A Simple Box Model of the Nitrogen Cycle in Boston Harbor and the Massachusetts Bays

Using a model to understand nitrogen cycle dynamics can help determine the effects of moving effluent discharges from Boston Harbor to Massachusetts Bay.

E. ERIC ADAMS, JIM W. HANSEN, RAFAEL L. LAGO, PAM CLAYTON & XUEYONG ZHANG

The Massachusetts Water Resources Authority (MWRA) currently operates two wastewater treatment plants — one on Deer Island and one on Nut Island — that discharge effluent into Boston Harbor. Beginning in 1995, the MWRA plans to start operating its new treatment plant on Deer Island with discharge through a deep ocean outfall in Massachusetts Bay (see Figure 1). Many residents on Cape Cod are concerned that, by moving the outfall offshore, water quality will improve in Boston Harbor, but it may become worse in Massachusetts and Cape Cod bays (hereafter referred to as Mass Bay, or simply bay). This concern has focused on nitrogen because it is the limiting nutrient in the growth of marine algae. Growth of excessive quantities or noxious forms of algae could have detrimental impacts on water quality (through eutrophication), on higher rungs of the food chain (*e.g.*, whales) and even on human health (red tides).

Clearly, the change in water quality in Mass Bay will depend, in large part, on just how much of the existing effluent that enters Boston Harbor is already being transported into the bay. For a conservative substance, mass loading to the harbor from the existing treatment plants must be balanced by transport to the bay; otherwise, its concentration in the harbor would keep increasing. However, nitrogen is not conservative. Nitrogen cycles among different organic and inorganic forms include ammonia, nitrate and nitrite. In addition, some organic nitrogen settles to the bottom where it is nitrified (converted to nitrate) in the presence of oxygen. It can then, in the absence of oxygen, be denitrified into nitrogen gas that escapes to the atmosphere.[1] Some nitrogen in the sedi-

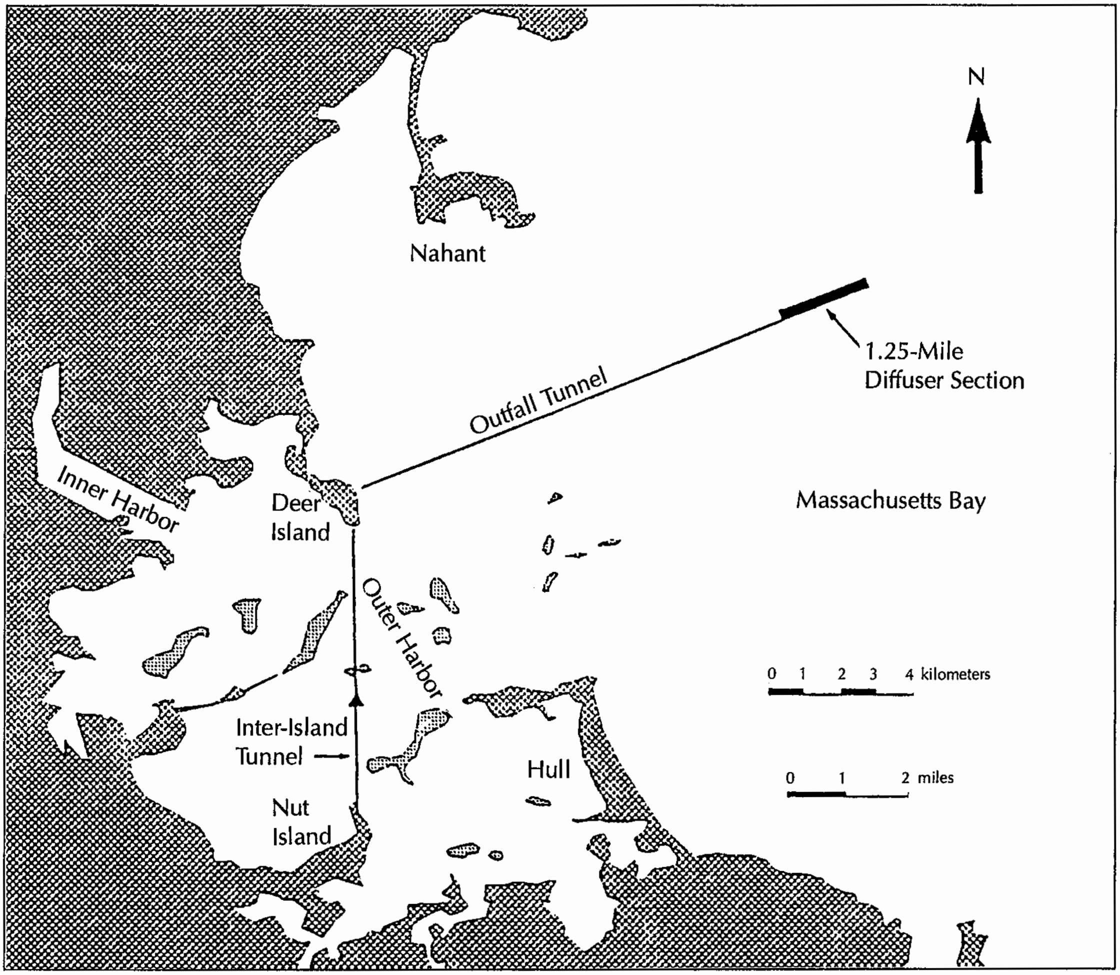

FIGURE 1. Location of the wastewater treatment plants and outfall tunnel.

ments is also buried. Thus, the harbor behaves to some extent as a tertiary treatment plant by removing nutrients prior to their "discharge" into Mass Bay. How efficient is this "plant"; *i.e.*, what percentage of the input nitrogen is lost? Estimates range from about ten percent[2] to as much as about 70 percent.[3]

A simple box model of nitrogen cycle dynamics in Boston Harbor and Mass Bay facilitates an understanding of these processes. The model represents many complex processes using simple linear relationships and it treats system properties (*i.e.*, nitrogen concentrations) as steady in time and well mixed in space over large boxes. However, even though the model is simple, it may provide more realistic answers (or at least bounds on answers) than some previous analyses because it attempts to represent both transport (hydrodynamics and particle settling) and biochemical factors.

Model Description

Basic Structure. The model has six types of nitrogen (see Figure 2). Five types occur in the water: NH_4, ammonia pool; NO_3, nitrate plus nitrite pool; DON, dissolved organic nitrogen pool; PON, particulate organic nitrogen pool; and, BIO, biological pool. One type occurs in the sediments: SED, sediment pool. Nitrogen in various phytoplankton and zooplankton is lumped into the BIO pool. This pool takes up nitrogen from the ammonia (NH_4) and nitrate plus nitrite (NO_3) pools. It excretes nitrogen in the form of NH_4, DON and PON as fecal pellets and dead plankton. The NO_3 pool represents both nitrate and nitrite, which is an intermedi-

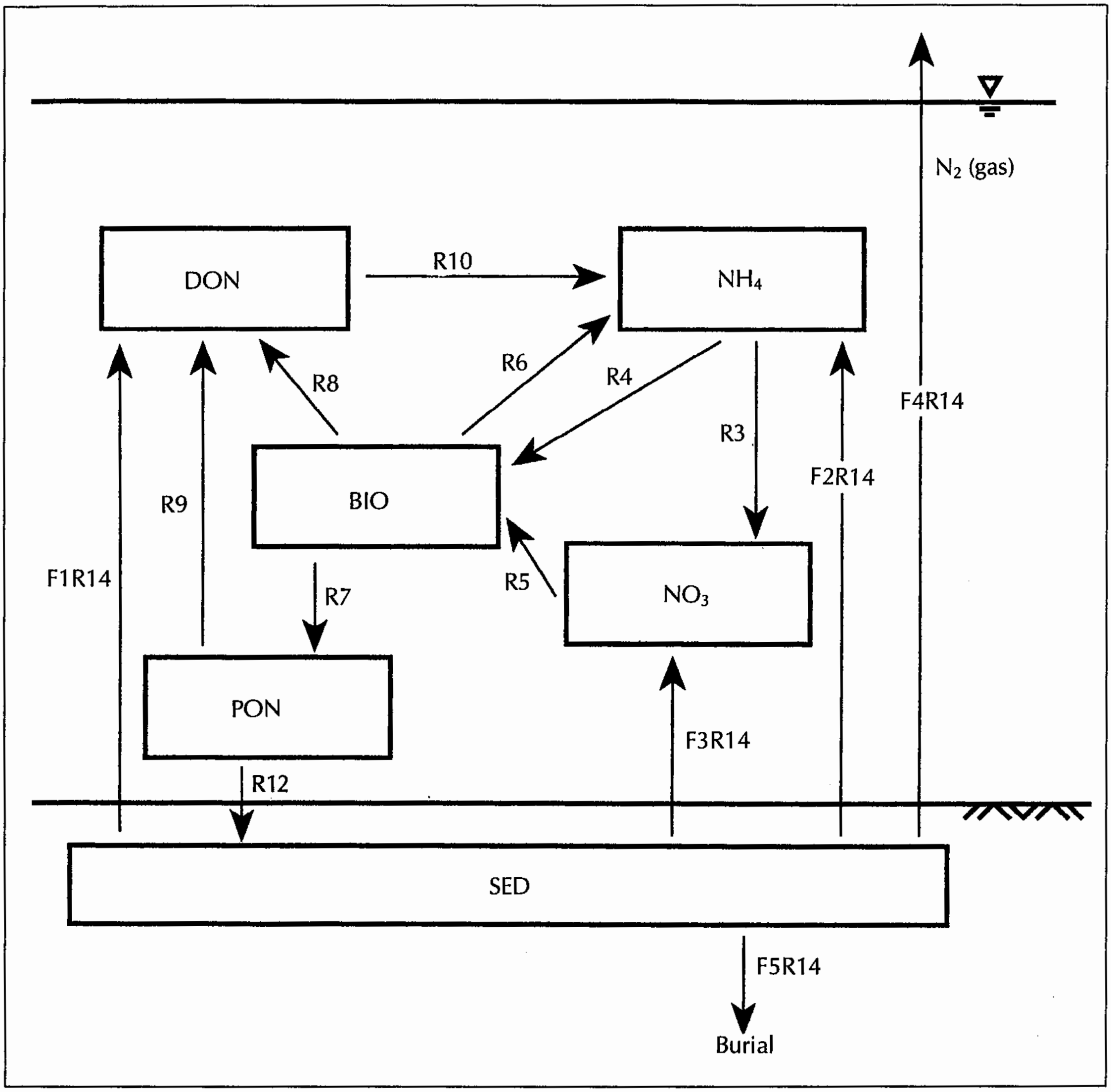

FIGURE 2. Schematic of the harbor nitrogen pools for the box model.

ate step in the oxidation of ammonia to nitrate and typically represents about one-tenth of the combined store of nitrate and nitrite. The NH_4 pool is fed by bacterial hydrolysis of DON, which in turn is fed by the breakdown of material in the PON pool.

The PON that settles out of the water column is also the source for the SED. Although nitrogen in the sediments exists in various forms and there are discrete oxic and anoxic layers, this model has a single sediment pool. Nitrogen is returned to the water column in various forms (DON, NH_4, NO_3) and some is lost from the system. The major loss is to nitrogen gas (denitrification), but some is lost to burial and dredging (lumped into a single term). Diffusion of dissolved nitrogen from the water column to the sediments and resuspension of SED nitrogen into the water column are neglected.

The hydrodynamic portion of the model is constructed by placing an assembly of nitrogen pools within each of two large boxes representing the harbor and the bay (Massachusetts Bay plus Cape Cod Bay) (see Figure 3). The waterborne pools in each box are then allowed to exchange with their respective pools through a volumetric exchange rate, Q_1, that simulates tidal flushing and dispersion. The ocean (Gulf

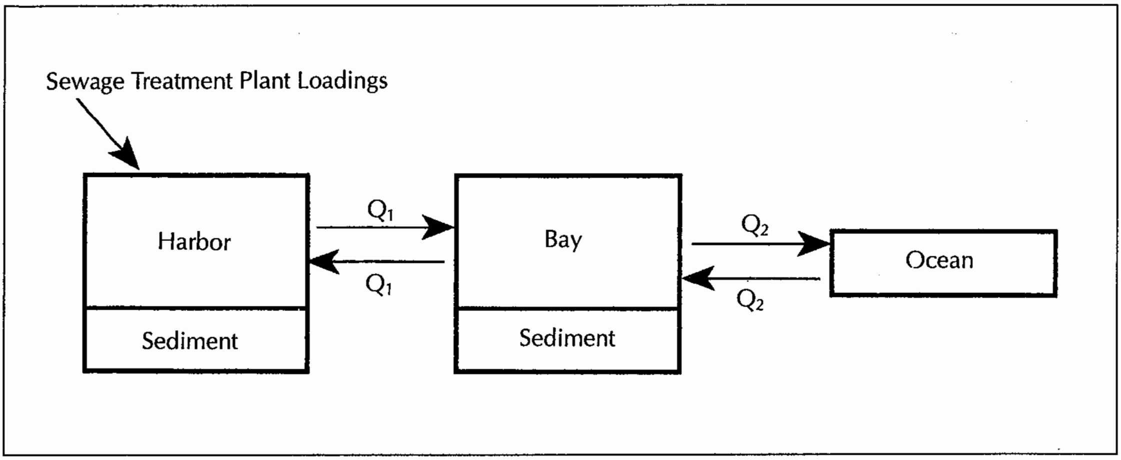

FIGURE 3. Connections among the harbor, bay and ocean boxes for the model.

of Maine) acts as a third box with an assumed constant background concentration of all relevant forms of nitrogen. The ocean and bay communicate through a second exchange rate, Q_2.

Rates. The state variables in the model are the inventories of nitrogen (moles) in each of the twelve pools. The connections between the pools are represented with first-order rate equations. Table 1 lists base case values of the rates for each connection between pools. The rates concerning the biochemical processes (R3 to R10) were taken in abbreviated form from an earlier model constructed by Najarian and Harleman that was applied to the Potomac River estuary.[4] Their model was more complicated. It included such factors as temperature and some nonlinearities as well as more types of nitrogen (*i.e.*, both nitrate and nitrite as well as both phytoplankton and zooplankton). The present model uses values that correspond to a temperature of about 10°C.

The effective exchange rates, Q_1 and Q_2, between the harbor and bay and between the bay and ocean can not be assigned *a priori* in a simple model with only two boxes. The tidal prisms that are physically transported between the boxes during each tidal cycle are known. However, since concentrations are not well mixed in each box (particularly, in the bay), computed fluxes would be overestimated if they were based on tidal prisms. Therefore, the exchange rates were based on empirical residence times. Since the reported residence times for the harbor, based on discharge at the existing treatment plants, range from about three to ten days,[5–8] a base case of five days was studied. For the bay, currents measured by Geyer *et al.* suggest a residence time of 20 to 45 days for surface waters,[9] although there is evidence that the time is significantly greater (up to six months) for bottom waters during periods of stratification. A value of 30 days was chosen for the base case.

Based on these residence times, a value of Q_1 equal to one-fifth of the harbor volume (600 million cubic meters[10]) per day (thus, Q_1 is roughly 120 million cubic meters per day) and a value of Q_2 equal to one-thirtieth of the combined harbor plus bay volumes (150 billion cubic meters[11]) per day (thus, Q_2 is roughly five billion cubic meters per day) were chosen. It can be shown analytically that these choices lead to a harbor residence time of 5.1 days for a conservative substance discharged to the harbor and a bay residence time of 30 days for a substance discharged to the bay. The harbor residence time is slightly greater than five days because it reflects a small amount of transport from the bay back into the harbor. A slightly higher value of Q_1 could have been chosen to yield a residence time of identically five days, but this option was considered unnecessary given the small difference.

The settling rate of PON and all of the rates concerning the sediment box are considered the least certain parameters. Equal sediment decay rates in the harbor (R14) and bay (R15) of 0.01 per day (d^{-1}) were based on U.S. Environmental

Protection Agency data.[12] A PON settling velocity of 0.001 centimeters per second was suggested as typical.[12,13] Assuming average harbor and bay depths of six[10] and 36 meters,[11] respectively, leads to a loss rate of 0.15 d^{-1} for the harbor (R12) and 0.025 d^{-1} for the bay (R13). The fractions of sediment nitrogen that are regenerated as ammonia (F2 equal to 0.35 in the harbor and F7 equal to 0.35 in the bay), nitrogen gas (F4 equal to 0.4 in the harbor and F9 equal to 0.1 in the bay), nitrate (F3 equal to 0.05 in the harbor and F8 equal to 0.45 in the bay), and dissolved organic nitrogen (F1 equal to 0 in the harbor and F6 equal to 0.1 in the bay), as well as the fractions lost to burial (F5 equal to 0.2 in the harbor and F10 equal to 0 in the bay) were established based on typical sediment texture and available denitrification measurements.[2]

Loadings. Monthly average nitrogen concentrations, measured in the effluent of the Deer and Nut Island treatment plants from May 1989 to October 1991, were used to calculate an average annual treatment plant loading for each type of nitrogen (see Table 2). Although effluent from the Deer Island plant enters President Roads shipping channel near the boundary between Boston Harbor and Mass Bay — hence, some nutrients enter the bay on ebb tide — the entire treatment plant loading was put into the harbor in order to be consistent with the interpretation of harbor residence time measurements (and, hence, the model exchange rate Q_1). Average effluent concentrations and their range for the Deer Island effluent are presented in Table 3. Since data were not available separately for dissolved and particulate forms of organic nitrogen (only total organic nitrogen), it was assumed that the organic nitrogen was fifty percent DON and fifty percent PON. Note that the total nitrogen loading of 2.4 million moles per day, or 880 million moles per year for the two-and-one-half-year period, compares with an estimate of 790 million moles per year for effluent reported by Menzie *et al.*[10] The same reference reports a total nitrogen loading to the harbor from all sources as 930 million moles per year that includes 80 million moles per year from sludge (which ceased in December 1991) and 70 million moles per year combined from rivers, runoff, groundwater and air.

TABLE 1
Base Case Parameter Estimates

Parameter	Description	Value
Q_1	Harbor/Bay Exchange Rate (Harbor Residence Time)	1.2×10^8 m^3/d (~ 5 d)
Q_2	Bay/Ocean Exchange Rate (Bay Residence Time)	5×10^9 m^3/d (~ 30 d)
R3	NH_4 to NO_3 Rate	0.1 d^{-1}
R4	NH_4 to BIO Rate	0.5 d^{-1}
R5	NO_3 to BIO Rate	0.05 d^{-1}
R6	BIO to NH_4 Rate	0.005 d^{-1}
R7	BIO to PON Rate	0.015 d^{-1}
R8	BIO to DON Rate	0.015 d^{-1}
R9	PON to DON Rate	0.025 d^{-1}
R10	DON to NH_4 Rate	0.006 d^{-1}
R12	PON to SED Rate (Harbor)	0.15 d^{-1}
R13	PON to SED Rate (Bay)	0.025 d^{-1}
R14	SED Decay Rate (Harbor)	0.01 d^{-1}
R15	SED Decay Rate (Bay)	0.01 d^{-1}
F1	SED to DON Fraction (Harbor)	0.0
F2	SED to NH_4 Fraction (Harbor)	0.35
F3	SED to NO_3 Fraction (Harbor)	0.05
F4	SED to N_2 Fraction (Harbor)	0.4
F5	SED to Burial Fraction (Harbor)	0.2
F6	SED to DON Fraction (Bay)	0.1
F7	SED to NH_4 Fraction (Bay)	0.35
F8	SED to NO_3 Fraction (Bay)	0.45
F9	SED to N_2 Fraction (Bay)	0.1
F10	SED to Burial Fraction (Bay)	0.0

Another important loading to the system is the background nitrogen washed into the bay from the ocean (Gulf of Maine) with the tide. In principle, this ocean source also includes some treatment plant nitrogen originally discharged to the harbor, but this contribution can be shown to be negligible. For example, with a treatment plant loading of 2.4 million moles per day and Q_2 equal to 5 billion cubic meters per day, the average

TABLE 2
Annual Average Loadings from Deer & Nut Island Treatment Plants

Nitrogen Type	Loading (moles/day)	Percent
DON	509,000	21
NH_4	1,130,000	47
NO_3	256,000	11
PON	509,000	21
Total	2,404,000	100

bay concentration of total nitrogen from treatment plant sources would be about 0.5 microMolar (μM) — a factor of 30 less than the average ocean concentration shown in Table 3.

The bay also receives loading from other sources including groundwater, other treatment plants and other non-point sources. However, these additional sources too are small compared with the ocean source.[14] The loadings to the bay were calculated from the bay/ocean exchange flow rate, Q_2, times the ocean concentrations. Average ocean concentrations (see Table 3) in turn came largely from an annual bay survey of Gulf of Maine boundary stations (Stations 1, 12 and 13 reported in Tables 1 to 6 of Townsend *et al.*[15]). Measurements did not distinguish BIO from PON, so the reported PON values were split equally between PON and BIO. There also were no measurements of DON. Therefore, it was assumed that DON concentrations were 2.5 times the measured PON (following measurements by Howes and Taylor in New Bedford Harbor[16]). While the data in Table 3 represent averages from six cruises over about a year (from October 1989 to August 1990), the actual data showed significant seasonal variability. For these reasons, and because the bay loadings rely on an uncertain bay/ocean exchange rate, there is less confidence about the nitrogen loadings to the bay than about the treatment plant loadings to the harbor.

Solution Procedure. The model consists of a set of twelve coupled, linear first-order differential equations representing the twelve nitrogen pools (six each in the harbor and in the bay). Letting A represent the 12 by 12 matrix of rate constants, $\vec{L}$ the 12 by 1 column vector of loadings, and $\vec{N}$ the 12 by 1 column vector of nitrogen inventories:

$$\frac{d\vec{N}}{dt} = A\vec{N} + \vec{L} = 0 \qquad 1$$

TABLE 3
Simulated & Measured Nitrogen Concentration in the Harbor & Bay (in μM)

Nitrogen Type	Treatment Plant*	Harbor**	Bay***	Ocean****
DON§	330	11.8	6.8	5.0
	250–540	1.2–*36*§§	1.2–*13*	1.2–*9*
NH_4	740	2.8	0.15	0.6
	560–1,070	*0.8*–*7*	*0.2*–1.5	*0.05*–1.4
NO_3§§§	180	5.7	3.6	8.0
	14–610	*0.9*–13	*1.6*–13	*4*–13
BIO+PON	330	14.0	5.5	1.0
	250–540	0.5–*14.4*	0.5–*5.4*	0.2–1.8

Notes: * Average (upper) and range (lower) of measurements at Deer Island Sewage Treatment Plant from May 89 to October 91
** Model prediction (upper) and range of measurements from Reference 15 Sta. 6 (lower)
*** Model prediction (upper) and range of measurements from Reference 15 Stas. 8 & 9 (lower)
**** Average (upper) and range (lower) of measurements in the Gulf of Maine from Reference 15 Stas. 1, 12 & 13
§ "Measured" DON is 250 percent of reported BIO+PON
§§ Italicized values represent measurements during spring & summer
§§§ "Measured" NO_3 is the sum of reported NO_2 plus NO_3

TABLE 4
Simulated Nitrogen Inventories & Concentrations Due to Treatment Plant & Ocean Sources

	Run 1 (Treatment Plant & Ocean)		Run 2 (Treatment Plant Only)		Run 3 (Ocean Only)	
Nitrogen Type	**Inventory (moles × 10^6)**	**Concentration (μM)**	**Inventory (moles × 10^6)**	**Concentration (μM)**	**Inventory (moles × 10^6)**	**Concentration (μM)**
Harbor						
BIO	6.4	10.7	3.8	6.3	2.6	4.4
DON	7.1	11.8	3.0	5.1	4.0	6.7
NH_4	1.7	2.8	1.6	2.6	0.1	0.17
NO_3	3.4	5.7	1.7	2.9	1.7	2.9
PON	2.0	3.3	1.5	2.5	0.46	0.77
SED	29.8	—	22.9	—	7.0	—
Bay						
BIO	631.1	4.3	23.2	0.16	607.9	4.1
DON	1,006.3	6.8	29.1	0.2	977.2	6.6
NH_4	22.1	0.15	1.1	0.007	21.1	0.14
NO_3	527.1	3.6	6.4	0.04	520.7	3.5
PON	175.9	1.2	7.8	0.05	168.1	1.1
SED	439.7	—	19.4	—	420.3	—

Under the assumption of steady state (which ignores tidal and seasonal variations), $\vec{N}$ can be found by matrix inversion as:

$$\vec{N} = -A^{-1}\vec{L} \qquad 2$$

The equations were solved by a computer running matrix manipulation software.

Results

Base Case. Five runs were made using the base case parameters. Run 1 used the sewage treatment plant loadings to the harbor and the ocean loadings to the bay. Table 4 displays the simulated inventories of nitrogen in both the harbor and the bay. The table shows that nitrogen in the harbor is mainly in the active sediments (59 percent), while the bay shows a more even distribution among DON, BIO, NO_3 and SED. The distribution in the harbor is the result of high PON loading from the treatment plants in comparison with the ocean (see Tables 2 and 3) combined with a relatively slow sediment decay rate (0.01 d^{-1}) compared with other rates in the system.

Concentrations in each of the ten water column pools are also computed in Tables 3 and 4 by dividing the simulated inventories in the harbor by a harbor volume of 600 million cubic meters and by dividing the simulated inventories in the bay by a bay volume of 150 billion cubic meters. Table 3 also includes measured average concentrations and the annual range in concentration in the harbor and bay. Harbor concentrations are represented by Townsend *et al.*'s Station 6, actually located just east of Deer Island at the harbor mouth; bay concentrations are represented by Stations 8 and 9, located approximately 20 and 30 kilometers ENE of Deer Island.[15] As with the ocean loadings, it was assumed that DON equals 2.5 times the measured PON. In examining Table 3, it is clear that simulated concentrations fall within the general range of measurements. The agreement is best during spring and summer (when measured NO_3 and NH_4 are lowest and measured PON and BIO are largest).

The rate of denitrification in the harbor for

TABLE 5
Simulated Harbor Denitrification & Burial Rates as Percentages of Total Nitrogen Loading From the Existing Treatment Plants

		Loadings Include:		Nitrogen Loss in Harbor Sediments		
Run	**Description**	**Plant**	**Ocean**	**Denitrif. (%)**	**Burial (%)**	**Total (%)**
1	Base Case Parameters	Yes	Yes	5.0	2.5	7.5
2	Base Case Parameters	Yes	No	3.8	1.9	5.7
3	Base Case Parameters	No	Yes	1.2	0.6	1.8
4	Same as Run 2 Except Outfall Moved to Bay (Still Primary Treatment)	Yes	No	0.06	0.03	0.09
5	Same as Run 4 Except Secondary Treatment Assumed	Yes	No	0.04	0.02	0.06
6	Same as Run 2 Except Sediment Decay Rate Increased From 0.01 to 0.1 d^{-1}	Yes	No	3.8	1.9	5.70
7	Same as Run 2 Except PON Settling Velocity Increased From 10^{-5} to 10^{-4} m/sec in Harbor & Bay	Yes	No	8.2	4.1	12.3
8	Same as Run 2 Except Harbor Residence Time Increased From 5 to 10 Days	Yes	No	5.8	2.9	8.7
8*	Same as Run 2 Except Harbor Residence Time Decreased From 5 to 3 Days	Yes	No	2.7	1.3	4.0
9	Same as Run 2 Except Bay Residence Time Increased from 30 to 120 Days	Yes	No	3.9	1.9	5.8
10	Same as Run 2 Except PON Production Rate Increased From 0.015 to 0.05 d^{-1}	Yes	No	4.5	2.3	6.8
11	Same as Run 2 Except Fraction of Harbor Sediment Nitrogen Regenerated as N_2 Increased From 0.5 to 0.75	Yes	No	5.7	1.9	7.6
12	Combination of Runs 7–11	Yes	No	19.5	6.5	26.0
13	Combination of Runs 7–11	Yes	Yes	22.1	7.4	29.5

this run is 0.12 million moles per day, while the rate of burial plus dredging is 0.06 million moles per day. Table 5 expresses these rates as five and 2.5 percent, respectively, of the treatment plant loading of 2.4 million moles day. The value of five percent for harbor denitrification compares with an annual estimate of about eight percent extrapolated from denitrification measurements by Kelly and Nowicki.[2] Ongoing denitrification measurements (from April to September 1992) that were uncorrected for season or sediment type also indicate that about eight percent of harbor nitrogen is being denitrified.[17] Meanwhile, the 2.5 percent burial rate compares with Kelly and Nowicki's summary of measurements that indicates about a four percent rate.[2] Their estimates refer to a time when sludge was still being discharged to the harbor. Once the practice was stopped in December 1991, nitrogen loading (and, hence, harbor denitrification and burial rates) could be expected to fall by about ten percent.

The sources of nitrogen contributing to the harbor denitrification and burial rates in Run 1 include both the direct treatment plant loading to the harbor and the ocean loading. Runs 2 and

3 were made to help distinguish these two sources by including only the treatment plant nitrogen (for Run 2) and only the ocean nitrogen (for Run 3). Resulting concentrations are listed in Table 4. The computed harbor denitrification and burial rates, expressed as a percentage of the existing treatment plant nitrogen loading, are shown in Table 5. In each table, the sum of the results for Runs 2 and 3 equals the result for Run 1, which is to be expected since the model is linear. Data in Table 4 suggest that the majority (57 percent) of the total nitrogen concentration in the harbor comes directly from the treatment plants, and that only a minor fraction (three percent) of the total nitrogen concentration in the bay comes directly from the treatment plant. Comparing Runs 2 and 3 in Table 5 suggests that about 75 percent of the total nitrogen loss occurring in Boston Harbor is due to nitrogen discharged directly from the treatment plants, while 25 percent is imported from the Gulf of Maine. From Run 2, the fraction of treatment plant nitrogen that is simulated to be lost in Boston Harbor is about 5.7 percent with the remainder being transported to Mass Bay.

It is instructive to compare the simulated harbor sediment loss rate of 5.7 percent for Run 2 with an estimate that ignores biochemical recycling in the water. Particulate organic nitrogen represents approximately 21 percent of the harbor loading (see Table 2). Treating the harbor as a well mixed box characterized by a hydrodynamic residence time of five days and a characteristic settling time of seven days (average depth of six meters divided by a settling rate of 0.001 centimeters per second) suggests that approximately 42 percent of the solids settle in the harbor. If 60 percent of the settled PON is lost (40 percent to denitrification and 20 percent to burial), then the percentage of the total treatment plant nitrogen loading that is lost in the harbor would be approximately 5.3 percent (21 percent times 42 percent times 60 percent), close to the simulated 5.7 percent. The small difference may result from the fact that some of the dissolved nitrogen (NH_4, NO_3 and DON) generated by the sediments later becomes PON, resettles and is either denitrified or buried.

In order to evaluate the effect of moving the outfall (without changing the level of treatment), a fourth simulation was made, in which the treatment plant loading was moved from the harbor to the bay and the ocean loading was again omitted. Table 5 indicates that a small fraction of this loading will still be denitrified in Boston Harbor (about 0.06 percent). A total of 0.09 percent will be lost through a combination of denitrification, burial and dredging. The *net* effect of moving the outfall would be found by subtracting the latter percentage from the corresponding percentage of Run 2 (5.7 percent), yielding a value of 5.6 percent of the treatment plant loading. Thus, to the extent that the model formulation and parameters are realistic, the effect of the outfall relocation (leaving the level of treatment constant) will be to increase the effective nitrogen loading to the bay by somewhat less than six percent.

A final simulation (Run 5) was made to evaluate the combined effect of moving the outfall *and* implementing secondary treatment, which is scheduled for 1999. Effluent from an activated sludge plant is expected to contain nitrogen primarily in the form of ammonia and nitrate, with comparatively small percentages of organic nitrogen. Accordingly, the percentages of NH_4, NO_3, DON and PON are assumed to be 50, 40, 5 and 5, respectively. Total nitrogen loading is also expected to decrease somewhat following secondary treatment. For example, in a recent survey of U.S. sewage treatment plants compiled by Murcott and Harleman, the average total nitrogen removal rate reported for primary treatment was 15 percent, while that for biological secondary treatment was 31 percent.[18] Run 5 was based on the assumption that the total nitrogen loading will be reduced by 15 percent. Table 5 indicates that the absence of much settleable PON in the secondary effluent and the smaller total nitrogen loading result in even less denitrification in the harbor (about 0.04 percent) and total loss (about 0.06 percent) than predicted for Run 4, although both percentages are very small in absolute value. The net effect of moving the outfall and implementing secondary treatment will be a *decrease* in the effective flux of nitrogen to the bay of about nine percent (94 percent of the existing primary load that reaches the bay minus the future secondary load assumed to be equal to 85 percent of the existing primary load). It is recognized that these calculations are average loadings to the entire Massachusetts and Cape Cod bay system; the change in nitrogen composition accompanying secondary treatment may result in more rapid nitrogen uptake, which in turn could result in local regions of high productivity, an effect that cannot be computed in a two-box model.

Variations from the Base Case. In order to gauge the sensitivity of the calculations to model uncertainty, two sets of sensitivity tests were made. In the first set (not shown), the response of each of the twelve nitrogen pools to a systematic five-percent increase in each of the rates indicated in Table 1 was determined. This sensitivity analysis was used to understand which rates deserved further attention and to understand, in general, whether the biochemical or the transport (*i.e.*, hydrodynamic and settling) factors are more important. It appeared that two of the most important rates were the harbor/bay exchange rate and the PON settling rate, both essentially transport factors.

Sensitivity tests are often used as the first step in model calibration. At this point, no serious calibration was attempted because data show substantial seasonal variation that cannot be handled with a steady state model. Based on a comparison of measurements with the results of Run 1, some parameter adjustment would certainly be warranted, but the parameters appear to be reasonable.

Eight large-scale parameter changes were also tested (Runs 6 to 13). These tests were guided by results of the earlier sensitivity study. These changes, in most of the cases, were designed to increase loss of nitrogen in the harbor sediments. Table 5 shows the results of these changes in terms of the percentage of treatment plant nitrogen that is either denitrified or buried in the harbor. Like Runs 2 and 4, Runs 6 to 12 were made with the ocean loading turned off; hence, the results of the changes can be compared to the base case Run 2.

In Run 6, the decay rates in the sediment boxes (R14 and R15) were increased by ten times (from 0.01 to 0.1 d^{-1}). Original sensitivity had shown that this increase had no effect on denitrification. Table 5 shows it has no effect even for a large change. The result of an increase in decay rate corresponds to a decrease in sediment nitrogen inventory so that their product, which is proportional to the sediment-to-water nitrogen flux, is unchanged.

In Run 7, the PON settled at a faster rate (ten times faster than the base case). During spring PON may be dominated by fecal pellets from zooplankton. These pellets are hard and compact and settle much faster than other particulate matter. With the increased deposition rate, the sediment nitrogen losses were increased by a factor of about two (to a total of 12.3 percent).

In Runs 8, 8* and 9, the exchange rates, Q_1 and Q_2, were adjusted. Run 8 shows that increasing the residence time from five days to ten days results in an increase in sediment nitrogen loss by a factor of about one and one half (from 5.7 to 8.7 percent). However, the concentration of BIO plus PON in the harbor for this run is 18.9 μM with treatment plant loading only. It becomes 26.1 μM with both treatment plant and ocean loading. Both concentrations are higher than the range of measured concentrations shown in Table 3. Therefore, Run 8* was made in which the harbor residence time was decreased to three days. (This time is still within the range of field observations and is consistent with numerically simulated flushing rates made by Signell for regions near the harbor mouth that exchange rapidly due to the deep shipping channels.[19]) For this run, the nitrogen losses in the harbor sediments decrease to 4.0 percent, while the harbor concentration of BIO plus PON drops to 5.1 μM. If the ocean nitrogen loading is included, nitrogen losses in the harbor sediments total 5.2 percent and the harbor BIO plus PON concentration becomes 9.4 μM, well within the range of observations. The simulations suggest that the harbor residence time is more likely to be less than five days rather than more. Rather than massive denitrification, rapid flushing of the outer reaches of Boston Harbor may better explain why eutrophication has not been a problem in Boston Harbor and why nitrogen levels are as low as they are, despite the high loadings from the existing treatment plants. Run 9 shows that increasing the bay residence time from 30 to 120 days results in an insignificant increase in the nitrogen losses in the harbor sediments from 5.7 to 5.8 percent.

PON is created in the model from BIO

through zooplankton excretion and phytoplankton and zooplankton death. Run 10 reveals that increasing the governing rate (R7) from 0.015 to 0.05 d^{-1} results in an increase in nitrogen losses in the harbor sediments from 5.7 to 6.8 percent.

The fraction of the sediment decay that yields nitrogen gas is obviously one of the most critical model parameters. Run 11 suggests that increasing this fraction by 50 percent (from 0.4 to 0.6, with the remaining 0.4 split evenly between NH_4 and burial) results in a proportional increase in the harbor denitrification percentage from 3.8 to 5.7 percent and an increase in the nitrogen losses in the harbor sediments from 5.7 to 7.6 percent.

The final runs (Runs 12 and 13) were made by simultaneously using a combination of the changes tested in Runs 7 through 11. The PON settling rates were increased to 1.5 and 0.25 d^{-1} for the harbor and bay, respectively. The harbor and bay residence times were 10 and 120 days, respectively. The PON production rate was increased to 0.05 d^{-1}, and the sediment denitrification fraction was increased to 0.6. Run 12 includes treatment plant loading. Run 13 includes loading from both the treatment plants and the ocean. While each of the above changes might individually reflect reality, they do not appear to be realistic in combination, especially as a representation of annual average conditions. Nonetheless, the upper bounds on nitrogen loss in the harbor sediments of 19.5 (denitrification), 6.5 (burial) and 26 percent (total) indicated for Run 12 are still modest fractions of the treatment plant loading. They are comparable in absolute value with the decrease of about 15 percent that can be expected once secondary treatment is implemented. The upper bound on harbor denitrification of 22.1 percent indicated for Run 13 is less than one-third of some previous estimates (about 70 percent).

Summary & Conclusions

A simple box model was developed to study the nitrogen cycle in Boston Harbor and Massachusetts and Cape Cod bays and to provide bounding estimates of the amount of denitrification that occurs as the result of the discharge of nitrogen through the existing treatment plants. The following conclusions can be drawn from this study:

1. Using *a priori* parameter estimates, the amount of denitrification taking place in harbor sediments represents about five percent of the nitrogen loading from the treatment plant, while the loss due to sediment burial represents about 2.5 percent. The total nitrogen loss in harbor sediments is thus about eight percent. The denitrification rate of five percent compares with about eight percent computed by Kelly and Nowicki based on direct measurements.[2] Given all of the uncertainties, the fairly close agreement suggests that the model formulation and parameters are reasonable.

2. About 25 percent of the computed nitrogen loss in harbor sediments is due to background nitrogen that is transported to the harbor from the Gulf of Maine or from other sources in Mass Bay. The simulated percentage of treatment plant nitrogen that is lost is about six percent, meaning that 94 percent of the nitrogen loading to the harbor is being exported to Mass Bay.

3. Moving the outfall into Mass Bay (with no changes in the level of treatment) would thus increase loading to the bay by about six percent. Implementing secondary treatment will remove about 15 percent of the nitrogen, so the average nitrogen loading to the bay would decrease by nine percent compared with present conditions. This decrease is in addition to a similar loading reduction that occurred when sludge was no longer discharged to the harbor (after December 1991).

4. The model is sensitive to many parameters that are uncertain. Perhaps the most important is the harbor/bay exchange rate characterized by the harbor residence time. Comparing simulated and measured concentrations of biological and particulate organic forms of nitrogen suggests that rapid flushing of the outer reaches of Boston Harbor may be a better explanation than high rates of denitrification for the absence of eutrophication and the modest nitrogen concentrations observed in Boston Harbor, despite the high nitrogen loading from the existing treatment plants.

5. Using simultaneous upper bound estimates (leading to maximum denitrification and burial) for the most sensitive parameters yields a computed total nitrogen loss in harbor sediments of 26 percent of the treatment plant loading (using treatment plant loadings only). While substantially larger than the base case value of about six percent, it still suggests that most of the existing treatment plant nitrogen is being flushed to the bay. Similarly, the upper-bound estimate on harbor denitrification for both treatment plant and ocean loadings of about 22 percent, while substantially larger than the base case value of five percent, is significantly less than some previous estimates (about 70 percent) that have been made by extrapolating measurements without due consideration of transport processes.

6. As formulated, the model is oversimplified, particularly because its spatial representation is based on two boxes and the fact that it is steady state. Based on the sensitivity tests, additional sophistication could easily be justified. Additional steps, in increasing order of complexity, could include using more boxes, incorporating the nitrogen cycle dynamics into existing 2-D (depth-average) time-dependent hydrodynamic and transport models,[5,19] and, finally, incorporating the nitrogen cycle dynamics into 3-D time-dependent models that are beginning to be applied to Mass Bay. In the last two cases, attempts should also be made to calibrate model parameters.

7. Although more sophisticated models are certainly justified, the simple box model calculations are instructional, both as an educational tool (the original purpose of this study) and as a preliminary way to put boundaries on a complex problem.

ACKNOWLEDGMENTS — *This article grew out of a Spring 1992 undergraduate term project completed by Jim Hansen and Rafael Lago under sponsorship of the Massachusetts Institute of Technology's (MIT) Environmental Engineering Clinic. The matrix manipulation package used in the study was MATLAB. The authors thank the following people who contributed many helpful suggestions during the project: Drs. Mike Connor, Mike Mickelson and Meryl Albert of the MWRA; Anne Giblin, of the Marine Biological Laboratory; Jack Kelly, of Battelle Ocean Sciences; and, Gene Gallagher of UMass-Boston. The authors also appreciate the thorough reviews provided by anonymous reviewers.*

ERIC ADAMS *received a Ph.D. from MIT in 1975. He is currently a Senior Research Engineer in MIT's Parsons Lab, where he directs the Environmental Engineering Clinic, a program designed to allow students to work on public and private sector environmental engineering projects as part of their undergraduate education. He is also Associate Director for Research in MIT's Sea Grant College Program, where he has been active in Boston Harbor issues including the development of receiving water quality models used in facility planning for outfall siting and combined sewer overflow remediation.*

JIM HANSEN, *from Dillon, Montana, is a senior in MIT's Civil and Environmental Engineering Department. After graduation he hopes to work with an environmental consulting firm.*

RAFAEL LAGO *graduated with a B.S. in Civil Engineering from MIT last spring and is currently working for ABB Environmental Services, Inc., in Washington, D.C.*

PAM CLAYTON, *from Jackson, Mississippi, is a senior mathematics major at Tougaloo University, Tougaloo, Mississippi. She spent the summer of 1992 as an intern in MIT's Parsons Lab.*

XUEYONG ZHANG, *from Beijing, China, is a Ph.D. candidate in MIT's Civil and Environmental Engineering Department. He received an M.S. from MIT in 1990 and has eight years of experience working on physical and mathematical modeling at the Institute for Water Conservancy and Hydroelectric Power Research in Beijing.*

REFERENCES

1. Seitzinger, S.P., "Denitrification in Freshwater and Coastal Marine Ecosystems: Ecological and Geo-

chemical Significance," *Limnology and Oceanography*, Vol. 33, 1988, pp. 702–724.

2. Kelly, J.R., & Nowicki, B.L., "Sediment Denitrification in Boston Harbor," draft report submitted to the Massachusetts Water Resources Authority, 1992.

3. Christensen, J.P., "Nitrogen Loading to Boston Harbor and Export to Massachusetts Bay," Report No. 91-125, Oceanic Associates, Brunswick, Maine, 1991.

4. Najarian, T.O., & Harleman, D.R.F., "Real Time Model of Nitrogen Cycle Dynamics in an Estuarine System," Report No. 204, R.M. Parsons Laboratory, Massachusetts Institute of Technology, Cambridge, Mass., 1975.

5. Adams, E.E., Kossik, R.F., Cosler, D.J., MacFarlane, J.K., & Gschwend, P.M., "Calibration of a Transport Model Using Halocarbons From Sewage Effluent as Tracers," in *Estuarine and Coastal Modeling*, proc. of 1st Int'l Conf., ASCE, Newport, R.I., Nov. 1989, M.L. Spaulding *et al.*, eds., 1990, pp. 380–389.

6. Sung, W., "Some Observations on the Temporal Variation of Dissolved Copper and Zinc in Boston Harbor," *Civil Engineering Practice*, Vol. 6, No. 1, 1991, pp. 99–110.

7. Shea, D., & Kelly, J.R., "Transport and Fate of Toxic Contaminants Discharged by MWRA into Massachusetts Bay," report submitted to the Massachusetts Water Resources Authority, 1991.

8. Stolzenbach, K.D., *et al.*, "Boston Harbor Study of Sources and Transport of Harbor Sediment Contamination, Part I: Transport of Contaminated Sediment in Boston Harbor," summary final report submitted to the Massachusetts Water Resources Authority, 1992.

9. Geyer, W.R., *et al.*, "Draft Final Report: Physical Oceanographic Investigation of Massachusetts and Cape Cod Bays," submitted to the Massachusetts Bay Program, administered by Massachusetts Office of Coastal Zone Management, 1992.

10. Menzie, C.A., Cura, Jr., J.J., Freshman, J.S., & Potocki, B., "Boston Harbor: Estimates of Loadings," Report No. 91-4, Environmental Quality Department, Massachusetts Water Resources Authority, 1991.

11. Briggs, D.A., & Madsen, O.S., "Mathematical Models of the Massachusetts Bay, Part II: Analytical Models for One- and Two-Layer Systems in Rectangular Basins," Report No. 172, R.M. Parsons Laboratory, Massachusetts Institute of Technology, Cambridge, Mass., 1973.

12. United States EPA, Revised Section 301(h) technical support document, Government Printing Office, Washington, D.C., 1982.

13. Wang, R.-F.T., "Laboratory Analysis of Settling Velocities of Wastewater Particles in Seawater Using Holography," EQL Report No. 27, Env. Quality Lab., California Inst. of Tech., Pasadena, Calif., 1988.

14. Menzie-Cura and Associates, "Sources and Loadings of Pollutants to the Massachusetts Bays," Report MBP-91-01, Massachusetts Bays Program, Boston, 1991.

15. Townsend, D.W., *et al.*, "Seasonality of Oceanographic Conditions in Massachusetts Bay," Technical Report No. 83, Bigelow Laboratory for Ocean Sciences, West Boothbay Harbor, Maine, 1991.

16. Howes, B.L., & Taylor, C.D., "App. D: Nutrient Regime of New Bedford Outer Harbor Relating to Potential Inputs and Phytoplankton Dynamics, Vol. IV, Effluent Outfall," Phase 2 Facilities Plan, City of New Bedford, Mass., 1989.

17. Giblin, A., personal communication regarding data acquired by the Ecosystems Center of the Marine Biological Laboratory, 1992.

18. Murcott, S.E., & Harleman, D.R.F., "Performance and Innovation in Wastewater Treatment," Technical Note 36, R.M. Parsons Laboratory, Massachusetts Institute of Technology, Cambridge, Mass., 1992.

19. Signell, R.P., "Tide and Wind-Driven Flushing of Boston Harbor, Massachusetts," in *Estuarine and Coastal Modeling*, proc. of 2nd Int'l Conf., ASCE, Tampa, Fla., Nov. 1991, M.L. Spaulding *et al.*, eds., 1992, pp. 594–606.