Ninigret Cove Groundwater Study 2013. A Pilot Study to Assess the Importance of Shallow Groundwater Discharge of Nutrients into a Coastal Salt Pond Embayment

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Executive Summary

This study was conducted by staff and associates of the Salt Ponds Coalition for the purpose of assessing the shallow groundwater input of nutrients to a typical embayment of Quonochontaug Pond. The study site was selected for its accessibility to collect surface-water and groundwater inputs that are important variables for a hydrologic and chemical mass balance.

The study site is Ninigret Cove, an embayment along the northern shore of the eastern basin of Quonochontaug Pond. The Cove study site consists of a well-delineated watershed with one surface-water entity that flows into the Cove's water column. The bottom sediments of the Cove consist of a band of sand deposits, along the northern shore, that grade into fine-grained organic-rich muds.

In order to define the major nutrient inputs to Ninigret Cove's water column, the following were done. Ninigret Cove Brook (Figure 1) was monitored for flow and nutrient content on a monthly basis from May to December 2013. Minipiezometer wells were installed and monitored for water quality (temperature, dissolved oxygen, and salinity) and nutrient (nitrate, ammonium, and dissolved reactive phosphate) content during the study period. At the time of well sampling, water samples from the Ninigret Cove water column were collected. In mid September and late October, drive-point profiling of water quality and nutrients was done at two localities in the sand deposits.

The following are the findings of the study.

* Fresh groundwater discharge through the sand deposits occurred in June through August when rainfall was sufficient to recharge the shallow groundwater aquifer.
* During the above time period, nitrate was the major component of DIN (dissolved inorganic nitrogen) at the shoreline well MP-2A. At the two shallow offshore wells (MP-3B and MP-4C), ammonium was the major component of DIN although these wells were only sampled in September and October (Table 1).
* Drive-point profiling of the sand deposits in mid September and late October showed that brackish water penetrated these deposits to depths of 12 inches where ammonium and phosphate concentrations were high. Below this depth to about 24 inches, recirculated Ninigret Cove water mixed with ambient fresh groundwater to produce intermediate concentrations of salinity, ammonium, and phosphate.
* DIN and DIP mass balances were constructed using data from this study, data from the Salt Ponds Coalition monitoring database, previously published data on the water quality of Quonochontaug Pond, and some data from published scientific papers on coastal lagoons.
* For the DIN mass balance, surface-water input and benthic flux of ammonium from organic-rich muds account for 83% of all DIN inputs. Fresh and saline submarine groundwater discharge (SGD) of DIN account for only 5% of these inputs.
* For the DIP mass balance, the benthic flux of phosphate from the muds is the dominant input, 97% of all DIP inputs. Fresh and saline SGD of DIP is only 0.5% of all inputs.

* Comparing the published data of Moran et al. (2013) with the results from this study, the SGD of DIN to Ninigret Cove is only one-third the percentage of all inputs (surface water, atmosphere, and SGD) relative to that for Quonochontaug Pond. The percentage for SGD of DIP to Ninigret Cove is about twice that for Quonochontaug Pond. Moran et al's. (2013) SGD flux of DIN, normalized to the surface area of Quonochontaug Pond, is considerably smaller than that for Ninigret Cove. However, the two normalized fluxes of SGD-DIP are essentially the same. The concentrations of nitrate in shallow groundwater entering the sand deposits of Ninigret Cove are considerably higher than those for the whole of Quonochontaug Pond.
* One should be cautious to apply single-site groundwater study data for assessing the eutrophic status of Rhode Island's coastal salt ponds. In addition, it appears that shallow groundwater inputs of nutrients to these salt ponds is the major pathway for groundwater input as evidenced from the study of Moran et al. (2013).

Introduction

Enrichment of coastal waters from land-derived nitrogen is one of the most pervasive threats to present-day aquatic ecosystems (Bowen and Valiela, 2001). Human activities in the past century have resulted in a tremendous increase in nutrient inputs (nitrogen and phosphorus) to the coastal zone worldwide. This external loading of nitrogen and phosphorus is the driving force for eutrophication. Shallow coastal bays and lagoons are particularly vulnerable to rapid changes in human activities (McGlathery et al., 2007) that cause increased algal production, decreased light transparency, and depleted dissolved oxygen (Anderson and Conley, 2009). Indirect effects of eutrophication are the increase in bacteria, the production of algal toxins, nutrient recycling from benthic sediments, and changes in ecosystem structure (Anderson and Conley, 2009). Eutrophication of shallow coastal lagoons typically causes a shift in dominance from seagrasses and perennial macro algae to ephemeral, bloom-forming algae (McGlathery et al., 2007).

Previous studies of nitrogen enrichment of Rhode Island's coastal lagoons suggest that groundwater discharge of dissolved inorganic nitrogen (DIN) is a very significant input to the nitrogen budget of these water bodies. Nixon and Buckley (2007) estimated that between 53 and 70 percent of all DIN inputs to Quonochontaug Pond originate from groundwater. That means between 4,600 and 9,200 Kg DIN/Yr comes from groundwater input, or to normalize this to the surface area of the Pond, 15 to 31 Kg DIN/hectare/Yr. They used a groundwater DIN concentration range of 1.4 to 2.8 mg/Liter based on data obtained from relatively deep (35 feet well depth) to deep (greater than 85 feet well depth) residential wells that are located some distance north of the Salt Ponds (Lee and Ernst, 1997; RICRMC, 1999). This deeper groundwater may or may not ultimately discharge into the ponds.

Very recently, Moran et al. (2013) published a paper giving estimates of submarine groundwater discharge (SGD) of DIN and DIP to coastal ponds of Southern Rhode Island. Measurements of shallow groundwater DIN and DIP concentrations were combined with recent radium-based SGD fluxes and prior estimates of SGD determined from Darcy's Law, a hydrologic model, and total recharge to yield SGD nutrient fluxes to four of the major coastal ponds. Using their data for SGD input and atmospheric data from Nixon et al. (1995), combined with stream input to Quonochontaug Pond (SPC database for DIN concentration, www.saltpondscoalition.org/monitoring.html; Masterson et al. 2007 for modeled stream flow) results in a calculated SGD-DIN input of 26% for all DIN inputs to Quonochontaug Pond.

The two estimates of percentage of groundwater input of DIN relative to total DIN input to Quonochontaug Pond are substantially different. Deep-groundwater input of DIN estimated from Nixon and Buckley (2007) is about 61% and the shallow-groundwater input (Moran et al., 2013) is about 26% of all DIN inputs to Quonochontaug Pond. Eventually, this discrepancy needs to be addressed.

This study focuses on the water quality and nutrients in shallow groundwater that flow through coarse-grained sediments that fringe the northern shore of Quonochontaug Pond. Ninigret Cove, an embayment to this northeast shoreline, was chosen because the Cove and its watershed is of a manageable size where surface water and shallow groundwater can be easily sampled in a few hours, and because nutrient inputs appear to be well delineated. The ultimate purpose of this study was to determine whether a shallow groundwater system is a significant source of nutrient input to Quonochontaug Pond and, by proxy, to other Southern Rhode Island coastal ponds. This study was initiated two months before the paper by Moran et al. (2013) appeared in the scientific literature. While this study focused on an embayment to Quonochontaug Pond, it will be useful to compare the Ninigret Cove data with that for the whole of Quonochontaug Pond. Later, in the discussion section of this paper, comparison of data from the two studies will be made.

Methods

Study Site

Ninigret Cove is a small embayment located on the northeast shore of Quonochontaug Pond, a coastal lagoon in Southern Rhode Island (Figure 1). The Cove is fed by one major stream (Ninigret Cove Brook, Figure 1) that drains the Cove's watershed. The surface area of the Cove is about 12,620 m^2 and that of its watershed is approximately 355,000 m^2. The bottom sediments of Ninigret Cove consist of permeable sand deposits that occupy the northern part of the Cove and fine-grained organic muds (silt and clay) that occur throughout the rest of the Cove's bottom area. Ninigret Cove is flushed with brackish Quonochontaug Pond water that is a mixture of some freshwater drainage and marine salt water from Block Island Sound.

Freshwater input to Ninigret Cove comes from three sources: rainfall, surface-water drainage from the watershed, and groundwater flow from a shallow-water aquifer. Saline water input comes from the tidal exchange with the waters of the eastern basin of Quonochontaug Pond. Surface-water drainage and its nutrient content is measured at a sampling site on Ninigret Cove Brook (Figure 1), atmospheric input of nutrients to the Cove is taken from Avery Point in nearby Connecticut (Nadim et al., 2001), the nutrient content of the Ninigret-Cove water column is measured on surface- and bottom-water samples, and the nutrient content of eastern basin Quonochontaug Pond water is measured on samples taken from a long-term station (North Bill's Island) located 0.75 km southeast of the mouth of Ninigret Cove (Salt Pond Coalition Google Maps).

The predominant surface geology of the Ninigret Cove watershed is dominated by the Charlestown Moraine that occupies a one-mile swath of land just north of highway US1 and till mantle that extends from US1 downslope to Ninigret Cove (Boothroyd, Dowling, and McCandless, 2001). This till mantle is commonly a slightly-to-moderately compacted, light brown to dark yellowish-brown diamicton that consists of a non-stratified mixture of silt, sand, pebbles, cobbles, and boulders. The morphology and sedimentary characteristics of this material suggest a debris-flow mode of emplacement (Boothroyd, 2001). In general, this till mantle is less than 15-20 feet in thickness (Masterson et al., 2007) and overlies Permian age igneous rocks. The shallow aquifer underlying the Ninigret Cove watershed is part of the South Coastal Basin aquifer and may be 10 to 30 feet thick in the study area (Masterson et al., 2007). Two auger holes were drilled on the land surface to the northeast and northwest of mini-piezometer cluster MP-2. The general description of the sediment recovered from the northeast hole is medium brown, organic rich, silty clay soil in the upper 10 inches, underlain by 20 inches of tan, dry, silty clay. Below that was 10 inches of light tan, damp, clayey silt. Below that was 10 inches of grey-tan clayey silt and below this was 10 inches of light grey, dry, silty clay. Rock was encountered at 60 inches below the land surface. This was also the case at the bottom (56 inches) of the auger hole northwest of the MP-2 well cluster.

A conceptual diagram of the shallow groundwater system for Ninigret Cove is presented in Figure 2. Based on this conceptual model and data from several minipiezometer well clusters, fresh groundwater always flowed through the seepage face along the shoreline. During periods of low rainfall, groundwater offshore was a mixture of fresh and saline water.

Installation of Minipiezometer Wells

Beginning in June of 2013, minipiezometer wells were installed at three sites along the northern edge of Ninigret Cove (Figure 1). These wells were constructed from AMS stainless steel gas vapor tips with stainless steel screens placed over the inlet ports. The nipple at the top of the vapor tip was connected to a length of fluoropolymer tubing that extended through the Cove sediment from the well screen to some distance above the Cove's water level at high tide. The tubing was threaded through galvanized pipe with the vapor tip and well screen abutted against the bottom of the pipe. In all cases a hole was augured to a depth of a few inches above the desired depth of the well screen and the galvanized pipe, with the attached minipiezometer, was pounded to the desired depth. The hole with the galvanized pipe and minipiezometer was filled with sand from the adjacent pond bottom. At the MP-2 well cluster, one well was screened at 25 inches (MP-2A) and 38 inches (MP-2B) below the bottom of the Cove. At the MP-3 well cluster, one well was screened at 38 inches (MP-3A), another well at 25 inches (MP-3B), and a third well at 45 inches (MP-3C) below the bottom of the Cove. At the MP-4 well cluster, one well was screened at 44 inches (MP-4A), another well was screened at 38 inches (MP-4B), and a third well was screened at 25 inches (MP-4C) below the bottom of the Cove.

The lithology of the MP-2B well hole consisted of medium brown to grey muddy sands to a depth of 20 inches underlain by medium to dark grey silty sand to a depth of 30 inches. The bottom 8 inches of the hole was a grey fine sand that was in contact with the well screen at 38 inches depth. The lithology of the MP-3B well hole consisted of grey brown fine sand with some granules to a depth of 18 inches underlain by 7 inches of light-grey very-fine sand to a depth of 25 inches where the well screen was placed. The lithology of the MP-4B well hole consisted of medium grey medium to coarse sand to a depth of 12 inches underlain by dark grey slightly muddy fine sand to a depth of 30 inches. Below this was a thin layer (3 inches) of dark grey, slightly silty medium coarse sand with wood chips. Finally, the bottom of the hole to 38 inches consisted of grey fine to medium sand that was in contact with the well screen.

Drive Point Piezometer Profiling

In the middle of September and at the end of October 2013, when rainfall was at a minimum (1.2 inches for two months), a Retract-A-Tip (AMS) drive point sampler (Charette, 2007) was used to collect a profile of water samples in the sandy bottom sediments of Ninigret Cove. Water samples were pumped at 6 inch intervals to a depth of 42 inches (9/16/2013) and 38 inches (10/28/2013) below the Cove bottom. A stainless steel piezometer was driven just below the depth of interest and then retracted so that the well screen was placed at the desired depth. Water samples were pumped through fluoropolymer tubing using a portable peristaltic pump. Similar to sampling the minipiezometer wells, samples for water quality analysis were pumped into 100 ml plastic bottles and analyzed using a hand-held YSI Temperature-dissolved oxygen-salinity monitor or by digital thermometer, Winkler titration (DO), and portable refractometer (salinity). After collecting the water quality sample, the bottle was rinsed and filled with 30-40 ml of water that would be filtered later in the day.

Sampling and Analysis

In June and July 2013, the residential wells (RW-1 to RW-4, see Figure 1 for location) and some of the minipiezometer wells (MP-2A, MP-3A, MP-4A) were sampled. Water was collected from these residential wells and minipiezometer wells, filtered through glass fiber filters, and frozen for later analysis of nitrate, ammonium, and dissolved inorganic phosphorus (phosphate) by the University of Rhode Island Watershed Watch Laboratory (URIWW).

In August of 2013, minipiezometer wells MP-2B and MP-4B were installed and these wells along with MP-2A,MP-3A, MP-4A were sampled, filtered, and frozen for later analysis. In early September of 2013, minipiezometer wells MP-3B, MP-3C, and MP-4C were installed, and these as well as all of the above minipiezometer wells were sampled, filtered, and frozen for later analysis by URIWW. Finally, on October 17, 2013, all minipiezometer wells were sampled, filtered, and frozen for later analysis.

At the times when the minipiezometer wells were sampled, temperature-dissolved oxygen-salinity were measured on the pumped water using a Yellow Springs Instrument Model 85 handheld monitor. All minipiezometer well samples were filtered within hours after collection and frozen for future nutrient analysis. Several times during the study, additional minipiezometer well samples were left unfiltered and frozen for future analysis of total nitrogen (TN) and phosphorus (TP). When DIN and DIP are subtracted from TN and TP, the difference may be used to estimate the concentration of dissolved and particulate organic nitrogen and phosphorus in the sample.

During the duration of this study (June to December, 2013), Ninigret Cove Brook (Figure 1) was sampled one or two-times per month for flow and nutrient content. Approximately twice per month, flow was measured at a weir upstream from the nutrient sampling site using the bucket method. This consists of taking a plastic bucket, calibrated in liters, and collecting water over a specified time interval, usually three seconds. This procedure was done three times in order to achieve an average value.

In order to aid in the hydrologic analysis of surface-water and groundwater inputs to Ninigret Cove, an automatic rain gauge was installed about 750 feet from the study site and daily amounts of precipitation were recorded over the period June to October, 2013.

Finally, water samples were collected from the Ninigret Cove water column (surface and bottom water) at times when the minipiezometer wells were sampled. This sampling consisted of taking a plastic bottle and filling it either with water 6 inches below the water surface and/or 6 inches above the Cove bottom. Later in the day of sampling, the water samples were filtered and frozen for later nutrient analysis.

Nutrient analyses, nitrate-ammonium-dissolved reactive phosphate-total nitrogen and total phosphorus, were done at the URIWW laboratory (Linda Green, written communication). the Ammonium is analyzed by auto analyzer using a colorimetric technique to determine ammonia [URIWW-SOP-3 or SOP014]. Orthophosphate + nitrate + nitrite is analyzed by a simultaneous colorimetric procedure of dissolved reactive phosphorus (DRP) and nitrate + nitrite (NO_3) + NO_2) [URIWW-SOP-2 or SOP015]. Total nitrogen and total phosphorus are performed on unfiltered, digested water samples using the above colorimetric analyses.

<u>Results</u>

Water Quality and Nutrients for Minipiezometer Wells

Table 1 gives the nutrient and water-quality analyses for the minipiezometer wells that were screened at 25 inches in the sandy sediments of Ninigret Cove.

Table 1. Ammonium, nitrate, phosphate, dissolved oxygen, and salinity data in Ninigret Cove minipiezometer wells screened at 25 inches below Cove bottom.

Well	Date	Ammonium, ug/L	Nitrate, ug/L	Phosphate, ug/L	DO,mg/L	Salinity,ppt
MP-2A*	6/20/2013	184	635	3	1.4	5.0
	7/22/2013	46	315	5	2.7	0.1
	8/05/2013	33	345	5	4.9	0.1
	9/06/2013	30	320	1	4.9	0.1
	10/17/2013	21	763	1	4.0	0.2
MP-3B**	9/06/2013	153	10	1	2.1	0.1
	10/17/2013	933	12	3	1.5	20.0
	12/03/2013	1,722	211	2	1.2	10.0
MP-4C***	9/05/2013	578	37	31	4.0	0.0
	9/16/2013	561	10	5	————	————
	10/17/2013	618	4	3	3.3	19.9

* **MP-2A located on shoreline (Figure 2)**
MP-3B located 80 feet offshore (Figure 2)
*****MP-4C located 150 feet offshore (Figure 2)**

MP-2A is located at the shoreline between the sandy bottom sediments and the land surface. Figure 2 shows that this is the area of nearshore seepage or the seepage interface (Swarzenski et al., 2004). Except for the 6/20/2013 sampling, the ammonium concentrations in MP-2A are low and indicative of fresh groundwater concentrations that derive their chemistry from rainwater percolating through the unsaturated zone. In contrast, the nitrate concentrations are moderately high and also are indicative of fresh groundwater. Phosphate concentrations are all low except for the 9/05/2013 sampling at MP-4C. The well water at MP-2A appears to be of fresh water origin, even during September and October when rainfall was at a minimum (Figure 3) and there was little recharge of the shallow aquifer. MP-2A is located in the nearshore seepage zone where the shallow freshwater aquifer intersects the saline NInigret Cove (Figure 2). The average ratio of nitrate to ammonium for this well water is 7.5:1 (Table 1), a value significantly lower than that for Ninigret Cove Brook, 32:1. Apparently, there must be more organic nitrogen mineralization (producing ammonium) in the shallow groundwater discharging at MP-2A than in rainwater that percolates through the unsaturated zone and feeds the Brook. At MP-3B, also screened at 25 inches below the Cove Bottom but 75 feet offshore of MP-2A and at MP-4C screened at the same depth and located 150 feet offshore of MP-2A, the nitrate to ammonium ratio is either 0.02 or 0.03. Obviously, the well-water concentrations of ammonium and nitrate at these locations are different than those at MP-2A. However, the nitrogen chemistry for MP-3B and MP-4C represents the low rainfall period of mid September through October (Figure 3). If we take the average nitrate and ammonium concentrations at MP-2A for the same time period, then the nitrate to ammonium ratio is 21:1. This value indicates that well water at MP-2A (seepage interface) pumped during the low rainfall time period is still of a freshwater origin while that from MP-3B and MP-4C (offshore) is of a different origin. In addition, the salinity data for the October sampling of the two offshore minipiezometer wells (Table 1) indicates that the origin of this well water is some mixture of fresh and saline groundwater (Figure 2).

Table A from Appendix 1 gives the nutrient chemistry for minipiezometer wells screened at 38 and 44 inches below the Cove bottom. For the 38 inch well screen depths, the shoreline well MP-2B has an average nitrate concentration of 1,400 ug/L and ammonium concentration of 144 ug/L. The 80 foot offshore well MP-3A has an average nitrate concentration of 2,164 ug/L and an average ammonium concentration of 25 ug/L. And, the 150 foot offshore well MP-4B has an average nitrate concentration of 924 ug/L and an average ammonium concentration of 40 ug/L. Thus, the nitrate to ammonium ratio of well waters at the 38 inch depth from the shoreline to 150 feet offshore varies from 10:1 to 87:1 to 23:1. There appears to be a significant difference in the nitrogen signature between the shoreline well and the offshore wells.

For the minipiezometer wells screened at 44 inches below the Cove bottom, there are only two wells offshore. At MP-3C (Table A, Appendix 1), 80 feet offshore, the average nitrate concentration is 2,084 ug/L and the average ammonium concentration is 90 ug/L. At MP-4A (Table A, Appendix 1), 150 feet offshore, the average nitrate concentration is 32 ug/L and the average ammonium concentration is 32 ug/L. There is a very different nitrate to ammonium ratio for these two well waters; 23:1 at MP-3C and 1:1 at MP-4A. There appears to be a very significant difference in the nitrate signature between these two deep, offshore well waters. However, MP-3C was sampled only three times late in the study period while MP-4A was sampled five times from June 20 to October 17, 2013 (Appendix 1, Table A). Only the October sampling at MP-3C had a brackish salinity (8.6 ppt).

The phosphate concentrations were all low for all minipiezometer wells: 1-5 ug/L at 25 inches, 1-15 ug/L at 38 inches, and 3-8 ug/L at 44 inches below the Cove bottom. There was little difference between sampling times for each well and little difference between well depths (Table 1; Table A, Appendix 1).

Water Quality and Nutrients from Drive-Point Sampling

On September 16 and October 28, 2013, when rainfall on the watershed was very low (Figure 3), drive-point profiles of water quality (temperature, dissolved oxygen, and salinity) and nutrients (nitrate, ammonium, and phosphate) were made with an AMS Retract-A-Tip piezometer probe. The profiles of salinity, ammonium, and phosphate are presented in Figure 4. Since nitrate concentrations were low and somewhat constant (8-20 ug/L), they were not plotted in Figure 4. Figure 4A is the plot of pore-water salinity versus depth in the sandy sediments of Ninigret Cove at the MP-4 site sampled on September 16 and at the MP-3 site sampled October 28, 2013. Salinity at the MP-4 profile was near that of Ninigret Cove water down to a depth of 12 inches. At 18 inches depth, the salinity at MP-4 decreased sharply to about 2.5 ppt and thereafter was essentially fresh, with some mixing of saline water at 24 inches, to a depth of 42 inches (Figure 4A). Salinity at the MP-3 profile was high, 32 ppt, at 6 inches depth in the sandy sediments. At 12 inches depth, salinity decreased to nearly 10 ppt, suggesting that the pore water at this depth was a mixture of fresh and saline water. At 18 and 24 inches depth, MP-3 pore water had fresh salinities, 0.1 ppt, while at 30 and 36 inches depth, the water was mostly fresh with some mixing with saline water (4 ppt salinity) (Figure 4A).

Figure 4B shows the plot of ammonium concentrations versus depth in the sandy sediments at sites MP-4 and MP-3. At MP-4, ammonium concentrations increase sharply from the sediment surface (15 ug/L) to a depth of 6 inches (800 ug/L), then levels off to 770 ug/L at 12 inches, increases again to 1,100 ug/L at 18 inches, and then decreases sharply to about 430 ug/l at 24 inches and thereafter to about 50 ug/l at the 30 to 42 inch depths (Figure 4B). The MP-3 ammonium profile is similar to that for MP-4 in the upper 12 inches, increasing from 60 ug/L at the sediment surface to about 750 ug/L at 6 and 12 inches below the Cove bottom (Figure 4B). Thereafter, MP-3 ammonium decreases to 100 ug/L at 18 inches, and gradually declines to about 25 ug/L at 36 inches depth. At depth in the drive-point pore water, ammonium varies positively with salinity (R^2=0.45), a relationship that suggests high ammonium concentrations originate with recirculated saline Ninigret Cove water.

Figure 4C shows the plot of phosphate concentrations versus depth in the sandy sediments at MP-4 and MP-3. At MP-4, phosphate increases sharply from the sediment surface (6 ug/L) to 154 ug/L and 171 ug/L at 6 and 12 inches respectively. Thereafter, it decreases to 80 ug/L at 18 inches and then to low concentrations of between 8 and 20 ug/L at depths 24 to 42 inches (Figure 4C). At MP-3, phosphate concentration increases from 20 ug/L at the sediment surface to 65 ug/L at 6 inches depth in the sandy sediments. Thereafter, it decreases to between 9 and 23 ug/L at depths 18 to 36 inches below the Cove bottom. Phosphate varies positively with salinity at depth in the Ninigret Cove sandy sediments (R^2=0.7), suggesting, like ammonium, that high concentrations originate with recirculated saline Ninigret Cove water.

Dissolved Inorganic Nitrogen (DIN) and Phosphorus (DIP) Mass Balances

The DIN and DIP mass balances for Ninigret Cove consist of four input terms; surface water, atmosphere, submarine groundwater discharge, and benthic flux of ammonium and phosphate. The two output terms are sedimentation and export to Quonochontaug Pond. Calculated values for yearly input or output from each of these components are based on data from this study or from published reports for this system or similar systems are presented in Figure 5.

DIN and DIP Mass Input to Ninigret Cove Via Ninigret Cove Brook

The monthly or bi-monthly flow rates for Ninigret Cove Brook were measured with the bucket method whereby a calibrated plastic bucket was placed under a weir for a set period of time, usually 3 seconds. Monthly and bi-monthly samples for nutrient concentrations were taken on the same day as the flow measurements. Item number 3 in Appendix 2 lists the monthly and bi-monthly flow data and item number 4 lists the DIN and DIP concentrations and the calculated DIN and DIP mass input for Ninigret Cove Brook for the period May to December 15, 2013. The total DIN and DIP mass input of Ninigret Cove Brook for 7.5 months is 32.4 Kg DIN and 0.27 Kg DIP. If we assume that there are 9.5 months when most temperatures are above freezing, then the annual input of DIN and DIP to Ninigret Cove is **41.0 Kg DIN** and **0.34 Kg DIP**.

Atmospheric Deposition of DIN and DIP to Ninigret Cove

Callender (2013), using atmospheric deposition data for ammonium and nitrate at Avery Point, Connecticut (Nadim et al., 2001), estimated the annual nitrogen deposition rate for Quonochontaug Pond, 2,964 Kg/Yr. Using the ratio between the surface area for Ninigret Cove and that for Quonochontaug Pond (0.0042, Appendix 2, #1) and multiplying that by the DIN deposition rate for the Pond, one gets the DIN deposition rate for Ninigret Cove, **12.5 Kg/Yr**.

Callender (2013) estimated the DIP atmospheric deposition rate for Quonochontaug Pond to be 14 Kg/Yr. Multiplying this figure by the above ratio, on gets the DIP deposition rate for Ninigret Cove, **0.06 Kg/Yr**.

Submarine Groundwater Discharge (SGD) of DIN and DIP to Ninigret Cove

Submarine groundwater discharge (SGD) has been increasingly recognized as an important source of nutrients to shallow, coastal marine environments (Charette, 2007; Li et al., 2009). It is difficult to quantitatively characterize SGD due to its significant spatial and temporal variability (Li et al., 2009). In most cases, SGD can be divided between a terrestrial, freshwater hydraulic gradient component and a tidally-induced sea water recirculation component (Li et al., 2009; Charette, 2007; Burnett and others, 2006). Moran et al. (2013), in a recent study of SGD input of DIN and DIP to the coastal ponds of Southern Rhode Island, estimated that the average SGD to Quonochontaug Pond is **5 liters/m^2/day.** This value is an average of four methods to determine SGD (Moran et al., 2013): Radium-tidal prism model, Radium-residence time model, Hydrologic model, and Recharge.

1) Freshwater SGD-DIN

The average DIN concentration of minipiezometer well water pumped from the 25 inch depth in the sandy deposits at the northern edge of Ninigret Cove was 465+/-475 ug/L for the time period June to early September, 2013 (Table 1). This DIN concentration is a combination of 226+/-242 ug/L ammonium and 239+/-233 ug/L nitrate. Total rainfall for this time period was 15.4 inches (Figure 3). Thus, the SGD of DIN through these sandy sediments (0-25 inches) is 0.228 gm/m^2/3 mos. Multiplying this rate by the surface area of sandy sediments in Ninigret Cove (Appendix 2, #1), one gets a value of **0.506 Kg DIN/3 mos.** (Appendix 2, #6). If we include the 38 inch mini-piezometer well water (Appendix 1, Table A), then the average DIN concentration of well water from both 25 and 38 inches depth is 1,254+/-1,016 ug/L. This DIN concentration is a combination of 125+/-176 ug/L ammonium and 1,129+/-840 ug/L nitrate. The 38 inch deep well water has considerably more nitrate than the 25 inch deep well water. Multiplying this DIN concentration by the average SGD, one gets a value for the freshwater SGD-DIN input to Ninigret Cove of **1.363 Kg/3 mos.** (Appendix 2, #6). Therefore, the range in fresh SGD of DIN from the sandy sediments in Ninigret Cove for the period June 1 to September 6, 2013 is **0.51 to 1.36 Kg/3 mos.**

2) Saline, Tidally-Induced SGD-DIN

During the time period September 10 to October 31, 2013, rainfall was minimal with only 1.15 inches falling in two months (Figure 3). If we look at the October 17 DIN data in MP-3B and MP-4C (Table 1) and the drive-point profiles of ammonium and nitrate (nitrate is not shown in Figure 4 because concentrations were low with an average of 21+/-25 ug/L) at MP-4 (9/16/2013) and MP-3 (10/28/2013) (Figure 4B), it becomes obvious that the proportions of ammonium and nitrate for these samplings (middle September and October) are significantly different than the ratio for the earlier months. For the above minipiezometer well waters (25 inch depth), the average DIN concentration was 713+/-203 ug/L with 704+/-200 ug/L ammonium and 9+/-4 ug/L nitrate. The ratio of ammonium to nitrate for the middle of September and October is 78:1. On the other hand, this ratio was 0.9:1 for June to early September.

The drive-point DIN data averaged 852+/-148 ug/L with ammonium making up most of the DIN concentration, 832+/-137 ug/L. The ammonium to nitrate ratio of these profiles was 40:1. So, for the "dry" months of September and October 2013, the ammonium to nitrate ratio was between 40:1 and 78:1. Conversely, for the "wet" months of June to August, this ratio was 0.9:1. Also, the salinity data for the drive-point profiles (Figure 4A) showed that Ninigret Cove water (salinity 32 to 35 ppt) penetrated the sandy sediments at the northern edge of Ninigret Cove to depths of 12 inches on September 16 and 6 inches on October 28.

Thus, for the "dry months", September and October 2013, the average DIN concentration was 782+/-98 ug/L. When this is combined with the average SGD (5 liters/m^2/day), the surface area of sandy sediments (2,200 m^2) and the number of days (51), the saline SGD of DIN from these sandy sediments for the period September 10 to October 31, 2013 is **0.44 Kg/2 mos.**

3) Fresh and Saline SGD of DIN to Ninigret Cove

Combining the above data, one can calculate the annual SGD of DIN to Ninigret Cove. For the three-month "wet" period, fresh SGD of DIN ranged between 0.51 and 1.36 Kg. If we conclude that the "wet" period covers 10 months of the year (Figure 3), then the annual fresh SGD of DIN to Ninigret Cove varies from **1.70 to 4.53 Kg/Yr.** For the "dry" period of two months, the SGD of DIN to Ninigret Cove is **0.44 Kg/Yr.** So, the total, annual SGD of fresh and saline DIN to Ninigret Cove is estimated to be **2.14 to 4.97 Kg/Yr.**

4) Freshwater SGD-DIP

Following a similar reasoning for dissolved inorganic phosphorus (DIP) as that for DIN (see above), we can calculate the fresh SGD of DIP to Ninigret Cove. The concentration of DIP in minipiezometer wells screened at 25 inches (Table 1) and 38 inches (Appendix 1, Table 1) below the Cove bottom is 6.9+/-9 ug/L. Thus the "wet" month SGD of DIP to Ninigret Cove is calculated to be 0.0075 Kg/3 mos. (Appendix 2, number 8), and the yearly (10 months) SGD of DIP to the Cove is **0.025 Kg.**

5) Saline, Tidally-Induced SGD-DIP

As for the saline SGD of DIP to Ninigret Cove, the calculations listed in Appendix 2, number 9 yield the following observations. The minipiezometer wells MP-3B and MP-4C (25 inch depth well screen) and MP-3A and MP-4B (38 inch depth well screen) have an average DIP concentration of 4.0+/-2.2 ug/L for the sampling date 10/17/2013, a “dry” month. The drive-point profiles of phosphate (DIP) (Figure 4C) have average concentrations of 136+/-47 ug/L on 9/16/2013 (MP-4, 6-18 inches) and 44+/-29 ug/L on 10/28/2013 (MP-3, 6-12 inches). These DIP concentrations are so much larger than those in the minipiezometer wells that the average SGD of DIP to Ninigret Cove only includes the phosphate profile data (Figure 4C). Thus, the saline SGD of DIP for the two “dry” months is calculated to be **0.052 Kg** (Appendix 2, #9).

6) Fresh and Saline SGD of DIP to Ninigret Cove
Combining the above DIP data, the calculated total SGD of DIP to Ninigret Cove is 0.025 Kg (fresh) plus 0.053 Kg (saline) to equal **0.077 Kg/Yr**.

Benthic Flux of Ammonium and Phosphate
Finally, we must calculate the benthic flux of ammonium and phosphate from fine-grained bottom sediments (muds) that occupy much of Ninigret Cove. In early September 2013, a sediment core was taken in Ninigret Cove and incubated under dark conditions and at ambient temperature. The resultant benthic flux of ammonium was 43 mg NH_4^+/m^2/day and the benthic flux of phosphate (DIP) was 18 mg PO_4^{3-}/m^2/day. When the flux rates were combined with the surface area of muds in Ninigret Cove (10,400 m^2, Appendix 2, #1) and the number of days during the summer and early fall when these flux rates might occur (90), the resultant annual input of **ammonium** and **dissolved inorganic phosphorus t**o the Ninigret Cove water column is calculated to be **39.8 Kg NH_4^+/Yr** and **16.85 Kg DIP/Yr**.

Total Inputs of DIN and DIP to Ninigret Cove and Percentage of Total Inputs

DIN Inputs
Ninigret Cove Brook (Surface Water)= **41.0 Kg/Yr** (42%)
Atmospheric Deposition= **12.5 Kg/Yr** (13%)
Freshwater SGD= **1.70 to 4.53 Kg/Yr** (2-5%)
Saline SGD= **0.44 Kg/Yr** (0.5%)
Benthic Flux= **39.8 Kg/Yr** (41%)
Total DIN Inputs = 95.44 - 98.27 Kg/Yr

DIP Inputs
Ninigret Cove Brook (Surface Water)= **0.34 Kg/Yr** (2%)
Atmospheric Deposition= **0.06 Kg/Yr (**0.4%)
Freshwater SGD= **0.025 Kg/Yr** (0.1%)
Saline SGD= **0.052 Kg/Yr** (0.3%)
Benthic Flux= **16.85 Kg/Yr** (97%)
Total DIP Inputs = 17.33 Kg/Yr

DIN and DIP Mass in Ninigret Cove Water Column
The water column of the Salt Ponds and their coves and embayments receive dissolved and particulate nutrients from surface-water runoff, atmospheric precipitation, and shallow groundwater discharge. Therefore, the mass of DIN and DIP in the water column of Ninigret Cove, at any given time, is the product of the sum of the dissolved inputs minus their assimilation into algae and the deposition of decaying organic matter into bottom sediment.

The mass of DIN in the upper meter of the water column is 0.227 Kg and the mass of DIN in deeper waters is 1.726 Kg (Appendix 2, #11). Therefore, the total mass of DIN in the Ninigret Cove water column is **1.95 Kg**.

The mass of DIP in the upper meter of the Ninigret Cove water column is 0.099 Kg and the mass of DIP in deeper waters is 0.374 Kg (Appendix 2, #11). Therefore, the total mass of DIP in the Ninigret Cove water column is **0.47 Kg.**

<u>Sedimentation of Nitrogen and Phosphorus to Bottom Sediment</u>

Ammonium, nitrate, and phosphate are assimilated by phytoplankton in the photic zone (upper 1 to 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 bottom sediment. Additionally, particulate matter in atmospheric precipitation and surface-water runoff enter the Pond's waters and eventually become incorporated into bottom sediment.

The estimated sedimentation rate of fine-grained, low energy, lagoonal bottom sediments, 0.125 $gm/cm^2/yr$, was measured by Ford (2003). Using this sedimentation rate, the average percent organic carbon of these fine-grained sediments, the average C/N ratio of these sediments, and the surface area of these fine-grained sediments, an annual nitrogen sedimentation rate for Quonochontaug Pond is calculated to be 10,200 Kg (Appendix 2, #12). If we multiply this rate for Quonochontaug Pond by the ratio of the Ninigret Cove's fine-grained surface area to that of Quonochontaug Pond (0.0081), we obtain an annual mass sedimentation of nitrogen for Ninigret Cove of **82.23 Kg/Yr** (Appendix 2, #12).

Many estimates of total sedimentary phosphorus in coastal lagoons have been consulted (13 references, too numerous to list). The average weight percent is 0.057 (+/-0.021) (7 references); the average concentration is 570 (+/-361) mg/Kg (4 references); and the average P sedimentation rate is 1,529 (+/-337) $mgP/m^2/Yr$ (2 references). Using the above mass sedimentation rate for fine-grained sediments (muds) in Quonochontaug Pond, the surface area of Ninigret Cove muds, and the estimates for total sedimentary phosphorus in coastal lagoons (Appendix 2, #12), the average calculated phosphorus sedimentation rate is **10.24 Kg/Yr**.

<u>Export of DIN and DIP from Ninigret Cove to Quonochontaug Pond</u>

Water floods and ebbs into and out of Ninigret Cove as a result of semidiurnal tides that occur 1.9 times per day. The volume of water exchanged between Ninigret Cove and the eastern basin of Quonochontaug Pond, on each tidal cycle, is 9.34×10^6 liters (Appendix 2, #13). The average concentration of DIN for the Ninigret Cove water column is 72 (+/-7) ug/L and that for waters of the eastern basin of Quonochontaug Pond is 69 (+/-10) ug/L. Thus, more DIN leaves Ninigret Cove on an ebb tide than enters the Cove on a flood tide. Therefore, the annual export of DIN from Ninigret Cove is **19.43 Kg** (Appendix 2, #13).

The average DIP concentration for the Ninigret Cove water column is 16 (+/-7) ug/L and that for waters of the eastern basin of Quonochontaug Pond is 14.5 (+/-3) ug/L. Thus, like DIN, more DIP leaves the Cove on an ebb tide than enters the Cove on a flood tide. Therefore, the annual export of DIP from Ninigret Cove is **9.71 Kg** (Appendix 2, #13).

Total Outputs of DIN and DIP from Ninigret Cove and Percentage of Total Outputs

DIN Outputs
Sedimentation of Nitrogen to Bottom Sediment= **82.23 Kg/Yr** (81%)
Export of DIN from Ninigret Cove=**19.43 Kg/Yr** (19%)
Total DIN Outputs= 101.7 Kg/Yr

DIP Outputs
Sedimentation of Phosphorus to Bottom Sediment= **10.24 Kg/Yr** (51%)
Export of DIP from Ninigret Cove= **9.71 Kg/Yr** (49%)
Total DIP Outputs= 19.9 Kg/Yr

Discussion of DIN and DIP Mass Balances

DIN Mass Balance
Figure 5A is a schematic diagram showing the mass inputs, outputs, and water-column storage of dissolved inorganic nitrogen (DIN) for Ninigret Cove using data accumulated during this study in the summer and fall of 2013 (Appendix 1 and 2) and other data for Quonochontaug Pond (Callender, 2013). The largest single term of the DIN mass balance is the sedimentation of nitrogen. This term includes both inorganic and organic forms of nitrogen, but water column and benthic sediment data accumulated in this study do not distinguish between the two forms. However, since biological uptake of DIN is a major ecological process affecting the nitrogen chemistry of the water column, it is reasonable to postulate that much of this sedimentary nitrogen originates from dead algal detritus or in other words, algal blooms can cause a massive influx of labile particulate organic matter to surface benthic sediment (Zilius, 2011).

Benthic flux of ammonium and surface-water inputs of DIN are the next largest terms, both inputs, affecting the water column of Ninigret Cove. The first breakdown product of mineralization of sedimentary organic matter is ammonium (Gruber, 2008). If there is oxygen in the media, water or surfical sediment, then the process is called aerobic mineralization of organic matter or ammonification (Herbert, 1999). The sediment core from Ninigret Cove,taken in early September 2013, was incubated under oxic conditions (6 mg/L DO in core-top water) and the ammonium concentration in the core-top water resulted from the oxidation of sedimentary organic matter. It should be pointed out that only one sediment core was taken in Ninigret Cove. A companion study of sediment core incubations in the western basin of Quonochontaug Pond conducted in the summer of 2013 showed that three other sites had comparable benthic flux estimates, 48+/-31 mg NH_4^+/m^2/yr. However, this benthic flux of ammonium (43 mg $NH4^+$/m2/yr) into the water column of Ninigret Cove occurs only for about three months during the summer (July-September) when the average dissolved oxygen in the water column is about 6 mg/L and the temperature about 21 degrees C (Appendix 2, #10). For the other months of the year, benthic flux of ammonium to the overlying water column does not occur. In late October of 2012, three sediment cores were taken from the western basin of Quonochontaug Pond. This was a time of lower temperatures (16 degrees C) and higher dissolved oxygen concentrations (7-8 mg/L). Incubation data from these sediment cores did not yield any ammonium release to the core-top water.

The surface-water input of DIN to Ninigret Cove for the 2013 sampling year is 41.0 Kg/Yr (Figure 5). If we normalize this input to the surface area of Ninigret Cove (12,620 m^2), we get a value of 0.0032 Kg DIN/m^2/Yr. The surface-water input of DIN to Quonochontaug Pond is 2,110 Kg/Yr (Callender, 2013) and the surface area of Quonochontaug Pond is $3.0x10^6$ m^2 (Appendix 2, #1). Thus, the normalized surface-water input of DIN to Quonochontaug Pond is 0.0007 Kg DIN/m^2/Yr. This is about five times lower than the value for Ninigret Cove. Moran et al. (2013) presented surface-water DIN input data for Ninigret and Point Judith Ponds. The normalized value for Ninigret Pond was 0.0007 and for Point Judith Pond it was 0.0042 Kg DIN/m^2/Yr. The value for Ninigret Pond is the same as that for Quonochontaug Pond. However, the value for Point Judith Pond is much larger than that for either of the other two salt ponds. The Saugatucket River is a major source of nutrients to Point Judith Pond. The conclusion from the above analysis is that Ninigret Cove Brook is a more substantial source of dissolved inorganic nitrogen to Ninigret Cove than all other surface-water inputs to Quonochontaug Pond.

Atmospheric precipitation of inorganic nitrogen to the waters of Ninigret Cove is not an insignificant input term but was not measured on site. It was taken from the data of Nadim et al. (2001) who conducted the atmospheric deposition measurements at nearby Avery Point, New London, Connecticut. These data were the best and the site was closest to the Ninigret Cove study area. Nixon et al. (1995) estimated atmospheric inorganic nitrogen input to Narragansett Bay and Moran et al. (2013) used their data to estimate the atmospheric DIN input to Quonochontaug Pond. Their estimate for Quonochontaug Pond was 3,500 Kg DIN/Yr. Multiplying the ratio of the surface area of Ninigret Cove to that of Quonochontaug Pond (0.0042) (Appendix 2, #1), a value of 14.7 Kg DIN/Yr is obtained for the atmospheric input of DIN to Ninigret Cove. This value is not significantly different from the 12.5 Kg DIN/Yr estimate shown in Figure 5A. In fact, if we use the Nixon-Moran value, 14.7 Kg DIN/Yr, then the total DIN inputs (100.5 Kg/Yr) would nearly equal the total DIN outputs (101.7 Kg/Yr) (Figure 5A).

The last input term shown on Figure 5A is the groundwater input of DIN to Ninigret Cove. Appendix 2, #'s 6 and 7 present the detailed calculations for the fresh and saline submarine groundwater discharge (SGD) of DIN to Ninigret Cove. Before examining the details of these calculations, let us review the concept of SGD as a source of nutrients to Ninigret Cove waters.

Knee and Paytan (2011) have written an extensive review of the current knowledge on submarine groundwater discharge (SGD) and the associated fluxes of terrestrial nutrients, metals, etc. to coastal waters. SGD has been defined as "direct groundwater outflow across the ocean-land interface into the ocean" (Church, 1996). This includes both fresh groundwater flow originating from inland recharge areas and seawater that circulates through the coastal aquifer on tidal to seasonal timescales (Michael et al., 2005). Precipitation, aquifer characteristics, the presence of stream systems, waves, and tides all control the quantity and location of SGD (Knee and Paytan, 2011). Rainfall recharges the aquifer, maintaining the hydraulic gradient necessary to drive seaward the groundwater flow (Figure 2). Aquifer characteristics include the porosity, permeability, and hydraulic conductivity of the aquifer substrate. There are several ways to measure SGD. Direct methods include seepage meters, geochemical tracers (see Moran et al., 2013), and the water-balance approach, while a more indirect method is hydrogeologic modeling (Knee and Paytan, 2011).

There are two main components of SGD: freshwater and recirculated seawater (Burnett et al., 2003). Although fresh and saline SGD often occur concurrently, they can be distinguished from each other using chemical tracers. In the case of the Ninigret Cove groundwater study, these tracers include salinity and the relative proportions of ammonium and nitrate. The relative magnitudes of fresh and saline SGD can vary considerably from site to site (Knee and Paytan, 2011). These vary from 96% saline (Li et al., 1999) to 60% saline and 40% fresh (Knee et al., 2010). Fresh and total SGD fluxes are typically lower in magnitude than river fluxes at locations where rivers are present (Knee and Paytan, 2011). One further, and most important, piece of information about SGD is that recent studies have revealed that tidal pumping of seawater supplies labile organic matter to the recirculated brackish water in the coastal aquifer (Santos et al., 2009).

With this background concerning SGD, let us now examine the minipiezometer well and drive-point data from the Ninigret Cove groundwater study. Since this study was a pilot study to see if professional Salt Ponds Coalition personnel could conduct such a study, there were no provisions made to acquire hydraulic head data needed to estimate the flow of shallow groundwater through the sandy sediments in Ninigret Cove, about 20% of the bottom surface area (Appendix 2, #1). Thus, the average flow value for sandy sediments of Quonochontaug Pond was used (Moran et al., 2013). Therefore, the study utilized three clusters of mini-piezometer wells (Figure 1) and two instances of drive-point piezometer profiling. Three wells were installed in mid-June 2013, two wells in early August of 2013, and three wells in early September 2013. One drive-point profile was done in mid-September and another in late October 2013. In retrospect, it would have been best to install all 25 inch wells in June and all 38 inch wells in July. Then, the study could better monitor the fresh SGD flow of nutrients during the early summer of 2013 and the saline SGD flow of nutrients during the late summer, early fall of 2013.

The average SGD for sandy sediments in Quonochontaug Pond is 5 liters/m^2/day (Moran et al., 2013). This is comparable to that for Ninigret Pond but considerably lower than that for Point Judith and Winnapaug Ponds (Moran et al., 2013). This rate is definitely in the lower range of values quoted by Knee and Paytan (2011). The average DIN concentration of minipiezometer well water from the 25 inch depth in sandy sediments at the northern edge of Ninigret Cove (MP-2A) is 465 ug/L (Table 1) for the period June to early September 2013. However, MP-2A has 30 ug/L ammonium and 320 ug/L nitrate for the September 06 sample date (Table 2). MP-2A is located at the shoreline (Figure 1) and probably represents the seepage interface between the land and the Cove. MP-3B and MP-4C are located offshore (Figure 1) and have different proportions of average ammonium and nitrate; 153 and 578 ug/L ammonium and 10 and 37 ug/L nitrate (Table 2). These concentrations are just the reverse of those at MP-2A. The low nitrate values for September 6, 2013 suggest that the water chemistry in MP-3B and MP-4C has undergone some transformation. Since salinity is very low (Table 2), mixing of fresh and recirculated Cove water does not appear to be a plausible process. Thus, either denitrification (loss of nitrate) or the production of ammonium (conversion of nitrate to ammonium, dissimilatory nitrate reduction to ammonium, DNRA) is occurring as water flows from MP-2A to MP-3B to MP-4C. Both of these processes are anaerobic, that is they occur in the absence of dissolved oxygen. A glance at Table 2 shows that there is a moderate dissolved oxygen concentration in these well waters. However, recent work has shown that anaerobic “hot spots” can exist in oxic sedimentary environments (Burgin et al., 2011).

Table 2. Concentration of Ammonium, Nitrate, Dissolved Oxygen, and Salinity in Minipiezometer Well Water Screened at 25 Inches at Three Sites Sampled on September 6, 2013.

Well Site	Ammonium, ug/L	Nitrate, ug/L	DO, mg/L	Salinity, ppt
MP-2A	30	320	4.9	0.1
MP-3B	153	10	2.1	0.1
MP-4C	578	37	4.0	0.1

In any case, using the above ammonium and nitrate data for the period June to early September 2013, the fresh SGD of DIN is calculated to be 0.506 Kg/3 mos (Appendix 2, #6). If we include the 38 inch well depth data for ammonium and nitrate (Appendix 1), then the average DIN concentration of well water from both the 25 and 38 inch depth in the sandy deposits is 1,254 ug/L (Appendix 2, #6). There is a lot more nitrate than ammonium at the 38 inch well depth in MP-2B, MP-3A, and MP-4B (Appendix 1, Table A). This suggests that most of the well water at the 38 inch depth originates as fresh water in the shallow aquifer. Using the above data from both well depths, the fresh SGD of DIN is calculated to be 1.363 Kg/3 mos. (Appendix 2, #6).

During the time period September 10 to October 31, 2013, rain was minimal and the proportion of ammonium and nitrate at the offshore minipiezometer wells MP-3B and MP-4C indicated that this well water was composed mostly of recirculated Ninigret Cove water. That is, very low nitrate (20 ug/L) and very high ammonium (690 ug/L) (Table 1). In addition, the drive-point profiles taken at MP-4 (9/16/2013) and MP-3 (10/28/2013) showed that saline water penetrated to 18 inches (MP-4) and 12 inches (MP-3) during the above time period (Figure 4A). For the above minipiezometer wells screened at 25 inches, the average DIN concentration was 713 ug/L (Appendix 2, #7). The average drive-point DIN concentration was 852 ug/L with ammonium accounting for most of this concentration. So, minipiezometer well water screened at 25 inches and sampled for the two “dry” months yielded a saline SGD-DIN value of 0.40 Kg/2 mos. And, the drive-point porewater for these two “dry” months yielded a saline SGD-DIN value of 0.48 Kg/2 mos. Thus, the average saline SGD of DIN is 0.44 Kg/2 mos.

Converting the range of fresh SGD of DIN to Ninigret Cove, 0.51 to 1.37 Kg/3 mos., to a yearly value (10 months of the year) results in an annual fresh SGD of DIN of 1.69 to 4.54 Kg/Yr. Adding these values to the saline SGD of DIN to Ninigret Cove (0.44 Kg/2 mos.), the total groundwater SGD of DIN varies from 2.14 to 4.97 Kg/Yr (Figure 5A). Taking all the DIN inputs to Ninigret Cove (Figure 5A), groundwater represents between 2.2 and 5.1 percent.

The final mass balance term for DIN is the export of dissolved inorganic nitrogen from Ninigret Cove to the eastern basin of Quonochontaug Pond (Figure 5A). Details of the calculation for this term are given in Appendix 2, number 13. The most important aspect of this calculation is that the average DIN concentration of Ninigret Cove water is 72 (+/-7) ug/L, while the average concentration of DIN in waters of the eastern basin of Quonochontaug Pond is 69 (+/-10) ug/L (**http://www.saltpondscoalition.org/monitoring.html**). The reason for this difference probably relates to the the large load of DIN contributed by surface-water inflow (Ninigret Cove Brook). The average concentration of DIN in surface water (Ninigret Cove Brook) is 1,112 (+/- 272) ug/L and that for shallow groundwater is 1,254 (+/- 508) ug/L. These concentrations of DIN are not very different. What is different is the annual flow of surface water and shallow groundwater into Ninigret Cove; 40.1x10^6 liters/yr for surface water and 4.0x10^6 liters/yr for shallow groundwater. Thus, the ratio of surface water to shallow groundwater flow is 10:1 and the ratio of surface water to shallow groundwater DIN flux is 11:1 (Figure 5A).

DIP Mass Balance

Figure 5B is a schematic diagram showing the mass inputs and outputs of dissolved inorganic phosphorus (DIP) for the Ninigret Cove water column using data accumulated during this study in the summer and fall of 2013 (Appendix 1 and 2) and other data for Quonochontaug Pond (Callender, 2013). The largest single term of the DIP mass balance is the benthic flux of dissolved inorganic phosphorus. The next largest term is the sedimentation of phosphorus. It should be noted that the sedimentation term is smaller than the benthic flux term, a situation that is not possible over the long term, say an annual cycle. The benthic flux of phosphorus was measured on an incubated core taken from muddy sediments in Ninigret Cove in early September 2013. As is the case for DIN, the benthic flux of phosphorus is applied for a three-month period (July-September) when water temperatures are highest (21 degrees C) and dissolved oxygen is lowest (6 mg/L) (Appendix 2, #10). Sediment cores taken at the end of October 2012 from Quonochontaug Pond and incubated for several days showed that no phosphorus was released to the core-top water. In fact, phosphorus was adsorbed to oxidized surface sediment. So, throughout most of the year, lower water temperatures and higher dissolved oxygen concentrations result in the sequesterization of phosphorus within benthic sediment.

While surface-water input of DIP is larger than the atmospheric input, they are both small terms for the DIP mass balance. In particular, surface-water DIP input is much less important than that for DIN, 2% versus 42% (Figure 5A,B). Export of DIP from Ninigret Cove to the eastern basin of Quonochontaug Pond is 50% of outputs while that of DIN is 19%. One wonders if recirculated Ninigret Cove water is a possible cause of this situation as the difference between NInigret Cove water and the eastern basin of Quonochontaug Pond is 10% for DIP and 4% for DIN (Appendix 2, #13). More importantly, drive-point profiles of ammonium (essentially all of the DIN) and phosphate (DIP) show that the concentration increase of DIP is substantially greater than that for DIN (ammonium) in the upper 20 inches of the sandy sediments sampled during the “dry” months (Figure 4B,C). That is, a 10-fold increase in DIN and up to a 34-fold increase in DIP.

There is no difference in the fresh SGD of DIP for wells screened at 25 inches and those screened at 38 inches, 0.008 Kg/3 mos. (Appendix 2, #8). Thus, the annual fresh SGD of DIP to Ninigret Cove is 0.025 Kg/Yr (Appendix 2, #8). The DIP concentrations for MP-3B and MP-4C (both screened at 25 inches) sampled in the middle of the “dry” month (October 2013) are so low (4 ug/L) that the saline SGD of DIP for these wells is insignificant (0.002 Kg/2 mos.) (Appendix 2, #9). On the other hand, the drive-point profiles of phosphate (DIP) show high concentrations for the two “dry” months (September and October 2013), resulting in a saline SGD of DIP of 0.051 Kg/2 mos (Appendix 2, #9). Thus, the groundwater input of DIP to Ninigret Cove is 0.08 Kg/Yr (Figure 5B). Taking all the DIP inputs to Ninigret Cove (Figure 5B), groundwater represents 0.5 percent.

Comparison Between this Study and that of Moran et al.(2013)

In the summer 0f 2013, Moran et al. (2013) published a paper on submarine groundwater discharge (SGD) of inorganic nitrogen and phosphorus to the Coastal Ponds of Southern Rhode

Island. The Ninigret Cove groundwater study (Quonochontaug Pond) described in this manuscript began in June of 2013 and continued to early December 2013. Moran et al. (2013) sampled three sites in Quonochontaug Pond in August and October of 2007. Their site A is located in the northeast corner of Quonochontaug Pond, their site B in shady-harbor Cove just southwest of site A, and their site C was located at the northern edge of Harmonic Cove (Moran et al., 2013, Fig. 1). Ninigret Cove is located approximately 1 km southwest of their site B. It would be instructive to compare the SGD data of Moran et al. (2013) with that for Ninigret Cove since both studies used similar sampling techniques.

Table 3 gives the average DIN and DIP data for sampling depths at three sites in Quonochontaug Pond (Moran et al., 2013) and three sites in Ninigret Cove (this study).

Table 3. Average DIN and DIP concentrations at Moran et al. (2013) and Callender (this ms.) in shallow groundwater from Quonochontaug Pond. SGD-DIN and SGD-DIP fluxes were calculated by Callender using the average SGD for Quonochontaug Pond (Moran et al., 2013) and the average DIN and DIP concentrations listed in Table 2.

Site	Sample Depth, in.	DIN, ug/L ave., sdev.	DIP, ug/L ave., sdev.	SGD-DIN mmN/m2/yr	SGD-DIP mmP/m2/yr	House Den. houses/ha
A*	8,16	558, 151	80, 97	73	4.3	1.0
B*	8,12,16,20	204, 78	17, 23	27	1.6	1.7
C*	8,12,20,25	812, 471	64, 53	106	3.8	2.0
Nin. Cove**	25,38,44	1,060, 489	6, 5	138	0.35	1.1
Nin. Cove	DP-6,12,18	540, 382	33, 28	70	1.9	1.1
Nin. Cove	DP-6,12,18, 24,30	637, 405	87, 76	83	5.1	1.1

* Moran et al., 2013
** This Study
ave.= average; sdev.= standard deviation
mm= millimole
House Den.= housing density
ha= hectare
DP= drive point

It can be seen from Table 2 that, in general, DIN concentrations in Moran et al. (2013) for sites A and C fall within the range of DIN concentrations for the Ninigret Cove groundwater study (this study). Moran's sample depths were sampled twice in the late summer and fall of 2007 while this study sampled three minipiezometer-well clusters three to five times from June to October 2013. In addition, the drive-point profiles of DIN and DIP were taken in mid-September and late October 2013. Moran site B is located in Shady Harbor Cove which is about 1 km northeast of Ninigret Cove. However, the average DIN and DIP concentrations are considerably lower than those in Ninigret Cove.

In summary, if we take all the DIN and DIP groundwater data in Moran et al. (2013) and compare it with the data from this study, we get the following comparison as listed in Table 4.

Table 4. Summary table of DIN and DIP concentrations in groundwater from Quonochontaug Pond and the calculated SGD-DIN and SGD-DIP fluxes.

Study	Year Sampled	Months	Depth, inches	Ave. DIN, ug/L	Ave. DIP, ug/L	SGD-DIN, mmN,m2/yr	SGD-DIP, mmP/m2/yr
Moran et al., 2013	2007	August, October	8-25	392(336)	34(43)	31-62	1-2
This Study	2013	June-October	6-38	1,010(691)	20(40)	132-210	1.2-2.3

Number is parenthesis is standard deviation
mm= millimole

While the DIP shallow groundwater fluxes for Moran et al. (2013) and this study are very comparable, such is not the case for DIN groundwater fluxes into Quonochontaug Pond. Ninigret Cove appears to have significantly higher SGD-DIN fluxes (this study) than any of the other coves in Quonochontaug Pond (Moran et al., 2013). If we look at the nitrate and ammonium data from the two studies (this study, Table 1 and Appendix 1, Table A; Moran et al. 2013, Table 1), it is apparent that shallow groundwater in Ninigret Cove has considerably more nitrate, on the average, than other shallow groundwater in the Pond. For the 25 and 38 inch minipiezometer wells in Ninigret Cove, the average nitrate concentration is 1,034+/-809 ug/L. For all the sample depths at sites A-C in Quonochontaug Pond, the average nitrate concentration is 74+/-93 ug/L (Moran et al., 2013).

Finally, Moran et al. (2013) estimated that SGD-DIN input was 26% of all DIN inputs to Quonochontaug Pond. [Please note that this calculation included stream DIN input for Quonochontaug Pond from the Salt Ponds Coalition monitoring database]. A similar calculation of the DIN inputs to Ninigret Cove (Figure 5A) would estimate that SGD-DIN input was 2-5% of all DIN inputs to Ninigret Cove. These inputs included the benthic flux of ammonium, a term that was not included in the Moran et al. (2013) calculation. If we take the benthic flux of ammonium out of the total input of DIN to Ninigret Cove, then SGD-DIN would be 4-9% of all DIN inputs to Ninigret Cove. Even with deleting the benthic flux of ammonium, the percentage of SGD-DIN to DIN inputs to Ninigret Cove (9% maximum) is considerably smaller than that (26%) for Quonochontaug Pond as given by Moran et al. (2013) with the surface-water input from the Salt Ponds Coalition database.

Making the same calculation for phosphorus, the Ninigret Cove groundwater study estimated that SGD-DIP input was 0.5% of all DIP inputs (Figure 5B). Moran et al. (2013), with surface-water data from the Salt Ponds Coalition database, estimated that, for Quonochontaug Pond, SGD-DIP input was 9% of all DIP inputs. Again, if we delete the benthic flux of inorganic phosphorus from fine-grained Ninigret Cove bottom sediments, then the SGD-DIP input would be 16% of the total DIP input, a figure not drastically different than that of Moran et al. (2013).

Summary and Conclusions

In the Summer and Fall of 2013, the author and Mr. Richard Hosp conducted a hydrologic study of the Ninigret Cove watershed, Charlestown, Rhode Island.

This study included: (1) monitoring the flow and nutrient chemistry of Ninigret Cove Brook, the primary surface-water input to Ninigret Cove; (2) installing three clusters of minipiezometer wells, screened at 25, 38, 44 inches below the Cove bottom, and monitoring their water quality and nutrient chemistry; (3) monitoring the water quality and nutrient chemistry of Ninigret Cove's water column; and (4) monitoring rainfall in the watershed with an automatic recording rain gauge.

The lithology of Ninigret Cove's bottom sediments consists of medium sands, in the northern part of the Cove, grading into fine-grained, organic-rich muds that extend out to the mouth of the Cove.

Rainfall, which recharges the shallow groundwater aquifer, was quite variable during the study period, with 10.43 inches in June, 1.55 inches in July, 2.52 inches in August, 2.72 inches in early September, and 0.51 inches in October.

With these rainfall amounts, recharge of the shallow groundwater aquifer was sufficient to cause fresh groundwater discharge through the sandy sediments during the period June through August. Well MP-2A, screened at 25 inches and located at shoreline between the sandy bottom sediments and the land surface, had moderately high nitrate concentrations (404 ug/L) and moderately low ammonium concentrations (73 ug/L) during this period (Table 1).

However, low rainfall in most of September and all of October 2013 resulted in little recharge of the shallow aquifer with minimal fresh groundwater discharge through the upper 25 inches of sand deposits located offshore. During this period, brackish Ninigret Cove water recirculated through the offshore sands in response to tidal pumping. Wells MP-3B and MP-4C, screened at 25 inches and located offshore in sand deposits, had low nitrate concentrations (15 ug/L) and high ammonium concentrations (569 ug/L) during this low-rainfall period (Table 1).

Deeper well-screen depths (38 and 44 inches below the Cove bottom) always had high nitrate concentrations, 1,100 to 2,300 ug/L (except MP-4A) (Appendix 1, Table A). On the other hand, ammonium shows a gradient in concentration from 145 ug/L at MP-2B to 82 ug/L at MP-3C to 32 ug/L at MP-4A (Appendix 1, Table A). It appears that some geochemical process is attenuating ammonium as deeper groundwater flows offshore.

Drive-point profiling the sandy sediments at the northern edge of Ninigret Cove for nutrients and salinity (Figure 4) was conducted at the MP-3 and the MP-4 well cluster sites during mid September and late October 2013, the low rainfall months. The vertical distribution of salinity, ammonium, and phosphate showed that Ninigret Cove bottom water penetrated the shallow sandy sediments to depths of 6 inches (MP-3) and 12 inches (MP-4) during this period (Figure 4). Below these depths to about 18 to 24 inches, recirculated Ninigret Cove water mixed with ambient fresh groundwater to produce intermediate concentrations of the above constituents.

A dissolved inorganic nitrogen (DIN) mass balance (Figure 5A) was constructed using the data from this study, data from the monitoring database of the Salt Ponds Coalition, and some previously published data on the water quality of Quonochontaug Pond (Appendix 2, #1-13). The major inputs of DIN to Ninigret Cove are surface water (Ninigret Cove Brook, Figure 1) and benthic flux of ammonium. These two inputs constitute 83% of all DIN inputs. Combined fresh and saline submarine groundwater discharge (SGD) of DIN constitute 5% of all DIN inputs. Sedimentation of nitrogen is the primary output. The other output is export of DIN from Ninigret Cove, calculated from 5 years of water-column DIN data for the eastern basin of Quonochontaug Pond. While the average concentration of DIN in the Ninigret Cove water column is the result of 10 samplings during the study period, statistics (standard deviation about the mean) lend some credence to this calculation.

The dissolved inorganic phosphorus mass balance for Ninigret Cove is presented in Figure 5B. The same caveats noted for the calculation of the DIN mass balance apply to the DIP mass balance except that the sedimentation of phosphorus term is calculated from a compilation of 13 references for the average concentration of phosphorus in coastal lagoon bottom sediments (Appendix 2, #12). Contrary to the DIN mass balance, surface-water input of DIP to Ninigret Cove is very small, only 2% of all DIP inputs. The benthic flux of phosphate from fine-grained bottom sediments is 97% of all DIP inputs (Figure 5B). This benthic flux represents an input for three summer months (July-September) and is larger than the annual sedimentation of phosphorus term (Figure 5B). However, taken over an annual cycle, benthic flux of DIP would be smaller in magnitude than phosphorus sedimentation. The observation concerning the export of DIN from Ninigret Cove applies to the export of DIP.

In the summer of 2013, Moran et al. (2013) published a paper concerning submarine groundwater discharge of dissolved inorganic nitrogen and phosphorus to the Coastal Ponds of Southern Rhode Island. Quonochontaug Pond was one of four coastal ponds studied. In order to compare their estimates with this study for SGD inputs of DIP and DIP to total inputs, this author has added the stream input term to their Table 4 (Moran et al., 2013). In addition, this author has removed the benthic flux term from the total inputs of DIN and DIP. Table 4 is a summary of the comparison between Moran et al. (2013) data for Quonochontaug Pond and that in this study of Ninigret Cove, an embayment to Quonochontaug Pond. Moran et al. (2013) calculated the SGD-DIN flux to be 31-62 mmN/m^2/yr while this study calculated the SGD-DIN flux to be 132-210 mmN/m^2/yr. If we use just the 25 inch wells (Table 1), then our SGD-DIN flux would be 61 mmN/m^2/yr, a value identical to Moran et al's. (2013) upper value. The SGD-DIP values from both studies are essentially the same, 1-2 mmP/m^2/yr (Table 4).

Considering the above, SGD-DIN input to ninigret Cove is 9% of all DIN inputs while SGD-DIN input to Quonochontaug Pond (Moran et al., 2013) is 26% of all DIN inputs. And, SGD-DIP input to Ninigret Cove is 16% of all DIP inputs while SGD-DIP input to Quonochontaug Pond is 9% of all DIP inputs.

It appears that there may be considerable variability in the importance that SGD inputs of DIN and DIP play with the nutrient economy of Rhode Island's coastal salt ponds. Future studies of shallow groundwater input to these water bodies should consider multiple sites of investigation as evidenced by the study of Moran et al. (2013).

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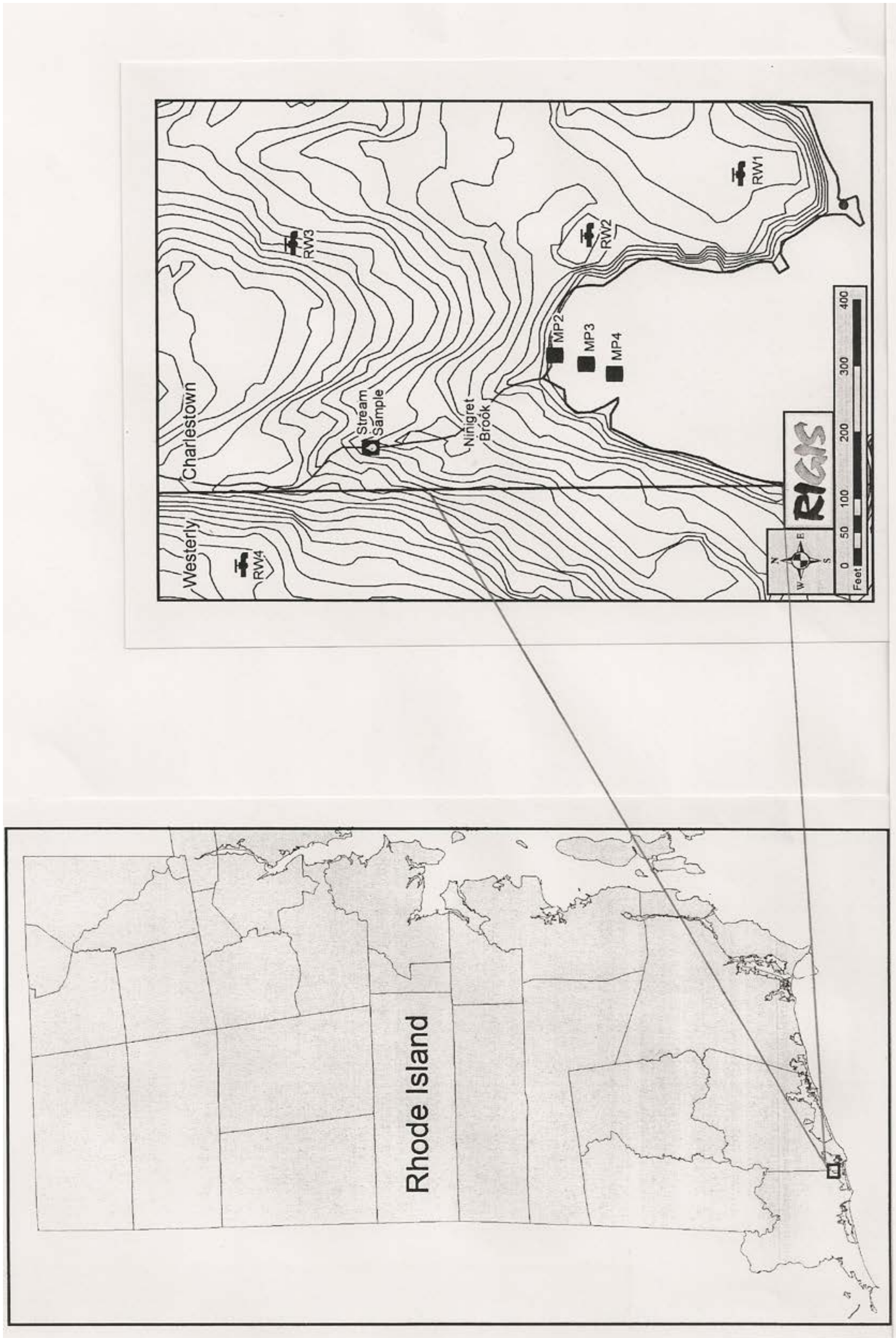

Figure 1. Study site in Ninigret Cove, an embayment on the northeast shore of Quonochontaug Pond. Minipiezometer wells were installed at MP2 (25 and 38 inch depth), MP3 (25, 38, and 44 inch depth), and MP4 (25, 38, and 44 inch depth). RW1-4 are residential wells in the Ninigret Cove watershed. Stream sample is the approximate location on Ninigret Cove Brook where flow was measured and nutrients sampled.

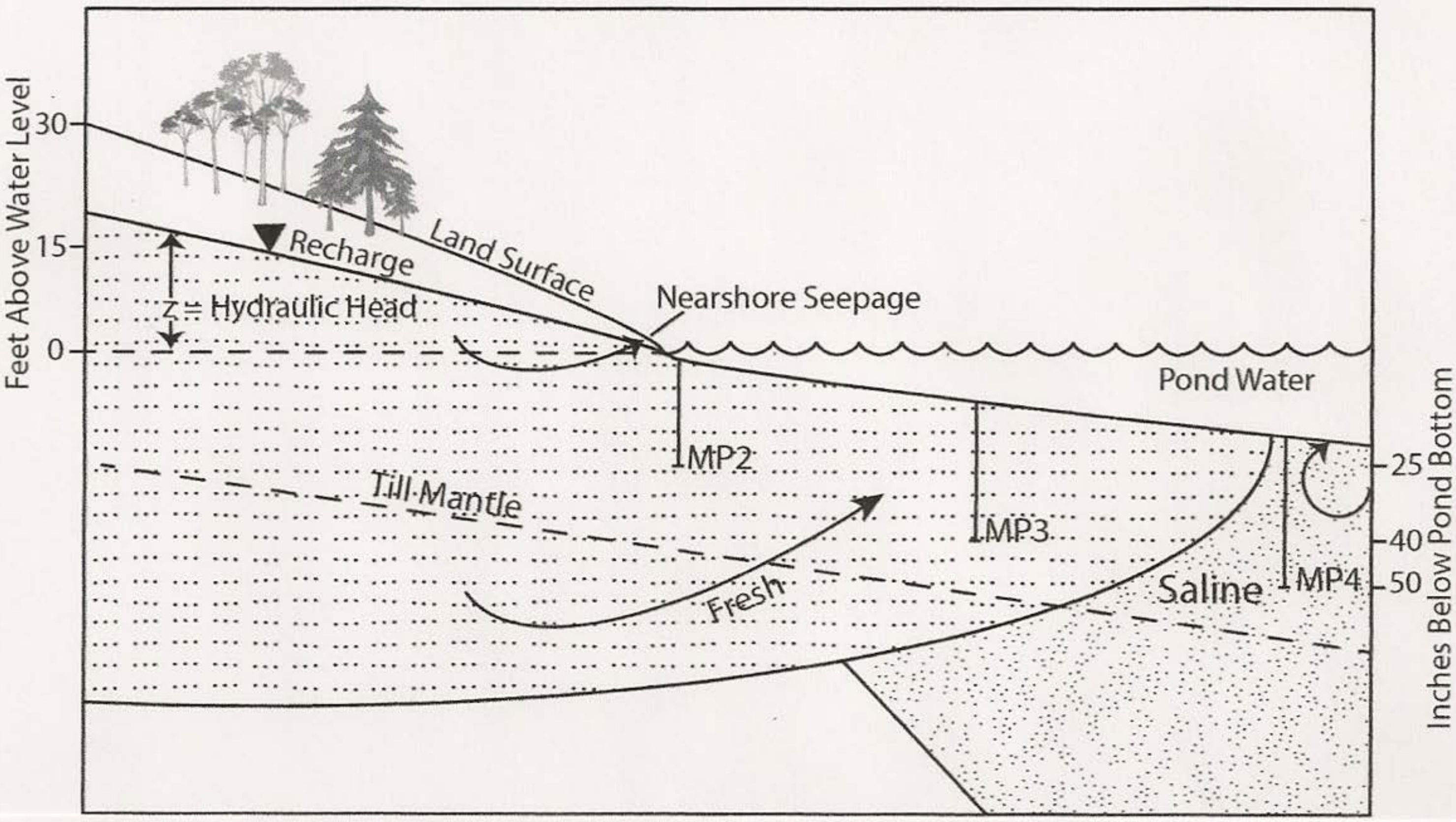

Figure 2. Schematic cross-sectional diagram of submarine ground water discharge (SGD) as depicted for the Ninigret Cove groundwater study. The till mantle line is the estimated depth of rock encountered at the bottom of the deepest auger holes. The hydraulic head is estimated from topographic elevations and logging of auger holes on land. The interface between fresh and saline groundwater is estimated from salinity of minipiezometer well water and drive-point profiles.

Schematic Diagram Showing the Amounts of Rain Falling on the Ninigret Cove Watershed, June to December 2013.

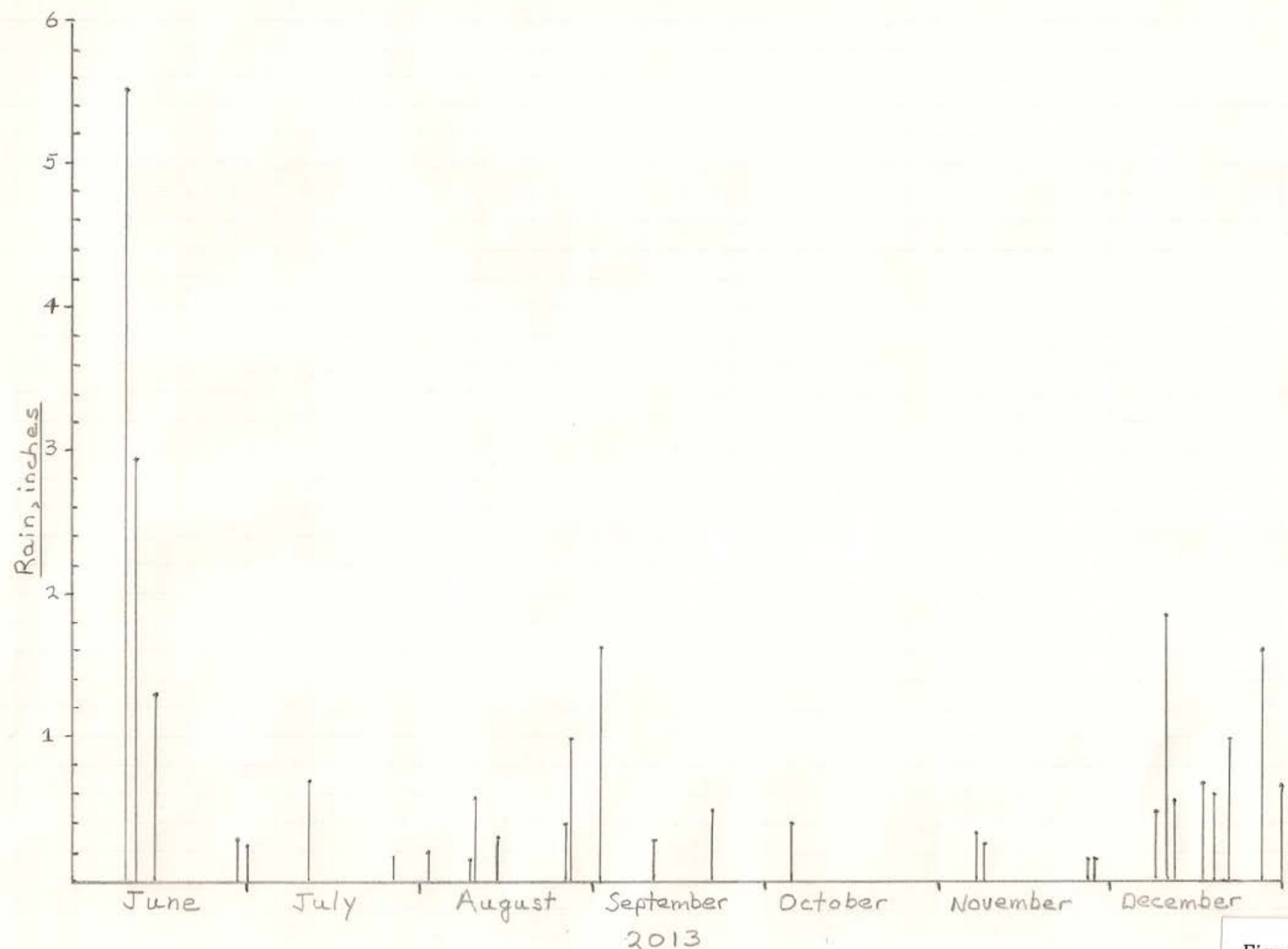

Figure 3

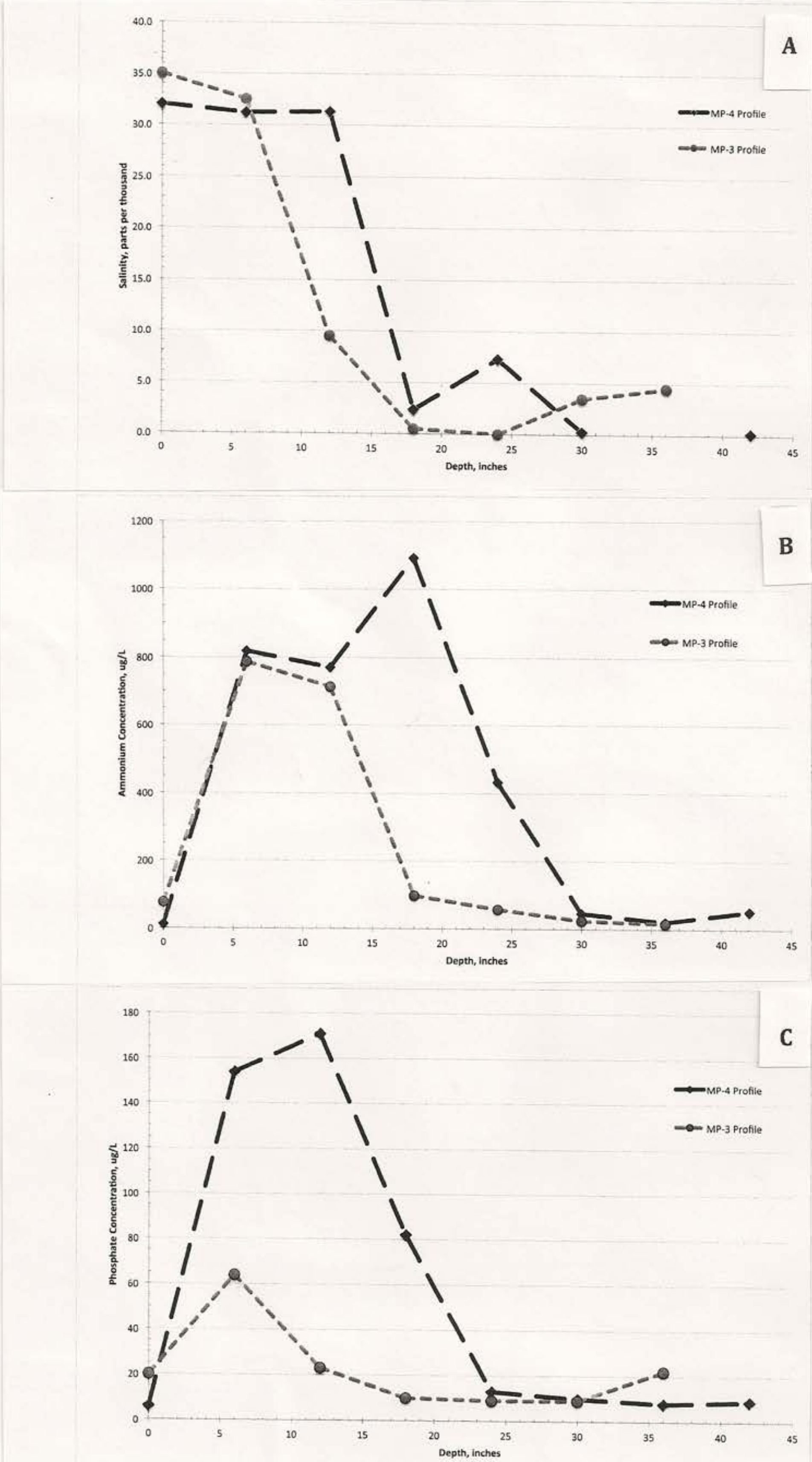

Figure 4. Drive-Point profiles at minipiezometer well cluster sites MP3 (10/28/2013) and MP4 (9/16/2013) in Ninigret Cove. **A**-Salinity (ppt), **B**-Ammonium (ug/L), and **C**-Phosphate (ug/L).

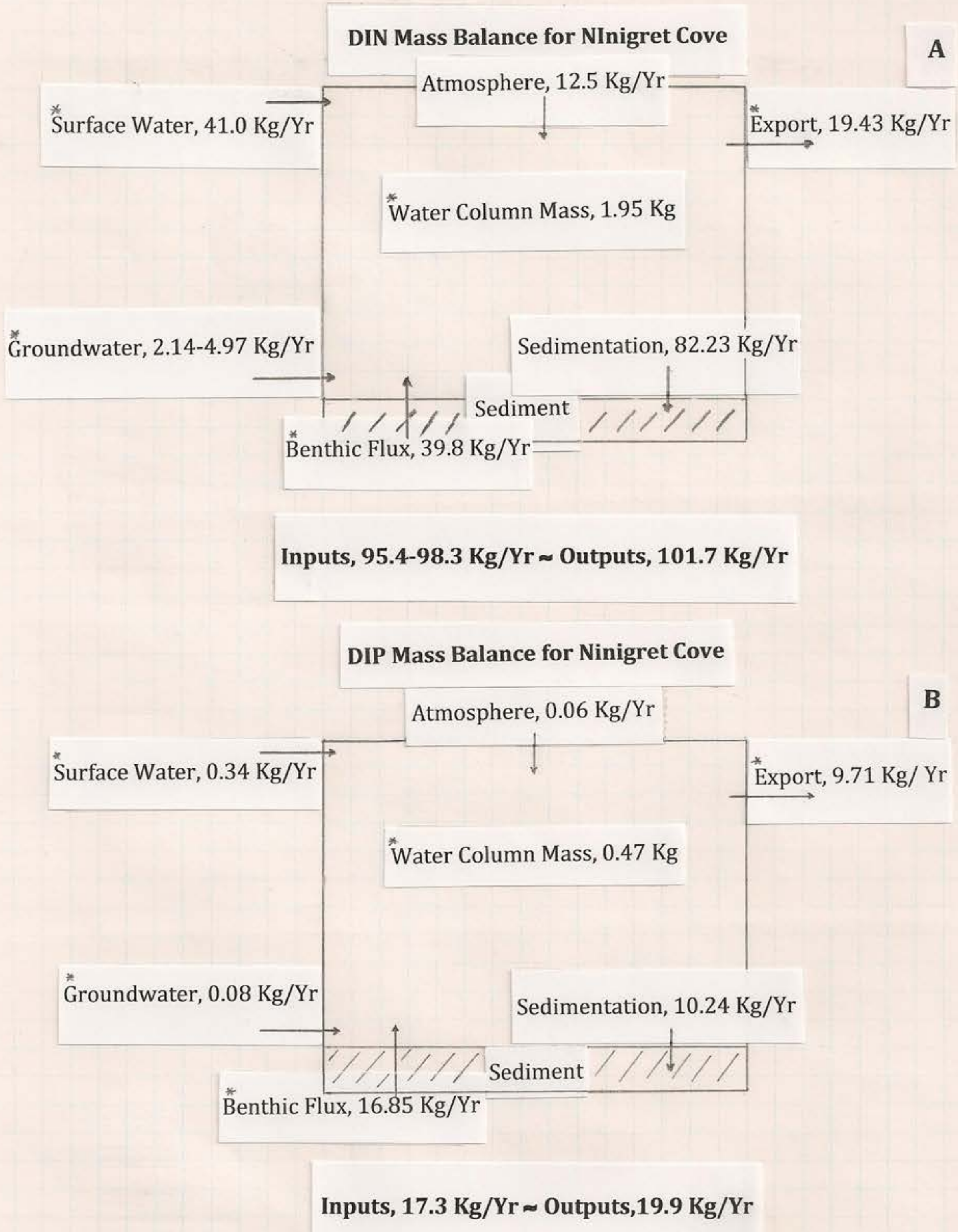

Figure 5. Schematic Box Diagrams of the Dissolved Inorganic Nitrogen (DIN) (A) and the Dissolved Inorganic Phosphorus (DIP) (B) Mass Balances for Ninigret Cove, Quonochontaug Pond, Charlestown and Westerly, Rhode Island. Terms marked with stars are derived mostly from data accumulated during the Ninigret Cove Groundwater Study and those with no stars are derived from published reports.

Appendix 1

Table A. Ammonium, nitrate, phosphate, dissolved oxygen, and salinity concentrations in Ninigret Cove minipiezometer wells screened at 38 and 44 inches below the Cove bottom.

Well	Date	Ammon., ug/L	Nitrate, ug/L	Phos., ug/L	DO, mg/L	Salinity, ppt	Screen Depth, in.
MP-2B*	8/01/2013	155	1,300	4	nd	nd	38
	8/05/2013	96	1,245	11	5.0	0.0	
	9/06/2013	48	1,566	2	5.0	0.1	
	10/17/2013	279	1,484	1	4.7	4.5	
MP-3A**	6/20/2013	74	2,851	5	3.7	4.5	38
	7/22/2013	17	2,138	11	4.6	0.2	
	8/05/2013	15	2,090	15	4.0	0.1	
	9/06/2013	6	1,910	1	4.0	0.1	
	10/17/2013	11	1,832	2	3.9	0.2	
MP-4B***	8/01/2013	32	1,283	7	nd	nd	38
	8/05/2013	73	790	9	1.9	0.2	
	9/06/2013	15	1,254	2	2.2	0.0	
	10/17/2013	40	367	7	1.0	6.6	
MP-3C**	9/06/2013	101	2,296	4	3.4	0.0	44
	10/17/2013	78	1,872	5	1.9	8.6	
	12/03/2013	66	2,297	7	3.3	3.0	
MP-4A***	6/20/2013	26	48	5	1.2	3.5	44
	7/22/2013	43	9	3	1.3	0.2	
	8/05/2013	32	15	8	1.5	0.2	
	9/06/20131	28	12	6	1.9	0.1	
	10/17/2013	30	92	8	1.6	0.3	

* Shoreline, ** Eighty feet offshore, *** One hundred fifty feet offshore
Ammon.= Ammonium

Phos.= Phosphate
DO= Dissolved oxygen
ppt= Parts per thousand
in.= Inches; nd= no data

<u>Appendix 2- Pertinent Data and Calculations</u>

1. Surface Areas

* Quonochontaug Pond- $3.0x10^6$ m^2
* Ninigret Cove Watershed- $3.55x10^5$ m^2
* Ninigret Cove- 12,620 m^2
* Ninigret Cove sand area- 2,220 m^2
* Ninigret Cove mud area- 10,400 m^2

2. Volumes

* Quonochontaug Pond- $5.4x10^6$ m^3
* Ninigret Cove- $9.3x10^3$

3. Ninigret Cove Brook Flow

Month of 2013	Flow, Liters/Month
May	4.29x10
June, 1st half month	6.48x10
June, 2nd half month	$3.11x10^6$
July	$3.0x10^6$
August, 1st half month	$0.5x10^6$
August, 2nd half month	1.16x10
September, 1st half month	2.38x10
September, 2nd half month	$1.11x10^6$
October	1.02x10
November	1.76x10
December	1.90x10

4. <u>DIN and DIP Mass Input to Ninigret Cove from Ninigret Cove Brook</u>

Month	DIN, ug/L	DIN Mass,Kg/Mo.	DIP, ug/L	DIP Mass,Kg/Mo.
May	1,185	5.1	10	0.043
June, 1st half	1,238	8.0	16	0.104
June, 2nd half	1,435	4.5	5	0.016
July	1,255	3.8	6	0.018
August, 1st half	441	0.2	16	0.008
August, 2nd half	1,025	1.2	7	0.008
Sept., 1st half	1,240	3.0	7	0.017
Sept., 2nd half	1,175	1.3	2	0.002
October	805	0.8	33	0.034
November	1,184	2.1	6	0.011
Dec., 1st half	1,251	2.4	4	0.008
TOTAL		32.4 Kg/7.5 mos.		0.269 Kg/7.5 mos.

5. <u>Atmospheric Input of DIN and DIP</u>
Callender (2013), using atmospheric deposition data for ammonium and nitrate at Avery Point, Connecticut (Nadim and others, 2001), estimated the annual nitrogen deposition rate for Quonochontaug Pond (2,964 Kg/Yr). The ratio of the surface area of Ninigret Cove (12,620 m^2) to that of Quonochontaug Pond (3,000,000 m^2) is 0.0042, which when multiplied by the Quonochontaug Pond atmospheric deposition rate gives the atmospheric deposition rate for Ninigret Cove, 12.5 Kg/Yr.

Callender (2013) estimated the dissolved phosphorus atmospheric deposition rate for Quonochontaug Pond to be 14 Kg/Yr. When this rate is multiplied by the above ratio of surface areas (0.0042), the atmospheric deposition rate of DIP for Ninigret Cove is calculated to be 0.06 Kg/Yr.

6. <u>Fresh Submarine Groundwater Discharge (SGD) of DIN</u>
The average SGD for Quonochontaug Pond is 5 liters/m^2/day (Moran et al., 2013).
The average DIN concentration of minipiezometer well water from the 25 inch depth in the sandy deposits at the northern end of Ninigret Cove is 465+/-475 ug/L (Table 1) for the period June to early September 2013.
Thus, the SGD of DIN through these sandy deposits for June-July-August is:
(5 liters/m^2/day)(465 ug/L)(98 days)= 2.28×10^5 ug/m^2/3 mos.
using the surface area of the sandy sediments in Ninigret Cove (2,220 m^2), then the SGD input of DIN for 3 mos. is 0.506 Kg.

If we include the 38 inch minipiezometer well water DIN data (Appendix 1, Table A), then the average DIN concentration of well water from both the 25 and 38 inch depth in the sandy deposits is 1,254+/-1,016 ug/L.
Thus, the SGD DIN through these sandy sediments for June-July-August is:
(5 liters/m^2/day)(1,254 ug/L)(98 days)= $6.14x10^5$ ug/m^2/3 mos.
using the above surface area, then the SGD input of DIN for 3 mos. is 1.363 Kg.

The range of fresh SGD of DIN from sandy deposits in Ninigret Cove for the period June 1 to September 6, 2013 is 0.51 to 1.36 Kg. For the year, this range is 1.70 to 4.53 Kg when we multiply the three-month range by 3.33 mos./yr.

7. Saline Submarine Groundwater Discharge (SGD) of DIN
During the time period September 10 to October 31, rain was minimal (1.15 inches) and the proportion of ammonium and nitrate changed at minipiezometer wells MP-3B and MP-4C. In addition, the drive-point profiles of ammonium, nitrate, and salinity taken at MP-4 (9/16/2013) and MP-3 (10/28/2013) showed that saline water penetrated the sandy deposits to a depth of 18 inches (MP-4) and 12 inches (MP-3) (Figure 4).

For the minipiezometer wells MP-3B and MP-4C, the average DIN concentration was 713+/-203 ug/L with 704+/-200 ug/L ammonium and 9+/-4 ug/L nitrate.

The drive-point DIN data (September 16 and October 28) averaged 852+/-148 ug/L with ammonium making up most of the DIN concentration, 837+/-137 ug/L. The ammonium to nitrate ratio for these two “dry” months was between 60:1 and 78:1 while this ratio for the three previous “wet” months was 0.9:1.

Therefore, minipiezometer well water at the 25 inch depth for the two “dry” months yielded a SGD-DIN value of 0.40 Kg/2 mos. And, the drive-point pore water for these two “dry” months yielded a SGD-DIN value of 0.48 Kg/2 mos. Thus, the average saline SGD of DIN is calculated to be 0.44 Kg/2 mos.

8. Fresh SGD of DIP
Following a similar reasoning for dissolved inorganic phosphorus (DIP) as that for DIN yields the following data:
Fresh SGD-DIP, 25 inch depth: (5 liters/m^2/day)(7 ug/L DIP)(2.220 m^2)(98 days)= 0.008 Kg/3 mos.
Fresh SGD-DIP, 25 and 38 inch depth: (5 liters/m^2/day)(6.8 ug/L DIP)(2.220 m^2)(98 days)=0.007 Kg/3 mos.
Therefore, the average fresh SGD of DIP= 0.0075 Kg/3 mos. = 0.025 Kg/Yr.

9. Saline SGD of DIP
The minipiezometer wells MP-3B and MP-4C (25 inch depth) and MP-3A and MP-4B (38 inch depth) have an average DIP concentration of 4.0+/-2.2 ug/L for the sampling time 10/17/2013, a “dry” month. This concentration results in an insignificant saline SGD of DIP, 0.002 Kg/2 mos.

The drive-point profiles of phosphate (DIP) (Figure 4C) have average concentrations of 136+/-47 ug/L on 9/16/2013 (MP-4, 6-18 inches) and 44+/-29 ug/L on 10/28/2013 (MP-3, 6-12 inches). Taking the average of these two concentrations, we calculate the saline SGD of DIP for the two "dry" months to be: (5 liters/m^2/day)(90 ug/L DIP)(2,220 m^2)(52 days)= 0.052 Kg/2 mos.

10. <u>Benthic Flux of Ammonium and Phosphate</u>
We must consider the benthic flux of ammonium and phosphate from organic-rich fine-grained muds that occupy 82% of the bottom sediments of Ninigret Cove. In early September 3013, a sediment core was taken from these muds, incubated under dark conditions (minimum exposure to light) and ambient temperature, and core-top water was stirred and sampled twice daily. The resultant benthic flux of ammonium was 42.5 mg/m^2/day. This rate was determined after 20.5 hours of incubation when the dissolved oxygen in well-stirred core-top water was 6.0 mg/L. The benthic flux of ammonium into the Ninigret Cove water column is:
(42.5 mg/m^2/day)(10,400 m^2)(90 days/yr) = 39.8 Kg NH_4^+/Yr

The resultant benthic flux of phosphorus (phosphate) as measured on the sediment core incubated in early September 2013 was 18 mg/m^2/day. This rate was also determined after 20.5 hours of incubation when the dissolved oxygen on well-stirred core-top water was 6.0 mg/L. The benthic flux of phosphate into the Ninigret Cove water column is:
(18 mg/m^2/day)(10,400 m^2)(90 days/yr) = 16.85 Kg PO_4^{3-}/Yr

The 90-day time period for the above Ninigret Cove sediment core incubation represents the months July-August-September. The table below, which gives the average bottom-water temperature and dissolved oxygen for the eastern basin of Quonochontaug Pond, shows why these three months were chosen.

Month	May	June	July	August	September	October
Temp,deg.C	12.7+/-0.6	17.1+/-1.3	21.0+/-0.7	21.5+/-0.5	19.9+/-0.6	16.1+/-2.5
DO, mg/L	8.0+/-0.5	6.6+/-0.3	6.1+/-1.0	6.3+/-0.6	5.8+/-0.6	6.9+/-0.4

May, June, and October had the coldest temperatures of the six-month period, 15.3+/-2.3 degrees C. These same months had an average bottom-water DO of 7.2+/-0.7 mg/L, compared to the average DO for July-August-September, 6.0+/-0.2 mg/L. Thus, the months of July-September had the warmest bottom-water temperatures (20.8+/-0.8 degrees C) and the lowest bottom-water dissolved oxygen (6.0+/-0.2 mg/L). Such conditions were most suitable for the bacterial breakdown (mineralization) of sedimentary organic matter.

11. <u>Mass of DIN and DIP in the Ninigret Cove Water Column</u>
The volume of the upper meter of the water column is 12,620 m^3, or 12.6x10^6 liters.
The concentration of DIN in the upper meter of water is 18 ug/L. Thus the mass of DIN in the upper meter of the water column is:
(12.6x10^6 liters)(18 ug/L)= 226.8x10^6 ug DIN= 0.227 Kg DIN

The volume of deeper waters in Ninigret Cove is 20,800 m^3 = 20.8x10^6 liters.
The concentration of DIN at 2 meters depth in the Ninigret Cove water column is 83 ug/L. Thus the mass of DIN in the deeper water column is:
(20.8x10^6 liters)(83 ug/L)= 1,726x10^6 ug DIN= 1.726 Kg DIN
Therefore, the total mass of DIN in the Ninigret Cove water column is 1.95 Kg DIN

The mass of DIP in the Ninigret Cove water column is as follows:
DIP concentration of surface water is 6 ug/L; DIP concentration of bottom water is18 ug/L
Therefore, the mass of DIP in the upper water column is:
$(12.6x10^6$ liters)(6 ug/L)= 0.099 Kg DIP
And, the mass of DIP in the deeper water column is:
$(20.8x10^6$ liters)(18 ug/L)= 0.374 Kg DIP
The total mass of DIP in the Ninigret Cove water column is 0.47 Kg DIP

12. Sedimentation of Nitrogen and Phosphorus to Ninigret Cove Bottom Sediment
The sedimentation rate of fine-grained sediments in Quonochontaug Pond is 0.125 $gm/cm^2/yr$ (Ford, 2003) and using the surface area of fine-grained sediments in Ninigret Cove (see below), the annual mass sedimentation rate of these muds is 13,000 Kg/Yr. The average weight % of organic carbon of fine-grained Quonochontaug Pond sediments is 5.9 and the C/N ratio is 9.3 (Ford, 2003). The surface area of these fine-grained sediments in Quonochontaug Pond is $12.9x10^5$ m^2 (Ford, 2003). Therefore the annual mass sedimentation of nitrogen for Quonochontaug Pond is:
(0.125 $gm/cm^2/yr$)(5.9%)(9.3)($12.9x10^9$ cm^2)= $0.0102x10^9$ gm N/Yr= 10,200 Kg N/Yr.

Using the ratio of the surface area of fine-grained bottom sediments in Ninigret Cove to that for Quonochontaug Pond (0.0081), the annual sedimentation of N in Ninigret Cove bottom sediments is 82.23 Kg.

The estimation of the phosphorus sedimentation rate for the fine-grained Ninigret Cove bottom sediments is as follows:
a. Average total phosphorus concentration of fine-grained sediment (muds) in Coastal Lagoons is:
weight %= 0.057+/-0.021 (7 references)
mg/kg= 570+/-361 (4 references)
mg $P/m^2/yr$= 1,529+/-337 (2 references)
b. Phosphorus Sedimentation Rate is:
(0.00057)(13,000 Kg sed/yr)= 7.41 Kg P/Yr
(570 mg P/kg sed)(13,000 Kg sed/yr)= 7.41 Kg P/Yr
(1,529 mg $P/m^2/yr$)(10,400 m^2 sur.area muds)= 15.90 Kg P/Yr

Therefore, the average sedimentation rate of phosphorus in Ninigret Cove fine-grained bottom sediments is 10.24 Kg P/Yr.

13. Export of DIN and DIP from Ninigret Cove to the Eastern Basin of Quonochontaug Pond
Semidiurnal tides occur in the eastern basin of Quonochontaug Pond, 1.9 times per day.
R. Hosp, who lives on the northeast shore of Ninigret Cove, estimates that the average monthly tidal range for Ninigret Cove is 29 inches (74 cm). This includes spring and neap tides.
The volume of water exchanged between the eastern basin of Quonochontaug Pond and Ninigret Cove is:
(12,620 m^2, sur. area of Ninigret Cove)(0.74 m) = 9,339 m^3 =$9.339x10^9$ cm^3 = $9.339x10^6$ liters.
The average DIN concentration of the Ninigret Cove water column is 72+/-7 ug/L
The average DIN concentration of the eastern basin of Quonochontaug Pond water column is 69+/-10 ug/L.
Therefore, the export of DIN across the mouth of Ninigret Cove is:
(72-69 ug/L)($9.339x10^6$ liters)(1.9 tidal cycles/day)(365 days/yr) = $19.430x10^6$ ug DIN/yr=

19.43 Kg DIN/Yr.

The average DIP of the Ninigret Cove water column is 16+/-7 ug/L and the average DIP of the eastern basin of Quonochontaug Pond water column is 14.5+/-3 ug/L.
The export of DIP across the mouth of Ninigret Cove is:

(16.0-14.5 ug/L)(9.339×10^6 liters)(1.9 tidal cycles/day)(365 days/yr)= 9.715×10^6 ug DIP/yr= 9.71 Kg DIP/Yr.