The Role of Benthic Sediment in Internal Recycling of Nitrogen and Phosphorus in a Southern Rhode Island Coastal Lagoon

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Executive Summary
During the summer of 2013, sediment cores were taken and processed to determine the importance of benthic recycling on the nitrogen and phosphorus mass balances of Quonochontaug Pond.

The sediment oxygen demand (the uptake of dissolved oxygen) of grey-black organic-rich muds from the Pond fall within the range of values for estuaries and lagoons that occupy the US Coastal Zone.

The average summer ammonium benthic flux for Quonochontaug Pond (2.14 mg/m²/hr) is consistent with the average summer benthic flux of ammonium for coastal US estuaries and lagoons (2.10 mg/m²/hr; Bailey, 2005. Measurements of Nutrient and Oxygen Fluxes in Estuarine and Coastal Marine Sediments: Literature Review. Univ. Md. Center for Environmental Science 05-091). And, the average summer benthic flux of phosphate for Quonochontaug Pond (0.81 mg/m²/hr) is significantly higher than the average for coastal US estuaries and lagoons (0.48 mg/m²/hr; Bailey, 2005. Measurements of Nutrient and Oxygen Fluxes in Estuarine and Coastal Marine Sediments: Literature Review. Univ. Md. Center for Environmental Science 05-091).

Bioturbation, the translocation of material between benthic sediment and bottom water by burrowing bivalves, is an important process affecting the benthic fluxes of ammonium and phosphate in an eelgrass bed in the western basin of Quonochontaug Pond. These enhanced benthic fluxes are seven (7) times greater than the summer average for the Pond as a whole.

Water-column remineralization of dissolved inorganic nitrogen (mostly ammonium) and phosphate contributes about 48% of the nitrogen and 49% of the phosphorus required for the growth of phytoplantonic algae in Quonochontaug Pond.

The annual benthic flux of ammonium and that of phosphate contribute about 31% of the nitrogen and 59% of the phosphorus required for the growth of this planktonic algae. The total utilization of nitrogen (79%) and phosphorus (108%) by phytoplankton does not add up to 100% due to some uncertainty in the data and the possibility that some other process is operative.

The late summer (August and September) benthic flux of ammonium contributes between 50 and 85 percent of the annual ammonium benthic flux. The late summer benthic flux of phosphate contributes 84% of the annual benthic flux of phosphate. This late summer benthic flux of phosphate is significantly greater than the average for US coastal estuaries and lagoons.

The external mass balance of dissolved inorganic nitrogen (DIN) for Quonochontaug Pond is essentially in balance (17,647 kgN/yr IN=17,250 kgN/yr OUT) with the benthic flux of ammonium contributing 59% of all DIN inputs and surface water-groundwater-atmospheric inputs each contributing about 12%.
The external mass balance of dissolved inorganic phosphorus (DIP) is substantially out of balance; 1,516 KgP/Yr IN and 1,959 kgP/Yr OUT. The benthic flux of phosphate contributes 88% of all DIP inputs and groundwater contributes 10%.

The high rate of benthic exchange of ammonium and phosphate between bottom sediment and bottom water during the late summer provides much of the DIN and DIP to the bottom waters of Quonochontaug Pond. Throughout most of the remaining year, benthic fluxes are minimal and the nutrient increases in the Pond’s bottom waters are a result of water-column remineralization processes. It appears that phosphate is more sensitive to dissolved oxygen depletion than ammonium in the bottom waters of Quonochontaug Pond.

**Introduction**

Enrichment of coastal waters from land-based nitrogen is one of the most pervasive threats to present-day aquatic ecosystems (Bowen and Valiela, 2001). Human activities in the past century have resulted in a tremendous increase in nutrient inputs (nitrogen and phosphorus) to the coastal zone worldwide (Howarth and Marino, 2006; Viktorsson, 2012). This external loading of nitrogen and phosphorus is the driving force for eutrophication. Shallow coastal bays and lagoons are particularly vulnerable to rapid changes in human activities (McGlathery et al., 2007) that cause increased algal production, decreased light transparency, and depleted dissolved oxygen (Anderson and Conley, 2009). Indirect effects of eutrophication are the increase in bacteria, nutrient recycling from benthic sediments, and changes in ecosystem structure (Anderson and Conley, 2009).

Previous studies of eutrophication of Rhode Island’s salt ponds (coastal lagoons) have focussed on the dissolved inorganic nitrogen (DIN) loading of these water bodies (CRMC, 1999; Nixon and Buckley, 2007). Generally, DIN consists of nitrate and ammonium with nitrate considered the main offending species. This is because nitrate is the predominant form of DIN entering the ponds from surface water, atmosphere, and groundwater (Callender, 2013; Callender, 2014; Nixon, 1982; Nixon and Pilson, 1983). While aquatic scientists believe that nitrogen is the primary cause of eutrophication in many coastal ecosystems (Howarth and Marino, 2006), Taylor et al. (1995), using the mesocosm approach, determined that nitrogen and phosphorus inputs enriched coastal lagoons more than nitrogen-alone treatments. Therefore, one cannot ignore the eutrophic impact of phosphorus loading even though nitrogen loading appears to be more important (Howarth and Marino, 2006).

Both nitrate and ammonium are utilized by algae for growth (Twomey et al., 2005; Collos et al., 2003), although at different rates and at different times during the growing season (Nixon and Pilson, 1983). While nitrate is the major form of DIN entering Rhode Island’s coastal lagoons (Callender, 2013; Callender, 2014), it appears to be utilized readily by algae. In fact, it is so important for the growth of micro algae, that the concentration of nitrate in the water column is very low during the growing season. The concentration of nitrate in the water column of Quonochontaug Pond averages about 16±3 ug/L per sampling year that lasts from May to October (SPC Monitoring Database). On the other hand, ammonium averages about 40±13 ug/L in surface waters but 68±24 ug/L in bottom waters (SPC Monitoring Database), and the concentration of bottom-water ammonium is increasing with time (SPC Status and Trends Report, 2013). Generally, higher concentrations of ammonium occur in the bottom waters of the western basin of Quonochontaug Pond where replenishment of oxygenated bottom water is decreased by restricted circulation of Block Island Sound water through the Breachway and the
narrates between the eastern and western basins of the Pond (The Tidal Page, Late Fall 2008) (Figure 1).

The increase in bottom-water ammonium is a common occurrence at most deep-water sites in southern Rhode Island coastal lagoons (Quonochontaug Pond, Ninigret Pond, Green Hill Pond, Point Judith Pond, and Potter Pond) (SPC Monitoring Database). Table 1 gives the summary data for bottom-water increases of ammonium and phosphate in Quonochontaug Pond, a coastal lagoon with four deep-water stations.

Table 1. Summary of Sampling Year (June to October) Bottom-Water Increase of Ammonium and Phosphate Relative to Surface-water Concentrations at Four Deep-Water Stations in Quonochontaug Pond. Delta (∆) NH$_4$+ and PO$_4^{3-}$ represent bottom water-surface water concentrations in ug/L.

<table>
<thead>
<tr>
<th>Year</th>
<th>Ave., SD ∆NH$_4$+</th>
<th>Months ∆NH$_4$+ $&gt;/=20$ug/L</th>
<th>Months</th>
<th>Ave., SD ∆PO$_4^{3-}$</th>
<th>Months ∆PO$_4^{3-}$ $&gt;/=10$ug/L</th>
<th>Months</th>
</tr>
</thead>
<tbody>
<tr>
<td>2013</td>
<td>39±43ug/L(18)</td>
<td>13</td>
<td>July,Aug.,Oct.</td>
<td>3±ug/L(6)</td>
<td>4</td>
<td>July</td>
</tr>
<tr>
<td>2012</td>
<td>28±27ug/L(28)</td>
<td>11</td>
<td>July,Sept.,Oct.</td>
<td>4±2ug/L(12)</td>
<td>1</td>
<td>June,Aug.,Sept</td>
</tr>
<tr>
<td>2010</td>
<td>22±14ug/L(21)</td>
<td>12</td>
<td>Aug.,Sept.</td>
<td>10±6ug/L(9)</td>
<td>7</td>
<td>July,Aug.</td>
</tr>
<tr>
<td>2009</td>
<td>27±18ug/L(6)</td>
<td>6</td>
<td>July,Sept.,Oct.</td>
<td>No Data</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Ave. = average; SD= standard deviation
Numbers in Parentheses are months where bottom-water concentrations were greater than surface-water concentrations
Five-Year Ave., SD of ∆NH$_4$+ = 29±6ug/L (2009-2013)
Four-Year Ave., SD of ∆PO$_4^{3-}$ = 8±4ug/L (2010-2013)
Molar ∆NH$_4$+ : ∆PO$_4^{3-}$ = 8.0:1

Delta NH$_4$+ and ∆PO$_4^{3-}$ are the average concentration differences between bottom and surface waters at deep-water stations (generally $>/=2.0$ meter water depth) for the years 2009 to 2013 (NH$_4$+) and 2010 to 2013 (PO$_4^{3-}$). What are the processes responsible for these average ammonium (29 ug/L) and phosphate (8 ug/L) increases in bottom waters relative to surface waters? Either remineralization of ammonium and phosphate in the oxic-hypoxic water column and/or regeneration of these nutrients in hypoxic-anoxic benthic sediment. The biogeochemical processes responsible for these nutrient species may be substantially different and will be discussed in later sections of this manuscript. A glance at Table 1 provides some justification for this observation; that is, ∆NH$_4$+ concentrations greater than 20 ug/L occur more frequently, on the average of 10 sampling months per year, than do ∆PO$_4^{3-}$ concentrations greater than 10 ug/L, on the average of 4 sampling months per year. In Table 1, the fourth and seventh columns list the sampling months where bottom-water concentrations of NH$_4$+ and PO$_4^{3-}$ were substantially greater than surface-water concentrations.

In order to determine whether benthic regeneration of ammonium and phosphate is the primary cause of substantial bottom-water concentration increases relative to surface-water concentrations of ammonium($>/=20$ ug/L) and phosphate ($>/=10$ ug/L), the author initiated a core incubation study of bottom sediments in the western basin of Quonochontaug Pond under
varying levels of dissolved oxygen. In the summer of 2013, the author undertook this study to determine how much ammonium and phosphate could emanate from fine-grained, organic-rich muds in deep-water areas (>2.0 m water depth) of Quonochontaug Pond. This study focuses on fine-grained, dark grey-black muds in the western basin of Quonochontaug Pond because bottom waters are significantly enriched in ammonium and sometimes phosphate, and the basin includes an extensive area of eelgrass (SPC Status and Trends Report, 2013). The ultimate purpose of this study was to determine whether benthic release of ammonium and phosphate enriches bottom waters of Quonochontaug Pond, and by proxy other southern Rhode Island coastal lagoons, during the warm summer months (July-September) when dissolved oxygen is decreased by respiration and oxidation of sedimentary organic matter.

Methods

Study Sites
Quonochontaug Pond is the second major coastal lagoon in southern Rhode Island east of the Pawcatuck River and Little Narragansett Bay. Figure 1 is a representative GIS image of Quonochontaug Pond and its watershed showing the three deep-water sampling stations in the western basin that have been monitored since 2008. The three sites where sediment cores were taken in the summer of 2013 are HC Buoy, HCCh, and JR. The full names for these stations are Harmonic Cove Buoy, Harmonic Cove Channel, and Judge’s Rock. Sediment cores were taken with a hand-held plastic tube fitted with a suction valve at the top end of the tube, below which was fitted a wooden clamp that held a plastic push rod and a rope for retrieving the core tube to the water surface (Figure 2). Before the bottom of the sediment core tube broke the water surface, a plastic core cap was attached to the bottom of the core tube so that the contained sediment core would not slide out of the core tube. A sediment core was taken at the above stations in mid July, mid August, and mid September, 2013. (Instead of a core at HCCh in September, a core was taken in Ninigret Cove, Figure 1).

The following are descriptive logs of the sediment lithology encountered at the three sites.

**HCBuoy, mid August:** 0-1 cm, sediment surface covered with many small bivalves; 1-8 cm, dark grey-black, somewhat fluid, silty-clay mud; 8-18 cm, dark grey-black, less fluid, silty-clay mud; 18-28 cm, dark grey-black, somewhat indurated (less water content), silty-clay mud. The length of the core was 28 cm.

**HCChannel, mid August:** 0-6 cm, dark grey-black, fluid, silty clay with dark grey-black organic tube structures sticking 1-2 cm above sediment surface; 6-14 cm, dark grey-black, moderately stiff, slightly sandy silty clay; 14-19 cm, dark grey-black, stiff, silty clay. The length of the core was 19 cm.

**Judge’s Rock, mid August:** 0-9 cm, dark grey-black, fluid, silty-clay mud; 9-16 cm, dark brown to grey-black, somewhat indurated or stiff, silty clay; 16-30 cm, same as 9-16 cm; 30-32 cm, same as 9-16 cm. The length of the core was 32 cm.

Core Incubations
After the sediment cores were taken, they were transported to shore and placed in a water bath that was flushed with cold well water. When the cores were not sampled, the core-incubation bath container was covered with a wooden box and a plastic tarp to keep out light and allow the core incubations to proceed in the dark (Figure 3). Before times of sampling, the core-top water was agitated with a stirring rod and disc (Figure 4) for three minutes. This procedure broke down any physical and chemical stratification of the core-top water column and allowed for a homogenous water sample to be taken.
Core-top water was mixed three times in a 24-hour period and water sampling was performed once or twice in the same 24-hour period based on the dissolved oxygen concentration. If the dissolved oxygen concentration in the core-top water decreased by more than 1.5 mg/L in an eight-hour time interval, then sampling of the core-top water was done twice in a 24-hour period. Otherwise, sampling of the core-top water was done once every 24 hours.

After stirring the core-top water, temperature, dissolved oxygen, and salinity were measured using a hand-held YSI Model 85 water-quality monitor. Then, if appropriate, sampling of the core-top water was done using plastic tubing attached to a wooden stick. The opening of the tubing was inserted to about 10 cm above the sediment surface and the water sample extracted with a 60-ml syringe. The syringe was fitted with a filter holder containing a GFC glass fiber filter and the filtered water placed in a plastic bottle that was stored in a freezer until transport to the University of Rhode Island Watershed Watch Laboratory (URIWWL). At the laboratory, under the direction of Ms. Linda Green, thawed water samples were analyzed for nitrate, ammonium, and dissolved reactive phosphate using auto analyzer colorimetric techniques appropriate for the analysis of nitrate, ammonium, and phosphate in saline water samples.

After sampling of the core-top water, the height of the core-top water column above the sediment surface was measured and recorded. This was done to compute the total volume of water from which the 60-ml sample was taken.

Calculations
The fluxes of oxygen, ammonium, and dissolved reactive phosphate across the sediment-water interface were calculated as:

\[
\text{Flux} = (m)(V)/A
\]

where \(m\) is the slope of the regression line obtained by plotting the concentration of a relevant species as a function of incubation time (ug or mg/L/hr), \(V\) is the volume of the water column (Liters), and \(A\) is the sediment surface area (cm\(^2\)). Examples of oxygen and nutrient concentrations versus time are given in Figures 5-9 (these are just examples of oxygen consumption or nutrient input versus time). Initial flux estimates have units of ug or mg species/cm\(^2\)/hour which are converted to the following units:

- for the Sedimentary Oxygen Demand (SOD) = mg O\(_2\)/cm\(^2\)/hour * 10,000 * 24/1000
  = gm O\(_2\)/m\(^2\)/day
- for NH\(_4\)\(^+\) Benthic Flux = ug NH\(_4\)\(^+\)/cm\(^2\)/hour * 10,000 * 24/1000
  = mg NH\(_4\)\(^+\)/m\(^2\)/day
- for PO\(_4\)\(^3-\) Benthic Flux = ug PO\(_4\)\(^3-\)/cm\(^2\)/hour * 10,000 * 24/1000
  = mg PO\(_4\)\(^3-\)/m\(^2\)/day

To compare with other published benthic flux data, mg NH\(_4\)\(^+\)/m\(^2\)/day is divided by 14 to get mMole NH\(_4\)\(^+\)/m\(^2\)/day and mg PO\(_4\)\(^3-\)/m\(^2\)/day is divided by 30.97 to get mMole PO\(_4\)\(^3-\)/m\(^2\)/day.
Results

Table 2 gives the results of three sets of core incubations from three sites in the western basin of Quonochontaug Pond conducted during the summer of 2013.

Table 2. Sediment Oxygen Demand, Benthic Flux of Ammonium, and Benthic Flux of Phosphate at Three Sites in the Western Basin of Quonochontaug Pond.

<table>
<thead>
<tr>
<th>Site</th>
<th>Date</th>
<th>SOD¹</th>
<th>NH₄⁺ Benthic Flux²</th>
<th>PO₄³⁻ Benthic Flux³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Judge’s Rock</td>
<td>7/3-5/2013</td>
<td>-1.78</td>
<td>33</td>
<td>25</td>
</tr>
<tr>
<td>Judge’s Rock</td>
<td>8/8-10/2013</td>
<td>-1.53</td>
<td>369</td>
<td>8</td>
</tr>
<tr>
<td>Judge’s Rock</td>
<td>9/10-12/2013</td>
<td>-1.14</td>
<td>304</td>
<td>37</td>
</tr>
<tr>
<td>HCBuoy</td>
<td>7/3-5/2013</td>
<td>-1.41</td>
<td>110</td>
<td>14</td>
</tr>
<tr>
<td>HCBuoy</td>
<td>8/8-10/2013</td>
<td>-0.69</td>
<td>1,051</td>
<td>191</td>
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<tr>
<td>HCBuoy</td>
<td>9/10-12/2013</td>
<td>-2.20</td>
<td>176</td>
<td>39</td>
</tr>
<tr>
<td>HCChannel</td>
<td>7/3-5/2013</td>
<td>-0.96</td>
<td>35</td>
<td>-4.4</td>
</tr>
<tr>
<td>HCChannel</td>
<td>8/8-10/2013</td>
<td>-1.79</td>
<td>65</td>
<td>0.0</td>
</tr>
<tr>
<td>Ninigret Cove</td>
<td>9/10-12/2013</td>
<td>-1.72</td>
<td>128</td>
<td>38</td>
</tr>
</tbody>
</table>

1- Sediment Oxygen Demand, gmO₂/m²/day
2- uM NH₄⁺/m²/hr
3- uM PO₄³⁻/m²/hr

Negative sign indicates flux into benthic sediment, positive sign indicates efflux from benthic sediment.

The average and standard deviation for Quonochontaug Pond are: SOD= -1.47±0.47 gm O₂/m²/day, NH₄⁺ Benthic Flux= 153±124 uM/m²/hr (without HCBuoy, 8/8-10/2013), and PO₄³⁻ Benthic Flux= 26.1±16.2 uM/m²/hr (without HCBuoy, 8/8-10/2013). The nutrient benthic flux rates for HCBuoy, 8/8-10/2013, were an order of magnitude higher than those for any other sampling time and were not used in the calculation of average and standard deviation about the mean value (average).

SOD results for the Judge’s Rock site appear to be relatively consistent, -1.48±0.32 gmO₂/m²/day for the three time-period incubations in July, August, and September. Cores from this site always encountered semi-fluid, dark grey-black, silty-clay muds in the upper 10 cm of the sediment column (see core description under Study Sites section). Thus, it is not unexpected that SOD values would be similar, month to month. On the other hand, the monthly SOD values for the HCChannel site (July and August) are significantly different (-1.38±0.59 gmO₂/m²/day) with the July value substantially less than the August value (Table 2). The surface sediment at this site also consisted of fluid, dark grey-black, silty-clay muds in the upper 6 cm of the sediment column but also included dark grey-black organic tube structures sticking up into the water column. The tube structures were more prevalent in the August sediment core. It is likely that these tube structures are worm tubes whereby bottom water is pumped across the sediment-water interface into the surface sediment. Their prevalence in the August
sediment core may explain the greater SOD value for this sampling. The monthly SOD values for the HCBuoy site are considerably more variable than the other two sites (-1.43±0.76 gmO$_2$/m$^2$/day) and can be explained by the fact that this site was located in an actively growing eelgrass meadow with many biological entities living on the sediment surface. In fact, the August sediment core contained many white-colored bivalve creatures congregated in the upper 1 cm of the sediment column. This may explain the low SOD value and the extremely high ammonium and phosphate benthic flux values (Table 2). These bivalves move through the upper few centimeters of the sediment column, causing mixing of bottom water with surficial sediment. This process is known as bioturbation (Stolt et al., 2011).

As for the ammonium and phosphate benthic flux data (Table 2), there appears to be little relationship with the SOD values, at least at the Judge’s Rock site. The ammonium flux is somewhat variable (235±178 uM/m$^2$/hr) while the phosphate benthic flux (32±6 uM/m$^2$/hr) and the SOD (-1.48±0.32 gm O$_2$/m$^2$/day) are both relatively constant. At the HCChannel site, both the August SOD and the ammonium benthic flux values are significantly higher than those for the July sampling. At the HCBuoy site, it is obvious that biturbation has greatly enhanced the benthic flux of ammonium and phosphate in the August 2013 core incubations (Table 2).

Comparison with Other Studies
Table 3 gives the sediment oxygen demand (SOD) and the average benthic flux of ammonium and phosphate, mostly for the summer months, from many studies of shallow marine sites along the Atlantic and Pacific Coasts of the United States (Bailey, 2005). The average SOD of Quonochontaug Pond (1.5±0.5 gmO$_2$/m$^2$/day) is very similar to the average SOD for other Atlantic Coast sites (1.4±0.9 gmO$_2$/m$^2$/day) (Table 3). West Coast sites appear to have a lower average SOD (0.8±0.4 gmO$_2$/m$^2$/day). Many of the SOD measurements for the Atlantic Coast sites were made on somewhat fluid, grey-black, silty-clay muds which was the sediment type used for the core incubations in Quonochontaug Pond. These sediments would have a strong affinity for dissolved oxygen in bottom waters.

The average benthic ammonium flux data from Quonochontaug Pond grey-black, somewhat fluid, silty-clay muds is 153±124 uM NH$_4^+$/m$^2$/hr, a value not too different from the ammonium benthic flux average of other Atlantic Coast sites (181±74 uM NH$_4^+$/m$^2$/hr). The average ammonium benthic flux data for the Pacific Coast sites is 99±108 uM NH$_4^+$/m$^2$/hr (Table 3), a value approximately one-half that for the Atlantic Coast sites.

The average phosphate benthic flux from Quonochontaug Pond’s silty-clay muds is 26±16 uM PO$_4^{3-}$/m$^2$/hr, significantly higher than that for the average of other Atlantic Coast sites (17.5±10 uM PO$_4^{3-}$/m$^2$/hr). The average phosphate benthic flux data for the Pacific Coast sites is 13.2±8.9 uM PO$_4^{3-}$/m$^2$/hr (Table 3), a value similar to the average for the Atlantic Coast sites but substantially smaller than the average for Quonochontaug Pond.

Biogeochemical Processes Affecting the Benthic Flux of Nutrients
Nitrogen
The most important biologically-mediated nitrogen processes that could occur in Quonochontaug Pond are nitrate and ammonium assimilation by phytoplankton, ammonification (or remineralization) of sedimentary organic matter, and nitrogen fixation (Gruber, 2008). The fertilization of phytoplankton by nitrate and ammonium is an aerobic, photo-autotrophic process that represents the production of labile organic matter sinking to the bottom of the water column and becoming incorporated into surficial bottom sediment. This labile organic matter is known
as phytoplankton debris and is the starting point for remineralization of particulate nitrogen (and phosphorus) in bottom water and surface benthic sediment. Nitrogen fixation may be a process that could enhance the nitrogen content of the water column but since there is no evidence (presence of cyanobacteria) of this process occurring in southern Rhode Island’s coastal salt ponds (lagoons), it will not be discussed here.

Table 3. Sediment Oxygen Demand (SOD) and Benthic Flux of Ammonium and Phosphate at Shallow Marine Sites along the Atlantic Coast and the Pacific Coast of the United States. (All data, except those for Quonochontaug Pond, taken from Bailey, 2005)

| Location                  | Months, Year | SOD \(^1\) | NH\(_4\)\(^+\) \(^2\) | PO\(_4\)\(^3-\) \(^3\) |
|---------------------------|--------------|-------------|----------------|----------------|---|
| Buzzards May, MA          | May-Sept, 1989 | 0.62±0.05 (8) | nd | nd |
| Waquoit Bay, MA           | May-Oct., 1992-94 | 3.23±0.95 (6) | 306±200 (6) | 36.7±39.3 (6) |
| Narragansett Bay, RI      | May-Oct, 1973-1974 | 1.68±0.96 (15) | 134±75 (14) | nd |
| Potter Pond, RI           | Summer, 1979-81 | nd | 178±162 (8) | 19.5±16.0 (8) |
| Quonochontaug Pond, RI    | Summer, 2013 | 1.47±0.47 (9) | 153±124 (8) | 26.1±16.2 (7) |
| L I Sound, NY             | Summer, 1975-76 | nd | 84.5±74.3 (7) | nd |
| Ches. Bay, VA             | Summer, 1989 | 0.58±0.27 (11) | 193±126 (11) | 22.2±39.4 (11) |
| Potomac R. Est.           | August, 1979 | 1.17±0.43 (4) | 302±223 (7) | 19.2±10.7 (6) |
| York R., VA               | Summer, 1983 | 1.24±0.54 (4) | 180±121 (4) | 15.1±18.0 (4) |
| CherryStone Inlet, VA     | Summer, 1990 | 1.63±0.77 (6) | 154±133 (6) | 7.77±8.40 (6) |
| Neuse R. Est., NC         | Summer, 1988 | 0.48±0.21 (7) | 99±87 (7) | 12.9±21.2 (7) |
| Pamlico So., NC           | 1977-1978 | 2.37±0.85 (11) | 177±106 (9) | 5.6±8.6 (11) |
| Gal. Bay, TX              | July, 1993 | 0.21±0.05 (3) | 13.6±14.2 (3) | 0.57±2.75 (3) |
| Tomales Bay, CA           | Summer, 1987-88 | 0.54±0.12 (12) | 167±92 (12) | 16.0±8.8 (12) |
| S.SF Bay, CA              | Spring, 1996 | 0.75±0.42 (13) | 26.5±51.1 (13) | 6.8±2.6 (13) |
| Buena Vista Lagoon, CA    | Summer, 2008 | 1.37±1.66 (7) | 63±114 (4) | 13.9±33.2 (6) |
| LaJolla Bight, CA         | Summer, 1972 | nd | 32.5±30.8 (5) | 2.86±4.5 (5) |
| Quartermaster Hbr., WA    | Summer, 2010 | 0.98±0.62 (6) | 288±159 (5) | 25.5±24.9 (6) |

1- gmO\(_2\)/m\(^2\)/day
2- uM NH\(_4\)\(^+\)/m\(^2\)/hr
3- uM PO\(_4\)\(^3-\)/m\(^2\)/hr

Numbers in parentheses are number of measurements; nd- No Data
The assimilation of nitrate and ammonium into organic nitrogen by marine phytoplankton that need to satisfy their nitrogen requirement for growth is the process that dominates the marine nitrogen cycle (Gruber, 2008). The assimilation of nitrogen by phytoplankton is strongly linked to the photosynthetic fixation of carbon as both elements are needed to build living organic tissue. The synthesis of organic matter by the coupled assimilation of $\text{CO}_2$, $\text{NO}_3^-$ or $\text{NH}_4^+$, and $\text{PO}_4^{3-}$ can be expressed by the following two equations (Gruber, 2008):

1) Using Nitrate: $106 \text{CO}_2 + 16 \text{NO}_3^- + \text{HPO}_4^{2-} + 78 \text{H}_2\text{O} + 18 \text{H}^+ = \text{C}_{106}\text{H}_{175}\text{O}_{42}\text{N}_{16}\text{P}_1 + 150 \text{O}_2$

2) Using Ammonium: $106 \text{CO}_2 + 16 \text{NH}_4^+ + \text{HPO}_4^{2-} + 48 \text{H}_2\text{O} + 14 \text{OH}^- = \text{C}_{106}\text{H}_{175}\text{O}_{42}\text{N}_{16}\text{P}_1 + 118 \text{O}_2$

In the ocean, most of this fixed organic nitrogen is recycled back to nitrate by the remineralization process in the water column. In the salt ponds, in this case Quonochontaug Pond, the remineralization process in the water column and surficial benthic sediment proceeds as ammonification, and nitrification (the oxidation of ammonium to nitrate) is insignificant relative to ammonification.

The term microbial loop describes a trophic-level pathway in the marine microbial food web where dissolved organic carbon (DOC) is returned to higher trophic levels via its incorporation into bacterial biomass, and then coupled with the classic food chain formed by phytoplankton-zooplankton-nekton. Heterotrophic bacteria utilize dissolved organic matter (DOM) as an energy source. The source of DOM is from phytoplankton, perhaps mediated by zooplankton grazing or viral lysis (Azam et al., 1983). Bacterial numbers are controlled by heterotrophic flagellates that are preyed upon by microzooplankton. By this process, some DOM is returned to the main food chain (Azam et al., 1983) and the particulate material left over (phytoplankton debris or particulate nitrogen) sediments to the bottom (www.ozcoasts.gov.au). Thus, heterotrophic organisms consume autotrophic organisms (phytoplankton) and through the microbial loop process release nutrients (N and P) to the water column. That is, since these bacteria are actively consumed by scavengers, they participate in the regeneration of nutrient elements (Carlson et al., 1994).

Aerobic respiration is a chemical process in which oxygen is used to make energy from carbohydrates and is basically the reverse of photosynthesis (www.ozcoast.gov.au/glossary). The function of aerobic respiration is to release the energy and nutrients in organic matter so that they can be assimilated by organisms. Areal rates of pelagic respiration are 2-4 times higher than benthic respiration rates (Hopkinson and Smith, 2004).

The chemical composition of organic matter in marine environments can be generalized by the following formula: $(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z$ where $x=106$, $y=16$, $z=1$ for marine organic matter (e.g. phytoplankton) having the Redfield composition (Kristensen, 2000). Organic matter is completely metabolized by bacteria to $\text{H}_2\text{O}$, $\text{CO}_2$, and inorganic nutrients using oxygen as an electron acceptor according to the following:

3) $(\text{CH}_2\text{O})_x(\text{NH}_3)_y(\text{H}_3\text{PO}_4)_z + x\text{O}_2 = x\text{CO}_2 + y\text{NH}_3 + z\text{H}_3\text{PO}_4 + x\text{H}_2\text{O}$

As the oxic zone in coastal marine sediments usually is limited to a thin uppermost layer, a large fraction of the sedimentary organic matter is buried in a more or less decomposed form in the
underlying anoxic layers. Here, anaerobic decomposition of organic matter is accomplished by a consortia of bacteria. Anaerobic decomposition occurs stepwise, involving several different functional types of bacteria. First, the large and normally complex polymeric organic molecules are split stepwise into water soluble amino acids, monosaccharides, and fatty acids by hydrolysis and fermentation under the production of energy and the release of inorganic nutrients (Kristensen, 2000).

4) \[8(CH_2O)x(NH_3)y(H_3PO_4)_z = xCH_3CH_2COOH + xCH_3COOH (Acetate) + 3xCO_2 + 3xH_2 + yNH_3 + zH_3PO_4\]

5) Then, Denitrification: \[CH_3COOH + 1.6 NO_3^- + 1.7 H^+ = 2 CO_2 + 0.7 N_2 + 2.8 H_2O\]

6) Then, Sulfate Reduction: \[CH_3COOH + SO_4^{2-} = 2 CO_2 + S^{2-} + 2H_2O\]

The balance between downward transport and consumption of oxygen and the penetration depth of oxygen in coastal marine sediments is controlled by temperature, organic supply, light, water currents, and bioturbation (Kristensen, 2000):

Temperature is the master variable controlling rates of chemical and biological processes in the marine environment (Kristensen, 2000). With respect to oxygen penetration in coastal marine sediments, higher temperatures decrease the solubility of oxygen in water and the lowest oxygen penetration occurs when the temperatures are highest, like in the summer months (Kristensen, 2000). As a consequence, the penetration depth and concentration of oxygen in sediments is lower during warm than cold periods and the gradient driving diffusive uptake of oxygen at the sediment-water interface is steeper during warm periods (Rasmussen and Jorgensen, 1992).

Organic matter in sediments is considered a complex mixture of more or less labile compounds (Berner, 1980). It is generally accepted that benthic oxygen uptake is directly related to the input of labile organic matter to the sediment (Kristensen, 2000). Variations in oxygen penetration caused by seasonal fluctuations in fresh detrital influx are most conspicuous in coastal regions experiencing spring and fall phytoplankton blooms (Jorgensen, 1996).

The direct influence of light on oxygen conditions in sediments is limited to shallow areas where light is sufficient to maintain positive net photosynthesis by benthic primary producers. The chemical microenvironment created by benthic primary producers may have a more pronounced impact on coastal ecosystems than their photosynthetic production of organic matter (Kristensen, 2000).

The actual thickness of the diffusive boundary layer and thus the penetration depth of oxygen into sediments is determined by the water flow velocity and the roughness of the sediment surface (Kristensen, 2000). At higher water flow velocities, the thickness of the boundary layer is reduced and an increase in the diffusion-dependent solute flux across the sediment-water interface occurs.

Coastal marine sediments underlying oxygenated waters are often perforated with tubes and burrows formed by bottom-dwelling animals such as polychaetes, crustaceans, and bivalves (Kristensen, 2000). The hypothetical vertical distribution of microbial processes (aerobic respiration, nitrification, manganese oxide reduction, denitrification, iron oxide reduction, sulfate
reduction) based on the availability of electron acceptors is influenced by macrobenthos in a number of ways (Kristensen, 2000):

Material is translocated continuously between reaction zones by feeding, burrowing, and tube construction.
New reactive substrates in the form of mucus secretions are introduced into the sediment independent of the sedimentation process.
Tubes and burrows are irrigated with oxic water by the ventilation activities of their inhabitants.

Tube or burrow structures differ in size, appearance, and composition according to the functional group and the size of the various infaunal species. The permeability of tube and burrow linings to solute diffusion can be an important determinant of the chemical and biological composition of the surrounding sediment and the tube or burrow habitat. Aller (1994) found that the diffusive permeability of linings from eight infaunal species of marine invertebrates was 10-40% of that in free solution.

**Phosphorus**
The major input of dissolved and particulate phosphorus to estuarine and coastal marine waters is riverine phosphorus, where most of the phosphorus is in the particulate form (Ruttenberg, 2003). Available data suggest that between 20% and 40% of this suspended particulate phosphorus is organic (Ruttenberg, 2003) and the remainder consists of inorganic forms apatite and P-sorbed ferric oxyhydroxides.

The net removal of phosphorus in coastal marine waters occurs by flocculation of humid-iron complexes in saline waters and biological uptake. Phosphorus in its simplest form, dissolved orthophosphate (PO$_4^{3-}$), is taken up by photosynthetic organisms at the base of the marine food web. The marine phosphorus cycle is linked to the marine carbon and nitrogen cycles through photosynthetic fixation of these elements by phytoplankton (see equations 1 and 2). Organic matter is an important primary carrier of phosphorus to marine sediments. Due to the shallower water column in coastal waters, less respiration (equation 3) occurs prior to deposition of phosphorus in benthic sediment.

The forms of phosphorus in coastal marine sediments include detrital and authigenic apatite (Ca-P), ferric iron-bound phosphorus, and organic phosphorus. Mobilization of sedimentary phosphorus by microbial activity during diagenesis causes a buildup of dissolved phosphate in benthic sediment pore waters, promoting the efflux of phosphate from benthic sediment to overlying bottom waters. The sorption or release of iron-oxide bound phosphorus is driven by the dissolved-oxygen concentration in bottom water overlying benthic sediment (Ruttenberg, 2003). With more dissolved oxygen and a positive redox potential, iron oxyhydroxide is formed at the sediment-water interface (see Figure 14) causing the sorption of phosphate. With less dissolved oxygen (i.e. hypoxia) and a less positive to negative redox potential, iron oxyhydroxide is dissolved, releasing dissolved phosphate to pore water.

Ruttenberg (2003) describes the important processes that occur during the transport to and early diagenetic transformations of phosphorus in marine sediments (see her Figure 3). Dissolved, detrital, and organically-bound phosphorus is transported to the coastal ocean by rivers. In coastal waters, biological uptake of phosphorus by photosynthetic activity, chiefly by phytoplankton, convert dissolved phosphate into organic phosphorus (phosphorus in synthesized organic matter) which sinks to the bottom. Some of this organic phosphorus is
remineralized in bottom waters by heterotrophic bacteria and zooplankton excretion and the remainder is deposited in benthic sediment. Once delivered to the sediment-water interface, organic phosphorus is subject to breakdown via microbial respiration (mineralization). A representative equation for oxygenic respiration is given below (Ruttenberg, 2003):

7) \[ C_{106}H_{179}O_{68}N_{16}P_{1} + 106O_2 = 106CO_2 + 64H_2O + 16NH_3 + H_3PO_4 \]

After oxygenic respiration, a well-documented sequence of electron acceptors (manganese oxide, nitrate, iron oxide, sulfate) are utilized by microbial communities. All of these respiration reactions result in a buildup of phosphate and other metabolites in pore waters. Generally, organic matter and iron oxyhydroxide are the primary sources of phosphorus that undergo steady-state diagenesis and release phosphate to benthic sediment pore water (Ruttenberg, 2003).

**Nitrogen Cycling in Quonochontaug Pond**

*Internal Mass Balance of Dissolved Inorganic Nitrogen (DIN)*

**Water Column.** The particulate matter, mostly phytoplankton cells, that is suspended in the water column and eventually sinks to the bottom upon mortality is undergoing rapid decomposition due to autolysis and bacterial attack. This decomposition process is called mineralization (also remineralization, regeneration), in which essential nutrients (species of carbon, nitrogen, and phosphorus) for algal growth are recycled within the water (and sediment) column and fuel the continual growth of plant matter. While the microbial loop (see section on nitrogen biogeochemical processes) cycles these nutrient species through zooplankton and phytodetritus, we will use plankton respiration as the main process that causes the mineralization of nutrient in the water column. Aerobic respiration is represented by equation 7 where organic matter (phytoplankton cells) with a set C-N-P composition is oxidized by molecular oxygen to stoichiometric concentrations of CO$_2$, NH$_3$, and H$_3$PO$_4$. Thus, through phytoplankton respiration, oxygen is consumed in the water column.

Quonochontaug Pond has lower dissolved oxygen concentrations in bottom waters than in surface waters, especially during the months of July, August, and September. For the sampling years 2008 to 2021, the difference between surface waters and bottom waters (\(\Delta_{\text{sur-bot}}\)) is, on the average, 1.25±0.38 mg/L dissolved oxygen (Callender, 2013). Appendix A lists the dissolved oxygen data for the 2013 sampling year and the 2008-2012 sampling years with calculations of dissolved oxygen consumed in the bottom waters. (The 2013 dissolved oxygen data was only available after calculations were made for the 2008-2012 data). For the 2013 sampling year, the oxygen consumption in bottom waters (respiration) was 50±41 gm O$_2$/m$^2$/yr. And, for the 2008-2012 sampling years, the oxygen consumption in bottom waters was 60±34 gm O$_2$/m$^2$/yr.

The photosynthetic quotient is the molar ratio of dissolved oxygen produced during the lysis of water in the light reactions of photosynthesis to carbon assimilated during the Calvin-Benson Cycle (Smith et al., 2012). This quotient varies between 1.42 (Smith et al., 2012) and 1.2 (Oviatt et al., 1986). For simplicity, we will use a value of 1.3 (www.soest.hawaii.edu/Krubin/CG325/lect24.pdf). Thus, the organic carbon remineralization rate for Quonochontaug Pond, where plankton respiration is converted to carbon mineralization, is 46±5 gm C/m$^2$/yr (60 gm O$_2$/m$^2$/yr divided by 1.3).
Now, we want to estimate the dissolved inorganic nitrogen (DIN) requirement for primary production in the water column of Quonochontaug Pond. The annual primary production of Quonochontaug Pond has been given by Moran et al. (2013) to be 96 gm C/m²/yr. In order to calculate the amount of DIN needed for algae growth in Quonochontaug Pond, the annual primary production must be divided by the C:N ratio of microalgae. The standard Redfield C:N ratio for marine plankton is 106:16 or 6.63:1 (Redfield, 1934). However, many elemental measurements of particulate organic matter from shallow ocean waters have yielded a somewhat higher ratio, 8.4:1. This average value was taken from many references including Kepkay et al. (1997), Frigstad et al., 2011, Doval et al. (digital.csic.es), Faganeli et al. (1988), Maksymouliska-Brossard and Piekarek-Jankowska (2001), and Chen-Tung et al. (1996). Thus, the DIN requirement for growth of microalgae (phytoplankton) in Quonochontaug Pond is 96 gm C/m²/yr  8.4 (C:N) = 11.4 gm N/m²/yr. Much of this DIN that fuels the growth of algae appears to be nitrate as this is the predominant form of inorganic nitrogen that enters Quonochontaug Pond from surface water, atmosphere, and groundwater inputs (Callender, 2013). If we compare the amount of inorganic nitrogen mineralized by plankton respiration, calculated as 46 gm C/m²/yr  8.4 (C:N) = 5.5 gm N/m²/yr, to the amount of inorganic nitrogen required for growth of microalgae (phytoplankton), 11.4 gm N/m²/yr, then water-column respiration or mineralization contributes 50% of the DIN required for microalgae growth.

**Benthic Sediment.** The other major component of the internal mass balance for DIN in Quonochontaug Pond is the benthic sediment. This sediment, on the bottom of Quonochontaug Pond, receives organic and inorganic particulate matter from the water column. The quantity and quality (ease of decomposition) of the organic matter that is deposited in the surface sediment of the Pond depends upon autotrophic and heterotrophic processes in the water column, which result in the production of phytodetritus and waste material from grazers that sediments to the bottom. These organic-rich surface sediments are zoned based on their dissolved oxygen content: an aerobic zone with rapidly declining dissolved oxygen and an anaerobic or anoxic zone where no dissolved oxygen exists. Biogeochemical processes consuming oxygen in the sediment column differ from those in the water column (Pena et al., 2010). The water column of Quonochontaug Pond is always oxic to slightly hypoxic, so biological production and respiration/remineralization of organic matter are the dominant processes. Consumption of oxygen in benthic sediments can greatly exceed the oxygen consumption in the water column (Pena et al., 2010). In the surface oxic zone of benthic sediment, oxidation of organic matter is the dominant process. This surface oxic zone is usually no more than 1 cm thick, especially in shallow coastal waters like Quonochontaug Pond. And, in the warm summer months when hypoxia may exist (Guarinello, 2009), the thickness of the benthic sediment oxic zone may be less than 0.5 cm. Underlying the surface oxic zone is the suboxic zone where nitrate, manganese oxide, and iron oxide respiration occur (Pena et al., 2010). This zone may be either non-existent or ephemeral in Quonochontaug Pond as nitrate concentrations in the bottom waters of the Pond are very low. Finally, the reduced (anoxic) zone underlies the suboxic zone and is the major locality of sulfate reduction in coastal marine waters (Pena et al., 2010). Equation 6 above represents the oxidation of organic matter by sulfate respiration.

The coupling between the water column and the benthic sediments is an important concept in marine biogeochemistry. In the water column, heterotroph organisms benefit from primary production and feed on the remains of autotrophic organisms (algae). Nutrients (N and P species) are remineralized by the heterotrophic community, channeling nutrients back to the primary producers (Sokoll, 2013). Dead cells, byproducts of grazers, and other organic detritus
form particles or aggregates which sink towards the bottom. Sinking aggregates are often densely populated with heterotrophic microorganisms (bacteria) that lead to degradation of organic matter as it sinks through the water column (Sokoll, 2013). At the Pond bottom and in the benthic sediment, organic matter is further degraded and the remineralized nutrients are released to bottom water and sediment porewater. Exchange between surface sediment and bottom water is accomplished by molecular diffusion and advective processes such as bioturbation. The regenerated nutrients help fuel primary production through mixing of the water column. This coupling between the water column and the benthos is called “benthic-pelagic coupling” (Sokoll, 2013). The coupling between the water column and the benthic sediments is much tighter in coastal environments than in the open ocean.

Fine-grained, silty-clay sediments occupy the deeper depressions in Quonochontaug Pond and are called low-energy lagoonal bottom sediments (Stolt et al., 2011). These sediments occupy approximately 43% of the bottom deposits of Quonochontaug Pond. The Judge’s Rock (JR) station in the Pond (Figure 1) contains just such deposits. Also, the Harmonic Cove Buoy (HCBuoy) station contains clayey-silt muds that support a sizable eelgrass meadow (Guarinello, 2009). This station also supports an abundant benthic invertebrate population (Stolt et al., 2011) which during August causes significant bioturbation between the benthic sediment and the bottom waters in the western basin of Quonochontaug Pond (Figure 1, Figure 11). The third station where several benthic flux measurement were made in the summer of 2013 is Harmonic Cove Channel (HCChannel). Sediment at this site is classified as a slightly clayey silt with some fine sand. During August, dark grey-black tubular structures rise above the sediment surface into the bottom water. These are thought to be worm tubes that are common in such coastal marine environments.

Appendix B lists the data and calculations for the annual benthic flux of ammonium from lagoonal bottom sediment in Quonochontaug Pond. Three core incubations were performed on sediments from the JR and HCBuoy stations in the summer of 2013 (July, August, September). Two core incubations were performed on the HCChannel station in July and August of 2013; and one core incubation was performed on sediment from the Ninigret Cove Embayment (located on the northeast shore of Quonochontaug Pond, Figure 1) in September of 2013. (This core incubation was done to aid the study of shallow groundwater input of nitrogen and phosphorus to Ninigret Cove benthic sediment). The results of these core incubations, with respect to the benthic flux of ammonium, are presented in Table 2. In late October of 2012, when water temperatures were declining and dissolved oxygen concentrations in bottom waters were elevated, one core incubation was performed at the JR, HCBuoy, and HCChannel stations. These ammonium fluxes are recorded in Appendix B.

A note about the seasonal calculation of ammonium benthic flux recorded in Appendix B. There are only four months of ammonium benthic flux measurements for Quonochontaug Pond; late October 2012, July 2013, August 2013, and September 2013. In the first case (1), I have assigned the October 2012 flux to the fall-winter-early spring months (240 days), the July 2013 flux to the early summer months (60 days), and the August and September 2013 fluxes to the late summer months (60 days). In the other case (2), I have assigned the July 2013 flux to the months of January-July (210 days) only because I have no flux measurements for the winter and spring. In general, July is a month where water temperatures are still rising and dissolved oxygen concentrations in bottom waters are still elevated. The July incubations were done in the first third of the month and represent the lowest ammonium fluxes measured during the summer of 2013 (Table 2). The fluxes measured in August and September are used to
designate the late summer (60 days) fluxes and represent the highest values measured during this study (Table 2). The October 2012 measurements represent the fall fluxes, October to December (90 days). The average of the two estimates is 8.1 gm N/m²/yr or 10,500 kg N/yr (Appendix B).

The average annual benthic flux of ammonium for Quonochontaug Pond is 10,500 kg N/yr or 8.1 gm N/m²/yr. We see from above that the nitrogen requirement of primary production in the water column of Quonochontaug Pond is 11.4 gm N/m²/yr or 34,286 kg N/yr, thus the annual benthic flux of ammonium contributes between 31 and 71% of this nitrogen requirement, depending on whether we use absolute fluxes (kg N/yr) or fluxes normalized to surface area. The discrepancy relates to the fact that the surface area of fine-grained, silty-clay muds is 43% of the total surface area of Quonochontaug Pond. Adding up the normalized water-column respiration and the benthic flux estimates of nitrogen supporting the primary productivity, we get 121% (8.1 + 5.7/11.4). Obviously, one or both of these contributions may have been overestimated. And/or, our estimation of the nitrogen requirement may be too low.

So, there are three possible sources of error in the above calculations. The nitrogen requirement of phytoplankton for growth; water-column respiration (remineralization of nitrogen); and the benthic flux of ammonium. The most obvious error is the bottom surface area of Quonochontaug Pond represented by fine-grained sediments. If we use the total surface area for Quonochontaug Pond (30x10⁵ m²), then the benthic flux becomes 3.5 gm N/m²/yr and its contribution to the nitrogen requirement phytoplankton growth is 31% (3.6/11.4). And, the total contribution from the two sources is 81%. This is much better but probably not realistic in that coarse-grained sediments (sands and gravels) are found in the near-shore environment of Quonochontaug Pond (Stolt et al., 2011; Guarinello, 2009). Another potential source of error is the C:N ratio that was used to convert primary production in carbon units to that in nitrogen units. This ratio is 8.4:1 and is substantially greater than the Redfield ratio, 6.6:1. If the Redfield ratio is used, then the nitrogen requirement for phytoplankton growth would be 14.5 gm N/m²/yr. And the total contribution of water-column respiration (remineralization) and benthic flux (regeneration) would be 95% (8.1 + 5.7/14.5). Obviously, this result would be more acceptable. However, the most accurate result probably lies somewhere between the two extremes listed above.

So, the internal mass balance for dissolved inorganic nitrogen in Quonochontaug Pond is as follows:

<table>
<thead>
<tr>
<th>C:N Ratio</th>
<th>N Required</th>
<th>Water-Column Respiration</th>
<th>Benthic Regeneration</th>
<th>% W-C</th>
<th>%Benthic</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.4:1</td>
<td>11.4</td>
<td>5.7</td>
<td>8.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>50</td>
<td>71</td>
</tr>
<tr>
<td>6.6:1</td>
<td>14.5</td>
<td>7.3</td>
<td>3.5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>50</td>
<td>24</td>
</tr>
</tbody>
</table>

1- Nitrogen required for the growth of planktonic algae, gm N/m²/yr.
2- Water-Column Respiration (Remineralization), gm N/m²/yr.
3- Benthic Regeneration (Benthic Flux of Ammonium), gm N/m²/yr.
   a- 12.9x10⁵ m² bottom sediment surface area.
   b- 30x10⁵ m² bottom sediment surface area.
4- Percent of nitrogen requirement for plankton growth by water-column respiration.
5- Percent of nitrogen requirement for plankton growth by benthic regeneration.
Given the major constraint mentioned above (surface area of fine-grained benthic sediment), then water-column remineralization of DIN provides 41% (5.5 gm N/m²/yr  13.4 gm N/m²/yr) and benthic flux (regeneration) of ammonium provides 60% (8.1 gm N/m²/yr  13.4 gm N/m²/yr). The term 13.4 gm N/m²/yr is the average nitrogen required for the growth of planktonic algae, as noted in the above table. The total of water-column respiration and benthic flux, 101%, appears to be a good approximation of 100%.

**External Mass Balance of Dissolved Inorganic Nitrogen (DIN)**

Callender (2013), in a white paper describing the detailed analysis of physical, water quality, and nutrient data as related to nitrogen and phosphorus cycling in Quonochontaug Pond, constructed an external DIN mass balance for the Pond. An external mass balance gives the quantitative sources of DIN into and from the water column. This DIN mass balance, with modifications related to the present study of benthic fluxes, is presented in Figure 10. The only difference between the Figure 10 version of the DIN mass balance and that given in Callender (2013) is that the groundwater input of DIN has been updated with recent data (Moran et al., 2013) and that the benthic flux of ammonium from bottom sediment to the water column has been added. The previous groundwater input of DIN was calculated from flow data of the US Geological Survey’s hydrologic model (Masterson et al., 2007) and nitrate data from Nixon and Buckley (2007), Kroeger et al. (2006), and Bowen et al. (2007). However, since most of the nitrate data was gleaned from groundwater studies on Cape Cod and deep well sites significantly north of the Pond, it was thought that a direct study of ground-water input to Quonochontaug Pond would better represent the mass input to the Pond. Such a study was conducted by Moran and others (2013) with the result that the annual groundwater input of DIN to Quonochontaug Pond is 2,100 kg/yr. And, as seen above, the annual benthic flux of ammonium to the water column of Quonochontaug Pond is 10,500 kg/yr (Figure 10). So, the external mass balance of DIN for Quonochontaug Pond is (Figure 10):

\[
\text{Input (Surface Water, Streams + Atmosphere + Groundwater + Benthic Flux)} = \text{Output (Sedimentation + Exchange with Block Island Sound)}
\]

Putting numbers to the terms, then \(\text{Input} \ (2,110 \text{ Kg/yr} + 2,964 \text{ Kg/yr} + 2,100 \text{ Kg/yr} + 10,500 \text{ Kg/yr}) = \text{Output} \ (11,300 \text{ Kg/yr} + 5,950 \text{ Kg/yr}),\)

or \(\text{Input} \ (17,674 \text{ Kg N/yr}) = \text{Output} \ (17,250 \text{ Kg N/yr})\)

Amazingly, the external DIN mass balance is essentially in balance! From the above, it is clear that benthic flux of ammonium is by far the largest input to the waters of Quonochontaug Pond and that surface water (streams), atmosphere, and groundwater inputs are considerably smaller and essentially equal to one another.

**Phosphorus Cycling in Quonochontaug Pond**

**Internal Mass Balance of Dissolved Inorganic Phosphorus (DIP)**

*Water Column.* A description of the biogeochemistry of particulate matter in the water column of Quonochontaug Pond is given in the first paragraph in the *Water Column* subsection under Internal Mass Balance of Dissolved Inorganic Nitrogen (DIN). Please refer to this paragraph as it essentially describes biogeochemical reactions pertaining to nitrogen and phosphorus in the water column of Quonochontaug Pond.
Quonochontaug Pond has lower dissolved oxygen concentrations in bottom waters than in surface waters, especially during the months of June-July-August. For the sampling years 2008 to 2012, the difference between surface waters and bottom waters (delta_{sur-bot}) is, on the average, 1.25±0.38 mg/L dissolved oxygen (Callender, 2013). Appendix A lists the dissolved oxygen data for the 2013 sampling year and the 2008-2012 sampling years with calculations of dissolved oxygen consumed in the bottom waters. For the 2013 sampling year, the oxygen consumption in bottom waters (respiration) was 50±41 gm O₂/m²/yr. And, for the 2008-2012 sampling years, the oxygen consumption in bottom waters was 60±34 gm O₂/m²/yr.

The photosynthetic quotient is the molar ratio of dissolved oxygen produced during the lysis of water in the light reactions of photosynthesis to carbon assimilated during the Calvin-Benson Cycle (Smith et al., 2012). This quotient varies between 1.42 (Smith et al., 2012) and 1.2 (Oviatt et al., 1986). For simplicity, we will use a value of 1.3. Thus, the organic carbon remineralization rate for Quonochontaug Pond, where plankton respiration is converted to carbon mineralization, is 46±5 gm C/m²/yr (60 gm O₂/m²/yr divided by 1.3).

Now, we want to estimate the dissolved inorganic phosphorus (DIP) required for primary production in the water column of Quonochontaug Pond. The annual primary production of Quonochontaug Pond has been given by Moran et al. (2013) to be 96 gm C/m²/yr. In order to calculate the amount of DIP needed for planktonic algae growth in Quonochontaug Pond, the annual primary production must be divided by the C:P ratio of microalgae. The standard Redfield C:P ratio for marine plankton is 106:1 (Redfield, 1934). However, many elemental measurements of particulate organic matter from shallow ocean waters have yielded a somewhat different C:P ratio, 118:1. This average value was taken from several references including Frigstad (2011), Faganelli et al. (1988), Copin-Montegot (1983). Using this C:P ratio, we calculate that 0.82 gmP/m²/yr (96 gm C/m²/yr 118 C:P) or 2,430 kgP/yr are needed to support the planktonic algae growth. If we use an updated N:P ratio (16.3:1) provided by Callender (2013), Downing (1997), and Nieuwerburgh (2004), then 0.70 gmP/m²/yr (11.4 gm N/m²/yr 16.3 N:P) or 2,100 kgP/yr are needed to support planktonic algae growth in Quonochontaug Pond. The average of these two estimates is 0.76 gmP/m²/yr or 2,280 kgP/yr.

Using the same C:P and N:P ratios to convert water-column remineralization (respiration) from carbon and nitrogen units to phosphorus units, the results are:

46 gm C/m²/yr 118 C:P = 0.39 gmP/m²/yr or 1,169 kgP/yr
5.5 gm N/m²/yr 16.3 N:P = 0.34 gmP/m²/yr or 1,020 kgP/yr

Taking the average of these values, water-column remineralization (respiration) of phosphorus is 0.365 gmP/m²/yr or 1,095 kgP/yr. The second number in all of the above phosphorus calculations converts gmP/m²/yr to kgP/yr by multiplying the former value by the surface area of Quonochontaug Pond (30x10^5 m²). If we compare the average value for water-column remineralization of phosphorus (0.365 gm P/m²/yr) to the phosphorus required for phytoplankton growth (0.76 gm P/m²/yr), then water-column remineralization of phosphorus supplies 48% of that required for plankton growth. This is the same percentage support that was calculated for nitrogen (48%).

**Benthic Sediment.** The other major component of the internal mass balance for DIP in Quonochontaug Pond is the benthic sediment. As a reminder, the description of biogeochemical processes operative in the benthic sediment of Quonochontaug Pond is detailed in the subsection **Benthic Sediment** under the Internal Mass Balance of Dissolved
Inorganic Nitrogen (DIN) section of Nitrogen Cycling in Quonochontaug Pond. These processes and coring logistics described for nitrogen also apply to phosphorus.

Appendix C lists the data and calculations for the annual benthic flux of phosphate from lagoonal bottom sediment in Quonochontaug Pond. Three core incubations were performed on sediments from the JR and HCBuoy stations in the summer of 2013 (July, August, September). Two core incubations were performed on the HCChannel station in July and August of 2013; and one core incubation was performed on sediment from the Ninigret Cove Embayment (located on the northeast shore of Quonochontaug Pond, Figure 1) in September of 2013. The results of these core incubations, with respect to the benthic flux of phosphate, are presented in Table 2. In late October of 2012, when water temperatures were declining and dissolved oxygen concentrations in bottom waters were elevated, one core incubation was performed at the JR, HCBuoy, and HCChannel stations. These phosphate fluxes are recorded in Appendix C.

The October 2012 benthic flux of phosphate was used to estimate the fall-winter-spring phosphate flux, \(-0.34 \text{ mgPO}_4^{3-}/\text{m}^2/\text{day} \) (Appendix C). Multiplying this value by 240 days (8 months) gives -0.082 gmP/m\(^2\)/yr, and multiplying this value by the fine-grained bottom sediment surface area (12.9x10\(^5\) m\(^2\)) gives -106 kgP/yr. The July 2013 benthic flux of phosphate (4.1±6.9 mgPO\(_4^{3-}/m^2/day\), Appendix C) was used to estimate the early summer period (June and July), and multiplying this value by 60 days gives 0.246 gmP/m\(^2\)/yr and 317 kgP/yr. The August and September benthic fluxes of phosphate (14.5±15.3 mgPO\(_4^{3-}/m^2/day\), Appendix C) were used for the late summer period, and multiplying the average benthic flux by 60 days gives 0.87 gmP/m\(^2\)/yr and 1,122 kgP/yr. Thus, the annual benthic flux of phosphate from benthic sediment in Quonochontaug Pond is 0.78 gmP/m\(^2\)/yr or 1,333 kgP/yr (Appendix C).

The internal mass balance of DIP for Quonochontaug Pond is as follows:

<table>
<thead>
<tr>
<th></th>
<th>P Required(^{1a})</th>
<th>P Required(^{1b})</th>
<th>W-C Respiration(^{2a})</th>
<th>W-C Respiration(^{2b})</th>
<th>B Flux(^{3a})</th>
<th>B Flux(^{3b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C:P=118:1</td>
<td>0.76</td>
<td>2,250</td>
<td>0.37</td>
<td>1,110</td>
<td>0.78</td>
<td>1,333</td>
</tr>
<tr>
<td>N:P=16.3:1</td>
<td>0.70</td>
<td>2,100</td>
<td>0.35</td>
<td>1,050</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1a- Phosphorus required for growth of planktonic algae, gmP/m\(^2\)/yr.
1b- Phosphorus required for growth of planktonic algae, kgP/yr.
2a- Phosphate released by plankton respiration (remineralization), gmP/m\(^2\)/yr.
2b- Phosphate released by plankton respiration (remineralization), kgP/yr.
3a- Benthic flux of phosphate, gmP/m\(^2\)/yr. (This value is independent of C:P and N:P ratio)
3b- Benthic flux of phosphate, kgP/yr. (This value is independent of C:P and N:P ratio)

If we use the C:P ratio for calculation of phosphorus required for phytoplankton growth and water-column respiration, then water-column remineralization supports 48% of plankton growth. And, benthic regeneration of phosphate supports 59% of plankton growth. If we use the N:P ratio for calculation of phosphorus required for phytoplankton growth and water-column respiration, then water-column remineralization supports 50% of plankton growth. And, benthic regeneration of phosphate supports 63% of plankton growth. On the average, water-column respiration and benthic flux provide 110% of the phosphorus required for plankton growth in the water column of Quonochontaug Pond. Some uncertainty in the data used to make the above calculations is probably the cause of this excess, 110% compared to 100%. However, it appears that estimates for water-column remineralization of phosphate (DIP) are relatively
consistent with respect to C:N:P stoichiometry and that the annual benthic flux of phosphate (DIP) provides the balance of phosphorus needed for growth of planktonic algae.

Looking at the data in Appendix C, it is apparent that the benthic fluxes of phosphate measured in August and September 2013 are significantly greater than those for other seasons (late summer, 14.5 mgPO$_4^{3-}$/m$^2$/day; early summer, 4.1 mgPO$_4^{3-}$/m$^2$/day; fall-winter-spring, -0.34 mgPO$_4^{3-}$/m$^2$/day). The late summer benthic flux of phosphate in Quonochontaug Pond (26 uMPO$_4^{3-}$/m$^2$/hr) is the largest value for summer benthic fluxes of phosphate listed in Table 3. That is, Potter Pond, RI (19.5 uMPO$_4^{3-}$/m$^2$/hr), Chesapeake Bay, VA (22.2 uMPO$_4^{3-}$/m$^2$/hr), Potomac River Estuary, VA (19.2 uMPO$_4^{3-}$/m$^2$/hr), York River Estuary, VA (15.0 uMPO$_4^{3-}$/m$^2$/hr), and Tomales Bay, CA (16.0 uMPO$_4^{3-}$/m$^2$/hr).

**External Mass Balance of Dissolved Inorganic Phosphorus (DIP)**

Callender (2013), in a white paper describing the detailed analysis of physical, water quality, and nutrient data as related to the nitrogen and phosphorus cycling in Quonochontaug Pond, constructed an external DIP mass balance for the Pond. This DIP mass balance, with a modification related to the present study of benthic fluxes and new estimates of atmospheric and groundwater input and breach way output, is presented in Figure 13. The main difference between the the Figure 13 version of the DIP mass balance and that given in Callender (2013) is that groundwater input of DIP has been taken from Moran et al. (2013) for submarine groundwater discharge (SGD) through coarse-grained sediments that occur along the northern shore of Quonochontaug Pond instead of using well data in the Pond’s watershed or SGD data from Cape Cod (Kroeger et al., 2006; Bowen et al., 2007). The other difference between Figure 13 and the external mass balance of DIP given in Callender (2013) is the term for the export of DIP from Quonochontaug Pond to Block Island Sound. The average dissolved phosphorus (DP) concentration is the eastern basin of Quonochontaug Pond is 13.7±2.1 ug/L while the average DP for eastern Long Island Sound is 12.8±6.2 ug/L (Boon, 2008). Thus, the export of DIP = (13.7-12.8 ug/L)(3.25x10$^8$ L/day)(365 days/yr) = 1,067 kgDIP/yr.

So, the external mass balance of DIP for Quonochontaug Pond, using Moran et al. (2013) SGD phosphorus data, the annual benthic flux of phosphate (this study, Appendix C), and new DP data from eastern Long Island Sound (Figure 11) is as follows:

**Input** (Surface Water, Streams + Atmosphere + Groundwater + Benthic Flux) = **Output** (Sedimentation + Exchange with Block Island Sound)

Putting numbers to the terms, then **Input** (19 kg/yr + 19 kg/yr + 185 kg/yr + 1,333 kg/yr) = **Output** (892 kg/yr + 1,067 kg/yr)

or, **Input** (1,516 kg DIP/yr) = **Output** (1,959 kg DIP/yr)

This external DIP mass balance is not as close to being in balance as the one for DIN. Both the sedimentation term and the breach-way out term have a significant level of uncertainty that may be responsible for this imbalance.
Discussion

 Oxygen Consumption in Bottom Water and Surface Sediment
Appendix A gives the average dissolved oxygen consumption in bottom waters of Quonochontaug Pond for the years 2008 to 2012 and 2013, 58±7 gmO\textsubscript{2}/m\textsuperscript{2}/yr. (The 2013 dissolved oxygen data was not available at the time that the initial calculations were made) This average is for 6 months, May to October. The average SOD (Table 2) is 1.38±0.41 gmO\textsubscript{2}/m\textsuperscript{2}/day and when multiplied by 180 days, gives an annual SOD of 248±74 gmO\textsubscript{2}/m\textsuperscript{2}/yr. Thus, the diffusive flux of oxygen into benthic sediment (SOD) is about four (4) times the oxygen consumption in bottom water. This compares with two and one-half times (2.5) for the diffusive flux of oxygen into sediment versus water-column reactions at a seasonally hypoxic site in the Baltic Sea (Reed et al., 2011).

Quonochontaug Pond experiences episodic hypoxia (Guarinello, 2009). In a detailed study of the Pond during the summers of 2007 and 2008, Guarinello (2009) found that the forcing functions for hypoxia were tides, photoperiod, wind and precipitation, and circulation patterns. The absolute amplitude of dissolved oxygen data were -7.0 mg/L (JR), -4.3 mg/L (HCBuoy), and -2.0 mg/L (HCChannel). Minimum values in dissolved oxygen were recorded between 6:30 and 8:15 am. Guarinello (2009) concluded that the western basin of Quonochontaug Pond is most vulnerable to hypoxia during Spring tides due to reduced water transport from Block Island Sound during flood tides. Additionally, moderate to high rainfall and low northeast wind stress can create water-column stratification and induce hypoxia.

If we use the above dissolved oxygen deficits in bottom water during hypoxic events in Quonochontaug Pond for the summers of 2007 and 2008, then the average oxygen consumption in bottom waters of the western basin of the Pond would be 417±193 gmO\textsubscript{2}/m\textsuperscript{2}/yr. These hypoxic events only occurred during a two-month period (60 days) during the summer. This average hypoxic oxygen consumption in bottom waters of the western basin of Quonochontaug Pond (417 gmO\textsubscript{2}/m\textsuperscript{2}/yr) is about 7 times greater than the annual oxygen consumption for the entire Pond (58 gmO\textsubscript{2}/m\textsuperscript{2}/yr). Since these oxygen consumption rates occurred for only two months of the year (Guarinello, 2009), one might expect that the annual oxygen consumption rate might be 64 gmO\textsubscript{2}/m\textsuperscript{2}/yr (58 + 417/6) 2 (gmO\textsubscript{2}/m\textsuperscript{2}/yr) for all of Quonochontaug Pond. This annual oxygen consumption rate in bottom waters of the Pond is still more than 3.5 times less than the diffusive flux of oxygen into benthic sediment (SOD=248 gmO\textsubscript{2}/m\textsuperscript{2}/yr).

Nitrogen Cycling in Quonochontaug Pond
Figure 10 shows the internal mass balance of dissolved inorganic nitrogen (DIN) for Quonochontaug Pond. The water-column respiration/mineralization of organic matter provides 48% of the inorganic nitrogen needed (34,286 KgN/yr) for the growth of phytoplankton (microalgae). If we include hypoxia during two summer months as an extreme of dissolved oxygen consumption in bottom water (see above), then water-column respiration/mineralization would provide 52% of the DIN needed for microalgae growth. The benthic flux of ammonium into bottom water from fine-grained bottom sediments provides an additional 31% of the DIN needed for microalgae growth.

There are several versions of the nitrogen cycle in marine aquatic systems. Paasche (1988) depicts the euphotic zone whereby phytoplankton take up nitrate and ammonium (DIN), are consumed by grazers that produce nitrogen detritus (non-living particulate organic nitrogen,
PON) that sinks into the aphotic zone and where a fraction of the PON is remineralized to ammonium, and eventually the remaining PON is deposited in benthic sediment and further remineralized to ammonium that fluxes into bottom water. Newell et al. (1988) and Billen and Lancelot (1988) further elaborate on the pathways of nitrogen regeneration through the plankton community in a mixed water column. The decomposition cycle includes heterotrophic bacteria, flagellates, and large protozoa. And, herbivores, such as zooplankton, ingest phytoplankton. The estimate of water-column respiration/mineralization presented in Figure 10 only represents respiration as the process that converts PON (micro algae) to ammonium. The other decomposer reactions, as mentioned above, are not represented and probably would add additional ammonium to the water-column respiration/mineralization mass.

Owens (2009) presents a detailed conceptual diagram for a well-mixed water column and a two-level benthic sediment column: a surface aerobic layer and an underlying anaerobic layer. Diffusion and advection of dissolved oxygen in bottom water penetrates and maintains the surface aerobic benthic sediment layer. Bioirrigation also helps to maintain the aerobic layer. Aerobic respiration/remineralization of PON releases ammonium to sediment pore water which diffuses across the sediment-water interface into bottom water. Owens (2009) also depicts nitrification/denitrification in the aerobic layer but these biogeochemical reactions do not appear to occur in the benthic sediments of Quonochontaug Pond. In the underlying anaerobic sediment, further breakdown of PON to ammonium occurs through ammonification (Owens, 2009). (Note: ammonification is the conversion of organic nitrogen to ammonium by bacteria). Billen and Lancelot (1988), in their paper concerning modeling benthic nitrogen cycling in temperate coastal ecosystems, emphasize that benthic sediments play two key roles with respect to the plankton system in coastal waters. First, benthic sediment acts as a regenerator of mineral nutrients for the water column. They note that benthic nitrogen release supplies between 30 and 70 % of nitrogen requirements for plankton growth. East Coast USA estuaries and bays (Buzzard's Bay, Narragansett Bay, Neuse River Estuary) are noted as examples (Billen and Lancelot, 1988). As can be seen from the above calculations (Figure 10), the benthic flux of ammonium from the fine-grained benthic sediment in Quonogochontaug Pond provides 31% of the nitrogen required for phytoplankton growth.

The second key role that benthic sediment plays with respect to phytoplankton growth in temperate coastal waters is that sediments are often the only site where anaerobic conditions exist. Such conditions are necessary to promote denitrification, a process which can result in the elimination of up to 25% of the nitrogen mineralized in benthic sediment (Billen and Lancelot, 1988). Denitrification will only occur in aquatic systems where nitrate-nitrogen is an important component of dissolved inorganic nitrogen (DIN), both in bottom water and sediment pore water. Such is not the case for Quonochontaug Pond, at least in the water column, which has only 11 ug/L nitrate in surface water and 11 ug/L nitrate in bottom water (SPC monitoring database, 2008-2013). By comparison, the average ammonium concentration in surface water is 48 ug/L and that in bottom water is 72 ug/L (SPC monitoring database, 2008-2013). The significant increase of ammonium in bottom water is partly a result of benthic remineralization of sedimentary organic matter and the exchange of ammonium across the sediment-water interface.

The benthic flux of ammonium (and phosphate) at the HCBuoy station in August of 2013 was considerably higher than that for July and September of 2013 at this station and for all three months at the JR station (Table 3). Figure 11 is a graphic representation of a photo of the core surface taken at the end of the August 2013 (see incubation of the sediment core from HCBuoy
station). One can clearly see many small, white bivalves at the sediment-water interface and the light-grey trail of one bivalve that migrated from a depth of several centimeters in the sediment column to the sediment surface. This station, HCBuoy, is located in an extensive bed of eelgrass (*Zostera marina*) (Stoll et al., 2011; SPC Status and Trends Report, 2013). Stoll et al. (2011) notes that the small bivalve, *Gemma gemma*, is prevalent in the benthic sediment of Quonochontaug Pond. They also note that a tube-dwelling amphipod, *Amphelisca abdita*, is very prevalent in the bottom sediments of the Pond. From the graphic representation of the core photo (Figure 11) and the elevated benthic fluxes of ammonium and phosphate in August 2013 (Table 2), it is obvious that biological irrigation or bioturbation is occurring in benthic sediment where benthic invertebrates are prevalent. The HCBuoy station is located in an extensive eelgrass meadow and is the only location where this biophysical activity occurs in the western basin of Quonochontaug Pond. The JR station, where benthic fluxes of ammonium are high but one-third the magnitude of that for the August 2013 HCBuoy station, has no such benthic biological activity (Figure 12).

*Phosphorus Cycling in Quonochontaug Pond*

Figure 13 shows the internal mass balance of dissolved inorganic phosphate (DIP) for Quonochontaug Pond. The water-column respiration/mineralization of organic matter provides 48% of the inorganic phosphorus needed (2,250 kgP/yr) for the measured growth of phytoplankton (microalgae). If we include hypoxia during two summer months as an extreme of dissolved oxygen consumption in bottom water (see discussion section on oxygen consumption), then water-column respiration/mineralization would provide 52% of the DIP needed for microalgae growth. Appendix C gives the calculation of the annual benthic flux of DIP, 1,333 kgP/yr. This benthic flux contributes 59% of the inorganic phosphorus required for microalgae growth. Adding these two flux estimates (Figure 13), respiration/mineralization (1,110 kgP/yr) and benthic flux (1,333 kgP/yr), results in a total inorganic phosphorus recycling input to the water column of 2,443 kgP/yr. This is 108% of the inorganic phosphorus required for phytoplankton (microalgae) growth. Some uncertainty in the data used to make these calculations is probably the reason why these two flux estimates add up to greater than 100%.

A glance at Appendix C reveals two interesting observations. The estimated benthic flux for October 2012 at stations JR, HCBuoy, and HCChannel is negative, that is, inorganic phosphate is taken up from bottom water by the binding of phosphorus to sediment particles (Slomp, 2011) and/or direct uptake by the surface layer of benthic sediment. The oxidized suspended sediment that binds the phosphorus eventually becomes part of the surface layer of benthic sediment. Figure 14 is a graphic representation of a photo taken from a sediment core at the JR station in late October 2012. The material at the sediment-water interface consists of 1.5 to 2.0 millimeters of medium to dark reddish brown flocculent silty clay overlying 3 millimeters of light-grey silty clay that overlies 0.5 meters of dark-grey silty clay. The redox condition of the three sediment layers is: brown-oxidized (aerobic), light grey-mildly reducing, dark grey-strongly reducing (anaerobic). The average October dissolved oxygen concentration in the bottom waters of Quonochontaug Pond is 7.1±0.4 mg/L for the years 2008-2013 (SPC Monitoring Database). Thus, oxygenated bottom waters are always in contact with the surface layer of benthic sediment during the fall months. And, by association, these conditions probably exist throughout the winter and spring. So, it is hypothesized that during this time (October to May), oxic conditions exist in the bottom waters and the surface benthic sediment layer of Quonochontaug Pond. Thus, the negative benthic flux of inorganic phosphate observed during this period. The October 2012 core incubation data at the JR station show a significant decrease in DIP concentration with time. The core incubation data from the HCChannel station are nearly
flat (no flux) and the core incubation data from the HCBuoy station showed a relatively strong DIP flux from the benthic sediment into the overlying water. However, since eelgrass areas occupy a small part of the fine-grained silty-clay sediment surface area of Quonochontaug Pond (SPC Status and Trends Report, 2008-2012), the weighted benthic flux of the HCBuoy station is small and that of the JR station dominates the Pond’s benthic environment at this time. While the fall-winter-early spring benthic flux of DIP was determined from the October 2012 core incubations that show adsorption of DIP in core-top water by an oxic surface benthic layer, there is another geochemical process that can affect the apparent uptake of inorganic phosphorus by benthic sediment. Particulate organic matter is the major carrier of reactive phosphorus to the sediment in most coastal areas (Slomp, 2011). And, as we have seen above, another potential source is iron-bound phosphorus (Fe-bound P).

The other interesting observation revealed by Appendix C is that the benthic flux of phosphate is very high for the months of August and September 2013 compared to fluxes from July 2013 and October 2012. The average bottom water dissolved oxygen concentration in Quonochontaug Pond for the months of August and September is 5.6±0.8 mg/L, a value significantly lower than that for October (7.1±0.4 mg/L). And, bottom-water hypoxic dissolved oxygen concentrations were consistently below 5.0 mg/L during these months in the years 2007 and 2008 (Guarinello, 2009). It seems that low bottom-water dissolved oxygen concentrations during the late summer (August and September) may result in environmental conditions that promote higher benthic fluxes of dissolved phosphate.

The distribution of seasonal benthic dissolved phosphate fluxes in Quonochontaug Pond appears to follow a similar pattern observed at other coastal marine sites. In Aarhus Bay, Denmark, Jensen et al. (1995) showed that the benthic flux of dissolved reactive phosphate (orthophosphate) was very low in the fall-winter-early spring (0-0.05 mM/m²/day) while in the summer the flux increased to 0.2-0.5 mM/m²/day. Nielsen et al. (2001), in their study of Randers Fjord, Denmark, showed that the benthic flux of phosphate varied between 0 kg/P/day in the winter to 100 kg/P/day in the spring to 300 kg/P/day in the summer. Both studies related the high summer/autumn maximum in benthic phosphate flux to sulfate reduction whereby the released sulfide reduced the iron-oxide-bound phosphate into the sediment porewater, thus causing a diffusive flux of phosphate from benthic sediment to bottom water.

The only benthic flux studies in southern Rhode Island coastal lagoons was conducted by Nowicki and Nixon (1985). They studied the benthic nutrient remineralization in Potter Pond. They determined that the flux of dissolved inorganic phosphate (DIP) ranged from a net uptake of -10 to a net release of +50 μM PO₄³⁻/m²/hour. A glance at Table 2 shows that this range of DIP benthic fluxes is comparable to those measured in Quonochontaug Pond (with the exception of that from the HCBuoy Station from August 2013). However, the annual benthic phosphate remineralization for Potter Pond was 5 mM P/m²/yr while that for Quonochontaug Pond was 25 mM P/m²/yr (Figure 13). For Potter Pond, the benthic flux of phosphate represented only 2% of the phosphorus needed for the growth of algae (Nowicki and Nixon, 1985) while for Quonochontaug Pond the benthic flux of phosphate represented 59% of the phosphorus needed for phytoplankton growth. However, for Potter Pond, macrophyte production was a major part of the Pond’s gross primary production whereas macrophyte production appears to be a minor part of the gross primary production of Quonochontaug Pond.

In general, the phosphorus cycle in coastal waters is similar to the nitrogen cycle. Gurel et al. (2005) envision that phytoplankton is the focus of nutrient activity (nitrogen and phosphorus).
Phytoplankton mortality produces nonliving particulate organic phosphorus (POP), which through hydrolysis and bacterial attack is mineralized to dissolved inorganic phosphate (PO$_4^{3-}$). In addition, zooplankton grazing produces some dissolved inorganic and organic phosphorus. Particulate matter in the water column reacts with the PO$_4^{3-}$ through adsorption/desorption and adsorbed inorganic phosphorus settles out to the benthic sediment as particulate inorganic phosphorus (PIP) (Gurel et al., 2005). In the sediment column, dissolved inorganic phosphorus (PO$_4^{3-}$) is released through decomposition of nonliving POP and desorption of particulate inorganic phosphorus (PIP) (Gurel et al., 2005). Thus, the buildup of phosphate in the sediment column results in the release of inorganic phosphorus across the sediment-water interface into bottom water. Changing dissolved oxygen concentrations in the bottom waters of coastal marine environments lead to very dynamic iron (Fe) and phosphorus (P) cycling in the surface benthic sediment column. This is due to the affinity of P to adsorb onto Fe-oxyhydroxides (FeOOH) (Sokol, 2013).

Ruttenberg (2003) describes the important biogeochemical processes that occur during the transport of P through the water column and the early diagenetic transformations of P within the sediment column. (Diagenesis is defined as the sum of all processes, chiefly chemical, by which changes in a sediment property are brought about after its deposition). In coastal waters, biological uptake of phosphorus by photosynthetic activity, chiefly phytoplankton, convert dissolved phosphate into POP (organic matter) that sinks to the bottom. Some of this phosphorus is remineralized in bottom waters by heterotrophic bacteria and zooplankton excretion and the remainder of this POP (phytodetritus) is deposited in benthic sediment. Once delivered to the sediment-water interface, this POP is subject to breakdown via microbial respiration/mineralization; that is, the oxidation of particulate organic matter to its dissolved mineral constituents (CO$_2$, NH$_4^+$, PO$_4^{3-}$). After oxygenic respiration, a well-documented sequence of electron acceptors (manganese oxide, nitrate, iron oxide, and sulfate) are utilized by microbial communities (Ruttenberg, 2003). All of these respiration reactions result in the buildup of phosphate and other metabolites in pore waters. Generally, organic matter and iron oxyhydroxide (FeOOH) are the primary sources of phosphorus that undergo steady-state diagenesis and release phosphate to benthic sediment porewater (Ruttenberg, 2003). A third biogeochemical process that affects phosphorus release from benthic sediment is sulfate reduction. Under sulfate reduction (see equation 6), sulfide is produced and combines with FeOOH to reduce the iron from a +3 oxic state to a +2 reduced state. This reduction of ferric iron to ferrous iron releases the FeOOH-adsorbed phosphate to sediment porewater and results in an enhanced flux of phosphorus across the sediment-water interface (Kraal et al., 2013).

It is apparent from the above discussion of phosphorus cycling in Quonochontaug Pond that aerobic respiration/remineralization and iron-sorbed phosphate recycling play an important role in promoting benthic fluxes of phosphorus in the Pond. For much of the year when bottom-water oxygen concentrations are high (7.0 mg/L and greater), iron-oxide sorption of phosphate results in an uptake of phosphate by benthic sediment (Appendix C, item 2a). During the early summer (June and July), aerobic respiration/remineralization is the predominant cause of positive fluxes from surface benthic sediment to the bottom waters. However, in the late summer (August and September), enhanced benthic fluxes of phosphorus into bottom water (Appendix C, item 2c) is not only the result of aerobic respiration/remineralization but also the result of sulfate reduction that by itself or in concert with iron recycling enhances the benthic flux of phosphorus. Hypoxic conditions in bottom waters at this time (Guarinello, 2009) may enhance the effect of sulfate reduction in the fine-grained organic-rich surface benthic sediment of Quonochontaug Pond.
Summary and Conclusions

During the summer of 2013 (July, August, September), sediment cores were collected from three stations in the western basin of Quonochontaug Pond (Figure 1).

The cores were incubated in the dark at nearly-ambient temperatures for a period of three or four days (Figure 3). Twice per day the water column was stirred (Figure 4) and the concentration of dissolved oxygen measured with a YSI handheld monitor.

Water samples were drawn from the mixed water column adjacent to the sediment-water interface, filtered through a glass fiber filter, and frozen for later analysis of nitrate, ammonium, and dissolved phosphate.

Sediment oxygen demand (SOD) at the Judge’s Rock (JR) site averaged -1.48 gm O$_2$/m$^2$/day with a standard deviation (SD) of ±0.32 gm O$_2$/m$^2$/day (Table 2). The low standard deviation of the SOD about the mean at the JR site suggests that biogeochemical processes affecting the uptake of oxygen were consistently similar during sampling period (July-September). Benthic sediment at the JR site consists of fluid, dark grey-black muds (silty clay).

SOD at the Harmonic Cove Channel (HCCh) site averaged -1.38 gm O$_2$/m$^2$/day with a standard deviation (SD) of ±0.59 gm O$_2$/m$^2$/day (Table 2). The SD at this site was somewhat greater than that for the JR site. Benthic sediment at this site consists of somewhat indurated, dark grey-black, sandy muds (silty clay). At the August 2013 sampling, dark grey-black organic tube structures protruded 1-2 cm above the sediment surface.

SOD at the Harmonic Cove Buoy (HCBuoy) site averaged -1.43 gm O$_2$/m$^2$/day with a standard deviation (SD) of ±0.76 gm O$_2$/m$^2$/day (Table 2). This large SD, 53% about the mean SOD, is considerably larger than that for the JR (23%) and HCCh (43%) sites. The HCBuoy core site is located in an extensive bed of eelgrass (*Zostera marina*) that hosts an extensive macro invertebrate population (see Figure 11). At the August 2013 sampling, small bivalves mixed the surface sediment extensively (Figure 11), resulting in a low SOD and a very high benthic flux of ammonium and phosphate (Table 2).

The average summer benthic oxygen demand of sediments (SOD) in Quonochontaug Pond (-1.47 ± 0.47 gm O$_2$/m$^2$/day, Table 2) is consistent with the average summer SOD’s for coastal US estuaries and lagoons, -1.22 ± 0.80 gm O$_2$/m$^2$/day (Table 3). The average summer ammonium benthic flux for Quonochontaug Pond (153 ± 125 microMoles N/m$^2$/hr, Table 2) is consistent with the average summer benthic flux of ammonium for coastal US estuaries and lagoons, 150 ± 91 microMoles N/m$^2$/hr, Table 3). And, the average summer benthic flux of phosphate for Quonochontaug Pond (26 ±16 microMoles P/m$^2$/hr, Table 2) is significantly higher than the average for coastal US estuaries and lagoons (15.5 ± 10 microMoles P/m$^2$/hr, Table 3).

Bioturbation, the translocation of sedimentary material between benthic sediment and bottom water by burrowing bivalves, is an important process affecting the benthic fluxes of ammonium and phosphate at the HCBuoy station in August of 2013 (Table 2). This station is located in an extensive eelgrass meadow. These enhanced benthic fluxes are seven (7) times greater for ammonium and seven (7) times greater for phosphate than the summer average for Quonochontaug Pond (see previous summary item and Table 2).
Water-column remineralization (respiration) of dissolved inorganic nitrogen (mostly ammonium) contributes about 48% of the nitrogen required for phytoplankton growth (Figure 10) while the annual benthic flux of ammonium contributes about 31% of the phytoplankton nitrogen requirement.

The late summer (August and September) benthic flux of ammonium contributes between 50 and 85 percent of the annual ammonium benthic flux (Appendix B).

The external mass balance of dissolved inorganic nitrogen (DIN) for Quonochontaug Pond is nearly in balance; In= 17,647 Kg N/Yr, Out= 17,250 Kg N/Yr (Figure 10). The benthic sediment remineralization of ammonium contributes 59% of all the DIN inputs while surface water-groundwater-atmosphere inputs each contribute about 12%.

Water-column remineralization (respiration) of dissolved inorganic phosphorus (DIP) contributes 49% of the phosphorus required for phytoplankton growth (Figure 13) while the annual benthic flux of phosphate contributes about 59% of the phytoplankton phosphorus requirement.

The late summer (August and September) benthic flux of phosphate contributes 84% of the annual phosphate benthic flux (Appendix C). This summer benthic flux of phosphate is significantly higher than the average for US coastal estuaries and lagoons (Table 3).

The external mass balance of dissolved inorganic phosphorus (DIP) for Quonochontaug Pond is substantially out of balance; In= 1,556 Kg P/Yr, Out= 1,959 Kg P/Yr (Figure 13). Much of this imbalance may be due to the uncertainty of the phosphorus sedimentation term and the exchange of DIP between Quonochontaug Pond and Block Island Sound. The benthic sediment remineralization of phosphate contributes 86% of all DIP inputs to the Pond while groundwater contributes 12%.

It appears that the high rates of benthic exchange (flux) of ammonium and phosphate during the late summer provides much of the DIN and DIP in the bottom waters of Quonochontaug Pond (Table 2). Throughout most of the year, October to June, benthic fluxes of ammonium and phosphate are minimal (Appendices B and C) and the nutrient increases in the Pond’s bottom waters are the result of water-column remineralization processes. It appears that phosphate is more sensitive to dissolved oxygen depletion than ammonium in the bottom waters of Quonochontaug Pond.

References


Figures
1- Location of sampling stations in Quonochontaug Pond.
2- Schematic diagram of sediment core sampler.
3- Schematic diagram of core incubation chamber.
4- Schematic diagram of plastic core tube with stirring rod.
5- Regression of dissolved oxygen versus time for a core from Judge’s Rock, 8/8-10/2013.
6- Regression of ammonium versus time for a core from Harmonic Cove Channel, 8/8-9/2013.
7- Regression of ammonium versus time for a core from Harmonic Cove Buoy, 7/3-4/2013.
8- Regression of dissolved inorganic phosphorus versus time for a core from Harmonic Cove Channel, 7/3-5/2013.
9- Regression of dissolved inorganic phosphate versus time for a core from Harmonic Cove Buoy, 7/3-5/2013.
10- Internal and external mass balance of DIN for Quonochontaug Pond.
11- Schematic diagram of photo from HCBuoy Station, August 2013.
12- Schematic diagram of photo from Judge’s Rock Station, August 2013.
13- Internal and external mass balance of DIP for Quonochontaug Pond.
14- Schematic diagram of photo from Judge’s Rock Station, October 2012.
Figure 3. Core incubation setup.
Regression of Dissolved Oxygen in Sediment Core Water Column versus Time of Incubation, Judge's Rock Core, 8/8-10/2013

y = -0.1117x + 5.3904
R² = 0.99243

Figure 5
Regression of Dissolved Ammonium in July Sediment Core Water Column versus Time of Incubation, Harmonic Cove Buoy, 7/3-4/2013
Regression of Dissolved Inorganic Phosphorus in July Sediment Core Water Column versus Time of Incubation, Harmonic Cove Channel, 7/3-5/2013

$Y = 0.468X + 0.85$

$R^2 = 0.835058$
Internal and External Mass Balance of DIN for Quonochontaug Pond

Atmosphere = 2,964 Kg N/yr

Surface Water = 2,110 Kg N/yr

Water Column

Photic Zone = 143 Kg N
Nitrogen Requirement, Phytoplankton = 34,286 Kg N/yr = 11.4 gmN/m²/yr
H₂O Column Remineralization (Respiration) = 16,500 Kg N/yr = 5.5 gmN/m²/yr
Aphotic Zone = 802 Kg N

10,500 Kg N/yr = 8.1 gm N/m²/yr
Sedimentation = 11,300 Kg N/yr

Groundwater = 2,100 Kg N/yr

Exchange with BI Sound = 5,950 Kg N/yr

Internal Mass Balance

Percent of N Requirement
W-C Remineralization = 48%
Benthic Remineralization = 31%

External Mass Balance: In = Out

Surf. H₂O + Atmos. + Groundwater + Benthic Flux = Sedimentation + Breachway Out
2,110 Kg N/yr + 2,964 Kg N/yr + 2,100 Kg N/yr + 10,500 Kg N/yr = 11,300 Kg N/yr + 5,950 Kg N/yr

17,674 Kg N/yr In = 17,250 Kg N/yr Out

Figure 10
Photo of Sediment Core from Judge's Rock Station, Quonochontaug Pond, August 2013

Medium Grey Sediment Surface

Dark Grey-Black Mud

Sediment Column

28 cm

Figure 12
Internal and External Mass Balance of DIP for Quonochontaug Pond

**Atmosphere** = 19 Kg P/yr

**Surface Water** = 19 Kg P/yr

**Photic Zone**
- 50 Kg P
- P Requirement, Phytoplankton = 2.250 Kg P/yr = 0.76 gP/m²/yr
- H₂O-Column Remineralization (Respiration) = 1.110 Kg P/yr = 0.37 gP/m²/yr

**Water Column**
- Exchange with B1 Sound = 1.067 Kg P/yr

**Aphotic Zone**
- 58 Kg P

**Groundwater** = 145 Kg P/yr

**Sedimentation** = 892 Kg P/yr

**Internal Mass Balance**
- Percent of P Requirement
  - W-C Remineralization = 48%
  - Benthic Remineralization = 59%

**External Mass Balance**: In = Out

Sur. H₂O + Atmos. + GW + Benthic Flux = Sedimentation + Breachway Out

\[ 19\text{KgP/yr} + 19\text{KgP/yr} + 145\text{KgP/yr} + 1,333\text{KgP/yr} = 892\text{KgP/yr} + 1,067\text{KgP/yr} \]

\[ 1,516\text{ Kg P/yr IN} = 1,959\text{ Kg P/yr OUT} \]

Figure 13
Photo of Sediment Core from Judge's Rock Station, Quonochontaug Pond, October 2012

- Water Column
- Oxygenated
- Dark reddish brown oxidized sediment surface, 1.5 mm thick
- Iron oxyhydroxide
- Light grey mud, 3 mm thick
- Dark grey-black mud (anoxic)
- 21 cm

Figure 14
Appendix A

Calculations of Water-Column Respiration

A. 2008-2012 Data

1. Surface area of Quonochontaug Pond = 30x10^5 m^2
2. Surface area of fine-grained silty clay lagoon bottom sediment in Quonochontaug Pond = 12.9x10^5 m^2
3. Volume of water in Quonochontaug Pond, 1-2.5 meters = (1.5 m)(12.9x10^5 m^2) = 19.35x10^11 cm^3 = 19.35x10^8 Liters
4. Volume of water in Quonochontaug Pond, 2.5-4.0 meters = 19.35x10^8 Liters
5. Volume of water below 1.0 meters at:
   - JR=19.4x10^8 Liters
   - HCBuoy=12.9x10^8 Liters
   - HCCChannel=38.7x10^8 Liters
   - NBI= 38.7x10^8 Liters
   - EBYC= 19.4x10^8 Liters
6. 2008-2012 Dissolved Oxygen Data

   a. JR: Surface=6.9 mg/L, Bottom=5.9 mg/L, Δs-b= 1.0 mg/L/12 hrs per day for 210 days
      Oxygen consumed=(1mg/L)(19.4x10^8 Liters)(105 days/yr)= 2,037x10^6 mg/yr divided by 12.9x10^5 m^2 = 158 gm O_2/m^2/yr
   b. HCBuoy: Surface=6.8 mg/L, Bottom=6.2 mg/L, Δs-b= 0.6 mg/L/12 hrs per day for 210 days
      Oxygen consumed=(0.6 mg/L)(12.9x10^5 Liters)(105 days/yr)= 813x10^6 mg/yr divided by 12.9x10^5 m^2 = 63 gm O_2/m^2/yr
   c. HCCChannel: Surface=6.9 mg/L, Bottom=6.1 mg/L, Δs-b= 0.8 mg/L/12 hrs per day for 210 days
      Oxygen consumed=(0.8 mg/L)(38.7x10^8 Liters)(105 days/yr)= 3,251x10^8 mg/yr divided by 12.9x10^5 m^2 = 252 gm O_2/m^2/yr
   d. NBI: Surface=6.8 mg/l, Bottom=6.3 mg/L, Δs-b= 0.5 mg/L/12 hrs per day for 210 days
      Oxygen consumption=(0.5 mg/L)(38.7x10^8 Liters)(105 days/yr)= 2,032x10^8 mg/yr divided by 12.9x10^5 m^2 = 158 gm O_2/m^2/yr
   e. EBYC: Surface=6.6 mg/L, Bottom=6.2 mg/L, Δs-b= 0.4 mg/L/hrs per day for 210 days
      Oxygen consumption=(0.4 mg/L)(19.4x10^8 Liters)(105 days/yr)= 815x mg/yr divided by 12.9x10^5 m^2 = 63 gm O_2/m^2/yr

The average of the five stations for water-column respiration= 139±79 gm O_2/m^2/yr

However, the surface area of Quonochontaug Pond water is 2.3 times that of fine-grained silty clays (30x10^5 m^2 divided by 12.9x10^5 m^2), so the normalized respiration rate (O_2 uptake) is 139 divided by 2.3= 60 gm O_2/m^2/yr.

If the average dissolved oxygen for surface water at the five stations is 6.8±0.2 mg/L, and we use the surface area of Quonochontaug Pond water (30x10^5 m^2) and an average volume of water below 1.0 meters (25.8±12.0x10^8 Liters), then the average water-column respiration or oxygen uptake in the water column below 1.0 meter depth is:

(0.7mg/L )(25.8±12.0x10^8 Liters)(105 days/yr)= 1,896x10^8 mg/yr divided by 30x10^5 m^2 = 63±29 gm O_2/m^2/yr
B. 2013 Dissolved Oxygen Data (Data not available at time of first writing)
   a. JR: $\Delta O_2$ (s-b)= 0.6 mg/L
      Oxygen consumed= (0.6 mg/L)(19.4x10^8 Liters)(105 days)= 1,222x10^8 mg/yr divided by
      30x10^3 m^2 = 41 gm O_2/m^2/yr
   b. HCBuoy: $\Delta O_2$ (s-b)= 0.9 mg/L
      Oxygen consumed= (0.9 mg/L)(12.9x10^8 Liters)(105 days)= 1,219x10^8 mg/yr divided by
      30x10^3 m^2 = 41 gm O_2/m^2/yr
   c. HCChannel: $\Delta O_2$ (s-b)= 0.07 mg/L
      Oxygen consumed= (0.07 mg/L)(38.7x10^8 Liters)(105 days)= 285x10^8 mg/yr divided by
      30x10^3 m^2 = 10 gm O_2/m^2/yr
   d. NBI: $\Delta O_2$ (s-b)= 0.8 mg/L
      Oxygen consumed= (0.8 mg/L)(38.7x10^8 Liters)(105 days)= 3,251x10^8 mg/yr divided by
      30x10^3 m^2 = 108 gm O_2/m^2/yr

The average of the four stations for water-column respiration= 50±41 gm O_2/m^2/yr

The overall average of the three estimates of water-column respiration is 58±7 gmO_2
/m^2/yr

Appendix B

Calculation of Annual Benthic Flux of Dissolved Inorganic Nitrogen (Ammonium), 2012 and 2013
A. Surface area of fine-grained silty-clay benthic sediments in Quonochontaug Pond= 12.9x10^6
m^2 (Ford; 2003; Guarinello, 2009).
A1. Method 1
   1. Benthic Flux of Dissolved Inorganic Nitrogen (Ammonium)
      a. October 2012- Judge's Rock, HCBuoy, HCChannel= 6.5±3.1 ugN/m^2/hr
         using this value for Fall-Winter-Early Spring, then 157 ugN/m^2/day x 240 days=
         0.038 gmN/m^2/yr or 49 kgN/yr
      b. July 2013- Judge's Rock, HCBuoy, HCChannel= 831±614 ugN/m^2/hr
         using this value for Early Summer (June and July), then 14.7 mgN/m^2/day x 60 days=
         0.882 gmN/m^2/yr or 1.138 kgN/yr
      c. August and September 2013-Judge's Rock,HCBuoy,HCChannel=4,884±3,622 ugN/m2/hr
         using this value for Late Summer (August and September), then 117.2 mgN/m^2/day x
         60 days= 7.032 gmN/m^2/yr or 9,071 kgN/yr

Therefore, the Annual Benthic Flux of Ammonium = 7.95 gmN/m^2/yr or 10,258 kgN/yr

A2. Method 2
   1. Benthic Flux of Dissolved Inorganic Nitrogen (Ammonium)
      a. July 2013- Judge's Rock, HCBuoy, HCChannel= 831±614 ugN/m^2/hr
         using this value for Winter-Spring-Early Summer, then 19.9 mgN/m^2/day x 210 days=
         4.18 gmN/m^2/yr or 5,392 kgN/yr
      b. August and September 2013- Judge's Rock, HCBuoy, and HCChannel= 2,847±1,712
         mgN/m^2/hr
         using this value for Late Summer (August and September), then 68.3 mgN/m^2/day x
         60 days= 4.10 gmN/m^2/yr or 5,289 kgN/yr
      c. October 2012- Judge's Rock, HCBuoy, and HCChannel= 6.5±3.1 ugN/m^2/hr
         using this value for Late Fall (October, November, December), then 0.157 mgN/m^2/day
x 90 days = 0.014 gmN/m²/yr or 18 kgN/yr

Therefore, the Annual Benthic Flux of Ammonium = 8.29 gmN/m²/yr or 10,699 kgN/yr

Appendix C

Calculation of Annual Benthic Flux of Dissolved Inorganic Phosphorus (Phosphate), 2012 and 2013

1. Surface area of fine-grained silty-clay benthic sediments in Quonochontaug Pond = 12.9x10⁵ m² (Ford, 2003; Guarinello, 2009).

2. Benthic Flux of Dissolved Inorganic Phosphate (DIP)
   a. October 2012 - Judge’s Rock, HCBuoy, HCChannel = -0.34 mgPO₄³⁻/m²/day
      using this value for Fall-Winter-Early Spring, then -0.34 mgPO₄³⁻/m²/day x 240 days = -0.082 gmP/m²/yr or -106 kgP/yr
   b. July 2013 - Judge’s Rock, HCBuoy, HCChannel = 4.1±6.9 mgPO₄³⁻/m²/day
      using this value for Late Spring-Early Summer (June and July), then 4.1±6.9 mgPO₄³⁻/m²/day x 240 days = 0.246 gmP/m²/yr or 317 kgP/yr
   c. August and September 2013 - Judge’s Rock, HCBuoy (Sept.), HCChannel, Ninigret Cove = 14.5±15.3 mgPO₄³⁻/m²/day
      using this value for Summer (August and September), then 14.5 mgPO₄³⁻/m²/day x 60 days = 0.87 gmP/m²/yr or 1,122 kgP/yr

3. Annual Benthic Flux of Phosphate
   October to May = -0.082 gmP/m²/yr or -106 kgP/yr
   June and July = 0.246 gmP/m²/yr or 317 kgP/yr
   August and September = 0.87 gmP/m²/yr or 1,122 kgP/yr
   Annual Benthic Flux = 0.776 gmP/m²/yr or 1,333 kgP/yr