Summary Descriptions of MWRA Monitoring Relevant to Ocean Acidification (Updated 5/2016)

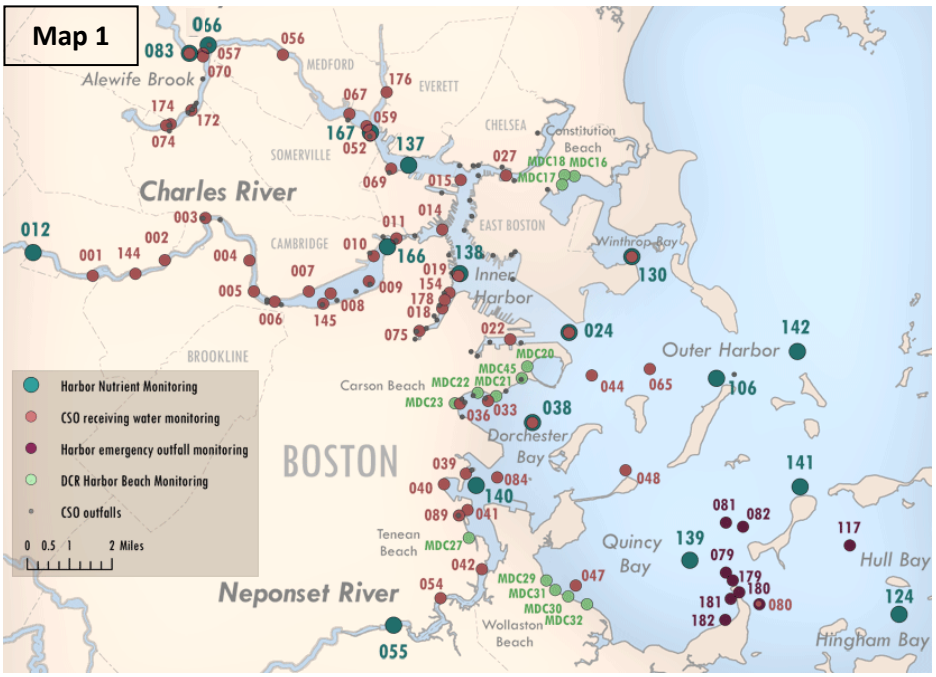
1. Monitoring of pH

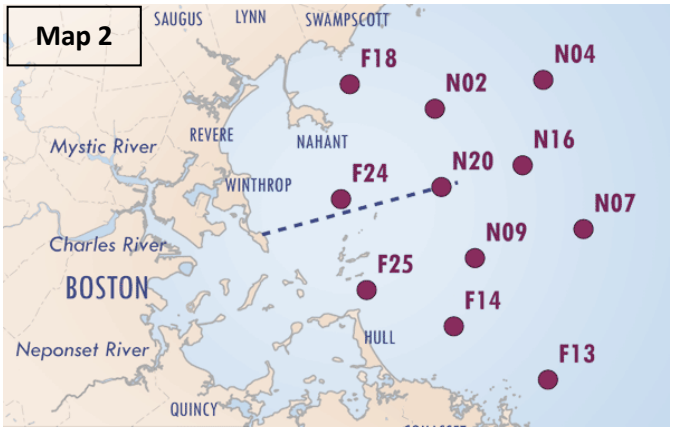
The Massachusetts Water Resources Authority (MWRA) has ongoing long-term monitoring programs in rivers, Boston Harbor, and Massachusetts Bay that include pH measurements. The pH measurements are made during surveys from vessels or the shore using in situ multi-parameter (e.g., temperature, salinity, and dissolved oxygen) sondes manufactured by YSI/Xylem and/or Hydrolab/OTT-Hydromet. The pH sensors are the glass electrode type with manufacturer-provided specifications for resolution and accuracy of 0.01 and 0.2 pH units respectively. Manufacturer-recommended methods and schedules for calibration (3-point using fresh buffers) and maintenance are carried out. However, the monitoring programs were not designed with the goal of detecting long-term pH trends such as ocean acidification (OA). Furthermore, while Quality Assurance Project Plans (QAPPs) have been followed, because pH is an auxiliary variable with respect to MWRA priorities (e.g., compared to dissolved oxygen), limited effort is applied to its quality control and quality assurance. It is likely that, to potentially be scientifically useful for detection of long-term trends, MWRA pH data will require substantial additional quality control and evaluation; to this end temperature and salinity observations, collected simultaneously with the pH data, are expected to be useful and are also available. Users should understand this context, and the disclaimer (http://www.mwra.state.ma.us/harbor/html/disclaimer2.htm).

For the purpose of attempting to detect long-term trends, the MWRA data most likely to be potentially useful is from our Harbor Monitoring Program (green stations on Map 1 below; more information at www.mwra.state.ma.us/harbor/html/bh_wq.htm). Several stations in the central and outer harbor (e.g., 106 & 142) have been visited consistently, at nominally 2-week frequency year-round since 1995, to collect measurements from at least a few depths spanning the water column (data available at http://www.mwra.state.ma.us/harbor/html/wq_data.htm under “Boston Harbor/Physical/All” section of table). Similar sampling has occurred, though typically concentrated somewhat more heavily during warmer months, since the mid-1990s at stations in rivers (red, Map 1) as part of our Combined Sewer Overflow monitoring program.

In Massachusetts Bay, pH measurements at 11 sites (Map 2 below) have been collected monthly near the surface, with samples also near the seafloor during stratified conditions (about May to October), since Sep 8, 2006 in a cooperative bacteria sampling program with the MA Department of Marine Fisheries (http://www.mwra.state.ma.us/harbor/html/mb_bacteria.htm).

There are additional pH datasets, but they are considered less likely to be useful for long term trend investigations. One dataset, collected by MWRA in the late 1990s, focused on conditions in effluent plumes from the Nut Island and Deer Island outfalls prior to shutdown of the former and relocation of the latter to Massachusetts Bay. Another relatively small pH dataset was gathered by MWRA in the vicinity of the current Massachusetts Bay outfall location (between N20 & N16, Map 2) during a 2001 study of its effluent plume. Finally, MWRA is aware of a late-1980s Boston Harbor study by the New England Aquarium that included pH; Bill Robinson, now at UMass Boston, oversaw that project and may know if data are available (https://www.umb.edu/academics/csm/faculty_staff/william_e._robinson).





(Finally, though less relevant to potential detection of long-term trends in ambient waters, it can be mentioned that MWRA routinely monitors the pH of the effluent leaving its Deer Island treatment plant, which is released from its Massachusetts Bay outfall. The outfall is located at the eastern end of the tunnel from Deer Island, indicated as the dashed line in Map 2 above.)

2. Other monitoring potentially relevant to ocean acidification research

After the NECAN (North East Coastal Acidification Network) stakeholders workshop in Gloucester MA on June 23, 2015, MWRA reviewed its monitoring studies to identify potential measurements of OA-related parameters in addition to the water column pH measurements summarized above.

This review documented that potentially relevant measurements have been made. We spoke with the researchers involved with collecting the data. Indications from those discussions are that since monitoring impacts of ocean acidification was not a project goal, data may not always have been gathered using methods

suitable for OA research. Additionally, in some cases the potentially most relevant data from an ocean acidification perspective were ancillary to the goals of MWRA's monitoring, and therefore were not reported and archived in MWRA's monitoring database. For example, only the rates of dissolved inorganic carbon (DIC) fluxes into or out of sediments were reported to MWRA, not the individual measurements from which the rates were calculated.

We would be happy to work with the researchers who collected these data, and any others in the NECAN community who are interested in potentially using them in OA-related investigations, to share data and to further evaluate their usability.

The studies we identified include:

Sediment metabolism. This 18-year study of sediment oxygen and nutrient metabolism in Boston Harbor and Massachusetts Bay tracked the recovery of sediments in Boston Harbor during and after MWRA's Boston Harbor project[1], and determined whether the relocated outfall discharge affected these processes in Bay sediments. Potentially relevant measurements include sediment pH profiles, sediment-water column DIC flux measurements, and porewater alkalinity profiles. Unfortunately, alkalinity profiles were only made for a few years, and the caveats mentioned above could affect the usability of other measurements for OA studies. We would suggest any interested scientist communicate directly with Anne Giblin (Marine Biological Laboratory, agiblin@mbl.edu) and the other researchers who collected these observations, to help assess whether the data can be of use.

Primary productivity. This study investigated primary productivity using ^{14}C dosing and incubations between 1993 and 2010 at multiple stations, depths, and surveys in Massachusetts Bay and Boston Harbor[2]. Pre-incubation measurements were made of initial DIC prior to dosing with ^{14}C. After the workshop, we asked Candace Oviatt's lab (University of Rhode Island, coviatt@uri.edu), which made these measurements, if the DIC data (not reported to MWRA) were still available. They were able to locate spreadsheets containing the results for 2001 to 2010, and sent them to MWRA. From a quick skim most spreadsheets contain all the DIC data from a single survey (there were 12 to 17 surveys per year), though a few of the 2001 spreadsheets contain results from multiple surveys.

We will maintain copies of the individual DIC spreadsheets in offline storage, but do not plan to extract the DIC data and load them into our monitoring database. We would recommend that any interested scientist review the project QAPPs and reports (available at http://www.mwra.state.ma.us/harbor/enquad/trlist.html) for details of when and where the data were collected, and work directly with Dr. Oviatt's lab help understand the DIC data prior to contacting us for the spreadsheets.

For more information on MWRA monitoring datasets—and/or to request data not already available at our website—contact Doug Hersh (douglas.hersh@mwra.com) or Dan Codiga (dan.codiga@mwra.com).

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[1] A recent open access paper summarizing some findings of this study is Tucker at al. 2014. Response of benthic metabolism and nutrient cycling to reductions in wastewater loading to Boston Harbor, USA. *Est. Coast. & Shelf Sci*. 151:54-68. The most recent QA plan for the project is online at http://www.mwra.state.ma.us/harbor/enquad/pdf/2010-05.pdf.

[2] The most recent QA plan that includes protocols for the productivity measurements is online at http://www.mwra.state.ma.us/harbor/enquad/pdf/2010-02.pdf.