Boston Harbor: a comparison of eutrophication-related water-quality before, and 36-months after 'offshore transfer'

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Boston Harbor: a comparison of eutrophicationrelated water-quality before, and 36-months after 'offshore transfer'

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EXECUTIVE SUMMARY

In September 2000, the Massachusetts Water Resources Authority (MWRA) transferred the wastewater discharges from the Deer Island treatment facility to Boston Harbor, 16 km offshore, for diffusion in the bottom-waters of Massachusetts Bay. This 'offshore transfer' ended the bulk of the discharges of wastewater from the City of Boston and surrounding communities to Boston Harbor.

Numerical modeling studies conducted by others before transfer, predicted that offshore transfer would lead to improvements in the water-quality of Boston Harbor, with only minimal impacts on the Bay. In this report, we compare the water-quality in the Harbor during the first 36-months after offshore transfer, with the water quality during a 3-to-8 year baseline period pre-transfer.

The focus of the report is on aspects related to eutrophication, or 'organic overenrichment', of the Harbor water-column. Others will address changes to other aspects of the Harbor, and to eutrophication-related and other aspects of the Bay. In the Discussion section of the report we compare the differences observed during the 36months, with the numerical model predictions.

The Massachusetts Water Resources Authority collected all water-quality data presented in the report. The data were collected at 10 stations, which were located in all 4 major regions of the Harbor. Water quality in the Harbor is compared before and after transfer at two levels; one at the level of the Harbor as a whole, and two, at the level of each of the individual stations.

The following are some of the differences in Harbor water-quality observed between the 36-months and baseline:

• Harbor-wide average concentrations of total nitrogen (TN) and total phosphorus (TP) during the 36-months were significantly, and -32% and -

- 28%, lower than baseline. For both nutrients, concentrations during the 36- months were significantly lower than baseline at all 10 stations. (Note, N and P are the two nutrients most responsible for over-enrichment of coastal systems).
- Harbor-wide average concentrations of dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP), and molar ratios of TN:TP and DIN:DIP, were all also significantly lower during the 36-months than baseline. DIN and DIP both accounted for ca. 70% of the decrease in TN and TP, respectively. (Note, DIN and DIP were the dominant fractions of the two nutrients in the wastewater discharged to the Harbor during baseline).
- Harbor-wide average concentrations of acid-corrected chlorophyll-<u>a</u> (chl-<u>a</u>) for the full 36-months were not significantly different from baseline, but the values during summers during the 36-months were. Average chl-<u>a</u> concentrations during summers during the 36-months were -36% lower than baseline. As for year-round N and P, the decreases during summers were significant at all 10 stations. (Based on N loading-chl-<u>a</u> relationships developed by others, the lowered N inputs to the Harbor were likely responsible for the decrease in chl-<u>a</u>).
- As for N and P, Harbor-wide average concentrations of particulate organic carbon (POC) for the full 36-months were significantly, and in this case, 28% lower than baseline. The decreases were again significant at all 10 stations. (Note, POC is a measure of suspended detritus + living material; elevated concentrations of POC can be a symptom of eutrophication).
- Harbor-wide average concentrations of total suspended solids (TSS), during the 36-months were not significantly different from baseline. As a result of the significant decrease for POC but not for TSS, the percent contribution of POC to TSS was significantly lower during the 36-months than baseline.
- For both measures of water clarity that we conducted, reciprocal attenuation coefficient (k) and secchi depth, Harbor-wide averages for the

full 36-months were also not significantly different from baseline. For \underline{k} , the differences at none of the 10 stations were also significant. For secchi depth, average values during the 36-months were significantly greater than baseline at only 1 station, and 'almost' significantly greater than baseline at two others..

- For the full 36-months, Harbor-wide average concentrations of dissolved oxygen (DO) and DO percent saturation (DO % sat.) in the bottom-waters of the Harbor were not significantly different from baseline. For both variables, however, averages during mid-summer during the 36-months, were significantly, and between 5% and 10% greater than baseline. The stations at which the increases were significant were located in the North Harbor and Central Harbor regions.
- Harbor-wide average salinity during the 36-months was also significantly, and in this case, +0.4 ppt (or +1%), greater than baseline. Average salinity was also significantly greater during the 36-months than baseline at all 10 stations.

For most variables for which comparisons could be conducted, the directions and sizes of the differences were basically as estimated from simple mass-balance calculations and more complex water-quality /hydrodynamic models. This applied especially for N, P, chl-a, POC, DO and salinity, and less so for TSS. The similarity of the observed and predicted differences would support (although not necessarily prove), the observation that offshore transfer was responsible for the differences.

INTRODUCTION

September 2000 saw completion of one of the final and most conspicuous milestones of the Boston Harbor Project (BHP), the transfer 16-km offshore of the wastewater discharged from the Deer Island wastewater treatment facility to Boston Harbor. This transfer, here termed 'offshore transfer', ended the bulk of the discharges of wastewater from the City of Boston and surrounding communities to Boston Harbor.

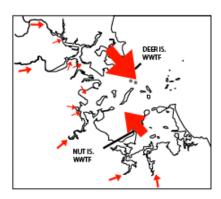
Earlier milestones of the BHP included the upgrade to secondary treatment at the Deer Island facility starting in 1997, and then transfer of Nut Island flows through the upgraded Deer Island facility in mid-1998. Figure 1 provides a schematic of the two transfers, first, 'inter-island transfer', and then, 'offshore transfer'. Rex et al. (2002) provides an overview of these, and the other milestones of the BHP.

Numerical modeling conducted by others before the two transfers predicted that 'offshore transfer' would be the milestone of the BHP that would most impact the Harbor (Signell et al. 2000, HydroQual and Normandeau 1995). The models predicted significant improvements in, especially eutrophication-related water quality of the Harbor, with only minimal impacts on the Bay.

Differences in water-quality have been observed in Boston Harbor during the first approximately two-years that followed transfer (Taylor 2003, Libby <u>et al.</u> 2003, Werme and Hunt 2003). Water-quality in bay-estuarine systems such as Boston Harbor can vary widely year-to-year. Thus, background processes could have contributed at least some of the differences observed during the first two years.

In this report we compare eutrophication-related water-quality in Boston Harbor between the first 36-months after offshore transfer (bottom panel, Fig. 1), and a 3- to 8-year 'baseline' period before transfer (top two panels, Fig. 1). With the addition of another year of post-transfer data, we can be more confident of any differences in water-quality that coincided with, or were caused by, offshore transfer.

<JULY 1998

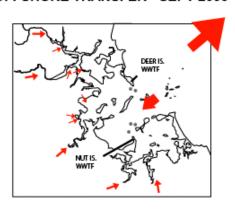


INTER-ISLAND TRANSFER - JULY 1998

DEER IS. WWITE

BASELINE PERIOD (< Sept. 2000)

OFFSHORE TRANSFER - SEPT 2000



36-MONTHS POST-OFFSHORE TRANSFER (Sept. 2000 through Aug. 2002)

Figure 1. Changes in locations of discharges from the two WWTFs during the baseline period, and between the baseline period and the first 36-months after offshore transfer. Arrows indicate flows from the WWTFs, rivers and shoreline non-point sources., and are roughly proportional to the historic N loads to the system (based on Alber and Chan 1994).

The 36-months post-transfer extended from 7 September 2000, the day after offshore transfer, through 31 August 2003. 'Baseline', which covered the last 3-to 8-years that the Harbor received discharges, extended from August 1993 (or August 1997 depending on variable), through 6 September 2000. In the Discussion section of the report, we compare the differences observed during the 36-months, with the differences predicted by numerical models.

Aspects addressed by the report

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

Others will address other aspects related to eutrophication of the Harbor, including rates of pelagic primary production, phytoplankton community structure, sediment redox characteristics, benthic metabolism and nutrient fluxes, and biomass and structure of the Harbor benthic invertebrate communities. Others too will report on the changes to the Bay.

The reasons we focused this report on eutrophication were as follows:

- The numerical modeling studies conducted before transfer, predicted that it would be aspects related to eutrophication of the Harbor that would be most changed by transfer (HydroQual and Normandeau 1995);
- N loadings to the Harbor from combined land plus air sources, before transfer, were estimated to be high (Kelly 1997, 1998), with the two wastewater treatment facilities contributing the bulk (>90%) of the elevated inputs;

- Numerous symptoms of eutrophication had been documented in the Harbor during baseline (some of these symptoms are summarized in Taylor 2001); and lastly,
- Eutrophication, or organic over-enrichment, is now widely recognized to pose a threat to coastal systems worldwide (Forsberg 1995), including those of the northeast USA

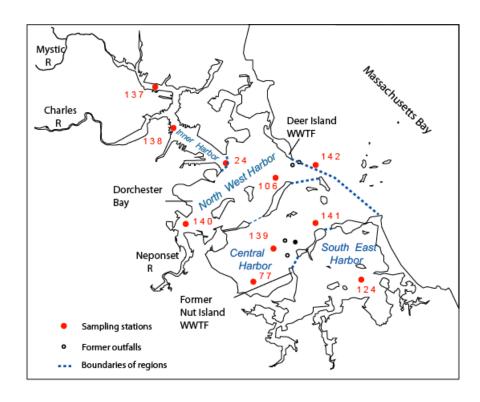
METHODS

Field sampling and laboratory analytical procedures

The Massachusetts Water Resources Authority (MWRA), the agency responsible for the transfer of discharges from Deer Island offshore, collected all the 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. 2). The names and coordinates of the 10 stations are listed in Table 1. The 10 stations were located in each of the 4 major regions of the Harbor; three in the Inner Harbor, three in the North West Harbor, three in the Central Harbor and one in the South East Harbor. Six of the 10 stations were located in the North Harbor, and 4 in the South 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. At all stations, measurements were conducted weekly from May through October, and every two weeks from November through April.



North Harbor = Inner Harbor + North West Harbor

South Harbor = Central Harbor + South East Harbor

Outer Harbor = North West Harbor + Central Harbor + South East Harbor

Figure 2. Sampling stations and regions. Locations of the sampling stations, former wastewater treatment facility (WWTF) outfalls, and the 4 major regions of Boston Harbor.

For most variables, measurements 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 following variables were monitored at both depths: dissolved inorganic nitrogen (DIN), ammonium (NH₄), nitrate + nitrite (NO₃₊₂), chlorophyll- \underline{a} (chl- \underline{a}), phaeophytin, total suspended solids (TSS), dissolved oxygen (DO), salinity and

temperature. For all these variables, excluding DO, all data presented are averages for the 2 depths. For DO, only data from the near-bottom depth are reported here.

Table 1. Locations of the stations sampled to track differences in Harbor water-quality between the 36-months and baseline.

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

The following variables were monitored at a single depth, which, in all cases, was the 'near-surface' depth: total N (TN), particulate N (PN), non-DIN, total P (TP), particulate P (PP), non-DIP and POC. TN was computed as total dissolved nitrogen (TDN) + PN, and TP as total dissolved phosphorus (TDP) + PP. Note, chl-<u>a</u> and TP data are available only after mid-1995.

Table 2 provides a summary of all 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 the individual stations, we used the non-parametric Mann-Whitney U test to test for differences between means between the two periods (SPSS 10.1, SPSS 2002). The Mann-Whitney U test was used in preference to conventional ANOVA, because of the frequent non-homogeneity of variance of the Harbor data. The Mann-Whitney U test also tended to be more conservative than ANOVA.

To determine differences for the Harbor as a whole, we used volume-weighted Harbor-wide averages. These were computed after Sung (1991), and as follows:

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

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 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).

Table 2. Summary of field and analytical methods.

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
Enterococcus b	Clesceri et al. (1998, Method 9230C)
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.

For both the Harbor-wide average values and for the values for each of the stations, the Mann-Whitney U test was applied to average monthly values. All average monthly values were 'de-seasonalized' before application of the Mann-Whitney U test; 'de-seseasonalization' was achieved using the multiplicative procedure outlined in SPSS (2002). For variables for a particular season, for instance for summer chl-<u>a</u> or midsummer DO, the test was applied to non-deseasonalized data.

Three levels of significance have been differentiated in the report. When the Mann-Whitney U test yielded \underline{p} values = or < 0.05, we considered the difference to be 'significant' (95% CL), and denoted these using a single asterisk (*). When \underline{p} was > 0.05 but < 0.10, we considered the difference 'almost significant' (90% CL), and used a '?' to denote this condition. For \underline{p} values > 0.10, the difference was considered 'not significant'.

RESULTS

Nitrogen

Total nitrogen (TN). One of the variables for which averages during the 36-months were significantly different from baseline was TN (Table 3). During baseline, TN averaged $30.9 \pm 6.4 \, \mu \text{mol l}^{-1}$; during the 36-months, it averaged $20.9 \pm 2.9 \, \mu \text{mol l}^{-1}$. The difference of -10.0-μmol l⁻¹, which was equivalent to -32% of average baseline concentrations, was significant (p = or < 0.05).

This difference between the two periods of -10.0-µmol l⁻¹ was, in turn, similar to the difference, in this case of -12.3-µmol l⁻¹, that we estimated from simple-mass balance calculations using estimates of the reduction in wastewater loadings of TN to the Harbor post-transfer (Table 4). For details of the mass-balance calculations and assumptions used in the calculations, see the footnote to the Table. For this report, we have assumed

Table 3. <u>Nitrogen concentrations</u>. Volume-weighted Harbor-wide average concentrations during the 36 months after transfer, and during baseline. Values are averages ± 1 x SD of average monthly values, with the \underline{n} value in parentheses. * = difference between periods 'significant' ($\underline{p} < 0.05$ but > 0.011); '?' difference 'almost' significant ($\underline{p} < 0.10$ but > 0.051).

Variable	Average values during		Difference between baseline and	
	Baseline	36-months	36-months	
TN	30.9 <u>+</u> 6.4	20.9 <u>+</u> 2.9	-10.0 (-32%) * *	
(μmol 1 ⁻¹)	(61)	(35)		
DIN (μmol l ⁻¹)	$11.8 \pm 6.4 $ (75)	4.8 ± 3.0 (36)	-7.0 (-59%) *	
DON (μmol l ⁻¹)	13.0 ± 3.7 (61)	11.9 <u>+</u> 1.9 (36)	-1.1 (-8%)	
NH ₄ (μmol l ⁻¹)	6.3 ± 3.4 (75)	1.1 <u>+</u> 0.7 (36)	-5.2 (-82%) *	
NO $_{3+2}$ (µmol 1^{-1})	5.5 ± 3.8 (77)	3.8 <u>+</u> 2.7 (36)	-1.7 (-31%) *	
PN (μmol 1 ⁻¹)	6.1 ± 2.4 (60)	4.2 ± 1.3 (35)	-1.9 (-31%) *	
DIN as %TN	38 <u>+</u> 17 (68)	24 <u>+</u> 13 (36)	-14 (-37%) *	
NH ₄ as %DIN	53 <u>+</u> 14 (75)	23 <u>+</u> 13 (36)	-30 (-57%) *	

the observed and estimated differences to be similar if the observed differences fell within 25% of the estimated difference. (Note, for TN, the difference of -2.3 μ mol l⁻¹ between the observed and the estimated difference was equivalent to only -19% of the estimated difference).

Table 4. <u>Observed versus estimated differences.</u> Comparison of observed and estimated differences in Harbor-wide average concentrations between the 36-months after transfer and baseline.

Variable	^a Difference in WWTF loadings	Observed difference during: 36-months	^b Difference estimated from difference in loadings	d Difference between observed and estimated, as % of estimated
		<u>NITROGEN</u> (μmol l ⁻¹)		
TN	-1324	-10.0*	-12.3	-19%
DIN	-918	-7.0*	-8.6	-19%
		PHOSPHORUS (μmol	1 ⁻¹)	
TP	-80	-0.58*	-0.75	-23%
DIP	-43.0	-0.40*	-0.4	0%
		° <u>CHLOROPHYLL-A</u>	<u>·</u> (μg l ⁻¹)	
Chl- <u>a</u>	n/a	-0.9	^d -0.9	-19%
		SOLIDS (mg l ⁻¹ for TS	S and µmol l ⁻¹ for I	POC)
TSS	-38	+0.25	-0.35	+171%
POC	-1780	-12.1 *	-15.6	-22%

^a Data are averages of average monthly loadings from the Deer Island and Nut Island WWTF combined, assuming that before transfer 50% of DI flows entered the Harbor, and after transfer, 5% of DI flows re-entered the Harbor. Also includes averages of average monthly loadings from the Charles, Mystic, Neponset and Weymouth rivers (all data are MWRA, unpublished). Units = kmol d⁻¹ for TN, DIN, TP, DIP, and POC, and ton d⁻¹ for TSS.

b Computed using reduction in wastewater loadings (MWRA, unpublished data), assuming midtide volume of Harbor of 643 x 10⁶ m³ (Stolzenbach and Adams 1998), and hydraulic residence time of the Harbor of 6 d (R. Signell, USGS Woods Hole, pers. comm.). Predicted change =((change in loadings x residence time)/mid-tide volume)-(concentration from re-entry from Massachusetts Bay).

^c Year-round, acid-corrected chl-^a.

^d Computed from predicted DIN changes assuming a change in DIN of 10 μmol l^{-1} yields a change in the same direction of acid-corrected chl-<u>a</u> of 1.0 μg l^{-1} .

e ((Observed difference – estimated difference)/estimated difference)*100

The fact that concentrations of TN in the Harbor were lower during the 36-months than baseline is confirmed in the time-series plot of TN in Figure 3. The plot also shows a difference in the seasonal pattern of TN between the two periods. During baseline, TN was typically elevated during late winter, and lowered during summer. Concentrations in the Harbor during the 36-months showed little evidence of a seasonal pattern.

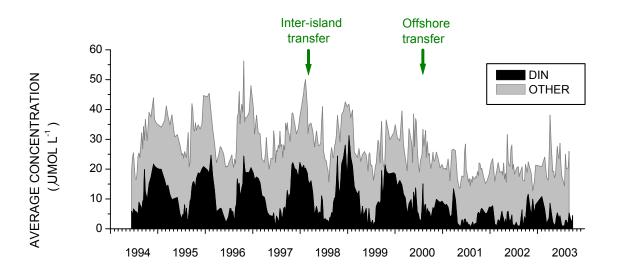


Fig. 3. <u>Total nitrogen (TN) partioned into DIN and non-DIN components.</u> Time-series plots of survey average, volume-weighted Harbor-wide average concentrations.

Average TN concentrations during the 36-months were also significantly lower than baseline at all 10 stations (Fig. 4). (For details of the notations used in this and subsequent Figures, see the footnote to the Figure). The differences at the individual stations ranged in size from -8.4-µmol l⁻¹ to -15.1-µmol l⁻¹. The two stations off of Deer Island (Stations 106 and 142) showed the two largest differences.

TN

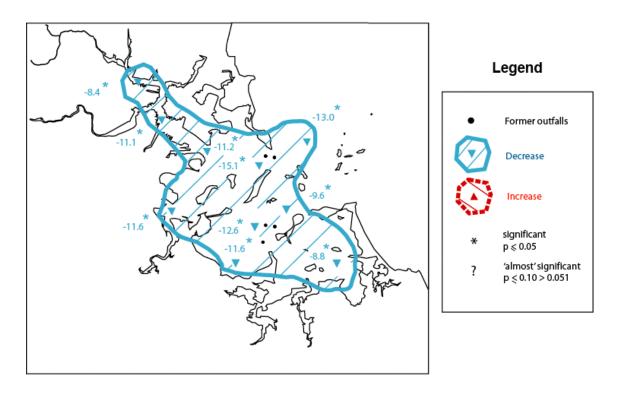


Fig. 4. Total nitrogen (TN). Differences in average concentrations (μ mol I⁻¹) between the first 36-months after offshore transfer and baseline, at the 10 stations sampled in the Harbor. 'Down-facing arrows' indicate stations at which subtraction of averages after transfer from averages before yielded negative values; 'up-facing arrows', indicate stations at which the opposite applied. 'Blue arrows' indicate differences that might be viewed as beneficial; 'red arrows', differences that might not be viewed as beneficial. 'Asterisks' are used to identify the stations at which the differences between the two periods were significant (p = or < 0.05). Hatched areas are used to enclose the stations at which the differences were significant; the hatched areas are not intended to serve as contours.

During each of the three 12-months that made up the 36-months, average TN concentrations were also significantly lower than baseline at all 10 stations (Fig. 5). The lowered concentrations, in both the North Harbor and South Harbor, and during all three 12-months, are confirmed in Figure 6. The plot also shows the shift in concentrations between the two regions after inter-island transfer in mid-1998. It also shows that the

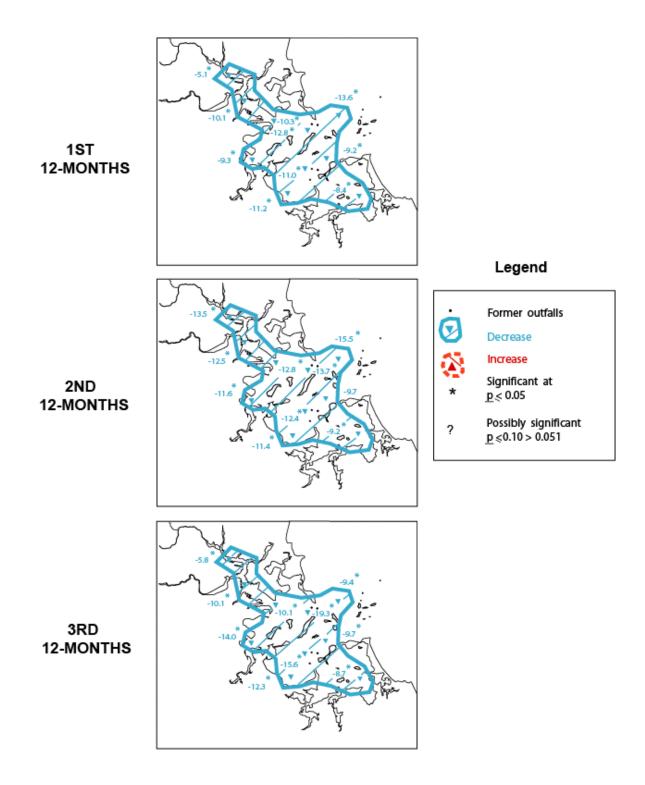


Fig. 5. Total nitrogen (TN). Changes in average concentrations (umol l ⁻¹) during each of the first, second and third 12-months after transfer.

The changes that followed both sets of transfers were superimposed on a background decrease in TN through the study.

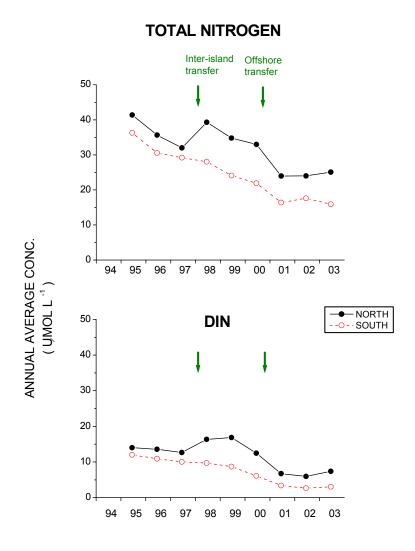


Fig. 6. <u>Changes in annual average TN and DIN in the North Harbor and South Harbor regions of Boston Harbor.</u> 'North Harbor' includes Stations 137, 138 and 024 in the Inner Harbor + Stations 106, 140 and 142 in the North West Harbor. The 'South Harbor' includes Stations 077, 139 and 141 in the Central Harbor region and Station 124 in the South East Harbor region.

Fractions of TN. For 4 of the 5 fractions of TN that we monitored, Harbor-wide averages after transfer were significantly different, and lower than baseline (Table 3).

The four fractions included dissolved inorganic nitrogen (DIN), ammonium (NH₄), nitrate + nitrite (NO₃₊₂) and particulate nitrogen (PN). The largest difference was observed for DIN, and specifically the NH4-fraction of the DIN. These too were the largest fractions of TN in the wastewater discharged to the Harbor during baseline (Taylor 2003).

For DIN, average concentrations for the 36-months were -7.0-µmol 1⁻¹ lower than baseline. This difference, which was equivalent to 59% of average concentrations during baseline, contributed ca. 70% of the decrease we saw for TN. It was also similar to the difference of -0.86-µmol 1⁻¹ we estimated from the decrease in DIN loadings; again, the difference between the observed and estimated differences was unlikely significant.

For NH₄, the difference between the two periods was -5.2- μ mol l⁻¹ (or -82% of baseline), for NO₃₊₂, -1.7- μ mol l⁻¹ (or -31%), and for PN, -1.9- μ mol l⁻¹ (or -31%). NH₄ contributed 74% of the difference we saw for DIN, and NO₃₊₂, the remaining 26%. (DIN contributed 70% of wastewater-TN, and NH₄, 94%, and NO₃₊₂, 6% of DIN discharged to the Harbor during baseline; Taylor 2003).

As for TN, average DIN concentrations during the 36-months were also significantly lower than baseline at all 10 stations (Fig. 7). At the individual stations, the sizes of the differences ranged from -5.9-µmol l⁻¹ to -8.2-µmol l⁻¹. Again, the two stations off of Deer Island, showed some of the largest, and in this case, two of the three largest decreases in DIN.

Nature of the N pool. As a result of the different size changes for the different N fractions, the nature of the N-pool of the Harbor water-column was also different after transfer (Fig. 8). Before transfer, DIN and DON contributed 38% and 42%, respectively, and approximately equal proportions of TN. After transfer, DIN contributed 22%, and DON, 57%, and more than one-half of the TN.

DIN

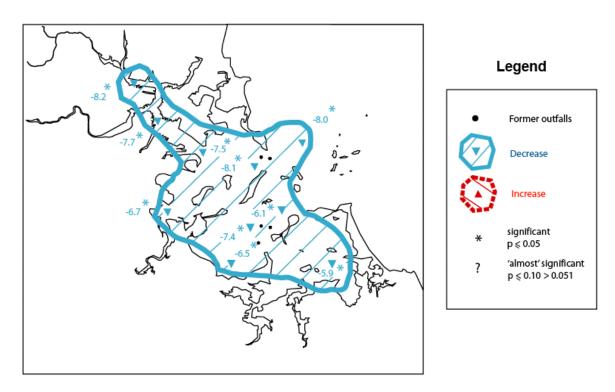


Fig. 7. <u>Dissolved inorganic nitrogen (DIN)</u>. Differences in average concentrations (µmol I ⁻¹) between the first 36-months after offshore transfer and baseline.

The nature of the DIN fraction of the N-pool was also changed. Before transfer, NH_4 contributed 53% of DIN, after transfer its percent contribution was reduced to 21%. NO_{3+2} contributed 47% of DIN before transfer, and 79% after. Before transfer, most of the DIN was contributed by the reduced fraction (NH_4); after transfer, the oxidized fractions (NO_{3+2}) contributed the bulk of the smaller pool.

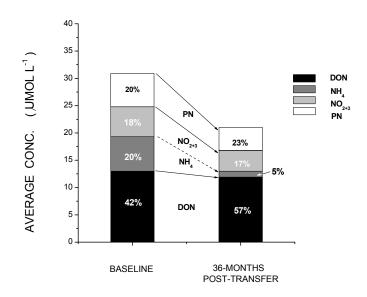


Figure 8. Nitrogen pool. Comparison of the nature of the TN pool of the Harbor water column for the periods before and 36-months after offshore transfer. Values in bars are percent contributions of the different constituents to the total pool.

Phosphorus

Total phosphorus (TP). We were also able to detect significant difference between the 36-months and baseline, for Harbor-wide average concentrations of TP (Table 5). During baseline, TP averaged $2.06 \pm 0.32 \, \mu \text{mol I}^{-1}$; during the 36-months, it averaged $1.47 \pm 0.29 \, \mu \text{mol I}^{-1}$. The difference of -0.58-μmol I⁻¹ was equivalent to -28% of baseline. The -28% difference was slightly smaller than the -32% difference we saw for TN.

As for TN, the difference observed between the two periods, in this case -0.58-µmol l⁻¹, was similar to the difference of -0.75-µmol l⁻¹, estimated from the decrease in TP loadings (Table 4). The lowered concentrations of TP in the Harbor during the 36-months are confirmed in the time-series plot of TP in Figure 9. Also shown in this plot is the persistence of the seasonal cycle of TP during the 36-months.

Table 5. <u>Phosphorus concentrations</u>. Comparison of volume-weighted Harborwide average concentrations between the 36 months after transfer, and baseline.

Variable	Average values	Average values during	
	Baseline	36-months	baseline and 36-months
TP (μmol l ⁻¹)	2.06 ± 0.32 (67)	1.47 ± 0.29 (36)	-0.58 (-28%)*
DIP (μmol l ⁻¹)	1.05 ± 0.37 (68)	0.65 ± 0.27 (36)	-0.40 (-38%)*
DOP (μmol l ⁻¹)	0.39 ± 0.24 (61)	0.37 ± 0.15 (36)	-0.01 (-3%)
PP (μmol 1 ⁻¹)	0.58 ± 0.18 (61)	0.45 ± 0.12 (36)	-0.13 (-22%) *
DIP as % TP	51 ± 16 (61)	44 ± 14 (36)	-7 (-14%)

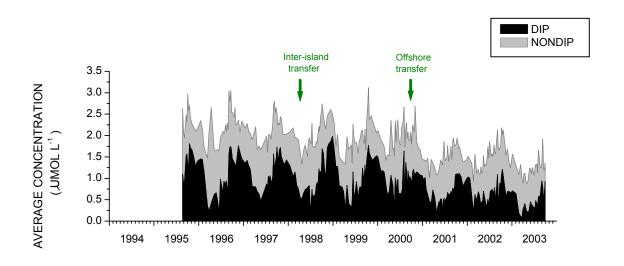


Figure 9. Total phosphorus (TP) partitioned into the dissolved inorganic phosphorus (DIP) and non-DIP fractions. Values are survey average, volume-weighted Harbor-wide averages.

At all 10 stations, average TP concentrations during the 36-months were also significantly lower than baseline (Fig. 10). The differences at the individual stations ranged in size from -0.4-µmol l⁻¹ at Station 124, to -0.8-µmol l⁻¹ at Station 142. Average TP concentrations were also significantly lower than baseline at all 10 stations, during each of the three 12-months that made up the 36-months (Fig. 11).

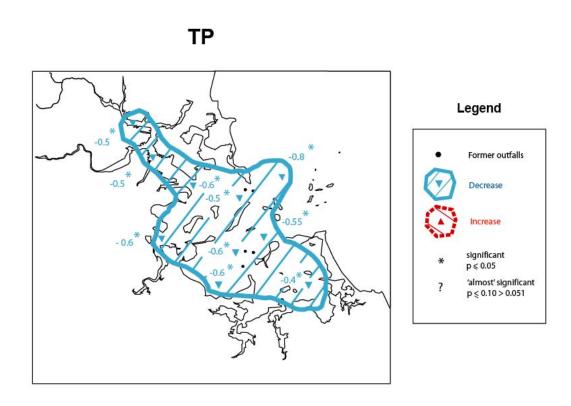


Fig. 10. <u>Total phosphorus (TP).</u> Differences in average concentrations (µmol I ⁻¹) between the baseline period and the 36-month period after offshore transfer.

Other P fractions. For two of the three fractions of TP that we monitored - dissolved inorganic phosphorus (DIP) and particulate phosphorus (PP), Harbor-wide average concentrations were also significantly lower during the 36-months than baseline. As for N, concentrations were lowered most for the dissolved inorganic fraction, DIP. During the 36-months, average DIP concentrations were -0.40-μmol 1⁻¹ lower than baseline.

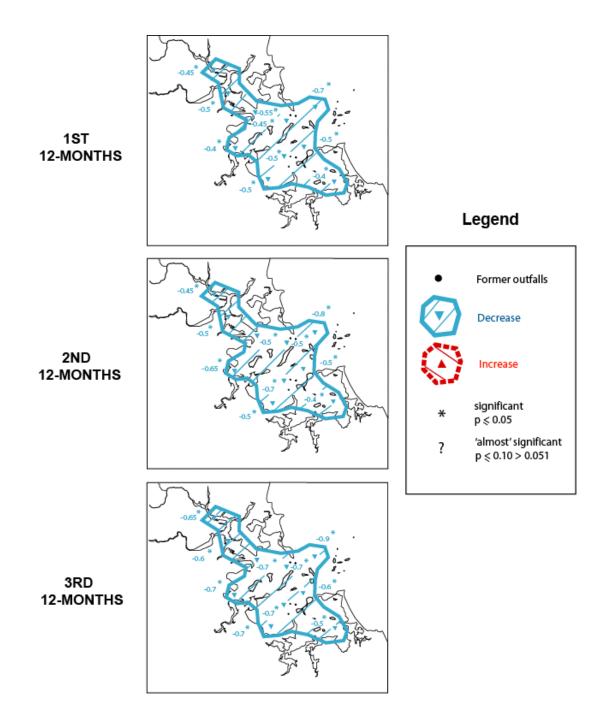


Fig. 11. Total phosphorus (TP). Changes in average concentrations (µmol l ⁻¹) during each of the first, second and third 12-months after offshore transfer.

This, which was equivalent to -38% of average baseline concentrations, was identical to the difference of -0.40- μ mol l⁻¹ we estimated from the decrease in wastewater-DIP loadings. The difference of -0.40- μ mol l⁻¹ accounted for 69% of the difference we saw for TP; this was in the same order as the 57% contribution that DIP made to TP in the wastewater discharged to the Harbor during baseline (Taylor 2003).

For DIP, average concentrations were also significantly lower during the 36-months than baseline at all 10 stations (Fig. 12). The differences at the 10 stations ranged in size from -0.33-µmol l⁻¹ (Station 140), to -0.47-µmol l⁻¹ (Station 137). As for DIN, the two stations off of Deer Island (Stations 106 and 142) showed two of the three largest decreases in DIP.

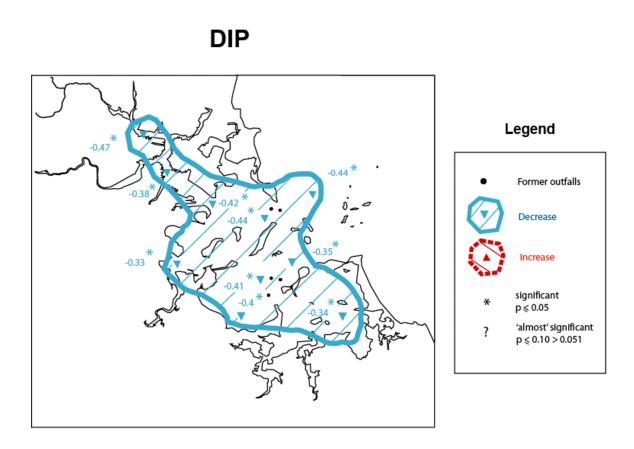


Fig. 12. Dissolved inorganic phosphorus (DIP). Differences in average concentrations (µmol ⁻¹) between the first 36-months after offshore transfer and baseline.

Differences in the P-pool. As for N, the nature of the TP-pool of the Harbor water column was also different after transfer (Fig. 13). Before transfer, DIP contributed 55%, and the bulk of TP. After transfer, its percent contribution to the now-smaller TP-pool was 44%. Unlike for N, where the DON fraction became the single largest fraction of the total-pool after transfer, for P, the DIP fraction remained the largest fraction after transfer.

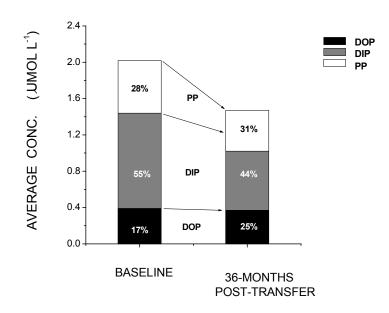


Figure 13. Phosphorus pool. Differences in the nature of the P pool of the Harbor water-column, before and 36-months after offshore transfer. Values in bars are percent contributions of the different constituents to the total P pool.

DOP contributed 17% of TP before transfer, and 25% after. The 25% contribution of DOP after transfer was smaller than the 57% that DON contributed to TN post-transfer. Both before and after transfer, PP contributed more of the TP-pool than did PN to TN. As for N, however, the percent contribution was similar during the two period; 28% of TP before transfer, and 31% after.

Molar ratios of N:P

Molar TN:TP. Harbor-wide average molar ratios of TN:TP during the 36-months were also significantly lower than baseline (Table 6, Fig. 14). During baseline, ratios averaged $15.2 \pm 3.2:1$; during the 36-months, they averaged $13.9 \pm 2.6:1$. The difference of -1.3:1 was equivalent to -9% of baseline, and was significant. The -9% difference was smaller than the -32% and -28% differences for TN and TP.

Table 6. <u>Molar ratios of N:P.</u> Comparison of volume-weighted Harbor-wide average ratios between the 36 months and baseline.

Variable	Average value	Average values during	
	Baseline	36-months	baseline and 36-months
TN:TP	15.2 ± 3.2 (61)	13.9 ± 2.8 (36)	-1.3 (-9%)*
DIN:DIP	$11.4 \pm 5.2 \\ (68)$	7.6 ± 5.9 (36)	-3.8 (-33%) *
DON:DOP	43 ± 33 (60)	35 ± 12 (36)	-7 (-17%)
PN:PP	10.0 ± 2.3 (61)	9.6 ± 1.8 (35)	-0.4 (-4%)

At the individual stations, average TN:TP ratios were significantly lower than baseline at 6 of the 10 stations; c.f. all 10 for TN and TP (Fig. 15). The 6 stations that showed the significant decreases were all located in the Outer Harbor. At the 6 stations, the differences ranged in size from -1.0:1 to -4.0:1. As for TN and TP, the two stations off of Deer Island showed the two largest decreases.

TN: TP

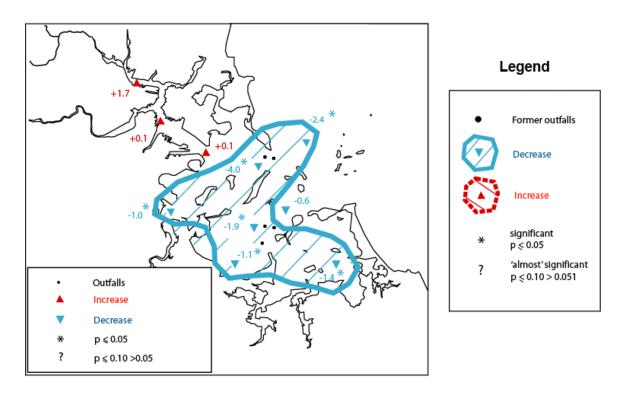


Fig. 15. Molar TN:TP. Differences in average molar ratios between the first36-months after offshore transfer and baseline.

During each of the three 12-months that followed transfer, average ratios of TN:TP were again significantly different from baseline only at certain stations; c.f TN and TP (Fig. 16). The stations that showed significant differences in turn differed between the three 12-months. Only at the two stations off of Deer Island were the differences, in all cases decreases, significant during all three of the 12-months.

Other molar N:P ratios. For only one of the three other N:P ratios that we monitored, specifically DIN:DIP, were Harbor-wide averages for the 36-months significantly different from baseline (Table 6, Fig. 14). During baseline, DIN:DIP averaged $11.4 \pm 5.2:1$; during the 36-months, they averaged $7.6 \pm 5.9:1$. The difference of -3.8:1 was equivalent to -33% of baseline, and was significant.

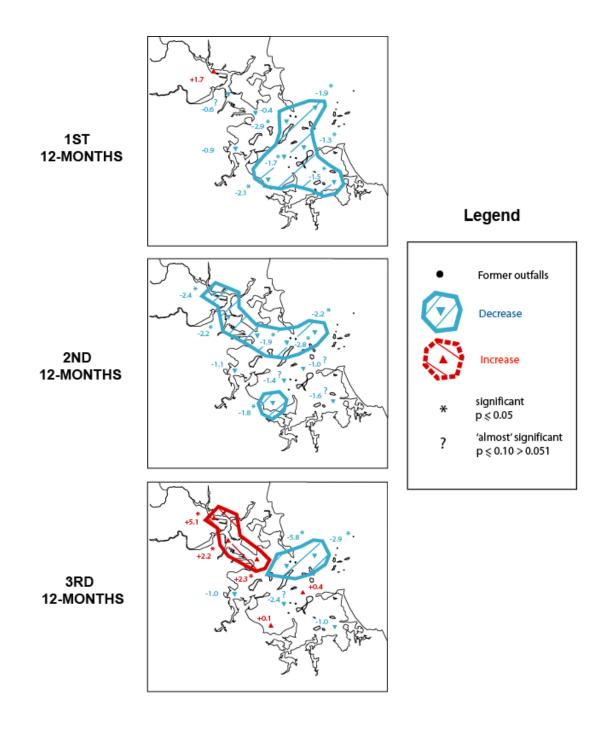


Fig. 16. Molar TN:TP. Changes in average ratios during each of the first, second and third 12-months after transfer.

For both of the remaining ratios, DON:DOP and PN:PP, subtraction of the Harbor-wide averages for the 36-months from the equivalent averages during baseline, yielded

negative values suggestive of decreases. In neither case, however, were the differences significant at p = 0.05 or less.

At the individual stations, average DIN:DIP ratios during the 36-months were significantly lower than baseline at 9 of the 10 stations (Fig. 17). At the 9 stations, the differences ranged in size from -1.0:1 to -4.8:1. Only at Station 137 in the upper Inner Harbor were average ratios during the 36-months not significantly lower than baseline.

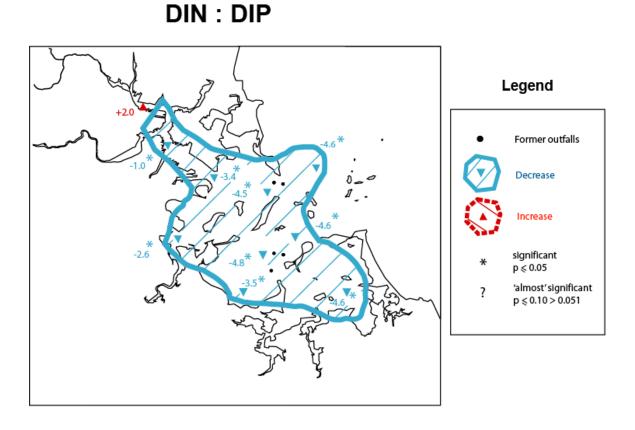


Fig. 17. Molar ratios of DIN:DIP. Differences in average ratios between the 36-months after offshore transfer and baseline.

Phytoplankton biomass (chlorophyll-a)

We were also able to detect significant differences between the 36-months and baseline for all three fractions of chlorophyll-<u>a</u> (chl-<u>a</u>) that we monitored; total chl-<u>a</u>, acid-corrected chl-<u>a</u>, and phaeophytin. (Table 7). Unlike for N and P, however, the differences were confined to particular seasons of the year, and regions of the Harbor. For the most part, the differences were also smaller than for N or P.

Table 7. Chlorophyll-a and phaeophytin. Comparison of volume-weighted Harborwide average concentrations between the 36 months after transfer and baseline.

Variable	Average values during		Difference between baseline and
	Baseline	36-months	36-months
	YEAR-ROU	ND DATA	
Total chl- <u>a</u> (μg l ⁻¹)	6.5 ± 4.1 (61)	5.2 ± 2.8 (36)	-1.3 (-20%)
Acid-corrected chl- <u>a</u> (μg l ⁻¹)	4.7 ± 3.1 (61)	3.8 ± 2.6 (36)	-0.9 (-19%)
Phaeophytin (μg l ⁻¹)	1.9 ± 1.3 (61)	1.4 ± 0.5 (36)	-0.5 (-26%) *
	SUMMER A	LONE ^a	
Total chl- <u>a</u> (μg l ⁻¹)	9.7 ± 3.8 (90)	6.3 ± 1.9 (49)	-3.4 (-35%) *
Acid-corrected chl- <u>a</u> (μg l ⁻¹)	6.9 ± 3.5 (91)	4.4 ± 1.6 (50)	-2.5 (-36%) *
Phaeophytin (µg 1 ⁻¹)	2.8 ± 1.3 (89)	1.8 ± 0.4 (48)	-1.0 (-36%) *

^a summer averages are averages of individual weekly surveys, rather than averages of average monthly values. 'Summer' refers to June 1 through September 30.

For total chl-a and acid-corrected chl-a, Harbor-wide average concentrations for the full

36-months were not significantly different from baseline. For both fractions, however, average concentrations during the summers during the 36-months were significantly lower than baseline. For phaeophytin, average concentrations for both the full 36-months and summers during the 36-months were lower than baseline.

During the 36-months, Harbor-wide average total chl- \underline{a} was -3.4- μ g l⁻¹, or-35%, lower than baseline. For acid-corrected chl- \underline{a} , the difference was -2.5- μ g l⁻¹, or -36% of baseline; this accounted for ca. three-fourths of the difference we see for total chl- \underline{a} . The remaining approximately one-fourth, or -1.0- μ g l⁻¹, was contributed by phaeophytin.

The time-series plot of total chl-<u>a</u> partitioned in acid-corrected chl-<u>a</u> and phaeophytin in Figure 18, confirms the lowered concentrations of especially acid-corrected chl-<u>a</u>, during summers during the 36-months. It also shows that unlike for N or P, the sizes of the decreases differed among the three summers that followed transfer.

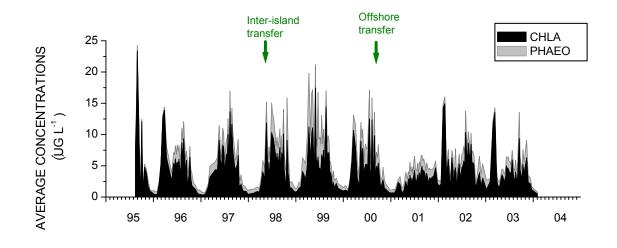


Fig. 18. <u>Total chl-a partitioned into the acid-corrected and phaeophytin fractions.</u> Values are survey average volume-weighted, Harbor-wide averages.

During two of the first three springs that followed transfer, and specifically during spring 2002 and 2003, the Harbor showed large peaks in acid-corrected chl-a. Similar spring-

peaks, presumably caused by spring phytoplankton blooms, were observed during certain years during baseline, for instance in 1996 and 2000, indicating that the two peaks after transfer were not transfer-related.

Average concentrations of acid-corrected chl-<u>a</u> during the full 36-months were significantly lower than baseline at only 1 of the 10 stations; c.f. all 10 stations for TN and TP (Fig. 19 top panel). During summers during the 36-months, however, average concentrations were significantly lower than baseline at all 10 stations (bottom panel). The differences at the 10 stations ranged in size from -0.7-µg l⁻¹ to -3.6-µg l⁻¹.

Unlike for TN and TP, the number of stations at which acid-corrected chl-<u>a</u> was lowered, differed among the three summers that followed transfer (Fig. 20). The number of stations at which concentrations were significantly lowered was smallest during summer 2002, and largest during summer 2001. Thus, not only were the differences for chl-<u>a</u> smaller than for N and P, but the differences were also more variable year-to-year.

As for N and P, concentrations of acid-corrected chl-<u>a</u> in both the North Harbor and South Harbor regions were lower after transfer than before (Fig. 21). As for N, the differences in the two regions that followed transfer followed an earlier shift in concentrations in the two regions after inter-island transfer in mid-1998. The size of the shift after inter-island transfer was not as large for chl-<u>a</u> as for N and P.

Suspended solids and water clarity

Total suspended solids (TSS) and particulate organic carbon (POC). As for year-round chl-<u>a</u>, Harbor-wide average concentrations of TSS during the 36-months were not significantly different from baseline (Table 8). During baseline, TSS averaged 3.6 ± 1.2 mg l⁻¹. During the 36-months, it averaged 3.8 ± 1.1 mg l⁻¹. The difference of +0.25 mg l⁻¹ was equivalent to +7% of baseline, and was not significant.

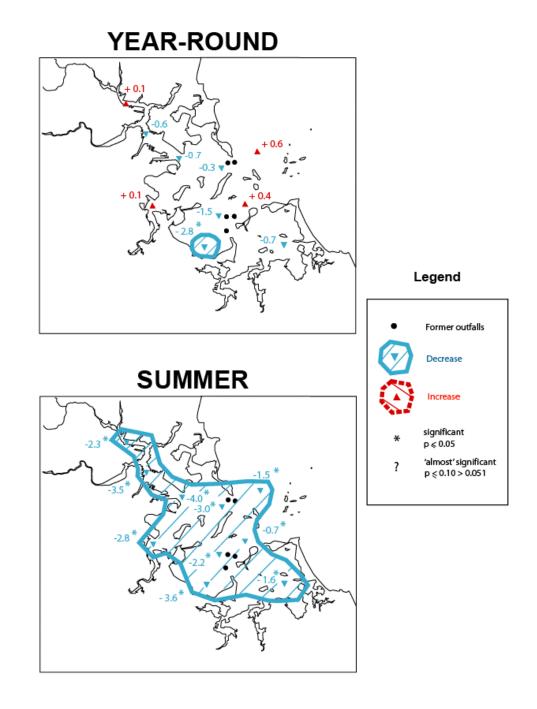


Figure 19. Acid-corrected chl-a. Spatial patterns of differences in year-round (top) and summer (bottom) average concentrations. Units are $\mu g I^{-1}$.

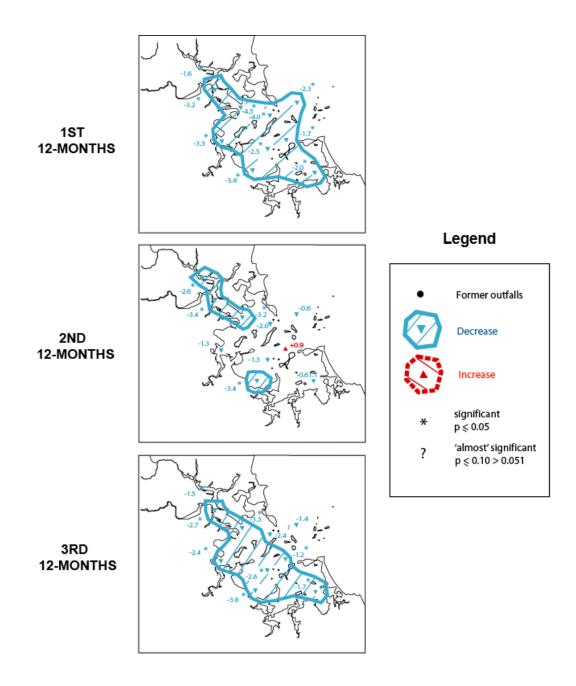


Fig. 20. Summer chlorophyll-a (chl-a). Changes in average summer concentrations (μ g l⁻¹) during each the first, second and third 12-months after transfer.

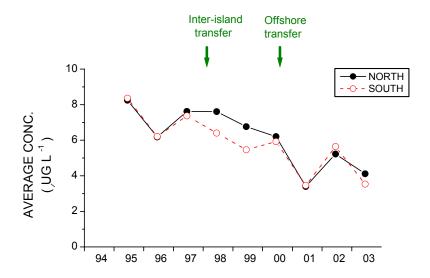


Fig. 21. <u>Average summer chl-a concentrations</u> in the North Harbor and South Harbor regions.

The positive difference of +0.25 mg l⁻¹ was unlike the negative value of -0.35-mg l⁻¹ estimated from the decrease in TSS loadings (Table 4). Both estimates were however small, and probably not significantly different from one another. The fact that TSS concentrations during the 36-months were no lower than baseline is confirmed in Figure 22.

For POC, unlike for TSS, but as for TN and TP, Harbor-wide average concentrations were significantly lower during the 36-months than baseline. During baseline, POC averaged $42.9 \pm 16.1 \, \mu \text{mol I}^{-1}$; during the 36-months it averaged $30.8 \pm 10.3 \, \mu \text{mol I}^{-1}$. The difference of -12.1- μ mol I⁻¹, which was significant, was similar to the difference of -15.6- μ mol I⁻¹ estimated from the decrease in wastewater POC loadings.

Table 8. Solids, POC and water clarity. Comparison of volume-weighted Harborwide average values between the 36 months after transfer and baseline.

Variable	Average during baseline	Average during 36-months	Difference between baseline and 36-months	
	SOLID	<u>S</u>		
TSS (mg l ⁻¹)	3.6 ± 1.2 (55)	3.8 ± 1.1 (36)	+0.25 (+7%)	
POC (μmol l ⁻¹)	42.9 <u>+</u> 16.1 (61)	30.8 ± 10.3 (36)	-12.1 (-28%)*	
POC as %TSS (by weight)	15 <u>+</u> 5 (48)	9 <u>+</u> 4 (36)	-6 (-42%)*	
	WATER C	LARITY		
<u>k</u> (m ⁻¹)	$0.53 \pm 0.12 \\ (73)$	0.52 ± 0.11 (36)	-0.01 (-2%)	
Secchi depth (m)	2.6 ± 0.6 (85)	2.7 ± 0.7 (36)	+0.1 (+4%)	

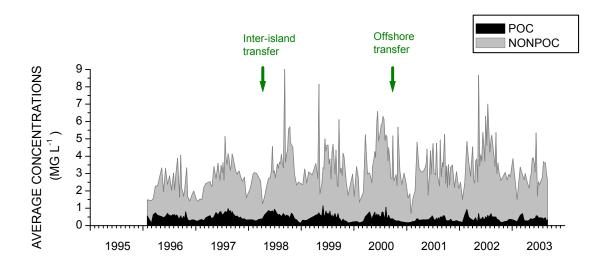


Figure 22. <u>Total suspended solids (TSS)</u> partitioned into the particulate organic carbon (POC) and non-POC fractions.

The lowered concentrations of POC during the 36-months are confirmed in the timeseries plot in Figure 23. The plots also show that for POC, as for chl-<u>a</u>, concentrations during the 36-months were lower than baseline especially during the summers. Unlike for chl-<u>a</u>, however, the differences for POC were sufficient to be significant for the full 36-months.

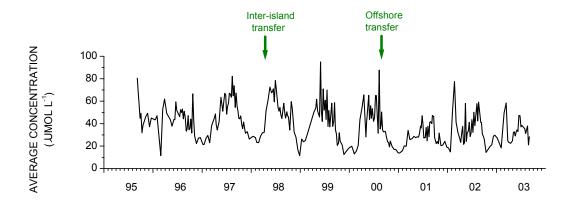


Fig. 23. Particulate organic carbon (POC). Time-series plot of volume-weighted, Harbor-wide average concentrations.

Both before and after transfer, POC contributed only a relatively small proportion of the TSS. The percent contribution was however significantly lower during the 36-months after transfer, than before. Before transfer, POC contributed 15 ± 5 % of TSS; during the 36-months, it contributed 9 ± 4 %. The difference of -6% was equivalent to -42% of baseline, and was significant.

Unlike for TN and TP, for TSS, average concentrations during the 36-months were significantly lower than baseline at only 1 of the 10 stations; specifically Station 137 in the upper Inner Harbor (Fig. 24). In fact at 5 of the 10 stations, all in the Outer Harbor, average TSS concentrations during the 36-months were significantly greater than baseline.

Fig. 24. Total suspended solids (TSS). Differences in average concentrations (mg l -1) between the first 36-months after offshore transfer and baseline.

For POC, as for TN and TP, average concentrations during the 36-months were significantly lower than baseline at all 10 stations (Fig. 25). The differences at the 10 stations ranged in size from -5.7-μmol l⁻¹ (at Station 137), to -14.6-μmol l⁻¹ (at Station 077). Unlike for TN and TP, the decreases were not necessarily largest off of Deer Island.

Water clarity. For both of the water-clarity variables that we monitored (reciprocal attenuation coefficient, \underline{k} , and secchi depth), Harbor-wide averages for the full 36-months were not significantly different from baseline (Table 8). This was as for year-round chl- \underline{a} and TSS. As can be seen in Figure 26, for both \underline{k} and secchi depth, average values during the 36-months fell within the range seen during baseline.

POC

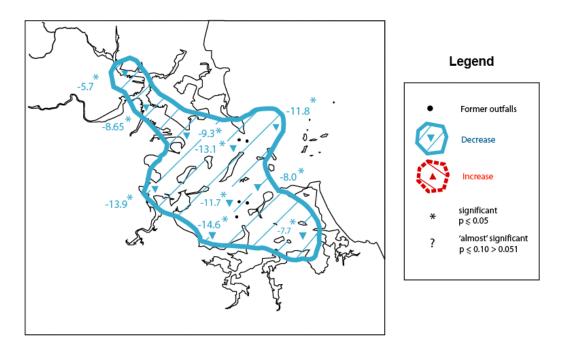
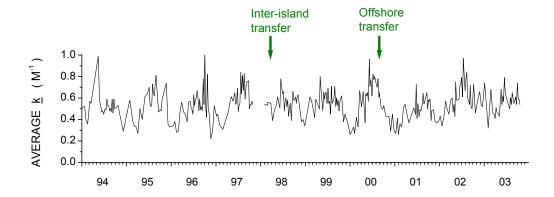


Fig. 25. <u>Particulate organic carbon (POC).</u> Differences in average concentrations (µmol I ⁻¹) between the first 36-months after offshore transfer and baseline.

During baseline, \underline{k} averaged $0.53 \pm 0.12 \text{ m}^{-1}$; during the 36-months, it averaged $0.52 \pm 0.12 \text{ m}^{-1}$. The difference of -0.01-m^{-1} was equivalent to -2% of baseline, and was not significant. For secchi depth, values averaged $2.6 \pm 0.6 \text{ m}$ during baseline, and $2.7 \pm 0.7 \text{ m}$ during the 36-months. Subtraction yielded a value of $\pm 0.1 \text{ m}$ (or $\pm 4\%$ of baseline), which as for \underline{k} , was not significant.

At none of the 10 stations were average \underline{k} values during the 36-months significantly different from baseline (Fig. 27 top). At two stations, the differences, one negative and the other positive, were 'almost' significant ($\underline{p} = \text{or} < 0.10$, but > 0.5). For secchi depth, the differences were significant at 1 station, and almost significant at two others (Fig. 27, bottom).

ATTENUATION COEFFICIENT (k)



SECCHI DEPTH

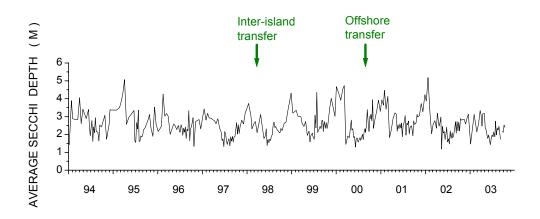
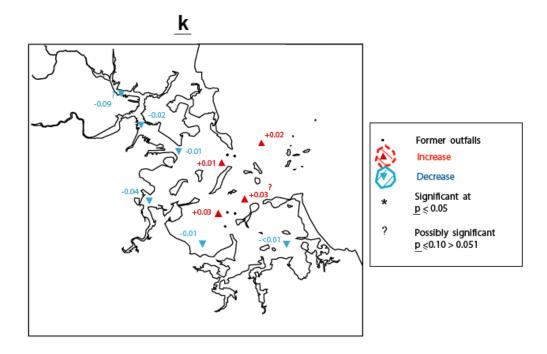


Fig. 26. Reciprocal attenuation coefficient and secchi depth. Time-series plot of volume-weighted, Harbor-wide average values.



SECCHI DEPTH

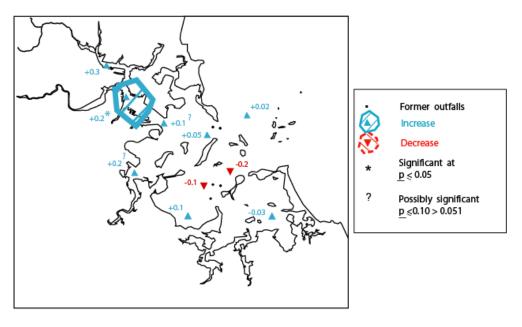
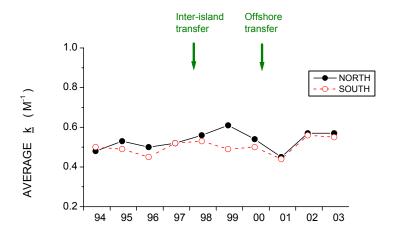


Fig. 27. Attenuation coefficient and secchi depth. Differences in average values between the first 36-months after transfer and baseline. Units are m⁻¹ for <u>k</u>, and m for secchi.

For both \underline{k} and secchi depth, average values during the 36-months, for both the North Harbor and South Harbor regions, fell within the range seen during baseline (Fig. 28). For both variables, but especially for secchi depth, values in the North Harbor and South Harbor regions differed between 'inter-island' transfer and 'offshore' transfer.

RECIPROCAL k



SECCHI DEPTH

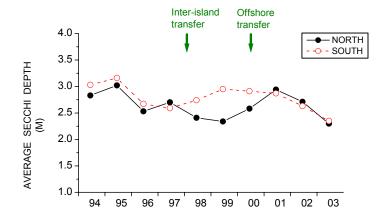


Fig. 28. Reciprocal k (top) and secchi depth (bottom). Changes in annual average values for the North Harbor and South Harbor regions of the Harbor.

Bottom-water dissolved oxygen (DO)

For neither of the DO variables that we monitored, bottom-water DO concentrations or DO % saturation, was Harbor-wide averages for the full 36-months significantly different from baseline (Table 9). For both variables, however, the differences were significant if we confined the analysis to 'mid-summer'; 'mid-summer' as used here refers to August plus September.

Table 9. Bottom-water dissolved oxygen (DO). Comparison of volume-weighted Harbor-wide average values between the 36-months after transfer and baseline.

Variable	Average values	Average values during		
	Baseline	36-months	baseline and 36-months	
DISSO	OLVED OXYGEN (D	O) (YEAR-RO	<u>OUND)</u>	
DO (mg l ⁻¹)	8.6 ± 1.2 (40)	9.1 <u>+</u> 1.4 (36)	+0.6 (+6%)	
DO (% saturation)	94.0 ± 6.3 (40)	93.3 ± 5.4 (36)	-0.7 (-1%)	
b DISS	SOLVED OXYGEN (DO) (MID-SU	MMER)	
DO (mg l ⁻¹)	7.0 ± 0.7 (33)	7.5 ± 0.6 (22)	+0.5 (+7%)*	
DO (% saturation)	87.4 ± 7.4 (34)	92.3 ± 7.4 (22)	+5.0 (+6%)*	

^a only data collected after May 1997, were used to compute baseline averages and to test for differences between baseline and 36-months.

^b average for the 'mid-summer' data were computed using data from individual sampling dates rather than the monthly averages used for the year-round data.

During baseline, mid-summer, bottom-water DO concentrations averaged 7.0 ± 0.7 mg l⁻¹. During the 36-months, they averaged 7.5 ± 0.6 mg l⁻¹. The difference of +0.5 mg l⁻¹ was equivalent to +7% of baseline, and was significant. For DO % saturation, values during mid-summer during baseline averaged 87.4 ± 7.4 %; during the 36-months, they averaged 92.3 ± 7.4 %. Again the difference, in this case, +5.0 % (or 6% of baseline), was significant.

The time-series plot of Harbor-wide average, bottom-water DO concentrations in Figure 29 shows concentrations for the full 36-months were not significantly different from baseline. During all three mid-summer periods after transfer, however, average concentrations were greater than average during all equivalent periods during baseline.

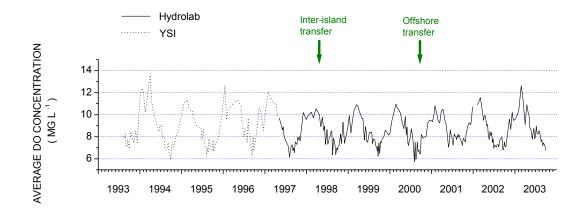


Figure 29. <u>Bottom-water DO concentrations</u>. Time-series plot of volume-weighted, Harbor-wide average concentrations through the baseline and 36-months after offshore transfer.

At the individual stations, year-round average concentrations of DO during the 36-months were significantly greater than baseline at 4 stations, all located in the Inner Harbor extending down into the North West Harbor (Fig. 30 top). For mid-summer concentrations of DO, the increases were significant at 7 stations; the same four that

showed increases for the year-round data, plus three others in the Central Harbor (bottom).

DO CONCENTRATION

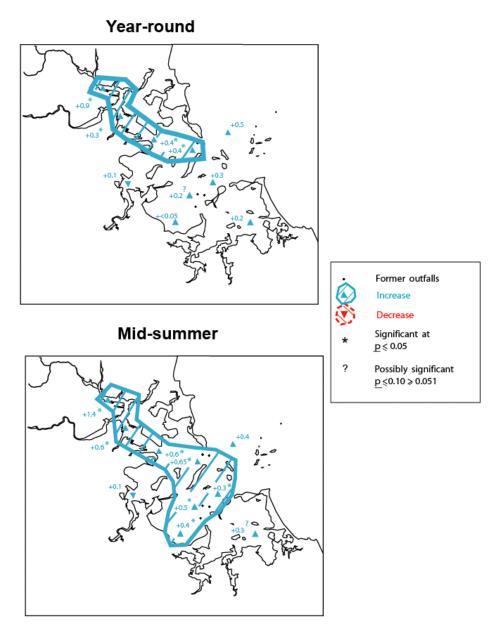


Fig. 30. Year-round (top) and mid-summer (bottom) bottom-water DO concentrations. Differences in average concentrations between the first 36-months after transfer and baseline. Units = mg I⁻¹

Unlike for TN, but as for summer acid-corrected chl-<u>a</u>, the numbers of stations at which mid-summer DO concentrations were significantly different from baseline differed

among the three 12-months (Fig. 31). The pattern among the three 12-months was however, different from that we saw for summer chl-<u>a</u>.

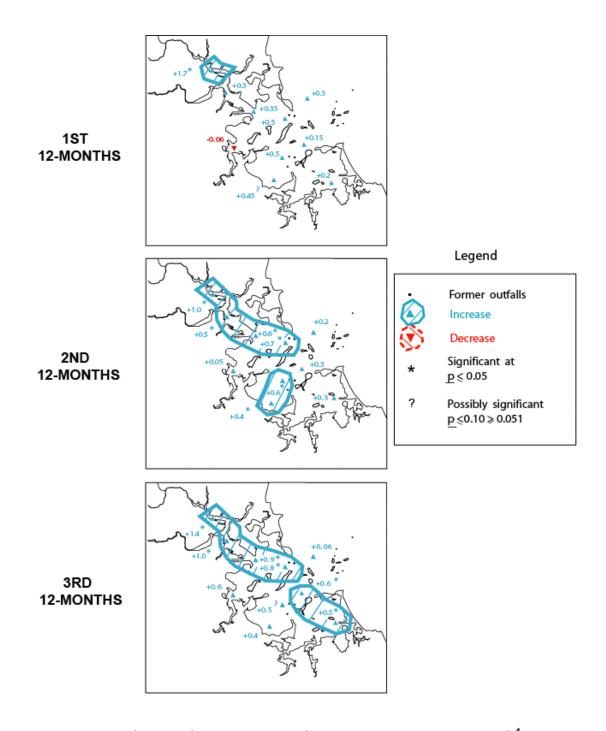


Fig. 31. Mid-summer, bottom-water DO. Changes in average concentrations (mg I⁻¹) during each of the first, second and third 12-months after transfer.

Salinity and water temperature

Salinity. For Harbor-wide average salinity, values during the 36-months were significantly greater than baseline (Table 10). During baseline, salinity averaged 30.3 ± 1.1 . During the 36-months, it averaged 30.7 ± 1.1 ppt. The difference of ± 0.4 ppt was

Table 10. <u>Salinity and temperature</u>. Comparison of volume-weighted Harbor-wide average values between the 36 months after transfer and baseline.

Variable	Average values	during	Difference between baseline and
	Baseline	36-months	36-months
Salinity (ppt)	30.3 ± 1.1 (75)	30.7 ± 1.1 (36)	+0.4 (+1%)*
Water temperature (°C)	9.9 ± 5.8 (75)	9.6 ± 5.1 (36)	-0.3 (-3%)

equivalent to +1% of baseline, and was significant. The difference was, however, too small to discern from the time-series plot of Harbor-wide average salinity in Figure 32.

At the individual stations, average salinity during the 36-months was significantly greater than baseline at 6 of the 10 stations (Fig. 33). Four of the 6 stations that showed the increases were located in the South Harbor; the other two in the outer North Harbor. The increases at the 6 stations ranged in size from +0.4 ppt to +0.8 ppt.

Water temperature. Unlike for salinity, Harbor-wide average water-temperature during the 36-months was not significantly different from baseline (Table 9). During baseline, water temperature averaged 9.9 ± 5.8 °C. During the 36-months, it averaged 9.6 ± 1.00 °C.

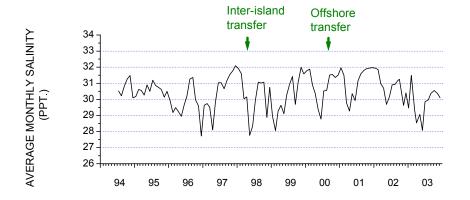


Fig. 32. Salinity. Time-series plot of volume-weighted, Harbor-wide averages.

SALINITY

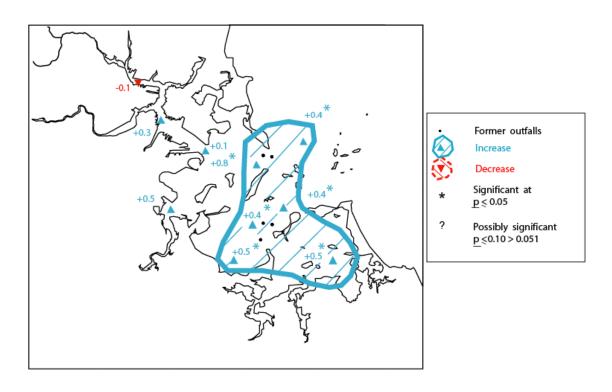


Fig. 33. **Salinity.** Differences in average values (ppt) between the 36-months after transfer and baseline, at each of the 10 sampling stations.

Water temperature. Unlike for salinity, Harbor-wide average water-temperature during the 36-months was not significantly different from baseline (Table 9). During baseline, water temperature averaged 9.9 ± 5.8 °C. During the 36-months, it averaged 9.6 ± 5.1 °C. The difference of -0.3-°C was equivalent to -3% of baseline, and was not significant.

Summary of the differences during the 36-months

Table 11 summarizes for 19 water-quality variables, the differences we observed between the 36-months and baseline. Note, 'solid arrows' signify differences that were significant for the Harbor as a whole; 'hollow arrows', differences that were significant only at certain stations, and 'dashes', differences that were significant for neither the Harbor as a whole nor individual stations.

The values adjacent to the arrows are the differences in Harbor-wide averages between the 36-months and baseline; the values in parentheses are these differences expressed as percent of Harbor-wide averages during baseline. For further explanations of the notations used in the Table, see the footnote to the Table. Arrows are color-coded to provide a qualitative assessment of the differences.

For 15 of the 19 variables, Harbor-wide average values during the 36-months were significantly different from baseline. These included year-round concentrations and ratios of N and P, year-round concentrations of POC, summer concentrations of chl-a, mid-summer levels of DO, and year-round salinity.

For two of the 19 variables, year-round TSS and year-round secchi depth, the differences between the two periods were not significant for the Harbor as a whole, but were significant at individual stations in the Harbor. For only one variable, year-round reciprocal <u>k</u>, were the differences between the two periods not significant for both the Harbor as a whole, and the individual stations.

Table 11. Summary of differences in Harbor water-quality between the 36-months and baseline.

VARIABLE	CHANGE DURIN 36-MONTHS	G
TN (umol I ⁻¹)		-10.0 (-32%)
DIN (umol I ⁻¹)		-7.0 (-59%)
DIN as %TN	* * * * * * * * * * * * * * * * * * *	-14 (-37%)
TP (umol I ⁻¹)		-0.58 (-28%)
DIP (umol l ⁻¹)		-0.4 (-38%)
DIP as % TP	\triangle	-7 (-14%)
TN:TP		-1.3 (-9%)
DIN:DIP	-	-3.8 (-33%)
TOTAL CHL- <u>A</u> (ug I ^{- 1}) (summer)		-3.4 (-35%)
'ACTIVE' CHL- <u>A</u> (ug I ⁻¹) (summer)		-2.5 (-36%)
PHAEOPHYTIN (ug I -1) (summer)		-1.0 (-36%)
POC (umol I ⁻¹)		-12.1 (-28%)
TSS (mg I ^{- 1})	abla	+0.25 (+7%)
POC as % TSS		-6.0 (-42%)
<u>k</u> (m ⁻¹)		-0.01 (-2%)
SECCHI DEPTH (m)	合	+0.1 (+4%)
DO CONC. (mg I ⁻¹) (mid-summer)	1	+0.5 (+7%)
DO % SAT. (mid-summer)	1	+5.0 (+6%)
SALINITY (ppt)		+0.4 (+1%)

Up-facing arrows indicate increases, down-facing arrows, decreases. Blue arrows indicate changes that might be interpreted as 'improvements'. Red arrows indicate changes that might be not be viewed as improvements. Gray hatched arrows denote differences that cannot at this time be assessed as beneficial or not.

DISCUSSION

Observed versus predicted changes

In this Section we compare the differences in Harbor water-quality observed during the 36-months, with the differences predicted to follow transfer by two sets of numerical models. The first set included two 3-D models, the Bays Hydrodynamic Model, BHM (Signell et al. 2000), and the Bays Eutrophication Model, BEM (HydroQual and Normandeau 1995). The second set included the 2-D box model used by Kelly (1998).

In the comparisons of observed - predicted changes conducted below, the changes predicted by the models have been used, in a sense, as 'standards', to determine whether offshore transfer was responsible for the changes. The use of the modeled changes for this purpose has been considered valid because both sets of models predicted the changes by 'numerically eliminating' the wastewater discharges to the Harbor.

In this report we consider the observed and predicted changes to be similar if the directions of the changes were the same, and the observed changes fell within a factor of 2.0 of the predicted changes. This relatively coarse comparison was necessary for two reasons: one, differences in locations/areas of the Harbor for which observed and predicted data were available; and, two, differences in boundary conditions and wastewater-nutrient inputs between the modeled and actual years.

3-D numeric model predictions. Table 12 compares for three variables, DIN, chl-<u>a</u> and DO, the difference observed for the Harbor as a whole for the full 36-months, and differences predicted by the BEM model for a single station at the mouth of the Harbor. The BEM model predictions are from HydroQual and Normandeau (1995), and apply to Station 2 used in their projections for the 'nearfield'; Station 2 lies between our Station 106 and 142 at the mouth of the Harbor.

Table 12. <u>Observed versus predicted changes.</u> Comparisons of the observed changes in average concentrations of DIN, chl-<u>a</u> and DO, with the changes predicted by the coupled hydrodynamic/water quality model BEM model, for the Harbor.

Variable	Observed			Predicted ^b		
	Baseline	36-months	Difference (%)	Baseline	Post-transfer	Difference (%)
DIN (μmol l ⁻¹)	11.8 ± 6.4 ^a (75)	$4.8 \pm 23.0^{\text{ a}}$ (24)	-7.0 (-59%) ^a	11.9 ± 5.5 ° (24)	5.1 ± 4.1 ° (24)	-6.8 (-57%) ^c
Chl- <u>a</u> (µg l ⁻¹) ^d	4.7 ± 3.1^{a} (61)	3.8 ± 2.8 ^a (24)	-0.9 (-19%) ^a	3.8 ± 2.1 ° (24)	2.3 ± 1.1 ° (24)	-1.5 (-39%) ^c
DO conc. (mg l ⁻¹)	8.6 ± 1.2^{a} (40)	9.1 ± 1.4 ^a (24)	+0.6 (+6%) ^a	9.2 ± 1.0 ° (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 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.

For DIN, the decrease we observed for the Harbor as a whole, of -7.0- μ mol l⁻¹ (or -59%), was almost identical to the decrease of -6.8- μ mol l⁻¹ (or -57%) predicted by the BEM model for Station 2. For year-round acid-corrected chl- α , the difference we observed, -0.9 μ gl⁻¹ (or -19%), was similar 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 difference of $+0.6 \text{ mg } 1^{-1}$ (or +6%) observed for the 36-months was also similar to the small difference of $+0.3 \text{ mg } 1^{-1}$ (or +4%) predicted by the BEM model. Again, for salinity, the observed increase of 0.4 ppt was similar, and in this case, almost identical to the increase of +0.5 ppt predicted by the BHM (Signell et al. (2000).

2-D numeric model. Table 13 compares for four variables (TN, DIN, DIP and TSS), the differences observed during the 36-months, and the differences predicted by Kelly (1998) for the North West Harbor. Note, the 'North Harbor' referred to by Kelly refers to the region we refer to as the 'North West Harbor'.

For TN, the difference we observed between the two periods for the North West Harbor of -13- μ mol l⁻¹ (or -38%), appears to have been slightly greater than the -6- μ mol l⁻¹ (or -24%) difference predicted by Kelly (1998). For DIN, the observed difference for the North West Harbor, -7.6- μ mol l⁻¹ (or -60%), was similar to the predicted difference, -5.5- μ mol l⁻¹ (or -50%).

For DIP, as for TN, the observed difference, in this case of -0.3- μ mol l⁻¹ (or -27%), was larger than the difference of -1.5- μ mol l⁻¹ (or -60%) predicted by Kelly. For DIN:DIP, however, the observed and predicted differences were similar; -4.6:1 and -5.5:1, respectively. For TSS, the observed difference of +0.4-mg l⁻¹ (or +11%) was unlike the predicted difference of -1.5 mg l⁻¹ (or -60%).

Table 13. <u>Observed differences versus differences predicted by Kelly (1998)</u>. Comparison of the observed and predicted difference in average concentrations of TN, DIN, DIP and TSS for the North West Harbor.

_	Th	is study	Kelly (1998)			
	Observed before	Observed 36-months	Difference	Observed before	Predicted post-transfe	Difference er
TN (μmol l ⁻¹)	33.8	20.8	-13 (-38%)	25	19	-6 (-24%)
DIN (μmol l ⁻¹)	12.7	5.1	-7.6 (-60%)	11	5.5	-5.5 (-50%)
DIP (μmol l ⁻¹)	1.1	0.7	-0.3 (-27%)	2.5	1.0	-1.5 (-60%)
TSS (mgl l ⁻¹)	3.7	4.2	+0.4 (+11%)	2.5	1.0	-1.5 (-60%)

The combination of the two sets of comparisons, indicate that for most of the variables for which both observed and predicted data were available, offshore transfer was likely responsible for much of the differences. For perhaps TN, DIP and TSS in the North West Harbor, background processes may have modified the differences predicted to follow transfer.

Conclusions

This study identifies, as it aimed to, a number of differences in water-quality in the Harbor between the first 36-months after offshore transfer and baseline. The differences were largest for N, P and POC, intermediate for chl-a, DO and salinity, and smallest for TSS, $\underline{\mathbf{k}}$ and secchi depth. For the most part the observed differences were as predicted, but a more comprehensive comparison of the observed and predicted differences might be merited.

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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.

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, PS, Geyer W.R, Keller A.A, Turner J.T, Borkman D, Oviatt, C.A. and C.D. Hunt C. D. 2003. 2002 annual water column monitoring report. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2003-9. 105 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. Esturaine, 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.

Taylor, D.I. 2003. 24 months after 'offshore transfer': an update of water quality improvements in Boston Harbor. Boston: Massachusetts Water Resources Authority. Report ENQUAD 2003-04. 94 p.

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



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