Harbor - Bay eutrophication-related water chemistry changes after 'offshore transfer'

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Harbor - Bay eutrophication-related water chemistry changes after 'offshore transfer'

prepared by

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#### **EXECUTIVE SUMMARY**

In September 2000, discharges from the Deer Island wastewater treatment facility to Boston Harbor were transferred 15-km offshore for diffusion into the bottom-waters of Massachusetts Bay. Numerical modeling conducted by others before transfer, predicted that the transfer would lead to improvements in the water-column of the Harbor with only minimal impacts on the Bay.

In the 3 years since transfer, significant improvements have been documented in the water-column of the Harbor. Small, localized changes have been reported in the Bay, focused in the nearfield region, the 10 km x 10 km area surrounding the Bay outfall. In this report, we examine for the first 24-months after offshore transfer, the differences in water-quality over the Massachusetts Bay – Boston Harbor system as a whole.

The report draws on data collected by two monitoring programs, both conducted by the Massachusetts Water Resources Authority, the agency responsible for the transfer of the discharges. The 'Bay' program monitored mainly in the Bay, with some representation in the Harbor; the 'Harbor' program monitored in the Harbor alone. The report uses data collected by the two programs at 52 water-column stations; 12 in the Harbor, and 40 in the Bay.

This report focuses on the water-column of the Harbor-Bay systems, and addresses specific aspects related to eutrophication, or 'organic over-enrichment'. The specific aspects addressed by the report included concentrations of N, P and Si, molar ratios of N:P and N:Si, concentrations of chlorophyll-<u>a</u>, concentrations of organic carbon, concentrations and percent saturation of dissolved oxygen (DO), and salinity.

For each of the variables, for the Harbor, Bay as whole and nearfield, we compared average values during the 24-months after transfer, with average values during a 3- to 8year baseline period before transfer. For each system, we conducted the comparisons for the system as a whole, and for each station sampled in the system. In the Discussion we compare the differences we observed in the nearfield and Harbor, with the predictions made by others using the numerical-models.

# **Overview of differences**

The following is a brief overview of some of the difference in water-quality we observed in the Harbor-Bay system between the 24-months and baseline. Note, the report addresses only the changes for the full 24-months after transfer, and (except for bottomwater DO) for the data averaged through the water-column at each station. Others will address differences during different seasons, and at different depths in the water-column.

*Nitrogen and phosphorus.* In the Bay, for system-wide average concentrations of both total nitrogen (TN) and total phosphorus (TP), we were able to detect a significant increase in the nearfield region ( $\underline{p} \le 0.05$ ), but not for the Bay as a whole. In the nearfield, average TN concentrations increased by +2.6 µmol l<sup>-1</sup> (or +16% of baseline). For total phosphorus (TP), the increase was +0.14 µmol l<sup>-1</sup> (or +14%).

In the Harbor, both variables showed significant decreases. For TN, the decrease was - 10.7-µmol l<sup>-1</sup> (or -34% of baseline). For TP, the decrease was -0.52-µmol l<sup>-1</sup> (or -25%). For both variables, the increases in the nearfield were smaller than, and about one-fourth the size of the decreases in the Harbor. In both systems, for both TN and TP, the dissolved inorganic fractions, were responsible for the bulk of the changes.

In the Harbor, for both the total and dissolved inorganic fractions of both N and P, the decreases were significant at all (or almost all) stations, indicating that the decreases occurred over most of the Harbor area. In the Bay, the increases in TN and TP were confined to stations in the nearfield; increases may have occurred outside of the nearfield, but we were unable to detect them.

For dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP), the increases in the Bay were confined to stations in the nearfield, except for three stations,

that were different for the two fractions, outside of the nearfield. The increases at the two sets of three stations could simply have been a function of the small sample-size at these stations.

*Molar ratios of N:P.* For system-wide average molar ratios of TN:TP, we were unable to detect a significant increase for the nearfield or Bay as a whole. The same applied at all individual stations in the nearfield and Bay. Thus, we were able to observe significant increases for both TN and TP in the nearfield, but not for concentrations of TN relative to TP. In the Harbor, as for TN and TP individually, TN:TP showed a significant decrease (of -1.6:1 or -11%).

For DIN:DIP, for the data averaged system-wide, we were able to detect a significant increase for the nearfield (in this case, +2.1:1 or +34%), but not for the Bay as a whole. For the Harbor, average ratios of DIN:DIP showed a significant decrease of -5.6:1 (or -49%). The increase in DIN:DIP in the nearfield was about one-third the size of the decrease in the Harbor.

*Silica.* For both total Si and dissolved inorganic Si (SiO<sub>4</sub>), for both the nearfield and Bay as a whole, we were unable to detect significant increases after transfer. This applied for both the data averaged system-wide, and for each of the individual stations. The pattern of differences among stations suggested a localized increase in SiO<sub>4</sub> in the nearfield, but at none of the nearfield stations were the increases significant.

In the Harbor, where sampling for Si was less intensive than for N and P, we were unable to detect significant decreases for either fraction. For SiO<sub>4</sub>, the decrease for the Harbor as a whole, and for two of the three stations in the Harbor, were 'almost significant ( $\underline{p} \le 0.1$  but  $\ge 0.051$ ). It could be that with longer-term monitoring, the decrease in SiO<sub>4</sub> in the Harbor will too be shown to be significant.

*Phytoplankton biomass (chlorophyll-<u>a</u>).* For both measures of chl-<u>a</u> that we examined, extracted chl-<u>a</u> and <u>in-situ</u> fluorescence chl-<u>a</u>, we were unable to detect significant

increases for the nearfield or Bay as a whole (c.f. the increases in the nearfield for N and P). For both chl-<u>a</u> variables, subtraction yielded positive values for the nearfield and Bay as a whole (of between  $+0.3 -\mu g l^{-1}$  and  $+0.6 -\mu g l^{-1}$ ), but in neither case were the increases significant. The same applied at the individual stations in the nearfield and Bay.

In the Harbor, system-wide average concentrations of extracted chl-<u>a</u> showed a significant decrease of  $-0.9-\mu g l^{-1}$  (or -19% of baseline). At the individual stations, the decrease was significant at 3 of the 12 stations. For fluorescence chl-<u>a</u>, perhaps because of small sample-size, the decreases in the Harbor was not significant; the 'Bay' program alone measured fluorescence chl-<u>a</u> in the Harbor.

**Organic carbon.** In the Bay, for neither the Bay nor nearfield, were we able to detect significant increases in average concentrations of total organic carbon (TOC). For particulate organic carbon (POC), the nearfield showed a significant increase of +4  $\mu$ mol l<sup>-1</sup> (or +18%). For the Bay as a whole, average POC concentrations were not significantly changed.

In the Harbor, subtraction yielded negative values for both TOC and POC. For TOC, which was sampled by the 'Bay' program alone, the decrease was not significant. For POC, which was sampled by both programs and therefore more intensively, the decrease of -12-µmol l<sup>-1</sup> (or -28%) was significant. The increase in POC in the nearfield was about one-third the size of the decrease in the Harbor.

*Bottom-water dissolved oxygen (DO).* For both DO variables that we monitored, bottom-water DO concentrations and bottom-water DO% saturation, we were unable to detect significant differences between the 24-months and baseline, for the Bay as a whole, nearfield, or Harbor. For both variables, this applied for the data averaged system-wide and for all stations in the three 'systems/regions'.

The pattern among stations of positive and negative differences suggested that the Harbor showed a small increase in bottom-water DO, and the nearfield and areas east and

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southeast of the nearfield, a smaller decrease after transfer. At none of the individual stations in either system, however, were the changes large enough to be detected.

*Salinity.* In the Bay, for neither the Bay as a whole nor nearfield, were we able to detect a significant decrease in salinity. For both Bay 'systems, and for almost all stations both inside and outside the nearfield, subtraction yielded positive values, suggestive of a background increase. It could be that this background increase (2002 was a dry year), dampened any decrease in salinity in the nearfield caused by transfer.

In the Harbor, for salinity averaged Harbor-wide and for most individual stations, average salinity after transfer was significantly greater than baseline. For the Harbor as a whole, the increase was +0.7 ppt (or +2% of baseline). The significant change in the Harbor was about twice the size of the, in this case, non-significant change in the Bay.

# **Cautionary comments**

For the variables that were sampled relatively intensively in particular systems, we can be relatively certain of the differences we observed during the 24-months. This would apply for instance for concentrations and molar ratios of N and P, extracted chl- $\underline{a}$ , POC, DO and salinity for both the Harbor and nearfield, and for Si, DIN:SiO<sub>4</sub> and TOC for the nearfield alone.

For the variables where sampling in a particular system was not as intense, for instance for Si, DIN:SiO<sub>4</sub> and TOC in the Harbor, and for all variables outside of the nearfield in the Bay (and hence for the Bay as a whole), we can be less certain of the differences. For these variables/systems, and also for all variables that were sampled relatively intensively but showed small differences (for instance for chl- $\underline{a}$  and DO), longer-term monitoring will increase our confidence in our estimates of the differences.

# **INTRODUCTION**

In September 2000, the wastewater discharges from the Deer Island wastewater treatment facility (WWTF) to Boston Harbor were transferred 15-km offshore, for diffusion into the bottom-waters of Massachusetts Bay. This transfer, which we refer to here as 'offshore transfer', was one of the final and most conspicuous milestones of the Boston Harbor Project (BHP).

Earlier milestones of the Project included upgrades to the systems of collection and treatment of the wastewater discharged to the Harbor before transfer, and that would with time be transferred offshore (for a review of the earlier milestones of the BHP see Rex <u>et</u> <u>al</u>. 2002). Offshore transfer ended the direct discharges of ca. 375 x  $10^6$  gal d<sup>-1</sup> (1.42 x  $10^6$  m<sup>3</sup> d<sup>-1</sup>) of secondary-treated wastewater to the Harbor.

Transfer changed the location at which the wastewater discharged to the Harbor-Bay system entered the Bay, but the total wastewater loadings to the Bay were little impacted. Before transfer, much of the wastewater discharged to the Harbor ultimately made its way to the Bay (Signell et al. 2000). Transfer changed the location of the inputs from 'surface' inputs at ca. 10 m depth in the very west of the Bay, to 'deep-water' inputs, at 30-m depth, 15 km offshore.

With transfer, the initial dilution of the wastewater discharged the Bay-Harbor system was also increased. Before transfer, the wastewater discharged at the mouth of the Harbor at the very west of the Bay had an initial dilution of ca. 20:1 (Battelle 1989). Since transfer, the initial dilution of the wastewater at the Bay outfall-diffuser system has been estimated to be 90:1 to 100:1 (Hunt <u>et al.</u> 2002).

Numerical modeling conducted by others before transfer, predicted transfer would lead to improvements in the water-column of the Harbor, with only minimal impacts on the Bay

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water-column (Walton 1990; HydroQual and Normandeau 1995, Signell <u>et al.</u> 2000). Much of the monitoring conducted since transfer has confirmed these predictions.

Taylor (2003, 2004), and to some extent Libby <u>et al</u>. (2003), have reported some of the improvements in the Harbor water-column. Libby <u>et al</u>. (2003) and Werme <u>et al</u>. (2003) have documented localized changes in the Bay water-column in the vicinity of the new outfall. Some comparisons have been conducted of the changes in the Harbor and Bay, but these have excluded much of the data available for the Harbor.

In this report, we attempt for the first 24-months after transfer, to quantify the changes in the water column of the Harbor-Bay system as a whole. The report focuses on the watercolumn alone; others will address changes to the sediments, fish and shellfish of the systems. The report also addresses only aspects related to eutrophication, or as defined by Nixon (1995), 'organic over-enrichment' of the systems.

For reasons of logistics the report addresses only specific aspects related to eutrophication of the Harbor-Bay water-column. Others will address changes to other eutrophication-related aspects, including water-column primary productivity, phytoplankton and zooplankton community-structure, benthic metabolism and nutrient fluxes, sediment redox characteristics, and biomass and structure of benthic invertebrate communities.

## **MATERIALS AND METHODS**

#### **Basic approach of the report**

In this report, we quantify the changes after transfer by comparing average water-column values during the first 24-months after transfer, with average values during a 3- to 8-year baseline period before transfer. We do this for the Harbor as a while, the Bay as a whole and for the nearfield region of the Bay, and then for each of the stations sampled in each of these systems/regions.

The 24-months after transfer extended from 7 September 2000, the day after offshore transfer, through 31 August 2002. For the Bay, the baseline period before transfer extended from February 1992 through 6 September 2000; for the Harbor, it extended from August 1993 through 6 September 2000.

For the boundaries of the Harbor, Bay and nearfield that we used in the report, and for the locations of each of the sampling stations, see Figure 1. For further details of the regions and stations within the Harbor, see Figure 2. In this report, unlike in most of our other reports, we have excluded Cape Cod Bay (CCB) from the system we term 'Massachusetts Bay'.

There were two reasons for this. First, the numerical models run before transfer predicted that the effects of the transfer would be largely confined to the nearfield, and would be attenuated well before CCB. Second, measurements that were conducted of the wastewater  $^{\delta 15}$ N isotope signal in the Bay after transfer, showed that the signal was attenuated well before CCB (Montoya <u>et al</u>. 2003).

In this report, we have partitioned Massachusetts Bay into the 'nearfield' and 'nonnearfield' regions. The nearfield, or the 10 km x 10 km area that enclosed the Bay outfall, was the area predicted to be the focus of much of the outfall signal. Note, the 'non-nearfield' is not the same as the area we term the 'farfield' in our other reports. The three farfield-stations in the Harbor, and five farfield-stations in CCB, are excluded from the 'non-nearfield'.

## Field sampling and laboratory analytical procedures

The report draws on data collected by two monitoring programs, both conducted by our agency, the Massachusetts Water Resources Authority (MWRA). The first program, which we refer to here as the 'Bay' program, was started in February 1992. It focused



Figure 1. Map showing study area, the 3 systems/regions making up the study area (Boston Harbor, Massachusetts Bay as a whole, and the nearfield region of the Bay), and the sampling stations within the systems/regions.

# **BOSTON HARBOR**



Figure 2. Locations of sampling stations, former wastewater treatment facility (WWTF) outfalls, and the four major regions of the Harbor - the Inner Harbor, the North West Harbor, the Central Harbor, and the South East Harbor.

mainly on Massachusetts Bay, with some representation in the Harbor (for work plan, see Libby <u>et al.</u> 2002).

The second program, which we refer to as the 'Harbor' program, was started in August 1993. It was the smaller of the two programs, and was confined to the Harbor (for work plan, see Rex and Taylor 2000). Comparisons now in progress indicate that the data generated by the two programs are for the most part, comparable (MWRA, unpublished data).

Data collected by the two programs at a total of 52 stations have been used in the report (Fig. 1). In the Harbor, samples were collected at 12 stations; the 'Harbor' program sampled 9 of the 12 stations, and the 'Bay' program, the remaining three. For coordinates of the Harbor stations, see Table 1. In the Bay, sampling by the 'Bay' program was conducted at 40 stations; 21 located in the nearfield (Table 2), and 19 outside of the nearfield (Table 3).

Table 1. Locations of stations sampled in Boston Harbor by the 'Harbor' and 'Bay' programs.

Program	Station ID	Latitude (N)	Longitude (W)			
	NORT	<u>TH HARBOR</u>				
Inner Harbor						
'Harbor'	138	42°21 59	71 ° 02 82			
'Harbor'	024	42 ° 20 59	71 ° 00 48			
'Bay'	F30	42°20.46	71 ° 00.48			
North West Ha	rbor					
'Harbor'	106	42 ° 20.00	70° 57.60			
'Harbor'	142	42°20.35	70 ° 55.89			
'Harbor'	140	42°18.35	71 ° 02.43			
'Bay'	F23	42 ° 20.34	71 ° 56.52			
	<u>SOUTH</u>	<u>I HARBOR</u>				
Central Harbor	r					
'Harbor'	077	42°1651	70° 59 31			
'Harbor'	139	42° 17.20	70° 58.10			
'Harbor'	141	42°18.30	70 ° 55.85			
'Bay'	F31	42 ° 18.36	70 ° 56.40			
South East Har	South East Harbor					
'Harbor'	124	42° 16.36	70° 53.86			

In the Harbor, the 9 stations sampled by the 'Harbor' program were sampled between 28 and 34 times per year; basically weekly from May through October, and every 2-weeks from November through April. The 3 stations in the Harbor sampled by the 'Bay' program were sampled 6 times per year; once per month in February, March, April, June, August and October.

Table 2.	Locations	of stations	in the	nearfield	region	of Massac	husetts	Bay	sampl	ed by
the 'Bay'	program									

Station ID	Latitude (N)	Longitude (W)
N01	12° 25 11	70° 51 84
NO2	42°25.14	70° 51.0 <del>4</del> 70° 70 32
NO2	42 25.00	$70^{\circ} 45.32$
NO4	42 20.10 42°26.64	70°40.74 70°44.42
N04 N05	$42^{\circ} 20.04$	70° 44.42 70° 43 56
N05 N06	42 24.90 42° 23 16	70 43.30 70° 42.06
NO7	42 25.10	70 42.90 70° 42.26
INU/	42 21.30	70 42.30 70° 44.04
INU8 NIOO	42 20.28	70 44.94 70° 47 46
N09	42 25.80	/0 4/.46
N10	42° 19.92	/0° 50.04
N11	42 <sup>°</sup> 21.66	70° 50.64
N12	42° 23.40	70° 51.24
N13	42°24.24	70° 49.50
N14	42 ° 24.60	70 ° 47.58
N15	42 ° 24.96	70° 45.66
N16	42°23.64	70 ° 45.18
N17	42°22.32	70 ° 44.76
N18	42°21.96	70 ° 46.68
N19	42°21.60	70 ° 48.60
N20	42°22.92	70° 49.02
N21	42°23.28	70°47.10

In the Bay, the 'Bay' program sampled the 21 nearfield stations as follows; twice per month in February, April, May, July, August and September, and once per month in March, June, October, November and December. The 'Bay' program sampled the 19 non-nearfield stations 6 times per year, with the timing of the 6 surveys as for its 3 Harbor stations.

Station ID	Latitude (N)	Longitude (W)
F05 F06 F07 F10 F12 F13 F14 F15 F16 F17	42°08.34 42°10.26 42°11.82 42°14.52 42°19.80 42°16.08 42°18.00 42°18.96 42°19.86 42°20.76	70° 39.00 70° 34.62 70° 30.96 70° 38.22 70° 25.38 70° 16.08 70° 48.48 70° 43.68 70° 39.00 70° 34.26
F18 F19 F22 F24 F25 F26 F27 F28 F29	42° 26.52 42° 24.90 42° 28.80 42° 22.50 42° 19.32 42° 36.48 42° 33.00 42° 24.60 42° 07.02	70° 53.28 70° 53.28 70° 38.22 70° 53.76 70° 52.56 70° 52.56 70° 33.90 70° 26.82 70° 25.98 70° 17.40

Table 3. Coordinates of the non-nearfield stations in Massachusetts Bay.

For 9 of the 10 stations sampled by the 'Harbor' program, sampling was started in August 1993. For the one remaining station, Station 077, sampling was initiated in May 1995. For 34 of the 40 stations sampled the 'Bay' program, sampling was started in February 1992. For the remaining six stations, Stations F26, F27, F28, F29, F30 and F31, sampling was started in February 1994.

The Harbor-outfall-Bay Transect used in the report extended from the Inner Harbor (specifically Station 138), out to the outfall (Station N21), and then down to the southeast

corner of the Bay (Station F29). Figure 3 shows the path of the Transect, and the identity and location of 16 stations along it.



Figure 3. Harbor - outfall - Bay Transect.

In this report, we use 25 water-column variables to quantify the changes in the Harbor-Bay water column during the 24-months. Seventeen of the 25 variables were measured directly (Table 4); the other 8 were computed indirectly from variables that were measured directly (for details of computations see Table 5). We also used a series of ratios of variables, and percent contributions to total variables, to help assess the changes.

Table 6 shows the stations and water depths at which each of the variables was measured. In the Harbor, 20 of the 26 variable, including dissolved inorganic N and P, ratios of dissolved inorganic N and P, extracted chl-<u>a</u>, DO and salinity, were measured at all 12 stations. The 6 remaining variables, including total Si, dissolved inorganic Si (SiO<sub>4</sub>), molar DIN:SiO<sub>4</sub>, fluorescence chl-<u>a</u>, TOC and DOC, were measured at the three Harbor stations sampled by the 'Bay' program.

In the Bay, 11 of the 25 variables, including dissolved inorganic N, P and Si, molar ratios of dissolved inorganic N, P and Si, and fluorescence chl-<u>a</u>, DO and salinity, were measured at all 40 stations. For the remaining 14 variables (9 of them in Table 4, and 5 in Table 5), measurements were conducted at a total of 14 Bay stations; 7 in the nearfield, and 7 outside of the nearfield.

At each station, measurements were conducted at between one and five depths, categorized as Depths A through E. In the Harbor, most variables sampled by the 'Harbor' program were measured at two depths, Depths A and E. For certain variables, measurements were conducted at one depth, Depth A. The variables sampled in the Harbor by the 'Bay' program were sampled at three depths (Depths A, C and E).

In the Bay, the 11 variables sampled by the 'Bay' program at all 40 stations, were sampled at all five depths. For the 15 variables that were sampled at 14 Bay stations, measurements were conducted at three depths at each station; specifically Depths A, C and E. The measurements conducted at different depths/stations in the different systems, represent the tiered sampling designs of the two programs.

VARIABLE	METHOD			
	'Harbor' program	'Bay' program		
Total dissolved nitrogen (TDN) and phosphorus (TDP)	Solarzano and Sharp (1980 <u>b</u> ), Skalar SAN <sup>plus</sup> autoanalyzer	D'Elia <u>et al</u> . (1997), Valderrama (1981), Technicon Autoanalyzer II		
Particulate carbon (PC) and nitrogen (PN)	EPA Method 440.0 (1997), Perkin Elmer CHN analyzer,	EPA Method 440.0 (1997). Menzel and Vaccaro (1964) Exeter Analyzer Model CE-440		
Particulate phosphorus (PP)	Solarzano and Sharp (1980 <u>a</u> ), Skalar SAN <sup>plus</sup> autoanalyzer	Solarzano and Sharp (1980 <u>a</u> ) Technicon Autoanalyzer II		
Ammonium (NH 4)	Fiore and O'Brien (1962), modified as in Clesceri <u>et al</u> . (1998; Method 4500-NH3 H), Skalar SAN <sup>plus</sup> autoanalyzer,	Oviatt and Hindle (1994), after Solarzano (1969), Technicon Autoanalyzer II		
Nitrate + nitrite (NO <sub>3+2</sub> )	Bendschneider and Robinson (1952), modified as in Clesceri <u>et al</u> . (1998; Method 4500-NO3 F), Skalar SAN <sup>plus</sup> autoanalyzer,	Bendschneider and Robinson (1952), Morris and Riley (1963), Technicon Autoanalyzer II		
Phosphate (DIP)	Murphy and Riley (1962), modified as in Clesceri <u>et al</u> . (1998; Method 4500-P F), Skalar SAN <sup>plus</sup> autoanalyzer,	Murphy and Riley (1962) Technicon Autoanalyzer II		
Biogenic silica	Not measured	Paasche (1973), Technicon Autoanalyzer II		
Silicate (SiO <sub>4</sub> )	Not measured	Brewer and Riley (1966), Oviatt and Hindle (1994), Technicon Autoanalyzer II		
Dissolved organic carbon (DOC)	Not measured	Sugimura and Suzuki (1988), Shimadzu 5000 Carbon Analyzer		
Extracted chlorophyll- <u>a</u>	Holm Hansen (1965) as in EPA (1992). Turner Designs Fluorometer Model 10AU	Arar and Collins (1992) Turner Designs Fluorometer Model AU		

Table 4. Summary of field and analytical methods used by the 2 monitoring programs.

# Table 4 continued

VARIABLE		METHOD
	'Harbor' program	'Bay' program
In situ fluorescence chl-a	Not measured	WET Labs WETStar Chlorophyll fluorometer
Dissolved oxygen (DO) concentrations and DO % saturation	Hydrolab Datasonde 4, Hydrolab manual	Seabird SBE-13, Weiss (1970)
Salinity	Hydrolab Datasonde 4, Hydrolab manual	Seabird SBE 9 CTD, CTD manual; or OS200 CTD, OS 200 manual

Table 5. List of derived variables, and methods of derivation of the variables.

Variable	Method of derivation
Total nitrogen (TN)	TN = TDN + PN
Dissolved inorganic nitrogen (DIN)	$DIN = NH_4 + NO_{3+2}$
Total phosphorus (TP)	TP = TDP + PP
Total silica (Total Si)	$Total Si = SiO_4 + biogenic silica$
Total organic carbon (TOC)	TOC = DOC + POC
Molar TN:TP	TN:TP = TN/TP
Molar DIN:DIP	DIN:DIP = DIN/DIP
Molar DIN:SiO <sub>4</sub>	$DIN:SiO_4 = DIN/SiO_4$

Table 6. Summary of stations and depths at which variables were measured to track changes in the Harbor and Bay. For depth classification, see footnote  $^{f}$ .

VARIABLE	HARBOR		BAY (nearfield)	Y (non-nearfield)	
	'Harbor' program	'Bay' program	'Harbor' program	'Bay' program	
Total N & P (TN, TP, TN:TP)	9 <sup>a</sup> stations at depth A alone	3 <sup>b</sup> stations at depths A + C + E	7 <sup>c</sup> stations, 3 depths A + C +E	8 <sup>d</sup> stations, 3 depths (A + C + E)	
Dissolved inorganic nutrients: DIN, DIP, DIN:DIP,	9 <sup>a</sup> stations at Depths A + E	3 <sup>b</sup> stations; 3 depths ( A + C + E) at F30 & F31; 5 depths (A + B + C + D + E) at F23	All 21 stations, at 5 depths (A + B + C + D + E)	19 <sup>e</sup> stations, 5 depths (A + B + C + D + E)	
Total Si	Not measured	3 stations, 3 depths $(A + C + E)$	As for total N &P	As for total N &P	
SiO <sub>4,</sub> DIN:SiO <sub>4</sub>	Not measured	As for dissolved inorganic N & P	As for dissolved inorganic N &P	As for dissolved inorganic N &P	
Extracted chl- <u>a</u> ,	9 <sup>a</sup> stations at Depths A + E	3 <sup>b</sup> stations as for DIN, DIP and DIN:DIP	7 ° stations, 5 depths (A + B + C + D + E)	$8^{d}$ stations, 5 depths (A + B + C + D + E)	
<u>In situ</u> fluorescence chl- <u>a</u>	Not measured	As for dissolved inorganic N & P	As for dissolved inorganic N &P	As for dissolved inorganic N &P	
TOC, DOC and POC	TOC, DOC not measured; POC Depth A 9 <sup>a</sup> stations	3 <sup>a</sup> stations, 3 depths (A + C +E)	As for total nutrients	As for total nutrients	
Dissolved oxygen (DO) conc., DO % saturation	9 <sup>a</sup> stations at Depths A + E	3 stations as for DIN & DIP	21 stations, 5 depths (as for DIN & DIP)	As for DIN & DIP	
Salinity	9 <sup>a</sup> stations at Depths A + E	3 stations as for DIN & DIP	21 stations, 5 depths (as for DIN & DIP)	As for DIN & DIP	

<sup>a</sup> 024, 077, 106, 124, 138, 139, 140, 141, 142; <sup>b</sup> F23, F30, F31; <sup>c</sup> N01, N04, N07, N10, N16, N18, N20; <sup>d</sup> F06, F13, F19, F22, F24, F25, F26, F27, <sup>e</sup> F05, F06, F07, F10, F12, F13, F14, F15, F16, F17, F18, F19, F22, F15, F16, F17, F18, F19, F22, F24, F25, F26, F27, F28, F29, <sup>f</sup> A= surface, B = mid-surface layer, C = mid-depth or chlorophyll maximum, D = mid-bottom layer, E = near- bottom.

Depth A was located between < 1 m ('Harbor' program) and < 3 m ('Bay' program) from the water surface. Depth B was located mid-way between Depths A and C. Depth C was located at the depth of the fluorescence chl-<u>a</u> maximum, and when this was not present, at the mid-depth of the water-column. Depth D was located mid-way between Depths E and C. Depth E was located within 1 m ('Harbor' program) or <5 m of the bottom ('Bay' program).

#### **Computations and statistical analyses**

For both each of the systems/regions (the Harbor, Bay as a whole and nearfield) and each of the stations in the systems/regions, the average values before and after transfer were compared using monthly-, rather than survey-average values. This was necessary to compensate for the different numbers of surveys conducted per month, at different times of the year, by the two programs.

For the systems/regions as a whole, the averages before and after transfer were compared using volume-weighted system-wide averages. It was necessary to volume-weight the averages, to account for the different numbers of stations sampled per region in both the Harbor and the Bay.

For the Harbor, system-wide volume-weighted averages were computed as follows (after Sung 1991):

*Volume-weighted average* = 
$$(\underline{a}*0.119) + (\underline{b}*0.418) + (\underline{c}*0.342) + (\underline{d}*0.12)$$

where,  $\underline{a}$  = average concentrations per survey for all stations in the Inner Harbor,  $\underline{b}$  = average concentrations per survey for all stations in North West Harbor,  $\underline{c}$  = average concentrations per survey for all stations in Central Harbor, and  $\underline{d}$  = average concentration per survey for all stations in South East Harbor.

The constants, 0.119, 0.418, 0.342 and 0.12, were the volumes of the respective regions expressed as a proportion of 1 (volumes from Sung 1991, citing Ketchum 1951). The system-wide volume-weighted averages were then averaged to provide monthly averages. For Massachusetts Bay as a whole, the volume-weighted averages were computed from monthly averages for the nearfield and non-nearfield, as follows:

*Volume-weighted average* =  $(\underline{a} * 0.034) + (\underline{b} * 0.966)$ 

where,  $\underline{a}$  = average monthly concentration for all stations in the nearfield and  $\underline{b}$  = average monthly concentration for all stations outside of the nearfield. The constants, 0.034 and 0.966, were the proportions that the respective regions contributed to the total volume of Massachusetts Bay (volume of nearfield = 3.870 x 10<sup>9</sup> m<sup>3</sup>, and of non-nearfield = 110.008 x 10<sup>9</sup> m<sup>3</sup>, S-Y Liang, MWRA unpublished data).

For all variables, for each system and individual stations, simple <u>t</u>-tests were used to compare the monthly averages between the two periods (SPSS 10.1, SPSS 2002). The Levene test was used to test for homogeneity of variance of the data before application of the <u>t</u>-test (SPSS 10.1, SPSS 2002). If the condition of homogeneity of variance was not met, the data were log  $_{10}$  or cosine transformed.

Three levels of significance were recognized. If the <u>t</u>-test yielded a <u>p</u> value equal to or less ( $\leq$ ) than 0.05, the difference was considered 'significant' and denoted using an asterisk (\*). If <u>p</u> values were between 0.051 and  $\leq$  0.10, the difference was considered 'almost' significant, and denoted using a superscript '?'. When <u>p</u> values were  $\geq$  0.11, the differences were considered 'not significant'.

In this report, we have considered the requirement of the <u>t</u>-test of serial independence of the data, to be met. In the Harbor, the one-month interval between averages used for the <u>t</u>-test was greater than the estimated 5- to 8-day hydraulic residence time of the Harbor (Signell <u>et al.</u> 2000). In the nearfield, correlation between chl-<u>a</u> concentrations measured

at 22-day intervals, which is less than the monthly interval used here, yielded an  $\underline{r}$  value of only 0.43 (Section 5 in MWRA 2003).

# RESULTS

# Nitrogen

*Total nitrogen (TN).* For concentrations of TN averaged 'system-wide', we were able to detect a significant decrease for the Harbor, no significant change for the Bay as a whole, and a significant increase for the nearfield (Table 7, Fig. 4). In the Harbor, TN concentrations averaged  $31.1 \pm 6.4 \mu mol l^{-1}$  during baseline, and  $20.4 \pm 3.0 \mu mol l^{-1}$  during the 24-months. The difference of -10.7-µmol l<sup>-1</sup> was equivalent to -34% of average baseline concentrations, and was significant (p < 0.01).

For the Bay as a whole, concentrations averaged  $19.0 \pm 4.1 \ \mu \text{mol} \ l^{-1}$  during baseline and  $19.25 \pm 3.1 \ \mu \text{mol} \ l^{-1}$  during the 24-months. The difference, in this case,  $+0.25 \ \mu \text{mol} \ l^{-1}$  was equivalent to +1% of baseline, and was not significant ( $\mathbf{p} = 0.79$ ). In the nearfield, average TN concentrations increased from  $16.1 \pm 5.2 \ \mu \text{mol} \ l^{-1}$  to  $18.7 \pm 2.8 \ \mu \text{mol} \ l^{-1}$ ; the difference of  $+2.6 \ \mu \text{mol} \ l^{-1}$  was equivalent to +16% of baseline, and was significant.

In terms of the absolute change in concentrations, the increase in TN in the nearfield of +2.6-µmol l<sup>-1</sup> was equivalent to ca. one-fifth of the decrease of -10.7-µmol l<sup>-1</sup> in the Harbor. In terms of the change expressed as a percent of baseline, the +16% increase in the nearfield was ca. one-half of the -34% decrease in the Harbor.

The time-series plots of average TN in Figure 4 confirm the increase in the nearfield and decrease in the Harbor. The plots also show that the nearfield, and possibly also the Bay as a whole, exhibited a background increase in TN through the baseline. If this increase persisted through the 24-months, the increase in TN in the nearfield was at least partly background.

Table 7. <u>Nitrogen concentrations</u>. Comparison of values averaged for the periods before and after offshore transfer. Values are averages ( $\pm 1 \ge 3D$ ) of average monthly values ( $\underline{n}$  = number of months).  $\underline{p}$  values were generated by  $\underline{t}$ -test. \* denotes significant at  $\underline{p} \le 0.05$ , '?' denotes almost significant with  $\underline{p}$  between 0.051 and 0.10.

BOS	TON HARBOR		
31.1 <u>+</u> 6.4 (60)	$20.4 \pm 3.0$ (24)	-10.7 (-34%)	<0.01 *
11.8 <u>+</u> 6.4 (75)	4.6 <u>+</u> 2.7 (24)	-7.2 (-61%)	<0.01 *
6.3 <u>+</u> 3.4 (75)	$1.0 \pm 1.1$ (24)	-5.3 (-84%)	<0.01 *
MASSACHU	<u>SETTS BAY</u> (as a whole)		
$19.0 \pm 4.1$ (53)	$19.25 \pm 3.1$ (11)	+0.25 (+1%)	0.79
$5.3 \pm 2.8$ (55)	$5.5 \pm 1.2$ (11)	+0.2 (+4%)	0.79
$1.2 \pm 0.4$ (57)	$1.2 \pm 0.2$ (12)	0 (-<1%)	0.83
MASSACHUS	<u>SETTS BAY</u> (nearfield)		
16.1 <u>+</u> 5.2 (75)	$18.7 \pm 2.8$ (21)	+2.6 (+16%)	< 0.01 *
4.3 <u>+</u> 2.5 (95)	$6.4 \pm 1.6$ (21)	+2.1 (+49%)	0.01 *
$1.0 \pm 0.4$ (95)	$2.3 \pm 0.8$ (21)	+1.3 (+130%)	<sup>a</sup> <0.01 *
	<b>BOS</b> $31.1 \pm 6.4$ (60) $11.8 \pm 6.4$ (75) $6.3 \pm 3.4$ (75) <b>MASSACHU</b> $19.0 \pm 4.1$ (53) $5.3 \pm 2.8$ (55) $1.2 \pm 0.4$ (57) <b>MASSACHUS</b> $16.1 \pm 5.2$ (75) $4.3 \pm 2.5$ (95) $1.0 \pm 0.4$ (95)	BOSTON HARBOR $31.1 \pm 6.4$ $20.4 \pm 3.0$ (24) $11.8 \pm 6.4$ $4.6 \pm 2.7$ (75) $(75)$ $(24)$ $6.3 \pm 3.4$ $1.0 \pm 1.1$ (75) $(75)$ $(24)$ MASSACHUSETTS BAY (as a whole) $19.0 \pm 4.1$ $19.25 \pm 3.1$ (53) $(53)$ $(11)$ $5.3 \pm 2.8$ $5.5 \pm 1.2$ (55) $(11)$ $1.2 \pm 0.2$ (57) $1.2 \pm 0.4$ $1.2 \pm 0.2$ (57) $(12)$ MASSACHUSETTS BAY (nearfield) $16.1 \pm 5.2$ $18.7 \pm 2.8$ (21) $4.3 \pm 2.5$ $6.4 \pm 1.6$ (95) $(21)$ $1.0 \pm 0.4$ (23) $\pm 0.8$ (95) $(21)$	<b>BOSTON HARBOR</b> $31.1 \pm 6.4$ $20.4 \pm 3.0$ (24) $-10.7 (-34\%)$ (24) $11.8 \pm 6.4$ $4.6 \pm 2.7$ (24) $-7.2 (-61\%)$ (5) $6.3 \pm 3.4$ $1.0 \pm 1.1$ (24) $-5.3 (-84\%)$ (75) <b>MASSACHUSETTS BAY (as a whole)</b> $19.0 \pm 4.1$ $19.25 \pm 3.1$ (11) $5.3 \pm 2.8$ $5.5 \pm 1.2$ (11) $5.3 \pm 2.8$ $5.5 \pm 1.2$ (11) $1.2 \pm 0.4$ (55) $1.2 \pm 0.2$ (12) $0 (-<1\%)$ <b>MASSACHUSETTS BAY (nearfield)</b> $16.1 \pm 5.2$ (75) $18.7 \pm 2.8$ (21) $4.3 \pm 2.5$ (95) $6.4 \pm 1.6$ (21) $+2.6 (+16\%)$ (95) $1.0 \pm 0.4$ (95) $2.3 \pm 0.8$ (21) $+1.3 (+130\%)$

<sup>a</sup> denotes data cosine transformed prior to <u>t</u>-test.



Fig. 4. <u>Time-series plots of system-wide average monthly concentrations of TN and DIN</u>, for the three systems. Vertical arrows show date of wastewater transfer offshore. Only data points from consecutive months are connected by lines.

Figure 5 shows the differences in average TN before and after transfer, at each of the stations sampled in the Harbor-Bay. For details of the notations used in this Figure, see the title and legend to the Figure. Basically, the shaded/hatched areas enclose the stations



Figure 5. <u>Total nitrogen (TN)</u>. Spatial patterns of changes in average TN concentrations between the periods before (Feb '92 thru Aug '00) and after offshore transfe (Sept '00 thru Aug '01). Changes at each station were determined from data averaged through the water column at the station. Up-facing triangles show stations at which subtraction of averages after transfer from averages before transfer yielded positive values. Down-facing triangles denote the opposite. Solid triangles enclosed by shaded (solid or hatched) areas show stations at which the changes were significant. Hollow triangles enclosed by open (solid or dashed) lines show stations at which the changes were 'almost significant'. Hollow triangles not enclosed by a shaded area or line, show stations at which the averages before and after transfer were not significantly different.

at which the differences between the two periods were significant. Note, these shaded areas simply group stations, and are not meant to be contours.

In the Harbor, average TN concentrations during the 24-months were significantly lower than baseline at all 12 stations, suggesting that the decrease in TN after transfer occurred over most of the area of the Harbor. In the Bay, average concentrations during the 24-months were significantly greater than baseline at 5 of the 14 stations at which we monitored TN.

The 5 stations that showed the significant increases in TN were located in the nearfield. (Note, TN was only sampled in the nearfield at 7 stations). At one of the two remaining nearfield stations, the increase was 'almost' significant ( $p \le 0.1$ , but  $\ge 0.051$ ). At only one of the 7 stations, Station N10 in the southwest corner of the nearfield, was the increase not significant (or 'almost' significant).

At none of the Bay stations outside of the nearfield, were average concentrations after transfer significantly different from baseline. It is perhaps worth noting that at Station F13 located south of the nearfield, subtraction yielded a positive value, as it did at all nearfield stations. At the two stations between the Harbor and nearfield (Stations F24 and F25), subtraction yielded negative values, as it did in the Harbor.

**Dissolved inorganic nitrogen (DIN).** For system-wide average concentrations of dissolved inorganic nitrogen (DIN), the pattern of changes among systems was basically as for TN; a significant decrease for the Harbor, no significant change for the Bay as a whole, and a significant increase for the nearfield (Table 7, Fig. 4). In the Harbor, average DIN decreased from  $11.8 \pm 6.4 \mu mol 1^{-1}$  during baseline to  $4.6 \pm 2.7 \mu mol 1^{-1}$  during the 24-months, or by -7.2- $\mu mol 1^{-1}$  (or -61%).

In the nearfield, average DIN concentrations increased from  $4.3 \pm 2.5 \ \mu mol \ l^{-1}$  during baseline to  $6.4 \pm 1.6 \ \mu mol \ l^{-1}$  during the 24-months. The increase of  $\pm 2.1 \ \mu mol \ l^{-1}$  was equivalent to  $\pm 49\%$  of baseline, and was significant. In terms of absolute concentrations,

this increase was equivalent to between one-third and one-fourth of the decrease of -7.2- $\mu$ mol l<sup>-1</sup> we saw for DIN in the Harbor.

In both the Harbor and nearfield, the changes in DIN contributed the bulk of the changes we saw for TN; ca. 67% of the decrease in TN in the Harbor, and ca. 80% of the increase in the nearfield. Both percent contributions were similar to the 70% that DIN was estimated to contribute to wastewater-TN discharged to the Harbor before transfer (Taylor 2003).

At the individual stations, the decreases in DIN in the Harbor were significant at all 12 stations (Fig. 6). In the Bay, average concentrations after transfer were significantly higher than baseline at 17 of the 40 stations. At three other Bay stations, the increases were 'almost' significant.

Fourteen of the stations that showed significant increases, plus two of the three at which the increases were 'almost' significant, were located in the nearfield. The three other stations that showed the significant increases were located east of the nearfield. Longerterm monitoring will allow us to determine whether the increases at these three stations were not simply the result of small sample-size.

At 4 stations located between the Harbor and nearfield (including Station N10 in the southwest corner of the nearfield), subtraction yielded non-significant negative values. While the differences at none of the 4 stations were significant, their proximity to one another and to the mouth of the Harbor, together suggested the decrease in DIN in the Harbor may have extended out as far as the southwest nearfield in the Bay.

Figure 7 compares average DIN concentrations before and after transfer at the 16 stations located along the Harbor-outfall-Bay Transect. The Figure confirms the extension of the decrease in the Harbor out into the west Bay. It shows a single peak in DIN at Station



Figure 6. **Dissolved inorganic nitrogen (DIN)**. Differences in average concentrations between the periods before and after 'offshore transfer', at individual stations sampled in the Harbor and Bay For legend, see Fig. 5.

N21 located over the outfall in the nearfield. Only at this one station along the Transect in the Bay, did average DIN concentrations after transfer approach the concentrations seen in the Harbor during baseline.

The Figure shows that the increase in the nearfield may have extended south of the nearfield. At none of the stations along the Transect in this area were the increases in DIN after transfer significant. The Figure also shows that any increase in DIN that may have extended south of the nearfield was attenuated well before CCB.



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Fig. 7. <u>DIN</u>. Average concentrations of DIN before and after offshore transfer, along a transect from Boston Harbor through the nearfield, to the south east corner of Massachusetts Bay. Data are averages for data collected year-round, averaged at the between 2 and 5 depths sampled at each station. ' **\*** ' indicates differences at station significant, '?' indicates difference 'almost' significant.

*Ammonium (NH<sub>4</sub>).* For NH<sub>4</sub>, the pattern of changes among systems was as for TN and DIN. In the Harbor, average concentrations of NH<sub>4</sub> during the 24-months were -5.3- $\mu$ mol l<sup>-1</sup> (or -85%) lower than baseline. In the nearfield, they were +1.3  $\mu$ mol l<sup>-1</sup> (or +130%) higher than baseline. The increase in the nearfield was, in this case, one-fourth the size of the decrease in the Harbor.

# **Phosphorus**

*Total phosphorus (TP).* For system-wide average concentrations of TP, we were able to detect a significant decrease for the Harbor as a whole, no change for the Bay as a whole, and a significant increase for the nearfield (Table 8, Fig. 8). In the Harbor, concentrations averaged  $2.06 \pm 0.32 \ \mu mol \ l^{-1}$  during baseline, and  $1.53 \pm 0.27 \ \mu mol \ l^{-1}$  during the 24-months. The difference of -0.52-µmol  $l^{-1}$  (or -25%) was significant.

Table 8. <u>Phosphorus concentrations</u>. Comparison of values averaged for the periodsbefore and after transfer of Deer Island flows offshore.

Variable	Baseline period	24-month period after transfer	Difference	p		
	BOSTON	HARBOR				
TP (μmol l <sup>-1</sup> )	$2.06 \pm 0.32$ (61)	1.53 <u>+</u> 0.27 (24)	-0.52 (-25%)	0.01 *		
DIP (µmol l <sup>-1</sup> )	$1.05 \pm 0.37$ (68)	$0.72 \pm 0.26$ (24)	-0.33 (-31%)	<0.01 *		
	MASSACHU	<u>SETTS BAY</u> (as a whole)				
TP (μmol l <sup>-1</sup> )	$1.09 \pm 0.22$ (32)	$1.10 \pm 0.11$ (11)	+0.01 (<+1%)	0.97		
DIP (µmol l <sup>-1</sup> )	$0.64 \pm 0.21$ (56)	$0.69 \pm 0.12$ (13)	+0.05 (+8%)	0.77		
MASSACHUSETTS BAY (nearfield)						
TP (μmol l <sup>-1</sup> )	$0.98 \pm 0.24$ (60)	$1.12 \pm 0.19$ (20)	+0.14 (+14%)	0.01 *		
DIP (µmol l <sup>-1</sup> )	$0.59 \pm 0.21$ (95)	$0.66 \pm 0.18$ (21)	+0.07 (+12%)	0.26		



Fig. 8. <u>TP and DIP</u>. Time-series plots of system-wide average monthly concentrations, in the three systems.

In the nearfield, average TP concentrations increased from  $0.98 \pm 0.24 \mu mol l^{-1}$  to  $1.12 \pm 0.19 \mu mol l^{-1}$ , or by+0.14  $\mu mol l^{-1}$  (or +14%). The size of the increase in the nearfield was, in this case, less than one-fourth the size of the decrease in the Harbor. For the Bay

as a whole, average TP concentrations after transfer were not significantly different from before.

The decrease in TP in the Harbor, and increase confined to the nearfield, are both evident in the time-series plots of TP in Figure 8. The plots also show that the Harbor showed a background decrease in TP through the baseline (discussed further by Taylor 2001); in the nearfield the opposite applied, and TP, like TN, showed a background increase through the baseline.

At the individual stations we were able to detect significant decreases in TP after transfer, at 11 of the 12 Harbor stations (c.f. all 12 for TN); at the 1 remaining station, the decrease was 'almost' significant (Fig. 9). In the Bay, TP showed significant increases at 6 of the 14 stations at which TP was monitored. As for TN, all 6 stations that showed the increases were located in the nearfield.

Only at one of the 7 stations in the nearfield, Station N10 located in the southwest corner of the nearfield, closest to Boston Harbor, was the increase in TP after transfer not significant. At this station, like at the stations in the Harbor and immediately east of the Harbor, subtraction yielded a negative value. Unlike the stations in the Harbor, the negative value was not significant.

*Dissolved inorganic phosphorus (DIP).* For system-wide average concentrations of DIP, we were able to detect a significant decrease for the Harbor, but were unable to detect a significant change (increase or decrease) for the nearfield or Bay as a whole. In the Harbor, average DIP concentrations decreased by -0.33-µmol 1<sup>-1</sup>; the decrease was equivalent to -31% of baseline. This decrease contributed ca. 60% of the decrease we saw for TP.

In the Bay, for both the nearfield and Bay, subtraction yielded positive values, but in neither case, was the increase significant. In the nearfield, subtraction yielded a value of +0.07 -µmol l<sup>-1</sup> (or +12%); this was equivalent to 50% of the increase we saw for TP, but



Fig. 9. <u>Total phosphorus (TP)</u>. Differences in average concentrations between the periods before and after offshore transfer. For Legend to Figure, see Figure 5.

unlike for TP, was not significant. The positive value of 0.07-µmol l<sup>-1</sup> for DIP in the nearfield was, in turn, equivalent to ca. one-fifth of the significant decrease of -0.33-µmol l<sup>-1</sup> we saw in the Harbor.

At the individual stations, average DIP concentrations during the 24-months were significantly lower than baseline at 9 of the 12 Harbor stations (Fig. 10). All 9 stations that showed the significant decreases were those sampled by the 'Harbor' program. It


Figure 10. <u>Dissolved inorganic phosphorus (DIP)</u>. Differences in average concentrations between the periods before and after offshore transfer. For Legend, see Figure 5.

may be that we were unable to detect significant decreases at the three stations sampled by the 'Bay' program, because of small sample-size.

In the Bay, significant increases in DIP were observed at 8 of the 40 stations; and at one other station, the increase was 'almost' significant. As expected, the 8 stations was less than the 17 that showed significant increases for DIN. Five of the 8 stations were located

in the center of the nearfield; the other three were located outside of the nearfield. Note, the three stations outside of the nearfield were different from the three that showed significant increases for DIN.

As for DIN, longer-term monitoring will allow the significance of the increases at the three stations outside of the nearfield to be verified. As for DIN, subtraction yielded negative values for DIP at stations east of the Harbor mouth, extending into the southwest nearfield. Again, the decreases at none of these stations were significant, but may be shown to be significant with time.

The pattern of change in DIP along the Harbor-outfall-Bay Transect was basically as for DIN (Fig. 11). DIP showed a decrease in the Harbor extending out into the southwest



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Fig. 11. <u>DIP</u>. Average concentrations of DIP before and after transfer, along the Harbor - outfall - Bay Transect.

nearfield, an increase in the nearfield with a single peak over the outfall, and then a sharp drop off within the nearfield. Again, south of the nearfield the wastewater-DIP signal attenuated well before CCB.

## **Molar ratios of N:P**

*Total nitrogen : total phosphorus (TN:TP).* For system-wide average molar ratios of TN:TP, we were able to detect a significant decrease for the Harbor, but no significant change for the nearfield or Bay as a whole (Table 9, Fig. 12). For the Harbor, average

 Table 9. Molar N:P ratios.
 Comparison of values averaged for the periods before and after transfer of Deer Island flows offshore.

Variable	able Baseline 24-month period period after transfer		Difference	р			
BOSTON HARBOR							
TN:TP	$15.2 \pm 3.2$ (60)	$13.6 \pm 2.4$ (24)	-1.6 (-11%)	<0.01 *			
DIN:DIP	$11.4 \pm 5.2$ (60)	5.8 <u>+</u> 3.2 (24)	-5.6 (-49%)	<0.01 *			
<b>MASSACHUSETTS BAY</b> (as a whole)							
TN:TP	$18.8 \pm 3.5$ (32)	$19.4 \pm 3.1$ (12)	+0.6 (+3%)	0.65			
DIN:DIP	7.1 <u>+</u> 2.7 (56)	$7.6 \pm 1.1$ (12)	+0.5 (+7%)	<sup>a</sup> 0.87			
MASSACHUSETTS BAY (nearfield)							
TN:TP	$18.1 \pm 4.0$ (58)	$17.1 \pm 3.2$ (21)	-1.0 (-6%)	0.28			
DIN:DIP	6.2 <u>+</u> 2.6 (94)	8.3 <u>+</u> 1.9 (21)	+2.1 (+34%)	0.001 *			

<sup>a</sup> data cosine transformed prior to <u>t</u>-test



Fig. 12. <u>Molar TN:TP and DIN:DIP</u>. Time-series plots of system-wide average monthly values in Boston Harbor, Massachusetts Bay and the nearfield.

TN:TP ratios decreased from  $15.2 \pm 3.2$ :1 during baseline, to  $13.6 \pm 2.4$ :1 during the 24months. The difference was -1.6:1 (or -11% of baseline) was significant. For neither the Bay nor nearfield, were the average ratios during the 24-months significantly greater than baseline. In the Harbor, the decreases in TN:TP were significant at 9 of the 12 stations; again the 9 stations were the stations sampled by the 'Harbor' program (Fig. 13). At none of the 14



Figure 13. <u>Molar TN:TP</u>. Differences in averages ratios between the periods before and after offshore transfer at individual stations. Values are averages through water column. For Legend to Figure, see Figure 5. stations at which TN:TP was sampled in the Bay, were the average ratios during the 24months significantly different from baseline.

**DIN:DIP.** For system-wide average ratios of DIN:DIP, we were able to detect a significant increase for the nearfield but not for the Bay as a whole, and a significant decrease for the Harbor (Table 9). In the nearfield, average ratios after transfer were +2.1:1 (or +34%) greater than baseline. This increase of +2.1:1 was between one-third and one-half the decrease of -5.6:1 (or -49%) in the Harbor.

At the individual stations, in the Harbor the decreases in DIN:DIP were significant at 9 of the 12 Harbor stations (Fig. 14); again, the 9 stations were those sampled by the 'Harbor' program. In the Bay, DIN:DIP showed significant increases at 12 of the 40 stations; and at one other, the increase was 'almost' significant.

All 12 stations that showed the significant increases (plus the one at which the increase was almost significant) were located in the nearfield; unlike for DIN and DIP individually, the increases were not significant at any of the stations outside of the nearfield. As for DIN and DIP, subtraction yielded negative values at a group of stations extending out from the mouth of the Harbor to the west nearfield.

The patterns of changes in DIN:DIP along the Transect were basically as for DIN and DIP (Fig. 15). The Harbor and west Bay showed lowered ratios. The nearfield showed a single peak over the outfall. Only at this one station in the Bay, did DIN:DIP ratios approach those seen in the Harbor during baseline. Again, the DIN:DIP signal seen in the nearfield attenuated well before CCB.



Figure 14. <u>Molar DIN:DIP</u>. Differences in average monthly ratios between the periods before and after offshore transfer. Differences are for ratios averaged through the water column at each station. For Legend to Figure, see Figure 5.



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Fig. 15. <u>DIN : DIP</u>. Average molar ratios of DIN:DIP before and after offshore transfer, along the Harbor - outfall - Bay Transect.

### Silica and molar N:Si

*Total silica (total Si) and dissolved inorganic silica (SiO<sub>4</sub>).* For system-wide average concentrations of both total Si and SiO<sub>4</sub>, we were unable to detect significant differences after transfer, for the Harbor, nearfield or Bay as a whole (Table 10; Fig. A-1). For the Harbor, for both Si fractions, subtraction yielded negative values. Unlike for N and P, the decreases were not significant.

For total Si, subtraction yielded a non-significant negative value of -1.7-µmol l<sup>-1</sup> (or -15% of baseline); for SiO<sub>4</sub>, it yielded a value of -2.2-µmol l<sup>-1</sup> (or -31% of baseline). For SiO<sub>4</sub>, the decrease was 'almost' significant. For neither fraction, and perhaps because of small

sample-size in the Harbor, the decreases in the Harbor were not significant. Note, the 'Bay' program alone sampled Si in the Harbor.

Table 10. <u>Total Si, SiO<sub>4</sub>, and molar DIN:SiO<sub>4</sub></u>. Comparison of values averaged for the periods before and after offshore transfer.

Variable	Baseline period	24-month period after transfer	Difference	Þ			
	BOSTON HARBOR						
'Total' silica (μmol l <sup>-1</sup> )	$11.4 \pm 3.9$ (31)	$9.8 \pm 2.1$ (10)	-1.7 (-15%)	0.21			
SiO <sub>4</sub> (µmol l <sup>-1</sup> )	$7.0 \pm 4.2$ (54)	$4.8 \pm 2.6$ (11)	-2.2 (-31%)	0.09 ?			
DIN:SiO <sub>4</sub> $1.7 \pm 1.2$ $1.9 \pm 1.7$ (51) (11)		+0.2 (+12%)	0.75				
	MASS	SACHUSETTS BAY (as	a whole)				
'Total' silica (μmol l <sup>-1</sup> )	$8.2 \pm 2.8$ (31)	$7.8 \pm 1.8$ (10)	-0.4 (-5%)	0.62			
SiO <sub>4</sub> (µmol l <sup>-1</sup> )	5.9 <u>+</u> 2.5 (56)	$4.8 \pm 1.5$ (11)	-1.1 (-19%)	0.17			
DIN:SiO <sub>4</sub>	$1.0 \pm 0.4$ (53)	$1.5 \pm 0.7$ (11)	+0.5 (+50%)	<0.01 *			
	MASS	ACHUSETTS BAY (nea	rfield)				
'Total' silica (μmol l <sup>-1</sup> )	$7.7 \pm 2.7$ (61)	$7.2 \pm 1.9$ (21)	-0.5 (-6%)	0.40			
SiO <sub>4</sub> (µmol l <sup>-1</sup> )	$5.2 \pm 2.2$ (94)	$5.0 \pm 1.5$ (21)	-0.2 (-4%)	0.62			
DIN:SiO <sub>4</sub>	$0.8 \pm 0.4$ (94)	$1.3 \pm 0.4$ (21)	+0.5 (+63%)	<0.01 *			

Unlike for N and P, we were unable to detect a significant increase for total Si or SO<sub>4</sub> for the nearfield. In fact for both fractions, subtraction yielded non-significant negative values for this particular area. The pattern of positive and negative values among stations in the Bay, suggested an increase in SiO<sub>4</sub> in the center of the nearfield, superimposed on a background decrease in SiO<sub>4</sub> over much of the remainder of the Bay (Fig. 16).



Figure 16. **Dissolved inorganic silica (SiO<sub>4</sub>).** Differences in average monthly concentrations between the periods before and after offshore transfer, at individual sampling stations. For Legend to Figure, see Figure 5.

In the Bay, subtraction yielded positive values at 7 of the 40 stations; 6 of the 7 stations that showed positive values were located in the center of the nearfield. At one of the 7 stations, specifically Station N14 located immediately north of the outfall, the increase was 'almost' significant. At two stations well southeast of the nearfield, the decreases were 'almost' significant.

In the Harbor, subtraction yielded negative values at all three stations at which  $SiO_4$  was measured; at two of the three stations, the decreases were 'almost' significant. Again, as for the data averaged Harbor-wide, it seems likely that longer-term monitoring will show the decreases, especially for  $SiO_4$ , to be significant in the Harbor. The same could well apply to the small, and at this time non-significant increase in  $SiO_4$  over the outfall.

The Transect plot of SiO<sub>4</sub> in Figure 17 confirms the possible decrease in concentrations in the Harbor, with little increase in the nearfield. Except at three stations in the center of the nearfield, average SiO<sub>4</sub> concentrations at the Bay stations were consistently lower after transfer than baseline. It may be that the SiO<sub>4</sub> increase seen over the outfall was dampened by the background decrease seen over most of the Bay. Note that, as for N and P, SiO<sub>4</sub> concentrations in the wastewater involved in the transfer (Butler <u>et al</u>. 1997) were orders of magnitude greater than in the Bay receiving-waters.

*Molar ratios of DIN:SiO*<sub>4</sub>. For system-wide average molar ratios of DIN:SiO<sub>4</sub>, we were unable to detect a significant change for the Harbor, but observed significant increases for both the nearfield and Bay as a whole (Table 11). For the Harbor, where the 'Bay' program alone measured DIN:SiO<sub>4</sub>, subtraction yielded a non-significant positive value of +0.2:1 (or +12%).

For both the nearfield and Bay, average DIN:SiO<sub>4</sub> ratios after transfer were significantly greater than baseline. The sizes of the increases were similar in the two Bay 'systems/regions'; +0.5:1 (or +63% of baseline) for the nearfield, and +0.5:1 (or +50%) for the Bay. The fact that the increases were similar for the nearfield and Bay as a whole is suggestive of a background increase.



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Fig. 17. <u>SiO<sub>4</sub></u>. Average concentrations of dissolved inorganic silica before and after offshore transfer, along the Harbor - outfall - Bay transect.

At the individual stations, we were unable to detect significant decreases in DIN:SiO<sub>4</sub> at any of the three stations at which we monitored DIN:SiO<sub>4</sub> in the Harbor (Fig. 18). In the Bay, subtraction yielded positive values at all except two of the 40 stations. At 25 of the Bay stations, the increases in DIN:SiO<sub>4</sub> were significant. The increases were 'almost' significant at three other stations.

Twenty of the 25 stations that showed significant increases were located in the nearfield; four of the remaining 5 stations, plus the three at which the increases were 'almost' significant, extended in a broad band southeast of the nearfield. The number of stations that showed significant changes in the Bay after transfer was greater for DIN:SiO<sub>4</sub> than for all other variables.





In the Harbor, subtraction yielded positive values for DIN:SiO<sub>4</sub> at all three stations at which the ratio was monitored. At none of the three stations, were the changes significant. As can be seen in the Transect plot of DIN:SiO<sub>4</sub> (Figure 19), at the Harbor stations, average ratios after transfer were almost identical to those during baseline.



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Fig. 19. <u>DIN :  $SiO_4$ </u>. Average molar ratios of DIN:SiO<sub>4</sub> before and after offshore transfer, along the Harbor - outfall - Bay Transect.

In the Bay, at all except one of the stations along the Transect, average ratios after transfer were consistently higher than baseline. DIN:SiO<sub>4</sub> showed a single peak over the outfall after transfer, but this was superimposed in a relatively large background increase in DIN:SiO<sub>4</sub>, which in the Transect plot, is readily evident south of the nearfield.

#### Phytoplankton biomass (chlorophyll-<u>a</u>)

For the two chlorophyll- $\underline{a}$  (chl- $\underline{a}$ ) variables that we measured, combined, extracted chl- $\underline{a}$  and  $\underline{in \text{ situ}}$  fluorescence chl- $\underline{a}$ , we were able to detect a significant decrease for the Harbor, but no significant change for the nearfield or Bay as a whole (Table 11). In this report, the two chl- $\underline{a}$  variables were examined in combination, to compensate for the different intensities of sampling of the two variables in the Harbor and Bay.

Table 11.	Extracted chl-a and in situ fluorescence chl-a.	Comparison of	values averaged
for the peri	ods before and after transfer of Deer Island flow	ws offshore.	

Variable	Baseline period	24-month period after transfer	Difference	р	
	BOS	TON HARBOR			
Extracted chl- <u>a</u> $(\mu g l^{-1})$	4.7 <u>+</u> 3.1 (61)	3.8 <u>+</u> 2.8 (24)	-0.9 (-19%)	0.05 *	
$\frac{\text{In situ}}{\text{chl-}\underline{a}} (\mu g l^{-1})$	$3.2 \pm 2.5$ (53)	$4.2 \pm 4.1$ (11)	+1.0 (+31%)	0.29	
<b>MASSACHUSETTS BAY</b> (as a whole)					
Extracted chl- <u>a</u> $(\mu g l^{-1})$	$2.2 \pm 1.7$ (54)	$2.5 \pm 1.9$ (11)	+0.3 (+14%)	0.71	
<u>In situ</u> fluorescence chl- <u>a</u> (μg l <sup>-1</sup> )	2.1 <u>+</u> 1.5 (53)	$2.7 \pm 2.1$ (11)	+0.6 (+29%)	0.28	
	MASSACH	<u>USETTS BAY</u> (nearfield)			
Extracted chl- <u>a</u> $(\mu g l^{-1})$	2.1 <u>+</u> 1.9 (93)	$2.5 \pm 1.9$ (24)	+0.4 (+19%)	0.25	
In <u>situ</u> fluorescence chl- <u>a</u> ( $\mu$ g l <sup>-1</sup> )	2.1 <u>+</u> 1.5 (94)	$2.5 \pm 1.9$ (21)	+0.4 (+19%)	0.44	

In the Harbor, where sampling for extracted chl-<u>a</u> was greater than for fluorescence chl-<u>a</u>, average extracted chl-<u>a</u> concentrations decreased from  $4.7 \pm 3.1 \ \mu g \ l^{-1}$  during baseline, to  $3.8 \pm 2.8 \ \mu g \ l^{-1}$  during the 24-months. The decrease of -0.9  $\ \mu g \ l^{-1}$  was equivalent to -19% of baseline, and was significant. The time-series plot of extracted chl-<u>a</u> in Figure 20 confirms the decrease in the Harbor.

In the Bay, where sampling was most intensive for fluorescence  $chl-\underline{a}$ , subtraction yielded positive values for both variables, for both the nearfield and the Bay as whole. For

fluorescence chl-<u>a</u>, the positive values for the two Bay systems/regions were almost identical;+0.4  $\mu$ gl<sup>-1</sup> for the nearfield, and +0.3  $\mu$ gl<sup>-1</sup> for the Bay as a whole. For neither the Bay nor nearfield, and unlike for N and P in the nearfield, were the increases in chl-<u>a</u> significant. **BOSTON HARBOR** 



Fig. 20. <u>Extracted chl-a</u>. Time-series plots of system-wide, average monthly values for each of the three systems.

At the individual stations, for extracted chl-<u>a</u> we were able to detect significant decreases in the Harbor at three of the 12 stations (Fig. 21). One of the three stations was located in the Neponset River area of the North West Harbor, and the other two in the



Figure 21. **Extracted chl-a**. Differences in average concentrations between the periods before and after offshore transfer. For Legend to Figure, see Figure 5.

Central

Harbor. For fluorescence chl-<u>a</u>, subtraction yielded positive values at the three Harbor stations at which it was measured; at one of the three, Station F23 at the mouth of the Harbor, the increase was 'almost' significant (Fig. 22).



Figure 22. **Fluorescence chl-a**. Differences in average concentrations between the periods before and after offshore transfer. Fore Legend to Figure, see Figure 5.

In the Bay, for both chl- $\underline{a}$  variables, subtraction yielded positive values at almost all stations, and at none of the stations, including those in the nearfield, were the increases significant. For extracted chl- $\underline{a}$ , the increases were 'almost' significant at two stations. For fluorescence chl- $\underline{a}$ , the increase was 'almost' significant at one station, located off of the mouth of the Harbor.

For both chl-<u>a</u> variables, both in the Harbor and the Bay, the numbers of stations that showed significant (or 'almost' significant) changes in chl-<u>a</u> after transfer were much smaller than for N and P. Also unlike for N and P, the few stations in the Bay that showed increases in chl-<u>a</u> that were 'almost' significant, were not focused in the nearfield.

The Transect plot of chl- $\underline{a}$  in Figure 23 shows the decrease in chl- $\underline{a}$  concentrations in the Harbor after transfer. Unlike for N and P, the decrease in chl- $\underline{a}$  in the Harbor appeared not to extend out into the west Bay (at least not along the Transect). In the Bay, again unlike for N and P, chl- $\underline{a}$  showed no large peak in the nearfield. In fact at Station N21, where the N and P peaks were largest, the increase in chl- $\underline{a}$  in the Bay after transfer was smallest.

At all 10 Bay stations along the Transect, and as noted earlier, at almost all stations in the Bay as a whole, average concentrations chl-a concentrations after transfer were consistently (although not significantly) greater than baseline. This is suggestive of a background increase. It is worth noting that despite this background increase, we were unable to detect a significant increase in chl-<u>a</u> at any of the Bay stations.

Based on the relationships demonstrated by others between average chl-<u>a</u> concentrations and N loadings to estuarine systems (Nixon et al. 1986), the decrease in chl-a in the Harbor was presumably a response to the decrease in N loadings to the Harbor that followed transfer. In the Bay, the increase in N loadings to the nearfield that followed transfer apparently caused no significant increase in chl-<u>a</u> (at least for the first full 24months, and for the data averaged through the water-column).



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Fig. 23. <u>Average chl-a</u> concentrations before and after transfer along the Harbor - nearfield - Bay transect. Note, the Harbor data are extracted chl-<u>a</u> data measured by the 'Harbor' program, and the Bay data are fluorescence chl-<u>a</u> data measured by the 'Bay' program.

## **Organic carbon**

For system-wide average concentrations of total organic carbon (TOC), we were unable to detect a significant decrease for the Harbor, or significant increase for the nearfield or Bay as a whole (Table 12, Fig. A-2). For the Harbor, subtraction yielded a negative value of -28-µmol<sup>-1</sup> (or -11%), but the decrease was not significant. As for Si, small sample-size could well have been responsible for our not being able to detect a significant decrease.

Table 12. <u>Total organic carbon (TOC)</u>, particulate organic carbon (POC), and ratios of <u>POC:chl-a (by weight)</u>. Comparison of values averaged for the periods before and after offshore transfer.

Variable	<sup>a</sup> Baseline period	24-month period after transfer	Difference	ġ				
	BOSTON HARBOR							
TOC (µmol l <sup>-1</sup> )	FOC $265 \pm 59$ $237 \pm 62$ $\mu mol l^{-1}$ )(16)(11)		-28 (-11%)	0.25				
POC (µmol l <sup>-1</sup> )	$43 \pm 16$ (61)	31 <u>+</u> 13 (24)	-12 (-28%)	<0.01 *				
POC:chl- <u>a</u> <sup>b</sup> $110 \pm 42$ $98 \pm 27$ (61) (24)		-12 (-11%)	0.34					
MASSACHUSETTS BAY (as a whole)								
TOC (µmol l <sup>-1</sup> )	$247 \pm 60$ (49)	221 <u>+</u> 64 (11)	-26 (-11%)	0.03 *				
POC $23 \pm 8$ $24 \pm 5$ (µmol l <sup>-1</sup> )       (51)       (12)         POC:chl- <u>a</u> <sup>b</sup> $125 \pm 64$ $115 \pm 29$ (61)       (24)		$24 \pm 5$ (12)	+1 (+4%)	0.83				
		$115 \pm 29$ (24)	-10 (-8%)	0.39				
	MASSACHU	SETTS BAY (nearfield)						
TOC (μmol l <sup>-1</sup> )	242 <u>+</u> 57 (78)	208 <u>+</u> 51 (21)	-34 (-14%)	0.02 *				
POC (µmol l <sup>-1</sup> )	22 <u>+</u> 8 (85)	26 <u>+</u> 7 (21)	+4 (+18%)	0.04 *				
POC:chl- <u>a</u> <sup>b</sup>	126 <u>+</u> 72 (61)	125 <u>+</u> 35 (24)	-1 (-<1%)	0.84				

<sup>a</sup> For TOC, the baseline period extends from Jan 1 1998 through Aug 5 2000 (data collected prior to this date was not used to compute average baseline values, because they were determined using a different method). For POC, the baseline extended from Aug 1995 through Aug 5 2000 for the data collected by the 'Harbor' program, and Feb 1992 through Aug 5 2000 for the data collected by the 'Bay' program. <sup>b</sup> POC:chl-<u>a</u> is a gravimetric rather than a molar ratio, and uses extracted (rather than fluorescence) chl-<u>a</u>.

For both the nearfield and Bay as a whole, average TOC concentrations during the 24months were significantly lower (rather than significantly higher) than baseline. For the Bay, the decrease was  $-26-\mu$ mol<sup>-1</sup> (or -11%); for the nearfield, it was  $-34-\mu$ mol<sup>-1</sup> (or -14%). A background decrease may have been responsible for the decreases in the two Bay systems/regions.

For system-wide average concentrations of particulate organic carbon (POC), we were able to detect a significant decrease in the Harbor, a significant increase in the nearfield, and no change for the Bay as a whole (Fig. 24). In the Harbor, average POC decreased by -12-µmol l<sup>-1</sup> (or -28%), and the fact that concentrations decreased, was as for chl-<u>a</u>.

In the nearfield, unlike for chl-<u>a</u>, POC concentrations showed a significant increase, in this case of +4- $\mu$ mol l<sup>-1</sup> (or +18%). The increase in the nearfield of +4- $\mu$ mol l<sup>-1</sup> was equivalent to ca. one-third of the decrease in POC in the Harbor. In neither the Harbor nor nearfield, were system-wide average, gravimetric POC:chl-<u>a</u> ratios after transfer significantly different from baseline.

For POC, at the individual stations we were able to detect significant decreases in concentrations in the Harbor at 9 of the 12 stations (Fig. 25). Again, the 9 stations that showed the significant decreases were the stations sampled by the 'Harbor' program. The decrease in POC over most of the area of the Harbor was as for N and P, but was more extensive than for chl-<u>a</u>.

In the Bay, average POC concentrations during the 24-months were significantly greater than baseline at two of the stations, both located in the center of the nearfield, and at one other station, east of the nearfield, the increase was 'almost' significant. The number of stations in the nearfield that showed significant increases was greater than for  $chl-\underline{a}$ , but smaller than for N or P.



Fig. 24. <u>Particulate organic carbon (POC)</u>. Time-series plots of system-wide average monthly concentrations of POC in the 3 systems.



Figure 25. <u>Particulate organic carbon (POC)</u>. Differences in average monthly concentrations between the periods before and after offshore transfer. For Legend to Figure, see Figure 5.

# Bottom-water dissolved oxygen (DO)

For both DO variables that we monitored, bottom-water DO concentrations and bottomwater DO percent saturation, we were unable to detect significant differences between the 24-months and baseline, for the Harbor, nearfield or Bay as a whole. This applied for both the data averaged system-wide (Table 13), and for all stations sampled in each of the systems/regions.

 Table 13.
 Bottom-water dissolved oxygen (DO).
 Comparison of average DO values for

 the periods before and after offshore transfer.

Variable	<sup>a</sup> Baseline period	24-month period after transfer	Difference	p		
	BOSTC	N HARBOR				
DO conc $(mg l^{-1})$	$8.6 \pm 1.2$ (40)	$8.8 \pm 1.3$ (24)	+0.2 (+2%)	0.61		
DO % sat.	DO % sat. $94.0 \pm 6.3$ $93.3 \pm 5.8$ (40) (24)					
MASSACHUSETTS BAY (as a whole)						
DO conc. $(mg l^{-1})$	9.5 <u>+</u> 1.4 (52)	9.1 <u>+</u> 1.4 (10)	-0.4 (-4%)	0.20		
DO % sat. $92.0 \pm 10.0$ $94.2 \pm 8.1$ (23) (12)		+2.2 (+2%)	0.73			
	MASSACHUSE	<u>TTS BAY</u> (nearfield)				
DO conc. $(mg l^{-1})$	$9.4 \pm 1.4$ (93)	9.1 <u>+</u> 1.3 (21)	-0.3 (-3%)	0.25		
DO % sat.	$92.4 \pm 10.3$ (93)	92.8 <u>+</u> 8.3 (21)	+0.4 (+<1%)	0.80		

<sup>a</sup> Baseline Harbor data are for June 1 1997 through September 6 2000. For the Bay, the baseline data are from February 1992 through September 6 2000.

For both DO variables, in both the Harbor and the Bay, average values during the 24months fell within the range seen during baseline (see time-series plot for DO concentrations in Fig. 26). During the mid-summers during the 24-months. bottom-water DO concentrations in the Harbor showed evidence of an increase (see also Taylor 2003), but no equivalent decrease was observed for the nearfield or Bay as a whole.



Fig. 26. <u>Bottom-water DO concentrations</u>. Time-series plots of system-wide average monthly values for each of the systems.

For neither DO concentrations (Fig. 27) nor DO % saturation (Fig. 28), were we able to detect significant changes after transfer for the year-round data, at any of the individual stations in the Harbor or Bay. For both variables, however, the pattern of positive and



Figure 27. <u>Dissolved oxygen (DO) conc</u>. Differences in average monthly DO concentrations between the periods before (Feb '92 thru Aug '00) and after offshore transfer (Sept '00 thru Aug '02).

negative values among stations suggested a small increase in DO in the Harbor, and decrease in the nearfield. Longer-term monitoring will allow verification (or not) of these changes.



Figure 28. **Bottom-water dissolved oxygen % sat.** Spatial pattern of the differences in year-round, average monthly % saturation values between the periods before and after offshore transfer. For Legend to Figure, see Figure 27.

The Transect plot in Figure 29, confirms the fact that any differences in bottom-water DO

in the Harbor and Bay after transfer were small. In the Harbor, at both the sets of stations, averages after transfer were consistently (although not significantly) greater than baseline. The converse applied at all stations along the Transect in the Bay. No sharp increase or decrease in bottom-water DO was observed within, or in the vicinity of the nearfield.



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Fig. 29. <u>Average bottom-water DO concentrations</u> before and after offshore transfer along the Harbor - nearfield - Bay transect. Note, in the Harbor averages at the two stations measured by the 'Bay' program were greater than at the stations measured by the 'Harbor' program, presumably because of differences in sample-size.

### Salinity

For system-wide average salinity, the Harbor showed a significant increase, the nearfield showed no significant change, and the Bay as a whole, showed a significant increase

(presumably in response to a background increase) (Table 14). In the Harbor, systemwide average salinity increased from  $30.5 \pm 1.2$  ppt during baseline, to  $31.2 \pm 0.9$  ppt during the 24-months. The increase of +0.7 ppt was equivalent to +2% of baseline.

 Table 14. <u>Salinity</u>. Comparison of values averaged for the periods before and after offshore transfer.

Variable	<sup>a</sup> Baseline period	24-month period after transfer	Difference	p
	BOST	ΓΟΝ HARBOR		
Salinity (ppt)	$30.5 \pm 1.2$ (55)	$31.2 \pm 0.9$ (24)	+0.7 (+2%)	0.02 *
	MASSACHU	<u>SETTS BAY</u> (as a whole)	)	
Salinity (ppt)	$31.7 \pm 0.5$ (56)	$32.0 \pm 0.4$ (12)	+0.3 (+1%)	0.04 *
	MASSACHUS	<u>SETTS BAY</u> (nearfield)		
Salinity (ppt)	31.6 ± 0.6 (94)	31.8 <u>+</u> 0.6 (22)	+0.2 (+1%)	0.25

In the nearfield, salinity averaged  $31.6 \pm 0.6$  ppt during baseline, and  $31.8 \pm 0.6$  ppt during the 24-months; the difference, in this case of +0.2 ppt (or +1%), was not significant (p = 0.25). For the Bay as a whole, system-wide average salinity during the 24-months was +0.3 ppt (or +1%), and significantly greater than baseline.

At the individual stations, the patterns of changes in salinity were basically as for the system-wide data (Fig. 30). In the Harbor, subtraction yielded positive values at all 12 stations, and at 8 of the 12, the increases were significant. In the Bay, subtraction yielded positive values at 37 of the 40 stations, and at 20 of the 37, the increases were significant (or almost significant).

The distribution of the Bay stations that showed significant or 'almost' significant increases is supportive of a background increase in salinity. This background increase in salinity could well have 'dampened' the small decrease in salinity in the nearfield expected to follow transfer.



Figure 30. **Salinity**. Differences in average monthly values between the periods before and after offshore transfer. For Legend to Figure, see Figure 27.

At all 16 stations along the Transect, average salinity after transfer was consistently (although not significantly) greater than baseline (Fig. 31). The low-salinity wastewater

signal is evident in the nearfield as a decrease in the size of the difference in salinity between the two periods.



Fig. 31. <u>Salinity</u>. Average salinity before and after transfer, along the transect from Boston Harbor, through the nearfield, to the south east corner of Massachusetts Bay. Data are averages of all 5 depths, for year-round data at each station.

## DISCUSSION

### Overview of the changes observed in the Harbor and Bay

Table 15 compares for 16 variables, the changes in the Harbor, Bay as a whole and nearfield, during the first 24-months after transfer. For details of the notations used in the Table, see the title of, and footnote to the Table. Basically, 'solid' arrows show variables for which the differences were significant for the system as a whole; 'open' arrows show

variables for which the differences were significant only at certain stations within the system.

		VARIABLE	BOSTON HARBOR		MASSACHUS BAY (nearfiel farfield)	SETTS Id +	NEARFIEL	D
Nutrients	_	TN (μmol I <sup>-1</sup> ) DIN ( umol I <sup>-1</sup> ) TP (μmol I <sup>-1</sup> ) DIP ( μmol I <sup>-1</sup> ) MOLAR TN:TP MOLAR DIN:DIP TOTAL SI ( μmol I <sup>-1</sup> ) SiO 4 ( μmol I <sup>-1</sup> )	♦ ♦ ♦ ♦ – –	-10.7 (-34%) -7.3 (-61%) * -0.52 (-25%) -0.33 (-31%) -1.6 (-11%) * -5.6 (-49%) *	<ul> <li>☆</li> <li>☆</li></ul>	+0.25 (+1%) +0.2 (+4%) +0.01 (<+1%) +0.05 (+8%) +0.6 (+3%) +0.5 (+7%)	<ul> <li>▲</li> <li>↓</li> <li>↓</li></ul>	+2.6 (+16%) * +2.1 (+49%) * +0.14 (+14%) * +0.07 (+12%) -1.0 (-6%) +2.1 (+34%) *
Chl <u>a</u>		EXTRACTED CHL- <u>A</u> ( $\mu$ g l <sup>-1</sup> ) FLUORESCENCE ( $\mu$ g l <sup>-1</sup> )	+	-0.9 (-19%) *	-	то.5 (тоож) ·	-	10.0 (TOS76)
Salinity DO Organic carbon	[ [	TOC ( µmol I <sup>-1</sup> ) POC ( µmol I <sup>-1</sup> ) DO CONC. (summer) (mg I <sup>-1</sup> ) DO % SAT. (summer) SALINITY (ppt)	- + - +	-12 (-28%) * +0.7 (+2%) *	↓ - -	-28 (-11%) * +1 (+4%) +0.3 (+1%) *	<ul> <li>↓</li> <li>↓</li></ul>	-34 (-14%) * +4 (+18%) * +0.2 (+1%)

Table 15. Summary of changes seen in the Harbor, the Bay as a whole and nearfield during the first 24-months after transfer of wastewater discharges from the Harbor to the Bay.

Footnote: 'Up-facing' arrows indicate increases; 'down-facing' arrows, decreases. 'Solid' arrows show differences significant (p = or < 0.05) for the system/region as a whole; 'open' arrows indicate differences significant (p = or < 0.05) at individual stations; 'dashes' show differences were not significant for the system/region as a whole or individual stations. Values next to arrows show differences in system-wide averages between 24-months and baseline; values in parentheses are the differences expressed as percent of baseline. Values are shown adjacent to arrows only when differences were significant for system as a whole or individual stations.

*Boston Harbor.* In the Harbor, we were able to detect significant differences between the 24-months and baseline (for either the Harbor as a whole or individual stations), for 9 of

the 16 variables. For all 9 variables, which included the concentrations and ratios of N and P fractions listed in the Table, concentrations of extracted chl- $\underline{a}$  and of POC, and salinity, the differences were significant for the Harbor as a whole.

For at least 5 of the remaining 7 variables, the decreases for the Harbor (for the Harbor as a whole and individual stations) were likely not significant because of small sample size. The 5 variables, which included the two Si fractions, DIN:SiO<sub>4</sub>, fluorescence chl-<u>a</u> and TOC, were only measured in the Harbor by the 'Bay' program. For a number of these variables, the changes at certain of the stations were 'almost' significant, and may be shown to be significant with time.

For the remaining two variables that showed no significant differences between the two periods in the Harbor, bottom-water DO concentrations and bottom-water DO % saturation, both programs conducted measurements in the Harbor, but the changes were too small to be detected (at least for the year-round data).

*Nearfield.* For 5 of the 9 variables that showed significant changes in the Harbor, we were able to detect significant changes for the nearfield as a whole. The 5 variables included concentrations of TN, DIN, TP, and POC, and molar ratios of DIN:DIP. For all 5 variables, average values after transfer were significantly greater than baseline. The increases were equivalent to between one-fourth and one-third of the sizes of the decreases in the Harbor.

For three of the 9 variables that showed significant changes in the Harbor, we were unable to detect significant changes for the nearfield as a whole, but were able to detect significant changes at individual stations in the nearfield. These variables included concentrations of DIP, molar ratios of TN:TP, and salinity.

For the one remaining variable that showed significant decreases in the Harbor, extracted chl-<u>a</u>, we were unable to detect significant changes for the nearfield or individual stations

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in the nearfield. Chl-<u>a</u> concentrations may have increased as specific depths in the nearfield or during particular seasons, but these were not addressed in this report.

For two variables, DIN:SiO<sub>4</sub> and TOC, that perhaps because of small sample size showed no significant change in the Harbor, we were able to detect significant changes for the nearfield as a whole. For both variables, the increases were presumably caused by background increases that were seen for the Bay as a whole.

*Bay as a whole.* For the Bay as a whole, we were only able to detect significant differences from baseline for three variables; specifically increases for molar ratios of DIN:SiO<sub>4</sub> and salinity, and decreases for concentrations of TOC. For all three variables, background changes (rather than transfer) were likely responsible for the changes.

### Comparison of observed and predicted changes

In this section we compare for the Harbor and the Bay, the differences we observed during the 24-months with the changes predicted by others using two sets of numerical models; one, the 3-D Bays Eutrophication Model (BEM) developed and run by HydroQual and Normandeau (1995), and two, the 3-dimensional ECOM-si hydrodynamic model developed and run by Signell <u>et al.</u> (2000).

The comparisons of the observed and predicted changes/differences are necessarily broad. Both models were run using historic boundary data, that were likely different from boundary conditions during the 24-months. Also, for the BEM model, historic estimates of the secondary-treated wastewater loadings involved in the transfer were used (HydroQual and Normandeau 1995).

For these reasons, in this report we assume that the observed and predicted changes are similar, if the observed differences fall within a factor of ca. 2.0 of the predicted differences. The purpose of these comparisons is not to calibrate the numerical models

(this would require other comparisons), but to simply identify any large discrepancies between the observed and predicted differences.

The predictions made by the models were generated by 'numerically transferring' the wastewater from the Harbor to the Bay, under controlled boundary conditions. Thus, similar observed and predicted changes would suggest (although not indicate conclusively), that transfer was responsible for the changes observed during the 24-months.

Table 16 compares for the Harbor and nearfield, for three variables (DIN, extracted chl-<u>a</u> and bottom-water DO concentrations), the changes during the 24-months and those predicted by the BEM model. The differences observed for salinity are compared with the changes predicted by the ECOM-si hydrodynamic model, later in the report.

For DIN, the decrease in the Harbor of -7.3- $\mu$ mol l<sup>-1</sup> (or -63% of baseline) was almost identical to the decrease of -6.8- $\mu$ mol l<sup>-1</sup> (or -57%) predicted by the BEM model. In the nearfield, the increase in DIN of +1.6  $\mu$ mol l<sup>-1</sup> (or +50% of baseline) may have been slightly greater than predicted (+0.9  $\mu$ mol l<sup>-1</sup> or +25%), but fell within a factor of two of the predicted change.

For chl-<u>a</u>, as for DIN, the fact that we observed a decrease in the Harbor was as predicted by the BEM model. The decrease in chl-<u>a</u> in the Harbor of -0.9- $\mu$ g l<sup>-1</sup> (or -19%) may have been slightly smaller than predicted (-1.5- $\mu$ g l<sup>-1</sup> or -39%), but fell within a factor of 2.0 of the predicted change. In the nearfield, the non-significant difference of +0.8  $\mu$ g l<sup>-1</sup> (or +32%) observed for chl-<u>a</u> was similar to the decrease of -0.4- $\mu$ g l<sup>-1</sup> (or -20%) predicted by the model.

For bottom-water DO concentrations, the difference of  $+0.3 \text{ mg l}^{-1}$  (or +3%) we observed in the Harbor during the 24-months, and that was non-significant, was almost identical to the predicted increase of  $+0.4 \text{ mg l}^{-1}$  (or +4%). Likewise, in the nearfield, the observed
Table 16. <u>Observed versus predicted changes.</u> Comparisons of the observed changes in average concentrations of DIN, chl-<u>a</u> and DO, with the changes predicted by the BEM model, for the Harbor and nearfield.

System		Observed			Predicted <sup>b</sup>	
	Baseline	24-months	Difference (%)	Pre-transfer	Post-transfer	Difference (%)
DISSOLVED INORGANIC NITROGEN (DIN) (µmol l <sup>-1</sup> )						
Boston Harbor	$11.8 \pm 6.4^{a}$ (75)	$4.6 \pm 2.7^{a}$ (24)	-7.3 (-63%) <sup>a</sup>	$11.9 \pm 5.5^{\circ}$ (24)	5.1 <u>+</u> 4.1 <sup>c</sup> (24)	-6.8 (-57%) °
Nearfield	3.3 <u>+</u> 2.9 <sup>d</sup> (94)	$4.9 \pm 2.5^{d}$ (21)	+1.6 (+50%) <sup>d</sup>	$3.4 \pm 3.2^{e}$ (24)	$4.3 \pm 3.6^{\circ}$ (24)	+0.9 (+25%) <sup>e</sup>
CHLOROPHYLL-A ( $\mu g l^{-1}$ ) f						
Boston Harbor	$4.7 \pm 3.1^{a}$ (61)	$3.8 \pm 2.8^{a}$ (24)	-0.9 (-19%) <sup>a</sup>	3.8 <u>+</u> 2.1 <sup>c</sup> (24)	$2.3 \pm 1.1^{\circ}$ (24)	-1.5 (-39%) <sup>°</sup>
Nearfield	2.6 <u>+</u> 2.1 <sup>d</sup> (95)	$3.5 \pm 2.6^{d}$ (24)	+0.8 (+32%) <sup>d</sup>	$2.0 \pm 1.0^{\circ}$ (24)	$1.6 \pm 0.8^{\circ}$ (24)	-0.4 (-16%) <sup>e</sup>
DO CONCENTRATION (mg l <sup>-1</sup> )						
Boston Harbor	$8.8 \pm 1.2^{g}$ (40)	9.1 <u>+</u> 1.7 <sup>g</sup> (24)	+0.3 (+3%) <sup>g</sup>	9.2 <u>+</u> 1.0 <sup>h</sup> (24)	9.5 <u>+</u> 1.0 <sup>h</sup> (24)	+0.3 (+4%) <sup>h</sup>
Nearfield	9.3 <u>+</u> 1.3 <sup>i</sup> (95)	9.2 <u>+</u> 1.1 <sup>i</sup> (24)	-0.1 (-1%) <sup>i</sup>	$9.4 \pm 1.0^{\mathrm{j}}$ (24)	$9.4 \pm 1.0^{j}$ (24)	-<0.1 (<-1%) <sup>j</sup>

For footnote to Table see next page

Footnote to Table 16:

<sup>a</sup> values are the averages for all stations sampled, for all depths; <sup>b</sup> from HydroQual and Normandeau (1995); <sup>c</sup> predicted values are for averages of surface and mid-depths, for 1 station (HydroQual station 2 in the Harbor, located in the vicinity of 'Harbor' program stations 106 and 142 and 'Bay' station F23), <sup>d</sup> values are averages of the values observed at Depths A through C, for all stations in the nearfield, <sup>e</sup> predicted values are for averages of surface and mid-depths, for 1 station, HydroQual Station 5 located in the nearfield, in the vicinity of 'Bay' program stations N11 and N12; <sup>f</sup> for Harbor, data are acid-corrected, extracted chl-<u>a</u>, and for Bay, fluorescence chl-<u>a</u>; <sup>g</sup> observed DO data for Harbor are averages for all stations, bottom depth only, <sup>h</sup> predicted DO data for Harbor are averages for mid- and bottom depths for 1 station (HydroQual station 2 in the Harbor, located in the vicinity of 'Harbor' program stations 106 and 142 and 'Bay' program stations F23); <sup>i</sup> DO data for nearfield are averages for Depths D through E; <sup>j</sup> predicted values are for averages of mid- and bottom depths, for 1 station 5 in the nearfield, in the vicinity of 'Bay' program stations N11 and N12.

non-significant negative value of -0.1-mg  $l^{-1}$  (or -1%), was almost identical to the decrease of -<0.1 mg  $l^{-1}$  (or-<1%) predicted for year-round, bottom-water DO.

For salinity, the increase in the Harbor during the 24-months of +0.6 ppt was almost identical to the increase of +0.5 ppt predicted by the ECOM-si hydrodynamic model (Signell <u>et al</u>. 2000). In the nearfield, where salinity showed a background increase (of ca. 0.3 ppt), the observed difference of +0.2 ppt, may have been different from the predicted decrease of -0.15 ppt.

## **Cautionary comments**

For all variables, differences we observed in the Harbor and Bay between the 24-months and baseline, reflect the combined effects of both transfer and of natural background changes/trends. The simple statistical analyses that we conducted in this report proved useful for identifying, for the Harbor, Bay and nearfield, some of the differences between the 24-months and baseline.

It did not however allow the separate contributions of transfer and of these natural background changes/trends, to be quantified. While the changes observed for the four variables were similar to those predicted by numerical models, it is not possible to state that offshore transfer alone was responsible for the changes we observed during the 24-months.

In certain cases, the changes caused by transfer may have been 'accentuated' by background changes/trends; in other cases, they may have been 'dampened'. In still others, they may not have been affected. Multi-variate ANOVA would allow the effects of transfer alone, and of transfer and background changes in combination, to be better quantified.

Based on the simple analysis conducted in this report, it appears that for most variables, the changes observed in the Harbor have been greater than those observed in the nearfield

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or Bay as a whole. Multi-variate ANOVA with Contrast would allow the significance of the differences in changes among systems to be tested.

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## APPENDIX A

**Supporting Figures** 



Fig. A-1. <u>Total Si and silicate (SiO4)</u>. Time-series plots of system-wide average monthly concentrations in the three systems.



Fig. A-2. <u>Total (TOC) and dissolved organic carbon (DOC)</u>. Time-series plots of system-wide average monthly concentrations.