A Detailed Analysis of Physical, Water-Quality, and Nutrient Data as Related to Nitrogen and Phosphorus Cycling in Quonochontaug Pond

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Introduction
During a year’s time (Fall 2011 to Fall 2012) since the author of the “Nitrogen Cycling in Coastal Rhode Island Salt Ponds” report wrote the first draft of the manuscript, he has continually updated the concept of nitrogen cycling in southeastern coastal Rhode Island salt ponds and the data used to support these concepts. More recently, he has done a thorough reading of the Guarinello Masters Thesis “Habitats in a Rhode Island Coastal Lagoon Experiencing Episodic Hypoxia” [2] that presents a detailed description of processes causing hypoxia in Quonochontaug Pond. In addition, he has also reread carefully the Ph.D. thesis by Kathryn Ford (25).

Quonochontaug Pond has been extensively monitored by the Salt Ponds Coalition (SPC), beginning in 2006. Thus there are 7 years to date (2006 to 2012) of surface and bottom-water temperature data and dissolved oxygen data; secchi-disk transparency data; and nitrate, dissolved inorganic phosphorus, total nitrogen, and total phosphorus data for surface and bottom-water samples at five (5) deep-water stations in Quonochontaug Pond (Figure 1). The temperature and dissolved oxygen and secchi-disk transparency data are measured bi-weekly from the middle of May to the middle of October. The nutrients in surface and bottom waters are collected and measured monthly from the middle of May to the middle of October. Finally, the surface and bottom-water ammonium data used in this analysis come from the years 2008 to 2012. The reason for this is that the University of Rhode Island (URI) Watershed Watch Program updated their ammonium analysis protocol in 2008 and thus ammonium data could be compared for the years 2008 to 2012 (L. Green, personal communication).

While Quonochontaug Pond is known locally as a Salt Pond, it is technically classified as a Coastal Lagoon, as are the other Rhode Island Salt Ponds. Coastal Lagoons are shallow brackish bodies of water, separated from the ocean by a barrier island or sand bank and are connected at least intermittently to the open ocean by one or more restricted tidal inlets. Coastal Lagoons generally average less than 2 meters in depth, although deeper waters may be encountered in channels. Due to their shallowness, Coastal Lagoon waters are generally well mixed, and only local stratification may develop in deeper areas. From a biologic standpoint, Coastal Lagoons differ from deeper estuaries. The photic zone extends to much of the seafloor and high rates of metabolism of benthic primary producers mediate nutrient recycling processes and result in strong benthic-pelagic coupling (26).

Dissolved Oxygen Depletion in Bottom Waters
Figure 2 is a plot of the average concentration of dissolved oxygen (DO), by month (May to September), of the five deep-water stations (Figure 2) that are monitored in Quonochontaug Pond (Quonnie Pond) for the years 2008 to 2011. It is obvious for the
months of May and September, surface- and bottom-water DO concentrations are similar. However, for the months of June to August, bottom waters are depleted in DO, by about 1.2 mG/L, relative to surface waters. This DO depletion in bottom waters may be due, in part, to temperature stratification of the water column. For instance, at the Harmonic Cove Channel Station (HCCh) for the 2011 sampling year (May to October), bottom-water temperatures were at least 2 degrees C lower than surface-water temperatures for the July 6 and July 20, 2011 sampling dates. At the Judge’s Rock Station (JR), these same conditions existed for the June 8 and July 20, 2011 sampling dates. At the North Bill’s Island Station (NBI), bottom waters were often 3 degrees C lower than surface waters for the period June 22 to August 3, 2011.

For the sampling year 2012, dissolved oxygen (DO) and temperature measurements were made bi-weekly at the five deep-water stations in Quonochontaug Pond (see Figure 1 for station locations). The average surface- and bottom-water temperatures for the months of July, August, and September show that there is 0.7 to 1.0 degrees C lower temperature in bottom waters from these five stations. Individually, the Judge’s Rock, Harmonic Cove Channel, and North Bill’s Island stations experienced the most significant temperature stratification; generally 2 degrees C lower temperature in bottom waters. Such temperature stratification occurred in June and July for the Judge’s Rock and Harmonic Cove Channel stations and in July-August-September for the North Bill’s Island Station.

The average surface- and bottom-water dissolved oxygen (DO) for the months of June to September 2012 show that there is a 0.5 to 0.7 mG/L oxygen depletion (surface-water DO minus bottom-water DO). Individually, the Judge’s Rock Station had the most bottom-water oxygen depletions (8 out of 10 samplings); and the largest DO depletion values of 4.1/2.1/1.8 mG/L. For the other stations, Harmonic Cove Channel and North Bill’s Island, had only three oxygen depletions out of ten samplings and these were of significantly-less magnitude (0.7 to 1.3 mG/L) compared to the Judge’s Rock dissolved oxygen depletions. The Judge’s Rock Station DO depletion data matched very well with temperature stratification, six out of ten samplings. The Harmonic Cove Channel Station was next with four matches.

For the sampling year March 31, 1999 to March 15, 2000 (1), bottom-water DO was also depleted relative to surface-water DO. During the months of August and September, 1999, DO in bottom waters was depleted by 2.5 mG/L relative to surface waters. For this period, bottom-water temperatures were 2-3 degrees C lower than surface-water temperatures (1).

**Hypoxia**

In an extensive study of the benthic habitats and hypoxia in Quonochontaug Pond (2), hypoxia was defined as dissolved oxygen concentrations below 4.8 mG/L. EPA identifies this DO concentration level as chronic and notes that a 2.3 mG/L DO value defines acute hypoxia (2).
Table 1. Occurrence of Hypoxic Events at Four Stations in Quonochontaug Pond, Summer 2007 and 2008. Data from Guarinello Thesis (2).

<table>
<thead>
<tr>
<th>Station</th>
<th>DO less than 4.8 mG/L</th>
<th>DO less than 2.3 mG/L</th>
<th>DO less than 1.4 mG/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>June 2-October 2, 2007</td>
<td>7/2-4, 8/4-6, 9/8-10, 2007</td>
<td>September 8-10, 2007</td>
</tr>
<tr>
<td>HCS</td>
<td>August 15-20, 2008</td>
<td>August 13 and 19, 2008</td>
<td>------------------------</td>
</tr>
<tr>
<td>BI</td>
<td>July 29-August 1, 2007</td>
<td>------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>BI</td>
<td>6/22-23, 7/25-26, 8/6-7, 8/15-16, 2008</td>
<td>------------------------</td>
<td>------------------------</td>
</tr>
</tbody>
</table>
| JR=Judge’s Rock; HC=Harmonic Cove; HCS=Harmonic Cove South; BI=Bill’s Island

In her thesis, Guarinello (2) presents plots of bottom-water dissolved oxygen (DO) concentrations at four stations in Quonochontaug Pond for the months of May to October for the years 2007 and 2008. These four stations, Judge’s Rock-Harmonic Cove-Harmonic Cove South-Bill’s Island, correspond to those monitored by Salt Ponds Coalition (SPC) (JR, HCBuoy, HCCChannel, NBI) [see Figure 1 for full names].

Table 1 presents time lines for the occurrence of hypoxic events at four stations in Quonochontaug Pond for the summer months of 2007 and 2008. For both years the Judge’s Rock (JR) and Harmonic Cove (HC) stations had many events where the DO concentration in bottom waters was below 4.8 mG/L. Harmonic Cove South (HCS) had the next largest number of events and Bill’s Island (BI) had the least number of events where bottom-water DO was less than 4.8 mG/L. Bottom-water DO concentrations below 2.3 mG/L occurred several times at the JR and HC stations, and twice at the HCS station (Table 1). The JR and HC stations had very few occurrences where bottom-water DO concentrations were less than 1.4 mG/L.

**Causes of Hypoxia**

The best studied and most widespread anthropogenic variable contributing to hypoxia is eutrophication [a process where water bodies receive excess nutrients that stimulate excessive plant growth; www.toxics.usgs.gov]. For a coastal salt pond or lagoon such as Quonochontaug Pond, the inputs of dissolved inorganic nitrogen are surface water runoff (mostly nitrate), atmospheric input (ammonium and nitrate), and groundwater (mostly nitrate). A recent calculation of the total DIN input to Quonochontaug Pond indicated that about 17,000 Kg of nitrate and ammonium enters the pond annually (see Figure 13). Approximately 60% of this input is estimated to be groundwater (3) [Figure 13 estimates 70%]. Since the watershed area of Quonochontaug Pond is serviced by septic systems, an appreciable quantity of this DIN input may be considered anthropogenic. In addition, surface-water stormwater runoff and atmospheric input contain substantial anthropogenic fractions. Nixon and Buckley (3) estimate that approximately 29 Kg DIN/ha/yr enter Quonochontaug Pond via these inputs. Bowen and Valiela (4) estimate that a nitrogen load of over 30 Kg N/ha/year entering Cape Cod salt ponds would eliminate eelgrass meadows in these ponds. While Quonochontaug Pond does contain some beds of eelgrass, they are not in a healthy condition. Also, Quonochontaug Pond receives the
lowest nitrogen inputs (3) compared to Green Hill and Point Judith Ponds which receive 60 and 66 Kg N/ha/yr respectively. Eelgrass beds are virtually absent in these ponds.

While eutrophication is a primary driving function for the occurrence of hypoxia in coastal salt ponds, it is not the only cause. In coastal waters, hypoxia typically occurs when water column stratification is established during warm summer months when rainfall is generally high and wind is low (2). A substantial fraction of the water column in Quonochontaug Pond is deep enough (greater than 2.5 meters in depth) for salinity and temperature stratification to occur.

Quonochontaug Pond experiences episodic hypoxia with occurrence patterns falling outside the bounds of typical hypoxia predictor variables (stratification and wind stress) (2). In the study of hypoxia in Quonochontaug Pond, the forcing mechanisms that influence the DO concentrations in bottom waters were tides, photoperiod, weather (wind, precipitation) and circulation (2). Photoperiod and eelgrass photosynthetic activity at the Judge’s Rock and Harmonic Cove sites was expected to influence temperature and DO distributions in the western basin of Quonochontaug Pond. Low wind stress was expected to result in reduced mixing of the water column and contribute to stratification and reduced DO concentrations in bottom waters (2). In addition, the residence time of waters in the pond (circulation pattern) might play an important role in lowering the DO concentration in bottom waters. A recent experiment with sediment cores from three stations in Quonochontaug Pond (JR, HC, HCS) sheds some light upon this phenomenon. Cores taken on October 23, 2012 were incubated, with original overlying water, for 7 days. The original DO concentration of these core-top waters was 8.8 mG/L. On October 26, 2012, the DO concentration in HCS (HCCh) core-top water was 8.5 mG/L, that in the JR core was 7.1 mG/L, and that in the HC (HCBoyu) core was 4.6 mG/L. After one week’s duration, the DO concentration in core-top water was 5.8 mG/L for HCS, 5.0 mG/L for JR, and 1.4 mG/L for the HC core. Obviously, the longer time that water was in contact with benthic sediment, the more dissolved oxygen was consumed in bottom water at the sediment-water interface.

Guarinello (2) found that the diel range in DO concentrations for the 2007 summer sampling period was 7.0 mG/L for the JR station and 4.3 mG/L for the HC station. Much smaller daily variations in DO concentration were 1.98 mG/L for the HCS station and 1.60 mG/L for the NBI station (2). Guarinello (2) concluded that “The western basin (where stations JR, HC, HCS are located) is most vulnerable to hypoxia during spring tides due to the reduced transport volume from RI Sound to the lagoon during flood tides”. This is a low flushing effect on waters in the western basin. In addition, moderate to high precipitation and low NE wind stress can create water column stratification and induce hypoxia (2).

Hypoxia and Dissolved Nitrogen Cycling- Theory
Hypoxic events are triggered by the isolation of bottom waters via salinity and temperature stratification and subsequent depletion of dissolved oxygen (DO) through respiration of organic matter (see equation 1). Observed DO depletion in an Australian estuary indicated a shift in the form of dissolved inorganic nitrogen (DIN) from nitrate
(NO$_3^-$) to ammonium (NH$_4^+$) during hypoxic events (5). Oxidation of organic matter at the sediment-water interface and within shallow (few mm thick) surficial sediment is represented by the following equation (6):

(1) $\text{OM} + a\text{O}_2 \rightarrow a\text{CO}_2 + b\text{NH}_4^+ + c\text{H}_3\text{PO}_4 + a\text{H}_2\text{O}$ where OM is organic matter of the form $(\text{CH}_2\text{O})_a(\text{NH}_4^+)_b(\text{H}_3\text{PO}_4)_c$ (this is known as aerobic respiration)

Several other reactions, if operative, can control the presence or absence and concentration of nitrate and ammonium in coastal marine waters.

(2) **Nitrification**: $2\text{O}_2 + \text{NH}_4^+ + 2\text{HCO}_3^- \rightarrow \text{NO}_3^- + 2\text{CO}_2 + 2\text{H}_2\text{O}$

(3) **Denitrification**: $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 84.8\text{HNO}_3 = 106\text{CO}_2 + 42.4\text{N}_2 + 148.4\text{H}_2\text{O} + 16\text{NH}_3 + 16\text{H}_3\text{PO}_4$

(4) **Dissimilatory Nitrate Reduction to Ammonium (DNRA)**: $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16} + 53\text{HNO}_3 = 106\text{CO}_2 + 69\text{NH}_3 + 53\text{H}_2\text{O}$

Denitrification converts nitrate to nitrogen gas (N$_2$) and thus removes biogenic nitrogen from the aquatic ecosystem. DNRA converts nitrate to ammonium, thus adding biologically active dissolved inorganic nitrogen (NH$_4^+$) to the aquatic system. Ammonium is the form of inorganic nitrogen taken up most readily by phytoplankton because nitrate must first be reduced to ammonium before it is assimilated into amino acids in organisms (7).

The majority of remineralization of organic matter in bottom waters occurs by means of aerobic respiration (see equation 1) with a maximum occurring shortly after deposition of a dying plankton bloom (6). Bottom-water oxygen declines as a result of benthic consumption and an increase in water-column stratification during the summer months. Aerobic remineralization of organic matter releases ammonium (NH$_4^+$) and phosphate (PO$_4^{3-}$) to bottom waters and hypoxic (slightly oxic) surface sediments. If concentrations of NH$_4^+$ and PO$_4^{3-}$ within surficial sediment interstitial water are greater than those in overlying bottom water, then diffusion will transport these nutrient ions across the sediment-water interface into bottom water.

When dissolved oxygen becomes low (hypoxic to anoxic conditions), then nitrate (NO$_3^-$) will be utilized to oxidize organic matter. Most likely nitrate will diffuse from bottom water into surficial bottom sediment where it will be denitrified (equation 3). Denitrification produces nitrogen gas that leaves the aquatic system and effuses into the atmosphere. Thus, denitrification is a process that cleanses the aquatic system of bioavailable inorganic nitrogen.

In the last decade, an alternate pathway for the reduction of nitrate has been defined using nitrogen isotopes. This process is known as dissimilatory nitrate reduction to ammonium (DNRA) and is described in equation 4. Researchers have found that DNRA rates are significantly higher during oxic/hypoxic conditions compared to anoxic conditions (5).
Also, shallow-water environments with benthic plants, such as eelgrass, produce abundant oxygen, during photosynthesis. This dissolved oxygen can diffuse into sediment and inhibit denitrification (9). In addition, it has been determined that DNRA is the favored pathway over denitrification at extremes in water temperature, <14 degrees C and >17 degrees C (8). Denitrification is favored only in the narrow water temperature range of 14-17 degrees C (8). This temperature effect implies that during the warm summer months, such as July to September in the northern temperature regions of the globe, DNRA may contribute ammonium to the water column and fertilize the growth of phytoplankton. However, data from a North Sea estuary indicates that at water temperatures from 17-23 degrees C, DNRA contributes only about 5 percent of the total ammonium production (8). Also, the percentage of the annual nitrogen load denitrified in various estuarine and coastal marine systems varies with the mean water residence time (9). Thus, RI coastal lagoons (salt ponds), with water residence times of days, can only denitrify about 5 percent of their total nitrogen load.

After nitrate and iron oxide are utilized to oxidize organic matter in benthic sediment, sulfate (SO$_4^{2-}$) is the next available terminal electron acceptor for this process and is described by equation 5.

\[
\text{(5) Sulfate Reduction: } \text{OM} + a/2\text{SO}_4^{2-} + a\text{H}^+ = a\text{CO}_2 + b\text{NH}_4^+ + c\text{H}_3\text{PO}_4 + a/2\text{H}_2\text{S} + a\text{H}_2\text{O}
\]

The water in Rhode Island salt ponds is brackish with an average salinity of about 30 parts per thousand (ppt). Thus, SO$_4^{2-}$ is the main anionic constituent of these waters and benthic sediment deposited in these salt ponds (coastal lagoons) are sulfidic. One only has to grab a handful of this sediment to smell the abundant H$_2$S. It has been found that DNRA is the favored pathway of dissimilatory nitrate reduction when sulfide is present near the sediment surface (10, 11).

I have not defined the utilization of ferric oxide (Fe(OH)$_3$) in these benthic sediments for a good reason. That is, observations of the water-sediment interface using sediment cores show that the thickness of the rust-colored ferric oxide layer in surface sediment is generally no greater than 1 mm. However, a most recent observation of three sediment cores taken during the fall from the western basin of Quonochontaug Pond may shed some light on this situation. When the cores were taken, there was very little rust-colored material at the sediment surface. As the cores, intact with overlying water, were kept for up to ten days, a thicker rust color developed (2 mm plus) and the dissolved oxygen in the bottom water adjacent to the sediment surface declined appreciably. More about this in the next section about inorganic nitrogen cycling in Quonochontaug Pond.

Recent studies on Long Island Sound hypoxia have found that the flux of dissolved organic matter (DOM) from sediment to overlying water can increase when the sediment surface becomes anoxic. DOM fluxing from the bottom sediment to overlying bottom water would amplify bottom-water hypoxia if the sediment-derived DOM is bacterially labile (12).
In summary, hypoxia can impact biogeochemical cycling of nitrogen in coastal marine systems through the loss of nitrate by denitrification, the release of ammonium and phosphate from benthic sediments, and the production of toxic hydrogen sulfide that inhibits denitrification and allows dissimilatory nitrate reduction to ammonium (DNRA) to occur (13).

**The Effect of Water-Column Stratification on Quonochontaug Pond’s Nutrient Chemistry**

**Temperature.** Table 2 presents delta temperature data for the five deep-water stations in Quonochontaug Pond. This delta (Δ) value represents the degrees C which separates the temperature in bottom water (lower temperature) from surface water. The data given in Table 2 is for the sampling years (May to October) 2011 and 2012. The water temperature data for these years is representative of other years in Quonochontaug Pond as recorded in the Salt Ponds Coalition database (E. Torello, personal communication). All five stations have several sampling dates where the delta degrees C is between 0.5 and 1.6. The Judge’s Rock and HCBuoy stations have several sampling dates during the summer months where this temperature stratification occurs. These stations are located in the western basin of Quonochontaug Pond where Guarinello (2) notes that hypoxia was most prevalent in 2007 and 2008. These two stations are also the most shallow (JR= 2.5 m; HCBuoy= 2.2 m) of the five deep-water stations in the Pond and thus are most subject to wind mixing. The other three stations (HCChannel, N. Bill’s Island, E.Basin YC) are somewhat deeper (3 to 4 m) and thus not as susceptible to wind mixing. This is reflected in the data of Table 2 where the delta degrees C of 1.0-4.0 occurs consistently during the summer months at these three stations.

Table 2. Time Span Where the Water Column in Quonochontaug Pond was Stratified with Respect to Temperature. Δ= delta= Temperature Difference, in degrees C, Between Surface Water and Bottom Water.

<table>
<thead>
<tr>
<th>Station</th>
<th>Year</th>
<th>Δ, 0.5-1.6 Degrees C</th>
<th>Δ, 1.0-4.0 Degrees C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Judge’s Rock</td>
<td>2011</td>
<td>5/25 – 8/3</td>
<td></td>
</tr>
<tr>
<td>Judge’s Rock</td>
<td>2012</td>
<td>8/8</td>
<td>5/30 – 7/25</td>
</tr>
<tr>
<td>HCBuoy</td>
<td>2011</td>
<td>5/25 – 8/3</td>
<td></td>
</tr>
<tr>
<td>HCBuoy</td>
<td>2012</td>
<td>5/30 – 6/27</td>
<td>7/11</td>
</tr>
<tr>
<td>HCChannel</td>
<td>2011</td>
<td>---------------------</td>
<td>5/25 – 8/3</td>
</tr>
<tr>
<td>HCChannel</td>
<td>2012</td>
<td>8/8</td>
<td>5/30 – 7/11</td>
</tr>
<tr>
<td>N.Bill’s Island</td>
<td>2011</td>
<td>---------------------</td>
<td>5/20 – 8/15</td>
</tr>
<tr>
<td>N.Bill’s Island</td>
<td>2012</td>
<td>7/11 – 9/05</td>
<td>5/30 – 6/15</td>
</tr>
<tr>
<td>EBayYC</td>
<td>2011</td>
<td>---------------------</td>
<td>5/20 – 8/10</td>
</tr>
<tr>
<td>EBayYC</td>
<td>2012</td>
<td>7/11 – 8/22</td>
<td>5/30</td>
</tr>
</tbody>
</table>

Sources of Temperature Data:
- 2011- Salt Ponds Coalition Database (reference 14)
- 2012- T. Dodd, Personal Communication

**Dissolved Oxygen.** Table 3 presents the number of occurrences of various levels of hypoxia (low dissolved oxygen) in bottom waters of Quonochontaug Pond for the months May to October, 2007 to 2012. The highest level of bottom-water dissolved oxygen
(DO) that can be designated as hypoxic is 4.6 mG/L (2). For simplicity sake, the author has rounded this up to 5.0 mG/L. The DO data of Guarinello (2) was produced by anchored in situ water-quality monitoring instruments and thus is very detailed for the sampling period May to October 2007 and 2008. One can see from Table 3 that the Judge’s Rock (61-70) and the HCBuoy (46-60) stations have a great number of occurrences at this level of DO (≤5.0 mG/L). The other two stations monitored by Guarinello (2), HCChannel (HCS) (11-27) and N.Bill’s Island (3-15), have much fewer occurrences at this DO level. The 2006-2012 data, from the Salt Ponds Coalition (SPC) database (14), were obtained by bi-weekly sampling and thus are not nearly as detailed. However, for the ≤5.0 mG/L occurrence level, three out of four stations had either 3 or 4 occurrences, 25 to 33 percent of the number of sampling times (12) during the sampling year (May to October).

The Guarinello DO data (2) also had some occurrences at the ≤3.0 mG/L level, although far fewer than at the ≤5.0 mG/L level (Table 3). Again, the Judge’s Rock (12-15) and the HCBuoy (9-11) stations had the most occurrences at this level. At the ≤1.4 mG/L DO level, these two stations had the only occurrences with Judge’s Rock having the most (9) in 2007.

The author (E. Callender) has made a subjective judgement that the DO levels of 4-5 mG/L in bottom waters of Quonochontaug Pond represent conditions where benthic sediment exerts little influence on the water column overlying the benthic sediment surface. On the other hand, bottom-water DO levels of ≤3.0 mG/L suggest that the benthic sediment may influence the nutrient chemistry (nitrogen and phosphorus compounds) of the water column overlying the sediment surface. More on this subject in the section concerning biogeochemical processes in benthic sediment.

Table 3. Number of Occurrences of Various Levels of Hypoxia (Low Dissolved Oxygen) in Bottom Waters of Quonochontaug Pond for the Months of May to October, 2007 to 2012.

<table>
<thead>
<tr>
<th>Station</th>
<th>Year</th>
<th>Number ≤5.0 mG/L</th>
<th>Number ≤3.0 mG/L</th>
<th>Number ≤1.4 mG/L</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>JR</td>
<td>2007</td>
<td>61</td>
<td>15</td>
<td>9</td>
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<tr>
<td>JR</td>
<td>2008</td>
<td>70</td>
<td>12</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>HCBuoy</td>
<td>2007</td>
<td>60</td>
<td>11</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>HCBuoy</td>
<td>2008</td>
<td>46</td>
<td>9</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>HCCCh</td>
<td>2007</td>
<td>27</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>HCCCh</td>
<td>2008</td>
<td>11</td>
<td>2</td>
<td>-----</td>
<td>2</td>
</tr>
<tr>
<td>NBI</td>
<td>2007</td>
<td>3</td>
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<td>-----</td>
<td>2</td>
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<tr>
<td>NBI</td>
<td>2008</td>
<td>15</td>
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<td>-----</td>
<td>2</td>
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<tr>
<td>JR</td>
<td>07-11</td>
<td>3</td>
<td>1</td>
<td>-----</td>
<td>14</td>
</tr>
<tr>
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<td>07-11</td>
<td>4</td>
<td>1</td>
<td>-----</td>
<td>14</td>
</tr>
<tr>
<td>HCCCh</td>
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<tr>
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<td>2012</td>
<td>3</td>
<td>1</td>
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<td>14</td>
</tr>
<tr>
<td>HCBuoy</td>
<td>2012</td>
<td>4</td>
<td>1</td>
<td>-----</td>
<td>14</td>
</tr>
<tr>
<td>HCCCh</td>
<td>2012</td>
<td>1</td>
<td>-----</td>
<td>-----</td>
<td>14</td>
</tr>
</tbody>
</table>
Dissolved Inorganic Nitrogen (DIN)
i.1999 Data (1) [April 20, 1999 to December 13, 1999].
Figure 3 shows the average surface-water nitrate (NO$_3^-$) concentration data for the sampling period. The NO$_3^-$ concentrations for the eastern and western basins of Quonochontaug Pond were very low (1-4 uG/L) for the period April 20 to October 16, 1999. After that, NO$_3^-$ concentrations rose to maximum values of 25 to 34 uG/L in December 1999. The consistently low NO$_3^-$ concentrations in the water column of Quonochontaug Pond from late April to mid-October 1999 suggest that plankton were using this inorganic form of nitrogen for nutrition and growth. In addition, such low NO$_3^-$ concentrations do not appear to reflect microbiological activity in the form of nitrification or denitrification.

Figure 4 shows the average surface- and bottom-water ammonium (NH$_4^+$) concentration data in the Pond’s eastern basin for the 1999 sampling period. From April 20 to August 15, 1999, bottom waters are not significantly enriched (bottom-surface) in NH$_4^+$ relative to surface waters. On September 15, 1999, a substantial phytoplankton bloom occurred (chlorophyll-a was 6-7 ppb, Figure 5) which “crashed” sometime afterward, as evidenced by a chlorophyll-a concentration of 1.5 ppb on October 13, 1999 (Figure 5). On September 15, 1999, bottom-water NH$_4^+$ concentration became 35 uG/L relative to surface water (5 uG/L), suggesting that the plankton bloom “crashed” between September 3 and September 15, 1999, releasing NH$_4^+$ by remineralization of sinking organic matter. Also, on September 15, 1999, bottom-water dissolved oxygen was depleted by 2.6 mG/L relative to surface water. After the occurrence of maximum NH$_4^+$ concentrations on October 13, both surface- and bottom-water NH$_4^+$ concentrations, which were identical, decreased rapidly from 70 uG/L to 20 uG/L on December 15, 1999. In conclusion, it seems obvious that the “crash” of the phytoplankton bloom caused the substantial bottom-water enrichment in NH$_4^+$ and probably the substantial dissolved oxygen depletion in bottom water as a result of aerobic remineralization (oxidation, see Equation 1) of deposited organic matter that consumes dissolved oxygen and releases ammonium.

ii. Average DIN Data (SPC Database) [2008-2011].
The average concentrations of nitrate (NO$_3^-$) in surface and bottom waters are nearly identical, with 25 to 28 uG/L for the month of May and 12 to 18 uG/L for the months of June to September. These concentrations are slightly higher than those in 1999 (Figure 3) but generally reflect the utilization of NO$_3^-$ for plankton and algae growth during the summer months.

Average ammonium (NH$_4^+$) concentrations in the bottom waters of Quonochontaug Pond for the years 2008-2011 are enriched nearly 30% relative to surface waters (Figure 6).
For the sampling year 2012 (L. Green, personal communication), average ammonium concentrations in bottom waters of the Pond were enriched about 40% relative to surface waters. There is a statistically significant positive relationship between bottom-water $\text{NH}_4^+$ enrichment (bottom-water concentration minus surface-water concentration) and the bottom-water dissolved oxygen deficit (surface-water DO minus bottom-water DO) for the 2008-2011 sampling years (Figure 7). The substantially higher concentration of $\text{NH}_4^+$ in surface water for the month of May (Figure 6) may be related to the lack of uptake by phytoplankton (chlorophyll-a = 1.9 ppb) during this month when the pond waters are still cold. The significant enrichment of $\text{NH}_4^+$ in bottom water during the month of May is difficult to explain since water-column stratification and bottom-water hypoxia are not common during this month (2). However, the correlation of ammonium increase in bottom water and the dissolved oxygen deficit in bottom water (Figure 7) does suggest that aerobic remineralization of sinking organic debris (Equation 1) is a very important process that causes ammonium enrichment in bottom waters of Quonochontaug Pond. However, at dissolved oxygen deficits $\geq 1.5$ mG/L, the large $\text{NH}_4^+$ increases in bottom water (average $= 70$ uG/L $\text{NH}_4^+$) may be the result of $\text{NH}_4^+$ release from surficial benthic sediment.

There are very few occurrences of hypoxia and ammonium enrichment in bottom waters at the five deep-water stations in Quonochontaug Pond for the sampling year 2008. This was the second year of Guarinello’s study (2) of the Pond and the first year that reliable $\text{NH}_4^+$ data in brackish waters was available (14). At the $\leq 4.8$ mG/L dissolved oxygen level (2), the average $\text{NH}_4^+$ enrichment in bottom water at three deep-water stations (JR, HCChannel, NBI) was $48 \pm 27$ uG/L. These occurred in the middle of June, July, and August (14).

Table 4 presented below gives the average ammonium enrichment and dissolved-oxygen deficit in bottom waters of Quonochontaug Pond for the years 2008-2011 as recorded in the SPC Database (14)

Table 4. Average (Av.) Ammonium Enrichment and Dissolved Oxygen Deficit in Bottom Waters of Quonochontaug Pond for the years 2008 through 2011.

<table>
<thead>
<tr>
<th>Station</th>
<th>Av.Ammonium Enrichment</th>
<th>Av.Diss. Oxygen Deficit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Judge’s Rock</td>
<td>$59 \pm 25(5)$ uG/L</td>
<td>$1.6 \pm 0.8(4)$ mG/L</td>
</tr>
<tr>
<td>Harmonic Cove Channel</td>
<td>$30 \pm 5(3)$ uG/L</td>
<td>$1.2 \pm 0.3(3)$ mG/L</td>
</tr>
<tr>
<td>North Bill’s Island</td>
<td>$56 \pm 55(10)$ uG/L</td>
<td>$0.7 \pm 0.6(9)$ mG/L</td>
</tr>
<tr>
<td>East Basin Yacht Club</td>
<td>$42 \pm 24(5)$ uG/L</td>
<td>$0.6 \pm 0.6(4)$ mG/L</td>
</tr>
</tbody>
</table>

Values are Mean, $\pm$ Standard Deviation, and Number of Occurrences ( ).

$\text{NH}_4^+$ Enrichment = Bottom-Water Concentration-Surface-Water Concentration.

Dissolved-Oxygen Deficit = Surface-Water Concentration-Bottom-Water Concentration.

Thus, the average ammonium enrichment in bottom waters of Quonochontaug Pond for the years 2008-2011 is 46 uG/L and the average bottom-water dissolved-oxygen deficit for this same period is 1.0 mG/L. For the 2012 sampling season, the average ammonium enrichment in bottom waters of the Pond is 21 uG/L and the average bottom-water
dissolved-oxygen deficit is 0.8 mG/L (data from L. Green, personal communication and T. Dodd, personal communication).

Guarinello (2) notes that the Judge’s Rock, Harmonic Cove Buoy (Harmonic Cove), and Harmonic Cove Channel (Harmonic Cove South) stations experienced the most occurrences of hypoxia in Quonochontaug Pond (see Table 3). However, the SPC Database (14) did not show that the Harmonic Cove Buoy station contained any significant dissolved-oxygen deficits or ammonium enrichments. The possible reason for this is that the Harmonic Cove Buoy station is not as deep as the others (≤2 meters) and it is located in such a position in Quonochontaug Pond (see Figure 1) that prevailing summer southerly winds do not encourage stratification of the water column. While this may be true, please see the section “Nitrogen Dynamics at the Harmonic Cove Buoy Station Located in an Eelgrass Site”. The more probable reason for no bottom-water ammonium enrichment at this station is that ammonium is retained by the eelgrass roots in the benthic sediment.

The average ammonium enrichment and dissolved oxygen deficit in bottom waters of Quonochontaug Pond for the 2008-2011 sampling years and months that the author estimates benthic sediment might be a factor is 47±13 uG/L and 1.0 ±0.4 mG/L. These occurrences of significant ammonium enrichment of bottom waters represent 18% of the total sampling times for the four sampling years. Considering bottom waters near hypoxia (DO≥5.0 to ≤6.0 mG/L), bottom-water ammonium enrichment equals 17±17 uG/L. For bottom waters at the hypoxia level (DO<4.8 mG/L), bottom-water ammonium enrichment equals 43±30 uG/L.

**iii. Particulate Organic Nitrogen.**

The nutrient analyses that are contained within the SPC database (14) do not give data for the concentration of particulate organic nitrogen (PON) in the waters of the Rhode Island salt ponds. The author has queried the literature and determined that a reasonable estimate of PON is to subtract the DIN (NO₃⁻ + NH₄⁺) concentration from the total nitrogen (TN) concentration of a water sample and multiply that result by 0.55 (15). So, bottom-water PON was regressed against ammonium enrichment in bottom water (bottom-surface concentration) in an effort to see whether this PON was the source of remineralized ammonium in oxic/near hypoxic/hypoxic bottom water and surficial benthic sediment. Figure 8 is a graphical representation of this regression, with a correlation coefficient (R²) of 0.63. This significant correlation between bottom-water ammonium enrichment and bottom-water PON suggests that the process of aerobic remineralization of organic matter (equation 1) is primarily responsible for ammonium enrichment. The ammonium-enrichment data presented in Figure 8 that is greater than 35 uG/L is thought to be of such a magnitude as to have originated from surficial benthic sediment through diffusional and advective transport from the surficial sediment to the bottom water. However, there is a cluster of 8 samples that have an ammonium-enrichment value of 30 uG/L (Figure 8). This ammonium-enrichment level may be the upper limit for aerobic remineralization of organic matter in oxic/near hypoxic bottom waters. The higher levels of ammonium enrichment, 35 to 85 uG/L, may be a result of
aerobic remineralization of recently deposited organic matter in hypoxic surficial benthic sediment (Figure 8).

**iv. Dissolved Phosphate.**

Although the primary focus of this paper deals with nitrogen cycling and nitrogen biogeochemistry in Quonochontaug Pond, there is strong evidence from microcosm studies (16) and estuarine/coastal marine literature (17) that phosphorus also plays an important role in the primary production of organic matter in coastal lagoons, estuaries, and shallow marine waters.

The Salt Ponds Coalition (SPC) water quality and nutrient database (14) was queried for dissolved phosphorus (PO$_4^{3-}$) in surface- and bottom-water of Quonochontaug Pond for the years 2007-2011. The average surface-water PO$_4^{3-}$ concentration was 16.6±6.1(88) uG/L and the average bottom-water PO$_4^{3-}$ concentration was 16.8±4.9(88) uG/L. [These numbers represent the mean, standard deviation, and number of samples]. The difference between bottom-water and surface-water PO$_4^{3-}$ concentrations (ΔPO$_4^{3-}$) at the five deep-water stations in Quonochontaug Pond ranged between 0 and 61 uG/L. The number of occurrences where ΔPO$_4^{3-}$ was greater than 1 was 31. The number of occurrences where ΔPO$_4^{3-}$ was ≃ 3 and <7 uG/L was 12; that for ΔPO$_4^{3-}$ ≃ 7 uG/L was 8; and that for ΔPO$_4^{3-}$ ≥ 15 uG/L was 7. The largest ΔPO$_4^{3-}$ concentrations occurred at the Judge’s Rock station (14 and 15 uG/L), the HCBuoy station (16 and 32 uG/L), the HCChannel station (29 uG/L), and the North Bill’s Island station (20 and 61 uG/L). Only three of these large ΔPO$_4^{3-}$ concentrations correspond to the large ΔNH$_4^{+}$ concentrations. It is probable that ΔPO$_4^{3-}$ concentrations of 20 uG/L or greater represent regeneration of phosphorus in surficial benthic sediment.

One can compare these 2007 to 2011 dissolved inorganic phosphorus (DIP) data from the Salt Pond Coalition (SPC) database (14) with that for the sampling year (May to October) 1999 (1). The average surface-water PO$_4^{3-}$ concentration was 13.6±3.6 (18) uG/L and the average bottom-water PO$_4^{3-}$ concentration was 18.5±5.1 (18) uG/L. These values are not statistically different from the SPC concentrations (see above). They are also not statistically different from the mean values for the entire sampling year (April 20, 1999 to February 15, 2000); 15.1 uG/L for surface water and 19.2 uG/L for bottom water. Figure 9 shows the distribution of surface and bottom water DIP for the above sampling year. While the mean ΔPO$_4^{3-}$ for the sampling year was 4.1 uG/L, there were three occasions when the difference between bottom and surface water exceeded 4.0 uG/L. These were on August 18, 1999 (15.5 uG/L), September 15, 1999 (21.4 uG/L), and January 7, 2000 (9.0 uG/L). As previously noted there was a substantial phytoplankton bloom on September 15, 1999 (Figure 5) which “crashed” soon afterwards. As noted above for the SPC DIP data, the two large ΔPO$_4^{3-}$ concentrations that occurred in August and September (21 and 16 uG/L) probably represent regeneration of phosphorus in surficial benthic sediment. Bottom-water dissolved oxygen concentration was 6.3 and 5.4 mG/L with DO deficits of 2.2 and 3.6 mG/L on the above two dates in the late summer of 1999. Kemp et al. (18) gave a relationship between dissolved oxygen (mG/L) and benthic-sediment effluxes of PO$_4^{3-}$ (DIP Flux) for the Chesapeake Bay that, if applied to the 1999 data from Quonochontaug Pond (1), would suggest that on these two late-summer dates
the high $\Delta$PO$_4^{3-}$ values are derived from surficial benthic sediment. All the rest of the $\Delta$PO$_4^{3-}$ values, from May to October 1999, average 4.5±2.3 uG/L, suggesting that for most of the summer months the increase in bottom-water DIP is the result of aerobic mineralization of particulate organic matter in the water column.

**Biogeochemical Processes in Bottom Waters and Surficial Benthic Sediment**

*i. General.*

In earlier sections of this paper the physical properties of the water column in Quonochontaug Pond, temperature and dissolved oxygen (DO), were discussed. Much of the data came from the Salt Ponds Coalition database (14) where discrete samples of surface and bottom water were averaged over the sampling period from mid-May to mid-October. For at least two of the five deep-water stations in Quonochontaug Pond, the temperature and DO data were collected from 2006 to 2012. For the other three stations the data were collected from 2007 to 2012. Unfortunately, discrete sampling is not the best way to measure hypoxic events in the bottom water of the Pond. Table 3 shows that only four hypoxic events (<3.0 mG/L DO) were recorded by discrete sampling at the Pond’s deep-water stations during the 2007 to 2012 time periods.

The best way to monitor very low DO events (<2.3 mG/L DO) is to deploy bottom-water monitoring devices that measure temperature, salinity, dissolved oxygen, etc. In 2007 and 2008, Guarinello (2) had four such devices deployed in the bottom waters of Quonochontaug Pond. Table 3 shows that there were 52 low-DO events ($\leq$3.0 mG/L DO) that may be classified as hypoxic. There were also 20 very-low-DO events ($\leq$1.4 mG/L DO) where the bottom waters approached an anoxic condition (2).

There were many instances (313) where the bottom-water DO was less than 5 mG/L but greater than 3.0 mG/L (Table 3). These instances would reflect oxic conditions in the bottom waters and are most likely the “normal” dissolved-oxygen situation for much of the summer sampling season (June to September). However, these DO conditions in the Pond’s bottom waters do represent appreciable utilization of oxygen in bottom waters as surface waters contain about 7.5 mG/L DO (Figure 2). It is worthy to note that the preponderance of the DO$\leq$5.0 and $\geq$3.0 mG/L events occur at the three deep-water stations (Figure 1) in the Western Basin of Quonochontaug Pond (293 of 313). This is an area of restricted ocean water replenishment (2).

A similar situation exists for $\leq$3.0 mG/L DO events; of the 56 events, 56 occur at the three stations in the Western Basin of the Pond, and, in fact, nearly all of these occur at the Judge’s Rock (JR) and the Harmonic Cove Buoy (HCBuoy) stations (Table 3). These events (DO$\leq$3.0 mG/L) are classified as “near hypoxic”. Finally, only 20 “real” hypoxic events occurred at the three stations in the Western Basin of Quonochontaug Pond (Table 3).
Below, Table 5 after Gruber (19), summarizes the most important biologically mediated nitrogen processes that may occur in Quonochontaug Pond.

<table>
<thead>
<tr>
<th>Process</th>
<th>Organisms</th>
<th>Redox Environment</th>
<th>Trophic Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$ Assimilation</td>
<td>Phytoplankton</td>
<td>Aerobic</td>
<td>Photo-Autotrophic</td>
</tr>
<tr>
<td>NH$_4^+$ Assimilation</td>
<td>Phytoplankton</td>
<td>Aerobic</td>
<td>Photo-Autotrophic</td>
</tr>
<tr>
<td>Ammonification</td>
<td>Bacteria/Zooplankton</td>
<td>Aerobic/Anaerobic</td>
<td>Heterotrophic</td>
</tr>
<tr>
<td>DNRA</td>
<td>Bacteria</td>
<td>Anaerobic</td>
<td>Chemo-Autotrophic</td>
</tr>
<tr>
<td>N$_2$ -Fixation</td>
<td>Cyanobacteria</td>
<td>Aerobic</td>
<td>Photo-Autotrophic</td>
</tr>
</tbody>
</table>

DNRA= Dissimilatory Nitrate Reduction to Ammonium.

Thus, there are at least three aerobic biologically-mediated processes that occur in Quonochontaug Pond during the summer months and possibly two anaerobic microbiologically-mediated processes. All of these processes can occur in the water column of the pond (especially bottom waters) and at least two can occur in surficial benthic sediment.

Although oxygenated bottom water overlies anoxic, fine-grained benthic sediment, often a thin layer of oxic sediment overlies the grey to dark grey anoxic sediment. Figure 10 is a photo of a sediment core taken at the Judge’s Rock station on October 23, 2012. The core and the suspended sediment generated during the coring process was allowed to settle and the photo was taken on November 2, 2012. One can see from Figure 10 that there is a 1-1.5 mm layer of dark, reddish-brown oxic sediment overlying 3 mm of light-grey sediment that overlies dark-grey sediment. The light-grey sediment is definitely in an acute hypoxic state (DO<1.3 mg/L) and the dark-grey sediment is anoxic. The bottom-water dissolved oxygen concentration was 8.6 mg/L at the time that the core was taken. Two days later the DO concentration 1 cm above the sediment surface was 6.9 mg/L. Obviously there was a sediment oxygen demand (SOD). In fact, seven days after the core was taken, the DO concentration in water 1 cm above the sediment surface was 5.0 mg/L. A sediment core taken at the Harmonic Cove Buoy station on October 23, 2012 had a significantly greater SOD with the DO in bottom water 1 cm above the sediment surface declining from 8.7 to 1.4 mg/L in seven days.

While it was stated above that two microbiologically-mediated nitrogen processes occurred in anaerobic redox environments, the discussion of the oxygen environment in Quonochontaug Pond suggests that the bottom waters are mostly oxic and mildly hypoxic. And, surficial benthic sediment is definitely hypoxic to acutely hypoxic, at least in late October, 2012. However, recent work (20) has discovered that biological oxygen demand in benthic environments can exceed the rate of oxygen resupply via diffusion, particularly in finely–textured and organic rich soils (and coastal marine sediments), resulting in anaerobic “hotspots” (microsites) and events. In fact, such anaerobic microsites can also occur in particulate organic matter (fecal pellets) suspended in bottom waters in coastal lagoons and coastal marine environments.
ii. Assimilation of Nitrate and Ammonium.

The assimilation of nitrate or ammonium into organic nitrogen by marine phytoplankton that need to satisfy their nitrogen demand for growth is the process that dominates the marine nitrogen cycle (19). 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 (19). The synthesis of organic matter by the coupled assimilation of CO$_2$, NO$_3^-$ or NH$_4^+$, and PO$_4^{3-}$ can be expressed by the following two equations (19):

(6) using NO$_3^-$; $106\text{ CO}_2 + 16\text{ NO}_3^- + \text{HPO}_4^{2-} + 78\text{ H}_2\text{O} + 18\text{ H}^+ = C_{106H_{175O_{42}N_{16}P_1} + 150\text{ O}_2}$

(7) using NH$_4^+$; $106\text{ CO}_2 + 16\text{ NH}_4^+ + \text{HPO}_4^{2-} + 48\text{ H}_2\text{O} + 14\text{ OH}^- = C_{106H_{175O_{42}N_{16}P_1} + 118\text{ O}_2}$

In the ocean, most of the fixed organic nitrogen is returned back to nitrate by the remineralization process. It is proposed for Quonochontaug Pond, a coastal lagoon, that much of this remineralization process may only proceed as ammonification and that nitrification (the oxidation of ammonium to nitrate) is insignificant relative to ammonification. Either this is the case or that nitrate is recycled so rapidly between phytoplankton and the water column that the water-column nitrate concentrations remain very low during the summer (12-18 uG/L). Nixon and Pilson (21) presented nutrient data for Ninigret Pond showing that nitrate concentrations varied from 11-17 uG/L during the months April to October 1975 and that ammonium concentrations averaged 24 uG/L for the same period. Ammonium was low (≈7 uG/L) for the months April to June and considerably higher (35-65 uG/L) for the months July to October (21). By comparison, the SPC database (for the years 2008-2011) gives an average ammonium concentration for surface waters in Quonochontaug Pond of 54±18 uG/L for the months May to September. Like nitrate, ammonium may be recycled between phytoplankton and the water column although it appears that nitrate may be the preferred form of dissolved inorganic nitrogen during the summer months (July to October) (22). This is not always the case for coastal lagoons. For example, Berre Lagoon, a large Mediterranean coastal Lagoon in France, had nitrate and ammonium distributions in 2005 and 2006 that averaged 20 uG/L and 10 uG/L respectively for the months May to September (23). Using the 2005 ammonium and nitrate uptake rates for the summer months (May to September) in Berre Lagoon (23), the daily estimated uptake of NH$_4^+$ and NO$_3^-$ in Quonochontaug Pond is 135 Kg and 108 Kg respectively. The daily standing stock of NH$_4^+$ and NO$_3^-$ in the pond surface waters is 174 Kg and 49 Kg respectively. Obviously there is ample ammonium but not enough nitrate to support the primary production of planktonic organic matter in Quonochontaug Pond during the summer months.

Nixon (22) estimates that the annual phytoplankton primary production for Ninigret Pond is 30 gC/m$^2$/yr or 50 mgC/m$^3$/day. Applying these primary production estimates to Quonochontaug Pond (surface area of 30x10$^5$ m$^2$ and an average water depth of 1.8 meters), and using a planktonic algae carbon to nitrogen ratio of 6.6, the estimated assimilation of nitrate and ammonium (Dissolved Inorganic Nitrogen, DIN) is calculated to be 14, 200 KgN/yr. The calculated DIN inputs to Quonochontaug Pond total 13, 200
KgN/yr using the higher estimate calculated by Nixon and Buckley (3). The DIN inputs to the Pond calculated by the author (Figure 13) total 17,097 KgN/yr. Obviously, not all of the external DIN inputs to Quonochontaug Pond are used to support phytoplankton productivity.

**iii. Aerobic Mineralization of Organic Matter.**
This process of aerobic mineralization of nitrogenous organic matter in the water column of coastal lagoons and shallow coastal marine systems is also called ammonification. Ammonification is defined as the decomposition of organic matter with the production of ammonium compounds especially by the action of bacteria on nitrogenous organic matter (Merriam-Webster Dictionary). Thus this mineralization of organic matter is the transformation of organic compounds back to inorganic compounds such as ammonium and urea. The first ammonification mineralization process that will be discussed is aerobic mineralization of sinking organic matter by heterotrophic animals and bacteria. These bacteria utilize carbon and energy (for growth) which comes from pre-formed organic material. For example, herbivorous zooplankton are heterotrophs because they consume phytoplankton for their carbon and energy needs (www.geo.cornell.edu). The key issue about this process is that dissolved oxygen in the water is the main oxidant for the destruction of organic matter and that CO$_2$, NH$_4^+$, and PO$_4^{3-}$ are released to the water column (see Equation 1). The vast majority of the oxidation of organic matter follows this reaction involving oxygen as the terminal electron acceptor (19). Figure 7 shows the relationship between dissolved-oxygen deficit in bottom water (surface DO-bottom DO) versus the ammonium increase in bottom water (bottom NH$_4^+$-surface NH$_4^+$). While the correlation coefficient, R$^2$, is not the strongest, it is statistically significant due to the large number of samples (35). The significance of this relationship is that oxygen is consumed while ammonium is released by this mineralization process. Figure 8 shows that an increase in particulate organic nitrogen (PON) is accompanied by an increase in bottom-water ammonium enrichment. This relationship has a relatively strong correlation with an R$^2$ of 0.63. This PON originates from the rapid sedimentation of phytoplankton blooms that have crashed and consists of easily degradable organic matter that is rapidly attacked by heterotrophic bacteria.

The difference between the surface-water and bottom-water daily standing stock of ammonium in Quonochontaug Pond is 70 KgN. Using average ammonium regeneration rates for Swedish coastal waters (40 nMol NH$_4^+$/L/day) (24), the calculated ammonium regeneration for Quonochontaug Pond would be 90 KgN/day. The comparison between the two numbers assumes that the bottom-water increase in ammonium for Quonochontaug Pond is due to regeneration of rapidly-sinking particulate organic matter whose origin is decaying phytoplankton mass.

In October of 2012, sediment cores were taken at the JR and HCCh stations (see Figure 1). Core-top water samples were taken at the time of coring and 3, 7, and 10 days after the coring date (October 23, 2012). Core-top water samples were sent to the URI Watershed Watch Laboratory for nitrate, ammonium, phosphate (DIP), total N and total P analyses. Subsequent to the withdrawal of the core-top water sample, dissolved oxygen was measured by the Winkler titration.
The ammonium concentrations in the core-top water at the JR station showed no trend with time ($R^2 = 0.004$). They remained high (55±10 uG/L) throughout the incubation period. This may be a result of the fact that core-top water dissolved oxygen (DO) concentrations were of a sufficient level (8.5 to 5.0 mG/L) to maintain an oxic sediment-water interface. In fact, a picture of the sediment-water interface at the end of the core incubation (after 10 days) shows a marked 1.5 mm thick reddish-brown surficial sediment layer in contact with the overlying water (Figure 10). The oxic interface may have “trapped” any of the ammonium in the underlying sediment pore water from fluxing into the overlying water. This developed oxic surficial sediment layer adsorbed phosphate from the core-top water, indicated by a significant decrease in phosphate concentration over the time interval of the incubation (14 to 6 uG/L, $R^2 = 0.68$). This is a common occurrence in freshwater and marine sediments where phosphate is adsorbed onto iron oxhydroxide particles that form at the oxic sediment-water interface (65).

The ammonium concentrations in the core-top water at the HCCh station showed a somewhat significant decrease with time, from 70 to 47 uG/L ($R^2 = 0.49$). The DO in the core-top water showed a very significant negative trend with time, from 8.6 to 5.6 mG/L ($R^2 = 0.89$, slope = -0.22 mG/L/day). However, at the end of the incubation time interval, there was a 5-10 mm thick reddish-brown surficial sediment layer in contact with the core-top water. However, this oxidized surficial sediment layer did not cover the entire sediment surface and was intermingled with light-grey sediment. It is probable that microbenthos in this surficial sediment may be affecting the ammonium in the overlying water. The core-top water phosphate concentrations showed a very significant positive trend with time, 13 to 22 uG/L ($R^2 = 0.98$). This distribution implies that as DO in core-top water decreases, phosphate is released from surficial sediment. As mentioned above, the oxic surficial sediment layer does not cover the entire surface of the core and it is probable that the portion of the sediment surface covered by the light-grey sediment is the source of the phosphate release.

In summary, the above core-incubation data at two deep-water stations (JR and HCCh) in Quonochontaug Pond indicate that during the Fall (October 2012), when bottom-water dissolved oxygen concentrations are initially high (DO=8.5 mG/L), a well-developed oxic sediment-water interface will definitely adsorb phosphate from overlying bottom waters and possibly retard any ammonium flux from benthic sediment. Any irregularity in this oxic interface may result in a benthic flux of phosphate from underlying suboxic or anoxic sediment.

iv. Nitrogen Dynamics at the Harmonic Cove Buoy Station Located in an Eelgrass Meadow.

The Harmonic Cove Buoy station (HCBuoy) in Quonochontaug Pond (see Figure 1) is located in moderately-shallow waters ($\leq 2$ meters) underlain by eelgrass (Zostera marina). Harmonic Cove waters are underlain by extensive beds of eelgrass (2, 25). The Harmonic Cove Buoy station (HCBuoy) is the one station of the five deep-water stations in Quonochontaug Pond where extensive beds of Zostera marina exist. The water depth at the HC Buoy station is approximately 2 meters and secchi-disk transparency reaches the bottom on most sampling occasions. Therefore, light reaches these aquatic
macrophytes and nourishes plant growth through photosynthesis. The HCBuoy station is the only one sampled routinely in Quonochontaug Pond where this situation exists. Therefore, this station will be designated as the vegetated site while the other four deep-water stations will be designated as the “bare” or unvegetated sites. The Judge’s Rock (JR) station has water depths approaching 2.7 meters. There is a sparse eelgrass presence at this station. The Harmonic Cove Channel (HCCh) station has water depths approaching 4 meters and no eelgrass. The North Bill’s Island (NBI) station also has water depths of 4 meters and no eelgrass. The East Basin Yacht Club (EBYC) station has water depths of about 2.8 meters and no eelgrass.

The following table (Table 6) gives the four-year annual (May to October) mean and standard deviation about the mean for three nitrogen species in surface and bottom waters of Quonochontaug Pond. In addition it presents the mean dissolved oxygen concentration for bottom waters. The vegetated site is the HCBuoy station and the unvegetated (“bare”) sites are the other four deep-water stations in Quonochontaug Pond that are sampled routinely (Figure 1).

Table 6. Average Surface- and Bottom-Water Nitrogen Species Concentrations and Bottom-Water Dissolved Oxygen Concentration in Quonochontaug Pond for the Sampling Years (May to October) 2008 to 2011. All Concentrations of Nitrogen Species are in Micrograms Per Liter (uG/L) and the DO Concentration is in Milligrams Per Liter (mG/L). The ± Values are Standard Deviation About the Mean.

<table>
<thead>
<tr>
<th>Site(s)</th>
<th>NO$_3^-$ (S)</th>
<th>NO$_3^-$ (B)</th>
<th>NH$_4^+$ (S)</th>
<th>NH$_4^+$ (B)</th>
<th>PON (S)</th>
<th>PON (B)</th>
<th>DO (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vegetated</td>
<td>18±12</td>
<td>15±10</td>
<td>34±19</td>
<td>37±22</td>
<td>203±47</td>
<td>237±89</td>
<td>6.8±1.1</td>
</tr>
<tr>
<td>“Bare”</td>
<td>15±1.4</td>
<td>17±1.5</td>
<td>37±4</td>
<td>54±10</td>
<td>210±33</td>
<td>224±34</td>
<td>6.2±1.1</td>
</tr>
</tbody>
</table>

Vegetated Site= Harmonic Cove Buoy Station.
“Bare” Sites= Judge’s Rock, Harmonic Cove Channel, North Bill’s Island, and East Basin Yacht Club Stations.
(S)= Surface Water; (B)= Bottom Water
PON= Particulate Organic Nitrogen= (Total N-(NO$_3^-$ + NH$_4^+$)) x 0.55.

Table 6 shows that nitrate concentrations for both surface and bottom waters at both the vegetated (eelgrass) and non-vegetated (“bare”) sites are low. However, there is a slight difference between the two types of sites. At the eelgrass site (Harmonic Cove Buoy Station) bottom-water NO$_3^-$ is slightly depleted relative to surface-water NO$_3^-$.

While the standard deviations indicate that there is no statistical difference between the two concentrations, it is interesting to note that this site has a shallow water depth (≤2 meters) that should promote extensive mixing of the water column. Such mixing would homogenate the nitrate concentrations in the water column. Is even a slight decrease in bottom-water NO$_3^-$ at this vegetated site indicative of denitrification, even though the rate must be quite small?

The ammonium data for the eelgrass site versus that for the unvegetated (“bare”) sites in Quonochontaug Pond give a different picture about nitrogen cycling and retention (Table 6). Bottom waters at the vegetated site (Harmonic Cove Buoy Station) are not significantly enriched in NH$_4^+$ compared to surface waters at this station (ΔB-S=3 uG/L).
However, bottom waters at the four non-vegetated ("bare") sites (the other four deep-water stations) do show significant enrichment in NH$_4^+$ compared to surface waters ($\Delta$B-S=17 uG/L). Surface waters at all five stations have essentially the same NH$_4^+$ concentration (Table 6). Extensive studies of eelgrass beds in shallow coastal bays and lagoons (26, 27, 28) indicate that eelgrass and their associated sediment is a nitrogen sink and that pore water ammonium nourishes their growth. The ammonium data in Table 6 appears to support this observation in that bottom-water NH$_4^+$ is not enriched at the vegetated eelgrass site, implying that NH$_4^+$ is retained in the benthic sediment. By contrast, the non-vegetated sites show significant enrichment in bottom-water NH$_4^+$ concentrations. These ammonium data further imply that much of this bottom-water enrichment is due to the flux of NH$_4^+$ from benthic sediment to overlying bottom waters. More about this in the next section. Recently released 2012 nutrient data (L. Green, personal communication) support the above conclusion about ammonium. The vegetated site (HCBuoy) has a $\Delta$B-S =10 uG/L while the “bare” sites have a $\Delta$B-S=21 uG/L.

A further look at Table 6 reveals another effect of eelgrass on nitrogen in the bottom waters of Quonochontaug Pond. At the vegetated site, particulate organic nitrogen (PON) shows a decided increase in concentration in bottom water relative to surface water ($\Delta$B-S=34 uG/L). The non-vegetated sites show a much lower increase in bottom-water relative to surface-water PON ($\Delta$B-S= 14 uG/L). The implication of this observation is that eelgrass leaves rising above the sediment surface trap suspended particulate matter settling through the water column. Such an effect of higher particle trapping by submersed plant beds has been observed in Chesapeake Bay (29). This particle trapping of suspended sediment results in higher organic content of the particulate matter settling to the bottom and augments surficial sediment pore-water nutrient pools.

As stated in the last part of the Aerobic Mineralization of Organic Matter section, in October 2012, sediment cores were taken from three deep-water stations in the western basin of Quonochontaug Pond. One of these stations was HCBuoy (Figure 1), a site where the distribution of eelgrass is prevalent. As at the other two core sites (JR and HCCCh), there was no time trend in ammonium concentration. Ammonium (NH$_4^+$) concentrations remained high (60±4 uG/L) throughout the incubation period of ten days. Dissolved oxygen (DO) concentration had a very significant, steep negative trend ($R^2 = 0.98$, slope = -1.1 mG/L/day), starting at 8.6 mG/L and ending at 1.4 mG/L. The HCBuoy core had a slanted sediment-water interface and after several days of incubation, the core surface consisted of approximately equal parts of medium brown and light grey colors. Also, several decayed eelgrass “leaves” protruded through the sediment surface. From this description it is obvious that not all of the surface of the sediment core was oxidized. Since the initial condition of the surface of the sediment core consisted of grey, organic-rich material, significant DO consumption would be required to produce an oxidized sediment-water interface, even if that oxic condition covered only 50% of the sediment surface. Such a process is demonstrated by the above DO data for the core-top water at the HCBuoy core site.
The lack of any time trend for ammonium is somewhat puzzling at first glance. It has been shown that pore-water NH₄⁺ nourishes the growth of eelgrass (27, 28). This means that eelgrass plant roots in the sediment obtain their nitrogen growth demand from pore-water NH₄⁺. Obviously, the eelgrass at site HCBuoy retains the NH₄⁺ in sediment (Table 6) and would not utilize NH₄⁺ from the water column for its growth. The lack of any time trend in NH₄⁺ concentration in core-top water from the HCBuoy core is consistent with this explanation. An incubation study of eelgrass beds in a French Mediterranean Coastal Lagoon (66) shows that, if anything, NH₄⁺ is lost from the overlying water column at the end of the incubation. In fact, at the beginning of the HCBuoy core incubation, the NH₄⁺ concentration was 65 uG/L and at the end of the incubation period the concentration was 55 uG/L.

While the ammonium concentration in core-top water from the HCBuoy core showed little change with time, the phosphate (DIP) concentration had a very significant positive time trend (R² = 1.0, slope = 6.6 uG/L/day). The initial concentration was 14 uG/L PO₄³⁻ and after seven days the concentration was 61 uG/L PO₄³⁻. Any phosphate flux from the sediment to the overlying water would not be retarded due to the steep decline in dissolved oxygen in water above the sediment-water interface. In general, phosphate concentrations in seagrass sediment pore waters are of significant concentration to cause a positive flux to the overlying water when there are low dissolved oxygen concentrations at the sediment-water interface (66). At the end of the HCBuoy core incubation, the dissolved oxygen concentration in the core-top water was 1.4 mG/L.

v. Ammonification Under Hypoxic Conditions.

The process of transforming organic compounds back to inorganic compounds is called mineralization. Recycled nitrogen is primarily in the form of ammonium and urea which is rapidly broken down to NH₄⁺ by bacteria. Ammonium is regenerated from organic compounds by zooplankton excretion and by microbial decomposition of organic matter (30). It is presumed that excretion contributes the largest part of NH₄⁺ regeneration in the aerobic water column, while more of the microbial decomposition of organic matter is accomplished in benthic sediment (31). Earlier we discussed the mineralization of suspended organic matter in the aerobic water column of Quonochontaug Pond. In this section we will consider the ammonification of organic matter under low-oxygen conditions (hypoxia) in the bottom waters and surficial benthic sediment of Quonochontaug Pond.

Figure 7 shows the relationship between dissolved-oxygen deficit and ammonium enrichment in the bottom waters of Quonochontaug Pond for the years 2008 to 2011. While the SPC database contains only monthly averages of discrete samplings for dissolved oxygen and ammonium for the years 2008 to 2011, Guarinello’s thesis (2) reports that there were many instances of hypoxia recorded by bottom-water water-quality monitors for the summers of 2007 and 2008. Table 3 shows that there are many instances of hypoxic DO concentrations for the years 2007 and 2008 (2) but far fewer discrete monthly instances of hypoxic conditions in 2011 and 2012. It is presumed that the instances where bottom-water DO concentrations are less than 5.0 and greater than 3.0 mG/L represent times when ammonium regeneration in the water column is caused
by aerobic respiration (see Equation 1). It is further presumed that instances where bottom-water DO is less than about 3.0 mG/L and bottom-water ammonium increase is greater than 25±5 uG/L represent microbial decomposition of organic matter deposited in benthic sediment and the flux of NH$_4^+$ from benthic sediment to the overlying water column.

Figure 11 shows the relationship between bottom-water dissolved oxygen (≤5.0 mG/L) and bottom-water ammonium enrichment (bottom-surface concentration) for the five deep-water stations in Quonochontaug Pond for the years 2008 to 2011. There is a relatively strong correlation ($R^2 = 0.66$) between these two parameters suggesting that the benthic flux of NH$_4^+$ may be responsible for the ammonium enrichments that are greater than 25 uG/L. These enrichments appear to be generated at bottom-water DO concentrations less than 4.5 mG/L.

Table 7. Comparison Between Near Hypoxia and Hypoxia of Bottom Water Dissolved Oxygen and Bottom-Water Ammonium Increase in Quonochontaug Pond, 2008-2011.

<table>
<thead>
<tr>
<th>Near Hypoxia</th>
<th>Bottom H$_2$O DO, 5.2 mG/L</th>
<th>Bottom H$_2$O NH$_4^+$ Incr., 17uG/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hypoxia</td>
<td>Bottom H$_2$O DO, 4.2 mG/L</td>
<td>Bottom H$_2$O NH$_4^+$ Incr., 43uG/L</td>
</tr>
</tbody>
</table>

Table 7 confirms the bottom-water DO deficit and the bottom-water ammonium enrichment relationship for Quonochontaug Pond.

If we extend the relationship between bottom-water DO and bottom-water ammonium enrichment (Figure 11) to calculate ammonium enrichment concentrations for acute hypoxic conditions (≤1.5 mG/L DO, Table 3), then a figure of 95 uG/L results (see equation for the regression in Figure 11). Such values for bottom-water ammonium enrichment at the Judge’s Rock station have been observed for July 2008 and August 2011 (80 and 90 uG/L). In fact this station averages 52 uG/L for bottom-water ammonium enrichment for the years 2008 to 2011 and represents the best example of benthic flux that enriches the bottom water with ammonium. The average bottom-water ammonium enrichment at the North Bill’s Island station is 45 uG/L and represents the next best example of this process. The other three deep-water stations average 18 uG/L for bottom-water ammonium enrichment and suggests that mineralization of organic matter occurs in bottom water.

The literature on nutrient concentrations in coastal lagoon, estuarine, and shallow coastal marine waters gives an average bottom-water ammonium concentration of 43 uG/L (32,33,34). The average bottom-water ammonium concentration for Quonochontaug Pond for the years 2008 to 2011 is 51 uG/L. References 32 and 34 note that bottom-water ammonium concentrations of 61 and 37 uG/L overly benthic sediments that release ammonium to the water column.

The daily standing stock of NH$_4^+$ in the upper 1 meter (photic zone) of the water column of Quonochontaug Pond is 105 Kg. The daily standing stock of NH$_4^+$ in the bottom
meter of the water column of the Pond is 162 Kg. The difference between the bottom-water and the surface-water daily standing stock of ammonium is 57 Kg. Where does this mass of NH$_4^+$ come from? It is proposed that much of this extra mass of NH$_4^+$ in the bottom waters of Quonochontaug Pond comes from the exchange of NH$_4^+$ between surficial benthic sediment and the overlying bottom water. The only Rhode Island Salt Pond (coastal lagoon) that has been studied for the benthic flux of ammonium is Potter Pond (35). Nowicki and Nixon calculated that 450 mMoles NH$_4^+$/m$^2$/year was the yearly benthic ammonium flux rate for Potter Pond. Applying this value to Quonochontaug Pond (30x10$^5$ m$^2$ surface area), the calculated ammonium benthic flux for the Pond is 67 Kg NH$_4^+$-N/day when the Nowicki and Nixon value is divided by 365 days. The calculated ammonium benthic flux for Quonochontaug Pond is pretty close to that value that was calculated as the difference in the daily standing stock of bottom-water minus surface-water ammonium in the Pond (57 Kg NH$_4^+$-N/day). In fact, if we average available ammonium benthic flux data for several coastal lagoons and shallow marine systems (30) and apply this average value to Quonochontaug Pond, a value of 59±39 Kg NH$_4^+$-N/day is obtained.

A study of benthic ammonium release from surface sediments of the Gulf of Gdansk (southern Baltic Sea) (34) shows a statistically-significant correlation between dissolved oxygen in near-bottom waters and benthic diffusive fluxes of ammonium nitrogen. Applying these data to the occurrences of hypoxia in Quonochontaug Pond (Table 3), we calculate that for bottom-water DO concentrations of 5.0 mG/L, there is a benthic ammonium flux of 75 Kg NH$_4^+$-N/day and for DO concentrations of 3.0 mG/L, there is a benthic ammonium flux of 108 Kg NH$_4^+$-N/day. While these benthic fluxes of ammonium are somewhat higher than those calculated above, they do show that bottom-water hypoxia is a factor that stimulates ammonium release from benthic sediment.

A recent study in an Australian estuary (36) has shown that patchiness in the distribution of various types of benthic fauna can have a large effect on the benthic fluxes of ammonium. The dissolved oxygen in sediments containing small epifauna declined at a significant rate and these sediments recorded rapid efflux rates of ammonium. By contrast, the decline in dissolved oxygen in sediments containing burrowing infauna was much slower as was the rate of benthic ammonium release (36). These burrows may provide an oxic reservoir within the sediments, a situation that may slow down the decomposition of organic matter. Stolt et al. (37) conducted an extensive mapping study of Quonochontaug Pond and found that in areas where eelgrass was absent, fine-grained benthic sediment was dominated by tube-dwelling organisms that were visible at the sediment-water interface. This may be one reason why large bottom-water enrichments of ammonium are limited even though there have been extensive periods of hypoxia (2).

vi. Denitrification and Dissimilatory Nitrate Reduction to Ammonium. 
In the section on Hypoxia and Dissolved Nitrogen Cycling-Theory, both processes of denitrification and dissimilatory nitrate reduction to ammonium (DNRA) were shown to occur in the absence of dissolved oxygen and use nitrate to “oxidize” organic matter (Equations 3 and 4). In the last decade researchers have found that DNRA rates are significantly higher during oxic/hypoxic conditions compared to anoxic conditions (5).
In addition, shallow-water environments with benthic plants, such as eelgrass, produce abundant oxygen during photosynthesis. The dissolved oxygen diffuses into surficial benthic sediment and inhibits denitrification (9). Also, DNRA is favored over denitrification at extremes in water temperature, <14 and >17 degrees C (8). Finally, the percentage of the annual nitrogen load denitrified in various estuarine and coastal marine systems varies with the mean water residence time (9). Thus, Rhode Island coastal lagoons (salt ponds), with water residence times of days, can only denitrify about 5% of their total nitrogen load (9). The reasons, stated above, why denitrification may be the minor pathway for the oxidation of organic matter in Quonochontaug Pond are reinforced by the low, average nitrate concentrations in the Pond surface and bottom waters (Table 5). Assimilation of nitrate by phytoplankton growth during the summer months may be one major reason why NO$_3^-$ concentrations are so low (15-18 uG/L). Another reason may be that groundwater nitrate entering the Pond’s fringing shallow-water coarse-grained sediments is denitrified (38).

As we have seen above, nitrate concentrations in the water column of Quonochontaug Pond during the months of June through September (2008-2011 sampling years) are very low. Since the Salt Ponds Coalition does not sample during the other months of the year (November through April), the only nitrate data for the late Fall through the Winter is the data of Granger et al. (1) for 1999-2000. For the period November 1999 to February 2000, nitrate in both surface and bottom waters averaged 27±11 uG/L (see Figure 3). In early May 2010, NO$_3^-$ concentrations in surface and bottom waters at five deep-water stations in Quonochontaug Pond averaged 38±6 uG/L. The reason for these higher NO$_3^-$ concentrations in May 2010 is undoubtedly surface-water runoff from the watershed after torrential rains in early April 2010. At the same time in May 2010, NH$_4^+$ concentrations in surface and bottom waters averaged 110±17 uG/L and bottom-water temperatures averaged 14.8±1.8 degrees C. The reason for the elevated NH$_4^+$ concentrations was NOT watershed inputs as the ratio of NO$_3^-$/NH$_4^+$ in the brooks entering the eastern and western basins of Quonochontaug Pond was between 27 and 33 to 1.

It is proposed that during May 2010, the process of dissimilatory nitrate reduction to ammonium (DNRA) took place in Quonochontaug Pond. The following statements present information that may support this proposal. Some of these statements refer to criteria that have been advanced as supporting evidence for DNRA, especially in contrast to denitrification.

1) Temperature, ≤14 degrees C.
2) NO$_3^-$ concentrations should be evenly distributed between surface and bottom water during this time of the year (May) as the water column is not stratified with respect to temperature.
3) Also, NH$_4^+$ should be evenly distributed due to the above reasoning. Bottom-water NH$_4^+$ (120±22 uG/L) was somewhat elevated relative to surface-water NH$_4^+$ (100±12 uG/L). A minimal benthic flux of NH$_4^+$ during substantial oxic conditions may be the source of this increase.
4) Both NO$_3^-$ and NH$_4^+$ concentrations may be high in May as plankton growth is low and not utilizing these nutrients (chlorophyll-a concentrations 1.6±0.5 ppb).
5) Surface and bottom water, in May 2010, have high dissolved oxygen (DO) con-
centrations. Surface water=7.8±0.1 mG/L and bottom water=7.6±0.3 mG/L.
Considering these DO data, the upper few mm (up to 10 mm) of the benthic sediment column are oxic. Such conditions would inhibit denitrification.

6) DNRA is an anaerobic process (reaction). However, anaerobic microsites or “hotspots” can exist in marginally oxic sediments (20) or as patches associated with fecal pellets (39).

The DNRA reaction consumes 53 ug-atoms of NO$_3^-$ and produces 69 ug-atoms of NH$_4^+$; thus the ratio of NO$_3^-$/ NH$_4^+$ is 1.3 (see Equation 4). The average DNRA rates for temperate estuarine and coastal marine sediments is 1,500 uMoles NH$_4^+$-N/m$^2$/day (40, 41, 10). Applying this rate to Quonochontaug Pond for May 2010, it is calculated that the DNRA process produces 35 Kg NH$_4^+$-N/day. Using this number and combining it with other sources of NH$_4^+$-N to Quonochontaug Pond’s water column in May 2010, the accounting for NH$_4^+$-N is as follows:

- 0.03% Stream Input = 0.18 Kg NH$_4^+$-N/day
- 0.5% Atmospheric Input = 3.0 Kg NH$_4^+$-N/day
- 5.6% Benthic Flux = 33 Kg NH$_4^+$-N/day
- 5.9% DNRA = 35 Kg NH$_4^+$-N/day
- 88% Aerobic Mineralization = 523 Kg NH$_4^+$-N/day

In May 2010, the daily standing stock of NH$_4^+$-N was 594 Kg NH$_4^+$-N.

From the above accounting, DNRA is responsible for nearly 6% of the ammonium nitrogen in the month of May 2010. This figure is exactly the percentage contribution of DNRA to total ammonium at 15 degrees C calculated from a diagenetic model of nitrate reduction in temperate estuarine sediment (8).

There may be a few other times in 2010 and 2011 when DNRA is a process that converts moderate benthic nitrate concentrations to ammonium, but the May 2010 nitrate and ammonium data are the most consistent set suggesting that this process could occur in surficial benthic sediment of Quonochontaug Pond.

The availability of fixed nitrogen is considered by many researchers to be a major factor regulating primary productivity in shallow marine environments (9). While 79% of the earth’s atmosphere is composed of N$_2$, this major nitrogen reservoir is unavailable directly to plants and animals (9). Biological nitrogen fixation is the reduction of dinitrogen (N$_2$) to NH$_3$ (44).

$$N_2 + 8H^+ + 8e^- = 2NH_3 + H_2$$

The ammonia formed is subsequently incorporated into cellular material. The process of nitrogen fixation is catalyzed by the molybdo-iron enzyme nitrogenase (42). Nearshore coastal and estuarine areas are characterized by high primary production of plankton and rooted macrophytes (seagrasses) (21). Nitrogen, essential for plant growth, is generally found in short supply relative to estimated plant demands (42), especially in seagrass
meadows (43). This condition potentially favors the establishment of N₂-fixing microorganisms (44). Organic matter availability stimulates N₂ fixation and suggests that this process in coastal marine waters is an anaerobic one which, in aerobic marine waters, can only proceed in O₂-poor microzones or “hotspots” (20). These O₂-poor microzones in aerobic marine waters are important because nitrogenase, the enzyme complex mediating N₂ fixation, is inactivated by exposure to molecular oxygen (45).

In 1988, Howarth et al. (46) wrote that they found no data for planktonic nitrogen fixation in estuaries or coastal seas. They further wrote that unlike N₂ fixation by planktonic organisms, there were ample data with regard to N₂ fixation by benthic bacteria. By 2006, Howarth and Marino (47) noted that in estuarine and coastal marine waters with salinities greater than 12 parts per thousand, cyanobacteria capable of N₂ fixation were either present in very small numbers or absent from the plankton of the vast majority of mesohaline estuaries. They further note (47) that while N₂ fixation appears to be a rare process in saline estuaries and coastal seas, benthic cyanobacteria and cyanobacterial epiphytes on seagrasses often fix nitrogen at high rates and thus can contribute significantly to the N inputs of systems in which sufficient light penetrates to the bottom.

Although it appears that pelagic N₂ fixation is minimal, benthic N₂ fixation may be important in Quonochontaug Pond, especially in the eelgrass beds (47). Below is a table comparing average N₂-fixation rates for pelagic waters, bare benthic, and seagrass-covered benthic sediment areas of estuarine and coastal marine systems.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Average N₂-Fixation Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pelagic Waters</td>
<td>0.05±0.03 gN/m²/year</td>
<td>49</td>
</tr>
<tr>
<td>Uncolonised Marine Sed.</td>
<td>0.14±0.20 gN/m²/year</td>
<td>49</td>
</tr>
<tr>
<td>Vegetated Marine Sediment</td>
<td>1.0±0.14 gN/m²/year</td>
<td>5, 49</td>
</tr>
</tbody>
</table>

Vegetated Marine Sediment is specific for seagrass.

N₂-Fixation Rate numbers are expressed as Average±Standard Deviation about the Mean Value.

In the section on assimilation of nitrate and ammonium, it was calculated that 14,200 KgN/year were assimilated into the phytoplankton of Quonochontaug Pond. Yearly external nitrate and ammonium inputs to the Pond are 17,097 Kg/year (Figure 13). Obviously, external DIN inputs to Quonochontaug Pond satisfy the nitrogen demand of phytoplankton in the water column.

The only benthic metabolism study conducted on a Rhode Island Coastal Lagoon (salt pond) was that by Nowicki and Nixon (48) for Potter Pond. They estimated that the annual benthic macrophyte production was about 250 gC/m²/year. Using a C/N ratio of 6.6 (Redfield ratio), the nitrogen macrophytic production rate is calculated to be approximately 38 gN/m²/year. Applying this number to the benthic area in Quonochontaug Pond that was inhabited by eelgrass in 2007 (2), then the eelgrass-
inhabitated sediment in the Pond produces 22,800 KgN/year. However, Potter Pond may have a more diverse benthic floral composition than Quonochontaug Pond due to its eutrophic state and shallow average water depth. That is, Potter Pond may have both seagrass and macroalgae populations. If we use the benthic area of Quonochontaug Pond that is inhabited by eelgrass (6x10^5 m^2) and the average vegetated N_2-fixation rate in Table 8, then the eelgrass-assimilation rate for Quonochontaug Pond is calculated to be 680 KgN/year. Obviously this number for N assimilation is vastly inadequate to support the benthic macrophytic production reported for Potter Pond (48). As stated above, benthic macrophytic production in Potter Pond may not be a good substitute for Quonochontaug Pond. There are three factors that may bring the above comparison closer together. These are the proportion of seagrasses in Potter Pond, the C/N ratio of seagrass sediment, and the fact that sediment interstitial NH_4^+ may be the major nutrient that supports eelgrass growth in Quonochontaug Pond.

With respect to using benthic net production data for Potter Pond (48), other studies of macrophytic production in coastal lagoons (49, 50) indicate that seagrass production is about one-half (50%) of the total net production. Also, the C/N ratio for vegetated sediment in a Virginia coastal lagoon (51) averages about 10:1. If we use the above data and apply them to Quonochontaug Pond, then the 22,800 KgN/year value for benthic production in Quonochontaug Pond (using the Potter Pond benthic production number as a surrogate) becomes 7,600 KgN/year for the eelgrass assimilation rate in Quonochontaug Pond. Finally, ammonium uptake for the growth of eelgrass (52) has been measured to be 236 umol N/m^2/year. Using this number for Quonochontaug Pond’s eelgrass beds, the nitrogen requirement for the growth of this eelgrass is calculated to be 8,700 KgN/year. When this is combined with nitrogen fixation for the eelgrass, the total nitrogen production of eelgrass beds in Quonochontaug Pond is estimated to be about 9,400 KgN/year. This compares favorably with the estimate using the adjusted benthic net production number for Potter Pond. The above data indicate that nitrogen fixation represents 7% of the nitrogen needed for eelgrass growth in Quonochontaug Pond (680 KgN/yr N_2 fixation divided by 9,400 KgN/yr total N production). In a study of sources and fates of nitrogen in Virginia coastal bays, Anderson et al. (53) determined that nitrogen fixation represented 10% of all nitrogen sources.

**Nitrogen Cycling in Quonochontaug Pond**

Figure 12 is a diagram of conceptual models of N cycling in the water column and surficial benthic sediment column of Quonochontaug Pond. Figure 12A represents that portion of the Pond that is not inhabited by eelgrass and generally has water depths greater than 2.5 meters. Figure 12B represents that portion of the Pond that is inhabited by eelgrass (*Zostera marina*) and has water depths ≤2.0 meters. Non-eelgrass, deeper waters and their sediments represent 67% of the fine-grained surface area of Quonochontaug Pond and eelgrass habitats, shallow waters and their fine-grained sediments, represent 33% (2).

Probably the most important process in all waters of Quonochontaug Pond is the assimilation of NO_3^- and NH_4^+ by phytoplankton. In the Pond, this fixed nitrogen is recycled by remineralization of organic matter (PON in Figure 12A) to NH_4^+. 
(ammonification) and by excretion of zooplankton. Nitrification of NH$_4^+$ to NO$_3^-$ appears to be an insignificant process due to the very low NO$_3^-$ concentrations in the water column (Table 6). Apparently, NO$_3^-$ is the preferred form of inorganic nitrogen for phytoplankton growth in Quonochontaug Pond as summertime (May to September) NO$_3^-$ concentrations are very low (Figure 3) while surface-water NH$_4^+$ concentrations during the same period vary from low (June to August) to high (September and October) concentrations (Figure 4). There is a significant difference between the surface-water and bottom-water daily standing stock of ammonium in Quonochontaug Pond (57 Kg) which is, at least, partially related to ammonium regeneration by bacterial decomposition and zooplankton excretion. This process might be known as ammonification (mineralization) under oxic and near hypoxic conditions.

Under hypoxic conditions, the mineralization of organic matter is more intense. In shallow-water coastal marine systems, such as coastal lagoons, benthic sediments have a large effect on water-column nitrogen dynamics (54). Table 7 and Figure 7 confirm that there is a cause and effect relationship between bottom-water dissolved-oxygen deficit (oxygen consumption) and the enrichment of ammonium (ammonification of sinking and/or sedimented organic matter; equation 1). Bottom-water ammonium enrichment is greatest at the Judge’s Rock station, with a sampling-year average of 52 uG/L and values as high as 80 and 90 uG/L for some summer months. In many coastal lagoons and shallow coastal marine waters, high bottom-water ammonium enrichments (≥40 uG/L) occur where benthic sediments release ammonium to the water column (32, 34).

The difference in the daily standing stock of NH$_4^+$ between the upper meter and the lower meter of the water column in Quonochontaug Pond is 57 Kg N. Utilizing the ammonium benthic flux value for Potter Pond (35) and applying it to Quonochontaug Pond, an ammonium benthic flux of 67 Kg NH$_4^+$-N/day is obtained. When near-hypoxic dissolved oxygen (DO) concentrations (≤5.0 mG/L) in Quonochontaug Pond are applied to a bottom-water DO-benthic ammonium release relationship for surface sediments in the Gulf of Gdansk (southern Baltic Sea) (34), a benthic ammonium release rate of 75 Kg NH$_4^+$-N/day is obtained. For bottom-water DO concentrations of 3.0 mG/L (hypoxic conditions), the release rate is 108 Kg NH$_4^+$-N/day. These release rates are a little higher than those mentioned above for Quonochontaug Pond but tube-dwelling organisms dominate fine-grained benthic sediment in the Pond (37) and may provide an oxic reservoir within the sediment that slows down the decomposition of organic matter (36).

Nitrate concentrations in the water column of Quonochontaug Pond are very low during the sampling period from June to September. Thus, the rates of denitrification would appear to be at a minimum and the assimilation of nitrate by phytoplankton is the process that keeps nitrate concentrations low during this period.

However, for the period of late Fall, Winter, and Spring, nitrate concentrations are significantly higher than in the Summer. For the period November 1999 to February 2000, nitrate in surface waters of Quonochontaug Pond averaged 26±11 uG/L (see Figure 3 and reference 1). In early May 2010, NO$_3^-$ concentrations in surface and bottom waters at five deep-water stations in the Pond averaged 38±6 uG/L. At the same time (May
2010), NH$_4^+$ concentrations averaged 110±17 uG/L and bottom-water temperatures averaged 14.8±1.8 degrees C. If there is anytime when the process of dissimilatory nitrate reduction to ammonium (DNRA) is operative in Quonochontaug Pond, May 2010 seems to be a likely time. The average water temperature is approximately 14 degrees C, both NO$_3^-$ and NH$_4^+$ concentrations are high due to low numbers of phytoplankton (chlorophyll-a concentration 1.6±0.5 ppb), and while dissolved oxygen in both surface and bottom waters is near 100% saturation, anaerobic microsites or “hotspots” can exist in marginally oxic sediments (20). While only 40 uG/l NH$_4^+$ can be produced by DNRA at this time, the remainder of NH$_4^+$ in the water column is produced by benthic flux and aerobic mineralization of organic matter (PON and DON). In any case, DNRA produces only about 6% of the daily standing stock of NH$_4^+$ at this time (May 2010).

The foregoing discussion about nitrogen cycling in Quonochontaug Pond pertains to non-eelgrass, fine-grained sediment with an associated water column that exceeds 2.0 meters in depth. While eelgrass-habited sediment represents 33% of the benthic sediment surface area of Quonochontaug Pond, only one station resides wholly within this area. The water depth at the Harmonic Cove Buoy (HCBuoy) station is approximately 2 meters, the secchi-disk transparency often extends to the benthic sediment surface, and dissolved-oxygen concentrations in bottom water can exceed 100% saturation even at 7am. All these factors are requisite for the growth of eelgrass, *Zostera marina*. This vegetated site has a decidedly lower average bottom-water NH$_4^+$ concentration (37±22 uG/L) compared to the “bare”, non-vegetated, deep-water stations 54±10 uG/L (Table 6). In fact, bottom-water NH$_4^+$ concentrations at the HCBuoy station are not significantly higher than surface-water NH$_4^+$ concentrations (Table 6). This is due mostly to the fact that in shallow coastal bays, eelgrass beds and their associated sediment is a nitrogen sink and that pore water NH$_4^+$ nourishes their growth (26, 27, 28). Thus the benthic flux of NH$_4^+$ is minimal (Figure 12) and the shallow-water depth at this station (HCBuoy) results in similar concentrations of NH$_4^+$ in both surface and bottom water due to wind mixing. Also, the vegetated eelgrass site (HCBuoy) contains more than twice the concentration increase of PON in bottom water relative to surface water compared to the other four “bare” deep-water sites (Table 6). Thus, eelgrass traps sinking particulate organic matter that can nourish plant growth upon decomposition (mineralization).

Finally, table 8 lists some nitrogen fixation rates for pelagic waters, uncolonised marine sediment, and vegetated marine sediment in estuarine and shallow coastal marine systems. Pelagic waters appear to have a very low N$_2$ fixation rate while vegetated sediments have a relatively high rate. Nitrogen, essential for plant growth, is generally found in short supply, especially in seagrass meadows (43). This condition potentially favors the establishment of N$_2$-fixing microorganisms (44). Organic matter availability stimulates N$_2$ fixation suggesting that this process is an anaerobic one as nitrogenase, the enzyme complex mediating N$_2$ fixation, is inactivated by exposure to molecular oxygen (45). However, N$_2$ fixation can occur in aerobic environments due to the presence of O$_2$-poor microzones or “hotspots” (20). Such is the case for eelgrass-vegetated surface sediments in Quonochontaug Pond where bottom waters and possibly surficial benthic sediments always have some dissolved oxygen.
Using the adjusted benthic metabolism data from Potter Pond (48) and the surface area of Quonochontaug Pond inhabited by eelgrass (2), the eelgrass-assimilation rate by N\textsubscript{2} fixation for the Pond is calculated to be 680 Kg N/year. Since NH\textsubscript{4}\textsuperscript{+} is the major source of inorganic nitrogen that nourishes eelgrass growth (9,400 Kg N/year), N\textsubscript{2} fixation represents 7% of the nitrogen needed for eelgrass growth in Quonochontaug Pond.

**Nitrogen Mass Balance for Quonochontaug Pond**

i. **Dissolved Inorganic Nitrogen (DIN).**

Figure 13 is a schematic representation of a dissolved inorganic nitrogen balance for Quonochontaug Pond using water column and stream NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} data from the SPC database (14). The water column was broken up into 1 meter segments as described in Guarinello’s MS Thesis (2). The average NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} concentrations for surface-water samples taken in the sampling years 2008 to 2011 (14) were multiplied by the 1-meter volume of Quonochontaug Pond. The average deep-water concentrations of NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} from bottom-water samples were multiplied by the combination of 1-2, 2-3, 3-4, and 4-5 meter volumes of the Pond. This was done primarily because NH\textsubscript{4}\textsuperscript{+} concentrations were significantly higher in bottom waters than surface waters (14).

The Stream In DIN (NO\textsubscript{3}\textsuperscript{-} + NH\textsubscript{4}\textsuperscript{+}) annual mass was calculated using the average NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} concentrations at two stations entering the north shore of Quonochontaug Pond. These perennial streams (brooks) are Harmonic Cove Brook and Ninigret Cove Brook (14). Water volume streamflow data were taken from Masterson et al. (55).

The Breachway Out DIN annual mass for net flow from Quonochontaug Pond to Block Island Sound was calculated using the flow data from Guarinello’s MS Thesis and the NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} data from the SPC database (14) and Block Island Sound analyses.

The Atmosphere In DIN annual mass was calculated using the deposition of atmospheric nitrogen analyses reported by Nadim et al. (56) for the Avery Point site in nearby Connecticut. This was the nearest atmospheric monitoring site where reliable wet, dry, and bulk deposition data for NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} were available. The deposition data, expressed in Kg/ha/week, were multiplied by the surface area of Quonochontaug Pond (300 ha) and 52 weeks/year to get the annual mass of atmospheric NO\textsubscript{3}\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} falling onto the Pond.

The Groundwater In DIN annual mass was calculated using simulated groundwater flow data from the U.S. Geological Survey (55). Most of this groundwater flow contains NO\textsubscript{3}\textsuperscript{-} as NH\textsubscript{4}\textsuperscript{+} is adsorbed onto soil particles. The flow data were combined with NO\textsubscript{3}\textsuperscript{-} data from reference 3 (2.1 mG/L), reference 57 (3.06 mG/L), and reference 58 (5.74 mG/L) to calculate an average annual groundwater DIN mass input to Quonochontaug Pond.

Finally, an estimation of the sedimentation flux (accumulation) of nitrogen to surficial benthic sediment was made. Nitrate and ammonium are assimilated by phytoplankton in the photic zone (upper 2 meters of the water column) of Quonochontaug Pond. These phytoplankton either die or are consumed by zooplankton and the resultant detritus (suspended particulate matter) sinks to the bottom of the Pond and becomes incorporated
into surficial benthic sediment. Lagoon bottom, low energy, fine-grained sediment covers about 12.9 x 10^5 m² of the total bottom area (30 x 10^5 m²) of Quonochontaug Pond. The sedimentation rate for these fine-grained sediments is 0.125 gm/cm²/year (25). The average percent organic carbon in the Pond’s fine-grained surface sediments is 5.9 wt.% (2, 25) and the C/N ratio is 9.3 (25). Combining all these data produces an annual nitrogen sedimentation (accumulation) rate of 11,300 Kg/year. This is surprisingly close to the particulate nitrogen burial rate for a variety of estuaries listed in Boynton and Kemp (59) when their average rate (8.1 gm N/m²/yr) is applied to Quonochontaug Pond (10,125 Kg N/yr).

Thus, the Dissolved Inorganic Nitrogen (DIN) Mass Balance for Quonochontaug Pond is:

Mass DIN in Water Column + Export Out of DIN to Block Island Sound + Nitrogen Accumulation in Benthic Sediment = Stream DIN In + Atmosphere DIN IN + Groundwater DIN In (Figure 13).

When yearly mass numbers are attached to these terms (Figure 13), the mathematical balance becomes: Outputs 17,650 Kg N = Inputs 17,097 Kg. Surprisingly, the inputs nearly equal the outputs. The Stream and Atmospheric inputs are probably well-documented values. On the other hand, the sedimentation (accumulation) mass output and the groundwater mass input are best estimates from somewhat incomplete data. This is especially true for the groundwater mass input term because there are few (if any) groundwater NO₃⁻ numbers for shallow-water coarse-grained Rhode Island Salt Pond sediments. As for the sedimentation (accumulation) term, there were three sedimentation rates for Quonochontaug Pond sediments (25) and the C/N ratio (9.3) is based upon a few analyses (25).

**ii. Total Nitrogen (TN).**

Considering the fact that phytoplankton assimilate NO₃⁻ and NH₄⁺ for growth, then die and sometimes are consumed by zooplankton, particulate organic nitrogen (PON) and suspended particulate matter (SPM) should be included in the nitrogen mass balance for Quonochontaug Pond. Thus, total nitrogen concentrations were used to calculate Stream In. It is not known what fraction of this total nitrogen concentration is represented by PON and SPM. The Atmosphere In mass was corrected for input of organic nitrogen (56). And, Breachway Out was updated using total nitrogen data from the two stations in the eastern basin of Quonochontaug Pond. The Sedimentation Out term remained the same as for the DIN mass balance. The Groundwater In term was modified to include dissolved organic nitrogen (DON) using data from references 57 and 58.

The new values for NO₃⁻ + NH₄⁺ + PON mass in the water column of Quonochontaug Pond were calculated as follows. For the upper 1 meter of the water column, the DIN mass of 155 Kg (Figure 13) was subtracted from the TN mass of 1,059 Kg (Figure 14) and the difference was multiplied by 0.55 (15). Thus the mass of DIN + PON for the upper meter of the water column is 652 Kg (Figure 14). A similar calculation was made for the 2-5 meter volume of the water column and the resultant mass is 1,017 Kg (Figure 14). Using these masses for water column DIN + PON, the nitrogen mass balance for Quonochontaug Pond would be: Outputs 13,159 Kg ≈ Inputs 14,612
Finally, if we consider that total nitrogen encompasses the major nitrogen processes in the water column of Quonochontaug Pond (nutrient assimilation, mineralization, and formation of organic detritus), then the following mass balance results (Figure 14).

\[
\text{Water-Column Mass (2,707 Kg) + Export to Block Island Sound (7,300 Kg/yr) + Sedimentation (11,300 Kg/yr) = Stream In (3,234 Kg/yr) + Atmosphere In (3,510 Kg/yr) + Groundwater In (14,410 Kg/yr). Outputs 21,307 Kg = Inputs 21,154 Kg.}
\]

**Phosphorus Mass Balance for Quonochontaug Pond**

*No. Dissolved Inorganic Phosphorus (DIP).*

While the present state of knowledge concerning nutrient fertilization of coastal lagoons and shallow coastal marine waters clearly indicates that nitrogen is the most important limiting nutrient and at high concentrations causes eutrophication of these brackish and marine systems, mesocosm studies simulating Rhode Island coastal salt pond ecosystems (16) suggests that phosphorus can add to the above effect. Therefore, the author believes that it would be instructive to formulate a phosphorus mass balance for Quonochontaug Pond. The annual mass balance of dissolved inorganic phosphorus (DIP) is presented in Figure 15.

As for nitrogen, the DIP standing stock mass in the water column of Quonochontaug Pond is constructed using average surface- and bottom-water DIP concentrations for Quonochontaug Pond for the sampling years 2008-2011 (14) and multiplying these concentrations by the representative volumes of water for the upper 1 meter and the lower 2-5 meters of the water column. The Stream In DIP mass was calculated with the average brook concentration and the freshwater inflow data from the U. S. Geological Survey (55). The Atmosphere In annual DIP mass was calculated using near-coastal atmospheric deposition data (4,655 uG DIP/m²/yr) of Izquierdo et al. (60) and multiplying this value by the surface area of Quonochontaug Pond (30 x 10⁵ m²). Export of DIP through the Quonochontaug Pond breachway to Block Island Sound (0 Kg/yr) was calculated by subtracting the DIP concentration of Block Island Sound waters (16 uG/L; URI Watershed Watch and The Long Island Sound Study) from the average concentration of DIP at the North Bill’s Island station (16 uG/L; SPC Database).

The Groundwater In annual mass of DIP for Quonochontaug Pond (510 Kg/yr) was calculated using the average DIP flux for Point Judith-Potter-Green Hill-Ninigret Ponds (164 mg DIP/m²/yr) (61) and the surface area of Quonochontaug Pond (30 x 10⁵ m²). These groundwater DIP flux data of Kelly and Moran (61) were the best estimates and the most likely to be applied to Quonochontaug Pond as they were measured in four salt ponds northeast of Quonochontaug Pond. In addition, average shallow groundwater phosphorus data from several Cape Cod sites (75, 76) was combined with the above to give a best estimate of the Groundwater In term. The Accumulation (Sedimentation) of phosphorus in benthic sediment of Quonochontaug Pond (914 Kg/yr) was calculated by two different methods. First, mass sedimentation rates of Ford (25) and Garber (77) were multiplied by the average total phosphorus content of coastal lagoon bottom sediments (78, 79, 80). Secondly, the average N:P ratio of coastal lagoon and shallow marine bottom sediments (14:1) was divided into the nitrogen sedimentation rate (Figures 13 and 14- 11,300 Kg/yr) This average N/P ratio was determined from references 62, 63, 79, 81,
The results from these two methods were averaged to produce the Sedimentation Out term (914 Kg/Yr).

Using all of the above data for DIP input and output mass terms for Quonochontaug Pond, the DIP mass balance is given below (Figure 15):

\[
\text{Water-Column Mass (108 Kg) + Export to Block Island Sound (0 Kg/yr) + P Accumulation in Benthic Sediment (914 Kg/yr) = Stream In (22 Kg/yr) + Atmosphere In (14 Kg/yr) + Groundwater In (510 Kg/yr). Outputs 1,022 Kg = Inputs 546. Kg.}
\]

This mass balance for dissolved inorganic phosphorus (DIP) is not nearly as good as that for the DIN mass balance (Figure 13). The greatest uncertainties involved in the DIP mass balance calculations are the groundwater input of dissolved phosphorus and the phosphorus accumulation in fine-grained benthic sediment of Quonochontaug Pond.

\[\text{ii. Total Phosphorus (TP).}\]

Like the nitrogen mass balance, it is thought that total phosphorus might represent a more complete picture of phosphorus cycling in Quonochontaug Pond. The calculation for TP in all input and output terms except Groundwater In is relatively straightforward. The atmospheric TP flux is taken from reference 60; Stream In, Breachway Out, and Water-Column mass terms are computed with TP data from the SPC database (14) and the URI Watershed Watch database for the total phosphorus concentration in Block Island Sound. The Sedimentation term is the same as calculated for the DIP mass balance. The groundwater In term was modified to include dissolved organic phosphorus (DOP). This was calculated by multiplying the DIP groundwater flux by 1.4 based on the study of Taniguchi et al. (64). The resultant mass balance for Total Phosphorus is:

\[
\text{Outputs 4,457 Kg = Inputs 908 Kg. Obviously there is a tremendous imbalance for the total phosphorus mass balance. The main culprit in this imbalance is the Breachway Out term. As noted above, there are precious little data for phosphorus in the waters of Block Island Sound that lay off Quonochontaug Pond.}\]

As is the case for both nitrogen mass balances, the phosphorus mass balances are strongly dependent upon the mass accumulation (Sedimentation) in benthic sediment (Output) and the Groundwater In term (Input). The water-column masses of nitrogen and phosphorus are well constrained due to abundant analyses at five deep-water stations for the sampling years 2008-2011. For nitrogen, the Atmosphere In term is somewhat greater than the Stream In term, but both of these terms are significantly smaller than the Groundwater In term. For phosphorus, the Stream In term is slightly greater than the Atmosphere In term, but both of these are much smaller than the Groundwater In term. However, while the water-column masses of dissolved and total phosphorus at the station in the eastern basin of Quonochontaug Pond next to the breachway (NBI) are well constrained, the concentrations of these two forms of phosphorus in Block Island Sound are relatively obscure.
Nitrogen:Phosphorus Stoichiometry and the Focus of Nutrient Regeneration in Quonochontaug Pond

\textit{i. Introduction.}

Stoichiometry is defined by the Random House College Dictionary as “the calculation of the quantities of chemical elements or compounds involved in chemical reactions”. In freshwater and marine ecology, N:P stoichiometry is utilized to determine whether nitrogen or phosphorus is the limiting nutrient for primary production (67). In classic freshwater and marine ecology, phytoplankton stoichiometry has been utilized to assess nutrient limitation at the interface between abiotic (external inputs) and biotic (internal recycling) compartments of aquatic ecosystems (68). The chemical composition of marine seston (suspended particulate organic matter) is known to be relatively constant at a C:N:P molar ratio of 106:16:1 (69). This biogeochemical ratio has become widely known as the “Redfield ratio”. Redfield proposed that the nitrate:phosphate ratio of 16:1 in the ocean was controlled by the requirements of phytoplankton, which subsequently release nitrogen and phosphorus to the aquatic environment at this ratio as they were remineralized (70).

The biological pump of phytoplankton nutrients (C, N, P) is the sum of a series of biological and physical processes that transport carbon from surface waters to the deeper ocean waters (71). This mechanism is most important to the cycling of nutrients in the global ocean and is largely mediated by phytoplankton production in the photic zone, sinking of particulate matter (seston), and remineralization at depth and upward transport by eddy diffusion back into the photic zone. In coastal and shallow marine environments, controls on C:N:P stoichiometry are more complex as the sources and sinks of nutrients and the ecosystem community structure are more varied and dynamic (71).

The classic work of Alfred Redfield (69) provided marine scientists with a unified concept of nutrient stoichiometry which reflects continuous recycling of N and P between particulate organic matter and the dissolved inorganic nutrient pool in marine waters. This Redfield ratio has provided aquatic scientists with an important tool to understand nutrient dynamics and biogeochemical processes.

\textit{ii. Ammonium (and Phosphate) Study of Quonochontaug Pond.}

In the summer of 2010 (June to September), the author and a URI Coastal Fellow (Casey Tremper) conducted a weekly sampling of two deep-water stations in Quonochontaug Pond with the purpose of trying to understand the cycling of nitrogen and phosphorus in the water column. Two stations were sampled once per week from 6/11 to 9/21/2010; the Judge’s Rock (JR) station located in the far western basin and the East Basin Yacht Club (EBYC) station located in the far eastern basin of Quonochontaug Pond (see Figure 1).

Each weekly sampling date included surface- and bottom-water samples for temperature, dissolved oxygen, chlorophyll-a, and nutrients (NO$_3^-$, NH$_4^+$, Total N, PO$_4^{3-}$, and Total P). Water samples were fixed for dissolved oxygen on site and then analyzed by the Winkler titration later in the day. Chlorophyll-a analyses were conducted on filtered water samples by fluorometric analysis, and all nutrient analyses were analyzed by automated colorimetric analysis (autoanalyzer) under the direction of Linda Green of the URI.
Watershed Watch Program (URIWW). It is important to note that bottom-water samples for chlorophyll and nutrient analyses were collected using a special horizontally-oriented water sampler that was able to collect water just a few centimeters above the water-sediment interface.

The dissolved oxygen, chlorophyll-a, and nutrient data obtained in this study has been analyzed two different ways; A.- a comparison of surface- and bottom-water concentrations for several time intervals throughout the sampling period, and B.- bottom-water increases of NH$_4^+$ and PO$_4^{3-}$ for several time intervals throughout the sampling period.

A. Tables 9 and 10 present the physical/water quality and nutrient data for the JR and EBYC stations.


<table>
<thead>
<tr>
<th>Station</th>
<th>Days</th>
<th>Temp(s)</th>
<th>Temp(b)</th>
<th>DO(s)</th>
<th>DO(b)</th>
<th>ΔDOsat</th>
<th>Chl(s)</th>
<th>Chl(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JR</td>
<td>6/11-6/25</td>
<td>19.9</td>
<td>19.0</td>
<td>7.6</td>
<td>6.0</td>
<td>47%</td>
<td>4.4</td>
<td>10.0</td>
</tr>
<tr>
<td>JR</td>
<td>7/10-8/06</td>
<td>24.9</td>
<td>23.3</td>
<td>6.1</td>
<td>5.1</td>
<td>44%</td>
<td>6.3</td>
<td>9.9</td>
</tr>
<tr>
<td>JR</td>
<td>8/06-8/26</td>
<td>23.5</td>
<td>22.9</td>
<td>6.6</td>
<td>6.2</td>
<td>41%</td>
<td>5.5</td>
<td>8.6</td>
</tr>
<tr>
<td>EBYC</td>
<td>6/11-7/02</td>
<td>19.5</td>
<td>18.1</td>
<td>6.9</td>
<td>6.4</td>
<td>9%</td>
<td>4.6</td>
<td>5.8</td>
</tr>
<tr>
<td>EBYC</td>
<td>7/09-7/23</td>
<td>24.0</td>
<td>22.7</td>
<td>6.8</td>
<td>6.5</td>
<td>32%</td>
<td>5.1</td>
<td>7.8</td>
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<tr>
<td>EBYC</td>
<td>7/30-8/16</td>
<td>23.4</td>
<td>21.8</td>
<td>6.3</td>
<td>5.7</td>
<td>18%</td>
<td>4.4</td>
<td>7.2</td>
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<tr>
<td>EBYC</td>
<td>8/24-9/11</td>
<td>22.2</td>
<td>21.6</td>
<td>6.9</td>
<td>5.4</td>
<td>48%</td>
<td>4.6</td>
<td>7.7</td>
</tr>
</tbody>
</table>

JR = Judge’s Rock; EBYC = East Basin Yacht Club
(s) = surface water; (b) = bottom water
Temp. = Temperature in degrees C
DO = Dissolved Oxygen in mG/L
ΔDOsat. = % Dissolved Oxygen Saturation, surface water-bottom water
Chl = Chlorophyll-a in parts per billion (ppb)


<table>
<thead>
<tr>
<th>Station</th>
<th>Days</th>
<th>NH$_4^+(s)$</th>
<th>NH$_4^+(b)$</th>
<th>PO$_4^{3-}(s)$</th>
<th>PO$_4^{3-}(b)$</th>
<th>DIN/DIP(s)</th>
<th>DIN/DIP(b)</th>
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</thead>
<tbody>
<tr>
<td>JR</td>
<td>6/11-6/25</td>
<td>1.8</td>
<td>2.2</td>
<td>0.19</td>
<td>0.25</td>
<td>11:1</td>
<td>10:1</td>
</tr>
<tr>
<td>JR</td>
<td>7/10-8/06</td>
<td>1.3</td>
<td>2.3</td>
<td>0.20</td>
<td>0.34</td>
<td>7:1</td>
<td>7:1</td>
</tr>
<tr>
<td>JR</td>
<td>8/06-8/26</td>
<td>1.8</td>
<td>2.6</td>
<td>0.16</td>
<td>0.18</td>
<td>12:1</td>
<td>15:1</td>
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</table>
EBYC 6/11- 7/02  1.43  1.89  0.17  0.18  10:1  12:1
EBYC 7/09- 7/23  1.8  2.13  0.19  0.25  10:1  9:1
EBYC 7/30- 8/16  0.96  1.22  0.21  0.26  5:1  5:1
EBYC 8/24- 9/11  3.04  3.46  0.19  0.24  17:1  15:1

JR = Judge’s Rock; EBYC = East Basin Yacht Club
(s) = surface water; (b) = bottom water
Concentrations of NH₄⁺ and PO₄³⁻ are in micromoles per liter (µMol/L)
DIN/DIP surface and bottom are molar ratios
Table 10 Continued.

<table>
<thead>
<tr>
<th>Station</th>
<th>Days</th>
<th>TN(s)</th>
<th>TN(b)</th>
<th>TP(s)</th>
<th>TP(b)</th>
<th>TN/TP(s)</th>
<th>TN/TP(b)</th>
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<tr>
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<td>6/11-6/25</td>
<td>22.1</td>
<td>41.7</td>
<td>1.02</td>
<td>2.46</td>
<td>22:1</td>
<td>17:1</td>
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<td>7/10-8/06</td>
<td>25.2</td>
<td>33.4</td>
<td>1.70</td>
<td>2.57</td>
<td>15:1</td>
<td>13:1</td>
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<tr>
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<td>8/06-8/26</td>
<td>22.8</td>
<td>29.5</td>
<td>1.5</td>
<td>1.8</td>
<td>15:1</td>
<td>16:1</td>
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<tr>
<td>EBYC</td>
<td>6/11-7/02</td>
<td>22.5</td>
<td>24.1</td>
<td>0.98</td>
<td>1.3</td>
<td>23:1</td>
<td>18:1</td>
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<tr>
<td>EBYC</td>
<td>7/09-7/23</td>
<td>24.6</td>
<td>32.4</td>
<td>1.5</td>
<td>1.88</td>
<td>16:1</td>
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<td>EBYC</td>
<td>7/30-8/16</td>
<td>21.6</td>
<td>30.6</td>
<td>1.4</td>
<td>2.3</td>
<td>15:1</td>
<td>13:1</td>
</tr>
<tr>
<td>EBYC</td>
<td>8/24-9/11</td>
<td>22.1</td>
<td>31.5</td>
<td>1.29</td>
<td>2.26</td>
<td>17:1</td>
<td>14:1</td>
</tr>
</tbody>
</table>

Concentrations of TN and TP are in micromoles per liter (µMol/L)
TN/TP surface and bottom are molar ratios

Analysis of the JR water quality and nutrient data yields the following observations:
- July to early August 2010 had the most intense water temperature stratification,
  ∆T(surface water – bottom water) = 1.6 degrees C.
- June 2010 had the most intense DO deficit (surface water-bottom water), 1.7 mG/L;
  July 2010 is next with a DO deficit of 1.0 mG/L.
- Bottom-water chlorophyll-a concentrations were significantly higher than surface-water
  concentrations, 9.5±0.8 ppb versus 5.4±0.9 ppb.
- Nitrate concentrations were low and statistically similar in surface and bottom water;
  surface water = 12±4 uG/L and bottom water = 11±2.5 uG/L.
- Ammonium concentrations in surface water average 30±5 uG/L and bottom-water concentra-
  tions average 42±4 uG/L. The 7/10-8/26 sampling period had the greatest
  bottom water increase relative to surface water, 16 uG/L.
- Phosphate (dissolved inorganic phosphorus (DIP)) concentrations in surface water
  average 17±2 uG/L and bottom-water concentrations average 24±7 uG/L. The 7/10-
  8/06 sampling period had the greatest bottom water-surface water concentration increase
(13 uG/L) while the 6/11-6/25 and the 8/06-8/26 sampling periods had the lowest bottom water-surface water concentration increase (4 uG/L). These two sampling intervals had relatively high DO concentrations (6.6±0.4 and 6.7±0.3 mG/L) while the 7/10-8/06 sampling period had an average DO concentration of 4.8±0.2 mG/L.

- The DIN/DIP molar ratio for the 6/11-6/25 and 8/06-8/26 sampling periods average 11.5:1 for surface water and 12.5:1 for bottom water (Table 10). The 7/10-8/06 sampling period had a low ratio in both surface and bottom water, 7:1. During this time surface water DIN was lower than in the other sampling periods. This was also a time of higher chlorophyll-a concentration in surface and bottom water (Table 9) and lower dissolved oxygen in bottom water (see above). These two facts suggest that phytoplankton productivity consumed more DIN (NO₃⁻ and/or NH₄⁺) and that bottom-water near-hypoxia released DIP (PO₄³⁻) from surficial benthic sediment.

- The TN/TP molar ratio at the JR station averaged 17±4:1 for surface water and 15±2:1 for bottom water (Table 10). These ratios are very close to the Redfield ratio (16:1) and suggest that phytoplankton debris is the primary source of organic matter for the remineralization of nitrogen and phosphorus. This process can occur either in bottom waters or in surficial benthic sediment. Also, these TN/TP molar ratios indicate that nitrogen is the limiting nutrient for phytoplankton growth (73).

Analysis of the EBYC station water quality and nutrient data yields the following observations:

- June to the middle of August 2010, the temperature difference between surface and bottom water was 1.4±0.15 degrees C.
- There was little DO deficit for the period June to the middle of August 2010, 0.5±0.2 mG/L. For the period 8/24-9/11, the DO deficit was 1.5±1.8 mG/L.
- There was significantly more chlorophyll-a in bottom water than in surface water, 7.1±0.9 ppb versus 4.6±0.3 ppb.
- The average concentration of nitrate was low and statistically similar in both surface water (11±1 uG/L) and bottom water(11±2 uG/L).
- Ammonium concentrations in surface water averaged 33±16 uG/L and in bottom water they averaged 39±17 uG/L. Thus, the average bottom-water increase in ammonium relative to surface water was small, only 6 uG/L.
- Phosphate (DIP) concentrations in surface water averaged 18±2 uG/L and bottom water concentrations averaged 22±3 uG/L. Like the ammonium data, the bottom-water increase in phosphate relative to surface water was small, only 4 uG/L.
- The DIN/DIP molar ratios for the time intervals 6/11-7/23 are 10:1 for surface water and 11:1 for bottom water. Both ratios are somewhat lower than the Redfield ratio (16:1). The 7/30-8/16 sampling period had much lower ratios (5:1) in both surface and bottom water. The data in Table 10 shows that the ammonium (the major part of DIN) was significantly lower in concentration than in other sampling periods but that phosphate (DIP) concentration was about the same. This may be a time when phytoplankton utilization of NH₄⁺ occurred. For the 8/24-9/11 sampling period, the DIN/DIP molar ratio was 16:1 (Redfield ratio), suggesting that phytoplankton debris was the source of organic matter being remineralized.
- The TN/TP molar ratio at the EBYC station averaged 18±3:1 for surface water and 16±2:1 for bottom water (Table 10). Like the JR station, TN/TP molar ratios are not
significantly different from the Redfield ratio, suggesting that phytoplankton debris is the primary source of organic matter for the mineralization of nitrogen and phosphorus. And, like the JR station, TN/TP molar ratios indicate that nitrogen is the limiting nutrient for phytoplankton growth (73).

In summary, the 7/10-8/06 sampling period at the JR station had a significantly lower DIN/DIP molar ratio than the Redfield ratio suggesting that phytoplankton productivity consumed DIN in surface water and that benthic flux of phosphate (DIP) augmented the bottom-water concentration of dissolved phosphorus. For the EBYC station, the 7/30-8/16 sampling period had a very low DIN/DIP molar ratio (5:1) in both surface and bottom water. Ammonium concentrations were significantly lower than those in other sampling periods at this station but dissolved phosphate concentrations were about the same. Thus, phytoplankton utilization of ammonium may be an important biogeochemical process at this time.

B. Table 11 presents nitrate, ammonium, phosphate, total nitrogen and total phosphorus data for bottom water minus surface water concentrations for several 2010 sampling periods at the JR and EBYC stations in Quonochontaug Pond.

Table 11. Bottom Water Minus Surface Water Concentrations (Δ) of NO₃⁻, NH₄⁺, PO₄³⁻, TN, and TP for Various Sampling Periods during the Summer of 2010 (June to September) for the JR and EBYC Stations in Quonochontaug Pond.

<table>
<thead>
<tr>
<th>Station</th>
<th>Days</th>
<th>ΔNO₃⁻</th>
<th>ΔNH₄⁺</th>
<th>ΔPO₄³⁻</th>
<th>DIN/DIP</th>
<th>ΔTN</th>
<th>ΔTP</th>
<th>TN/TP</th>
</tr>
</thead>
<tbody>
<tr>
<td>JR</td>
<td>6/11-6/25</td>
<td>0.02</td>
<td>1.11</td>
<td>0.095</td>
<td>12:1</td>
<td>16.4</td>
<td>1.29</td>
<td>13:1</td>
</tr>
<tr>
<td>JR</td>
<td>7/09-7/23</td>
<td>0.0</td>
<td>0.89</td>
<td>0.168</td>
<td>5:1</td>
<td>10.1</td>
<td>0.87</td>
<td>12:1</td>
</tr>
<tr>
<td>JR</td>
<td>7/23-8/08</td>
<td>-0.05</td>
<td>1.11</td>
<td>0.147</td>
<td>8:1</td>
<td>10.1</td>
<td>0.87</td>
<td>12:1</td>
</tr>
<tr>
<td>JR</td>
<td>8/08-8/26</td>
<td>0.03</td>
<td>0.78</td>
<td>0.028</td>
<td>29:1</td>
<td>8.3</td>
<td>0.50</td>
<td>17:1</td>
</tr>
<tr>
<td>JR</td>
<td>8/27-9/02</td>
<td>-0.05</td>
<td>0.59</td>
<td>0.030</td>
<td>18:1</td>
<td>6.0</td>
<td>0.38</td>
<td>16:1</td>
</tr>
<tr>
<td>EBYC</td>
<td>6/11-7/09</td>
<td>-0.04</td>
<td>0.50</td>
<td>0.030</td>
<td>18:1</td>
<td>6.0</td>
<td>0.38</td>
<td>16:1</td>
</tr>
<tr>
<td>EBYC</td>
<td>7/11-8/10</td>
<td>0.03</td>
<td>0.59</td>
<td>0.068</td>
<td>9:1</td>
<td>9.2</td>
<td>0.94</td>
<td>10:1</td>
</tr>
<tr>
<td>EBYC</td>
<td>8/13-9/02</td>
<td>-0.04</td>
<td>0.68</td>
<td>0.078</td>
<td>9:1</td>
<td>9.2</td>
<td>0.94</td>
<td>10:1</td>
</tr>
</tbody>
</table>

JR = Judge’s Rock; EBYC = Easy Basin Yacht Club
All Δ values are in micromoles per liter (μM/L) and represent bottom water-surface water Concentrations
DIN/DIP and TN/TP ratios are molar ratios

The DIN/DIP molar ratios for the sampling period 7/09-8/08 at the JR station (5:1 and 8:1, Table 11) confirm the presence of a similar ratio (7:1) in Table 10 for the sampling
period 7/10-8/06. In both cases the elevated concentration of DIP (PO$_4^{3-}$) in bottom water is the reason for these low N/P ratios. Undoubtedly, benthic flux of phosphate from surficial benthic sediment is the reason for elevated bottom-water phosphate concentrations and low DIN/DIP molar ratios. The high DIN/DIP molar ratio for the sampling interval 8/08-8/26 at the JR station (29:1, Table 11) is also the result of bottom water phosphate concentration. But this time $\Delta$PO$_4^{3-}$ is very small (bottom water and surface water phosphate concentrations are nearly equal). This was a time when surface water and bottom water dissolved oxygen concentrations were equal and relatively high (7.0 mG/L) and benthic surficial sediment may have been oxidized, thus trapping phosphate with iron oxyhydroxides (65).

The DIN/DIP molar ratios for the sampling periods 7/11-8/10 and 8/13-9/02 at the EBYC station (9:1 and 9:1, Table 11) are significantly lower than those for the 6/11-7/09 sampling period. These DIN/DIP molar ratios (9:1) for the above sampling periods (7/11-8/10 and 8/13-9/02) confirm the presence of similar ratios (7±2:1) in Table 10 for the sampling periods 7/09-7/23 and 7/30-8/16. The reason for this is that the PO$_4^{3-}$ concentrations are significantly higher in Table 10 (calculation method A) as compared to $\Delta$PO$_4^{3-}$ values in Table 11 (calculation method B). As stated above for the JR station, the cause of this lower N/P molar ratio is benthic flux of phosphate from surficial benthic sediment. Several times during the 8/01-8/30 sampling period, bottom-water dissolved oxygen concentrations declined to 4 or 5 mG/L. However, the $\Delta$PO$_4^{3-}$ values for the EBYC station are significantly lower than those for the JR station (Table 11) as well as those for $\Delta$NH$_4^+$. It appears that benthic flux of phosphate at the EBYC station is not as important a factor for increasing bottom-water phosphate concentrations as it is at the JR station.

TN/TP molar ratios for both the JR and EBYC stations average 13±2.7:1 and probably are a result of biogeochemical processes acting on phytoplankton debris. This average TN/TP molar ratio (13:1) is less than 20:1, suggesting that nitrogen is the limiting nutrient in Quonochontaug Pond for the 2010 sampling year (73).

In summary, the DIN/DIP molar ratios for the sampling period 7/11-9/02 at the EBYC station (9:1) are significantly lower than the June-early July ratio (18:1) at this station. These lower N/P molar ratios (9:1) correspond to low bottom water dissolved oxygen concentrations; 5 mG/L on 8/06, 5.5 mG/L on 8/27, and 3.3 mG/L on 9/02. During these times, benthic phosphate release from surficial benthic sediment resulted in the enrichment of bottom waters and thus caused the low N/P ratio. In contrast, the 6/11-7/09 sampling period had a relatively high DIN/DIP molar ratio (18:1) and represents a time when bottom water dissolved oxygen averaged 6.5±0.3 mG/L. Such dissolved oxygen levels would keep bottom-water phosphate concentrations lower by maintaining a surficial oxic layer at the sediment-water interface and thus trapping phosphate in the surficial benthic sediment column.

A comparison between DIN/DIP molar ratios in Tables 10 and 11, which represent the summary data for calculation methods A and B, shows that there is general agreement between the two methods. For the JR station, the sampling period of 7/09-8/08 was a
time of low N/P ratios (7:1, Table 10 and 6:1, Table 11) caused by benthic phosphate release into bottom waters. For the EBYC station, the sampling period of 7/09-8/16 was a time of low N/P ratios (7:1, Table 10 and 9:1, Table 11) also caused by benthic phosphate release into bottom waters. As for high DIN/DIP molar ratios (significantly greater than the 16:1 Redfield ratio), the only time period that this occurred was 8/08-8/26 at the JR station (DIN/DIP = 29:1) when bottom-water ammonium concentrations (47±17 uG/L) were somewhat higher than at the other time periods. The average bottom-water phosphate concentration (17±4 uG/L) was lower than that for other sampling periods (31±12 uG/L) at this station. This was a time of high bottom water dissolved oxygen concentration (6.6±0.3 mG/L). A possible explanation is that a benthic flux of ammonium occurred at this time.

As for the TN/TP molar ratios (Tables 10 and 11), there is little departure from the 16:1 Redfield ratio. The average molar ratio for all sampling periods and both depths at both the JR and EBYC stations is 15±3:1, essentially the Redfield ratio. This means that at any time and at both surface and bottom water sampling depths during the 2010 ammonium recycling study of Quonochontaug Pond, nutrient (nitrogen and phosphorus) uptake and mineralization in the water column of the Pond was mediated by phytoplankton growth and subsequent decomposition of phytoplankton debris. As noted above, this average TN/TP molar ratio (15:1) indicates that nitrogen was the limiting nutrient for the Pond in the 2010 sampling year.

Recently released nutrient data for the 2012 sampling season (L. Green, personal communication) was added to the nutrient analyses in the SPC database (14). These data for the sampling years 2007-2012 were subjected to stoichiometric analysis and grouped in the following way. May, surface and bottom water; June to September, surface and bottom water; and October, surface and bottom water. The following are the summary findings of these analyses.

DIN (NO$_3^-$ + NH$_4^+$) averages 64±9 uG/L (3.6±0.5 uM/L) in surface waters and 84±17 uG/L (4.7±1.0 uM/L) in bottom waters. The $\Delta$DIN (bw-sw) (20 uG/L) is due to NH$_4^+$. DIP averages 15±4 uG/L (0.47±0.13 uM/L) in surface waters and 16±2 uG/L (0.52±0.07 uM/L) in bottom waters. The $\Delta$DIP (bw-sw) was very small (1 uG/L).

All DIN/DIP molar ratios are below 10:1 suggesting that nitrogen is the limiting nutrient for these waters (72) in May.

For the growing season (June-September), DIN/DIP molar ratios for surface and bottom waters were identical (5.5:1 and 5.4:1), suggesting that NH$_4^+$ concentrations were controlled by phytoplankton uptake.

October is the only sampling time when bottom water DIP is lower than surface water DIP, suggesting that DIP is “sorbed” onto oxic sediment at the sediment-water interface (see JR core incubation data for October 2012). Total nitrogen (TN) averages 330±45 uG/L (23.6±3.2 uM/L) in surface waters and 460±40 uG/L (32.8±2.9 uM/L) in bottom waters. Total phosphorus (TP) averages 34±10 uG/L (1.13±0.24 uM/L) in surface waters and 38±12 uG/L (1.28±0.24 uM/L) in bottom waters. The $\Delta$TN (bw-sw) (130 uG/L) is
significantly greater than the ΔTP (bw-sw) (4 μG/L). Using the molar concentrations for these delta values, the ΔTN/ΔTP ratio = 61:1, suggesting that phosphorus is the limiting nutrient during October 2012 (73).

The molar TN/TP ratios average 25:1 for all five stations and all sampling times (150) and depths (surface and bottom) except for October surface waters. This ratio (25:1) suggests that there is some phosphorus limitation as well as nitrogen limitation for these waters (73).

**Summary and Conclusions**

1. Quonochontaug Pond is a coastal lagoon, a shallow brackish body of water separated from Block Island Sound by a barrier island.

2. Five deep-water stations (JR, HCBuoy, HCCH, NBI, EBYC; see Figure 1) were sampled from 2007 to 2012. Both surface and bottom waters were collected at the above stations.

3. Water-quality data (temperature, dissolved oxygen, secchi disk depth, and chlorophyll-a) were collected biweekly and nutrient data (NO₃⁻, NH₄⁺, total nitrogen, dissolved inorganic phosphorus, total phosphorus) were collected monthly from the middle of May to the middle of October.

4. Significant dissolved-oxygen depletion in bottom waters (ΔDO≥1.0 mG/L, surface DO-bottom DO) generally occurs in the summer months, July-September.

5. Hypoxic events, where bottom-water dissolved oxygen is less than 4.8 mG/L, occurred many times in the summers of 2007-2012 (Tables 1 and 3).

6. Hypoxia is primarily caused by eutrophication (nitrogen inputs) but its development is aided by water-column stratification (temperature and salinity) and wind stress.

7. Decomposition of phytoplankton debris is the primary cause of bottom-water depletion of dissolved oxygen and the recycling of inorganic nutrients in the water column.

8. On September 15, 1999, bottom-water ammonium concentration was significantly higher than surface water, 35 μG/L versus 5 μG/L. A phytoplankton bloom crashed between September 3 and 15, releasing ammonium by the remineralization of sinking organic matter (phytoplankton debris). Also, at this time, bottom-water dissolved oxygen was depleted by 2.6 mG/L relative to surface water.

9. For the sampling years 2008-2012, average ammonium concentrations in bottom waters are enriched 40% relative to surface waters. There is a significant correlation between this ammonium enrichment and bottom-water dissolved oxygen deficit. The Judge’s Rock station had the greatest NH₄⁺ enrichment (59±25 μG/L) and the greatest DO deficit (1.6±0.8 mG/L). The East Basin Yacht Club station had a significantly lower
NH₄⁺ enrichment (42±24 uG/L) and a significantly lower DO deficit (0.6±0.6 mG/L). The Harmonic Cove Channel station had the lowest NH₄⁺ enrichment (30±5 uG/L) but an intermediate DO deficit (1.2±0.3 mG/L).

10. The difference between bottom-water and surface-water phosphate concentrations (ΔPO₄³⁻) ranged from 0 to 61 uG/L. The largest average ΔPO₄³⁻ concentrations occurred at the JR station (15 uG/L), the HCBuoy station (24 uG/L), the HCChannel station (29 uG/L), and the NBI station (40 uG/L). Only three of the 15 largest ΔPO₄³⁻ concentrations correspond to large ΔNH₄⁺ concentrations.

11. Nitrate and ammonium assimilation by phytoplankton was the primary biogeochemical process that controlled the concentration of nutrients in surface water (photic zone). Ammonification (mineralization of organic matter) was the primary process that controlled the concentration of NH₄⁺ in bottom waters of Quonochontaug Pond. Occasionally, under hypoxic conditions, benthic release of NH₄⁺ from surficial benthic sediment occurred. Under near-hypoxia (DO ≤5.0 mG/L), the ammonium increase in bottom water was 17 uG/L. Under hypoxia (bottom water DO <4.0 mG/L), the ammonium increase in bottom water was 43 uG/L.

12. While phytoplankton uptake of phosphate controlled the concentration of this nutrient in surface water, there were many instances when benthic release of PO₄³⁻ was a factor that affected the concentration of this nutrient in bottom water. This was especially the case when bottom-water dissolved oxygen was below 5 mG/L.

13. Nitrogen dynamics at the HCBuoy site, located in an extensive bed of eelgrass, was different than that at the other four deep-water sites in Quonochontaug Pond. Average ammonium concentration (37±22 uG/L) in bottom waters at this vegetated site was significantly lower than those (54±10 uG/L) in bottom waters from the other four “bare” sites. Eelgrass and its associated sediment is a nitrogen sink and pore-water ammonium nourishes its growth.

14. The HCBuoy station, a vegetated site, has significantly more particulate organic nitrogen (PON) in bottom water than the other four “bare” sites. The eelgrass leaves that rise above the sediment surface trap suspended particulate matter settling through the water column.

15. The difference in daily standing stock of NH₄⁺ between surface and bottom water in Quonochontaug Pond is 57 Kg NH₄⁺ -N. Applying average ammonium benthic flux data for several coastal lagoons and shallow marine systems (30) to Quonochontaug Pond, a value of 59±39 Kg NH₄⁺ -N/day is obtained. Thus, benthic flux of NH₄⁺ may be responsible for some of the increased concentrations of ammonium in the bottom waters of Quonochontaug Pond.

16. Stoichiometric analysis of 2010 weekly nutrient data for two stations (JR and EBYC) in Quonochontaug Pond clearly show two biogeochemical processes that affect the nutrient chemistry of the Pond. Under normal oxic conditions, the distributions of
inorganic nitrogen and phosphorus are controlled by phytoplankton uptake in the photic zone and mineralization (aerobic oxidation of phytoplankton debris) in the lower water column (aphotic zone). When near hypoxia (DO ≤ 5 mG/L) and hypoxia (DO ≤ 4 mG/L) occur, some benthic release of ammonium to bottom water occurs and there is a definite release (flux) of phosphate from surficial benthic sediment to bottom water. These two biogeochemical processes are prevalent in other shallow coastal marine ecosystems (74) whereby phytoplankton utilization of nutrients affect benthic-pelagic exchange by (a) enhancing gradient-driven transport across the sediment-water interface and (b) upon mortality, sediment labile phytodetritus promotes remineralization in or on surficial benthic sediment.

17. It is proposed that during May 2010, the process of dissimilatory nitrate reduction to ammonium (DNRA) took place in Quonochontaug Pond. It is calculated that the DNRA process produces 35 Kg NH₄⁺-N/day, approximately 6% of the daily ammonium nitrogen in Quonochontaug Pond for the month of May 2010.

18. Eelgrass meadows in Quonochontaug Pond can assimilate some ammonium nitrogen by the fixation of atmospheric nitrogen gas. This nitrogen fixation (680 KgN/yr) represents 7% of the nitrogen needed for eelgrass growth in the Pond (9,400 KgN/yr).

19. Stoichiometric analysis of all dissolved and total nitrogen and phosphorus data for the sampling years 2008 to 2012 indicate that nitrogen is the primary nutrient limiting the primary production of Quonochontaug Pond. However, at certain times of the year, phosphorus is also limiting to the growth of phytoplankton in the Pond. This phosphorus limitation appears to be driven by lower releases of phosphate from oxic surficial benthic sediment that “sorbs” the dissolved inorganic form of this element.

20. A conceptual model of nitrogen cycling in Quonochontaug Pond has two compartments; bare, non-vegetated sites (four deep-water stations) and a site colonized by eelgrass (HCBuoy). The left-side panel in Figure 12 represents the author’s interpretation of physical, water quality, and nutrient data for four deep-water stations in Quonochontaug Pond (JR, HCCH, NBI, and EBYC; Figure 1). There are major external inputs of NO₃⁻ and NH₄⁺ from surface-water runoff, atmosphere, and groundwater. The dissolved inorganic nitrogen (DIN) in the Pond’s waters are controlled by phytoplankton assimilation, mortality and zooplankton excretion, and sinking of phytoplankton debris to bottom waters and surficial benthic sediment where aerobic mineralization recycles particulate organic nitrogen (PON) back to NO₃⁻ and NH₄⁺. Some of this PON accumulates in surficial benthic sediment where alternative decomposition pathways produce NH₄⁺ and possible some N₂ as a result of denitrification. There is a possibility that dissimilatory nitrate reduction to ammonium (DNRA) occurs in the Spring when water-column concentrations of nitrate are elevated.

21. On the right-side panel of Figure 12, a somewhat different conceptual model of nitrogen cycling in eelgrass meadows is depicted. Nitrogen fixation (the conversion of atmospheric N₂ to NH₄⁺) and mineralization of PON to NH₄⁺ produce the primary nutrient that nourishes the growth of eelgrass.
22. Figure 13 is a box model that depicts the DIN (NO₃⁻ and NH₄⁺) mass balance for Quonochontaug Pond. The mass balance is somewhat biased to groundwater input, primarily that of nitrate. There are few data for the concentration of NO₃⁻ in groundwater that enters Quonochontaug Pond. One wonders if denitrification may reduce this mass input (38) as groundwater enters coarse sand deposits located along the northern fringe of the Pond.

23. Figure 14 depicts the total nitrogen (TN) mass balance for Quonochontaug Pond. Considering the fact that phytoplankton assimilate NO₃⁻ and NH₄⁺ (DIN) for growth, then die and sometimes are consumed by zooplankton, particulate organic nitrogen (PON) and suspended particulate matter (SPM) should be included in the nitrogen mass balance of the Pond. While the sedimentation of organic nitrogen term remains the same as for the DIN mass balance, the groundwater in term was updated to include DON. The additional mass of TN in the water column and the export of TN to Block Island Sound nearly offset the additional stream and groundwater inputs of total nitrogen (TN). Canada geese may add 22 Kg N/year to the sedimentation term of the Pond, but their input is small relative to other terms of the total nitrogen mass balance (Figure 14).

24. The dissolved inorganic phosphorus (DIP) mass balance for Quonochontaug Pond (Figure 15) is more tenuous than the nitrogen mass balance as several of the terms use DIP data that was not collected on the Pond. These include atmospheric and groundwater input; and the phosphorus sedimentation term was calculated by dividing the nitrogen sedimentation term by a N:P ratio of 23.7:1. This ratio is significantly above the Redfield ratio of 16:1. Because of these estimates, the DIP mass balance constructed for Quonochontaug Pond is substantially out of balance; 1,022 KgP/yr Out and 546 KgP/yr In (Figure 15). The TP (total phosphorus) mass balance, not depicted in a figure, was 4,457 KgP/yr Out and 908 KgP/yr In. This great imbalance is driven by the disparity in TP concentrations in the eastern basin of Quonochontaug pond and the waters of Block Island Sound.

25. For both the nitrogen and phosphorus mass balances of Quonochontaug Pond, the sedimentation Out, the Breachway Out, and the groundwater In terms have the most uncertainty. There are few data for nitrogen in benthic sediment and no data for phosphorus. Thus, literature data for C:N and N:P ratios in bottom sediment were useful in constructing these sedimentation terms. While groundwater flow data were available from the USGS groundwater and surface water flow model (55), there are few nitrate concentration data for groundwater flowing through bottom sediment into the Pond.

Acknowledgements
The author thanks Linda Green of the URI Watershed Watch Program for supplying the 2012 nutrient analyses of the southeastern Rhode Island salt ponds that are sampled by Salt Ponds Coalition (SPC). As always, Linda performs expert nutrient analyses and without her input SPC would not have such a valuable nutrient database for these salt ponds.
The author also wishes to acknowledge Mr. Tom Dodd and Ms. Barbara Engel for their dedicated effort in providing bi-weekly sampling, dissolved-oxygen analyses, and chlorophyll filtration during the sampling months (May to October) for the years 2008 to 2012. Their dedication to this effort, under good and bad weather conditions, is most admirable and deeply appreciated.

And finally, the author gratefully acknowledges the extensive help of Ms. Elise Torello. Ms. Torello prepared the database for SPC’s water quality and nutrient data. The author used this database for nearly all the tabular and graphic data presented in this report. In addition, Ms. Torello used her extensive gift of computer skills to prepare the sharp graphics presented in Figures 1 and 12. Figure 12 was prepared from the author’s sketch and notes and he (Callender) takes full responsibility for the content.

References


Figure 2

Average Concentration of Surface- and Bottom-Water Dissolved Oxygen in Quonochontaug Pond, 2008 to 2011
Figure 3

Concentration of Nitrate in Surface Water of the Western and Eastern Basins of Quonochontaug Pond, April to December 1999

- Western Basin
- Eastern Basin

Nitrate Concentration, µg/L

Date:
- 27-Mar
- 6-May
- 15-Jun
- 25-Jul
- 3-Sep
- 13-Oct
- 22-Nov
- 1-Jan
Concentration of Surface and Bottom Water Ammonium in the Eastern Basin of Quonochontaug Pond, April to December 1999

Figure 4
Concentration of Surface-Water Chlorophyll in Quonochontaug Pond,
April to December 1999

Figure 5
Average Concentration of Surface- and Bottom-Water Ammonium in Quonochontaug Pond, 2008-2011

Figure 6
Ammonium Increase versus Dissolved Oxygen Deficit for Bottom Waters in Quonochontaug Pond, May through September, 2008-2011

Figure 7

R² = 0.63284

Figure 8
Figure 9

Surface-and Bottom-Water Dissolved Inorganic Phosphorus (DIP) Concentrations in Quonochontaug Pond, 1999 and 2000
Figure 12

Conceptual models of nitrogen benthic-pelagic coupling in shallow coastal waters with unacknowledged sediment (A) and seagrass-habitat sediment (B).

These conceptual models represent nitrogen cycling in Quonochontaug Pond as explained in the text.
Atmosphere In- 2,964 Kg/Yr

Stream In- 2,110 Kg/Yr

Upper 1 meter Water Column- 155 Kg

Breachway Out- 5,950 Kg/Yr

Lower 2-5 meters Water Column- 245 Kg

Groundwater In- 12,023 Kg/Yr

Sedimentation- 11,300 Kg/Yr

Dissolved Inorganic Nitrogen Mass Balance, Quonochontaug Pond

Mass NO₃⁻ and NH₄⁺ in Water Column + Export NO₃⁻ + NH₄⁺ to Block Island Sound + Accumulation of Nitrogen in Benthic Sediment = Stream In + Atmosphere In + Groundwater In

400 Kg + 5,950 Kg/Yr + 11,300 Kg/Yr = 2,110 Kg/Yr + 2,964 Kg/Yr + 12,023 Kg/Yr

17,650 Kg Out = 17,097 Kg In

Figure 13
Total Nitrogen Mass Balance for Quonochontaug Pond

Mass TN in Water Column + Export TN to Block Island Sound + Accumulation of Nitrogen in Benthic Sediment = Stream In + Atmosphere In + Groundwater In

$$2,707\ Kg + 7,300\ Kg/Yr + 11,300\ Kg/Yr = 3,234\ Kg/Yr + 3,510\ Kg/Yr + 14,410\ Kg/Yr$$

$$21,307\ Kg\ Out = 21,154\ Kg\ In$$
Dissolved Inorganic Phosphorus Mass Balance for Quinechontan Pond

Mass of DIP in Water Column + Export DIP to Block Island Sound + Accumulation (Sedimentation) of Phosphorus in Benthic Sediment = Stream In + Atmosphere In + Groundwater In

\[ 108 \text{ Kg} + 0 \text{ Kg/yr} + 914 \text{ Kg/yr} = 22 \text{ Kg/yr} + 14 \text{ Kg/yr} + 510 \text{ Kg/yr} \]

1,022 Kg Out = 546Kg In