2009 Benthic Nutrient Flux Annual Report

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Introduction

The Benthic Nutrient Cycling portion of the Massachusetts Water Resources Authority's (MWRA) Outfall Monitoring Program was designed to monitor biogeochemical processes in depositional sediments of Boston Harbor and Massachusetts Bay. These data have been used to assess changes in parameters relevant to eutrophication (e.g.: organic carbon loading, sediment oxygen demand, nutrient flux, denitrification), particularly in the context of changing wastewater disposal practices. These data have also been used to examine benthic-pelagic coupling, specifically by providing data for the Bays Eutrophication Model. This summary report presents the status of both systems through the 2009 sampling season, with data from 2009 highlighted as appropriate. It includes as Appendix I a PowerPoint file that was presented at the Monitoring Program's Annual Technical Meeting for 2009, held April 29, 2010. Slides from the presentation "Benthic Nutrient Cycling: 2009" are referred to in the report. For a more in-depth discussion of these studies, see Tucker et al., 2008 and references therein (http://www.mwra.state.ma.us/harbor/enquad/pdf/2008-14.pdf).

The benthic flux component of the monitoring program began in its current design in 1993. From 1993 through 2000, the focus was on monitoring recovery of Boston Harbor as significant improvements in wastewater treatment and discharge were being implemented. Monitoring was also conducted in Massachusetts Bay and Stellwagen Basin in order to establish a baseline dataset for those environments. In September, 2000, a new outfall became operational, diverting wastewater from the historical outfall sites within Boston Harbor to a deepwater site 9 miles offshore in Massachusetts Bay. At this point, the focus shifted to Massachusetts Bay, and to watching for signs of any unexpected or significant impacts in the area near or even "downstream" of the new outfall. Monitoring of Boston Harbor continued in order to document further changes after the removal of effluent discharge.

Data presented in this report are from sediment samples collected four times a year: in May, to capture the deposition of the spring phytoplankton bloom; in July and August, to capture the warmest part of the season; and in October, before the breakdown of thermal stratification in Massachusetts Bay. Sediment cores were collected by box corer from three stations in Massachusetts Bay near the location of the ocean outfall and one station in Stellwagen Basin, which serves as a reference station (Appendix I: Slide 2) and by SCUBA from four stations in Boston Harbor (Appendix I: Slide 13). Survey dates, site coordinates, and field data for 2009 may be found in Appendix II. Details of field and laboratory protocols may be found in Tucker and Giblin, 2008 (http://www.mwra.state.ma.us/harbor/enquad/pdf/2008-06.pdf).

Both Boston Harbor and western Massachusetts Bay have been monitored extensively under this monitoring program. We have documented remarkable recovery in the harbor, which began with treatment upgrades before the outfall was relocated, and, nine years since the ocean outfall became operational, no discernible change in the bay.

Massachusetts Bay

One of the concerns for the benthic environment in the vicinity of the bay outfall was that organic matter deposition to the sediments might increase, either as direct input from the effluent or from stimulation of primary production, leading to a degradation of the benthic habitat. Accordingly, we have measured organic carbon and chlorophyll in the top few centimeters of sediments at our study sites (three nearfield and one farfield in Stellwagen Basin; Appendix I: Slide 2). We have seen no change in organic carbon content at any of our stations (measurements are reported as percent dry weight, made on the top 2 cm of

sediment); annual average values are typically between about 1.2% and 1.5%, although values under 1% and over 2% have been observed (Appendix I: Slide 3, top). In 2009, individual survey values from MB01 displayed this range, starting with a high of 2.4% in May (likely related to an early-season pulse of chlorophyll, described below) and declining to 0.8% in October. Otherwise, organic carbon ranged between 1% and 1.6% at all stations and for all surveys. Similarly, we have not detected a change in benthic chlorophyll *a* (reported as areal inventory for the top 5 cm of sediment) between the two periods. Annual averages typically range between about 5 to 7 ug cm⁻², but may vary considerably both spatially and temporally (Appendix I: Slide 3, bottom). For example, in 2009, we observed an apparent local and short-term increase in chlorophyll *a* at Station MB01 in May that was absent from the other 3 stations and for the rest of the sampling year (Appendix I: Slide 4). The May inventory for Station MB01 was 13.6 ug cm⁻², whereas values for the rest of the stations and surveys were on the low end of observations, ranging from 1 to 4 ug cm⁻². In fact, 2009 was the second year in a row with relatively low sediment chlorophyll (nearfield survey average of 3.9 and 3.6 ug cm⁻² for 2008 and 2009, respectively).

Consistent with the lack of change in organic matter deposition has been the lack of change in redox indictors. Eh profiles in both nearfield and farfield sediments continued to show highly oxidized conditions throughout the 2009 sampling season (Appendix I: Slide 5). As is typical, a redox potential discontinuity was often undetectable by visual inspection. That is, cores from Massachusetts Bay often retained the grey-green color indicative of oxygenated sediments down to the bottom of the core.

Changes in sediment oxygen demand (SOD) that may have indicated an adverse impact of the outfall have also been absent (Appendix I: Slide 6). In fact, the overall average for the nearfield in the post-relocation period (2001-2009; 14.6 mmol m⁻² d⁻¹) is slightly lower than for the pre-relocation period (1994-2000; 16.2 mmol m⁻² d⁻¹), although the difference is not meaningful given the variability in the data, which was also larger in the pre-relocation period. In 2009, the average rate of oxygen consumption by nearfield sediments was 12.7 mmol m⁻² d⁻¹, among the lowest in the monitoring record. Average SOD at the farfield station is essentially the same for the two periods (11.6 and 11.1 mmol m⁻² d⁻¹) was among the lowest observed. Sediment chlorophyll levels noted above suggest two successive years of relatively little phytoplankton deposition to these sediments, which may have contributed to low SOD as well as nutrient fluxes (below).

Fluxes of dissolved inorganic nitrogen (DIN = $NH_4^+ + NO_3^- + NO_2^-$) have followed a similar pattern (Appendix I: Slide 7). Again, there is overlap in the range of observations reported before and after outfall relocation, but the overall nearfield average for the "after" period is only about half that of the "before" period (0.4 compared to 0.8 mmol m⁻² d⁻¹). DIN flux for the past two years, in particular, has been quite low, averaging less than 0.2 mmol m⁻² d⁻¹. Rates in the farfield show a decline as well, (from 0.3 to 0.1 mmol m⁻² d⁻¹). This declining trend has been in the NH_4^+ component of the flux (Appendix I: Slide 8, top), which is sometimes directed into the sediment (observed more frequently during the post-relocation period). Average NH_4^+ flux before relocation was 0.6 mmol m⁻² d⁻¹; after relocation it is 0.2 mmol m⁻² d⁻¹. Whereas NH_4^+ was the major component of the DIN flux during the baseline period, $NO_3^- + NO_2^-$, which has shown on average no change (Appendix I: Slide 8, bottom), now comprises an equivalent flux. In the nearfield, average NH_4^+ flux was < 0.1 mmol m⁻² d⁻¹ in 2009 compared to a nitrate flux of 0.15 mmol m⁻² d⁻¹. In the farfield, there was an average NH_4^+ influx of about 0.1 mmol m⁻² d⁻¹ in 2009 compared to a nitrate flux of 0.1 mmol m⁻² d⁻¹.

Phosphate (PO₄⁻) fluxes have followed similar decreasing trends in both magnitude and variability. Phosphate fluxes have always been small, but in the period since outfall relocation, they have been particularly so, and have fluctuated between efflux and influx (Appendix I: Slide 9, top). These weak fluxes are often qualified by very low coefficients of determination (r^2) for the linear regressions used to calculate them. For the 2009 sampling season, there was essentially no net PO_4^- flux from nearfield sediments and a very small flux, $< 0.02 \text{ mmol m}^{-2} \text{ d}^{-1}$, from the farfield.

Silica fluxes are typically sizable, but they too have shown a downward trend and a decrease in variability (Appendix I: Slide 9, bottom). Average silica flux for the pre-relocation period was 4.7 mmol $m^{-2} d^{-1}$ and 4.3 mmol $m^{-2} d^{-1}$ for the nearfield and farfield, respectively, and 3.2 and 3.5 for the post-relocation period. In 2009 silica fluxes were similar and among the lowest in the record for both areas, averaging 2.4 mmol $m^{-2} d^{-1}$ for the survey year.

The pre- to post-relocation comparison for denitrification includes the caveats that sampling frequency, stations sampled, and methods have changed during the monitoring program. This lack of evenness in the dataset precludes comparing period averages, but we nevertheless believe a valid assessment of change may be made. The trends we see roughly track those of the other fluxes, that is, the data show higher rates and greater variability in the earlier period and no noticeable change at the time of the outfall diversion) (Appendix I: Slide 10). The change in methods implemented in 2004 has allowed us to measure denitrification at all four stations and all surveys. Since then, rates have averaged 1.5 and 1.3 mmol N m⁻² d⁻¹ for the nearfield and farfield, respectively, with summer high rates in 2006 at MB02 and MB03 reaching about 3.5 mmol N m⁻² d⁻¹, not dissimilar from some of the higher rates reported in the earlier period. Rates for 2009 were typical, averaging 1.4 and 1.3 mmol N m⁻² d⁻¹ for the nearfield and farfield accounts for over 70% of the combined DIN + denitrification flux, a characteristic that has been noted throughout the program (Appendix I: Slide 11).

In summary, we have not observed any negative impacts to depositional sediments at three stations in the vicinity of the ocean outfall (Appendix I: Slide 12). That is, we have observed no indication of increased organic matter loading at these sites, nor have we detected a change in redox conditions. There has also been no increase in sediment oxygen demand or nutrient fluxes, nor any discernible change in denitrification. Variability in these parameters seems to vary with region-wide biological and physical phenomena.

Boston Harbor

Treatment upgrades that reduced solids loading to Boston Harbor initiated recovery of harbor sediments at our four monitoring stations (Appendix I: Slide 13) before the effluent was diverted offshore. These changes were reflected in the organic carbon content of harbor sediments, which decreased in step with these changes, and was particularly noticeable at two stations, BH03 and BH08A, that had been most directly affected by sludge disposal (Appendix I: Slide 14). The concurrent appearance of large colonies of tube building amphipods (*Ampelisca sp.*) in the harbor accelerated the removal of organic matter by stimulating benthic nutrient cycling. Organic carbon content of nearly 4% at Station BH03 has declined to about 2.2% for the post-relocation period, which is very similar to the four-station average for the period.

Sediment chlorophyll as a measure of organic matter content in shallow water environments like the harbor is complicated by the fact that it may include both phytoplankton deposition and in situ production. Chlorophyll *a* inventories for surface sediments have varied widely (Appendix I: Slide 15, top) depending on production, which may be limited by light in the harbor as well as by grazing. Accordingly, there has been no change in average chlorophyll inventories since outfall relocation (Appendix I: Slide 15, bottom). Largest inventories and most variability have often been observed at Stations BH02 and QB01, where benthic organisms were relatively sparse and benthic diatoms were often noted. The presence of *Ampelisca* communities, e.g. at BH03 and BH08A, typically corresponded to lower chlorophyll *a* levels. In 2008 and 2009, when another amphipod (*Leptocheirus pinguis*) became abundant in the harbor, chlorophyll *a* levels fell at BH02 and QB01, presumably in response to this new

grazing pressure. Profiles through the top 5 cm (Appendix I: Slide 16) show that the 2009 season started with high concentrations in the spring that did not persist until the July survey. For example, at Station BH02 in May (Appendix I: Slide 16, Fig. a), concentrations over $10 \ \mu g \ cc^{-1}$ were measured as deep as 2-3 cm; integration over the top 5 cm yielded an inventory of almost 34 $\ \mu g \ cm^{-3}$; by July the inventory was about $10 \ \mu g \ cm^{-3}$, which was approximately the baseline level for all four stations in 2009.

Colonization of the harbor by large numbers of *Leptocheirus pinguis* began in 2007, and was associated with elevated rates of SOD and nutrient fluxes at Station BH02. In 2008, *Leptocheirus* was even more abundant, and fluxes increased further at Station BH02 and became elevated at Station BH08A (Appendix I: Slide 17). In 2009, amphipod abundance declined, and fluxes began to return to levels more typical of the post-relocation period.

During the first stages of harbor cleanup, SOD at some harbor stations was among the highest reported in the literature. Peaks in SOD corresponded to peak amphipod abundance. Rates began to abate before effluent diversion, as less organic carbon was being delivered to the harbor and sediment stores were burned off. Accordingly, the range of rates reported for the pre-diversion period is large, with an average for the period of 62 mmol $m^{-2} d^{-1}$ (Appendix I: Slide 18). Through 2006, the post-relocation average had declined to 34 mmol $m^{-2} d^{-1}$, a reduction of nearly 50%. In 2007, however, with the appearance of *Leptocheirus*, harbor average SOD began to climb due to high rates at BH02 (survey year average = 75 mmol $m^{-2} d^{-1}$), and increased further in 2008 due to very high rates at BH02 and BH08A (106 and 102 mmol m⁻² d⁻¹, respectively). In 2009, SOD was back to post-relocation "normal" at BH08A $(33 \text{ mmol m}^{-2} \text{ d}^{-1})$ and, although still high, had declined at Station BH02 as well (65 mmol m $^{-2} \text{ d}^{-1})$. The resulting four-station annual average was 41 mmol m⁻² d⁻¹, down from 77 mmol m⁻² d⁻¹ in 2008 and approaching 2001-2006 values. We have traditionally benchmarked harbor SOD averaged for the July and August surveys against summer rates reported for a range of coastal systems by Nixon in 1981 (Appendix I: Slide 19). In this comparison of likely maximum rates, we also see a return in 2009 to levels more typical of the post-relocation, pre-Leptocheirus period.

DIN fluxes closely follow the pattern set by SOD (Appendix I: Slide 20). DIN fluxes were high and variable during the pre-relocation period, and included declining rates related to effluent treatment achieved prior to diversion. During this period the average DIN flux was about 5 mmol m⁻² d⁻¹. For the first 6 years after diversion, DIN flux had fallen to an average of 2.7 mmol m⁻² d⁻¹. In 2008, the annual average had increased back up to 4.5 mmol m⁻² d⁻¹. In 2009, DIN fluxes fell back to 2.5 mmol m⁻² d⁻¹, a rate very characteristic of the 2001-2006 period.

Within the DIN flux increase of 2007-2008 was a change in the relative proportion of the components of the DIN (Appendix I: Slide 21). Over half of the flux was comprised of $NO_3^- + NO_2^-$, whereas NH_4^+ is more typically the major component of DIN fluxes associated with high rates of SOD. Again we invoke amphipods to explain this observation; bioturbation aerates the sediments and stimulates nitrification, and flushes nutrient-rich porewaters out of the sediments. We observed this phenomenon at Station BH03 and BH08A during the peak years of *Ampelisca* colonization, and now we have seen it at Station BH02 and again at BH08A with *Leptocheirus*. This effect persisted at Station BH02 into 2009 despite reduced numbers of amphipods and a reduced total flux.

The bioturbation effects noted above also influence denitrification rates. Throughout the monitoring program, denitrification has been quite variable and at times quite high, although rates were apparently declining along with DIN fluxes until 2007, when they both began to increase at the stations with *Leptocheirus* (Appendix I: Slide 22). In 2009, however, denitrification at Station BH02 reached the maximum in our record, 16 mmol N m⁻² d⁻¹, even though DIN fluxes declined. We speculate that a more moderate level of bioturbation may have created very favorable conditions for denitrification: sufficient aeration to stimulate nitrification coupled with a porewater residence time long enough to allow the denitrifiers access to the resulting NO₃⁻. At our harbor stations, denitrification generally accounts for

between 30% and 60% of the combined N flux (DIN + denitrification) out of the sediments (Appendix I: Slide 23).

In the early stages of harbor monitoring, we compiled a budget of nitrogen sinks versus inputs as part of an assessment of denitrification as a mitigator of nitrogen loading. For that time, around 1991-1994, Kelly (1997) gave N loading to the harbor as $8470 \text{ mmol N m}^2 \text{ y}^{-1}$ and burial within the harbor as 200 mmol N m⁻² yr⁻¹. Our average for denitrification was about 1200 mmol m⁻² d⁻¹. The result was that denitrification could account for only 14% of the inputs, with burial accounting for 2%, and export the remaining 84% (Appendix I: Slide 24, left). In this early period we had less spatial coverage in our measurements than in recent years (two stations rather than 4), although we had more complete temporal coverage (5 surveys instead of 4, including one during winter). Accounting for these differences, we have compiled a new budget. The overriding change has been in the reduction in loading effected by effluent diversion; recent estimates are about 14% of the early figures (Taylor, 2006). Assuming that burial rates have remained the same, we arrive at a budget in which denitrification now removes ~60% of inputs (Appendix I: Slide 24, right), consistent with typical continental shelf systems (Seitzinger and Giblin, 1996).

Phosphate and silica fluxes have generally paralleled the patterns we have observed in SOD and DIN fluxes, and have also returned to post-relocation "normal" levels after increases in 2007-2008. The prediversion average for PO_4^- was 0.34 mmol m⁻² d⁻¹, and had dropped to 0.17 mmol m⁻² d⁻¹ in the 2001-2006 period. The 2009 average was 0.12 mmol m⁻² d⁻¹ (Appendix I: Slide 25, top). Silica fluxes are regulated more by dissolution chemistry than by biogeochemistry, and although they follow the general pattern as the other fluxes, they have not declined to the same extent. They averaged 6.8 mmol m⁻² d⁻¹ for the pre-relocation period, 5.2 for 2001-2006, and 6.1 mmol m⁻² d⁻¹ for 2009(Appendix I: Slide 25, bottom). Regeneration of dissolved silica is important in maintaining a nutrient stoichiometry that supports diatom growth.

Redox indicators at our harbor stations continue to show improved conditions in recent years. In contrast to sediments from Massachusetts Bay, harbor sediments typically show a transition from brown to blacker, apparently anoxic sediments that corresponds to a drop in Eh (Appendix I: Slide 26). However all four stations now have deeper oxidized layers than were present in the early years. The most recent improvements have been at Station BH02, which had lagged behind the other three stations until it was colonized by *Leptocheirus* in 2007.

To summarize, depositional sediments of Boston Harbor have recovered dramatically in the relatively short time since cleanup efforts began. Sediment oxygen demand and nutrient fluxes during the period after outfall relocation are on average lower than baseline rates, even though rate decreases began during the baseline period. Recent spikes in these processes (2007-2008), driven by a *Leptocheirus pinguis* bloom, have abated with amphipod abundance; however, they point out that similar episodes are likely to occur during the current period of lower change: the harbor remains a relatively rich habitat. In contrast to the other fluxes, denitrification spiked in 2009 at one station, presumably due to ideal conditions provided by "just the right amount" of bioturbation. Overall, however, denitrification has also decreased compared to baseline. Even so, due to the very large reduction in nitrogen loading achieved by the outfall diversion, its importance as a nitrogen sink has increased.

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APPENDIX I

2009 Benthic Nutrient Cycling MWRA Workshop 2010





















































Conclusions for 2009 Boston Harbor

SOD and nutrient fluxes at Station BH02 and BH08A returning to post-relocation levels from elevated rates observed in 2008

Reduced fluxes related to reduced amphipod abundance

Post-relocation SOD and nutrient fluxes remain lower than baseline

High summer rates of denitrification at Station BH02

Relative importance of denitrification increased with reduction of loading; now accounts for ~60% of the N budget

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APPENDIX II

FIELD RESULTS

Appendix II. Station names, survey IDs, date of survey, station locations, near-bottom water sampling depth, temperature, dissolved oxygen (D.O.) and salinity for Boston Harbor and Massachusetts Bay stations visited in 2009.

Station	Survey	Date	Latitude	Longitude	Dept h (m)	Temp. (°C)	D.O. (mg/L)	Salinity (psu)
					()		(8,)	(1)
BH02	NC091	5/18/2009	42.34348	-71.00211	10	10.1	9.64	31.1
	NC092	7/14/2009	42.34362	-71.00205	9	14.4	8.20	30.4
	NC093	8/11/2009	42.34372	-71.00235	8	15.8	9.18	30.5
	NC094	10/14/2009	42.3436	-71.00191	12	10.9	9.16	31.1
BH03	NC091	5/18/2009	42.33055	-70.96175	8	10.4	9.67	30.7
	NC092	7/14/2009	42.33075	-70.96165	8	16.2	8.21	29.9
	NC093	8/11/2009	42.3306	-70.96181	7	16.7	8.68	30.3
	NC094	10/14/2009	42.3308	-70.96172	10	10.9	9.17	31.1
BH08A	NC091	5/18/2009	42.29080	-70.92226	9	11.1	9.51	31.0
	NC092	7/14/2009	42.29077	-70.92229	7	17.5	8.03	30.0
	NC093	8/11/2009	42.29102	-70.92198	7	16.5	9.81	30.7
	NC094	10/14/2009	42.291	-70.92218	9	11.0	9.21	31.2
QB01	NC091	5/18/2009	42.29348	-70.98766	4	12.1	9.35	30.3
	NC092	7/14/2009	42.29357	-70.98760	3	18.6	7.43	29.6
	NC093	8/11/2009	42.2937	-70.98801	3	17.8	8.65	30.4
	NC094	10/14/2009	42.29355	-70.98787	5	11.0	9.34	30.8
MB01	NC091	5/19/2009	42.40303	-70.83723	32	3.9	9.35	32.4
	NC092	7/13/2009	42.40302	-70.83728	33	7.4	10.05	31.8
	NC093	8/10/2009	42.40298	-70.83735	32	8.2	9.91	31.8
	NC094	10/13/2009	42.40318	-70.83725	33	9.3	6.69	31.7
MB02	NC091	5/19/2009	42.39245	-70.83440	32	3.9	9.36	32.4
	NC092	7/13/2009	42.39248	-70.83430	33	7.7	10.07	31.7
	NC093	8/10/2009	42.39258	-70.83425	33	8.3	9.95	31.7
	NC094	10/13/2009	42.39257	-70.83435	33	9.6	7.15	31.6
MB03	NC091	5/19/2009	42.34775	-70.81638	33	4.2	9.71	32.3
	NC092	7/13/2009	42.34789	-70.81603	32	7.8	9.23	31.7
	NC093	8/10/2009	42.34792	-70.81622	32	8.0	8.65	31.8
	NC094	10/13/2009	42.348	-70.81612	35	9.8	7.25	31.6
MB05	NC091	5/19/2009	42.41642	-70.65179	44	3.8	11.02	32.7
	NC092	7/13/2009	42.41658	-70.65202	41	6.9	10.47	32.1
	NC093	8/10/2009	42.41665	-70.65195	38	8.6	10.37	32.0
	NC094	10/13/2009	42.41645	-70.65197	42	8.8	7.69	31.8



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