January 1992

Sediment Denitrification in Boston Harbor

Massachusetts Water
Resources Authority

Environmental Quality Department
Technical Report No. 92-2

SEDIMENT DENITRIFICATION

IN BOSTON HARBOR

by

John R. Kelly
Barbara L. Nowicki

prepared by:
Battelle Ocean Sciences
397 Washington Street
Duxbury, MA 02332
(508) 934-0571, and

University of Rhode Island
Narragansett Bay Campus
Narragansett, RI 02882

prepared for:
Massachusetts Water Resource Authority
Charlestown Navy Yard
100 First Avenue
Boston, MA, 02129
(617) 242-6000

Environmental Quality Department Technical Report Series No. 92-2

January 1992

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 INTRODUCTION

Denitrification in soft-bottom sediments of shallow coastal marine ecosystems produces nitrogen gas from inorganic nitrogen dissolved in seawater or sediment pore water. In doing so, dissolved inorganic nitrogen that could be available to photosynthetic organisms as a nutrient for primary production is converted to a form that is nonnutritive, unutilized, and, thus, exported from the water to the atmosphere by degassing. Studies in the 1980s (cf. Seitzinger, 1988) suggested that sediment denitrification may remove a substantial fraction of the nitrogen load to some coastal waters.

Direct measurements of denitrification have not been made in Boston Harbor prior to this study. Kelly (1991) raised the issue that a large fraction of the very high nitrogen loading to the Harbor may be exported. An unknown is how much export might occur via denitrification and subsequent loss to the atmosphere, as opposed to flushing, which provides an indirect source of biologically available nitrogen to offshore waters. Better definition of the routes and magnitude of nitrogen export from the Harbor is critical to enable solid understanding of the present coupling of Boston Harbor and Massachusetts Bay nutrient dynamics, especially relative to the future situation when the Massachusetts Water Resources Authority (MWRA) discharge of nitrogen will be diverted from Boston Harbor directly to Massachusetts Bay.

This report presents denitrification (as well as oxygen flux) measurements made for four sediment types representing different areas of Boston Harbor. A synchronous study (Giblin *et al.*, 1992) measured metabolism and dissolved inorganic nutrient (nitrogen and phosphorus) fluxes at the same stations.

This report has two major parts. Section 2 (Methods and Results) was prepared by Dr. Barbara Nowicki and Dr. John R. Kelly, based on the measurements made by Dr. Nowicki. The section presents the methodology used to estimate the flux of dinitrogen gas (N_2) from sediment cores taken from Boston Harbor. Section 3 (Discussion) was prepared by Dr. John R. Kelly and interprets N_2 fluxes with respect to the sedimentary environment of Boston Harbor and with respect to other fluxes of nitrogen in, around, and through Boston Harbor.

2.0 METHODS AND RESULTS

2.1 METHODS

2.1.1 Sediment Core Collection and Transfer to Gastight Chambers

Stations were located by using a Northstar 800 GPS/Loran C system. The Northstar system automatically chooses between the GPS (Global Positioning System) and Loran C, depending on best accuracy. The GPS has an absolute accuracy of approximately 100 m, and the Northstar automatically corrects the latitude/longitude position when the system is in the Loran mode. Latitude/longitude positions were checked at fixed calibration points in Boston Harbor. Stations for core studies were occupied during grab sampling conducted from September 16-20, 1991 (Kelly and Kropp, 1992); the core stations reoccupied four of those for which grab sampling was successful (Appendix).

On September 23, 1991, scuba divers retrieved two sediment cores (0.005 m^2) from each of four stations in Boston Harbor, along with other cores taken for companion flux studies (Giblin *et al.*, 1992). Cores were carefully pushed into the sediment to a minimum of 10 cm, then capped top and bottom. Core locations are shown in Figure 1 and station descriptions are given in Table 1. The cores were maintained in the dark in a cooler filled with seawater at ambient temperatures (15.1-16.5 °C), and were returned to the laboratory within 2.5 h of meeting the sampling boat and divers at the dock. A single carboy of water taken by a diaphragm pump from throughout the water column in the Harbor, filtered nominally to 1.0 μm, was also returned to laboratory and used to replace overlying water in all of the cores used for flux measurements.

The sediment cores were in excellent condition. The surface sediments (1 cm) of cores from Stations T2, T3, and T7 were light brown and well-oxygenated while lower layers were black in color. The cores from Station T8 were sandy and light-brown throughout. Live, apparently healthy benthic organisms were noted in all of the cores.

One of the two replicate cores from each station was chosen and the surface 5 cm of the core was transferred to a gastight chamber that had the same diameter as the collection core. For Station T2, both of the collected sediment cores were transferred to chambers, and one was designated as the

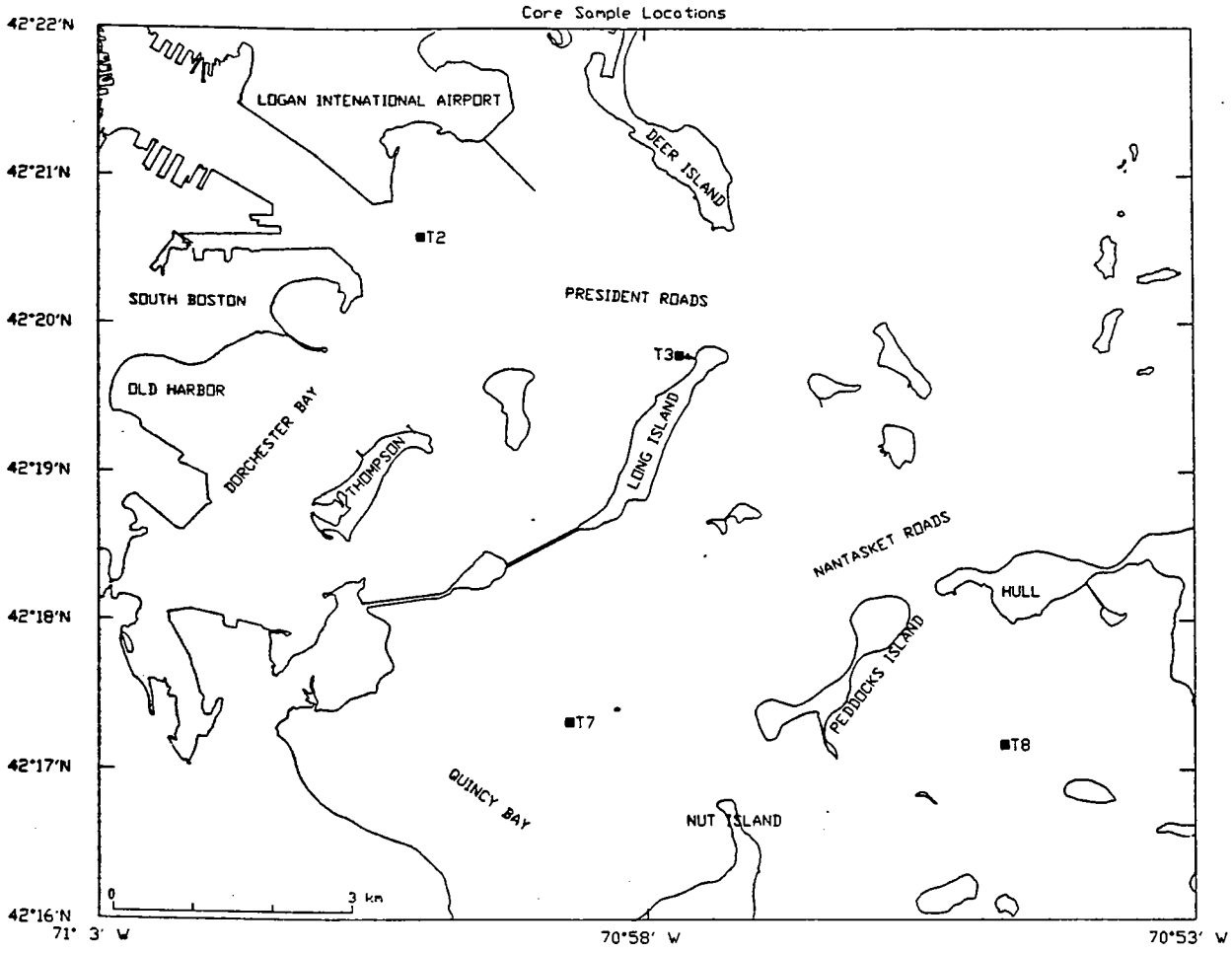


Figure 1: Map of Core Stations in Boston Harbor

Table 1: Boston Harbor Sediment Core Locations for Flux Studies (September 23, 1991).

Station	Core No.	Depth (m)	Lat. Long.	TD	H_2O Temp (°C)	Site Desc.
T2	3A,3B	12	42°20.59 71°00.04	14037.96 25857.84	16.5	Fine silt
T3	4A,4B	7	42°19.79 70°57.69	14026.73 25836.36	15.1	Fine silt
T7	1A,1B	6	42°17.32 70°58.7	14045.12 25829.39	15.9	Brown sand w/shell
T8	2A,2B	13	42°17.17 70°54.73	14020.24 25799.78	15.4	Hard sand

TD: Time delay.

"anoxic control core" (see Section 2.1.3). The transfer to incubation chambers was accomplished with minimal disturbance of the sediment-water interface (cf. Seitzinger *et al.*, 1980).

A description of the gastight chambers for denitrification measurements is given by Seitzinger *et al.* (1980) and Nowicki (1991). Briefly, the chambers were designed to hold an intact sediment layer, an overlying water column, and an air space above these two. The chambers were constructed of two sections of glass-walled pipe (total height: = 21.6 cm; diameter: = 7.8 cm), joined at the center with an O-ring and a metal clamp. Three glass stopcocks, sealed at the ends with rubber serum stoppers, served as sampling ports.

All sediments, once enclosed in gastight chambers, had their overlying waters carefully replaced with the Boston Harbor water (ca. 800 mL per chamber) that was collected at the time of core retrieval. The Boston Harbor water used in water exchange was sparged with He/O_2 to remove 95-99% of the ambient N_2 dissolved in seawater. Removal of nitrogen gas in the overlying water is necessary to detect the flux signal because there is such a large background concentration of N_2 in ambient seawater and the atmosphere (Seitzinger *et al.*, 1980). Following the initial water exchange, the air space (gas phase = 62 mL volume), was replaced with a helium/oxygen (He/O_2) gas mixture in the experimental cores, and with helium alone in the anoxic control core. Flushing with He/O_2 rapidly and effectively removed any remaining nitrogen gas introduced with water exchange, but also kept the oxygen concentration of the overlying water near the intended ambient values (or anoxic, in the case of the control core). Prior to each incubation (see Section 2.1.3), the gas phase in each chamber was flushed two to three times daily. This procedure ensured that any N_2 flux from sediments into the overlying in the intervening period was removed, establishing desired initial conditions of low N_2 concentration in the water/gas phase.

The sediment chambers were maintained in the dark at ambient collection temperatures. Each chamber was stirred continuously with a magnetic stir-bar positioned at the interface between the water and gas phases. The stirring rate (approximately 200 rpm) was adjusted to be fast enough to maintain a constant flow of water and particles across the sediments and to resuspend sediments slightly. The magnetic stir-bars mounted inside each chamber were rotated by an air-driven magnet mounted on top of each chamber. The air pressure driving the magnetic stirrers was carefully controlled to maintain constant and equal stirring rates for all chambers. The purpose of stirring is to

keep water and gas phases homogeneous and equilibrated with respect to the gases of interest (Seitzinger *et al.*, 1980).

2.1.2 Gas Sampling

Measurements of the concentrations of nitrogen and oxygen in the gas phase of each chamber were made by withdrawing gas samples through the chamber sampling ports. Replicate 50-μL samples were withdrawn using a gastight syringe that was preflushed with helium and then inserted through a rubber serum stopper in the sampling port. To prevent atmospheric contamination of N_2, the sampling port, syringe, and gas chromatography (GC) injection port were flushed continuously with helium during sampling; additionally, chambers were opened only when a slight positive pressure from the appropriate gas mixture was applied (cf. Seitzinger *et al.*, 1980).

Nitrogen (N_2) and oxygen (O_2) were measured by injecting gas samples into a Hewlett-Packard Model 5890A gas chromatograph equipped with a thermal conductivity detector. An 1/8 in. stainless steel column (2 m) packed with 5-Å molecular sieve (45/60 mesh) was operated at room temperature with a He carrier gas flow of 35 mL/min. Calibration curves were run with each set of samples, using a certified standard gas mixture (3% N_2, 20% O_2, balance He). Gas and water phases rapidly equilibrate in the system; therefore fluxes into the water from the sediments may be calculated knowing the changes in N_2 and O_2 sampled in the gas phase during an incubation and the volume of gas in each chamber (Seitzinger *et al.* 1980).

2.1.3 Estimating Denitrification: Correction for a Diffusive Flux Artifact

The method used here to calculate biological denitrification rates followed the method originally developed by Seitzinger *et al.* (1980), as slightly modified by Nowicki (in prep). Since the method involves stripping the overlying water and gas phases of nitrogen gas (see above), an artifact is introduced. Nitrogen gas dissolved in pore waters degasses from the sediment column because a diffusive gradient has been created between the overlying water and sediment pore waters. Equilibration of pore water and overlying water dissolved N_2 concentrations is not as rapid as equilibration between water and gas phases, and thus N_2 continues to "bleed" out of the sediments into the water over time. The total measured N_2 flux (F_t) estimated by increase of N_2 in the water/gas phase during

a sealed (but aerobic) incubation may be characterized as: $F_t = F_p + F_d$, where F_p is the production of N_2 (the flux due to denitrification activity that is if interest) and F_d is degassing flux, a physical diffusion process induced by maintaining a relatively N_2-free environment in the water and gas phases.

In theory, F_d should decrease over time as the sediment pore waters gradually become equilibrated with the overlying water/air. Based on several tests and calculations, the original method used a strategy of waiting to incubate cores for a period of time (about 6 to 10 days) thought to be sufficient to diminish F_d. The assumption was that by waiting long enough, F_t will approximate F_p (Seitzinger *et al.*, 1980; Seitzinger, 1987).

Seitzinger (1987) also used an anoxic control to assess non-biological flux of N_2 (i.e., F_d). Briefly, a core was treated in the same fashion as an experimental core, except that the gas used for sparging the overlying water, and for filling the gas phase of this chamber was helium alone, without oxygen. Any residual oxygen in the core quickly became removed by daily gas-phase flushes. Studies of Seitzinger have shown that nitrate nitrogen (NO_3) disappeared from the pore waters and overlying water of anoxic cores treated in this manner. Any residual N_2 production observed in the anoxic core may be assumed to be due to a background physical flux (due to pore-water degassing) since biological production of N_2 gas through denitrification has been blocked by anoxia and the lack of an NO_3 source. Seitzinger made checks on a core *following* measurements of F_t.

Nowicki (in prep) describes the use of a replicate core as an anoxic control incubated *in parallel* with an experimental core. The control core is treated in exactly the same fashion as an experimental core throughout the measurement period in the laboratory; the only difference is that the gas used for sparging and for flushing the chamber is helium alone, without oxygen. This modification allows one to correct for physical degassing *at the same time* incubations are made. Simple subtraction of the anoxic control core flux (F_d) from the rate measured synchronously in an experimental core (F_t) estimates F_p.

The difference between the calculated denitrification rates using parallel control-corrected and uncorrected methods is not necessarily large and depends on the timing of the incubation relative to establishment of an N_2-impoverished overlying water/gas phase. In general, the parallel correction

method will yield denitrification estimates that are lower than those using the original method if rates are measured within six to ten days after collection. The advantages of the modification are that it allows a direct correction for F_d and enables measurements to be made with less waiting time (Nowicki, in prep).

2.1.4 Description of the Incubations for Boston Harbor Sediments

Three incubations were done to measure sediment N_2 release and O_2 uptake in experimental cores from all four stations. In parallel, a replicate control core from Station T2 followed the same series of incubations, but was kept continuously anoxic. During an incubation a chamber was completely sealed; no exchanges of either the gas or water phases were made. The first two incubations provided a) two separate flux estimates of F_t from sediments at each four stations under aerobic conditions similar to those measured in bottom waters of Boston Harbor and b) two separate estimates of F_d under anoxic conditions from one core. Because only five chambers were available, the one anoxic control was used as a correction to estimate F_p in all cores. All cores started with approximately the same concentration of N_2 in water and sediments and minor differences in sediment porosity could have only a small effect on the rate of degassing (Nowicki, in prep.); thus use of a single control was deemed sufficient. As a check, however, the third incubation provided a direct measure of F_d for *all* cores after completion of F_t measurements.

During days 0-3 following collection, the cores were flushed as described in Section 2.1.1. Incubation #1 occurred during days 3-5, included a three-point flux measurement, and was terminated prior to a fourth measurement because oxygen concentrations in the cores were becoming low enough (5 mg O_2 L^{-1}) to perhaps affect N_2 production rates. After Incubation #1, air and water phases were flushed to return to initial conditions similar to Incubation #1.

Incubation #2 occurred during days 7-18 following core collection. This was a long incubation during which oxygen concentrations in the chambers were allowed to decline naturally over time to 0 mg O_2 L^{-1}. The chambers were allowed to become anoxic during this incubation and both N_2 and O_2 flux rates were measured during the period of decreasing O_2 concentration. This additional sampling was not requested as part of the original contract, but the data are included in the Appendix to provide a complete time course for concentrations in water over the sediments. The O_2 and N_2 flux

regressions to estimate F_t for Incubation #2 include only the first four measurements during the incubation period, taken before oxygen concentrations decreased to a level that may have affected the linearity of N_2 production.

For the final flux estimate, the chambers remained sealed and Incubation #3 occurred during days 22-28 following core collection. All chambers were completely anoxic, and N_2 fluxes reflect a degassing of the background nitrogen gas remaining in the sediment pore waters.

2.1.5 Data Analysis, Error Analysis, and Analytical Quality Control

The slope of the linear regression of the amount of N_2 or O_2 in the gas phase of the sealed chamber versus time provides a direct estimate of flux as mass per unit time. Dividing this slope by the sediment surface area in the chamber yields an area-based rate. Each point in the linear regressions consisted of two or more replicate samples of the gas phase of the sealed chambers at a given time. Initial rates of nitrogen gas production and oxygen uptake were always linear over time in all cores. An analysis of variance was used to calculate 95% confidence limits around the slopes of regressions of nitrogen concentration over time. The coefficient of variation for the slopes of all of the daily standard curves obtained during the 30-day course of sampling was $\pm 4\%$.

Observed fluxes of N_2 gas in experimental cores were corrected for the background flux of N_2 observed in the anoxic control core. Since both the experimental core flux and the anoxic control core flux have an error term [95% CI (confidence interval)] associated with them, the error in the resulting corrected N_2 flux was calculated (propagated) according to Ramette, (1981) as follows.

$$R \pm r = (A \pm a) - (B \pm b),$$

$$r = \sqrt{a^2 + b^2},$$

where A and B are N_2 fluxes for experimental and control cores with their associated error terms (a, b), and r is the propagated error in the final corrected N_2 flux.

2.2 RESULTS

Just prior to the core collection, the flux stations were chosen from a larger set occupied in a benthic survey to be representative sites from different regions of Boston Harbor, but the sites also varied in depth and in sediment character (Table 1). Measurable fluxes of N_2 gas from the sediments were recorded at all four stations for the first two incubations, and rates well exceeded that measured in the control core (Figure 2). A summary of calculated flux rates for all cores is provided in Table 2, which also includes control corrected and uncorrected rates for N_2; further details are provided in the Appendix.

The anoxic control core flux declined over time, which was to be expected if sediment pore waters degassed over time. The control core flux was 58 μmol N_2 m^{-2} h^{-1} for the 3-5 days following collection (Incubation #1), 27 μmol N_2 m^{-2} h^{-1} for days 7-11 (Start of Incubation #2) and 9 μmol N_2 m^{-2} h^{-1} for days 22-28 (Incubation #3). In comparison, the anoxic incubations on the experimental cores at Incubation #3 gave flux estimates of 5 to 17 μmol N_2 m^{-2} h^{-1}. Considering the associated measurement errors and subsequent estimate uncertainties, all four of the experimental core flux 95% CIs (Table 2) overlapped with that of the control core from Station T2. The results confirm it is reasonable to correct all four stations using the single anoxic control fluxes over the course of the first two incubations, and this has been done in Table 2.

Confidence intervals for flux estimates are included only for nitrogen flux. These show larger CIs for the first incubation than for the second because the regressions for incubation #1 included only three points in time, whereas the second included four points. The first incubation was cut short after three measurements to avoid any potential inhibition of flux by lowered oxygen concentration in the overlying water. However, the results of Incubation #2 suggest that N_2 flux rates remain linear at O_2 concentrations as low as 0.5 mg O_2 L^{-1}. Therefore, future incubations could be run over the longer period to increase the precision of the estimate.

Using corrected rates of Table 2 (used through the rest of this report, unless specified), the denitrification rates varied by location. Rates were lowest, about 24 to 30 μmol N_2 m^{-2} h^{-1}, for Station T8 in Hingham Bay. Rates were highest, 95 to 97 μmol N_2 m^{-2} h^{-1} at Station T3 in the northern Harbor off Long Island. Rates at Station T7 in Quincy Bay were second-highest (80 to 85 μmol N_2 m^{-2} h^{-1}) and

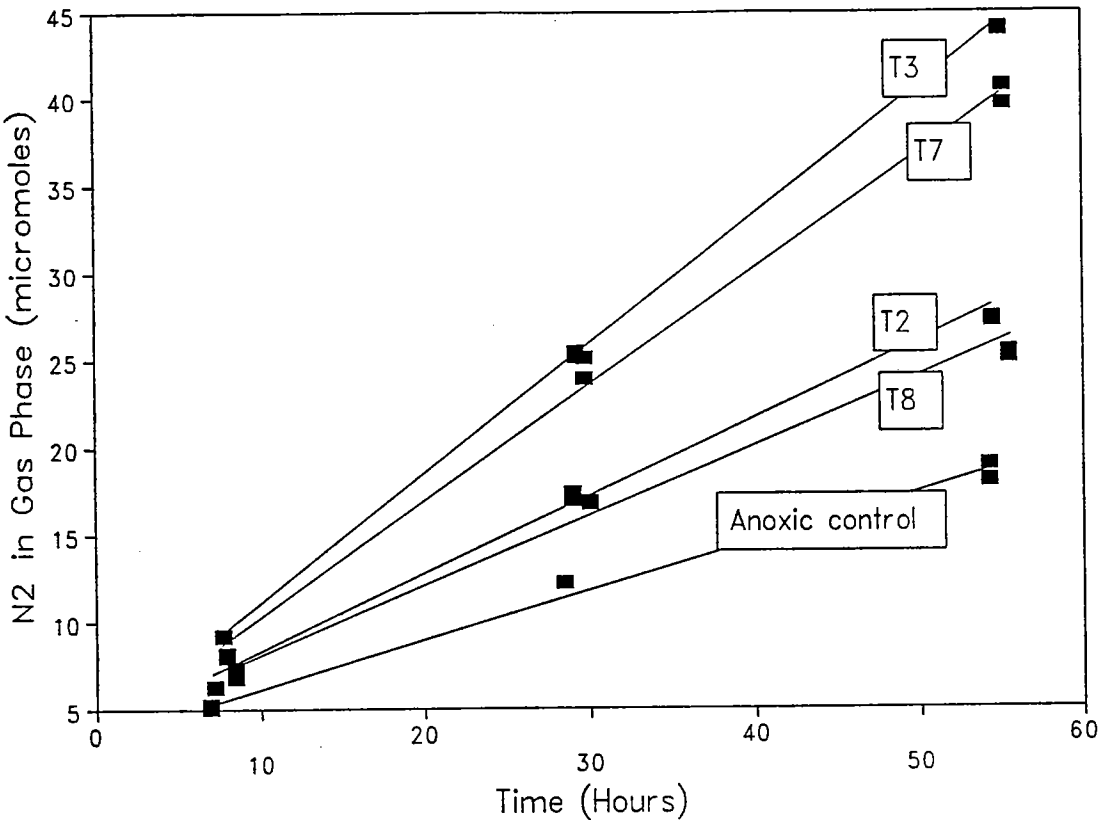


Figure 2: N_2 Increase during Incubation #1.

Lines are drawn by eye. Data and regressions are given in the Appendix.

Table 2. Summary of Flux Measurements in Boston Harbor

Station	Incubation	Days	O_2 Flux ($mg\ O_2\ m^{-2}\ h^{-1}$)	N_2 Flux[a] ($\mu molN_2\ m^{-2}\ h^{-1}$)	Anoxic Control Flux[a,b] ($\mu molN_2\ m^{-2}\ h^{-1}$)	Corrected N_2 Flux[a] ($\mu molN_2\ m^{-2}\ h^{-1}$)
T2	1	3-5	-33	94±9	58±7	36±11
	2	7-11	-28	74±2	27±3	47±4
	3	Anoxic	—	17±5	9±2	—
T3	1	3-5	-33	155±2	58±7	97±7
	2	7-11	-28	122±4	27±3	95±5
	3	Anoxic	—	12±2	9±2	—
T7	1	3-5	-36	143±12	58±7	85±14
	2	7-11	-38	107±2	27±3	80±4
	3	Anoxic	—	16±5	9±2	—
T8	1	3-5	-32	82±8	58±7	24±11
	2	7-11	-27	57±5	27±3	30±6
	3	Anoxic	—	5±2	9±2	—

[a]Errors show 95% CIS around slopes of regressions, determined as described in Section 2.1.5.
[b]For incubations #1 and #2, this value is from single control core taken at Station T2.

Station T2 on the flats just outside the entrance to the Inner Harbor were in the range of 36 to 47 μmol N_2 m^{-2} h^{-1}. The corrected rates measured for each core were remarkably consistent across incubations #1 and #2; the 95% CIs for fluxes at each station overlapped for the two measurements.

In contrast to the range in N_2 flux, oxygen metabolism (uptake of O_2 by the sediment) had markedly less variability across stations (Table 2). Rates ranged from about 27 to 38 mg O_2 m^{-2} h^{-1} and were consistent across measurements at each station. Station T7 in Quincy Bay had the highest oxygen metabolism, but only slightly higher than the other three stations (Table 2). As discussed in Giblin *et al.* (1992), oxygen metabolism rates measured in these denitrification studies were similar to rates measured on separate cores incubated in companion nutrient flux and metabolism studies.

At the end of the flux studies, the Boston Harbor water being used for replacing overlying water of the cores was analyzed for nutrients (Table 3). Values were slightly higher than the original concentrations at collection in the Harbor (see Giblin *et al.*, 1992), as expected, because of decomposition from being held in the dark for a month. Even so, the nutrient concentrations (specifically NH_3, NO_3, NO_2, and PO_4) in replacement water were within the range observed in Fall in the Harbor (Robinson *et al.*, 1990) and, notably, NO_3 concentrations were not sufficient to alter denitrification in the sediments.

Table 3: Nutrient Concentrations in Filtered Boston Harbor Water Used for Incubations.[a]

Nutrient	μM
NO_{2+3}	5.6
PO_4	1.72
SiO_2	4.02
NH_3	11.18
NO_2	0.66

[a]Concentrations were measured at end of studies and, thus, are slightly higher than are the *in situ* concentrations at collection.

3.0 DISCUSSION

3.1 DENITRIFICATION RATES IN BOSTON HARBOR SEDIMENTS

3.1.1 Boston Harbor Compared to Other Coastal Marine Areas

Denitrification rates measured in Boston Harbor sediments were within the range of values reported in the literature for coastal marine sediments. The benthic flux of N_2 at Stations T3 and T7, respectively averaged 96 and 82.5 μmol N_2 m^{-2} h^{-1} (or 192 and 165 μmol m^{-2} h^{-1} as *N*, i.e. when doubled to account for the diatomic nature of the gas). These rates are at the high end of rates estimated for many of the coastal sediments that have been examined (by the direct technique used here, or by other techniques), although there are reports of rates in the range of 200 to slightly over 1000 μmol N m^{-2} h^{-1} (Seitzinger, 1988). Seitzinger (1988) reported rates (*not parallel-control corrected*) as high as 109 μmol N m^{-2} h^{-1} for silt/clay sediments in Narragansett Bay, which is the nearest estuary for which direct denitrification rates are available. Narragansett Bay receives less nutrient loading than Boston Harbor (Kelly, 1991).

The rate of sediment denitrification apparently increases with nutrient loading (Seitzinger, 1988). Nowicki and Oviatt (1990) reported (uncorrected) denitrification rates in the Marine Ecosystem Research Laboratory (MERL) experimental mesocosms. One control set of tanks only Narragansett Bay water, and another set received daily nutrient additions to bring total nutrient loading to a level comparable to Boston Harbor. The relative change in denitrification rates between nutrient enriched and control situations was about a factor of four, which is similar to the relative range observed across sites in Boston Harbor (see Table 2).

At the four Boston Harbor stations, sediment metabolism and nutrient cycling were measured by Giblin *et al.* (1992). They have reported that nitrous oxide gas (N_2O), a possible endproduct of nitrification/denitrification activity, was measurable but very small and of no significance to the total N flux from the sediment.

Giblin *et al.* (1992) compared predicted denitrification from their measurements, applying a stoichiometric model, to the rates measured directly, as reported here. Denitrification rates by the direct

method were higher than one would predict from using the measured O/N flux ratios, as compared to expected aerobic organic matter decomposition stoichiometry. However, when total metabolism (including oxygen uptake and an estimate of anoxic metabolism) was considered, their model predicted fluxes only slightly lower than the rates of N_2 flux reported here. Given these findings, using O/N flux stoichiometry to infer denitrification is unwise; furthermore, additional comparisons of the methods are advisable.

3.1.2 Spatial Variation of Benthic Fluxes

Benthic nutrient fluxes in September 1991 varied at the four stations in the Harbor (Giblin *et al.*, 1992). However, the spatial variation in dissolved inorganic nitrogen (DIN) flux (DIN = ammonium + nitrate + nitrite) did not coincide with the pattern of denitrification. For DIN, rates were highest at T2, which had relatively low denitrification rates.

The pattern of fluxes relative to total organic carbon (TOC) content of the sediments was revealing. Station sediment chemistry data (surface 2 cm) was gathered by grab sampling during the week prior to core collection at points within 150 m of each the flux core collections (see Appendix and also Kelly and Kropp, 1992). These data show a factor of four variation in percent TOC across the stations. Station T8 had the lowest percent TOC in the grab sampling. The location for Station T8 core collection was slightly to the south of the grab station; by the visual sediment descriptions, the core station was sandier than the grab station and may therefore have had lower organic content. Flux Station T2 was slightly to the East of grab Station T2, and in deeper water. Denitrification fluxes have been plotted versus percent TOC using the grab station data (Figure 3). The result shows a strong linear relationship between N_2 flux and organic content, the sediment organic content and denitrification both decreasing in the order T3 > T7 > T2 > T8. To our knowledge, this is the first evidence that shows a strong correlation of sediment organic content and denitrification in nature.

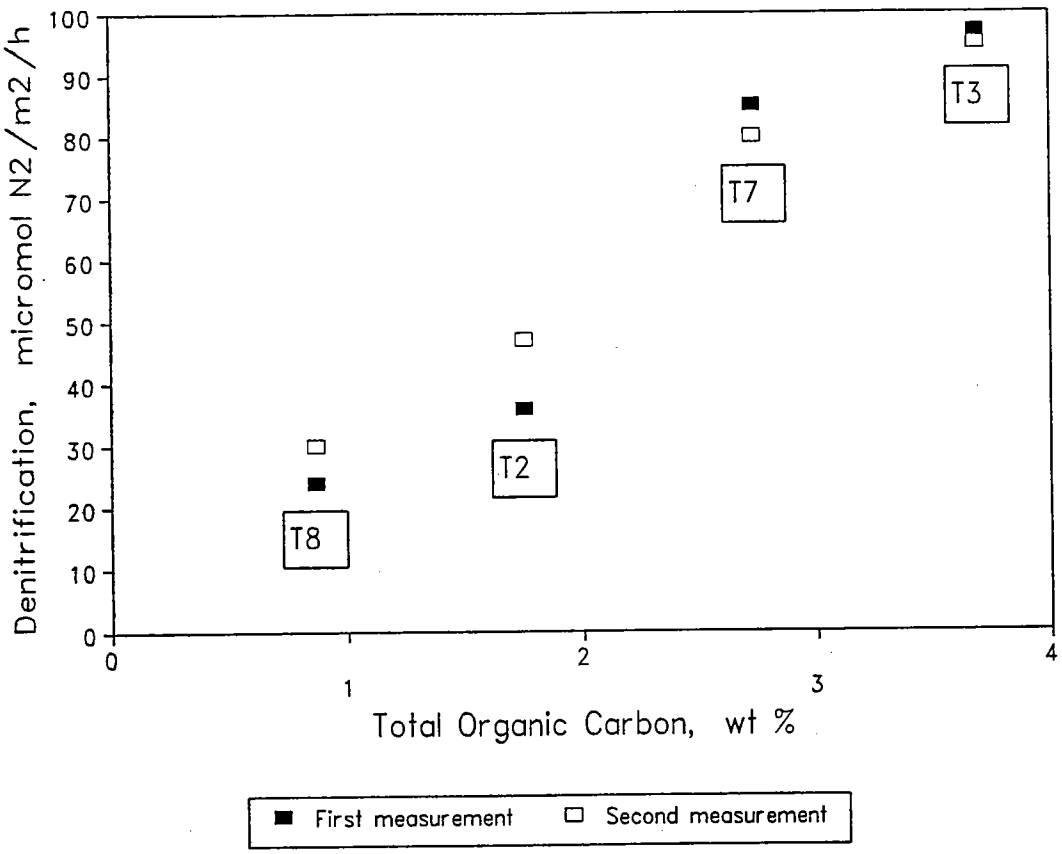


Figure 3: Relationship between Sediment Denitrification and Total Organic Carbon in Sediments.

A linear regression described the pattern, $Y = 26.3\ X + 2.25$ (n=8, r^2 =0.97).

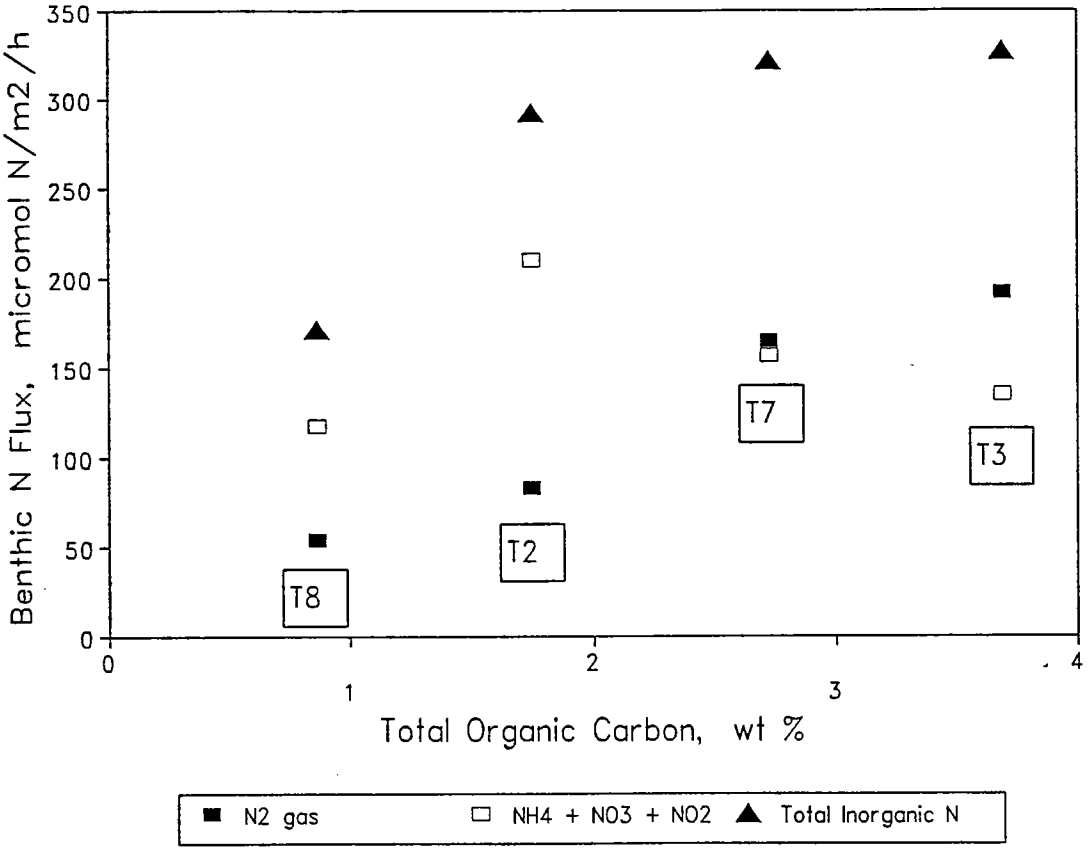


Figure 4: Benthic Flux of N_2 and DIN as Related to Total Organic Carbon in Sediments.
Average fluxes for a station are compared (all as μmol N). Total inorganic N is the sum of N_2 and DIN.

As shown in Figure 4, where all N fluxes are expressed in the same units, DIN fluxes did not follow the denitrification pattern with enrichment but seemed to increase to an intermediate carbon content, then decrease with higher carbon enrichment. Kelly *et al.* (1985) observed this same type of pattern of DIN flux when it was plotted against nitrogen loading in experimental mesocosms.

The consequence of the two flux patterns, i.e., of denitrification and DIN, is that total N flux from the sediments approached a maximum at a TOC content between 2% to 3% dry weight (Figure 4). In sediments with higher organic content, the N flux as N_2 equaled or exceeded the DIN flux, and thus constituted more than 50% of the total N flux (up to 58% at Station T3). In contrast, in sediments with lower sediment TOC content, the majority of the flux was as DIN. For Station T8, about 31% of the flux was as N_2 and for Station T2 about 28% of the flux was as N_2. Seitzinger's (1988) summary suggests that a range of 15% to 75% of the total benthic N flux may occur through denitrification for the dozen coastal marine sites where she was able to find data. All the sites in Boston Harbor lay within this range.

3.1.3 Denitrification As Sensitive to Harbor Recovery

It has been known for some time that benthic nutrient and denitrification fluxes are sensitive to changes in nutrient loading and organic deposition, including both decreases (Smith *et al.*, 1981) and increases (Kelly and Nixon, 1984; Kelly *et al.*, 1985; Seitzinger, 1988). The relationship between sediment TOC and denitrification in Boston Harbor confirms that the direct measure of denitrification may well be a good indicator of changes in nutrient discharge practices. The prediction from Figure 3 would be that a decreased sediment denitrification rate would ensue in the Harbor as loading deceases.

Figure 3 shows denitrification as related not to loading but to organic content. What is not known at present is whether denitrification is really coupled with the *concentration* of carbon stored in the surface sediments, or whether it is linked primarily to the variation in the *flux* of carbon to the sediments (cf. Kelly and Nixon, 1984). The distinction on controlling mechanisms (concentration versus flux) might be important with regard to the pace of recovery. For example, if denitrification were controlled by carbon flux, the denitrification response might be faster than if it were controlled

by stored carbon, for it can take some time for the stored reservoir to be metabolized. Importantly, the pace of denitrification response could affect the recovering Harbor's nutrient budget and its apparent conversion of input nitrogen to N_2 gas loss.

At the upper end of the gradient of enrichment (greater than 2% TOC), DIN fluxes might not be as sensitive to change as denitrification (Figure 4). In contrast, at lower enrichment levels one might look for *simultaneous* decreases in denitrification and DIN flux as an indicator of response to decrease in nutrient inputs. Thus, the patterns seen here suggest that data on *all* forms of benthic nitrogen flux could provide valuable information on the progress of Harbor recovery.

3.1.4 Extrapolation of Denitrification to an Annual Value for Boston Harbor

The most appropriate timeframe for comparing different processes and rates for a nutrient budget is over an annual cycle. Denitrification has been measured only during September 1991; DIN flux has been measured during September of 1991 and 1992 only. We need to measure these rates at different seasons and temperatures to arrive at a better annual value. However, an extrapolation, as is often done for such flux data, is made here so that rates can be seen in the context of the Harbor nutrient budget. The extrapolation requires both spatial and temporal considerations, because the other elements of the Harbor budget have been examined as average Harbor-wide values.

The spatial consideration takes advantage of the Harbor-wide sediment sampling (Kelly and Kropp, 1992), from which Harbor averages are derived. The average surface sediment TOC content for 32 stations through the northern and southern Harbor areas (including the four of this study) was about 2.5%, with the range from 0.28% to 3.7%. Station T3 of these flux studies had the second highest value, 3.69%. From Figure 3 and the average TOC value of 2.5%, the average denitrification rate would be about 67 μmol N_2 m^{-2} h^{-1} (or 134 μmol N m^{-2} h^{-1}). Since the areas sampled were biased to silt/clay and soft-bottom depositional areas and the simple average does not weight the relative proportion of the Harbor covered by different sediment types, the average TOC value derived here is most likely to be maximal and thus lead to maximal estimates of denitrification.

A common procedure to average across time uses a relationship between flux and temperature (Nixon *et al.*, 1976, 1980). Denitrification usually is slower at colder temperatures, but there appears to be

insufficient data to describe a flux/temperature relationship in nature (Seitzinger, 1988). Data generated in the MERL experiment discussed previously (Nowicki and Oviatt, 1990) are suitable, however. From the experiment, there were data across a temperature range from 4 to 18 °C. Fluxes (uncorrected, $n=11$) showed the common strong exponential relationship to temperature (r^2 = 0.78), where the Q_{10} (relative flux increase for each 10 °C rise in temperature) was 3.8, similar to that seen for metabolism and nutrient flux (e.g., Nixon *et al.*, 1976, 1980). Using the slope of the flux/temperature relationship, along with the average September flux for Boston Harbor as a whole (above), combined with a month-by-month temperature distribution for the Harbor (Robinson *et al.*, 1990), monthly denitrification fluxes were calculated. The sum of all months gives the annual value of 666 mmol N m^{-2} $year^{-1}$. As an average rate, this represents 76 μmol N m^{-2} h^{-1}, which is 57% of the estimated Harbor average for September 1991 (134 μmol N m_{-2} h_{-1}).

This preliminary estimate is based on few data and tentative extrapolations. We anticipate refining the estimate through additional measurements at these stations at different seasons of the year.

3.2 PRESENT STATUS OF THE BOSTON HARBOR NUTRIENT BUDGET

Several important aspects of the Harbor nitrogen budget either have been measured, estimated, or can be calculated from data in the literature. Accordingly, one can construct a rough budget of nitrogen flow and examine the relative importance of sediment denitrification as a sink for nitrogen in the context of other rates. A tentative nitrogen budget is compiled here and presented on an annual basis. Rates are also expressed as a fractions of the known annual nitrogen input to the Harbor (Figure 5).

3.2.1 Input

Menzie *et al.* (1991) recently estimated the annual total nitrogen input to Boston Harbor at about 13,086 metric tons, about 74% of which (~9663 metric tons) is delivered to the northern Harbor area north of a line of division extending along the length of Long Island (Figure 1). The area-based loading for the whole Harbor is 8643 mmol N m^{-2} $year^{-1}$ (Figure 5), with the northern Harbor receiving more on an area basis than the southern Harbor [i.e., about 13,500 versus 4286 mmol N m^{-2} $year^{-1}$ (see Kelly, 1991)]. For both the northern and southern areas of the Harbor, over 90% of the estimated load is from the MWRA discharges to the Harbor (as effluent, plus sludge in the case of the northern Harbor). On either a subdivided or a whole basis, Boston Harbor receives very high nitrogen loading as compared to most coastal marine areas, more even than some of the most intensively fertilized agricultural fields (Kelly and Levin, 1986; Nixon *et al.*, 1986).

3.2.2 Internal Cycling

Phytoplankton production has been estimated to be on the order of 325 to 350 g C m^{-2} $year^{-1}$ in the Boston Harbor area and immediately offshore (Michelson, 1991; Cura, 1991). The estimate is low as compared to some other highly enriched coastal waters, but there may be limiting factors other than nutrients (Kelly, 1991). Assuming a probable maximum of 350 g C m^{-2} $year^{-1}$ and Redfield stoichiometry (6.625 atoms C per atom of N) implies an uptake requirement of 4403 mmol N m^{-2} $year^{-1}$ for the Harbor. The input is well in excess of this, and primary producers appear to incorporate a maximum of only 51% of the input into net production (Figure 5). Commonly, in eutrophic

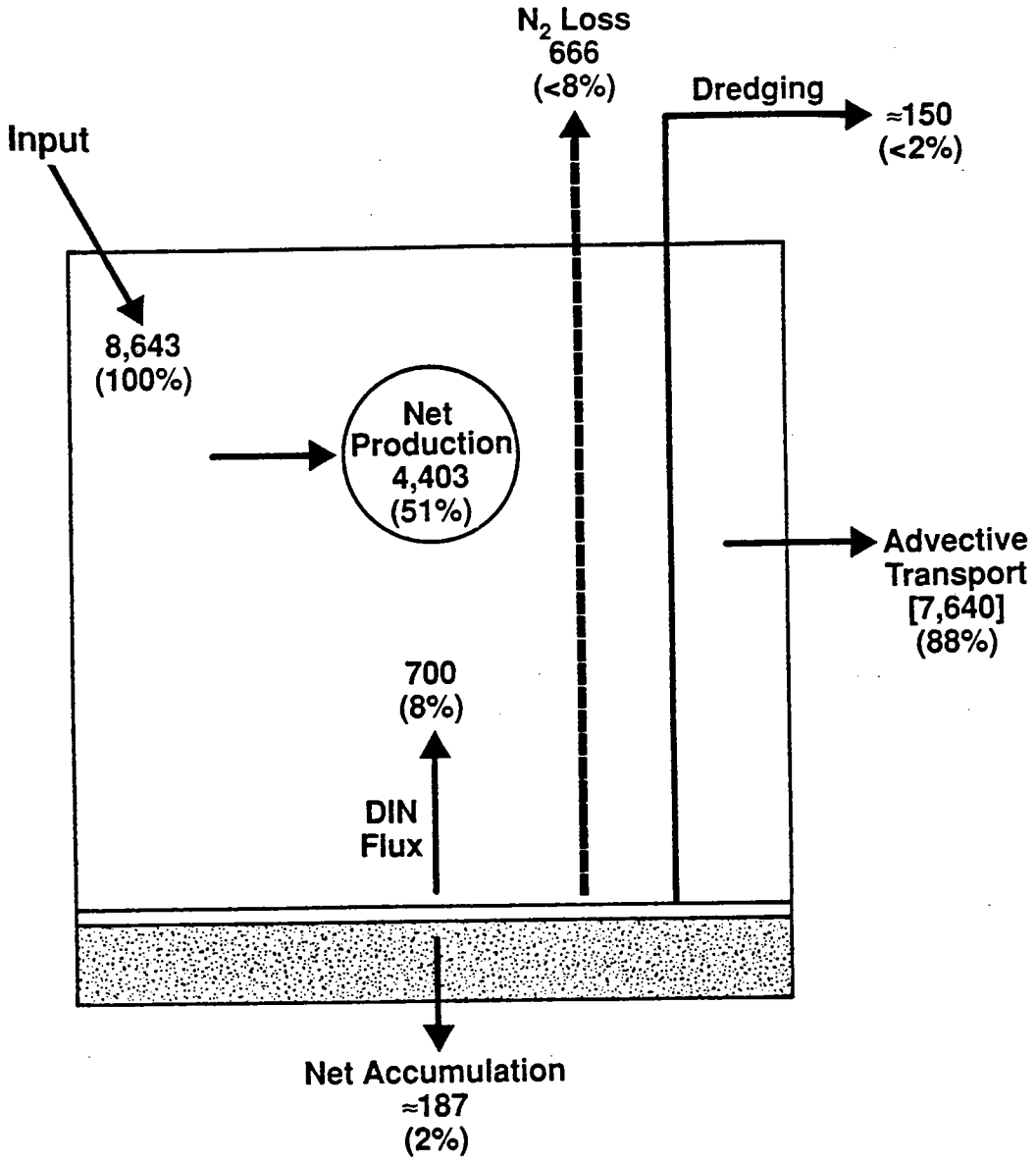


Figure 5: Tentative Nitrogen Budget for Boston Harbor.

Units are mmol N m^{-2} $year^{-1}$. Brackets around advective transport highlight that the estimate was derived by difference.

systems, nitrogen input exceeds the nitrogen demand for net primary production (Kelly and Levin, 1986). Water-column nutrient recycling has not been estimated, but several measurements now have been made of benthic nutrient flux (Giblin *et al.*, 1991 and 1992). DIN flux at the four denitrification stations during September 1991 ranged from 118 to 210 μmol N m^{-2} h^{-1} (Giblin *et al.*, 1992). In September 1990, at 3 stations in the northern Harbor, the average DIN flux was about 264 μmol N m^{-2} h^{-1} (Giblin *et al.*, 1991); water temperatures in 1990 were 18 to 20 °C, compared to 15 to 16.5 °C in September 1991. The two northern Harbor stations of the present (1991) study had an average of about 172 μmol N m^{-2} h^{-1} as DIN. The difference in nutrient flux rates between 1990 and 1991 could be accounted for by the difference in temperature, but there may be other factors that contribute to the interannual differences (Giblin *et al.*, 1992).

DIN flux data for Boston Harbor across a wide temperature range are presently lacking. Similar to the extrapolation for denitrification, one can extrapolate to a rough annual value by using temperature data for Boston Harbor from Robinson *et al.* (1990). Following Kelly (1991), assuming an exponential relationship based on Nixon *et al.* (1976), and an average Harbor benthic DIN flux of 155 μmol N m^{-2} h^{-1} at 15.5 °C (four station average for 1991), the extrapolated estimate of annual DIN flux is roughly 700 mmol N m^{-2} $year^{-1}$. This estimate places Boston Harbor in the mid-range for benthic DIN fluxes observed for coastal areas; it would represent roughly 15% to 18% of implied phytoplankton uptake (if production is 350 g C m^{-2} $year^{-1}$), a percentage that is on the low side but within the range measured in other systems of similar depth and having similar phytoplankton primary production rates.

Compared to the input of nitrogen to Boston Harbor, the extrapolated flux of DIN to the water from the sediments of the Harbor is small (Figure 5). It represents only 8% of the loading, a percentage that may be typical of highly nutrient-enriched coastal ecosystems (Kelly *et al.*, 1985).

The estimated annual DIN and denitrification fluxes are similar, suggesting on the average that loss as N_2 represents about one-half of the total inorganic N flux from the benthos. However, stations differed with respect to the relative proportion of total N flux as N_2 (Figure 4), and the extrapolated annual estimates should be used with care to make such a comparison.

3.2.3 Internal Sinks

Many researchers have grappled with getting estimates of the net sediment accumulation rate for Boston Harbor. The estimated suspended loads from land sources to Boston Harbor (9.8×10^{10} g $year^{-1}$; Menzie *et al.*, 1991) amounts to roughly 900 g m^{-2} $year^{-1}$, which can be converted to about 0.1 cm $year^{-1}$ as an accumulation rate if spread evenly across the whole Harbor. However, some of the suspended load is organic and substantial mass must be lost before burial. Solids input estimated by Menzie *et al.* (1991) does not include possible input from marine erosion (Knebel *et al.*, 1991) or possible import of marine muds from Massachusetts Bay. The most reliable estimates for recent accumulation Harbor-wide roughly match the estimated solids-input value and range from about 0.05 to 0.2 cm $year^{-1}$, though some small areas may accumulate at the rate of centimeters annually (cf. Knebel *et al.* 1991). Accumulation estimates from core-based studies, in the above range, may be considered "apparent," and, thus, maximum estimates of the actual rates because bioturbation has not been fully considered in the modeling and normally its inclusion lowers the estimate from that of the apparent sediment accumulation.

The value of 0.1 cm $year^{-1}$ is assumed and used here; it represents about 900 g dry solids m^{-2} $year^{-1}$ using appropriate porosity. The average TOC content measured for surface (2 cm) sediments measured in depositional areas throughout the Harbor in September (Kelly and Kropp, 1992), was about 2.5% of dry weight. Assuming a C/N (atoms) ratio of 8, this converts to 187 mmol N m^{-2} $year^{-1}$. This rate of accumulation into the sedimentary environment represents a small fraction of the nitrogen input to the Harbor, about 2%.

Retention in sediments usually is far less than the amount of N flowing through the benthos because deposited organic nitrogen is rapidly utilized and recycled primarily as ammonium (but also as nitrite or nitrate) — the inorganic endproducts of metabolism (Kelly and Nixon, 1984). In the case of Boston Harbor, the flow *through* the benthos, represented by the combined releases of DIN and N_2 gas, appears to be about 1366 mmol N m^{-2} $year^{-1}$. In contrast, the flow *to* the benthos (flow through + accumulation) appears to be on the order of 1553 mmol N m^{-2} $year^{-1}$ (i.e., 1366 + 187) spatially averaged over the Harbor. Using these numbers, the amount annually retained in the sediments is 12% of that being deposited, a value in line with other coastal areas.

Accumulation of the added nitrogen within the water column cannot be significant. To begin, the flushing is fast (days to weeks; Signell, 1991) and N concentrations seem in part determined by flushing (cf. Kelly, 1991). Recent nutrient data of Robinson *et al.* (1990) suggest no substantial change in water-column nutrient concentrations over about 1987 to 1989, a period over which loading has been fairly constant, if not slightly decreasing. If water-column accumulation were on the order of sediment accumulation (2%), then it should be detectable. For example, at 187 mmol N m^{-2} $year^{-1}$, this would represent 32 mmol N m^{-3} $year^{-1}$ using an average depth of 5.8 m for the Harbor (Robinson *et al.* 1990), or 32 μM N as a water column concentration. The average N concentration (as DIN + particulate N) in the Harbor is on the order of 11 to 12 μM N (Kelly, 1991). Thus, retention of even as small as 2% of the input would more than triple the existing water column concentration and would be highly detectable. Since little change over a number of years has been seen, there must be very small water-column retention.

3.2.4 Export

There are several possible routes of nitrogen export from the Harbor. These include removal by fishing, removal through dredging, loss as N_2 gas from sediment denitrification, and transport to offshore through advective water exchange (flushing). Each route is considered separately below, although flushing loss can be estimated only by difference.

Fishery harvest. The poundage of fish or shellfish caught in coastal marine waters can be visually impressive. However, on a theoretical basis, removal of nitrogen by harvest must be a small term in Boston Harbor's nitrogen budget, as it is elsewhere. Nixon (1988), for example, suggests that the fisheries yields (fin and shellfish) of coastal areas are usually less than 0.5% of the net primary production (on a carbon basis), which in this case would amount to, converted to nitrogen, <22 mmol N m^{-2} $year^{-1}$ ($<0.25\%$ of N input). Using 1987-1989 data for the commercial filter-feeding bivalve harvest (*Mya arenaria*, the soft-shell clam), which is regulated and tabulated by the Massachusetts Division of Marine Fisheries (DMF) (J. Kennedy, Newburyport, personal communication), and appropriate conversions to nitrogen, one can calculate that bivalve harvest may represent on the order of 10^{-3} mmol N m^{-2} $year^{-1}$. DMF data on the harvest of lobster, the other major commercial shellfish species, more difficult to use since the lobsters migrate in and out of the Harbor, nevertheless suggests a harvest removal of N of similar magnitude to the soft-shell clam harvest. Thus, the

unsurprising conclusion is that nitrogen export through fish and shellfish harvest can only remove a fraction of a percent of the input. The estimates are too uncertain but also too small to include in Figure 5.

Dredging. The MWRA (1988) cited a Harbor-wide dredging estimate based on the United States Army Corps of Engineers data as about 0.2 cm $year^{-1}$. Using more recent compilation on dredging and disposal to the Massachusetts Bay Disposal Site (EPA, 1989), one can estimate the long-term solids removal from Boston Harbor as on the order of 8.2×10^{10} g $year^{-1}$. Spread across the Harbor area (1.08×10^{8} m^2), it represents an average of about 760 g m^{-2} $year^{-1}$ as dry solids, or slightly less than the annual sediment accumulation values estimated above. Using a range of 0.25% to 0.31% N as dry weight of sediment (values similar to the average Harbor value converted from TOC above) as recorded at the dredge material disposal area in deeper waters of Massachusetts Bay (EPA 1989), this amounts to 136 to 168 mmol N m^{-2} $year^{-1}$. Thus, some 1.5% to 2% of the annual nitrogen input may be dredged and exported farther out into Massachusetts Bay.

Dredging and sediment accumulation, as calculated here, appear to be of similar magnitude with respect to N fluxes (Figure 5). However, it is unknown to what degree dredging removes sediment accumulation; the estimates are reached in very different ways, and it is difficult to know if the areas dredged capture only material not accumulated in undredged depositional areas, or whether some periodic (e.g., high wind events) postdepositional resuspension and redistribution occurs. There could be some double-counting in a budgetary sense if dredging and accumulation are considered to be independent, but in reality are not.

Denitrification. As calculated in Section 3.1.4, assuming a temperature-dependent flux rate, an annual estimate for export from the Harbor as gaseous N_2 loss to the atmosphere may be about 666 mmol N m^{-2} $year^{-1}$. The value could be underestimated if fluxes at high midsummer temperatures are unusually high and do not follow the assumed exponential relationship. The denitrification value is similar to the present DIN flux estimate (Figure 5). The present denitrification estimate, based on the only direct evidence of the rate of denitrification, represents less than 8% of the nitrogen input. This pathway is important and certainly one of the larger terms of the internal budget.

Advective exchange. The main mechanism for Harbor export would appear to be advective exchange

and transport to Broad Sound and western Massachusetts Bay. Unfortunately this export can be estimated only by difference. The sum of retention and export fluxes — sediment accumulation, dredging removal, and denitrification — amounts to 1003 mmol N m^{-2} $year^{-1}$. It is unclear if sediment accumulation estimates do or do not incorporate the dredging removal, and, thus, whether there is double counting. Given the small size of the estimates, even with their considerable uncertainty, this is a second-order concern with respect to the purpose of this budgeting exercise. A factor of 2 or more modifications of sediment accumulation or dredging estimates for these pathways have very little impact on the overall budget.

With only 1003 mmol N m^{-2} $year^{-1}$ otherwise lost, the remaining 7640 mmol N m^{-2} $year^{-1}$ of the input (88%) is not directly accounted for. There may be some minor additional sinks, but primarily this must exit the Harbor in the strong and regular tidal flushing. Thus, even when these new direct measurements of denitrification loss, a previously unknown part of the budget, are included in the accounting, the conclusion is that the majority of the present input to Boston Harbor could exit into western Massachusetts Bay. If one also adds the dredged solids that are discharged some 20 miles to the east of Boston at the Massachusetts Bay Disposal Site (MBDS), then the present budget suggests roughly 90% of the input (Figure 5) could be passed to Massachusetts Bay. The new direct estimates for denitrification in the overall input/output budget give empirical evidence to support the notion by Kelly (1991) that transport offshore of nitrogen delivered to the Harbor is very efficient and thus supports an observed nitrogen enrichment of the water column in Broad Sound and western Massachusetts Bay as far as 5 to 10 miles offshore from the Harbor entrances.

3.3 CONCLUSIONS:
DENITRIFICATION MEASUREMENTS AND NITROGEN BUDGET IMPLICATIONS

Denitrification rates measured in some parts of Boston Harbor are quite high, but comparable to rates estimated in a few other highly enriched coastal sediments. Denitrification-mediated flux of N_2 gas represented roughly 28% to 59% of the total benthic flux of inorganic nitrogen recycled by the sediments, varying with location in Boston Harbor. This range is in line with other studies (cf. Seitzinger, 1988).

Within the Harbor, a strong relationship between denitrification and organic content of the surface sediments is evident. Even though rates appeared especially high in some high organic areas, denitrification does not produce an nitrogen loss that is large in comparison to the input of nitrogen. This statement comes with the caveat that spatial and temporal extrapolations of the existing denitrification data have been made to make the comparison. Additional studies should provide data to improve the confidence of the extrapolations. Clearly, the seasonal variation of sediment denitrification should be assessed to validate/improve the tentative budget. Additionally, sediment stations with intermediate organic carbon content or sandier sediments should be considered for sampling. Because of the strong relation between fluxes and sediment quality and the known responsiveness of benthic fluxes to nutrient loading changes, denitrification could provide a valuable indicator of the pace of Harbor recovery with sludge abatement (December 1991) and effluent diversion (1995).

The provisional budget of nitrogen constructed here suggests that Boston Harbor, although receiving a very high load of nitrogen, may inefficiently trap or metabolize it. The present information indicates that as much as 90% of the input could be passed to Massachusetts Bay and slightly less than 8% may be lost to the atmosphere as N_2 gas from denitrification in the sediments. The consequences of a hypothesized strong nutrient coupling of Boston Harbor and Massachusetts Bay need to be kept in mind in the continued monitoring, forecasting, and interpretation of ecological changes in the Harbor and Bay over the next few years as the MWRA makes major changes to sludge and effluent disposal practices.

4.0 REFERENCES

Cura, J.J. 1991. Review of phytoplankton data: Massachusetts Bay. Environmental Quality Department Technical Report No. 91-1. Massachusetts Water Authority Resources, Boston MA. 27+ pp.

Giblin, A.G., J. Tucker, and C. Hopkinson. 1991. Sediment oxygen demand and nitrogen flux in Massachusetts Bay. Environmental Quality Department Technical Report No. 91-5. Massachusetts Water Authority Resources, Boston MA.

Giblin, A.G., C. Hopkinson, J. Tucker. 1992. Metabolism and nutrient cycling in Boston Harbor sediments. Environmental Quality Department Technical Report No. 92-1. Massachusetts Water Authority Resources, Boston MA.

Kelly, J.R. 1991. Nutrients and Massachusetts Bay: A synthesis of eutrophication issues. Environmental Quality Department Technical Report No. 91-10. Massachusetts Water Authority Resources, Boston MA.

Kelly, J.R., and S.W. Nixon. 1984. Experimental studies of the effect of organic deposition on the metabolism of a coastal marine bottom community. Mar. Ecol. Prog. Ser. 17:157-169.

Kelly, J.R., and S.A. Levin. 1986. A comparison of aquatic and terrestrial nutrient cycling and production processes in natural ecosystems, with reference to ecological concepts of relevance to some waste disposal issues. Pp. 165-203. in Kullenberg, G. (Ed.), *The Role of the Oceans as a Waste Disposal Option,* D. Reidel Publishing.

Kelly, J.R., and R.K. Kropp. 1992. Benthic recovery following sludge abatement in Boston Harbor: Baseline survey 1991. Draft report to Massachusetts Water Resource Authority. February.

Kelly, J.R., V.B. Berounsky, C.A. Oviatt, and S.W. Nixon. 1985. Benthic-pelagic coupling and nutrient cycling across an experimental eutrophication gradient. Mar. Ecol. Prog. Ser. 26:207-219.

Knebel, H., R.R. Rendigs, and M.H. Bothner. 1991. Modern sedimentary environments in Boston Harbor, Massachusetts. J. Sed. Petrol. 61:791-804.

MWRA. 1988. Secondary Treatment Facilities Plan. Massachusetts Water Resources Authority, Boston, MA.

Menzies, C.A., J.J. Cura, J.S. Freshman, and B. Potocki. 1991. Boston Harbor: Estimates of loadings. Environmental Quality Department Technical Report No. 91-3. Massachusetts Water Resources Authority, Boston MA.

Michelson, A.R. 1991. Analysis of the spatial and temporal variability of primary production in Boston Harbor, Massachusetts and Cape Cod Bays. Ms. thesis, Boston University. 64 pp.

Nowicki, B.L. 1991. The fate of nutrient inputs to estuaries: Evidence from estuarine mesocosms. Ph.D. thesis, University of Rhode Island, Graduate School of Oceanography, Kingston, R.I.

Nowicki, B.L., and C.A. Oviatt. 1990. Are estuaries traps for anthropogenic nutrients? Evidence from estuarine mesocosms. Mar. Ecol. Prog. Ser. 66:131-146.

Nixon, S.W. 1988. Physical energy inputs and the comparative ecology of lake and marine eco systems. Limnol. Oceanogr. 33:1005-1025.

Nixon, S.W., C.A. Oviatt, and S.S. Hale. 1976. Nitrogen regeneration and the metabolism of coastal marine bottom communities. Pp. 269-283 in Anderson, J.M. and A. Macfadyen (Eds.), The Role of Terrestrial and Aquatic Organisms in Decomposition Processes. Blackwell Scientific Publications, Oxford, England, United Kingdom.

Nixon, S.W., J.R. Kelly, B.N. Furnas, C.A. Oviatt, and S.S. Hale. 1980. Phosphorus regeneration and the metabolism of coastal marine bottom communities. Pp. 219-242 in Tenore, K.R. and B.C. Coull (Eds.), Marine Benthic Dynamics. University of South Carolina Press, Columbia SC.

Nixon, S.W., C.A. Oviatt, J.Frithsen, and B. Sullivan. 1986. Nutrients and the productivity of estuarine and coastal marine ecosystems. J. Limnol. Soc. South Afr. 12(1/2):43-71.

Ramette, R.W. 1981. Chemical equilibrium and analysis. Chapter 3 in *Limitations of experimental measurements.* Addison-Wesley Publishing Co., Reading, MA.

Robinson, W.E., T.J. Coffey, and P. A. Sullivan. 1990. New England Aquarium's Ten Year Boston Harbor Monitoring Program. First Report (March 1987-July 1989) New England Aquarium, Boston MA. 108+ pp.

Seitzinger, S., S. Nixon, M.E.Q. Pilson, S. Burke. 1980. Denitrification and N_2O production in near-shore marine sediments. Geochim. Cosmochim. Acta 44:1853-1860.

Seitzinger, S. 1988. Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. Limnol. Oceanogr. 33(4, Part 2):702-724.

Shea, D., and J.R. Kelly. 1992. Transport and fate of toxic contaminants discharged by MWRA into Massachusetts Bay. Environmental Quality Department Technical Report (in preparation). Massachusetts Water Authority Resources, Boston MA.

Signell, R.P. 1991. "Applications and limitations of depth-averaged circulation modeling in Boston Harbor, Massachusetts." To appear in Spaulding, M. (Ed.), Proceedings of the 2nd Estuarine and Coastal Modeling Conference, Tampa, FL. November 1991.

Smith, S.V., W.J. Kimmerer, E.A. Laws, R.E. Brock, and T.W. Walsh. 1981. Kaneohe Bay sewage diversion experiment: Perspectives on ecosystem responses to nutritional perturbation. Pac. Sci. 35:279-395.

Appendix

Part 1.
Flux data and concentration—time plots

DENITRIFICATION MEASUREMENTS FOR MASS BAY B. NOWICKI

REGRESSION ANALYSIS - NITROGEN

CORE #	DAY #	ELAPSE TIME (hrs)	TOTAL N2 IN GAS PHASE (umoles)
ANOXIC CONTRL	3	7	5.27
		7	5.02
	4	28.5	12.2
		28.5	12.18
	5	54.25	18.96
		54.25	17.94
		54.25	18.06
	7	7.25	2.54
		7.25	2.88
	8	30	6.47
		30	5.88
	9	58.2	10.7
		58.2	9.4
	11	98.25	14.5
		98.25	14.2
	13	151	18.6
		151	18.1
	14	175.6	20.7
		175.6	20.9
	16	222.9	25.5
		222.9	24.2
	18	269	27.7
		269	28.9
	22	27.6	5.16
		27.6	4.54
	24	69	6
		69	6.33
	25	98.6	7.37
		98.6	7.19
	28	167.6	11.22
		167.6	10.25

Regression Output:

Constant	3.618104
Std Err of Y Est	0.661768
R Squared	0.989573
No. of Observations	7
Degrees of Freedom	5
X Coefficient(s)	0.275094
Std Err of Coef.	0.012628

N2 FLUX = 58 umoles N2/m2/hr

(FIRST FOUR POINTS)

Regression Output:

Constant	2.150015
Std Err of Y Est	0.59733
R Squared	0.985913
No. of Observations	8
Degrees of Freedom	6
X Coefficient(s)	0.127439
Std Err of Coef.	0.006219

N2 FLUX = 27 umoles N2/m2/hr

Regression Output:

Constant	3.402699
Std Err of Y Est	0.451944
R Squared	0.968495
No. of Observations	8
Degrees of Freedom	6
X Coefficient(s)	0.042501
Std Err of Coef.	0.003129

N2 FLUX = 9 umoles N2/m2/hr

DENITRIFICATION MEASUREMENTS FOR MASS BAY B. NOWICKI

CORE #	DAY #	ELAPSE TIME (hrs)	TOTAL N2 IN GAS PHASE (umoles)
T-2	3	7.25	6.2
		7.25	6.28
	4	29	16.94
		29	17.33
	5	54.5	27.37
		54.5	27.14
	7	7.5	4.2
		7.5	4.5
	8	30.25	11.9
		30.25	11.6
	9	58.5	21.8
		58.5	21.6
	11	98.5	35.9
		98.5	36.5
	13	151.25	70.8
		151.25	72.4
	14	175.9	82.2
		175.9	80.7
	16	223.2	95.8
		223.2	95
	18	269.3	103
		269.3	104
	22	27.8	6.35
	24	69.25	11.45
		69.25	10.24
	25	98.8	13.57
		98.8	14.07
	28	167.8	18.03

Regression Output:

Constant	3.463907
Std Err of Y Est	0.722965
R Squared	0.995269
No. of Observations	6
Degrees of Freedom	4
X Coefficient(s)	0.443397
Std Err of Coef.	0.015285

N2 FLUX = 94 umoles N2/m2/hr

(FIRST FOUR POINTS)

Regression Output:

Constant	1.401708
Std Err of Y Est	0.37537
R Squared	0.999258
No. of Observations	8
Degrees of Freedom	6
X Coefficient(s)	0.351184
Std Err of Coef.	0.003908

N2 FLUX = 74 umoles N2/m2/hr

Regression Output:

Constant	4.962103
Std Err of Y Est	0.913059
R Squared	0.957218
No. of Observations	6
Degrees of Freedom	4
X Coefficient(s)	0.082636
Std Err of Coef.	0.008735

(ANOXIC) N2 FLUX = 17 umoles/n2/m2/hr

DENITRIFICATION MEASUREMENTS FOR MASS BAY B. NOWICKI

CORE #	DAY #	ELAPSE TIME (hrs)	TOTAL N2 IN GAS PHASE (umoles)
T-3	3	7.75	9.21
		7.75	9.12
	4	29.25	25.4
		29.25	25.14
	5	55	44.07
		55	43.9

Regression Output:

Constant	3.550906
Std Err of Y Est	0.18899
R Squared	0.999882
No. of Observations	6
Degrees of Freedom	4
X Coefficient(s)	0.736601
Std Err of Coef.	0.003994

N2 FLUX = 155 umoles N2/m2/hr

7	7.75	7.6
	7.75	7.6
8	30.5	21
	30.5	20.6
9	58.75	38.4
	58.75	37.9
11	98.8	60.1
	98.8	59.6
13	151.6	84.3
	151.6	86.6
14	176.3	93.4
	176.3	92.5
16	223.3	105.6
	223.3	106.6
18	269.6	114.4
	269.6	112.7

(FIRST FOUR POINTS)

Regression Output:

Constant	3.404554
Std Err of Y Est	0.658641
R Squared	0.999151
No. of Observations	8
Degrees of Freedom	6
X Coefficient(s)	0.576005
Std Err of Coef.	0.006853

N2 FLUX = 122 umoles N2/m2/hr

22	28.2	6.18
	28.2	6.04
24	69.5	10.12
	69.5	9.08
25	99.2	10.92
	99.2	10.57
28	168.2	14.22
	168.2	14.07

Regression Output:

Constant	5.085936
Std Err of Y Est	0.615198
R Squared	0.965852
No. of Observations	8
Degrees of Freedom	6
X Coefficient(s)	0.055481
Std Err of Coef.	0.004259

(ANOXIC) N2 FLUX = 12 umoles N2/m2/hr

DENITRIFICATION MEASUREMENTS FOR MASS BAY B. NOWICKI

CORE #	DAY #	ELAPSE TIME (hrs)	TOTAL N2 IN GAS PHASE (umoles)
T-7	3	8	8.15
		8	7.97
	4	29.75	23.9
		29.75	25.1
		29.75	23.9
	5	55.25	40.71
		55.25	39.67

Regression Output:

Constant	3.305598
Std Err of Y Est	1.011097
R Squared	0.995056
No. of Observations	7
Degrees of Freedom	5
X Coefficient(s)	0.677918
Std Err of Coef.	0.02137

N2 FLUX = 143 umoles N2/m2/hr

7	8.25	6.5
	8.25	6.9
8	30.75	18.4
	30.75	18.5
	59.2	32.8
	59.2	32.6
11	99.25	53.4
	99.25	52.6
13	151.9	77.4
	151.9	79.6
14	176.6	81
	176.6	80.3
16	223.7	86
	223.7	85.7
18	269.8	94.7
	269.8	93

(FIRST FOUR POINTS)

Regression Output:

Constant	2.649263
Std Err of Y Est	0.299265
R Squared	0.999775
No. of Observations	8
Degrees of Freedom	6
X Coefficient(s)	0.507738
Std Err of Coef.	0.003113

N2 FLUX = 107 umoles N2/m2/hr

22	28.3	5.84
24	69.75	10.12
	69.75	12.14
25	99.4	13.32
	99.4	12.61
28	168.4	17.33
	168.4	17.55

Regression Output:

Constant	5.100896
Std Err of Y Est	1.092881
R Squared	0.939909
No. of Observations	7
Degrees of Freedom	5
X Coefficient(s)	0.075638
Std Err of Coef.	0.008553

(ANOXIC) N2 FLUX = 16 umoles N2/m2/hr

DENITRIFICATION MEASUREMENTS FOR MASS BAY B. NOWICKI

CORE #	DAY #	ELAPSE TIME (hrs)	TOTAL N2 IN GAS PHASE (umoles)
T-8	3	8.5	6.78
		8.5	7.18
		8.5	7.31
	4	30	16.75
		30	16.83
	5	55.5	25.44
		55.5	25.04

Regression Output:

Constant	4.14994
Std Err of Y Est	0.776435
R Squared	0.99254
No. of Observations	7
Degrees of Freedom	5
X Coefficient(s)	0.388196
Std Err of Coef.	0.015051

N2 FLUX = 82 umoles N2/m2/hr

	7	8.5	5
		8.5	4
	8	31.25	9.2
		31.25	9.4
	9	59.75	19.6
		59.75	17.4
		59.75	19
	11	99.5	28.3
		99.5	28.3
	13	152.25	44
		152.25	43.9
	14	176.9	50.6
		176.9	50

(FIRST FOUR POINTS)

Regression Output:

Constant	1.918735
Std Err of Y Est	1.002716
R Squared	0.989645
No. of Observations	9
Degrees of Freedom	7
X Coefficient(s)	0.268556
Std Err of Coef.	0.010383

N2 FLUX = 57 umoles N2/m2/hr

	17	23	22.6
			22.3
	18	46	24.89

	22	28.5	3.26
		28.5	3.43
	24	70	5.63
		70	5.93
	25	99.6	5.71
		99.6	5.6
	28	168.6	7.16
		168.6	7.28

Regression Output:

Constant	3.185439
Std Err of Y Est	0.601568
R Squared	0.859757
No. of Observations	8
Degrees of Freedom	6
X Coefficient(s)	0.025247
Std Err of Coef.	0.004163

(ANOXIC) N2 FLUX = 5 umoles N2/m2/hr

DENITRIFICATION MEASUREMENTS FOR MASS BAY B. NOWICKI

CORE COLLECTION = SEPT. 23, 1991

CORE #	DAY #	ELAPSE TIME (hrs)	O2 CONC (mg/l)	TOTAL O2 IN GAS PHASE (umoles)	TOTAL N2 IN GAS PHASE (umoles)
ANOXIC CONTRL	3	7	0.02		5.27
			0.01		5.02
	4	28.5	0.02		12.2
			0.02		12.18
	5	54.25	0.02		18.96
			0.02		17.94
			0.02		18.06
	7	7.25	0.01		2.54
			0.01		2.88
	8	30	0.02		6.47
			0.02		5.88
	9	58.2	0.02		10.7
			0.02		9.4
	11	98.25	0.02		14.5
			0.02		14.2
	13	151	0.03		18.6
			0.02		18.1
	14	175.6	0.02		20.7
			0.02		20.9
	16	222.9	0.03		25.5
			0.02		24.2
	18	269	0.02		27.7
			0.01		28.9
	22	27.6	0.025		5.16
			0.02		4.54
	24	69	0.01		6
			0.02		6.33
	25	98.6	0.02		7.37
			0.02		7.19
	28	167.6	0.02		11.22
			0.02		10.25

DENITRIFICATION MEASUREMENTS FOR MASS BAY B. NOWICKI

CORE #	DAY #	ELAPSE TIME (hrs)	O2 CONC (mg/l)	TOTAL O2 IN GAS PHASE (umoles)	TOTAL N2 IN GAS PHASE (umoles)
T-2	3	7.25	8.28	562	6.2
			8.18	554	6.28
	4	29	6.62	452	16.94
			6.66	455	17.33
	5	54.5	4.71	323	27.37
			4.81	329	27.14
	7	7.5	8.13	561	4.2
			8.1	559	4.5
	8	30.25	6.88	472	11.9
			6.71	460	11.6
	9	58.5	5	339	21.8
			4.99	338	21.6
	11	98.5	2.82	191	35.9
			2.83	192	36.5
	13	151.25	0.56	38	70.8
			0.57	39	72.4
	14	175.9	0.058	4	82.2
			0.066	5	80.7
	16	223.2	0.046	<0.00002	95.8
			0.045	<0.00002	95
	18	269.3	0.049	0	103
			0.05	0	104
	22	27.8	0.02		6.35
	24	69.25	0.02		11.45
			0.02		10.24
	25	98.8	0.02		13.57
			0.02		14.07
	28	167.8	0.02		18.03

DENITRIFICATION MEASUREMENTS FOR MASS BAY B. NOWICKI

CORE #	DAY #	ELAPSE TIME	O2 CONC	TOTAL O2 IN GAS PHASE	TOTAL N2 IN GAS PHASE
		(hrs)	(mg/l)	(umoles)	(umoles)
T-3	3	7.75	8.25	560	9.21
			8.37	567	9.12
	4	29.25	6.58	449	25.4
			6.63	453	25.14
	5	55	4.87	334	44.07
			4.89	335	43.9
	7	7.75	8.05	555	7.6
			8.08	557	7.6
	8	30.5	6.66	457	21
			6.65	456	20.6
	9	58.75	4.74	321	38.4
			4.71	319	37.9
	11	98.8	2.59	176	60.1
			2.6	176	59.6
	13	151.6	0.53	36	84.3
			0.54	37	86.6
	14	176.3	0.13	9	93.4
			0.13	9	92.5
	16	223.3	0.04	<0.00002	105.6
			0.04	<0.00002	106.6
	18	269.6	0.04	0	114.4
			0.04	0	112.7
	22	28.2	0.02		6.18
			0.02		6.04
	24	69.5	0.02		10.12
			0.02		9.08
	25	99.2	0.02		10.92
			0.01		10.57
	28	168.2	0.02		14.22
			0.02		14.07

DENITRIFICATION MEASUREMENTS FOR MASS BAY B. NOWICKI

CORE #	DAY #	ELAPSE TIME	O2 CONC	TOTAL O2 IN GAS PHASE	TOTAL N2 IN GAS PHASE
		(hrs)	(mg/l)	(umoles)	(umoles)
T-7	3	0	8.31	564	8.15
			8.19	555	7.97
	4	29.75	6.5	443	23.9
			6.54	446	25.1
			6.53	445	23.9
	5	55.25	4.51	309	40.71
			4.54	311	39.67
	7	8.25	8.06	556	6.5
			7.94	548	
			7.97	550	6.9
	8	30.75	6.14	421	18.4
			6.05	415	18.5
	9	59.2	3.75	254	
			3.76	254	32.8
			3.77	255	32.6
	11	99.25	0.7	48	53.4
			0.69	47	52.6
	13	151.9	0.059	4	77.4
					79.6
	14	176.6	0.04	3	81
			0.04	3	80.3
	16	223.7	0.041	<0.00002	86
			0.04	<0.00002	85.7
	18	269.8	0.047	0	94.7
			0.046	0	93
	22	28.3	0.01		5.84
	24	69.75	0.02		10.12
			0.03		12.14
	25	99.4	0.02		13.32
			0.02		12.61
	28	168.4	0.02		17.33
			0.02		17.55

DENITRIFICATION MEASUREMENTS FOR MASS BAY B. NOWICKI

CORE #	DAY #	ELAPSE TIME (hrs)	O2 CONC (mg/l)	TOTAL O2 IN GAS PHASE (umoles)	TOTAL N2 IN GAS PHASE (umoles)
T-8	3	8.5	8.4	569	6.78
			8.43	571	7.18
			8.53	578	7.31
	4	30	7.19	491	16.75
			7	481	16.83
	5	55.5	5.06	347	25.44
			5.01	344	25.04
	7	8.5	8.52	588	5
			8.49	586	4
	8	31.25	7.15	490	9.2
			7.2	494	9.4
	9	59.75	5.41	366	19.6
			5.42	367	17.4
			5.43	368	19
	11	99.5	3.24	219	28.3
			3.24	220	28.3
	13	152.25	0.84	57	44
			0.83	57	43.9
	14	176.9	0.145	10	50.6
			0.143	10	50
	17	23	0.02	<0.00002	22.6
			0.02	<0.00002	22.3
	18	46	0.02	0	24.89
	22	28.5	0.01		3.26
			0.01		3.43
	24	70	0.02		5.63
			0.02		5.93
	25	99.6	0.02		5.71
			0.01		5.6
	28	168.6	0.01		7.16
			0.02		7.28

DENITRIFICATION MEASUREMENTS FOR MASS BAY

REGRESSION ANALYSIS - OXYGEN

CORE #	DAY #	ELAPSE TIME (hrs)	TOTAL O2 IN GAS PHASE (umoles)	
ANOXIC CONTRL	3	7		
	4	28.5		ANOXIC CONTROL OXYGEN CONC = 0 UMOLES
	5	54.25		
	7	7.25		
	8	30		
	9	58.2		
	11	98.25		ANOXIC CONTROL OXYGEN CONC = 0 UMOLES
	13	151		
	14	175.6		
	16	222.9		
	18	269		
	22	27.6		
	24	69		
	25	98.6		ANOXIC CONTROL OXYGEN CONC = 0 UMOLES
	28	167.6		

DENITRIFICATION MEASUREMENTS FOR MASS BAY

CORE #	DAY #	ELAPSE TIME (hrs)	TOTAL O2 IN GAS PHASE (umoles)	
T-2	3	7.25	562	
		7.25	554	
	4	29	452	
		29	455	
	5	54.5	323	
		54.5	329	
	7	7.5	561	
		7.5	559	
	8	30.25	472	
		30.25	460	
	9	58.5	339	
		58.5	338	
	11	98.5	191	
		98.5	192	
	13	151.25	38	
		151.25	39	
	14	175.9	4	
		175.9	5	
	16	223.2	<0.00002	
		223.2	<0.00002	
	18	269.3	0	
		269.3	0	
	22	27.8		
	24	69.25		CORE WAS ANOXIC DURING THIS TIME
	25	98.8		
	28	167.8		

Regression Output:

Constant	594.44
Std Err of Y Est	3.921089
R Squared	0.998862
No. of Observations	6
Degrees of Freedom	4
X Coefficient(s)	-4.91262
Std Err of Coef.	0.082899

O2 FLUX = -33 mg O2/m2/hr

(FIRST FOUR POINTS ONLY)

Regression Output:

Constant	587.3437
Std Err of Y Est	7.991921
R Squared	0.997504
No. of Observations	8
Degrees of Freedom	6
X Coefficient(s)	-4.07381
Std Err of Coef.	0.083196

O2 FLUX = -28 mg O2/m2/hr

DENITRIFICATION MEASUREMENTS FOR MASS BAY

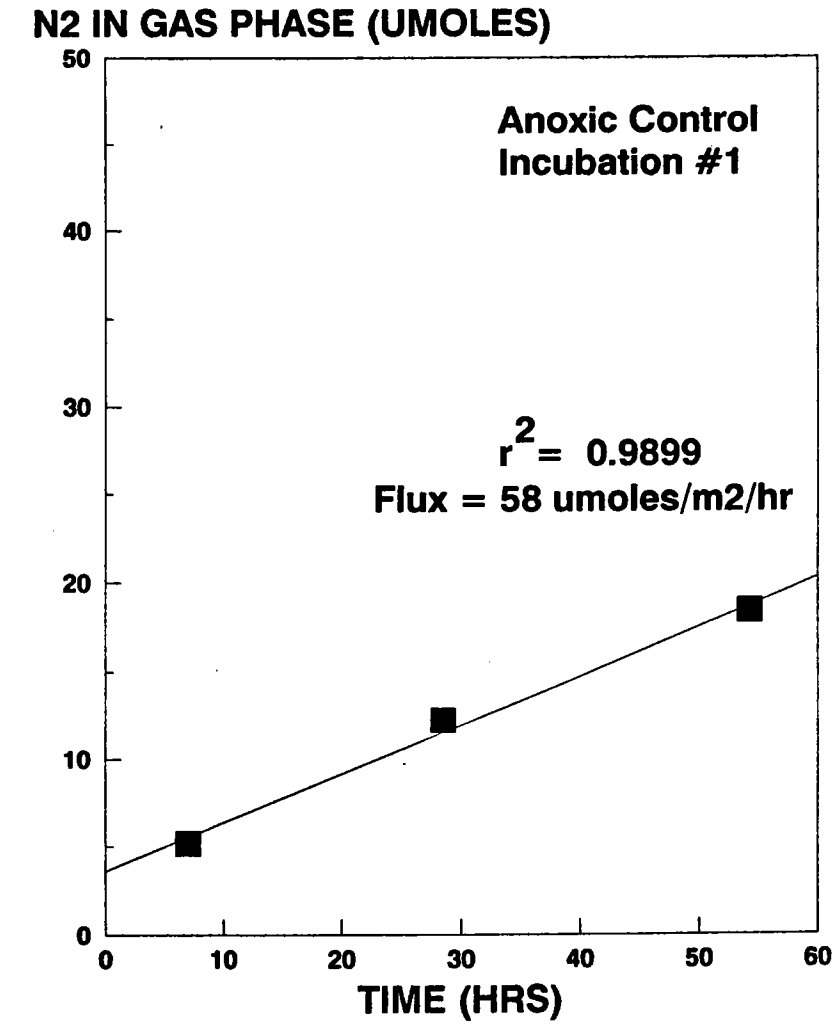
CORE #	DAY #	ELAPSE TIME (hrs)	TOTAL O2 IN GAS PHASE (umoles)	
T-3	3	7.75	560	Regression Output:
		7.75	567	Constant 597.9724
	4	29.25	449	Std Err of Y Est 5.580836
		29.25	453	R Squared 0.997626
	5	55	334	No. of Observations 6
		55	335	Degrees of Freedom 4
				X Coefficient(s) -4.83606
				Std Err of Coef. 0.117954
				O2 FLUX = -33 mg O2/m2/hr
	7	7.75	555	(FIRST FOUR POINTS ONLY)
		7.75	557	Regression Output:
	8	30.5	457	Constant 582.9336
		30.5	456	Std Err of Y Est 10.99424
	9	58.75	321	R Squared 0.995579
		58.75	319	No. of Observations 8
	11	98.8	176	Degrees of Freedom 6
		98.8	176	
	13	151.6	36	X Coefficient(s) -4.20447
		151.6	37	Std Err of Coef. 0.114388
	14	176.3	9	
		176.3	9	O2 FLUX = -28 mg O2/m2/hr
	16	223.3	<0.00002	
		223.3	<0.00002	
	18	269.6	0	
		269.6	0	
	22	28.2		
	24	69.5	CORE WAS ANOXIC DURING THIS TIME	
	25	99.2		
	28	168.2		

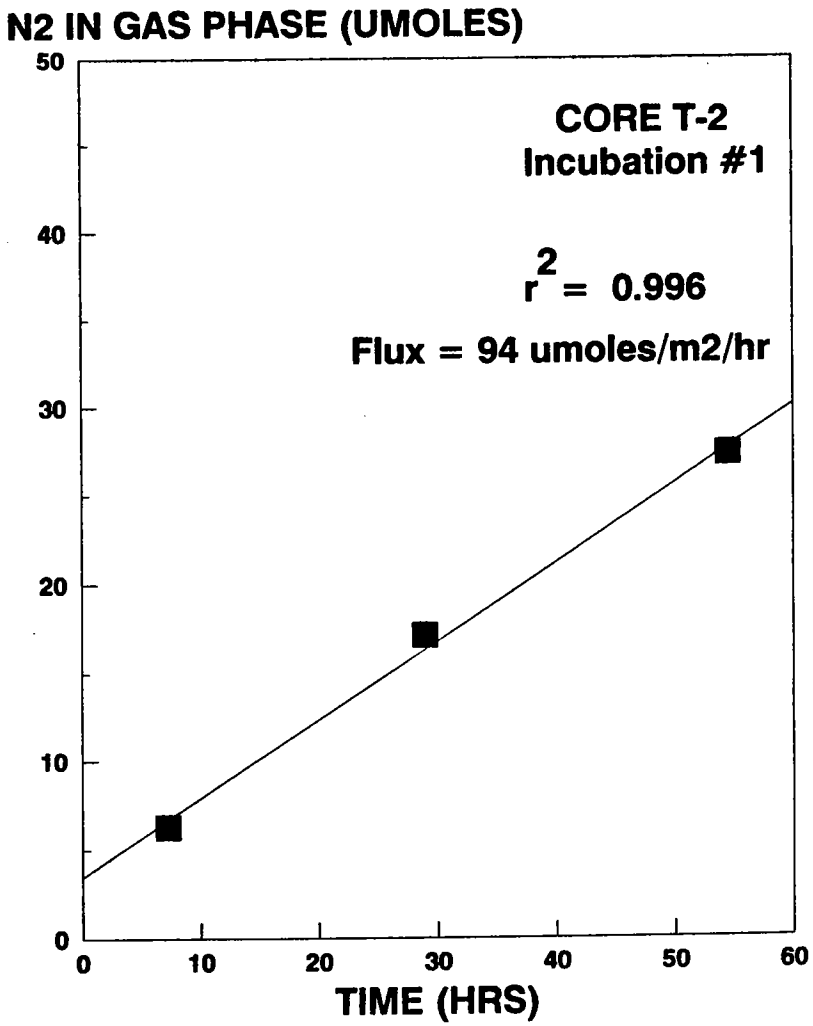
DENITRIFICATION MEASUREMENTS FOR MASS BAY

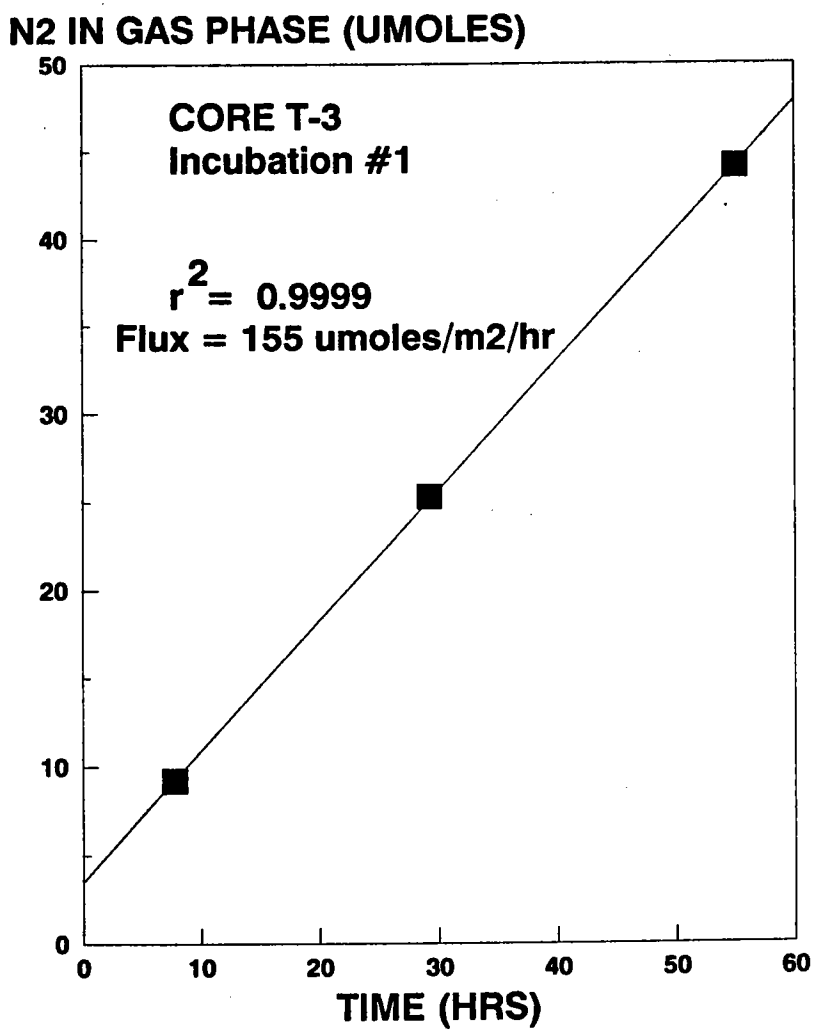
CORE #	DAY #	ELAPSE TIME (hrs)	TOTAL O2 IN GAS PHASE (umoles)	
T-7	3	8	564	Regression Output:
		8	555	Constant 601.7509
	4	29.75	443	Std Err of Y Est 3.071387
		29.75	446	R Squared 0.999245
		29.75	445	No. of Observations 7
	5	55.25	309	Degrees of Freedom 5
		55.25	311	X Coefficient(s) -5.28045
				Std Err of Coef. 0.064915
				O2 FLUX = -36 mg O2/m2/hr
	7	8.25	556	(FIRST FOUR POINTS ONLY)
		8.25	548	Regression Output:
		8.25	550	Constant 592.0911
	8	30.75	421	Std Err of Y Est 7.729327
		30.75	415	R Squared 0.99859
	9	59.2	254	No. of Observations 10
		59.2	254	Degrees of Freedom 8
		59.2	255	
	11	99.25	48	X Coefficient(s) -5.56486
		99.25	47	Std Err of Coef. 0.07392
	13	151.9	4	
	14	176.6	3	O2 FLUX = -38 mg O2/m2/hr
		176.6	3	
	16	223.7	<0.00002	
		223.7	<0.00002	
	18	269.8	0	
		269.8	0	
	22	28.3		
	24	69.75	CORE WAS ANOXIC DURING THIS TIME	
	25	99.4		
	28	168.4		

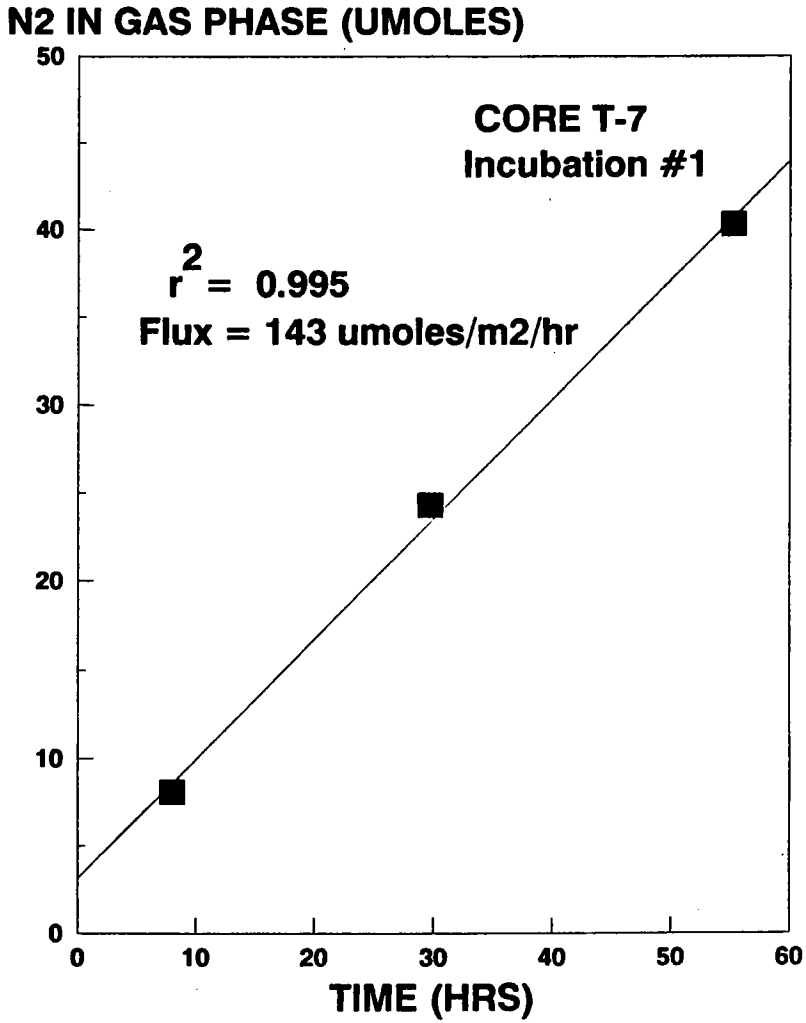
DENITRIFICATION MEASUREMENTS FOR MASS BAY

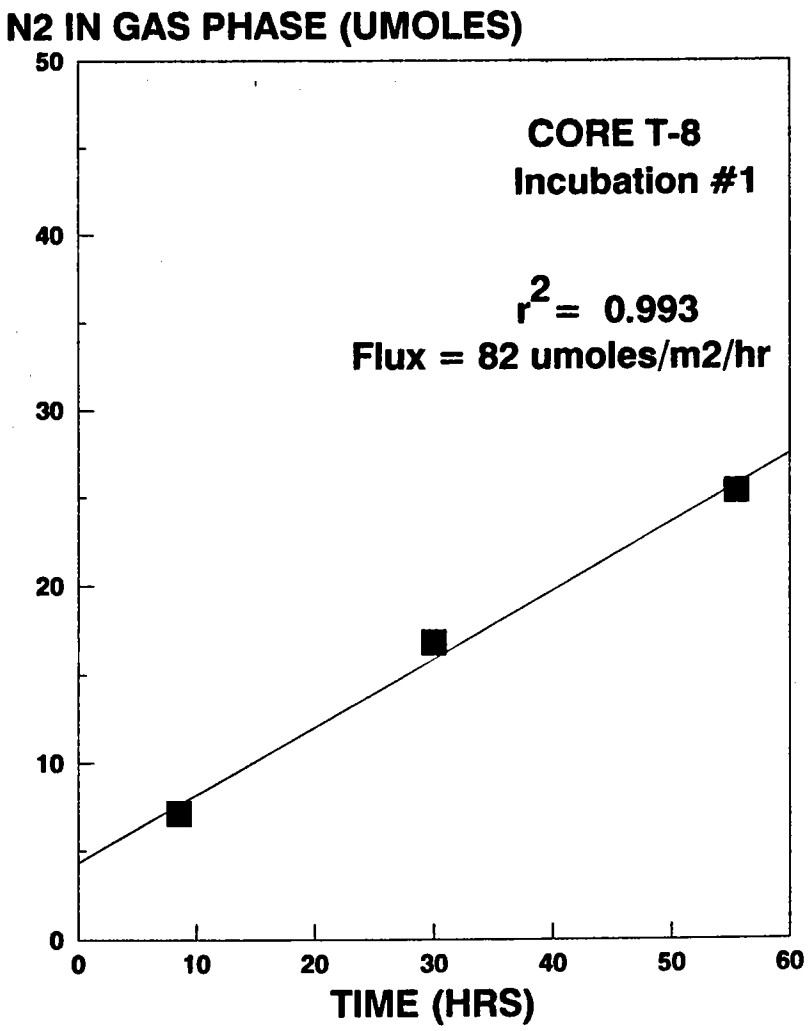
CORE #	DAY #	ELAPSE TIME (hrs)	TOTAL O2 IN GAS PHASE (umoles)	
				Regression Output:
				Constant 617.9767
T-8	3	8.5	569	Std Err of Y Est 10.22343
		8.5	571	R Squared 0.991578
		8.5	578	No. of Observations 7
	4	30	491	Degrees of Freedom 5
		30	481	
	5	55.5	347	X Coefficient(s) -4.80833
		55.5	344	Std Err of Coef. 0.198179
				O2 FLUX = -32 mg O2/m2/hr
	7	8.5	588	(FIRST FOUR POINTS ONLY)
		8.5	586	Regression Output:
	8	31.25	490	Constant 617.5158
		31.25	494	Std Err of Y Est 6.627693
	9	59.75	366	R Squared 0.998006
		59.75	367	No. of Observations 9
		59.75	368	Degrees of Freedom 7
	11	99.5	219	
		99.5	220	X Coefficient(s) -4.06257
	13	152.25	57	Std Err of Coef. 0.068628
		152.25	57	
	14	176.9	10	O2 FLUX = - 27 mg O2/m2/hr
		176.9	10	
	17	23	<0.00002	
			<0.00002	
	18	46	0	
	22	28.5		
	24	70	CORE WAS ANOXIC AT THIS TIME	
	25	99.6		
	28	168.6		

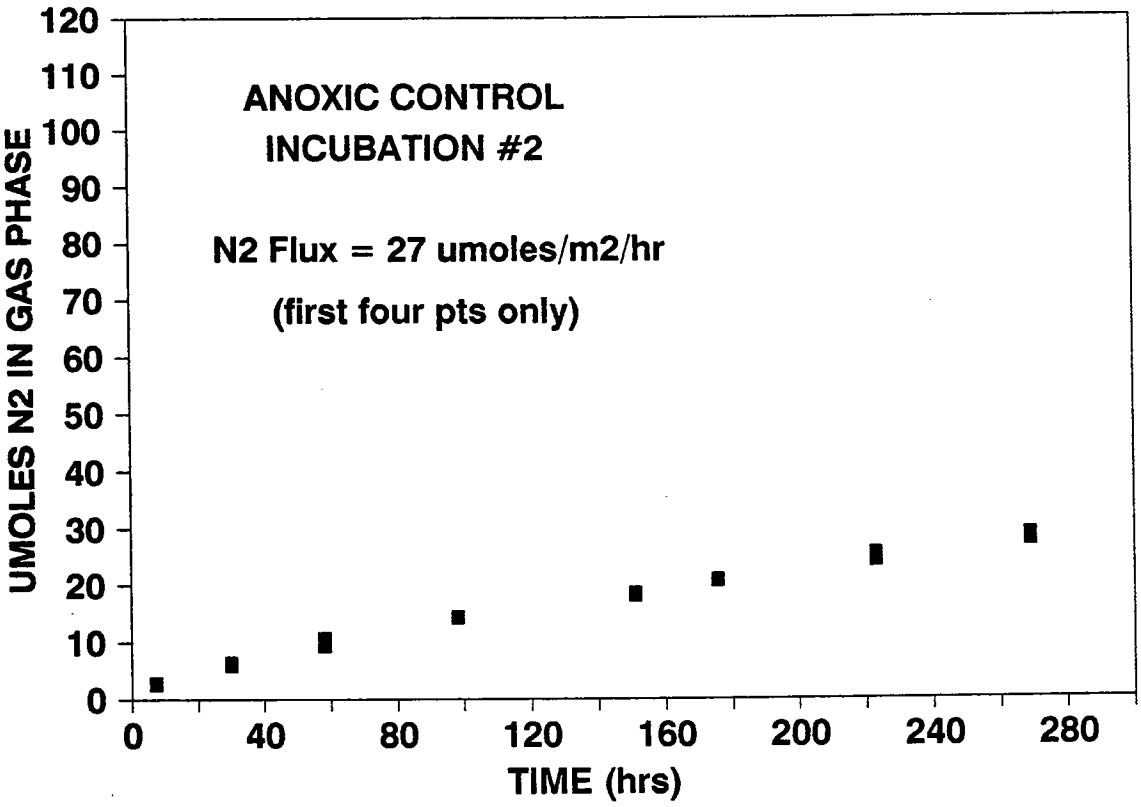

N2 IN GAS PHASE (UMOLES)
Anoxic Control
Incubation #1
r2= 0.9899
Flux = 58 umoles/m2/hr
TIME (HRS)
0
10
20
30
40
50
60

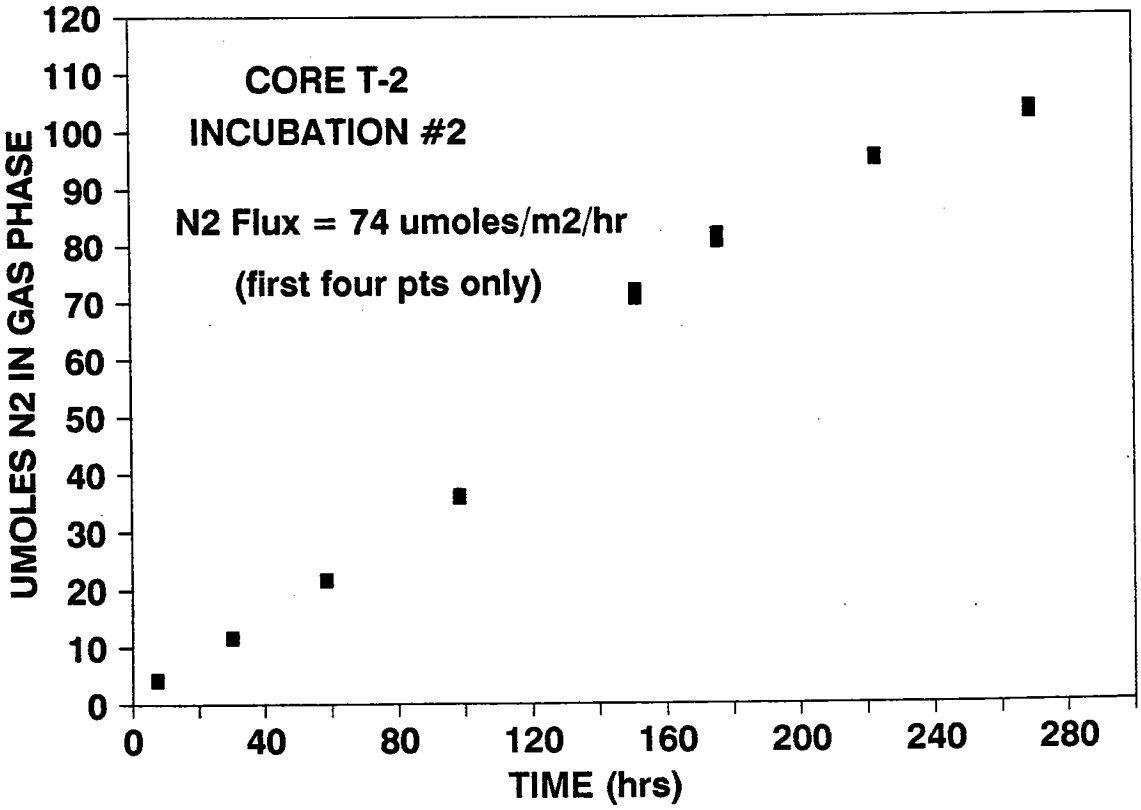

N2 IN GAS PHASE (UMOLES)
CORE T-2
Incubation #1
r2= 0.996
Flux = 94 umoles/m2/hr
TIME (HRS)
0
10
20
30
40
50
60

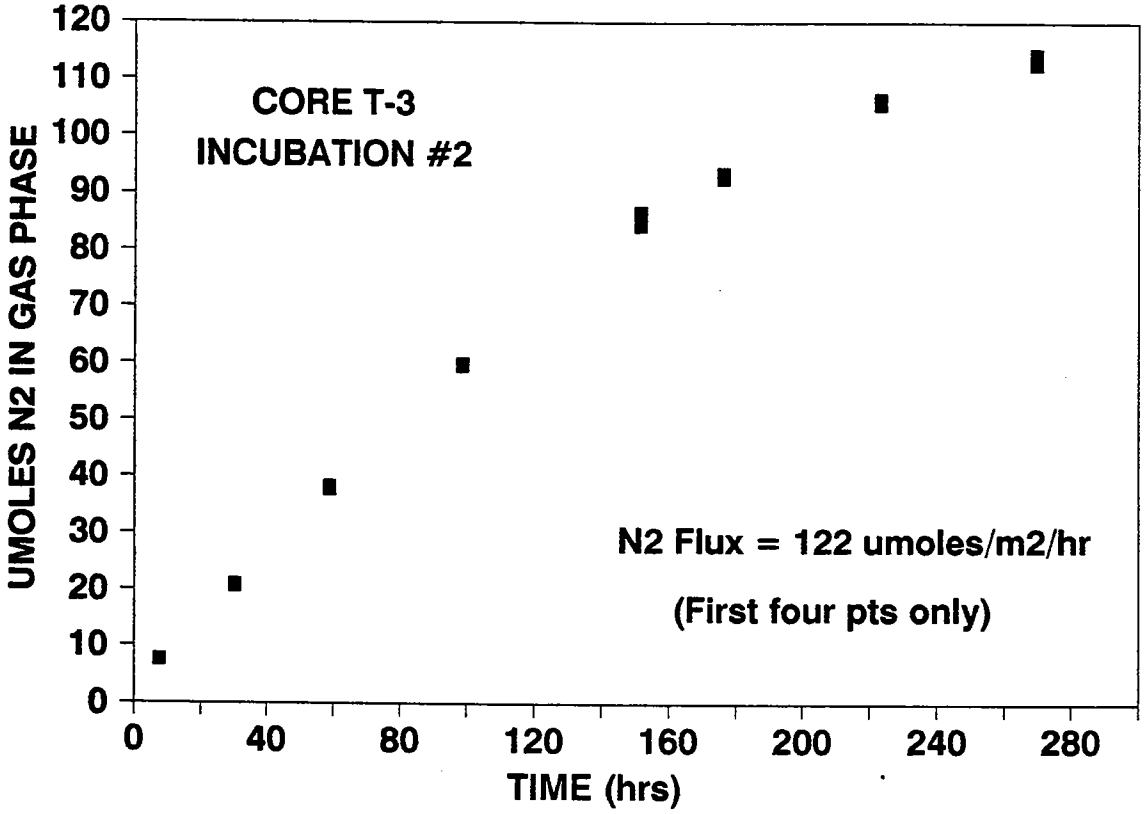

N2 IN GAS PHASE (UMOLES)
CORE T-3
Incubation #1
r2= 0.9999
Flux = 155 umoles/m2/hr
0
10
20
30
40
50
0
10
20
30
40
50
60
TIME (HRS)

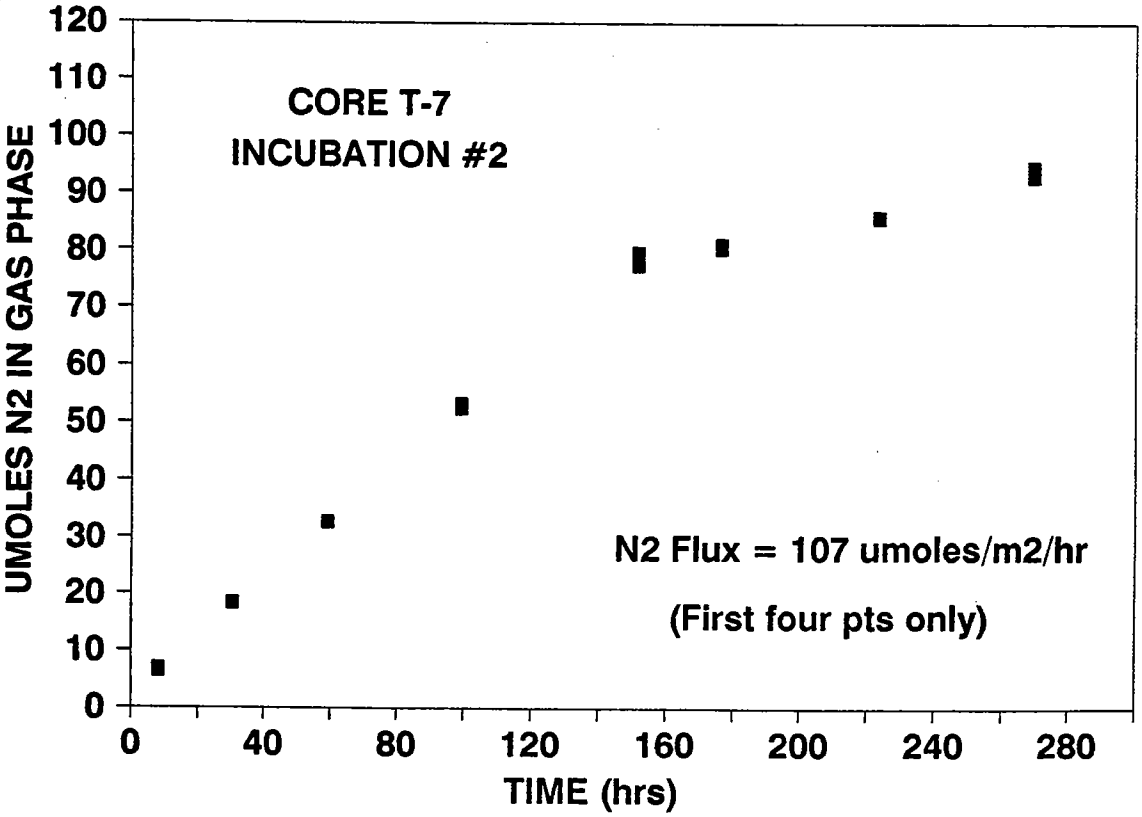

N2 IN GAS PHASE (UMOLES)
CORE T-7
Incubation #1
r2= 0.995
Flux = 143 umoles/m2/hr
0
10
20
30
40
50
0
10
20
30
40
50
60
TIME (HRS)

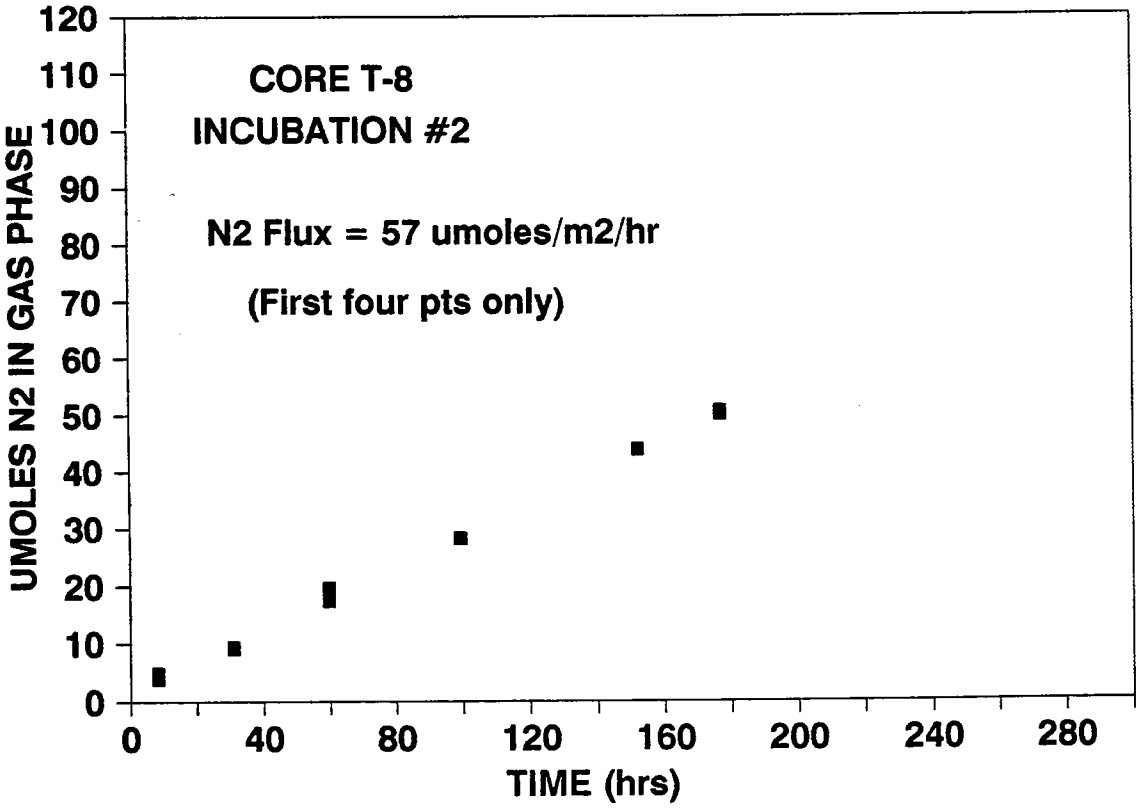

N2 IN GAS PHASE (UMOLES)
CORE T-8
Incubation #1
r2= 0.993
Flux = 82 umoles/m2/hr
50
40
30
20
10
0
0
10
20
30
40
50
60
TIME (HRS)

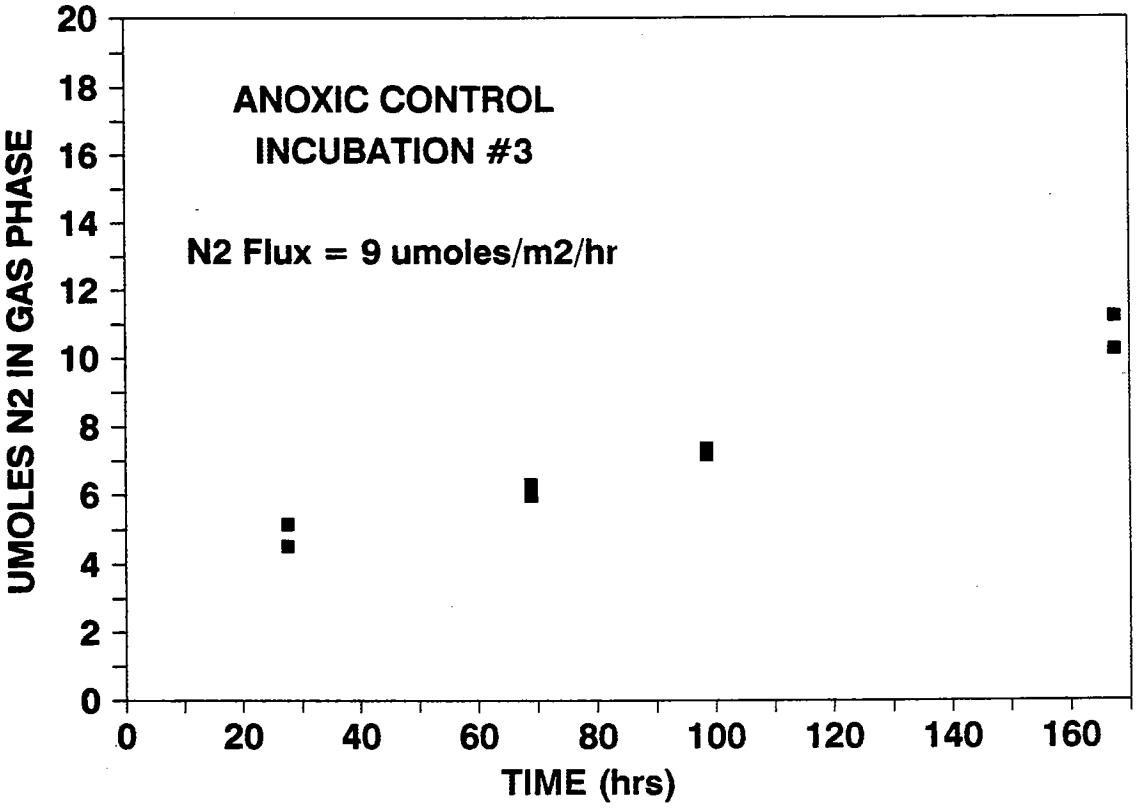

ANOXIC CONTROL
INCUBATION #2
N2 Flux = 27 umoles/m2/hr
(first four pts only)
UMOLES N2 IN GAS PHASE
TIME (hrs)
0
10
20
30
40
50
60
70
80
90
100
110
120
0
40
80
120
160
200
240
280

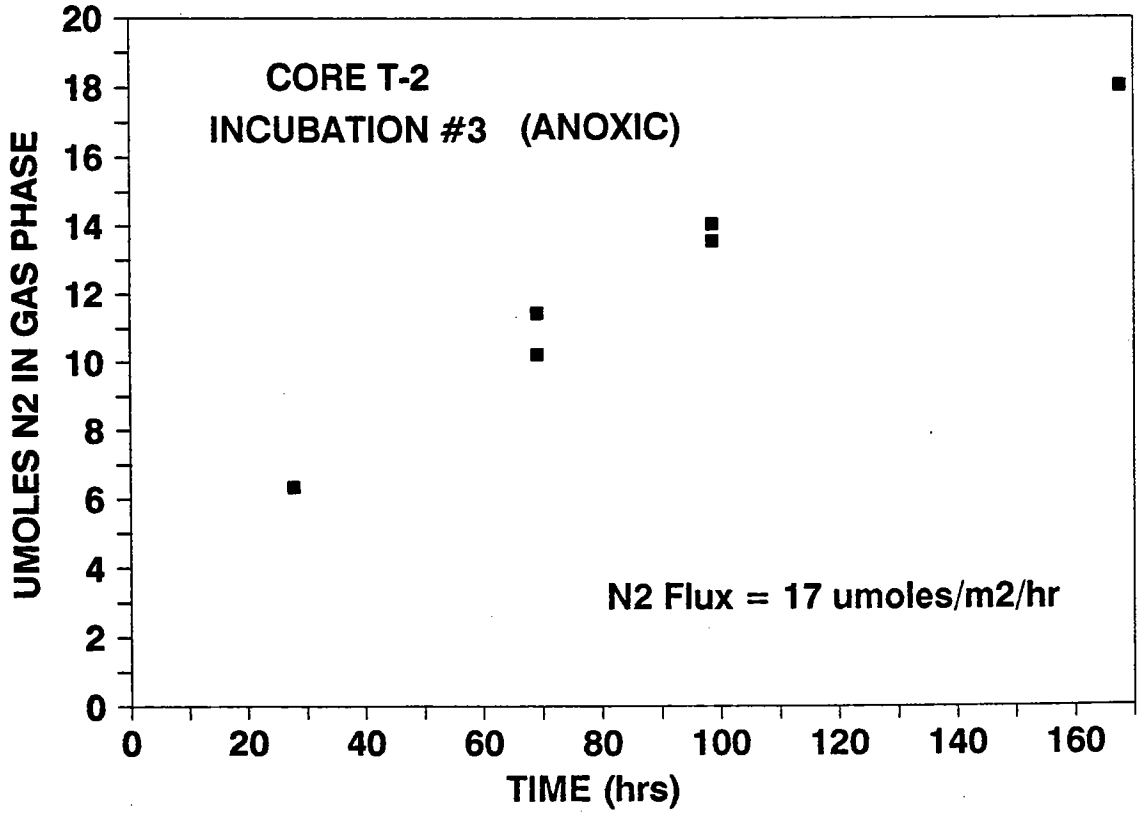

CORE T-2
INCUBATION #2
N2 Flux = 74 umoles/m2/hr
(first four pts only)
UMOLES N2 IN GAS PHASE
TIME (hrs)
0
10
20
30
40
50
60
70
80
90
100
110
120
0
40
80
120
160
200
240
280

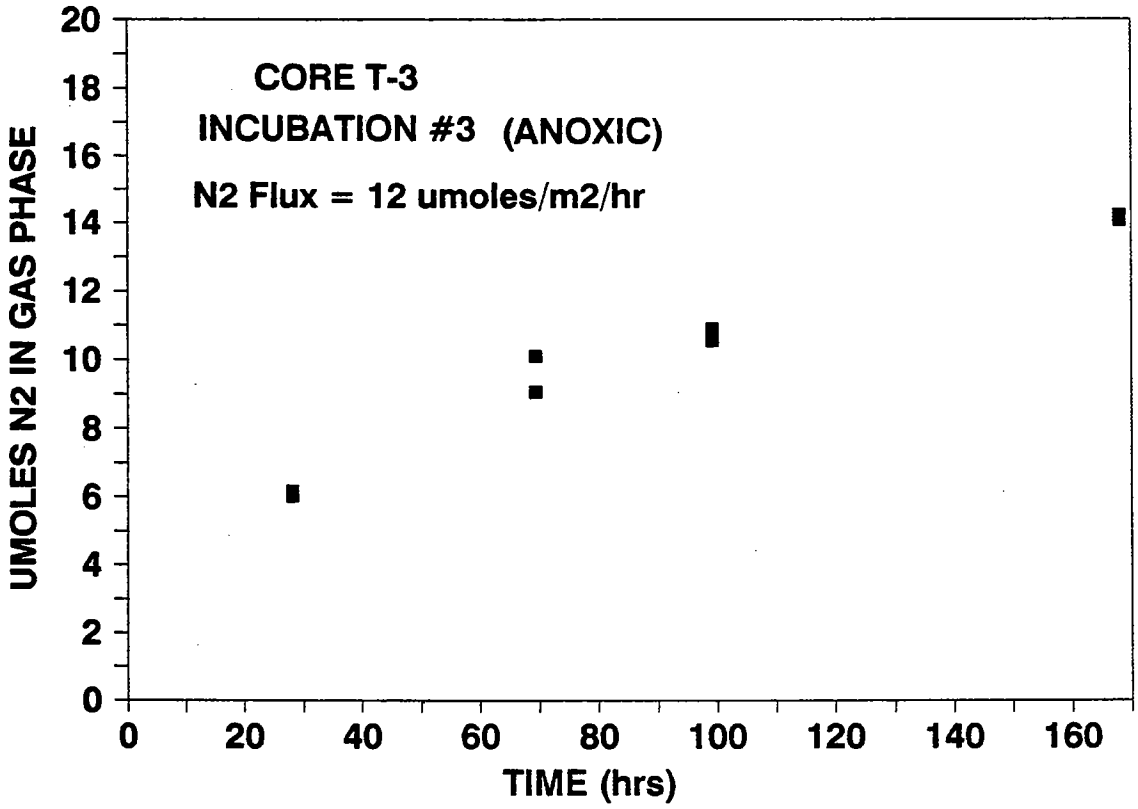

CORE T-3
INCUBATION #2
N2 Flux = 122 umoles/m2/hr
(First four pts only)
UMOLES N2 IN GAS PHASE
TIME (hrs)
0
10
20
30
40
50
60
70
80
90
100
110
120
0
40
80
120
160
200
240
280

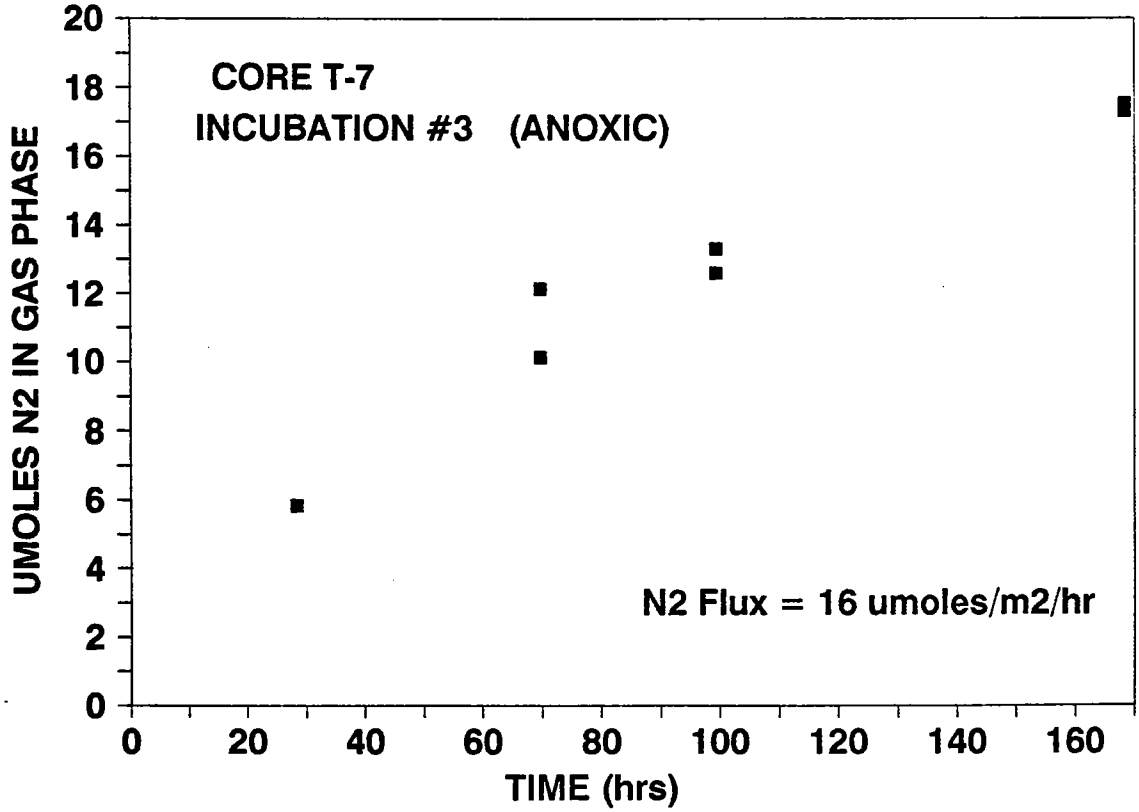

CORE T-7
INCUBATION #2
N2 Flux = 107 umoles/m2/hr
(First four pts only)
UMOLES N2 IN GAS PHASE
TIME (hrs)
0
10
20
30
40
50
60
70
80
90
100
110
120
0
40
80
120
160
200
240
280

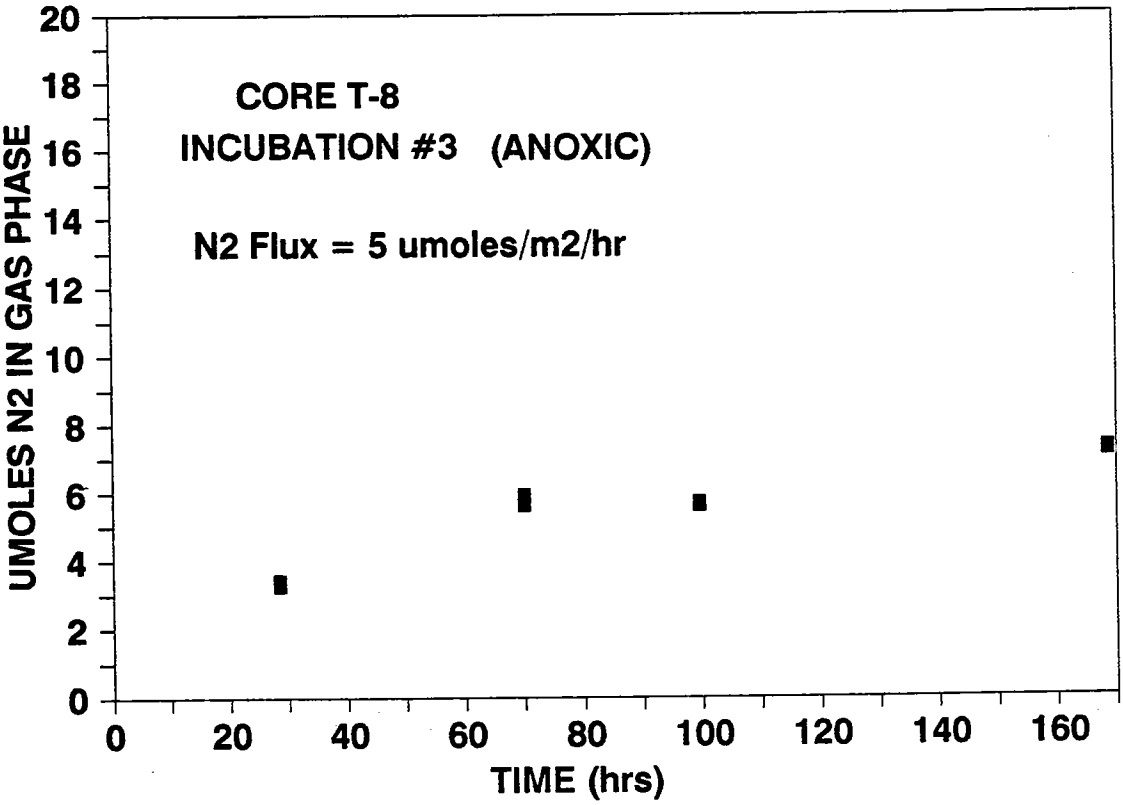

CORE T-8
INCUBATION #2
N2 Flux = 57 umoles/m2/hr
(First four pts only)
UMOLES N2 IN GAS PHASE
TIME (hrs)
0
10
20
30
40
50
60
70
80
90
100
110
120
0
40
80
120
160
200
240
280


ANOXIC CONTROL
INCUBATION #3
N2 Flux = 9 umoles/m2/hr
UMOLES N2 IN GAS PHASE
TIME (hrs)
0
2
4
6
8
10
12
14
16
18
20
0
20
40
60
80
100
120
140
160


CORE T-2
INCUBATION #3 (ANOXIC)
N2 Flux = 17 umoles/m2/hr
UMOLES N2 IN GAS PHASE
TIME (hrs)
0
2
4
6
8
10
12
14
16
18
20
0
20
40
60
80
100
120
140
160


CORE T-3
INCUBATION #3 (ANOXIC)
N2 Flux = 12 umoles/m2/hr
UMOLES N2 IN GAS PHASE
TIME (hrs)
0
2
4
6
8
10
12
14
16
18
20
0
20
40
60
80
100
120
140
160


CORE T-7
INCUBATION #3 (ANOXIC)
N2 Flux = 16 umoles/m2/hr
UMOLES N2 IN GAS PHASE
TIME (hrs)
0
2
4
6
8
10
12
14
16
18
20
0
20
40
60
80
100
120
140
160


CORE T-8
INCUBATION #3 (ANOXIC)
N2 Flux = 5 umoles/m2/hr
UMOLES N2 IN GAS PHASE
TIME (hrs)
0
2
4
6
8
10
12
14
16
18
20
0
20
40
60
80
100
120
140
160

Appendix

Part 2.
Station locations and sediment quality data

Station locations [from Kelly and Kropp, 1992].

Note small differences in latitude/longitude relative to core Stations (Table 2) as well as differences in depth as noted in text. A difference of 0.01′ equals about 18 m.

Station	Date and Time (EDT)	Grab	Latitude Longitude	LORAN Time Delays	Depth (m)	Comments
T2	09/18/91	1	42°20.57′N 71°00.12′W	14038.6 25858.4	7.4	3/4 full grab. No worms. Strong odor. Sediment level flat.
		2	42°20.57′N 71°00.12′W	14038.4 25858.1	7.1	Same as Rep. 1.
		3	42°20.58′N 71°00.12′W	14038.2 25858.0	7.4	Identical to Reps. 1 and 2.
		4	42°20.58′N 71°00.11′W	14038.5 25858.2	7.1	Grab cleaned with DCM and acetone. Level surface. 3/4 full. 0.04 m^2 grabs with bio screens.
T3	09/17/91	1	42°19.81′N 70°57.72′W	14026.8 25836.6	8.1	Full grab. Surface undisturbed and level. Brown floc over anoxic mud. Much detritus, light silt.
		2	42°19.80′N 70°57.71′W	14026.7 25836.5	7.7	Full grab. Same as Rep. 1
		3	42°19.80′N 70°57.70′W	14026.5 25836.4	7.8	Same as Reps 1 and 2.
		4	42°19.80′N 70°57.72′W	14026.8 25836.6	7.9	Same as Reps. 1, 2, and 3. Decon grab with acetone and DCM. Using 0.04 m^2 grab with bio screens.
T7A	09/16/91	1	42°17.36′N 70°58.71′W	14044.9 25829.6	5.2	Good grab 3.4 full. Undisturbed – brown floc overlying anoxic mud.
		2	42°17.37′N 70°58.70′W	14044.9 25829.6	5.0	Good grab 3/4 full. Same as Rep 1.
		3	42°17.37′N 70°58.69′W	14044.9 25829.6	5.2	Same as Reps 1 and 2.
		4	42°17.38′N 70°58.70′W	14044.9 25829.6	5.0	3/4 full grab. Undisturbed surface. Decon grab using acetone and DCM. Using 0.04 m^2 grab with bio screens.
T8	09/17/91	1	42°17.12′N 70°54.75′W	14020.6 25799.6	12.7	1/2 to 3/4 full grab. Undisturbed surface sloping on all sides. Much detritus. Fine silt. Snails.
		2	42°17.12′N 70°54.75′W	14020.6 25799.6	12.7	1/2 to 3/4 full grab. Acceptable. Sediments undisturbed and sloping on all sides. Fine silt. Snails.
		3	42°17.12′N 70°54.75′W	14020.6 25799.6	12.3	Full grab (removed foot pads). Slightly overpenetrated. Sediments undisturbed sloping on one side. Same as Reps. 1 and 2.
		4	42°17.12′N 70°54.75′W	14020.7 25799.7	12.6	Full grab. Same as Reps 1, 2, and 3. Decon grab using acetone and DCM. Using 0.04 m^2 grab with bio screens.

Sediment characteristics measured at grab stations [from Kelly and Kropp, 1992].

Station	TOC	*C. perfringens*	% Gravel	% Sand	% Silt	% Clay
T2	1.75	22900	0.2	63.6	27.8	8.5
T3	3.69	207000	0	44.1	39.1	16.8
T7	2.73	13700	1.8	57.3	27.3	13.6
T8	0.87	7330	0	12.1	52.2	35.7

The Massachusetts Water Resources Authority
Charlestown Navy Yard
100 First Avenue
Charlestown, MA 02129
(617) 242-6000