because of a host of variables (water column depth, temperature, mixing, rates of primary productivity, etc.) generally associated with the constantly changing nature of coastal waters (see Tyler, 1986). A more precise method for determining the potential for anoxic events in coastal marine sediments and overlying waters is to simultaneously measure sediment surface oxygen uptake and subsurface sulfate reduction rates (Jorgensen, 1977; Howes, et al., 1984; Martens and Klump, 1984), and to couple these measurements with water column mixing data. These methods, however, while precise, are expensive, labor-intensive and not generally amenable for routine monitoring or survey work.

In order to make management decisions concerning water quality and coastal marine resources, a simple yet reliable means of assessing sediment oxygen demand over time is required. The technique should be suitable for use in routine monitoring or survey work, yet sensitive and responsive enough to detect changes (both positive and negative) in sediment oxygen demand. Such a technique must be capable of assessing when a sediment system is critically impacted such that a real

potential for sediment and water column hypoxia/anoxia exists. The overall objective of this project was to develop such a method and test it over a wide range of sediment samples from Buzzards Bay with varying degrees of organic loading.

The basic method examines the relationship between labile organic carbon content and benthic metabolism (sediment oxygen demand) of a range of sediment types from sandy to highly organic fine grained sediments. Because it is the input of labile organic carbon that ultimately drives benthic oxygen demand, we hypothesize that sediment oxygen demand will be positively correlated to the quantity of labile organic matter in these sediments. We determined the reactive carbon content of these various sediment types using a bioassay in which the labile organic matter was mineralized to carbon dioxide (CO_2) and the total CO_2 production from an incubated sediment sample is quantified. These measurements were compared with simultaneous measurements of sediment oxygen uptake in parallel incubations of sediment cores from the same sites.

Methods:

Station Location and Description

Sediment samples for this investigation were collected either by box core or by diver from six stations in New Bedford Outer Harbor and Buzzards Bay (Figure 2). Exact station locations are presented in Table 1. The sites were chosen to encompass the major sediment types found in the Outer Harbor (Table 2). Benthic stations 2 and 1 include the current and proposed outfall locations, respectively, for the New Bedford Sewage Treatment Facility. Station 3 has a relatively sandy substrate with low organic content and station 4 has a muddy/sandy substrate with an intermediate organic content. Site 6 represents an organic-rich nearshore

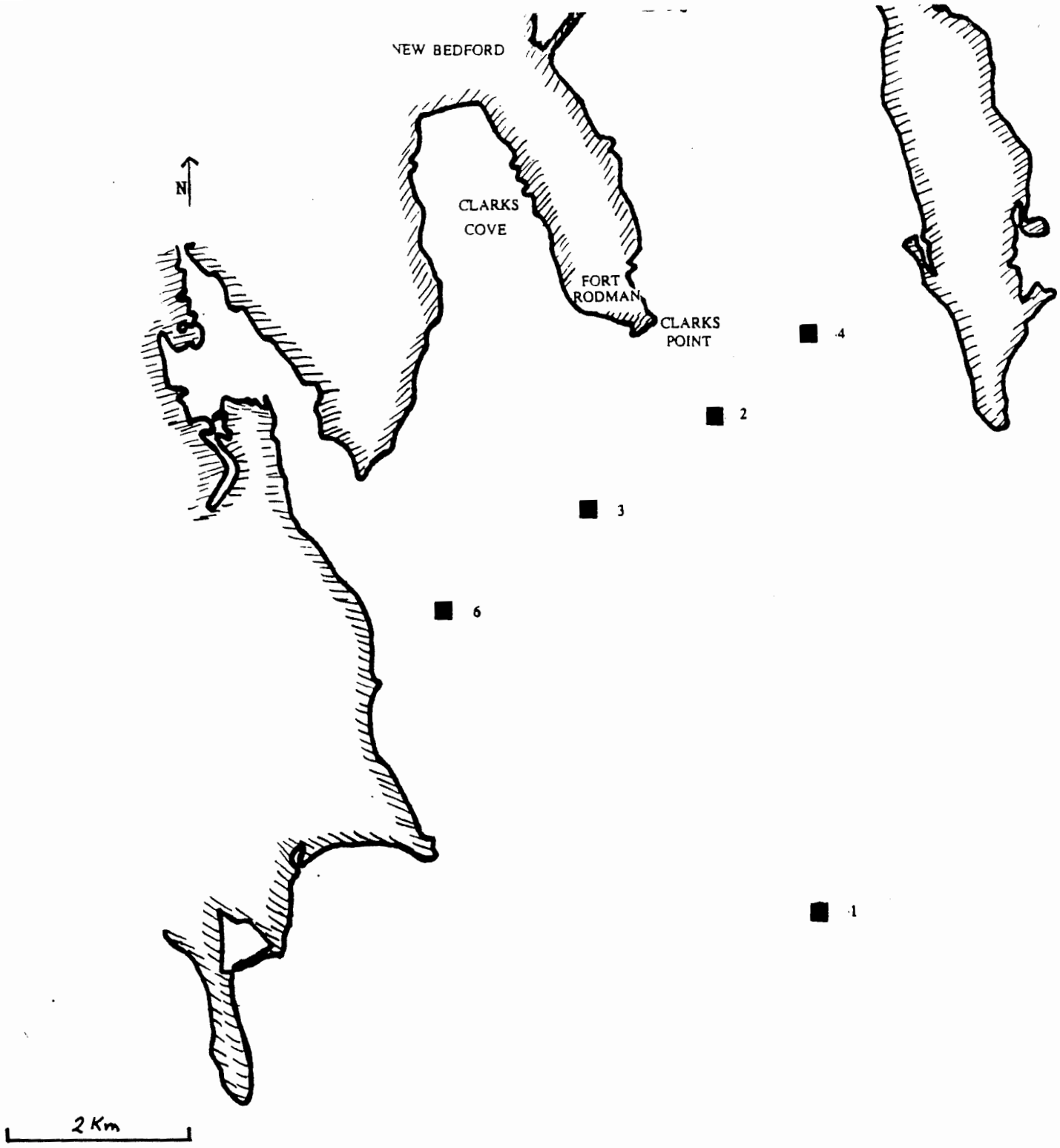

Figure 2 - Benthic sampling stations in New Bedford Outer Harbor and Buzzards Bay.

Table 1. Sediment Locations: Sediment Nutrient Cores/Infaunal Community Samples

Station No.	LORAN Time/Delays	Latitude/ Longitude	General Location	Depth (m)
1	14,205.2 43,975.2	41°32.29'N 70°52.77'W	Mid/Outer Harbor Entrance	13.4
2	14,199.0 43,994.3	41°35.01'N 70°53.44'W	Near present outfall	9.1
3	14,205.0 43,990.5	41°34.31'N 70°53.96'W	South of Clark's Point	7.6
4	14,193.0 43,998.0	41°35.70'N 70°52.92'W	East of Clark's Point	7.6
5	14,221.3 43,956.3	41°29.27'N 70°53.34'W	Station R	18.3
6	14,218.0 43,989.5	41°33.75'N 70°55.71'W	East of Nonguitt	7.9

Table 2. New Bedford Outer Harbor Sediment Grain Size Analysis

Station No.	Sediment Type[a]	Sand %	Silt %	Clay %	Phi Sizes						
					>4	>5	>6	>7	>8	>9	>10
1	Silty mud	14.0	47.3	38.7	11.8	12.4	13.4	9.7	7.0	8.1	23.6
2	Silty mud	11.3	48.4	40.4	12.8	14.1	12.1	9.4	7.4	6.1	40.4
3	Sand	95.0	2.4	2.6	1.2	0.5	0.0	0.7	0.0	0.0	2.6
4	Muddy sand	83.2	9.9	6.9	4.4	2.2	1.5	1.7	0.7	0.5	5.7
5	Silty mud	18.1	50.5	31.3	17.3	13.9	11.4	8.0	5.5	5.1	20.7
6	Silt	6.3	63.9	29.7	31.0	12.4	12.8	7.7	5.4	4.6	19.7

[a] Based on Folk (1974).

sediment, whereas station 5 is an unimpacted Buzzards Bay sediment and has been a long-term study site by investigators at WHOI (Sanders, 1958, 1960).

Two sediment collections were made, summer (July) and winter (January-February) in order to investigate any possible seasonal differences in the pool of labile organic carbon. Sediment samples for each of the seasonal time points were obtained on two cruises per season. Winter sediments were collected on 30 January and 13 February 1989 and summer sediments were collected on 12 and 18 July 1989.

Ship time and personnel required for obtaining the samples were provided by a related project evaluating the nutrient regime of New Bedford Outer Harbor sediment (Howes and Taylor, 1989). This companion project provided necessary data on sediment total organic carbon pools and in situ sediment oxygen demand, anaerobic sediment metabolism (sulfate reduction), and chemical oxygen demand at each sampling site. As quantitative measurements of sediment oxygen demand were made simultaneously with estimates of labile organic carbon content in sediments from each site, we were provided the opportunity in this project to compare sophisticated measurements of sediment biogeochemical processes with simpler, more easily obtainable estimates of labile sedimentary organic carbon pools obtained by measuring carbon dioxide production.

Determination of biologically labile organic matter content of sediments:

Surface sediments (0-5 cm) obtained from each benthic station on each date were sieved through a 1.0 mm screen to remove animals and large shell fragments. Duplicate 100 cm^3 samples of each sediment were slurried with 150 ml of 1.0 um-filtered seawater in a 500 ml sealed flask and incubated in the laboratory at 25° C. Control flasks containing only seawater were set up in the same manner. The slurries were amended with $(NH_4)_2SO_4$ and K_2HPO_4 (10 mM each) and regularly

aerated with carbon dioxide-free air (Linde specialty gas, dry grade) to ensure that oxygen and nutrients were not limiting. The sealed flasks were connected to duplicate base traps (0.2N NaOH) connected in series. When the sediment reactors were aerated, metabolically produced CO_2 was swept into the NaOH traps where the CO_2 was quantitatively absorbed (Figure 3). Preliminary experiments demonstrated that the carbon dioxide was quantitatively recovered in the initial NaOH trap with the second trap serving as a back-up. The system was tested with CO_2-free distilled water in place of sediment to ensure that no source of CO_2 contamination existed which would introduce CO_2 into the reactors. Furthermore, control experiments were conducted in which known quantities of CO_2 (up to 10 mg of CO_2-C) were injected into the reactor system and subsequently flushed into and absorbed by the 0.2N NaOH traps. These experiments demonstrated that the experimental system used was effective at trapping $\geq$ 95% of the added CO_2 (Table 3).

In a separate experiment, a sediment core obtained from station 2 in New Bedford Harbor on 13 February 1989 was sectioned at 7 cm intervals; duplicate samples of 100 cm^3 of sediment from each section were incubated in sealed flasks according to the procedures described above. The purpose of this experiment was to measure changes in CO_2 production with increasing sediment depth (and decreasing labile organic carbon content).

In all sediment incubation studies performed, the sediment slurry pH was measured at the beginning and end of the incubation, as well as periodically during the incubation, to ensure that the oxidation of reduced sulfur did not lower the sediment pH to an extent that respiration was inhibited and/or CO_2 was released via the dissolution of carbonate.

FIGURE 3

SCHEMATIC OF EXPERIMENTAL SYSTEM FOR THE COLLECTION OF MICROBIALLY-PRODUCED CARBON DIOXIDE FROM SEDIMENT/SEAWATER SLURRIES

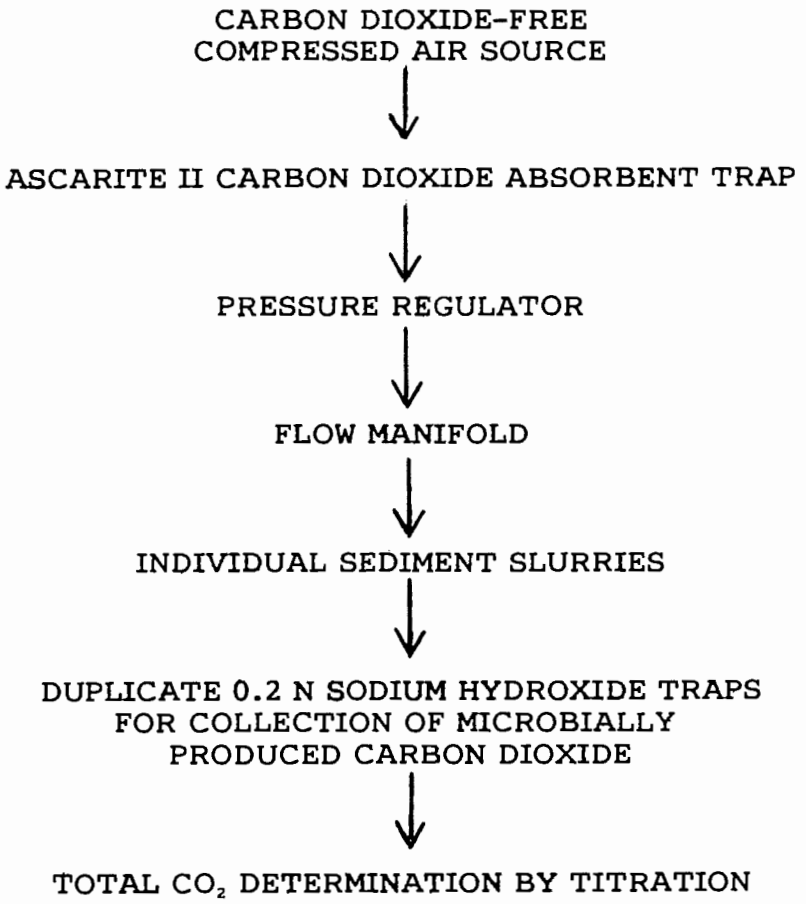

Table 3. Percent Recovery of CO_2-Carbon Injected into Experimental CO_2 Collection System

Experiment No.	ml CO_2 added	mg CO_2-C added	mg CO_2-C recovered	% Recovery of added CO_2-C
1	3	1.59	1.50	94.3
2	3	1.59	1.49	93.7
3	5	2.65	2.62	98.9
Mean	-	-	-	95.6 $\pm$ 2.8

Quantification of Carbon Dioxide

The metabolically produced CO_2 captured in the 0.2N NaOH traps was quantified by alkalinity determination by titration (Black, 1965; Standard Methods, 1985). We found this to be a simple yet reliable means of quantifying CO_2 as it provided a direct integration of the total CO_2 produced. In this method, the CO_2 absorbed in the 0.2N NaOH traps was precipitated as barium carbonate by the addition of excess barium chloride (5 ml of 1 M $BaCl_2 \cdot 2\ H_2O$ per CO_2 trap). The barium carbonate was removed by centrifugation and the supernatant titrated for residual alkalinity with 0.5N hydrochloric acid. After the amount of unreacted alkali (0.2N NaOH) was determined by titration, the amount of CO_2 that combined with 0.2N NaOH in the base traps could be determined by simple substraction (Black, 1965). We calibrated this method for determining CO_2 over a wide range of concentrations of both gaseous CO_2 (0-20 mg CO_2) and Na_2CO_3 (0-0.1 M). In all instances, the method was precise, accurate and highly sensitive (Figure 4).

Determination of carbonate content of sediments

In order to correct for carbon dioxide present as carbonate, subsamples of all the initial sediments added to the reactor flasks and samples of the sediment remaining in each flask after the incubations were completed were acidified with 18N H_2SO_4 to pH 1.0 or less in a sealed serum vial and incubated overnight. The amount of acid-volatile carbon dioxide released in each vial was then measured by thermal conductivity gas chromatography. This assay was conducted in order to correct for CO_2 collected during the incubations that may have evolved from the dissolution of inorganic carbonates.

Determination of total sediment organic content

Replicate subsamples of each initial sediment sample, in addition to subsamples of the sediment remaining in each reactor flask at the conclusion of the incubations, were dried at 60° C and ground to a fine powder with a glass rod. One gram of dry sediment was then acidified with 5N H_3PO_4 to volatilize carbonates, washed with ultrapure distilled water to remove the H_3PO_4 and dried again at 60° C. High carbonate sediments (stations 3 and 4) were acidified a second time with concentrated HCl, washed, and dried in order to be sure that all carbonate had volatilized. These samples were analyzed for particulate organic carbon and nitrogen on a Perkin Elmer Model 2400 CHN analyzer. These measurements were made to determine the total organic matter pool (labile and refractory or nondecomposable) of each sediment sample and together with the labile organic carbon measurements described above indicate the percentage of labile organic carbon in the sediment samples.

Determination of sediment organic matter remineralization rates

Data concerning the rates of sediment organic matter remineralization were provided by a related project evaluating the nutrient regime of New Bedford Outer Harbor which was conducted for Camp, Dresser, McKee, Inc. (Howes and Taylor, 1989). Organic matter mineralization was determined by the measurement of sediment oxygen uptake. Rates of sediment oxygen uptake were determined in enclosed 15 cm x 20 cm long subcores carefully obtained from the box core samples or taken by diver. The O_2 concentration in the gently stirred overlying water (nominal 2 liters volume) was monitored at 15 min intervals using an Endeco Type Pulsed Dissolved Oxygen and Temperature Recorder.

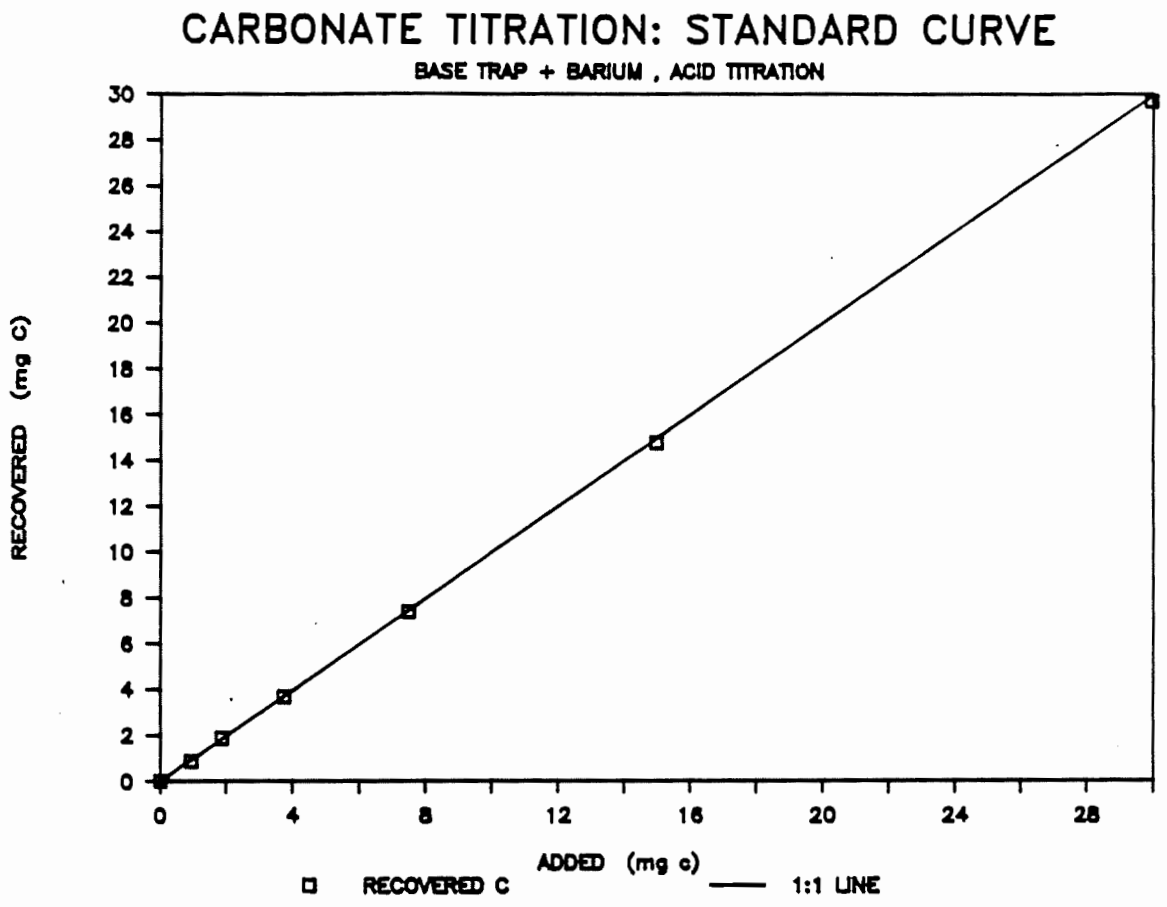

Figure 4 - Standard curve for the quantification of carbon dioxide by alkalinity titration.

Sediments were held from time of collection through the incubation period at in situ temperatures using temperature-controlled baths to ensure the accurate measurement of environmental rates. The water overlying the sediment samples was replaced with 0.22 um filtered water from the collection site in order to eliminate effects of phytoplankton respiration. The activity for each station was measured in quadruplicate cores and oxygen consumption rates were determined from the slopes of the time series oxygen concentration curves. Data were expressed as the average of 3 or 4 replicates. In cases where one replicate was widely divergent from the remaining three, it was eliminated from the computation of the average.

Results and Discussion:

Time Course Experiments - The cumulative CO_2 production (mg CO_2-C per 100 cm^3 of sediment) resulting from the extended incubation of New Bedford winter and summer sediments is presented in Tables 4 and 5, respectively. The same data, presented as umoles CO_2 per cm^3 of sediment are graphically presented in Figures 5 and 6. In all experiments, the sediment slurries continued to evolve significant amounts of carbon dioxide throughout the incubation, even after 377 days. The data indicate that the CO_2 production observed was the result of heterotrophic bacteria decomposing labile organic matter contained within the sediments upon their collection, and was not the result of CO_2 contamination or the dissolution of inorganic sedimentary carbonate.

The latter observation is supported both by the seawater controls which were conducted with each incubation, and by measurements of inorganic carbonate pools (Table 6) and of sediment slurry pH (Table 7) made at the start and end of each extended incubation. The seawater controls provided both the contribution of the

Table 4. Cumulative Labile Carbon Production Measured as mg CO2-C Obtained from Extended Incubations

I. Winter Sediments
Collected "1/30/89" (Stations 1,3,5) and "2/13/89" (Stations 2,4,6)

	mg C - CO2					
Days	S-1	S-2	S-3	S-4	S-5	S-6
9	9.92	11.70	3.38	12.29	12.75	16.44
	(1.11)	(0.52)	(2.76)	(1.08)	(0.78)	(2.16)
25	15.30	18.81	5.12	14.74	13.92	22.14
	(3.27)	(1.05)	(2.76)	(2.68)	(2.13)	(0.26)
41	23.21	25.94	6.22	20.42	17.27	30.05
	(0.68)	(2.01)	(2.97)	(5.97)	(3.07)	(2.10)
58	27.47	30.24	10.85	33.92	28.75	41.11
	(0.81)	(2.56)	(3.35)	(0.61)	(5.20)	(3.80)
94	52.14	55.26	25.87	50.86	43.73	62.44
	(10.51)	(5.57)	(3.42)	(0.61)	(0.70)	(2.53)
150	83.56	96.31	36.85	79.00	72.30	88.76
	(8.32)	(2.12)	(3.79)	(0.10)	(1.61)	(2.54)
234	111.49	129.99	50.46	103.85	94.10	106.97
	(3.65)	(2.04)	(4.99)	(1.92)	(10.10)	(6.48)
357	126.44	151.51	66.27	127.50	115.19	121.34
	(5.87)	(19.60)	(15.21)	(7.60)	(14.28)	(18.50)

Values are the mean carbon as CO2 produced from duplicate flasks and corrected for a seawater blank.
Numbers in parentheses indicate Standard Deviation of replicate samples.
Values represent total CO2-carbon produced per 100cm3 of sediment.

Table 5. Cumulative Labile Carbon Production Measured as mg CO2-C Obtained from Extended Incubations

II. Summer Sediments
Collected "7/12/89" (Stations 1,3,5) and "7/18/89" (Stations 2,4,6)

	mg C - CO2					
Days	S-1	S-2	S-3	S-4	S-5	S-6
8	5.77	8.22	3.60	4.08	6.16	9.36
	(1.73)	(0.41)	(0.50)	(0.08)	(-)	(1.25)
24	13.61	18.51	12.12	13.59	15.75	22.44
	(4.82)	(1.61)	(3.10)	(0.04)	(0.62)	(1.49)
40	24.2	27.63	16.73	18.66	19.35	28.86
	(5.11)	(2.67)	(3.30)	(2.04)	(1.58)	(1.61)
57	29.20	30.49	17.21	22.02	20.66	31.68
	(4.59)	(4.32)	(3.91)	(1.80)	(1.85)	(0.91)
93	50.45	62.8	32.52	44.90	41.71	52.83
	(7.36)	(2.53)	(6.10)	(7.81)	(1.05)	(1.26)
149	86.93	101.98	45.76	81.82	83.97	93.31
	(10.37)	(2.77)	(4.52)	(4.78)	(21.96)	(0.42)
233	123.14	138.43	56.72	114.39	98.06	119.86
	(16.13)	(0.70)	(0.99)	(7.80)	(25.99)	(2.59)
356	151.64	171.74	68.72	139.64	114.07	134.65
	(15.40)	(1.80)	(6.49)	(5.98)	(24.98)	(5.53)

Values are the mean carbon as CO2 produced from duplicate flasks and corrected for a seawater blank.
Numbers in parentheses indicate Standard Deviation of replicate samples.
Values represent total CO2-carbon produced per 100cm3 of sediment.

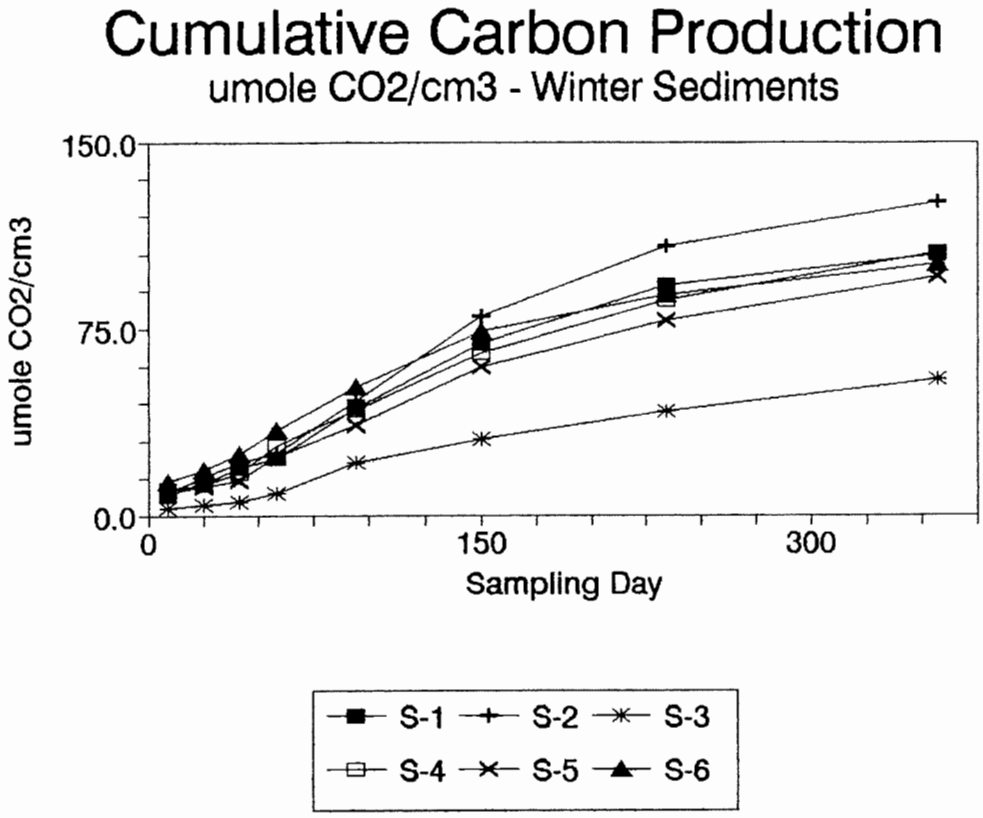

Figure 5 - Cumulative labile carbon production measured as umole CO_2/cm^3 obtained from extended incubation of sediments collected on 30 January 1989 and 13 February 1989 (winter samples). Values are the mean carbon produced from duplicate flasks, corrected for a small seawater blank.

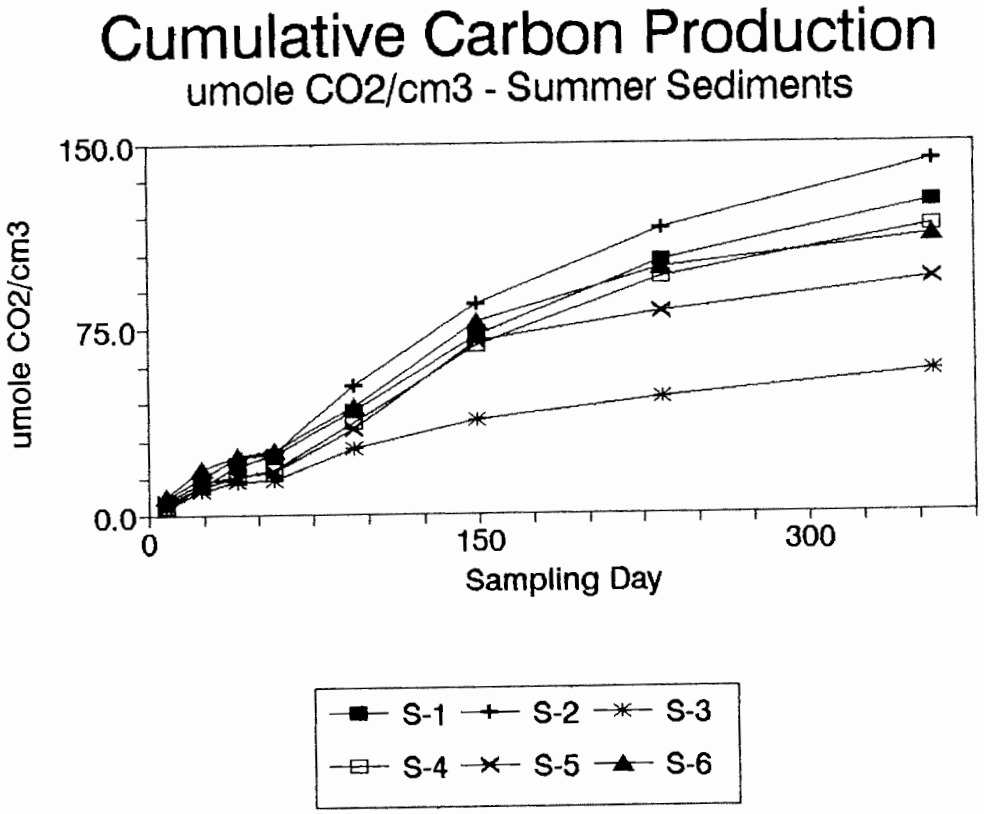

Figure 6 - Cumulative labile carbon production measured as umole CO_2/cm^3 obtained from extended incubation of sediments collected on 12 July 1989 and 18 July 1989 (summer samples). Values are the mean carbon produced from duplicate flasks, corrected for a small seawater blank.

Table 6. Mean Cumulative CO2-C (mg) Produced in Each Reactor Flask (per 100 cm3 sediment)

I. Winter Sediments

Station	X CO2-C-Final	X CO3-C-Final	Total CO2-C+CO3-C	X CO3-C-Initial	X CO2-C Final Corrected
S-1	126.44	20.59	147.03	27.32	119.71
S-2	151.50	55.96	207.46	60.45	147.01
S-3	66.27	160.32	226.59	170.20	56.39
S-4	127.50	98.34	225.84	106.94	118.90
S-5	115.19	36.78	151.97	32.86	119.11
S-6	121.34	25.31	146.65	29.92	116.73

II. Summer Sediments

Station					
S-1	151.64	35.79	187.43	32.59	154.84
S-2	171.74	75.12	246.86	70.45	176.41
S-3	68.72	170.14	238.86	166.15	72.71
S-4	139.64	88.79	228.43	98.22	130.21
S-5	114.07	35.19	149.26	31.03	118.23
S-6	134.65	40.88	175.53	36.33	139.20

Table 7. pH of Initial Starting Sediments and Final Sediments in Flasks after Extended Incubations

Station	pH-initial sediment	pH-final sediment
I. Winter Sediments		
S-1	7.20	7.40
S-2	7.11	6.90
S-3	7.35	7.30
S-4	7.36	7.20
S-5	6.97	6.80
S-6	7.07	7.10
II. Summer Sediments		
S-1	7.36	7.20
S-2	7.16	7.30
S-3	7.50	7.35
S-4	7.46	7.20
S-5	7.48	7.35
S-6	7.15	7.20

seawater added to the slurries to the total CO_2 respiration measured, and served as a control for the possible leakage of CO_2 into the sealed flasks from the atmosphere. In all cases, the seawater controls were less than 1% of the sediment CO_2 signal, indicating that these sources were minimal contributors to the total CO_2 produced.

Similarly, in all incubations the amount of CO_2 resulting from the volatilization of carbonate contained in the sediment slurries was $\leq$ 1% of the total respiration rate. This was shown by the fact that the carbonate content of the sediment slurries remained similar before and after the incubations (Table 6). Carbonate dissolution did not occur because the pH of the sediment slurries remained greater than 7.0 throughout the incubations, thus maintaining the stability of $CaCO_3$ in solid phase. The pH of the slurries generally dropped 0.1 to 0.2 pH units during incubation which might be expected from the oxidation of H_2S and FeS contained within the initial sediments.

The time course of CO_2 evolution followed a similar pattern of gradually diminishing rates in all sediments investigated. These included both winter (Figure 5) and summer (Figure 6) surface sediment collections from New Bedford Harbor, a summer collection from Little Pond, a coastal salt pond located in Falmouth, MA, (Figure 7), and a depth distribution study using a sediment core obtained from station 2 in New Bedford Harbor (Figure 8). The gradual reduction in CO_2 evolution observed in these incubations is in accordance with current models of decomposable organic matter in marine sediments which state that there is a small, very labile pool of organic matter, and a larger, more slowly decomposing pool of organic matter. The bulk of the organic matter, however, is refractory and relatively resistant to degradation (Westrich and Berner, 1984).

Significant differences in CO_2 production were found with location in New Bedford Outer Harbor (Figures 5 and 6). In both seasons, the station nearest to the

existing outfall (station 2) was found to have the highest CO_2 release, whereas station 3, one of the two sandy sites, had the lowest release. In general, the seasonal effect was one of magnitude - i.e., the stations maintained their relative differences but the absolute mass of CO_2 produced per cm^3 of sediment was higher in summer than in winter. This is most likely due to the higher rate of delivery of fresh organic matter to the sediments during the spring and summer periods as a result of higher rates of primary production (Smayda, 1988). Differences observed between stations appear to be related to organic matter loading, both from the outfall and natural phytoplankton production. One of the surprising findings of this study was the similarity in estimates of labile organic matter content among the majority of the stations.

Similar time course experiments were also conducted on sediments collected during the winter from Little Pond, an organic rich coastal salt pond (Figure 7). Similar rates of CO_2 production were observed in Little Pond as the most organically rich sites in New Bedford Harbor. Unfortunately, the majority of the sediments investigated in this study appear to have similar organic matter loadings such that large differences in organic matter content were not seen by our technique. However, it is still possible to partially test the validity of the technique by investigating changes in CO_2 production measured with increasing depth in the sediment. This experiment was carried out using sediment cores from the current outfall site (station 2) in New Bedford Harbor. Given the absence of deep bioturbation at this site, a decrease in labile organic matter (LOM) was expected with increasing sediment depth because of the increasing age of organic matter, and, hence, the longer period for decompositional processes to be acting upon it. This was indeed the observed result (Figures 8A and B) with the highest CO_2 production measured within the shallowest sediments and the lowest CO_2 production measured

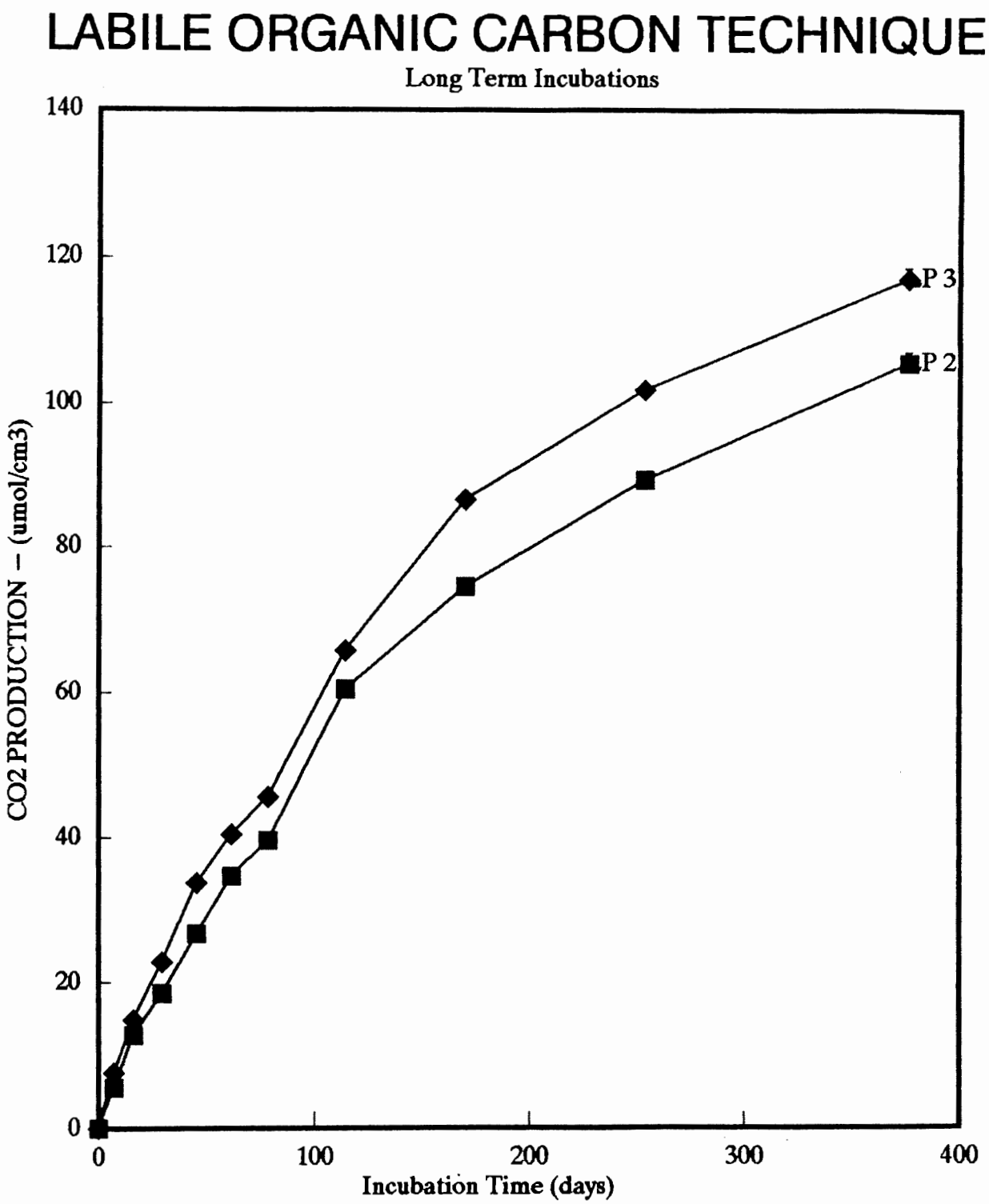

Figure 7 – Cumulative labile carbon production measured as umole CO_2/cm^3 obtained from extended incubation of sediments collected from Little Pond, Falmouth, MA. Values are the mean carbon produced from duplicate flasks, corrected for a small seawater blank.

LABILE ORGANIC CARBON TECHNIQUE

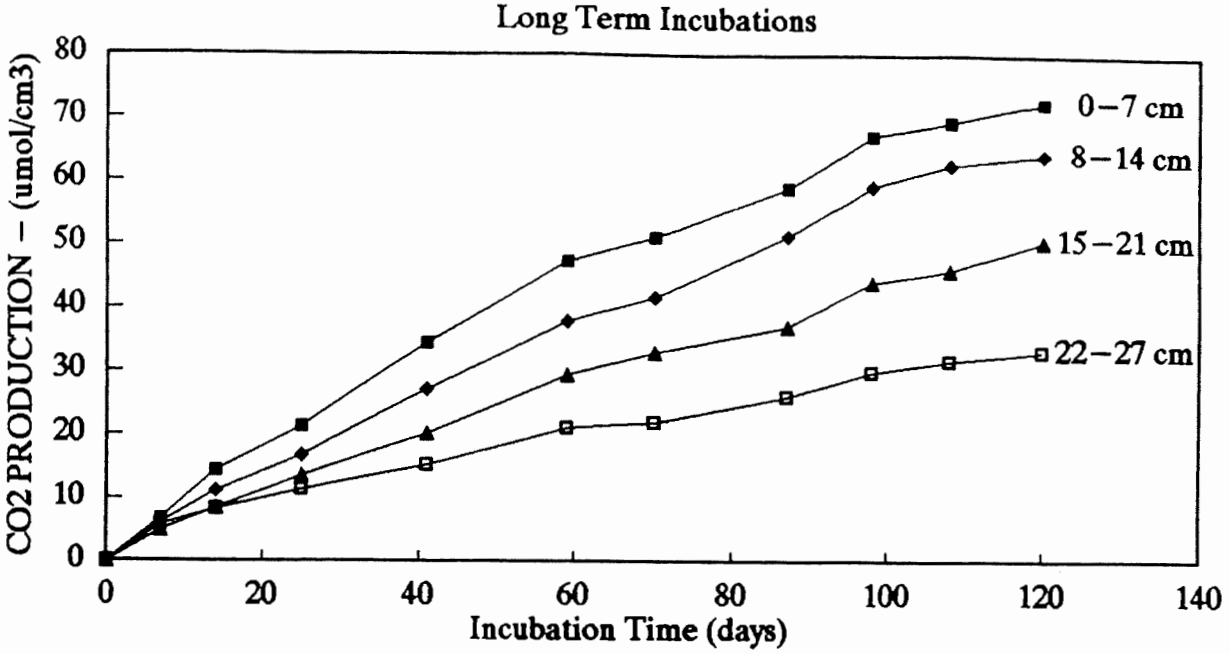

Figure 8A - Cumulative labile carbon production measured as umole CO_2/cm^3 obtained from extended incubation of subsamples collected at different depth intervals of a sediment core collected from station 2, New Bedford Harbor. Values are the mean carbon produced from duplicate flasks, corrected for a small seawater blank.

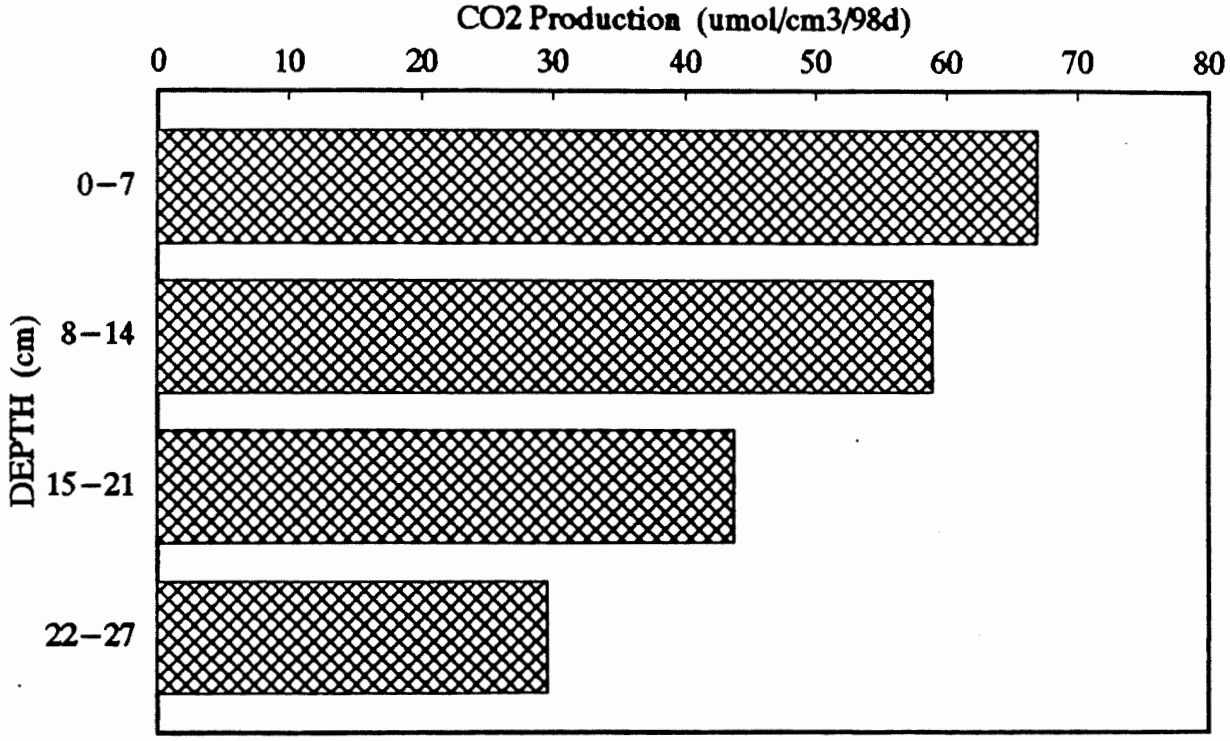

Figure 8B - The relationship between cumulative CO_2 production (94 days) and depth in the sediment core.

at depth. These differences with depth were maintained from day 25 through day 377 of the sediment incubations. Differences in the initial rates were not significant due to the early intra-treatment variation. These depth profile experiments (Figure 8A and B) suggest that the CO_2 production technique is indeed measuring differences in the labile organic matter pools which are known to diminish with sediment depth. In addition, the fact that differences in CO_2 production either between depths or between stations were maintained throughout the incubations in all the time course experiments also suggests that this CO_2 evolution technique may have some utility in screening sediments for relative organic matter loading rates. It is this consistent difference which is required in order to shorten the incubation period from nearly 400 days to something more manageable for routine work. Unfortunately, given the inconsistent results in the 7-14 day incubations, the required longer incubation almost certainly means that the assay will reflect a mixture of the highly and intermediately labile organic matter pools.

Labile Organic Matter Pool and Sediment Oxygen Demand - Taken in total, the time course experiments indicate that the CO_2 production technique does yield results which are consistent with sediment organic matter loading rates. However, in order to develop a utilizable technique for surveying potential high oxygen demand areas, the relationship between labile organic matter (LOM) and in situ sediment oxygen demand (SOD) must be quantified.

In order to make such comparisons of LOM and SOD it is first necessary to determine at what incubation time the comparison is to be made. We determined this time (days) by calculating the annualized CO_2 production at each time point in the incubation for comparison to the annual SOD at each station in New Bedford Outer Harbor, the latter being determined in a companion study (Howes and Taylor, 1989).

Since both the summer and winter sediment collections yielded similar time courses (Figures 5 and 6) and nearly similar CO_2 production rates, the data have been pooled for this particular determination (Figure 9). In all cases the initial determination (9 days) was significantly higher than the subsequent measurements. This is likely the result of a stimulation in sediment respiration caused by oxygenating and slurrying the sediments. More important to the development of the technique, however, is the similarity in calculated annual rates from incubation times of between 40 and 150 days (Figure 9). The coastal pond sediments also showed a similar trend. The consistency of rate over this interval makes an incubation period of approximately 100 days the most likely to yield reproducible results. Fortunately, the 100 day CO_2 evolution also gives the best fit to the annual SOD at each station (see arrows, Figure 9). A better comparison of the LOM and SOD is presented in Figure 10 in which the 94 day LOM (closest to 100 day) for both the summer and winter determinations is plotted against the annual SOD for the six New Bedford Harbor stations. Given the narrow range of SOD observed it is not possible to ascertain a relationship with LOM at the present time. However, the data do fall about the 1:1 line (Figure 10), suggesting that assays of LOM in areas of lower and higher SOD may define a usable relationship. Rates of SOD in the present study are in the intermediate range for marine systems. However, a two order of magnitude difference exists in sediments from marine ecosystems and a greater portion of this range needs to be investigated as a next step in the development of a LOM/SOD technique.

Labile versus Total Organic Carbon - The total organic carbon content of the New Bedford Harbor sediments sampled before and after extended incubation are presented in Table 8. As stated above, the total organic carbon pool within a

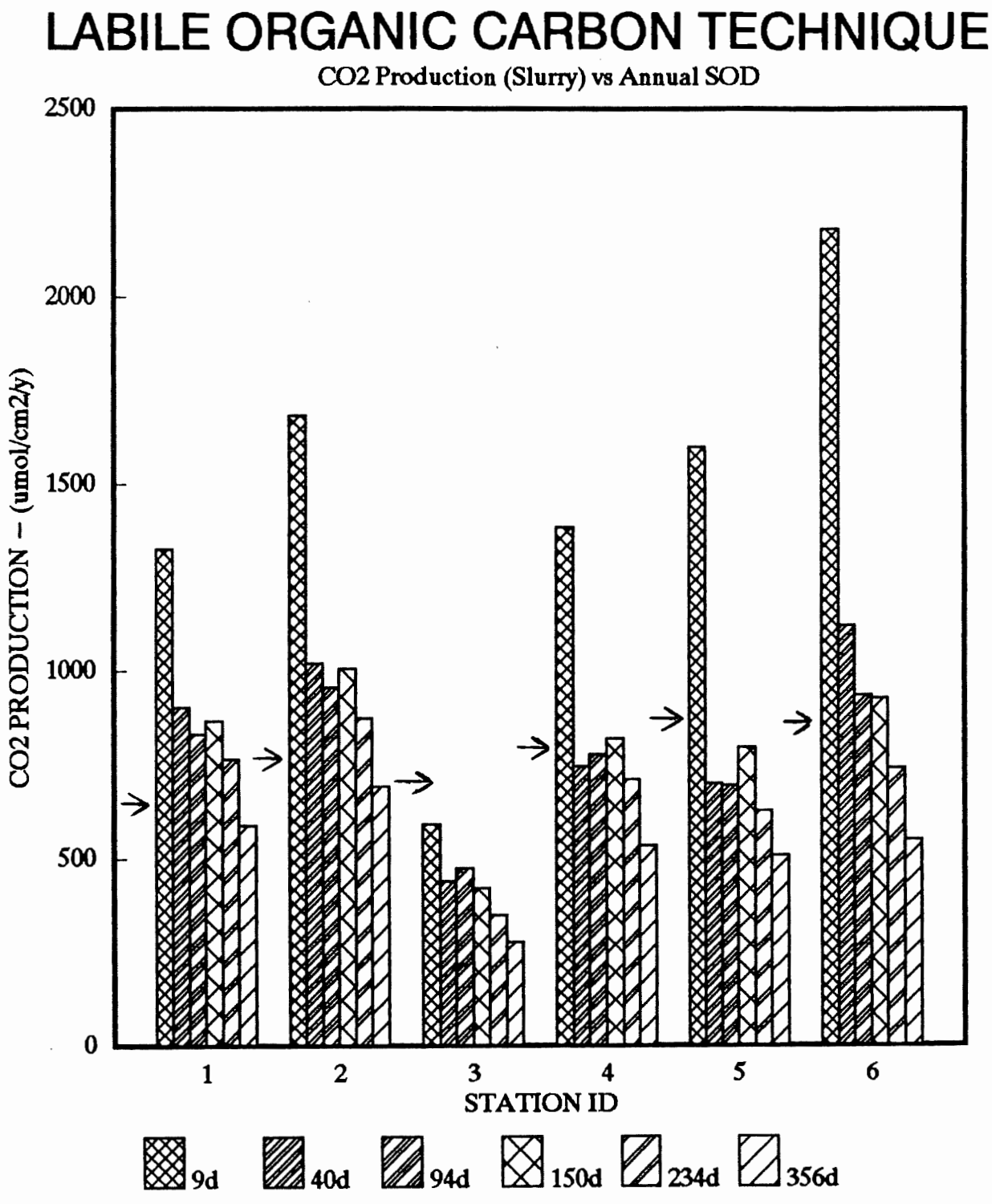

Figure 9 - Average CO_2 production from summer and winter sediments at each station in New Bedford Harbor with measured sediment oxygen demand indicated by the arrows; CO_2 production was adjusted to 365 days and integrated to cm^2.

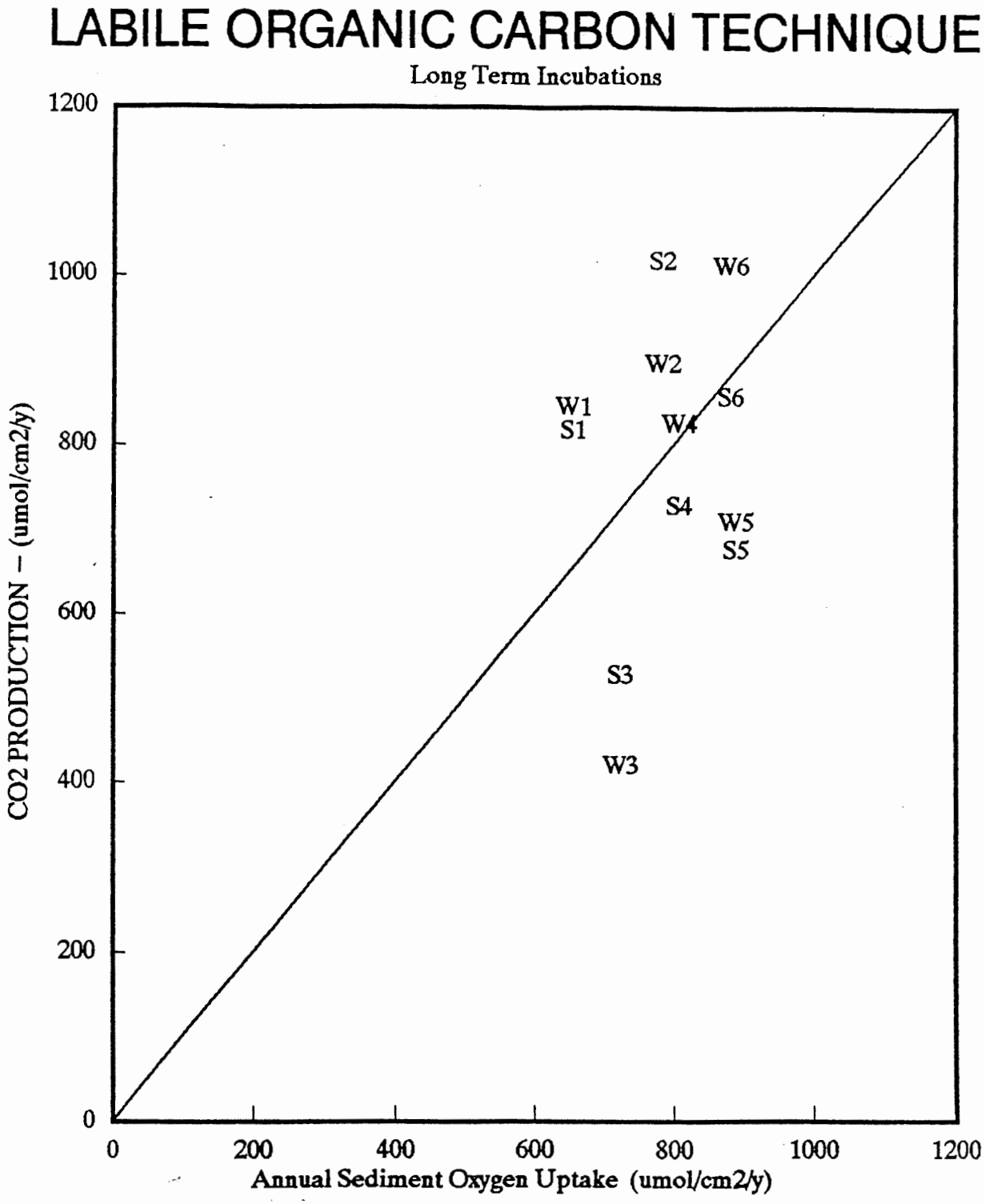

Figure 10 – Comparison of labile organic carbon in sediment samples from New Bedford Harbor as estimated from Sediment Oxygen Demand (SOD) and cumulative CO_2 production; cumulative CO_2 production at 94 days, adjusted to 365 days and integrated to cm^2.

Table 8. Organic Carbon Content of Initial Starting Sediments and Final Sediments after Extended Incubations

Station	mg Organic Carbon per g dry wt. sediment Initial Sediment	Final Sediment
I. Winter Sediments		
S-1	24.20	23.95
S-2	24.90	28.85
S-3	2.30	3.00
S-4	2.50	13.90
S-5	17.30	16.20
S-6	24.10	21.15
II. Summer Sediments		
S-1	23.00	23.50
S-2	29.50	28.85
S-3	1.80	2.10
S-4	3.10	3.80
S-5	20.20	18.70
S-6	21.60	21.15

Values were obtained by CHN elemental analysis after acidification to remove carbonate.

natural sediment is composed of organic matter with decomposition rates ranging from seconds to 1000s of years. In general, it is assumed that the bulk of the organic matter pool is refractory and is not significant in supporting system respiration (SOD). Our data suggest that this is the case for the fine grained sediments (Table 2) as generally less than 10% of the organic matter pool is mineralized even after one year (Figure 11). There was also no apparent difference observed between summer and winter sediments in % lability of organic matter. In strong contrast, in the sandy sediments (stations 3 and 4) almost 50% of the total organic matter pool was remineralized to CO_2 during these incubations. In addition, strong seasonal differences were found in these sediments with the highest proportion of LOM observed in the summer collection.

These results are consistent with our conceptual model of sediment carbon flow in the New Bedford Harbor system where the sandy sediments represent long-term areas of low sediment accumulation despite the fact that these sites are receiving similar amounts of organic matter deposition (on the short-term) as are adjacent locations. The net effect is a limited (low) but labile organic matter pool at these locations. These same conclusions can be made whether the LOM is determined by the CO_2 production technique (this study) or by the sediment oxygen demand technique (Howes and Taylor, 1989), indicating that the CO_2 production technique may have some utility in evaluating sediments for labile organic carbon.

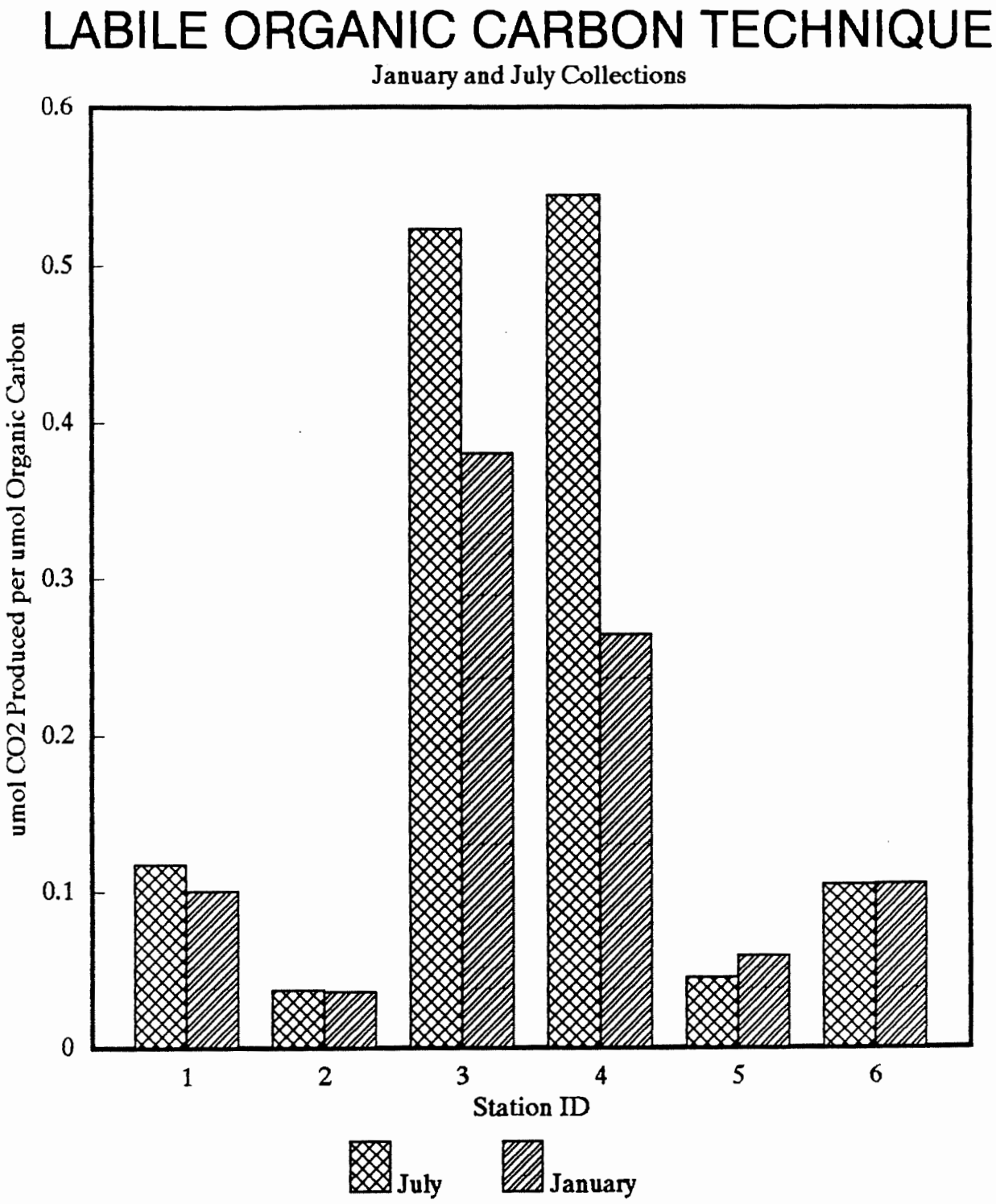

Figure 11- Average CO_2 production per umole of organic carbon for summer and winter sediments at each station in New Bedford Harbor; cumulative CO_2 production for 356 days; sediment organic carbon content determined by CHN elemental analysis after acidification.

References:

Black, C.A. (Ed.). 1965. Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties. Amer. Soc. Agronomy, Inc. Publisher, Madison, WI, pp. 1380-1385.

Cline, J.D. 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. Limnol. Oceanogr. 14:454-458.

Folk, R.L. 1974. Petrology of Sedimentary Rocks. Hemphill Publ. Co., Austin, Texas, 182pp.

Howes, B.L., J.W.H. Dacey, and G.M. King. 1984. Carbon flow through oxygen and sulfate reduction pathways in salt marsh sediments. Limnol. Oceanogr. 29:1037-1051.

Howes, B.L. and C.D. Taylor. 1989. Nutrient regime of New Bedford Outer Harbor. Infaunal community structure and the significance of sediment nutrient regeneration to water column nutrient loading. Report submitted to Camp, Dresser, and McKee, Inc.

Jorgensen, B.B. 1977. The sulfur cycle of a coastal marine sediment (Limfjorden, Denmark). Limnol. Oceanogr. 22:814-832.

Jorgensen, B.B. 1982. Mineralization of organic matter in the sea bed - the role of sulphate reduction. Nature 296:643-645.

Martens, C.S. and J.V. Klump. 1984. Biogeochemical cycling in an organic-rich coastal marine basin. 4. An organic carbon budget for sediments dominated by sulfate reduction and methanogenesis. Geochim. Cosmochim. Acta 48:1987-2004.

National Research Council. 1984. Ocean disposal systems for sewage sludge and effluent. National Academy Press, Washington, DC.

Sanders, H.L. 1958. Benthic studies in Buzzards Bay. I. Animal-sediment relationships. Limnol. Oceanogr. 3:245-258.

Sanders, H.L. 1960. Benthic studies in Buzzards Bay. II. The structure of the soft-bottom community. Limnol. Oceanogr. 5:138-153.

Science Applications International Corp. 1987. Buzzards Bay REMOTS Survey. New Bedford to Station "R" Transect. Report #SAIC-87/7535, Newport, RI, 2 pp.

Smayda, T.J. 1988. Assessment of primary productivity and eutrophication potential in New Bedford Outer Harbor in response to nutrient regime and potential inputs. Final Report to Camp, Dresser and McKee, Inc., Mackerel Cove Assoc., Saunderstown, RI.

Standard Methods for the Examination of Water and Wastewater. 1985. 16th edition. Amer. Public Health Assoc., Washington, DC, pp. 285-287.

Tyler, M.A. 1986. Flow-induced variation in transport and deposition pathways in the Chesapeake Bay: The effect of phytoplankton dominance and anoxia. In: D.A. Wolfe (Ed.), Estuarine Variability. Academic Press, Orlando, FL, pp. 161-176.

U.S. Congress, Office of Technology Assessment. 1987. Wastes in Marine Environments. OTA-0-334, U.S. Government Printing Office, Washington, DC, 119 pp.

Westrich, J.T. and R.A. Berner. 1984. The role of sedimentary organic matter in bacterial sulfate reduction: the G model tested. Limnol. Oceanogr. 29:236-249.