NYSG Completion Report Instructions & Required Format

Please include the following information for your project. The text of this report should be at least 5-8 pages and be composed for an audience of your peers. Other formats, or reports with incomplete sections, will not be accepted. The expectation is that information or material will be provided under each section.

Report Written By: _Caitlin Young________ Date: ___2-10-14_________

A. Project Number and Title: R/CTP-44-NYCT '*Sources and Fate of Nitrogen in North Shore Embayment's*

Project Personnel:
Dr. Gilbert Hanson, Principal Investigator
Dr. Teng-Fong Wong, Co- Principal Investigator
Caitlin Young, NYSG Scholar
Neal Stark, Senior Research Support Specialist
Josephine Durand, Graduate Research Assistant
Ron Paulsen, Suffolk County Department of Health Services Personnel
Jonathan Wanlass, Suffolk County Department of Health Services Personnel

B. Project Results::

C1. Meeting the Objectives:

Objective 1. Following a grid of transects, as shown in figure 1, use a combination of temperature and resistivity measurements to estimate the amount of groundwater entering Port Jefferson (PJH) and Stony Brook Harbors (SBH) using the Trident probe and SuperSting resistivity.

1. Results: Resistivity and Trident transects were performed in SBH (April 2011, August 2011) and in PJH (March-April 2012). Overall Trident surveys indicated a pattern spatially heterogeneous diffuse freshwater discharge along shoreline. Offshore locations did not exhibit freshening at the sampling depth of 60cm beneath the sediment water interface (see attached report, chapters 3 and 5).
   Resistivity transects in SBH and PJH revealed previously unknown freshwater plumes extending beneath the harbors for a distance of tens of meters offshore (see attached manuscript draft from Durand et al). These plumes are capped by a layer of marine mud which acts as an aquitard to offshore SGD. Inland hydraulic gradient due to steep topography of the embayment topography drives freshwater offshore.

Objective 2. Identify major plumes of groundwater entering Port Jefferson Harbor and Stony Brook Harbor. Sample within those plumes using a Trident probe. Use barge mounted Geoprobe to obtain sediment cores

2. Results: Using data from results of Objective 1, major groundwater plumes were identified in SBH and PJH. These plumes were the sites of further investigation, including porewater sampling. Due to sediment compaction, we were unable to obtain sediment cores offshore. Instead, cores were obtained in the intertidal and subtidal zones at SBH and analyzed for sediment composition (see chapter 3 in attached dissertation for full results). In PJH, a barge mounted Geoprobe was used to install permanent multi-level sampling wells that were used to take samples along two shore perpendicular transects; one located at Centennial Beach and one located in Belle Terre.

Objective 3. Identify any variations in SGD in the spring and fall periods following periods of highest and lowest recharge to the groundwater and how these impact overall nitrogen loading to the harbors.

3. Results: Variations in spring and fall periods were examined in SBH during 2011 and in PJH during 2012. Nitrate concentration data sets from May and October were analyzed by t-test to determine if a significant seasonal difference exists. October concentrations were found to be significantly higher ($p=0.007$), with an average concentration of 310µmol L^{-1}, as compared to 200µmol L^{-1} during May. During May maximum nitrate values are observed in at the high tide point but in October maximum nitrate values are observed in the fresh water zone at the base of the intertidal marsh, just prior to discharge. See attached dissertation chapter 3 'DENITRIFICATION AND NITRATE BIOGEOCHEMISTRY IN A SUBTERRANEAN ESTUARY OF STONY BROOK HARBOR' (figures 16d and 18d for an extended discussion of seasonal trend results)

    An additional study was performed to investigate nutrient dynamics in the subterranean estuary over two spring neap tidal cycles. This study found salinity and oxygen was consistently stratified over the spring-neap period, but nitrate and phosphate concentrations varied between the two periods. A large terrestrial hydraulic gradient resulted in a stable salinity depth profile despite daily two meter tidal oscillations. Fresh groundwater contained high concentrations of nitrate, averaging 6.3±2.7mgL-1NO3--N (450±193µmol L-1) at a depth of 9.1m. Maximum inorganic phosphate concentrations, averaged 0.13mgL-1 PO4-3-P (4.2µmol L-1), at sampling depth 1.8m. Mass balance models were used to estimate fresh and saline fractions of discharge during spring and neap tide periods. Spring tide discharge was estimated at 1.3 L min-1m-1 and 48.0 L min-1m-1 for freshwater and saltwater respectively. Neap tide discharge was estimated at 6.5 L min-1m-1 and 28.0 L min-1m-1 for fresh and saltwater respectively. These differences in salt vs fresh water factions of SGD resulted in water table over height during spring tide. Consequently, water-table over height causes migration of the freshwater discharge point along the beach face resulting in variation of nutrient concentrations. See attached dissertation chapter 2 'NUTRIENT DYNAMICS IN A SUBTERRANEAN ESTUARY OVER TWO SPRING-NEAP TIDAL CYCLES' for full report on this study.

Objective 4. Use piezometers to collect samples in the subterranean estuary. Transects will be 8-10 meters long, consisting of 10-15 sampling points with depth into the sediment ranging from 0-2m. Use these samples to define zones of salinity. Collect sub-bottom pore water samples to characterize the *in situ* nitrogen concentrations from the seawater sediment interface to a maximum depth of 60cm.

4. A total of 7 piezometer transects were completed during this study; 3 in SBH, 1 in Setauket Harbor and 3 in PJH. These samples were used to examine spatial and seasonal trends in nitrate discharge into three Long Island Sound Embayments. In SBH the coastal aquifer consisted of an upper saline plume, underlying freshwater zone and deep saline zone at the two piezometer transect locations. Denitrification rates were found to be spatially heterogeneous, with the percent of nitrate denitrified ranging 0 to 35% at low tide discharge points and up to 47% during transport to the embayment floor in offshore discharge zones. See attached dissertation chapter 3 'DENITRIFICATION AND NITRATE BIOGEOCHEMISTRY IN A SUBTERRANEAN ESTUARY OF STONY BROOK HARBOR' for a full discussion of these results. In PJH, piezometer profiles at Centennial beach revealed a freshwater discharge zone that outcrops at the beach surface at low tide. The lack of upper saline plume prevents incorporation of dissolved organic carbon and therefore reduces denitrification potential in this portion of the coastal aquifer. A second site in PJH was located in Belle Terre.

At this site the existence of an upper saline plume produced maximum denitrification rates in shallow sediments of the low tide zone.

Sub bottom porewater samples were collected in PJH and used in conjunction with a ^{222}Rn survey to estimate nutrient flux to the harbor during spring discharge time period. This study revealed three nitrogen input mechanisms to PJH via SGD; in the southern end of the harbor high porewater nitrate concentrations coincide with high ^{222}Rn concentrations, linking SGD with nitrate inputs that originate upgradient in the shallow aquifer. Along the east and north east harbor shoreline, low nitrate and high ^{222}Rn values were the result of harbor water circulation through sediments in the intertidal zone in a low density housing area, which limited the amount of nitrate entering the harbor from this portion of the coastal aquifer. Finally, the western shore of the harbor exhibited trends of low ^{222}Rn and low nitrate concentrations, indicating SGD was not a significant process along the western shore of PJH. In conclusion, nitrate inputs from SGD_{total} were estimated to be 800mol d^{-1} (11kg d^{-1}). Although this estimate is restricted to shoreline discharges of nitrate and does not account for input entering the harbor through offshore mud sediments, it is similar to the nitrogen input to the harbor from the Port Jefferson Sewage Treatment Plant (STP), which currently averages 12.2 kg N d^{-1}. Estimates of nitrate input to Port Jefferson Harbor (this study) are ~1.2% of total SGD nitrogen inputs to Long Island Sound from all of Suffolk County (Scorca and Monti, 2001). For a full description of this study, including tables and figures, please see chapter 5 in the attached dissertation 'EMBAYMENT SCALE ASSESSMENT OF SUBMARINE GROUNDWATER DISCHARGE NUTRIENT LOADING TO PORT JEFFERSON HARBOR, LONG ISLAND NY'.

Objective 5. Analyze all samples for nitrogen species, phosphate and major electron donors. Use this information to determine the major nitrate attenuation/generation processes.

5. Results: This process was performed throughout the study. See attached dissertation chapters 2-5 for a detailed report of nitrogen attenuation rates and mechanisms for SBH, PJH and Setauket Harbor

Objective 6. Integrate SGD survey data and geochemical data using GIS to generate maps for use by relevant authorities to create effective watershed management policies.

6. Results: SGD survey and geochemical data was made into maps for PJH as described above in dissertation chapter 5, 'EMBAYMENT SCALE ASSESSMENT OF SUBMARINE GROUNDWATER DISCHARGE NUTRIENT LOADING TO PORT JEFFERSON HARBOR, LONG ISLAND NY'. Given the restricted nature of piezometer transects, it was determined that data from SBH sampling was not applicable to harborwide mapping of SGD.

Objective7. Apply study results to existing nitrogen loading models and distribute study results via publication and at local and national conferences.

7. Results: Study results have been presented at numerous national and local conferences;

   2014: 'N_2O Formation Mechanisms in Sandy Unconfined Coastal Aquifers' Goldschmidt Geochemistry Conference June 8-13

   2013: 'Distribution of submarine groundwater discharge into Port Jefferson Harbor, Long Island Sound, NY' American Society of Limnology and Oceanography, February 18-22

2012: ‘Nitrogen transformations during oxic SGD in Stony Brook Harbor, NY American Geophysical Union, December 3-7

2012: ‘Fate of nitrogen during oxic submarine groundwater discharge into Stony Brook Harbor, New York’ Goldschmidt Geochemistry Conference, June 24-29

2011: ‘Groundwater nitrate attenuation during transport through a subterranean estuary in a Long Island Sound embayment’ American Geophysical Union, Dec 5-9

C2. Scientific Abstract: Long Island Sound experiences periods of hypoxia attributed to eutrophication, but the magnitude of nitrogen contributed to surface water via submarine groundwater discharge (SGD) entering Long Island’s north shore embayments is not well characterized. The coastal aquifer, where fresh groundwater mixes with saline coastal water is termed the subterranean estuary (STE). Advective flow combined with sharp salinity and dissolved oxygen gradients make the STE a zone of intense geochemical cycling. However, the fate of nitrogen during transit through Long island embayment STEs is not well understood, particularly how sediment heterogeneity influences nitrogen attenuation in discharge zones.

Nitrate attenuation mechanisms, principally denitrification, were investigated in three Long Island north shore embayments; Stony Brook Harbor, Setauket Harbor and Port Jefferson Harbor. In Stony Brook Harbor an investigation of freshwater nitrate dynamics over two spring-neap tidal cycles found oscillations in depth stratified nitrate concentrations. Calculation of fresh fraction discharge revealed that water table over-height is responsible for these oscillations, which result from shore perpendicular movement of the coarse sediment freshwater discharge point.

High resolution sampling of STE porewater from Stony Brook Harbor and Setauket Harbor revealed discharge of freshwater continues for tens of meters offshore, which results in two zones of nitrogen removal. When SGD discharges into surface water near low tide through coarse-grain sand or marsh sediments, denitrification rates are 15 - 50% lower than when SGD passes through into a fine grain sediment layer offshore.

In Port Jefferson Harbor, results from a combined shallow porewater nitrate concentration and geochemical tracer (^{222}Rn) study indicate SGD accounts for similar nitrogen flux to surface water as direct inputs from a local sewage treatment plant. Overall, embayment scale sediment heterogeneity is positively correlated with availability of dissolved organic carbon, which in turn controls the extent of microbially mediated denitrification found in each of the studied embayments.

C3. Problems Encountered:

Major difficulties were as follows

a) Data Collection: Due to full tidal flushing, collection of SGD rate data in Setauket harbor was not possible. A number of methods were tried, including manual seepage meters, automatic seepage meters and ^{222}Rn measurements. The conclusion was that these methods did not provide reliable estimates of SGD for this harbor. Therefore, we used porewater Cl^- profiles in an advective-diffusion model to estimate SGD rates for three different zones of the harbor. See attached dissertation chapter 4 ‘NUTRIENT RELEASE FROM A GROUNDWATER FED TIDAL FLAT IN SETAUKET HARBOR, LONG ISLAND NY’ for a full description of porewater modeling results.
b) Sample analysis: Results from PJH were delayed by approximately 1 year due to slow sample analysis. Samples for dissolved N_2/Ar measurements were sent to UC Davis Stable Isotope Laboratory for analysis, with an initial turn around estimate of 6 weeks. Unfortunately

results were not received for ~1year. Data was received at the end of December, 2013. Consequently, this final report does not include all data analysis, as denitrification estimates were not possible without N_2/Ar data. In lieu of this data, we instead used a coupled ^{222}Rn and porewater nitrogen concentration survey to examine how SGD transports nitrate to surface water in PJH. Results from this work are detailed in chapter 5 of the attached dissertation ‘EMBAYMENT SCALE ASSESSMENT OF SUBMARINE GROUNDWATER DISCHARGE NUTRIENT LOADING TO PORT JEFFERSON HARBOR, LONG ISLAND NY’

C4. New Research Directions:

Two additional research directions were pursued during this project.

1. Radon concentration mapping of surface water in conjunction with shallow porewater sampling: We wished to directly address the proposed installation of seepage pits to redirect sewage away from the Sewage Treatment Plant on Stony Brook University campus (SCSD no.21), which was proposed by Suffolk County legislature to lower the total maximum daily limits (TMDLs) of nitrogen entering surface body waters. It was proposed that the seepage pits would alleviate nitrogen loading to surface waters. We wished to test this hypothesis by examining spatially distributed nitrogen inputs to PJH.

   Results from this new research direction are detailed in ‘EMBAYMENT SCALE ASSESSMENT OF SUBMARINE GROUNDWATER DISCHARGE NUTRIENT LOADING TO PORT JEFFERSON HARBOR, LONG ISLAND NY’. The primary conclusion is that SGD carries ~11kg NO_3^-/day to PJH during shoreline discharge, which is similar to loading from the existing sewage treatment plant outfall (~12.2kg-N/d). Therefore, the proposed seepage pits are unlikely to reduce the amount of nitrogen entering the harbor, but will instead delay nitrogen loading in accordance with groundwater travel time.

2. Thermal infrared mapping of surface waters. During this project, we investigated the feasibility of thermal infrared mapping to distinguish areas of diffuse SGD. The data was used in NASA and SeaGrant proposal calls. The result was funding for NYSG Proposal SG14014 ‘"*The role of submarine groundwater discharge (SGD) in promoting hypoxia in Smithtown Bay*" and for NASA graduate student scholarship (J.Tamborski)

C5. Interactions:

C6. Presentations and Publications:

Presentations:

<u>Young, C.R</u>, G.N Hanson. 2014 ‘N_2O Formation Mechanisms in Sandy Unconfined Coastal Aquifers’ Goldschmidt Geochemistry Conference, Sacramento CA, 8-13 June

<u>Young, C.R</u>, J. Tamborski, A.D Rogers, G.N Hanson 2013: ‘Distribution of submarine groundwater discharge into Port Jefferson Harbor, Long Island Sound, NY’ American Society of Limnology and Oceanography, New Orleans, LA 18-22 February. Presentation

Young, C.R, J. Durand, G.N Hanson, 2012: 'Nitrogen transformations during oxic SGD in Stony Brook Harbor, NY American Geophysical Union, San Francisco, CA 3-7 December. Poster

Young C.R and G.N Hanson 2012: 'Fate of nitrogen during oxic submarine groundwater discharge into Stony Brook Harbor, New York' Goldschmidt Geochemistry Conference, Montreal, Canada 24-29 June. Poster.

Young, C.R. and G.N. Hanson 2011: 'Groundwater nitrate attenuation during transport through a subterranean estuary in a Long Island Sound embayment' American Geophysical Union, San Francisco, CA 5-9 December. Poster.

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D. Accomplishments: Complete the following sub-sections:

D1. Impacts & Effects:

This project is expected to have significant impact on decision making for regional land management organizations and government bodies. Overall, results from this study show that Long Island groundwater, which is known to contain high concentrations of nitrate, does not undergo more than 35% denitrification during submarine groundwater discharge in areas where discharge rates are in excess of 25cm/d. Seasonal trends show that denitrification rates are significantly lower in spring than in fall, which may affect coastal eutrophication as nutrients are added during the bloom phase of surface water phytoplankton life cycle.

Findings from this project indicate that it the installation of sewage seepage pits to offset surface water discharges from a sewage treatment plant does not provide a positive environmental impact. Instead, nitrogen added to the surficial aquifer will ultimately impact Long Island Sound harbors via SGD. Results from this study should be disseminated to state and local environmental regulation offices in order to provide data for sewage treatment plant decision making.

D2. Scholar(s) & Student(s) Status:

NYSG Scholar Caitlin Young- Scholar was awarded a Thesis Completion Award (TCA) by SeaGrant for the summer of 2013. Thesis defense was completed in November of 2013, and graduation awarded in December of 2013. Post-graduation, the NYSG scholar is employed as a Postdoctoral Associate in the Geological Sciences department at University of Florida, in the research group of Dr. Jonathan Martin.

Non-financially supported students

1. Josephine Durand: Contributed to collection and processing of geophysical data. She has an anticipated graduation date of August 2014. J.Durand will be publishing at least one paper detailing the geophysical results on the STE investigation at SBH (see attached). She will additionally be co-authoring the 2 of the remaining papers that result from R-CTP-44.
2. Joseph Tamborski: Contributed to collection of porewater data in PJH, thermal infrared data in PJH and ^{222}Rn surveys. J.Tamborski will be co-authoring 1 of the papers that result from R-CTP-44. He is currently supported by SG14014.

D3. **Volunteers:** Provide information about any volunteers (citizens or students) who worked on the project. Indicate their activity and amount of time (hours) they participated.

Michael Thorpe- Graduate student in Geosciences. Assisted with collection of porewater samples for trace metal analysis in PJH. Approximate amount of time spent on project was 6 months.

*Tsou ShuHsing***-** Undergraduate student in Marine sceinces assisted in collection of seepage meter data in PJH in May and July of 2012.

Adrien Pernet- Undergraduate exchange student from France. Assisted with sediment core sampling and processing of sediment potential denitrification rates in SBH. Amount of time spent on project was 6 weeks in July-August of 2011.

D4. **Patents:** N/A

E. **Stakeholder Summary:**

'Sources and Fate of Nitrogen in North Shore Embayment's ' was designed to gain a better understanding of how nitrogen, a nutrient that can cause coastal eutrophication, is transported through coastal aquifers during sumarine groundwater discharge (SGD) to Long Island's north shore embayments. The project investigated three major harbors of Long Island Sound; Stony Brook Harbor (SBH), Setauket Harbor and Port Jefferson Harbor (PJH). In each harbor a spatial survey was conducted to determine areas of SGD. Results from these spatial surveys indicated that highest rates of SGD are found at or near the low tide zone, with rates ranging 25 cm/d to 102cm/d, and areas with the greatest SGD is found on the western shore of SBH and the eastern shore of PJH. This is likely due to large topographic inland relief of these two shorelines, which generates higher hydraulic head in the surficial aquifer, driving groundwater down gradient towards the coast. In all three harbors SGD was also observed offshore, through marine mud cap that covers the harbor bottoms at a maximum distance of 60m from mean low tide. This is the first investigation to observe this type of SGD in Long Island Sound embayments, where rates through the mud cap ranged 0 to 2cm/d, significantly lower than rates measured in permeable sediments at low tide.

Nitrogen transformations during SGD were examined in all three harbors. Major findings for Stony Brook Harbor indicate that denitrification attenuates less than 35% of the nitrate discharging in the low tide zone, but nitrate undergoes ~47% denitrification during transport to the base of the mud cap in the offshore zone. Nitrate discharges were higher during spring than fall, which may provide an excess of nutrients to surface waters during the time of algal spring bloom. In Setauket Harbor, modeled nutrient consumption and production indicated the harbor was a net sink for freshwater sourced nitrate, but was a net source of dissolved organic carbon. This was due to reducing conditions in the central portion of the harbor, which promoted denitrification during freshwater transport to the base of the mud layer. Finally, in Port Jefferson Harbor nutrient measurements were coupled with dissolved ^{222}Rn concentrations (a SGD geochemical tracer) which provided insight into nitrogen loading from the entire coastline. This data was compared to direct nitrogen inputs from a local sewage treatment plant that discharges to Port Jefferson Harbor. It was determined that nitrogen inputs from shoreline SGD were approximately equivalent (11kg NO_3^--N /d) to average reported inputs from the sewage treatment plant (12.2kg N/d). These results have direct implcations for land management planning, particularly proposals to install inland sewage seepage pits as an alternative to sewage treatment plant direct discharge. Given that shoreline SGD currently provides an equivalent amount of nitrogen as direct inputs, the addtion of nitrogen to the shallow aquifer is unlikely to lower the total amount of nitrogen input to Port Jefferson Harbor. Instead, additions of nitrogen to groundwater will most likely increase the SGD nitrogen loading to Port Jefferson Harbor.

In conclusion, this study has demonstrated the importance of submarine groundwater discharge to surface water nitrogen loading in Long Island Sound embayments. We found limited denitrification along shorelines with high discharge rates, indicating the coastal aquifer does not fully attenuate groundwater derived nitrogen. Results from this study highlight the importance of land based nitrogen loading mitigation, as in most cases the coastal aquifer does not act as a zone of denitrification.

F. **Pictorial:** Please see attached the completed dissertation of SeaGrant scholar Caitlin Young. See also attached manuscript draft by Durand, Young, Hanson and Wong.