5 years after transfer of Deer Island flows offshore: an update of water-quality improvements in Boston Harbor

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5 years after transfer of Deer Island flows offshore: an update of water- quality improvements in Boston Harbor

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EXECUTIVE SUMMARY

In September 2000, the Massachusetts Water Resources Authority (MWRA) transferred the flows from the Deer Island wastewater treatment facility (WWTF) offshore, for diffusion into the bottom waters of Massachusetts Bay. This transfer, which we refer to here as 'offshore transfer', ended over a century of direct WWTF discharges to the Harbor.

A number of reports have documented the changes in the water-column of the Harbor during the first two to three years after transfer. The purpose of the following report was to update these earlier reports, and document the changes over the first 5 years after the transfer. With an additional two years of post-transfer data, we can be more confident of any changes that might have occurred in the Harbor.

To identify the changes since transfer, we compare water quality in the Harbor during the 5-years with water quality during a 5- to 7-year baseline period before the transfer. This report, like our earlier reports, focuses on eutrophication-related water quality, because it was this aspect of the Harbor that was predicted by earlier numerical models, to be most changed by transfer.

MWRA collected all water-quality data used in the report. The data were collected at 10 stations, located in the four major regions of the Harbor; the Inner Harbor, North West Harbor, Central Harbor and South East Harbor. Table I summarizes some of the differences in the Harbor water-column between the 5-years and baseline. Only differences significant at $p \le 0.05$ are presented in the Table.

'Solid arrows' indicate variables where the differences between the two periods were significant for the data averaged Harbor-wide. The 'hollow arrows' indicate variables, where the differences were not significant for the data averaged Harbor-wide, but were significant at certain stations. The 'dashes' indicate variables where the differences were not significant for the data averaged Harbor-wide or for any of the stations.

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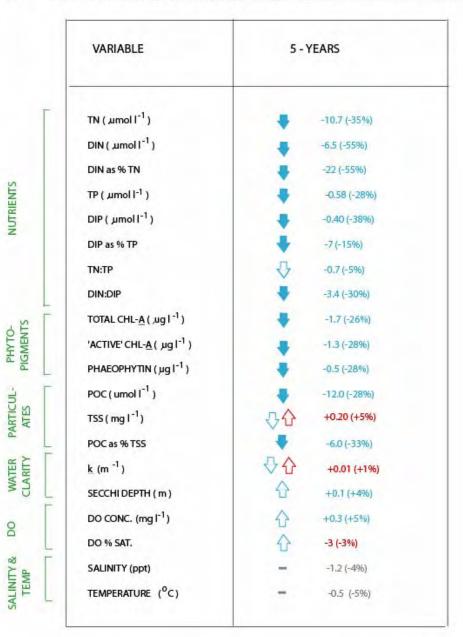


Table 1. Summary of differences in Harbor water-quality between the 5-years and baseline.

Blue arrows indicate change that might be interpreted as an 'improvement'. Red arrows indicate change that might not be viewed as an improvement. Gray symbols indicates a change that cannot be assessed as an improvement or non-improvement. Values adjacent to arrows indicate the difference in the Harbor-wide averages between the 5-years and baseline. This difference expressed as a percent of the average during baseline is shown in parentheses.

For 18 of the 20 variables shown in Table I, the averages after transfer were significantly different from baseline, for either the data averaged Harbor-wide, or for individual stations. For 12 of the 18 variables, the differences were significant for the data averaged Harbor-wide; for 6 of the 18 variables, the differences were significant only at individual stations.

For concentrations of most of the N and P nutrients, and especially for the dissolved inorganic fractions, the Harbor-wide averages after transfer were significantly different (and in all cases, lower) than baseline. The decreases were also significant at most or all of the 10 stations, suggesting that the decreases were observed over most of the area of the Harbor.

For most of the N and P nutrients that showed significant decreases (excluding the particulate fractions), the decreases were also observed during all four seasons, but were largest during fall and winters, the seasons when concentrations in the Harbor tend to be seasonally greatest.

For concentrations of chlorophyll-<u>a</u> (chl-<u>a</u>), a measure of phytoplankton biomass, Harborwide average concentrations during the 5-years were also significantly lower than baseline, presumably in response to the reduction in N loadings that followed transfer. The decreases were confined to a localized area of the Central Harbor, and were largest during summers, the season when concentrations in the Harbor tended to be highest.

The Harbor also showed significantly lowered concentrations of particulate organic carbon (POC), a measure of detrital mass, during the 5-years. As for N and P, the decreases were observed over most of the area of the Harbor. As for chl-<u>a</u>, but unlike for N and P, the decreases were most pronounced during summers, again when concentrations were seasonally greatest.

For TSS, the Harbor-wide averages during the 5-years were not significantly different from baseline. (Note, the bulk of the decrease in wastewater loadings of TSS occurred

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before offshore transfer, and the decrease after offshore transfer was much smaller than for N or P). Significant differences in TSS were observed between the 5-years and baseline, at individual stations. At stations in the Inner Harbor, and perhaps along the west margin of the Harbor, concentrations were lower than baseline. At the mouth of the Outer Harbor, the opposite applied.

For both attenuation coefficients (\underline{k}) and secchi depth, the Harbor-wide averages during the 5-years were not significantly different from baseline. Both variables indicated elevated clarity in the Inner Harbor extending along the west margin of the Harbor. The \underline{k} data in turn indicated significantly lowered clarity at the mouth of the Outer Harbor, perhaps extending into the South Harbor.

For neither dissolved oxygen (DO) concentrations nor DO % saturation, were the yearround, Harbor-wide averages after transfer significantly different from baseline. Both variables, however, showed significant increases for the data averaged Harbor-wide, during the 'mid-summers' after transfer. For the year-round data, average DO concentrations were significantly elevated compared to baseline, at stations in the mid- to upper Inner Harbor.

For only two of the 20 variables, salinity and water-temperatures, were the averages after transfer not significantly different from baseline, for both the Harbor-wide averages and the averages for the individual stations. The fact that these variables were not significantly different between periods, suggests that background environmental changes were not responsible for other differences in water quality observed between the two periods.

In the Discussion section of the report we compare the differences observed for the 5years, with the differences predicted by others before transfer, using 3-D numerical models. For all four variables where such comparisons were possible (dissolved inorganic nitrogen, chl-<u>a</u>, DO concentrations, and salinity), the observed differences were within \leq 15% of the predicted differences.

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The similarity of the observed and predicted differences indicates that, at least for these four variables, the transfer of the WWTF discharges offshore was largely responsible for the differences observed between periods. A more sophisticated statistical analysis would allow a better separation of the effects of the transfer from background environmental changes that might have occurred over the same period.

INTRODUCTION

In September 2000, the flows from the Deer Island (DI) wastewater treatment facility (WWTF) to Boston Harbor were transferred 16-km offshore, for diffusion into the bottom-waters of Massachusetts Bay (Rex <u>et al.</u> 2000). This transfer, which we refer to here as 'offshore transfer', ended over a century of direct WWTF discharges to the Harbor.

Before this transfer, non-oceanic loadings of materials that cause or exacerbate 'eutrophication', and specifically of total nitrogen (TN), were estimated to be among the highest reported for bays or estuaries in the USA (Kelly 1997). The WWTFs that at the time discharged to the Harbor, were in turn responsible for the bulk (>90%) of these elevated loadings of TN (and TP) (Alber and Chan 1994).

Numerical modeling studies conducted by others before the transfer (HydroQual and Normandeau 1995; Signell <u>et al</u>. 2000), predicted that the transfer of the WWTF discharges offshore would lead to improvements in eutrophication-related Harbor water-quality. Some of the changes in the Harbor water-column since transfer have been documented by Libby <u>et al</u>. (2006), Taylor (2004) and Rex <u>et al</u>. (2002).

Most of these studies, however, focused on the first two to three years after the transfer. The purpose of the following report was to update these reports, and document the changes during the first 5 years after transfer. With an additional two years of post-transfer data now available, we can be more certain of the changes that have taken place in the Harbor.

To identify the changes in the Harbor, and we used the same approach in some of our earlier reports, we compared eutrophication-related conditions in the Harbor watercolumn during the first 5-years after transfer, with conditions during a baseline period before transfer. We did this at two levels; one at the level of the Harbor as a whole, using

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Harbor-wide averages, and the other, at the level of the individual stations sampled in the Harbor, to determine the spatial extents of the differences.

In this report we also took the comparison a step further, and compared water quality before and after transfer during different seasons, to determine whether the sizes and the nature of the changes in the Harbor were different during different seasons. The changes in the Harbor were then compared (where possible) with the changes predicted by others before transfer, using numerical models.

The earlier model predictions were made by 'numerically transferring' the WWTF discharges offshore, meaning that the predicted changes could be used to determine the extent to which the changes were caused by transfer of WWTF discharges. In this study, the 5-years after transfer extended from 7 September 2000, the day after the actual transfer, through 31 December 2005. The 'baseline' period extended from August 1993 (or August 1997, depending on variable), through 6 September 2000.

Aspects of water quality addressed

This report, like Taylor (2004), focuses on aspects related to eutrophication, or as defined by Nixon (1995), 'organic over-enrichment' of the Harbor water-column. Specific aspects of eutrophication addressed included; concentrations of N and P (the two nutrients most responsible for eutrophication), phytoplankton biomass (measured as chlorophyll-<u>a</u>), concentrations of total suspended solids (TSS), concentrations of particulate organic carbon (POC), water-clarity, and bottom-water dissolved oxygen (DO).

Others have addressed other aspects related to eutrophication of the Harbor, including rates of pelagic primary production (Libby <u>et al</u>. 2006), structure of the phytoplankton communities (Libby <u>et al</u>. 2006), sediment redox characteristics (Maciolek <u>et al</u>. 2006), benthic metabolism and nutrient fluxes (Tucker <u>et al</u>. 2005), and biomass and structure of

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the benthic invertebrate communities (Maciolek <u>et al</u>. 2006). Others have addressed the changes to Massachusetts Bay.

We focused the report on eutrophication of the Harbor, because of the recent scientific interest in eutrophication of coastal aquatic ecosystems (Nixon 1995, Bricker <u>et al</u>. 1999), and the numerous symptoms of eutrophication that had been documented in the Harbor before transfer (some of these symptoms have been described in Taylor 2001). Loadings of N and P to the Harbor had been shown to be elevated compared to other bays and estuaries (Kelly 1997, 1998).

The discharges from the WWTFs, that would in turn be transferred offshore, had been shown to be responsible for the bulk of these elevated loadings (Alber and Chan 1994). The report focused on the water-column, because prior to the transfer, the wastewater was discharged directly to the water-column, and the water-column is often the part of an aquatic ecosystem that responds most rapidly to changes in external inputs.

METHODS

Field sampling and laboratory analytical procedures

The Massachusetts Water Resources Authority (MWRA), the agency responsible for the transfer of the DI discharges offshore, collected all the Harbor water-quality data used in the report. The data were collected as part of the Boston Harbor Water Quality Monitoring (BHWQM) project. For details of the BHWQM project, see its Quality Assurance Project Plan (Rex and Taylor 2000).

All water-quality data were collected at 10 sampling stations (Fig. 1). The names and coordinates of the 10 stations are listed in Table 1. Note: the 10 stations were located in each of the 4 major regions of the Harbor; three in the 'Inner Harbor' region, three in the 'North West Harbor', three in the 'Central Harbor', and one in the 'South East Harbor' region.

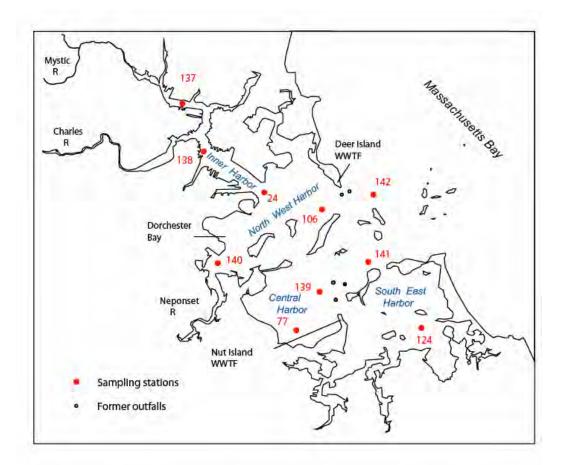


Figure 1. <u>Map showing locations of the 10 sampling stations</u>, the former Deer Island and Nut Island WWTF outfalls, and the 4 major regions of the Harbor. In this report, the term 'North Harbor' refers to the Inner Harbor plus North West Harbor. 'South Harbor' refers to the Central Harbor plus South East Harbor.

At 8 of the 10 stations, sampling was initiated in August 1993; at two of the 10 stations, specifically Station 077 and 137, sampling was initiated in June 1994 and June 1995, respectively. Sampling at these stations was added during the course of the study, to increase the spatial coverage of the Harbor. At all stations, measurements were conducted weekly from May through October, and every two weeks from November through April.

For most variables, measurements at each station were conducted at two depths; one, 'near-surface' (at ca. 0.3 m below the water surface), and the other, 'near-bottom' (or ca.

0.5 m above the Harbor bottom). The variables monitored at both depths included dissolved inorganic nitrogen (DIN), ammonium (NH₄), nitrate + nitrite (NO₃₊₂), chlorophyll-<u>a</u> (chl-<u>a</u>), phaeophytin, total suspended solids (TSS), dissolved oxygen (DO), salinity and temperature.

Table 1. Locations of the stations sampled to track differences in Harbor water quality between the 5-years and baseline.

Region	Station name	Station ID	Latitude (N)	Longitude (W)
	<u>NORTH H</u> A	ARBOR		
Inner Harbor	Mouth Mystic River New England Aquarium Mouth Inner Harbor	137 138 024	42° 23.20 42° 21.59 42° 20.59	71° 03.80 71° 02.82 71° 00.48
North West Harbor	Long Island Calf Island Neponset River/ Dorchester Bay	106 142 140	42 ° 20.00 42 ° 20.35 42 ° 18.35	70° 57.60 70° 55.89 71° 02.43
	SOUTH HA	ARBOR		
Central Harbor	Inner Quincy Bay Hangman Island Nantasket Roads	077 139 141	42° 16.51 42° 17.20 42° 18.30	70° 59.31 70° 58.10 70° 55.85
South East Harbor	Hingham Bay	124	42° 16.36	70° 53.86

For all these variables, excluding DO and the variables that were measured at 'nearsurface' alone, all data presented in the report were averages for the two depths. For DO, only the data from the 'near-bottom' depth were reported; this being the depth where any differences in DO would be of most concern. The variables sampled at 'near-surface' alone included, total N (TN), particulate N (PN), non-DIN, total P (TP), particulate P (PP), non-DIP and POC. Concentrations of TN were estimated indirectly by summing concentrations of total dissolved nitrogen (TDN) and PN for each sample collected at the 'near-surface' depth. Similarly, concentrations of TP were estimated by summing concentrations of total dissolved phosphorus (TDP) and PP. Note, for chl-<u>a</u> and for TP, data were only available after mid-1995.

Table 2 provides a summary of the field procedures and analytical techniques employed in the study. All standard operating procedures for all analytical techniques are archived at the MWRA Central Laboratory, Deer Island, Winthrop, MA 02152. All data used in the report are archived in the EM & MS Oracle database (MWRA Environmental Quality Department, Charlestown Navy Yard, Boston MA 02129), and are available on request.

Data and statistical analysis

In this report, for both the Harbor as a whole, and for the individual stations, we used the non-parametric Mann-Whitney U test to test whether means after transfer were significantly different from the means during baseline (SPSS 10.1, SPSS 2002). We used the Mann-Whitney U test in preference to conventional ANOVA, because for many of the variables, especially at individual stations, the requirement of non-homogeneity of variance of the data could not be met (even with data transformation).

To test for differences between periods for the Harbor as a whole, we applied the Mann-Whitney U test to volume-weighted Harbor-wide averages. These 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 concentration for all stations in the Inner Harbor, \underline{b} = average concentration for all stations in North West Harbor, \underline{c} = average concentration for all stations in Central Harbor, and \underline{d} = average concentration for all stations in South East

1 auto 2. Summary of fictu and analytical memous.	Table 2.	Summar	y of field and	analytical methods.
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VARIABLE	METHOD
TDN ^a and TDP ^a	Solarzano and Sharp (1980b), Whatman G/F filters
PN ^a	Perkin Elmer CHN analyzer, Whatman GF/F
PP ^a	Solarzano and Sharp (1980 <u>a</u>), Whatman GF/F
Ammonium ^b	Fiore and O'Brien (1962), modified as in Clesceri et al. (1998; Method 4500-NH3 H), Skalar SAN ^{plus} autoanalyzer, Whatman GF/F filters
Nitrate + nitrite ^b	Bendschneider and Robinson (1952), modified as in Clesceri et al. (1998; Method 4500-NO3 F), Skalar SAN ^{plus} autoanalyzer, Whatman GF/F filters
Phosphate ^b	Murphy and Riley (1962), modified as in Clesceri et al. (1998; Method 4500-P F), Skalar SAN ^{plus} autoanalyzer, Whatman GF/F filters
Chlorophyll <u>a</u> ^b , phaeophytin ^b	After Holm Hansen (1965) as described in EPA (1992). Sequioa Turner Model 450 fluorometer, Whatman GF/F filters
Secchi depth ^d	20 cm standard (all-white) secchi disc
<u>k</u> ^d	Li Cor PAR sensor Model LI-193 SB
TSS ^b	Clesceri et al. (1998, Method 2540D), using nucleopore filters
Dissolved oxygen ^c	YSI 3800 through July 1997, Hydrolab Datasonde 4 thereafter
Salinity ^b and water temperature ^b	YSI 3800 through July 1997, Hydrolab Datasonde 4 thereafter

^a = surface samples only, ^b = samples/measurements taken surface plus bottom, ^c = measurement taken at bottom only, ^d = profile through water column.

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).

For the year-round data, (for both the Harbor-wide averages and the averages for individual stations), we applied the Mann-Whitney U tests to average monthly data, rather than to data from individual surveys. This precaution was necessary to avoid biasing the findings by the different intensities of sampling during different periods of the year. For the data for the individual seasons, we applied the test to the averages for individual surveys.

In this report, unlike in Taylor (2004), none of the data were 'de-seasonalized' before we applied the Mann-Whitney U tests to the data. Thus, the tests (as applied) compare the averages before and after transfer, with each of the averages inclusive of any seasonal 'signal' within the period. To separate out 'any seasonal differences in responses, we then applied the Mann-Whitney U tests to the survey averages, for individual seasons.

In this report we have recognized three levels of significance. When the Mann-Whitney U test yielded <u>p</u> values ≤ 0.05 , we considered the difference to be 'significant' (at 95% CL), and used an asterisk (*) to denote this condition. When <u>p</u> was > 0.05 but ≤ 0.10 , we considered the difference 'almost significant' (i.e. significant at 90% CL), and used a '?' to denote this condition. When the <u>p</u> values were > 0.10, we considered the difference 'not significant'.

RESULTS

I. DIFFERENCES BETWEEN THE 5-YEARS AND BASELINE

Nitrogen

Total nitrogen (TN). During the 5-years after offshore transfer, Harbor-wide average concentrations of TN were significantly lower than baseline (Table 3). During the baseline, TN concentrations averaged $30.9 \pm 6.4 \mu \text{mol } \text{l}^{-1}$. During the 5-years, they

averaged $20.2 \pm 2.9 \ \mu \text{mol} \ l^{-1}$. The difference of $-10.7 \ \mu \text{mol} \ l^{-1}$ was equivalent to -35% of average baseline values, and was significant at $p \le 0.05$ (Mann-Whitney U test).

Table 3. <u>Nitrogen concentrations</u>. Comparison of volume-weighted Harbor-wide average concentrations between the 5-years after transfer, and baseline. Values are averages $\pm 1 \times SD$ of average monthly values, with the <u>n</u> value in parentheses.

Variable	Average values	lues during Difference between bas		<u>p</u>	
	Baseline	5-years	and 5-years		
TN $(\mu mol l^{-1})$	30.9 ± 6.4 (61)	20.2 ± 2.9 (62)	-10.7 (-35%)	<0.01 *	
DIN (μmol l ⁻¹)	11.8 <u>+</u> 6.4 (75)	5.3 <u>+</u> 3.5 (62)	-6.5 (-55%)	<0.01 *	
DON $(\mu mol l^{-1})$	13.0 ± 3.7 (61)	11.6 <u>+</u> 1.9 (62)	-1.5 (-11%)	0.075 ?	
\mathbf{NH}_4 (µmol l ⁻¹)	6.3 <u>+</u> 3.4 (75)	1.2 ± 0.9 (62)	-5.1 (-81%)	<0.01 *	
NO $_{3+2}$ (µmol l ⁻¹)	5.5 <u>+</u> 3.8 (77)	4.1 ± 3.2 (62)	-1.4 (-25%)	0.02 *	
PN (μ mol l ⁻¹)	6.1 <u>+</u> 2.4 (60)	4.1 <u>+</u> 1.3 (60)	-2.0 (-33%)	0.06 ?	
DIN as %TN	39 <u>+</u> 17 (68)	17 <u>+</u> 14 (62)	-22 (-55%)	<0.01 *	
NH 4 as %DIN	53 <u>+</u> 14 (75)	29 ± 15 (62)	-29 (-51%)	<0.01 *	

The fact that TN concentrations were lowered after transfer is readily evident in the timeseries and bar-chart plots of the Harbor-wide average concentrations in Figures 2 and 3, respectively. The time-series plots show also that the strong seasonal cycle of concentrations seen before transfer was 'dampened' during the 5 years after transfer.

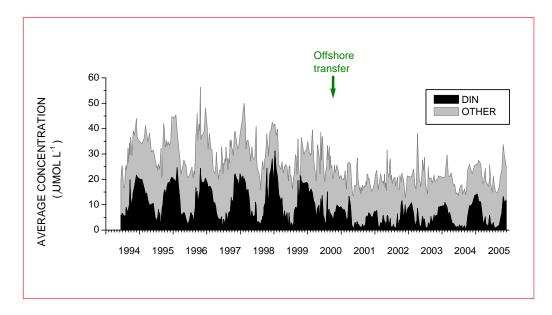


Fig. 2. <u>Total nitrogen (TN) partioned into DIN and non-DIN components.</u> Time-series plots of survey average, volume-weighted Harbor-wide average concentrations.

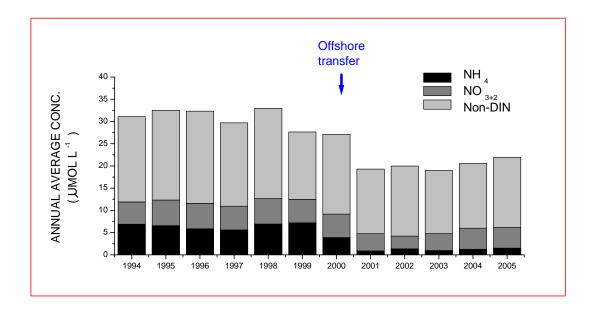


Fig. 3. <u>Annual average, Harbor-wide average concentrations of TN partitioned into the NH₄</u>. <u>NO₃₊₂</u>. and non-DIN fractions, 1994 through 2005.

As can be seen in the bar chart plot, the annual average TN-concentrations during each of the 5 years were consistently lower than during all years during baseline. During the 5-years after the discharges were ended, TN concentrations showed a background increase. The increase was between one-fourth and one-third the size of the decrease that followed transfer.

At the individual stations, average TN concentrations were significantly lower during the 5-years than baseline at all 10 stations (Fig. 4). At the individual stations the decreases ranged in size from -9- μ mol l⁻¹ to -14- μ mol l⁻¹. Expressed as percent of baseline, they ranged from -21% (Station 137), to -46% of baseline (Station 106). (Note; the shaded areas in this and later Figures simply enclose the stations that showed differences significant at $p \le 0.05$. The shading is not meant to be a contour plot).

The fact that the decreases were significant at all 10 stations suggests that after transfer average concentrations of TN were lower than baseline over most of the area of the Harbor. Some of the largest decreases were observed at stations located closest to the former DI (Stations 106 and 142) and NI outfalls (Station 139), but decreases were also observed up into the Inner Harbor and down into Hingham Bay.

For the TN-data averaged Harbor-wide, significant decreases were also observed during all four seasons (Table 4). Thus, concentrations after transfer were significantly lower than baseline year-round. Both in absolute and percent terms, the decreases were largest during fall and winter, when before transfer concentrations tended to be seasonally greatest, and smallest during spring and summer, when concentrations tended to be smallest.

During three of the four seasons, and specifically during summer, fall and winter, the decreases in TN were significant at all 10 stations (Fig. 5). During the remaining season, spring, the decreases were significant at 6 stations extending over most of the area of the Outer Harbor, and 'almost' significant at one other station located at the mouth of the

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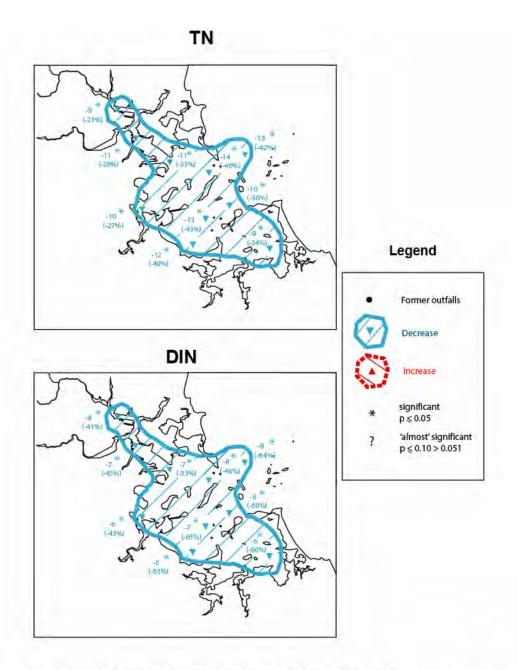


Fig. 4. Total nitrogen (TN) and dissolved inorganic nitrogen (DIN). Differences in average concentrations (μ mol l⁻¹) between the first 5-years after offshore transfer and baseline, at the 10 stations. 'Down-facing triangles' indicate stations at which subtraction of averages after transfer from averages before transfer yielded negative values; 'up-facing triangles' ndicate stations at which the opposite applied. 'Blue triangles' indicate differences might be viewed as beneficial; 'red triangle,' differences might not be viewed as beneficial. 'Asterisks' are used to identify the stations at which the differences between the two periods were significant (p < 0.05). '?' indicates stations at which the differences were significant at p > 0.05, but < 0.10.

Table 4.	Differences in average N concentrations between the 5-years and b	aseline,
by season	<u>n.</u> 'Spring' = April, May, 'Summer' = June, July August, September,	'Fall' =
October,	November, 'Winter' = December, January, February, March.	

Fraction	Difference (μ mol l ⁻¹ , % baseline)			
	Spring	Summer	Fall	Winter
TN	-7.8 (-27%) *	-7.1 (-28%) *	-12 (-36%) *	-15.4 (-42%) *
DIN	-5.1 (-52%) *	-3.1 (-59%) *	-8.7 (-63%) *	-10.4 (-54%) *
$ m NH_4$	-3.8 (-81%) *	-2.5 (-75%) *	-7.0 (-78%) *	-7.8 (-85%) *
NO ₃₊₂	-1.2 (-24%) *	-0.4 (-23%) ?	-1.7 (-35%) ^{ns}	-2.6 (-26%) *
PN	-2.0 (-31%) *	-3.0 (-38%) *	-1.7 (-27%) *	-1.6 (-35%) *
DON	-1.3 (-10%) ^{ns}	-1.3 (-10%) ^{ns}	1.25 (-9%) ^{ns}	-1.25 (-9%) ^{ns}

Inner Harbor. (Note, at the three stations located closest to river mouths, the decreases during spring were not significant.)

Fractions of TN. For three of the 5 fractions of TN that we monitored, Harbor-wide average concentrations during the 5-years were also significantly lower than baseline (at $p \le 0.05$). The three fractions that showed the significant decreases were dissolved inorganic nitrogen (DIN), and the two fractions of DIN; specifically ammonium (NH₄) and nitrate + nitrite (NO₃₊₂).

For DIN, the concentrations after transfer were -6.5- μ mol l⁻¹ (or -55%) lower than baseline. This decrease of -6.5- μ mol l⁻¹, in turn accounted for most (and 60%) of the

decrease in TN of -10.7 μ mol l⁻¹. Note, DIN too contributed most, and in this case, 73% of the TN in the secondary-treated wastewater discharged to the Harbor during baseline (MWRA unpublished data).

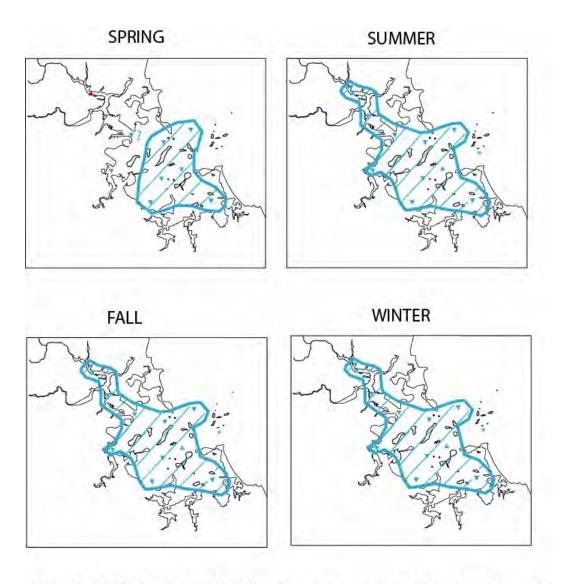


Figure 5. Total nitrogen (TN). Differences in average concentrations (umol l⁻¹) between the 5-years and baseline, at the 10 stations, during the four seasons. Legend as in Figure 4.

Average NH₄ concentrations during the 5-years were -5.1- μ mol l⁻¹ (or 81%) lower than baseline, and accounted for 78% of the decrease in DIN. NO₃₊₂ accounted for the remaining -1.4- μ mol l⁻¹ or 22% of the decrease in DIN. Note, NH₄ too accounted for

most (and in this case >95%) of the DIN in the secondary-treated wastewater discharged to the Harbor during baseline (MWRA, unpublished data).

For both particulate nitrogen (PN) and dissolved organic nitrogen (DON), subtraction of the Harbor-wide averages after transfer from the averages before transfer yielded negative values, suggestive of decreases. For both variables, the differences were 'almost' significant (p > 0.05, but ≤ 0.10 ; 90% C.L.). With longer-term monitoring, these differences may or may not be shown to be significant.

For DIN, as for TN, the decreases were significant at all 10 stations (Fig. 4). (The same applied for NH_4 and NO_{3+2} , MWRA unpublished data). At the individual stations, the decreases in DIN ranged in size from -6-µmol l⁻¹ to -8-µmol l⁻¹. As for TN, the stations located closest to the former DI outfalls (Stations 106 and 142) showed some of the largest decreases.

For three of the fractions of TN, specifically DIN, NH₄ and PN, the decreases in Harborwide average concentrations were significant during all four seasons (Table 4). For DIN and NH₄, the decreases were largest during winter; for PN, they were largest during summer. (For the respective fractions, as for TN, the decreases were largest during the seasons when concentrations before transfer were seasonally greatest).

For NO_{3+2} , the Harbor-wide average concentrations showed significant decreases during winter and spring, but not during summer or fall. For DON, the Harbor-wide averages before and after transfer were not significantly different during any of the four seasons.

Nature of the TN pool. Figure 6 compares the nature of the TN-pool of the Harbor water-column before and after transfer. Before transfer, DIN and DON contributed most and similar proportions of the TN (38% and 42%, respectively). After transfer, the percent contribution of DON was increased to more than one-half (57%), the percent contribution of DIN was decreased to about one-fourth (26%), and the percent contribution of PN remained unchanged at 20%.

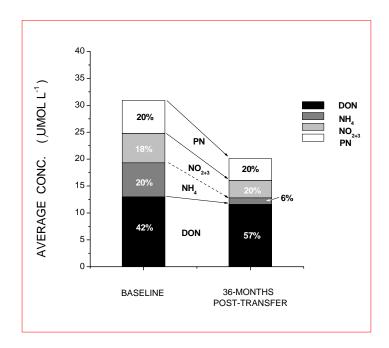


Figure 6. <u>Nitrogen pool</u>. Comparison of the nature of the TN pool of the Harbor water column between the baseline period, and the first 5-years after wastewater discharges to the Harbor were ended. Values in bars are the percent contributions of the different constituents to the total pool.

The nature of the DIN fraction of the TN-pool was also changed. Before transfer, NH_4 and NO_{3+2} contributed similar proportions (and 53% and 47%) of the TN. After transfer, the percent contribution of NO_{3+2} was increased to three-fourths (77%); and NH_4 decreased to about one-fourth (and 23%). The background increase in NO_{3+2} during the 5 years (Fig. 4), will also have contributed to the increase in the percent contribution of NO_{3+2} .

Phosphorus

Total phosphorus (TP). During the 5-years, Harbor-wide average concentrations of TP were also significantly lower than baseline (Table 5). During baseline, TP concentrations averaged $2.06 \pm 0.32 \,\mu\text{mol}\,l^{-1}$; during the 5-years they averaged $1.48 \pm 0.31 \,\mu\text{mol}\,l^{-1}$.

The difference of -0.58-µmol l⁻¹ was equivalent to -28% of baseline, and was significant. The -28% decrease was slightly smaller than the -34% decrease for TN.

Table 5.	<u>Phosphorus concentrations</u> .	Comparison of volume-weighted Harbor-wide
average co	ncentrations, between the 5-year	rs after transfer and baseline.

Variable	Average values during		Difference between baseline	p
	Baseline	5-years	and 5-years	
TP (μmol l ⁻¹)	2.06 <u>+</u> 0.32 (67)	1.48 ± 0.31 (63)	-0.58 (-28%)	<0.01 *
DIP $(\mu \text{mol } l^{-1})$	1.05 ± 0.37 (68)	0.65 ± 0.27 (63)	-0.40 (-38%)	<0.01 *
DOP $(\mu \text{mol } l^{-1})$	0.39 <u>+</u> 0.24 (61)	0.40 ± 0.22 (63)	+0.01 (+3%)	0.85 ^{ns}
PP (μmol l ⁻¹)	0.58 ± 0.18 (61)	0.42 ± 0.12 (63)	-0.15 (-26%)	<0.01 *
DIP as % TP	51 <u>+</u> 16 (61)	43 <u>+</u> 16 (63)	-7 (-15%)	<0.01 *

The fact that the concentrations of TP were lowered after transfer is evident in the timeseries and bar chart plots of Harbor-wide average concentrations of TP in Figures 7 and 8. The seasonal cycle of TP was also 'dampened' after transfer, but less so than for TN. Also unlike for TN, TP showed no evidence of a background increase through the 5 years after transfer.

The scatter plot of annual average concentrations of TN versus TP (Fig. 9) shows that during the years after transfer when the TP concentrations were lowest, the concentrations of TN were also lowest. The shallower slope of the observed data relative to the diagonal line (which represents the 1:10 TP:TN ratio), suggests that the decrease for TP was smaller relative to the decrease for TN.

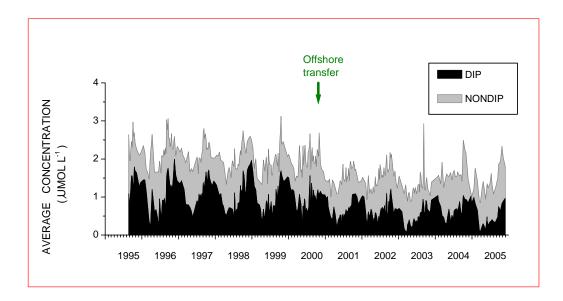


Fig. 7. <u>Total phosphorus (TP) partioned into DIP and non-DIP components.</u> Time-series plots of survey volume-weighted Harbor-wide average concentrations.

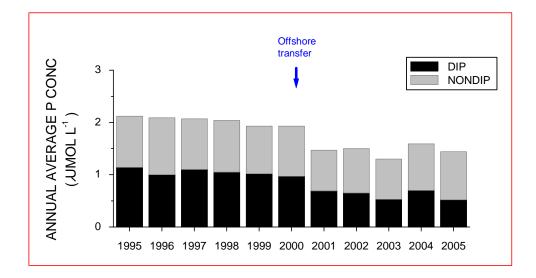


Figure 8. <u>Annual Harbor-wide average TP concentrations</u> partitioned into the DIP and non-DIP fractions, 1995 through 2005.

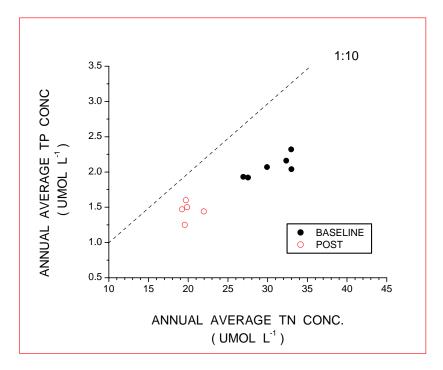


Fig. 9. <u>**TP versus TN**</u>. Data are annual, volume-weighted Harbor-wide averages. Note: diagonal line represents a 1 : 10 ratio of TP:TN.

The decreases in TP were also significant at all 10 stations (Fig. 10). The sizes of the decreases ranged from -0.4- μ mol l⁻¹ to -0.8- μ mol l⁻¹. The decreases were largest in the outer North East Harbor and the mid- Central Harbor, the locations of the former WWTF outfalls. Thus, the decreases were also observed over most of the area of the Harbor, as they were for TN.

For the data averaged Harbor-wide, and as for TN, the decreases were also significant during all four seasons (Table 6). Again as for TN, the decreases were largest during winter and smallest during summer. The differences in the sizes of the decreases during winter and summer were smaller than for TN, accounting for the smaller 'dampening' of the seasonal cycle after transfer for TP than TN.

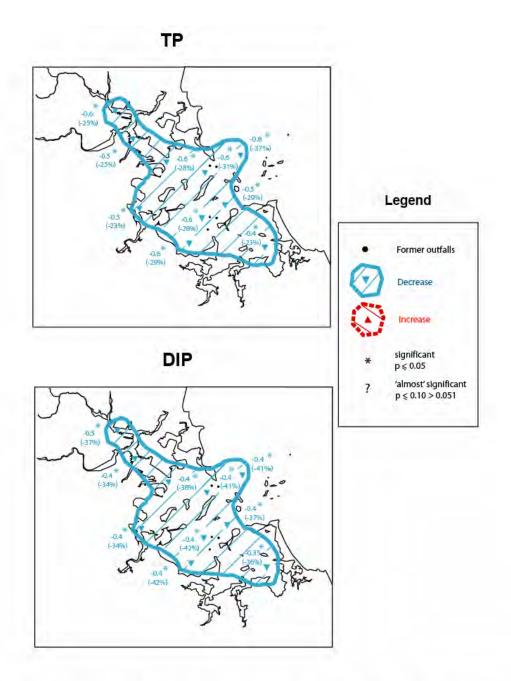


Fig. 10. Total phosphorus (TP) and dissolved inorganic phosphorus (DIP). Differences in average concentrations (µmol I⁻¹) between the 5-years after offshore transfer and baseline, at the 10 stations

Other P fractions. For two of the three fractions of TP that we monitored, DIP and PP, Harbor-wide averages during the 5-years were also significantly lower than baseline. For DIP, average concentrations decreased by -0.40-µmol l⁻¹ (or -38%) between the two

periods; for PP, they decreased by 0.15-µmol l⁻¹ (or -26%). For DOP, as for DON, the averages before and after transfer were not significantly different.

Fraction	Spring		ol I ⁻¹ , % baseline) Fall	Winter
TP	-0.58 (-32%) *	-0.53 (-26%) *	-0.61 (-25%) *	-0.65 (-33%) *
DIP	-0.24 (-39%) *	-0.34 (-37%) *	-0.61 (-40%) *	-0.46 (-40%) *
PP	-0.24 (-36%) *	-0.21 (-29%) *	-0.1 (-21%) *	-0.08 (-19%) ?
DOP	-0.08 (-17%) ^{ns}	-0.02 (-4%) ^{ns}	-0.16 (-47%) ^{ns}	-0.05 (-16%) ^{ns}

Table 6. Seasonal differences in P concentrations between the 5-years and baseline.

As for N, the dissolved inorganic fraction (DIP) accounted for most (69%) of the decrease in TP. In fact, the 69% contribution by DIP was almost identical to the 68% that DIN contributed to the TN-decrease. As for DIN, the decrease in DIP was also significant at all 10 stations (lower panel, Fig. 10).

Differences in the TP-pool. The nature of the TP-pool of the Harbor water-column was also changed after transfer (Fig. 11). The percent contribution of DIP decreased from 51% before transfer, to 44% after. (Note, both before and after transfer, DIP contributed a greater proportion of the TP pool than did DIN of TN.) Conversely, the percent contribution of DOP was increased from 19% to 27%. The percent contribution of DOP remained unchanged, and 28%.

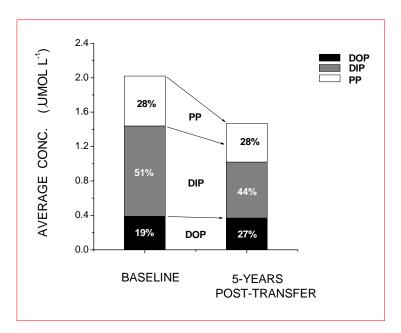


Figure 11. <u>Total phosphorus pool</u>. Differences in the nature of the TP pool of the Harbor water-column, before and 5-years after offshore transfer.

Molar ratios of N:P

Molar TN:TP. Unlike for TN and TP, the Harbor-wide average ratios of TN:TP during the 5-years were not significantly different from baseline (Table 7). During baseline, TN:TP ratios averaged 15.2 ± 3.5 :1; during the 5-years, they averaged 14.4 ± 3.5 :1. Subtraction yielded a negative value of -0.7:1 (or -5%), but the difference was not significant.

Both before and after transfer, and especially during winters, average TN:TP ratios in the Harbor varied widely between years (Fig. 12 and 13). This variability was such that the annual averages during the 5 years spanned the range of averages during baseline. The fact that the annual averages were not consistently lower than baseline during all 5 years after transfer was unlike for TN and TP.

Variable	Average values Baseline	s during 5-years	Difference between baseline and 5-years	p
TN:TP	15.2 ± 3.2 (61)	14.4 ± 3.5 (61)	-0.7 (-5%)	0.17 ^{ns}
DIN:DIP	11.4 ± 5.2 (68)	8.0 <u>+</u> 5.5 (63)	-3.4 (-30%)	<0.01 *
DON:DOP	43 ± 33 (60)	35 <u>+</u> 15 (61)	-8 (-18%)	0.15 ^{ns}
PN:PP	10.0 ± 2.3 (61)	9.6 <u>+</u> 1.8 (62)	-0.5 (-5%)	0.27 ^{ns}

Table 7.Molar ratios of N:P.Comparison of volume-weighted, Harbor-wideaverage ratios between the 5-years after transfer, and baseline.

At the individual stations, average TN:TP ratios during the 5-years were significantly different from, and in both cases significantly lower than baseline, at two of the 10 stations (Fig. 14). The two stations were Stations 106 and 139, the stations located closest to the former DI and NI WWTF outfalls, respectively. At two other stations, also located in the Outer Harbor, the decreases were 'almost' significant.

During the 5-years, the Harbor-wide average TN:TP ratios were significantly different from baseline during one of the four seasons, specifically winter (Table 8). Average TN:TP ratios during the winters after transfer were -2.2:1 (or -12%) lower than baseline. During the other three seasons, the averages after transfer were not significantly different from baseline.

Thus, the Harbor did show significant decreases in ratios of TN:TP, as it did for the concentrations of TN and TP individually, but the decreases were smaller, and more spatially localized and seasonally restricted than for TN and TP.

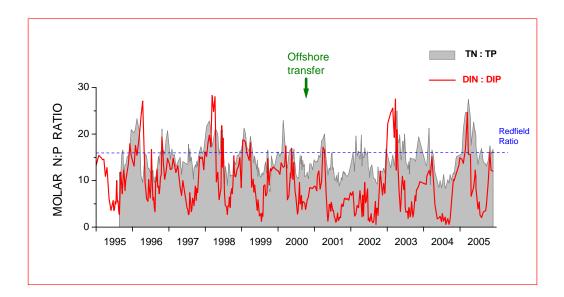


Fig. 12. <u>Molar ratios of TN:TP and DIN:DIP.</u> Time-series plots of survey volume-weighted Harbor-wide averages. Also shown is the Redfield Ratio of 16:1.

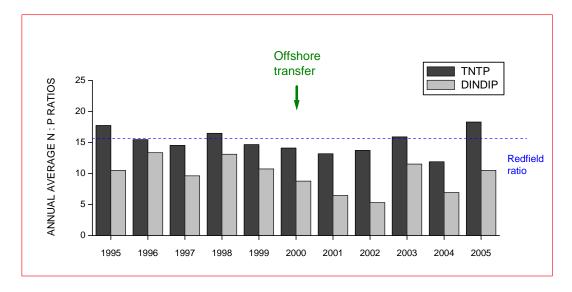


Fig. 13. Molar N:P ratios. Annual Harbor-wide average molar N:P ratios, 1995 through 2005.

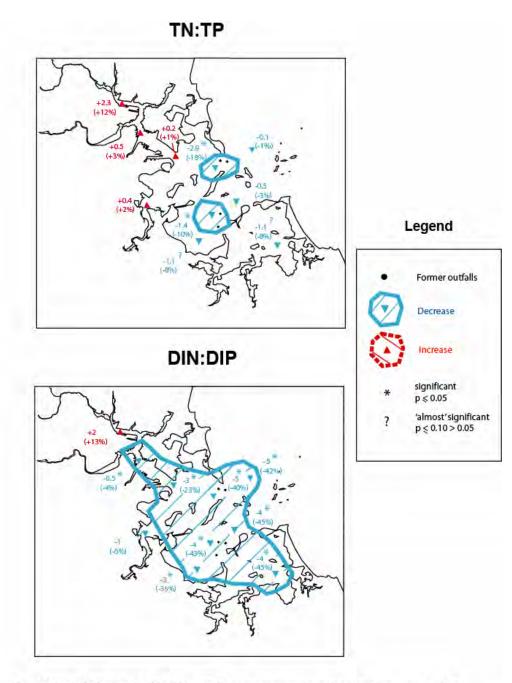


Fig. 14. Molar TN : TP and DIN : DIP. Differences in average molar ratios between the first 5-years after offshore transfer and baseline, at the 10 Harbor stations.

Other molar N:P ratios. For one of the other three N:P ratios that we monitored, specifically DIN:DIP, the Harbor-wide averages during the 5-years were significantly different from, and in this case lower than baseline (Table 7). For the other two N:P

Fraction		Difference (% baseline)		
	Spring	Summer	Fall	Winter
TN:TP	-1.4 (-9%) ^{ns}	-0.1 (-1%) ^{ns}	-0.9 (-6%) ^{ns}	-2.2 (-12%) *
DIN:DIP	-3.8 (-33%) ^{ns}	-3.3 (-48%) *	-3.8 (-31%) *	-3.2 (-20%) *
PN:PP	-1.0 (-10%) ^{ns}	-1.4 (-13%) *	+0.7 (+8%) ^{ns}	+0.1 (<+1%) ^{ns}
DON:DOP	+3.8 (+12%) ^{ns}	-5.4 (-13%) ^{ns}	-16.6 (-36%) ^{ns}	-11.1 (-23%) ^{ns}

Table 8.Seasonal differences in N:P ratiosbetween the 5-years and baseline, by season.

ratios, PN:PP and DON:DOP, subtraction yielded negative values, but as for TN:TP, the differences were not significant.

For DIN:DIP, the Harbor-wide averages decreased from 11.4 ± 5.2 :1 during baseline, to 8.0 ± 5.5 :1 during the 5-years. The difference of -3.4:1 was equivalent to -30% of baseline, and was significant. This -30% decrease was smaller than the -55% and -40% decreases for concentrations of DIN and DIP, respectively. Thus, the decrease for DIN:DIP was greater than for TN:TP, but smaller than for DIN or DIP.

Average DIN:DIP ratios in the Harbor also showed significant decreases at 8 of the 10 stations; c.f. two stations for TN:TP (Fig. 14). The 8 stations that showed the significant decreases were located in the main basin of the Outer Harbor extending up into the Inner Harbor. Only at Stations 137 and 140, the two stations located at river mouths, were the decreases not significant.

During the individual seasons, the Harbor-wide average ratios of DIN:DIP were significantly lower than baseline during summer, fall and winter; only during spring, were the averages after transfer not significantly different from baseline. For PN:PP, the averages after transfer were significantly lower than baseline during summer, but not the other three seasons. For DON:DOP, we were unable to detect significant differences between periods, during any of the four seasons.

Phytoplankton biomass (chlorophyll-a)

For all three fractions of chlorophyll-<u>a</u> (chl-<u>a</u>) that we monitored (total chl-<u>a</u>, acidcorrected chl-<u>a</u>, and phaeophytin), the Harbor-wide averages during the 5-years were significantly different, and lower than baseline (Table 9). For total chl-<u>a</u> (the sum of acid-corrected chl-<u>a</u> plus phaeophytin), concentrations decreased from $6.5 \pm 3.9 \ \mu g \ l^{-1}$ during baseline, to $4.8 \pm 2.4 \ \mu g \ l^{-1}$ during the 5-years. The difference of $-1.7 \ \mu g \ l^{-1}$ was equivalent to -26% of baseline, and was significant.

 Table 9.
 Chlorophyll-a and phaeophytin.
 Comparison of volume-weighted Harborwide average concentrations between the 5-years after transfer, and baseline.

Variable	Average values during Baseline 5-years		Difference <u>p</u> between baseline and 5-years	
Total chl- <u>a</u> (µg l ⁻¹)	6.5 ± 3.9 (61)	4.8 ± 2.4 (63)	-1.7 (-26%)	0.03 *
Acid-corrected chl- \underline{a} (µg l ⁻¹)	4.7 <u>+</u> 3.1 (61)	3.3 <u>+</u> 2.2 (63)	-1.3 (-28%)	0.05 *
Phaeophytin $(\mu g \Gamma^1)$	1.9 ± 1.3 (61)	1.4 ± 0.5 (63)	-0.5 (-28%)	<0.01 *

For acid-corrected chl-<u>a</u>, the fraction most often used to measure phytoplankton biomass, the Harbor-wide averages during the 5-years were -1.3 μ g l⁻¹, or -28% lower than baseline. For phaeophytin, or 'degraded' chl-<u>a</u>, the average concentrations were -0.5 μ g l⁻¹, or -28%. For all three fractions, the percent decreases were in the same order as for both TN (-34%) and TP (-28%).

The fact that the concentrations of chl-<u>a</u> after transfer were lower than baseline is evident in the time-series and bar chart plots of the three fractions (Figures 15 and 16). As is evident in the time-series plots, for all three fractions the decreases were largest during summers, the season when concentrations in the Harbor tended to be seasonally greatest. The fact that the decreases were largest during summers was unlike for TN and TP.

During the 5 years, for all three chl-<u>a</u> fractions, the annual averages were lower than baseline during four of the 5-years (2001, 2003, 2004 and 2005). During the remaining years (2002), average concentrations were higher than during the other four years and within the range of the elevated averages during baseline. (The fact that average chl-<u>a</u> concentrations during all 5 years were not lower than baseline was unlike for TN or TP).

As can be seen in the scatter plot of annual average $chl-\underline{a}$ concentrations versus TN (Fig. 17), the years that the Harbor showed lowered $chl-\underline{a}$, were, with the exception of 2002, the years after transfer that the Harbor showed the lowered TN concentrations. During 2002 concentrations of $chl-\underline{a}$ in the Harbor were elevated, despite the concentrations of TN being lowered.

At the individual stations, the average concentrations of acid-corrected chl-<u>a</u> after transfer were significantly lower than baseline, at two stations (Stations 077 and 139), both located in the Central Harbor region (Fig. 18). At one other station, Station 124, in the South East Harbor, and as for the other two stations, also located in the South Harbor, the decrease was 'almost' significant.

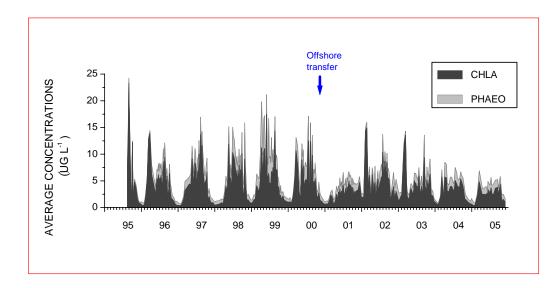


Fig. 15. <u>Total chl-a partitioned into the acid-corrected and phaeophytin fractions.</u> Values are survey volume-weighted, Harbor-wide averages.

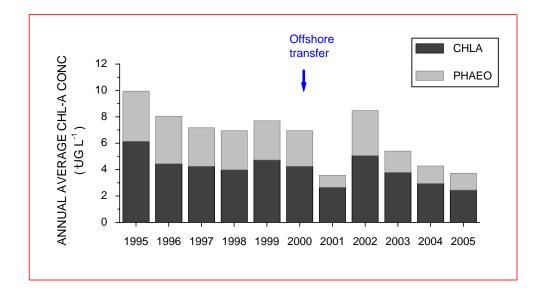


Fig. 16. Annual average total chl-a partitioned into the acid-corrected and phaeophytin fractions.

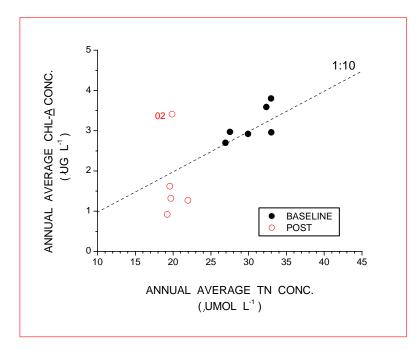


Fig. 17. <u>Acid-corrected chl-a versus TN</u>. Data are annual, volume-weighted Harbor-wide averages. Diagonal line represents ratios of concentrations of chl-<u>a</u>:TN of 1:10.

Thus, as for TN and TP, the Harbor showed a significant decrease in year-round average $chl-\underline{a}$ after transfer, but the decrease was more localized than for TN or TP. The fact that subtraction yielded negative values at all 10 stations suggests that with longer-term monitoring could well show the decreases in $chl-\underline{a}$ to have been significant over a larger area of the Harbor than indicated by the two stations alone.

For phaeophytin, average concentrations during the 5-years were significantly lower than baseline at three stations, and 'almost' significantly lower at two others (lower panel, Figure 18). Two of the three stations at which the decreases were significant were the two stations that showed significant decreases for acid-corrected chl-<u>a</u>. As for acid-corrected chl-<u>a</u>, subtraction yielded negative values at all 10 stations.



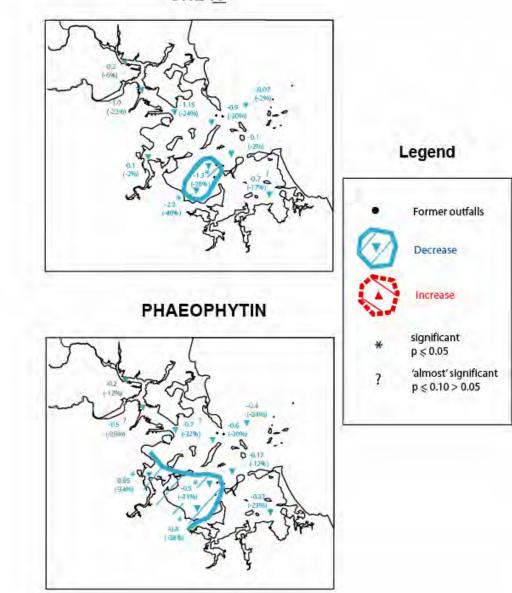


Fig. 18. <u>Acid-corrected chl-a and phaeophytin</u>. Differences in average concentrations (ug 1⁻¹) between the first 5-years after offshore transfer and baseline, at the 10 Harbor stations.

For all three fractions, the Harbor-wide averages during the 5-years were significantly different, and in all cases lower than baseline, during summers, but not during spring, fall

or winter (Table 10). During summers after transfer, average total chl-<u>a</u> concentrations were -3.7- μ gl⁻¹ (or -39%) lower than during baseline. For acid-corrected chl-<u>a</u>, they were -2.7 μ gl⁻¹ (or -39%) lower. and for phaeophytin, -1.07 μ gl⁻¹ (or -37%) lower.

Table 10. Seasonal differences in average concentrations of total chl-a, acidcorrected chl-a and phaeophytin between the 5-years and baseline.

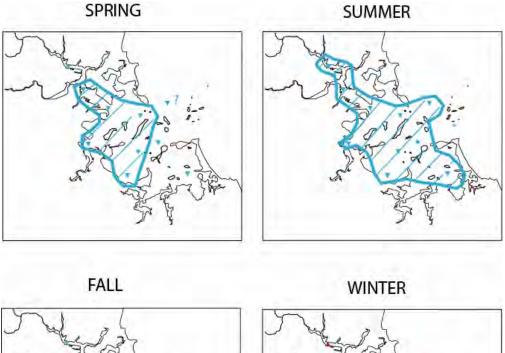
Fraction	Spring	Difference (µg l ⁻¹ , Summer	% baseline) Fall	Winter
Total chl- <u>a</u>	-4.2 (-49%) ^{ns}	-3.7 (-39%) *	-0.2 (-4%) ^{ns}	+0.8 (+25%) ^{ns}
Acid-corrected chl-a	-2.9 (-49%) ^{ns}	-2.7 (-39%) *	-0.4 (-14%) ^{ns}	+0.6 (+27%) ^{ns}
Phaeophytin	-1.4 (-50%) ^{ns}	-1.0 (-37%) *	<0.01- (<-1%) ^{ns}	+0.1 (+7%) ^{ns}

For all three chl-a fractions, the nature and the spatial extents of the changes after transfer, varied widely between seasons. Figure 19 the seasonal differences for acid-corrected chl-<u>a</u> (Fig. 19). For this fraction, average concentrations showed significant decreases at 6 stations during spring, and all 10 stations during summer. During fall, at none of the stations were the differences between periods significant.

During winters, subtraction yielded positive values at all except one of the stations, and at two of the stations that showed positive values, the averages after transfer were significantly greater than baseline. Both stations were located in the outermost Outer Harbor (Stations 142 and 141). At two others (Stations 24 and 106), both located in the North Harbor, the increases were 'almost' significant.

Thus, the decreases in concentrations of chl-<u>a</u> that followed transfer, were more seasonally restricted than for TN or TP. The decreases in chl-a observed for the year-

round data were driven by decreases during summer and spring, when the concentrations were lowered over most of the area of the Harbor. The decreases during spring and summer were, in turn, 'dampened' by the smaller, but still significant increases in chl-<u>a</u> observed at the mouth of Harbor, during the winters after transfer.



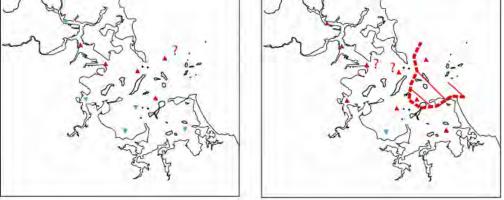


Figure 19. <u>Acid-corrected chl-a.</u> Differences in average concentrations between the 5-years and baseline, at the 10 stations, during the four seasons. Legend as in Figure 4.

POC and suspended solids

Particulate organic carbon (POC). During the 5-years, Harbor-wide average concentrations of POC were also significantly lower than baseline (Table 11). Average concentrations decreased from 42.9 ± 16.1 -µmol l⁻¹ during baseline, to 30.9 ± 10.2 µmol l⁻¹ during the 5-years, or by -12 µmol l⁻¹ (or -28%). The -28% decrease was similar to the -26% to -35% decreases for TN, TP and chl-a.

Table 11. **POC and total suspended solids**. Comparison of volume-weighted Harborwide average values during baseline and the first 5-years after offshore transfer.

Variable	Average values Baseline	during 5-years	Difference between baseline and 5-years	Ð
POC (μmol l ⁻¹)	42.9 <u>+</u> 16.1 (61)	30.9 ± 10.2 (60)	-12 (-28%)	<0.01 *
$TSS (mg l^{-1})$	3.6 ± 1.2 (55)	3.8 <u>+</u> 1.1 (63)	+0.2 (+5%)	0.14
POC as %TSS (by weight)	18 <u>+</u> 6.5 (55)	12 <u>+</u> 3 (60)	-6 (-33%)	<0.01 *
POC: Chl- <u>a</u> (by weight)	226 <u>+</u> 234 (62)	145 <u>+</u> 68 (62)	-81 (-36%)	0.32

As for chl-<u>a</u>, the decreases in POC were largest during the summers after transfer; summer being the season when POC concentrations in the Harbor tend to be seasonally greatest (Fig. 15). During each of the 5 years after transfer, the annual Harbor-wide average concentrations of POC were consistently lower than in all years during baseline (Fig. 16).

The fact that the annual averages during all 5 years were lower than baseline was as for TN and TP, but unlike for chl-<u>a</u>. Unlike for TN and TP, however, and this is evident in

the bar-chart plot of the annual average values, the decrease in POC started before offshore transfer, and in 1997 or 1998.

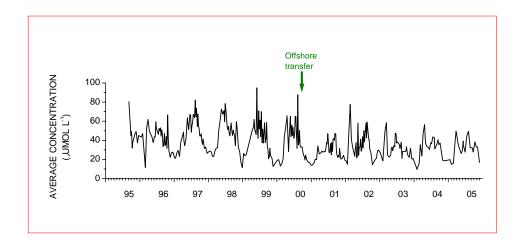


Fig. 20. <u>Particulate organic carbon (POC)</u>. Time-series plot of survey volume-weighted, Harbor -wide average concentrations.

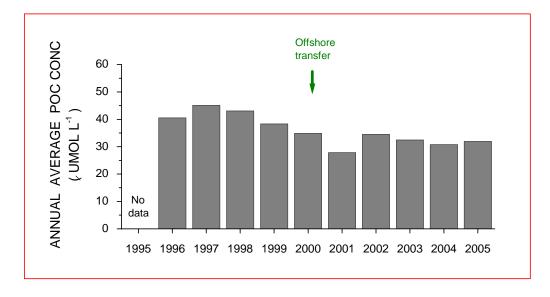


Fig. 21. Annual average POC concentrations, 1996 through 2005.

At the individual stations, averages POC concentrations after transfer were significantly lower than baseline at all 10 stations; c.f. two stations for chl-<u>a</u> (Fig. 22). The decreases

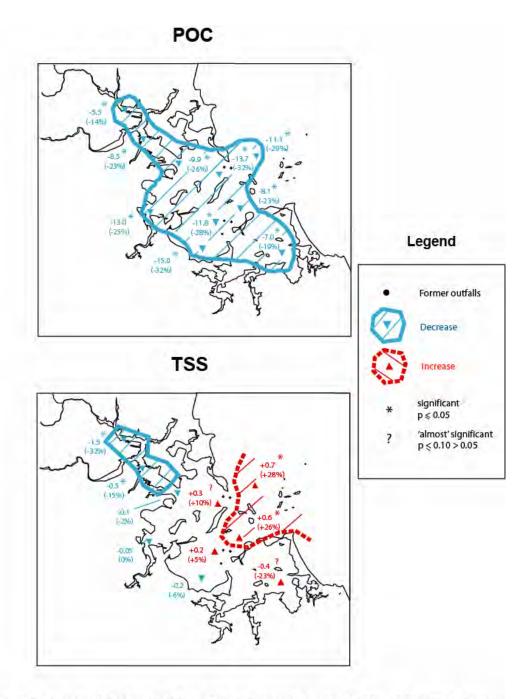


Fig. 22. Particulate organic carbon (POC) and total suspended solids (TSS). Differences in average concentrations (µmol I ⁻¹ for POC and mg I ⁻¹ for TSS) between the first 5-years after offshore transfer and baseline, at the 10 Harbor stations.

at the individual stations ranged in size from -5.5 μ mol l⁻¹ (at Station 137), to -15.0 μ mol l⁻¹ (at Station 077). In percent terms, the decreases were largest at the stations located closest the two sets of former WWTF outfalls, as was the case for TN and TP.

Among the four seasons, the Harbor wide averages during the 5-years were significantly different from, and in all cases lower than baseline, during spring, summer and fall, but not winter (Table 12). The decreases ranged in size from -15.6 μ mol l⁻¹ during fall, to -21.1 μ mol l⁻¹ during summer. In percent terms, they ranged from -34% of baseline during spring, to -40% of baseline during fall.

Table 12.Seasonal differences in average TSS and POC concentrations between the5-years and baseline.

Fraction	Spring	Difference (% b Summer	baseline) Fall	Winter
POC (µmol l ⁻¹)	-17.3 (-34%) *	-21.1 (-38%) *	-15.6 (-40%) *	+2.3 (+8%) ^{ns}
TSS (mg l^{-1})	+0.32 (+9%) ^{ns}	-0.31 (-7%) ^{ns}	+0.56 (+17%) ^{ns}	+0.48 (+18%) ^{ns}

Total suspended solids (TSS). Unlike for POC, the Harbor-wide average concentrations of TSS for the 5-years were not significantly different from baseline (Table 11). During baseline, TSS concentrations averaged $3.6 \pm 1.2 \text{ mg l}^{-1}$. During the 5-years, they averaged $3.8 \pm 1.1 \text{ mg l}^{-1}$. The difference of +0.2 mg l⁻¹ was equivalent to +5% of baseline, and was not significant (at $p \le 0.05$).

The fact that average TSS concentrations during the 5-years were not significantly different from baseline is evident in both the time-series and bar chart plots of the Harbor-wide average concentrations (Figures 23 and 24, respectively). The seasonal

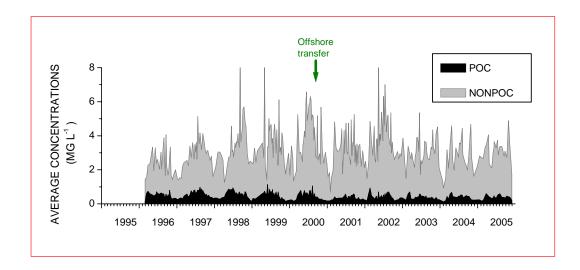


Figure 23. **Total suspended solids (TSS)** partitioned into the particulate organic carbon (POC) and non-POC fractions.

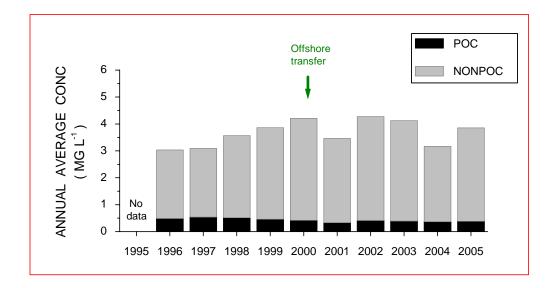


Fig. 24. Annual average TSS concentrations partitioned into the POC and non-POC fractions.

pattern of TSS after transfer was also not consistently different from the pattern during baseline. (Note, both before and after transfer, non-POC or inorganic suspended material contributed the bulk of the TSS).

At the individual stations, average TSS concentrations after transfer were significantly different from baseline at four stations (Fig. 22). At two stations, both located in the Inner Harbor (Stations 137 and 138), average concentrations after transfer were significantly lower than baseline. At two stations at the mouth of the Outer Harbor (Stations 141 and 142), the opposite applied.

For TSS averaged Harbor-wide, we were unable to detect significant differences between the two periods, for any of the four seasons (Table 12). During three of the four seasons (fall, winter and spring), subtraction yielded positive (and in all cases, non-significant) values; during summer, subtraction yield a negative value, but again this was not significant.

POC as % TSS. During the 5-years after transfer, the percent contribution of POC to TSS was also significantly lower than baseline (Table 11). During baseline, POC contributed $18 \pm 6.5\%$ of TSS; during the 5-years, it contributed $12 \pm 3\%$. The difference of -6% was equivalent to -33% of baseline, and was significant. Thus, the Harbor showed no decrease in TSS after transfer, but it did show a decrease in the % organic content of the TSS (measured as POC). Unlike for POC as % TSS, Harbor-wide average ratios of POC : chl-<u>a</u>, a measure of detrital:phytoplankton biomass, were not changed.

Water clarity

Vertical attenuation coefficients (k) and secchi depth. For both measures of water clarity that we conducted (\underline{k} and secchi depth), the Harbor-wide averages during the 5-years were not significantly different from baseline (Table 13). For both variables,

subtraction yielded values that were +1% to +2% of baseline, and the differences were not significant. This was as for TSS, but unlike for chl-<u>a</u> and POC.

Variable	Average values	during	Difference between baseline	p
	Baseline	5-years	and 5-years	
<u>k</u> (m ⁻¹)	0.52 ± 0.12 (73)	0.53 ± 0.12 (64)	+0.01 (+1%)	0.85
Secchi depth (m)	2.65 ± 0.60 (85)	2.70 ± 0.70 (64)	+0.05 (+2%)	0.56

Table 13.Water clarityComparison of volume-weighted Harbor-wide averagevalues during baseline and the first 5-years after offshore transfer.

The fact that the water clarity in the Harbor after transfer was not different from baseline is evident in both the time-series (Fig. 25) and bar chart plots (Fig. 26) of the two variables. For both variables, the Harbor-wide averages varied widely between successive surveys, perhaps masking any changes in clarity that might have followed transfer.

For both variables, as for TSS, the differences between the two periods were significant only at certain stations (Figure 27). For <u>k</u>, the averages after transfer were significantly lower than baseline at one station (Station 137 in the upper Inner Harbor), and significantly greater than baseline at one other (Station 141 in the Central Harbor). For secchi depth, at two stations in the Inner Harbor (Stations 137 and 138), average values after transfer were significantly greater than baseline.

The grouping of the stations that showed positive and negative values, and the fact that they were similar for the two variables, suggests that the Harbor may have experienced an increase in clarity in the Inner Harbor and along the west margin of the Harbor, and a decrease in clarity over much of the main body of the Outer Harbor. (Note, the k data

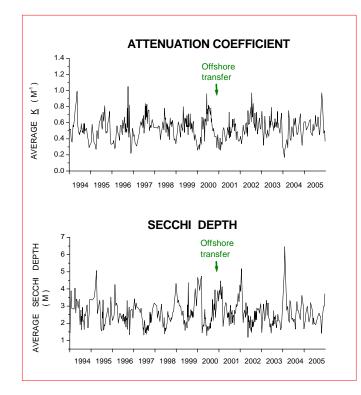


Fig. 25. <u>Vertical attenuation coefficients (k) and secchi depths.</u> Values are survey-average, volume-weighted Harbor-wide averages.

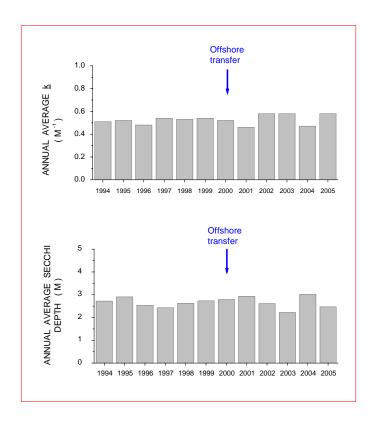
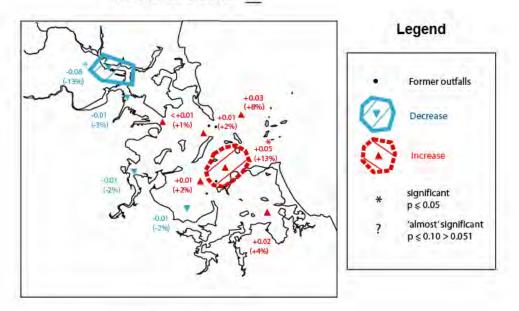


Fig. 26. <u>k and secchi depth</u>. Annual, volume-weighted, Harbor-wide average values, 1994 through 2005.

RECIPROCAL k



SECCHI DEPTH

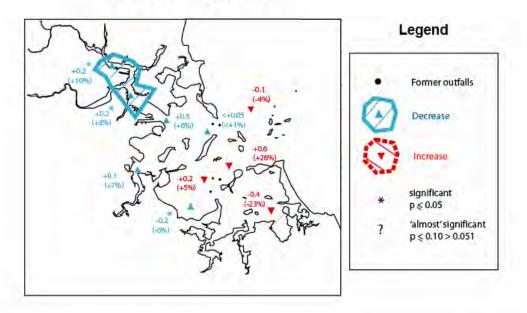


Fig. 27. <u>**k** and secchi depth.</u> Differences in average values (m) between the first 5-years after offshore transfer and baseline, at the 10 Harbor stations.

have been reported as reciprocal values, so negative values for \underline{k} correspond with positive values for secchi depth).

For both \underline{k} and secchi depth, and again as for TSS, the Harbor-wide averages after transfer were not significantly different from baseline during any of the four seasons (MWRA unpublished data).

Bottom-water dissolved oxygen (DO) concentrations and % saturation

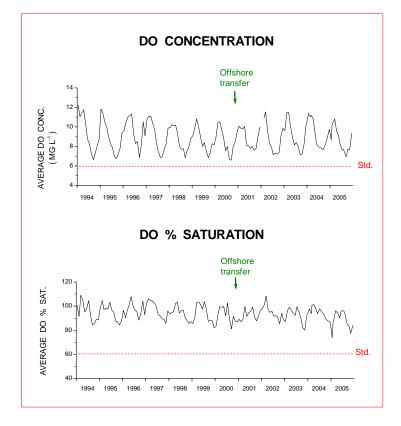
For both DO variables, as for TSS and water clarity, we were unable to detect significant differences between the Harbor-wide averages for the 5-years, and baseline (Table 14). For both variables, subtraction yielded differences that were equivalent to \pm 3% of baseline, and the differences were not significant

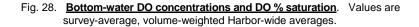
Table 14.Bottom-water dissolved oxygen (DO).Comparison of volume-weightedHarbor-wide average values between the 5-years after transfer, and baseline.

Variable	Average values Baseline ^a	during 5-years	Difference between baseline and 5-years	p
$\frac{\mathbf{DO}}{(\mathrm{mg } l^{-1})}$	8.6 ± 1.2 (40)	8.9 <u>+</u> 1.3 (64)	+0.3 (+3%)	0.34
DO (% saturation)	95 <u>+</u> 7 (40)	92 <u>+</u> 6 (64)	-3 (-3%)	0.18

only data collected after May 1997 were used to compute baseline averages and to test for differences between periods.

The time-series (Fig. 28) and bar chart plots (Fig. 29) confirm the fact that bottom-water DO values in the Harbor for the full 5-years after transfer were not significantly different from baseline. As is evident in the time-series plots, the Harbor showed increased





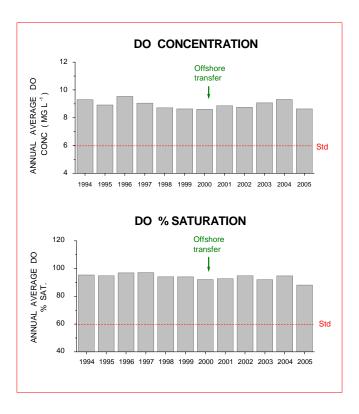


Fig. 29. Bottom-water DO concentrations and % saturation. Annual, volume-weighted, Harbor-wide average values, 1994 through 2005.

DO concentrations during the summers after transfer (top panel), but the same increase was not seen for DO % saturation (bottom panel).

During each of the summers before transfer, bottom-water DO concentrations in the Harbor dropped down to levels only just above the State Standard of 6 mg l⁻¹. During each of the summers after transfer, concentrations fell to higher levels, well above the State standard (discussed further below). (It is worth noting that average DO% saturation values have fallen to lower seasonal lows during the last three years than in all previous years).

At the individual stations, for both DO variables, the averages after transfer were significantly different from, and in all cases greater than baseline, at a single station, Station 137 in the upper Inner Harbor (Fig. 30). At this one station, average DO concentrations during the 5-years were +0.8 mg 1^{-1} (or +11%) greater than baseline; for DO % saturation, the increase was +6.6 % (or +9%).

For DO concentrations, subtraction yielded positive (but non-significant) values at all 9 other stations; for DO % saturation, subtraction yielded positive (but again non-significant) values at 5 other stations, extending from the mouth of the Inner Harbor over the main body of the Outer Harbor. Again, longer-term monitoring may (or may not) show any, likely small, increases in these other areas to be significant.

For both DO variables, the Harbor-wide averages for the 5-years were not significantly different from baseline during any of the four seasons (Table 15). If the 'mid-summer' data were separated out from the 'summer' data, however, the average DO concentrations during 'mid-summers' during the 5-years were +0.4 mg l^{-1} (or +6%), and significantly greater than during 'mid-summers' during baseline. 'Mid-summer', as used here, refers to August + September.

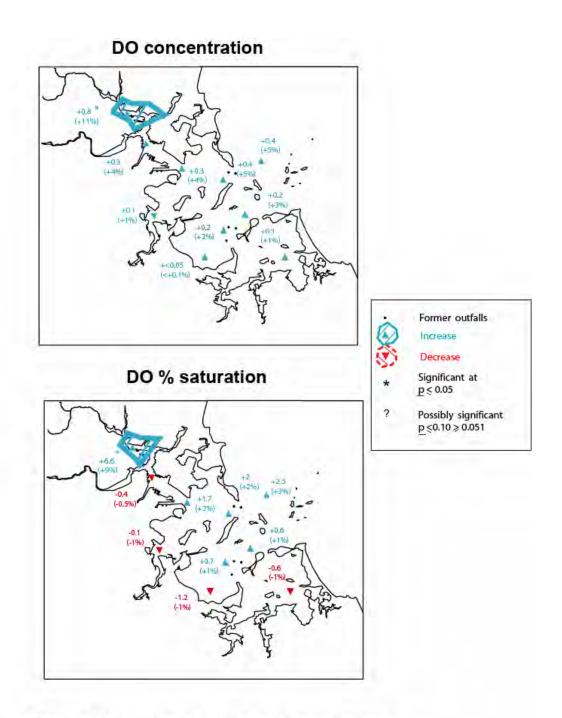


Fig. 30. Bottom-water DO concentrations and DO % saturation. Differences in average values between the first 5-years after transfer, and baseline at the 10 stations. Units = mg I⁻¹ for concentrations, and % for saturation.

Table 15.Seasonal differences in average bottom-water DO concentrations and DO% saturation values between the two periods.

Fraction		Differe	nce (% baseline)		
	Spring	Summer	Mid- summer	Fall	Winter
DO (mg l ⁻¹)	-0.15 (-2%) ^{ns}	-0.16 (-2%) ^{ns}	+0.39 (+6%) *	+0.24 (+3%) ^{ns}	+0.59 (+6%) ^{ns}
DO(%)	-5.8 (-6%) ^{ns}	-1.5 (-2%) ^{ns}	-0.2 (<-1%) ^{ns}	-0.8 (<-1%) ^{ns}	+0.3 (<+1%) ^{ns}

For bottom-water DO concentrations, the stations that showed significant differences varied widely among seasons (Fig. 31). Only during two of the seasons, 'mid-summer' and fall, were increases in bottom-water DO concentrations observed at individual stations. During mid-summers, significant increases in bottom-water DO concentrations were observed at 6 stations, extending from the upper Inner Harbor to Deer Island, and then into the Central Harbor.

During fall, subtraction yielded positive values at all 6 stations in the North Harbor and one station in the Central Harbor, but at only one, Station 137 in the upper Inner Harbor, were the increases significant. During winters, we were unable to detect significant differences (increases or decreases) in DO between the two periods, at any of the 10 stations.

During spring, average DO concentrations during the 5-years were significantly lower than baseline at three of the stations all located in the South Harbor (Stations 077, 124

and 139). At one other, Station 140 in the Neponset River area of Dorchester Bay, the decrease was 'almost' significant. These localized decreases in DO during the spring periods after transfer, will likely have 'dampened' the increases in bottom-water DO expected to follow the ending of wastewater discharges to the Harbor.

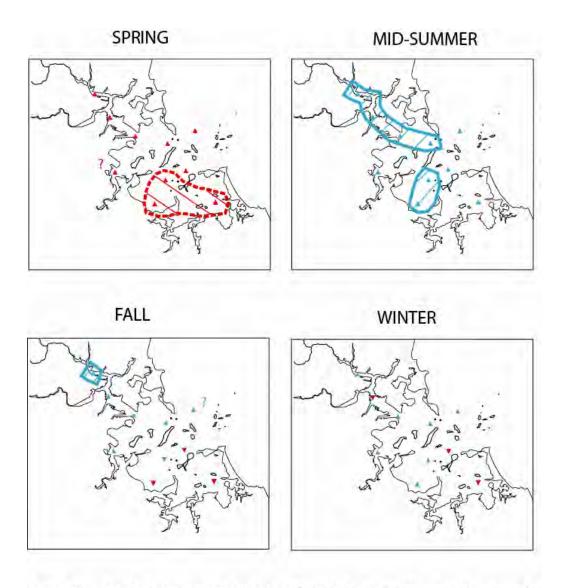


Figure 31. Dissolved oxygen concentrations. Differences in average concentrations between the 5-years and baseline, at the 10 stations, during the four seasons.

II. SUMMARY OF DIFFERENCES BETWEEN PERIODS

Year-round data. Table 16 summarizes, for 20 water-quality variables, the differences between the 5-years and baseline. The data used for this Figure are year-round data; the differences observed at different seasons are not represented. The symbols are as in the previous Figures, except that 'arrows' are used in place of 'triangles'. Note, also that only differences significant at $p \le 0.05$ are indicated in the Table; differences that were 'almost' significant are not included.

The 'solid arrows show variables where the differences between periods were significant for the data averaged Harbor-wide; the 'hollow' arrows indicate variables where the differences were significant only at individual stations. The 'dashes' indicate variables where the differences were not significant for the data averaged Harbor-wide or for individual stations.

The differences observed among the 20 variables can be partitioned into three categories. The first category, which included 12 variables, showed the largest differences, and in all cases decreases. The 12 variables included concentrations of the total and dissolved inorganic fractions of N and P, the percent contributions of DIN and DIP to TN and TP respectively, molar ratios of DIN:DIP, and concentrations of chl-<u>a</u>, phaeophytin and POC.

For all these variables, the decreases were significant for the data averaged Harbor-wide. For most of the 12 variables, chl-<u>a</u> and phaeophytin excluded, the decreases were also significant at all (or almost all) of the 10 stations. For chl-<u>a</u> and phaeophytin, the decreases were confined to localized areas of the Central Harbor extending up into the west North West Harbor region.

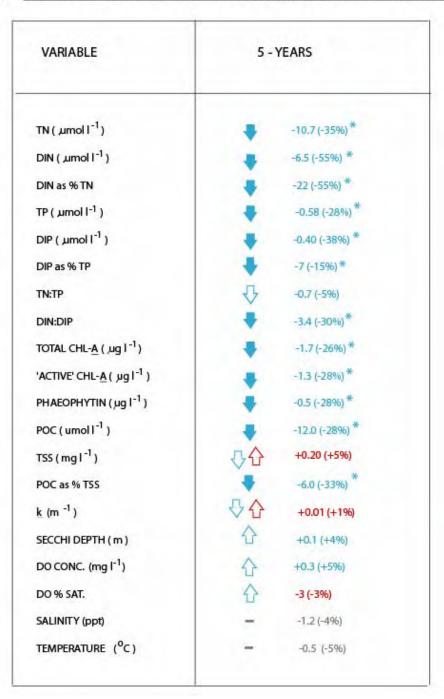


Table 16 Summary of differences in Harbor water-quality between the 5-years and baseline.

For most of these variables, the decreases were largest during the seasons when concentrations in the Harbor water-column tended to be seasonally greatest. This was winter for the total and dissolved inorganic fractions of N and P, and for DIN:DIP, and summer for the particulate fractions of N and P, and for chl-<u>a</u>, phaeophytin and POC.

The second category included the 6 variables that showed no significant differences between the two periods for the data averaged Harbor-wide, but did show significant differences at individual stations. These variables included molar ratios of TN:TP, concentrations of TSS, \underline{k} and secchi depth, and the two DO variables (DO concentrations and % saturation).

For all 6 variables, the differences were significant at 4 or less stations, and the differences were confined to localized areas of the Harbor. For many of these variables, which compared to the first category of variables showed relatively small changes, the subtraction yielded negative values (suggestive of decreases) in certain areas of the Harbor, and positive values (suggestive of increases) in others.

The third category of variables included only two variables, salinity and water temperature. For both of these variables, the differences between the two periods were not significant for either the data averaged Harbor-wide, or the data from each of the individual stations (see Appendix A for data). The absence of detectable difference for these variables, suggests that the differences we observed between periods for the other variables, were not the result of large differences in background environmental conditions between the periods.

Seasonal data. Table 17 shows, for the same 20 variables, the differences in averages between the 5-years and baseline, for each of the four seasons. For most of the N and P variables, the decreases were significant for the data averaged Harbor-wide, for all four seasons. For most of these variables, the decreases were largest during winters and fall, the seasons when before transfer, average concentrations tended to be greatest.

SEASON								VA	RIABLE											
	TN (Junol (⁻¹)	DIN (µmol l-1)	DIN as % TN	TP (Jumol I ⁻¹)	DIP (umol I ⁻¹)	DIP as % TP	TN :TP	DIN: DIP	тотаL CHL-A (лg I ⁻¹)	'ACTIVE' CHL-A (Jug I- ¹)	РНАЕОРНҮТІN (лід І ⁻¹)	TSS (mg l ⁻¹)	POC (µmol I ⁻¹)	POC as % TSS	k (m-1)	SECCHI DEPTH (m)	DO % SAT	DO CONC. (mg L ⁻¹)	SALINITY (ppt)	TEMPERATURE (^O C)
SPRING						₽	↔	₽	₽	₽	₽	↔			ns	ns	₽	₽	ns	ns
SUMMER						₹	ns			•		\mathcal{D}	+	-	\mathcal{O}	↔	(合)	(合)	\mathcal{D}	ns
FALL		٠			٠	∇	$\overline{\nabla}$		ns	ns	ns	0₽		+	ns	ns	ns		ns	ns
WINTER						$\overline{\mathbf{Q}}$			↔	↔		00	ns	ns	☆	₽	ns	ns	ns	ns

Table 17. Summary of seasonal differences in Harbor water-quality between the 5-years and baseline.

For the three chl-<u>a</u> variables, the averages after transfer were significantly lower than baseline for the data averaged Harbor-wide, during summers, and at individual stations during spring. During fall, we were unable to detect significant differences between the two periods, for the data averaged Harbor-wide or individual stations. During winters,

For the three chl-<u>a</u> variables, the averages after transfer were significantly lower than baseline for the data averaged Harbor-wide, during summers, and at individual stations during spring. During fall, we were unable to detect significant differences between the two periods, for the data averaged Harbor-wide or individual stations. During winters, certain stations showed significant increases in concentrations of the three fractions.

For POC, and POC as % of TSS, the average values after transfer were significantly different from baseline, for the data averaged Harbor-wide, during spring, summer and fall. During winters, we were unable to detect significant differences between the two periods for both variables, for the data averaged Harbor-wide or the individual stations.

For TSS, \underline{k} and secchi depth, at the level of the Harbor as a whole, the averages after transfer were not significantly different from baseline during any of the four seasons. All three variables, however showed significant differences at individual stations, during specific seasons; during all four seasons for TSS, and two of the four seasons (summer and winter) for \underline{k} and secchi depth.

For both bottom-water DO variables, the averages after transfer were significantly different, and in this case greater than baseline, for the data averaged Harbor-wide, during part of one of the four seasons, specifically 'mid-summer'. During two of the other three seasons, the differences were significant at individual stations, for one or both of the DO variables depending on season.

DISCUSSION

Comparison with the first 36-months after transfer

Table 18 compares the differences in water quality reported here for the first 5-years after transfer with the differences reported earlier, by Taylor (2004) for the first 36-months after transfer. For 14 of the 20 variables, the directions and levels of significance of the differences for the 5-years (or lack of differences in the case of water-temperature), were the same as for the first 36-months.

The 14 variables included the total and dissolved inorganic fractions of N and P, the % contributions of DIN to TN, molar DIN:DIP ratios, concentrations of phaeophytin, POC, and TSS, secchi depths, the two DO variables, and water-temperature. For these variables the fact that the differences during the 5-years were as for the 36-months, suggests that the bulk of the differences after transfer occurred during the first 36-months.

For an additional four of the 20 variables, the directions of the differences for the 5-years were as for the 36-months, but the levels of significance for the 5-years were greater than for the 36-months. For two of the four variables, total chl-<u>a</u> and acid-corrected chl-<u>a</u>, the size of the difference was increased between the 36-months and 5-years. For the other two variables, DIP as % TP and <u>k</u>, the increased <u>n</u> value for the post-transfer period, was likely responsible for the increased significance of the differences, between the 36-months and 5-years.

For two other variables, TN:TP and salinity, the levels of significance of the differences during the 5-years were smaller than for the 36-months. For these variables, background environmental processes, in this case reduced river inflows during 2002, were likely responsible for the greater differences for the 36-months than 5-years. River inflows to the Harbor are enriched with TN relative to TP (MWRA unpublished data).

VARIABLE	5 - YEA	RS	36-M	ONTHS
TN (سرا ⁻¹)		-10.7 (-35%)		-10.0 (-27%)
DIN (umol I ⁻¹)		-6.5 (-55%)		-7.0 (-59%)
DIN as % TN		-22 (-55%)		-14 (-37%)
TP (µmol l ⁻¹)		-0.58 (-28%)		-0.58 (-28%)
DIP (µmol I ⁻¹)		-0.40 (-38%)		-0,4 (-38%)
DIP as % TP	+	-7 (-15%)	$\overline{\Omega}$	-7 (-15%)
TN:TP	\mathcal{O}	-0.7 (-5%)		-1.3 (-9%)
DIN:DIP		-3,4 (-30%)	-	-3.8 (-33%)
TOTAL CHL- <u>A</u> (,ug l ⁻¹)		-1.7 (-26%)	\$	-1,3 (-20%)
'ACTIVE' CHL-A (µg l ⁻¹)		-1.3 (-28%)	5	-0.9 (-19%)
PHAEOPHYTIN (µg l ⁻¹)		-0.5 (-28%)		-0.5 (-26%)
POC (µmol I ⁻¹)		-12.0 (-28%)		-12.1 (-28%)
TSS (mg l ⁻¹)	心心	+0.20 (+5%)	心心	+0.25 (+7%)
POC as % TSS		-6.0 (-33%)		-6.0 (-33%)
<u>k</u> (m ⁻¹)	☆☆	+0.01 (+1%)	-	-0,01 (-1%)
SECCHI DEPTH (m)		+0.1 (+4%)		+0.1 (+4%)
DO CONC. (mg l ⁻¹)		+0.3 (+5%)	分	+0.3 (+5%)
DO % SAT.	合	-3 (-3%)		+2 (+2%)
SALINITY (ppt)	-	-1.2 (-4%)	1	+0.4 (+1%)
TEMPERATURE (⁰ C)	-	-0.5 (-5%)	-	-0.3 (-396)

Table 18. Summary of differences in Harbor water-quality between the 5-years and baseline. Also shown are the differences between the first 36-months after transfer and baseline (from Taylor 2004).

Observed versus predicted changes

Bays Hydrodynamic (BHM) and Eutrophication Models (BEM). Table 19 compares for three variables, concentrations of DIN, acid-corrected chl-<u>a</u>, and DO, the differences observed for the 5-years, and the differences predicted by HydroQual and Normandeau (1995) using the 3-D BHM/BEM model. Note, only broad comparisons can be conducted of the two sets of data, because the modeled predictions were generated using 1991 boundary data.

Also, the model predictions that were reported for specific times of the year, for specific locations within the Harbor, rather than for the year-round or seasonal, Harbor-wide averages emphasized in this report. In this report we have considered the observed differences to be 'similar' to the differences predicted by the BEM model, if the observed differences fell within \pm 20% of the predicted differences.

For DIN, the decreases we observed for the Harbor as a whole, of -6.5- μ mol l⁻¹ (or -55%), were almost identical to the decreases of -6.8- μ mol l⁻¹ (or -57%) predicted by the BEM model for Station 2. For year-round acid-corrected chl-<u>a</u>, the difference we observed, -1.3 μ gl⁻¹ (or -28%), was again almost identical to the difference of -1.5 μ gl⁻¹ (or -39%) predicted by the BEM model.

For year-round bottom-water DO concentrations, the small (and in this case, nonsignificant) value of +0.3 mg Γ^1 (or +3%) for the 5-years, was identical to that of +0.3-mg Γ^1 (or +4%) predicted by the BEM model. For salinity, the observed, but non-significant difference of 1.2 ppt was slightly greater than the 0.5 ppt difference predicted by the BHM (Signell <u>et al.</u> 2000). Both sets of salinity values, however, were small, and even small differences in background (river or oceanic) conditions between the two different periods covered by the two studies, could account for the difference.

Comparison with 2-D box model. Table 20 compares for six variables (TN, DIN, DIN as %TN, DIP, molar DIN:DIP, and TSS), the differences we observed for the 5-years for

Table 19. **Observed versus predicted changes.** Comparisons of the differences in average concentrations of DIN, chl-<u>a</u> and DO observed for the 5-years, and the changes predicted by the coupled hydrodynamic/water quality BHM/BEM model.

VARIABLE		OBSERV	ED		PREDICTED				
	Baseline	5 years	Difference (%)	Baseline	5 years	Difference (%)			
DIN (µmol l ⁻¹)	11.8 ± 6.4^{a} (75)	5.3 ± 3.5^{a} (62)	-6.5 (-55%) ^a	11.9 ± 5.5 ° (24)	5.1 ± 4.1 ° (24)	-6.8 (-57%) ^c			
Chl- \underline{a} (µg l ⁻¹) ^d	4.7 ± 3.1^{a} (61)	3.3 ± 2.2^{a} (63)	-1.3 (-28%) ^a	3.8 ± 2.1 ° (24)	2.3 <u>+</u> 1.1 ^c (24)	-1.5 (-39%) ^c			
DO conc. (mg l ⁻¹)	8.6 ± 1.2^{a} (40)	8.9 <u>+</u> 1.3 ^a (64)	+0.3 (+3%) ^a	$9.2 \pm 1.0^{\circ}$ (24)	9.5 ± 1.0 ° (24)	+0.3 (+4%) ^e			

^a values are the averages for all stations sampled, for all depths for DIN and chl-<u>a</u>, and near-bottom depth alone for DO. Averages are for year-round data; ^b from HydroQual (1995); ^c predicted values are for HydroQual and Normandeau station 2, located between Stations 106 and 142; ^d data are acid-corrected, extracted chl-<u>a</u>; ^e predicted DO data for Harbor are averages for mid- and bottom depths for HydroQual station 2.

the North West Harbor, with the differences predicted for the same area by Kelly (1998). Note, the 'North Harbor' referred to by Kelly is equivalent to the region we refer to as the 'North West Harbor'. Also, all data in the Table cover the March through September period, to be compatible with the period sampled by Kelly in 1994.

Variable	Th	is study		Kelly (1998)				
	Observed before	Observed 5-years	Difference	Observed before	Predicted post-transfe	Difference er		
TN (μmol l ⁻¹)	27.4	19.3	-8.1 (-30%)	25	19	-6 (-24%)		
DIN (μmol l ⁻¹)	7.4	3.0	-4.4 (-59%)	11	5.5	-5.5 (-50%)		
DIN as % TN	28	12	-16 (-57%)	44	29	-15 (-34%)		
DIP (μmol l ⁻¹)	0.8	0.5	-0.3 (-39%)	2.5	1.5	-1.0 (-40%)		
Molar DIN:DIP	9.6:1	6.3:1	-3:1 (-34%)	4.4:1	3.7:1	-0.7:1 (-16%)		
TSS (mg l^{-1})	4.0	4.1	+0.1 (+1%)	2.5	1.0	-1.5 (-60%)		

Table 20. Comparison of the differences observed during the 5-years with the differences predicted by Kelly (1998).

For TN, we observed a decrease of -8.1-µmol l⁻¹ (or -30%) between the 5-years and baseline; Kelly predicted a decrease of -6-µmol l⁻¹ (or -24%). The observed decrease was, in terms of absolute concentrations, 35% greater than the modeled estimate, and based on our 20% criterion different from the modeled estimate. For DIN and DIN as %TN, the observed and predicted decreases were similar.

For DIP, the decrease of $-0.3 - \mu \text{mol } l^{-1}$ (or -39%) we observed was smaller, and in terms of absolute concentrations about one-third the size of the predicted decrease. This difference might simply be the result of the DIP concentrations observed in the Harbor during baseline being one-third the size of the concentrations measured during 1994. Expressed as a percent of baseline, the observed decrease of -39% for DIP was identical the predicted decrease of -39%.

For DIN:DIP, the observed decrease of -3.1:1 was similar to the predicted decrease of -3.7:1; in percent terms, however, the observed decrease was larger than the predicted decrease. As noted earlier, the DIN:DIP ratios in the Harbor vary widely year-to-year, and the difference could simply reflect background differences between the 5-years and the period modeled by Kelly.

For TSS, the fact that we were unable to detect a significant difference was unlike the decrease of -1.5 mg l^{-1} (or -60%) predicted by Kelly. This could be because our comparison of TSS concentrations during the periods before and offshore transfer does not capture the fact that the bulk of the decrease in wastewater loadings to the Harbor occurred with upgrades to treatment, before offshore transfer.

Both sets of models predicted the 'effects' of the transfer of the wastewater discharges by numerically 'eliminating' the wastewater discharges to the Harbor. The output from these models can therefore be used as a 'reference', to verify the changes we observed in the Harbor. It can also be used to verify whether the transfer of the WWTF discharges were responsible for the sizes and nature of any changes observed in the Harbor.

Conclusions

The primary purpose of this report was to compare Harbor water-quality during the first 5-years after offshore transfer with water quality during a baseline period, and then compare the observed differences with the differences predicted by others using

numerical models. The study was able to demonstrate significant differences in the Harbor water quality between the two periods.

For the few variables where comparisons could be made, the observed changes were similar to the changes predicted by others using the BHM/BEM models. The model predictions were made be 'numerically eliminating' the wastewater discharges to the Harbor. Therefore the similarity of the observed and predicted changes would indicate that the changes observed in the Harbor were, at least for these variables, the result of the transfer of the WWTF discharges offshore.

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LITERATURE CITED

Alber, M. and Chan, A. B. 1994. Sources of contaminants to Boston Harbor: revised loading estimates. Massachusetts Water Resources Authority Environmental Quality Dept. Technical Report No 94-1.

Bendschneider, K. and Robinson, R. J. 1952. A new spectrophotometric determination of nitrate in seawater. Journal of Marine Research 11: 87-96.

Bricker, S. B., C. G. Clement, D. E. Pirhalla, S.P. Orlando and D.R.G. Farrow. 1999. National Estuarine Eutrophication Assessment: Effects of Nutrient Enrichment in the Nations Estuaries. NOAA, National Ocean Service, Special Projects Office and the National Centers for Coastal Ocean Science. Silver Spring, MD: 71pp.

Clesceri, L. S., A. E. Greenberg, and A. D. Eaton. 1998. Standard Methods for the Examination of Water and Wastewater. 20th Edition. American Public Health Association, American Water Works Association, Water Environment Federation.

Fiore, J. and O'Brien, J. E. 1962. Ammonia determination by automatic analysis. Wastes Engineering. 33: 352.

Holm-Hanson. O, Lorenzen, C. J, Holmes, R. W, and Strickland, J. D. H. 1965. Fluorometric determination of chlorophyll. J. Cons. Int. Explor. Mer. 30: 3-15.

Hydroqual and Normandeau 1995. A water quality for Massachusetts and Cape Cod bays: calibration of the Bays Eutrophication Model (BEM). MWRA Environmental Quality Department Technical Report No. 95-8. Massachusetts Water Resources Authority, Boston MA 402 Kelly, J. R. 1997. Nitrogen flow and the interaction of Boston Harbor with Massachusetts Bay. Estuaries, 20, 365-380.

Kelly, J. R. 1998. Quantification and potential role of ocean nutrient loading to Boston Harbor, Massachusetts, USA. Marine Ecology Progress Series: 17353-65.

Libby P. S, Geyer W. R, Keller A. A, Turner J. T, Mansfield A. D, Borkman D. G. and Oviatt C. A. 2006. 2004 Annual Water Column Monitoring Report. Boston: Massachusetts Water Resources Authority. Report 2006-15. 177 p.

Maciolek N. J, Diaz R. J, Dahlen D. T. and Williams I. P. 2006. 2004 Boston Harbor benthic monitoring report. Boston: Massachusetts Water Resources Authority. Report 2006-01. 244 p.

Murphy, J. and Riley, J. 1962. A modified single solution for the determination of phosphate in natural waters. Anal. Chim. Acta. 27:31.

Nixon, S. W. 1995. Coastal marine eutrophication: A definition, social causes, future concerns. Ophelia 41: 199-219.

Rex, A. C. and Taylor, D. I. 2000. Combined Work/Quality Assurance Project Plan for Water Quality Monitoring and Combined Sewer Overflow Receiving Water Monitoring in Boston Harbor and its Tributary Rivers 2000. Boston: Massachusetts Water Resources Authority. Technical Report MS-067

Rex, A.C, Wu, D, Coughlin, K, Hall, M, Keay, K and D. I. Taylor. 2002. The State of Boston Harbor; Mapping the Harbor's Recovery. Boston: Massachusetts Water Resources Authority, Technical Report ENQUAD 2002-09. 42 p. Signell, R. P., H. L. Jenter and A. F. Blumberg. 2000. Predicting the physical effects of relocating Boston outfall. J. Estuarine, Coastal and Shelf Sci., 50: 59-72.

Solarzano, L, and Sharp, J. H. 1980 <u>a</u>. Determination of total dissolved phosphorus and particulate phosphorus in natural waters. Limnology and Oceanography, 25, 754-758.

Solarzano, L, and Sharp, J. H. 1980b. Determination of total dissolved nitrogen in natural waters. Limnology and Oceanography, 25, 750-754.

SPSS 2002. SPSS Advanced Statistics 10.0. Chicago.

Stolzenbach, K. D, and Adams, E. E. 1998. Contaminated Sediments in Boston Harbor. (pp. 170). Massachusetts Institute for Technology Sea Grant Publications, Cambridge, USA.

Sung, W. 1991. Observations on the temporal variations of dissolved copper and zinc in Boston Harbor. Civil Engineering Practice, Spring 1991, 99-110.

Taylor, D.I. 2001. Trends in water quality in Boston Harbor during the 8-years before offshore transfer of Deer Island flows. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2001-05. 54 p.

Taylor, D.I. 2004. Boston Harbor: a comparison of eutrophication-related water-quality before, and 36-months after 'offshore transfer'. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2004-04. 63 p.

Taylor, D.I. 2005. Patterns of wastewater, river and non-point source loadings to Boston Harbor, 1995 – 2003. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2005-08. 52 p. Tucker J, Kelsey S, Giblin A. E. and C. S. Hopkinson J. 2005. 2004 annual benthic nutrient flux monitoring report. Boston: Massachusetts Water Resources Authority. Report 2005-11. 68 p.

Werme, C. and C. Hunt. 2003. 2002 Outfall monitoring overview. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2003-12. 80 p.

APPENDIX A

Salinity and water temperature

Salinity. During the 5-years, Harbor-wide average salinity was not significantly different from baseline (Table A-1, Figure A-1). The same applied for each of the individual stations (Fig. A-2). Harbor-wide average salinity was also not significantly different from baseline for each of the four seasons (Table A-2).

Table A-1.Salinity and temperature.Comparison of volume-weighted Harbor-wide average values between the 5-years after transfer, and baseline.

Variable	Average values	during	Difference between baseline	p
	Baseline	5-years	and 5-years	
Salinity (ppt)	30.3 <u>+</u> 1.1 (75)	29.1 <u>+</u> 1.2 (64)	-1.2 (-4%)	0.17
Water temperature (°C)	9.9 <u>+</u> 5.8 (75)	9.3 <u>+</u> 6.1 (64)	-0.5 (-5%)	0.21

Variable	Difference (ppt and ° C, and then % baseline)			
	Spring	Summer	Fall	Winter
Salinity	-0.3 (-1%) ^{ns}	-0.1 (<-1%) *	-0.4 (-1%) ^{ns}	+0.45 (+1%) ^{ns}
Temperature	+0.3 (+3%) ^{ns}	-0.2 (-1%) *	-0.3 (-3%) ^{ns}	-1.2 (-36%) *

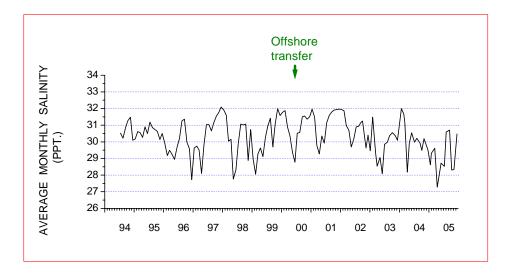


Fig. A-1. <u>Salinity</u>. Time-series plot of volume-weighted, Harbor-wide average salinity, 1994 through 2005. Note, data here are average monthly values.

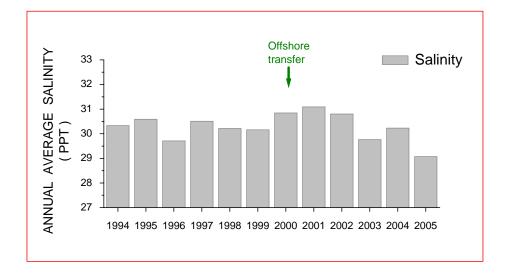


Fig. A-2. Annual Harbor-wide average salinity, 1994 -2005.

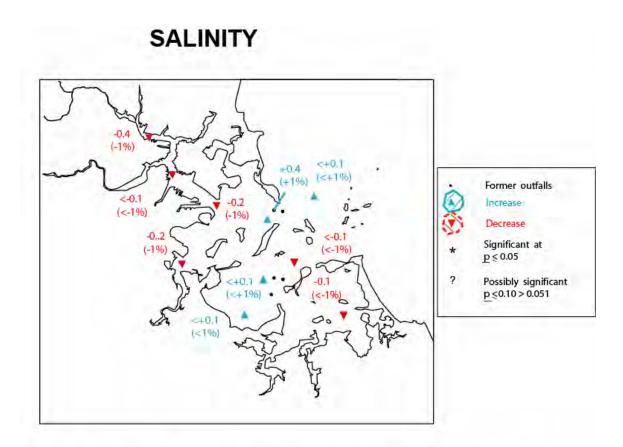


Fig. A-3. **Salinity.** Differences in average values (ppt) between the 5-years after transfer and baseline, at each of the 10 sampling stations.

Water temperature. Harbor-wide average water temperatures during the 5-years were also not significantly different from baseline (Table A-1, Fig. A-4, Fig. A-5). During 2002, annual average temperatures were greater than during the other four years after transfer. 2002 was also the year when average concentrations of chl- \underline{a} , and to a lesser extent POC, were elevated among the years after transfer.

At none of the 10 stations, as for salinity, were the average temperatures for the 5-years significantly different from baseline. At all stations, subtraction yielded small negative values, but at none of the stations were the differences significant (MWRA unpublished data, plots not shown).

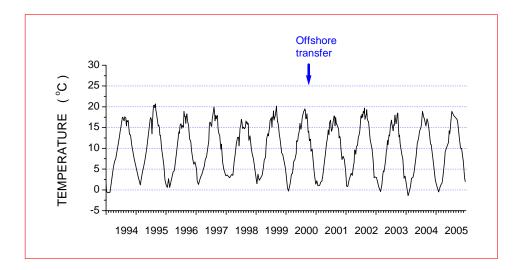


Fig. A-4. <u>Water temperature</u>. Time-series plot of volume-weighted, Harbor-wide average values. Vertical arrow shows completion date of offshore flow transfer.

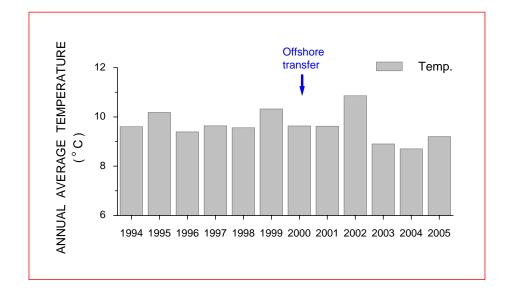


Fig. A-5. <u>Annual Harbor-wide average water temperatures</u>, 1994 -2005.



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