Quantifying Septic Effluent Nitrogen Loading and Processing in the Baffin Bay Watershed

Final Report

Publication CBBEP - 144
Project Number –2005
April 2021

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Executive Summary

Baffin Bay, TX exhibits excessive nitrogen (N) levels and displays various symptoms of eutrophication. However, the sources contributing to N loading are not well quantified. Previous studies have suggested septic/sewage as a primary source of the most substantial N species, dissolved organic nitrogen (DON), but this has not been directly investigated. To further explore the potential for septic systems to contribute N loading in Baffin Bay, this project aimed to 1) quantify nitrogen levels and characterize the isotopic composition of nitrogen species in groundwater directly adjacent to a septic system; 2) characterize transport and processing of nitrogen species in groundwater; and 3) provide a first estimate of septic N load processing in the Baffin Bay watershed using the Soil Treatment Unit Model (STUMOD).

Average concentrations of ammonium (NH_4^+), nitrate (NO_3^-) and DON in the two wells sampled in this study were below detection limit, 31.5 µM, and 32.1 µM, respectively, and at the surface water sites sampled were below detection limit, 0.74 µM, and 51.8 µM, respectively (n = 4 for each). Average nitrogen and oxygen isotopic composition of nitrate (δ^{15}N-, δ^{18}O-NO_3^-) in the well samples and one measurable surface water sample were (21.6, 14.5‰) and (26.1, 16.3‰). The δ^{15}N and δ^{18}O-NO_3^- values in the groundwater and surface waters suggest the majority of NO_3^- in both are from wastewater and is undergoing competing nitrification and denitrification processes. The average δ^{15}N values of DON in groundwater and surface water were 24.3 and 14.3‰ respectively. The SIAR isotope mixing model estimated septic/sewage as the primary source of DON (52.8 ± 12.2%) followed by atmospheric deposition (16.1 ± 11.1%), livestock waste (15.8 ± 10.8%) and fertilizer (14.1 ± 9.7%). The summer source apportionment was not significantly different from the winter suggesting the DON sources are relatively consistent during the year at the sampling location.

The Soil Treatment Unit Model (STUMOD) was used to determine whether N from septic drain fields should be reaching the groundwater in the watershed or if it should be fully processed before infiltrating the groundwater. The model suggests nitrogen in 98% of the drain fields should be processed prior to reaching the groundwater, however high NO_3^- and the associated stable isotope signature in the groundwater near the investigated site clearly indicate that this is not the case. If instead the majority of septic tanks in the watershed are functioning like those of the sandy soil types in the watershed, the 794 drain fields could be contributing ~ 1600 kg NO_3^-/yr directly to the groundwater.

Project results provide evidence that septic systems are potentially a significant source of N to the bay and may not be functioning properly. However, this study uses just one septic drain field to represent the watershed. Several more septic systems in varying soil types should be investigated to better characterize system efficacy and potential N loading. Stakeholders should encourage the local community to inspect and perform routine maintenance on septic systems in order to ensure greater nutrient processing efficiency thus preventing groundwater infiltration and subsequent discharge to the bay. The Baffin Bay Volunteer Water Quality Monitoring Group has provided valuable information about the high nutrient levels in surface waters of Baffin Bay over the last 7 years which has been accompanied by observations of high nutrient loading via groundwater discharge by the Murgulet Group at TAMU-CC. This project builds on that work by providing estimates of the significant nitrogen sources to the bay. Ultimately, this work aims to provide a foundation for stakeholders to develop informed nitrogen mitigation strategies.

Acknowledgements

We thank the members of the Murgulet group and Felix group for sample collection and filtering. We are grateful to the University of Pittsburgh Regional Stable Isotope Lab for Earth and Environmental Research for assisting in isotope analysis. Finally, we thank the Coastal Bend Bays & Estuaries Program for supporting this project.

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1. Introduction

Septic systems provide a cost-effective means of wastewater disposal in rural areas lacking access to a centralized wastewater treatment facility, however septic effluent can lead to groundwater quality decline and increased nitrogen (N) loading to coastal waters [*Withers et al.*, 2011; *Luscz et al.*, 2015]. Due to the anaerobic conditions in septic systems, a majority of N in the effluent exists as ammonium (NH_4^+) (70 to 90%) and dissolved organic N (DON) (10 to 30%) [*Lusk et al.*, 2017]. The effluent is discharged to the underlying soils where ideally, the N is processed to harmless forms of N (e.g. N_2). However, depending on the physical and chemical properties of the local soils and the depth to the water table, bioavailable forms of N (e.g. NH_4^+, NO_3^-) can percolate to the groundwater where favorable hydrologic connections exist, and subsequently be delivered to coastal waters (Figure 1). This increased bioavailable N loading to coastal waters can cause detrimental effects including eutrophication, harmful algal blooms and hypoxia [*Mallin*, 2013]. Groundwater N loading to estuaries is often overlooked and is difficult to characterize. However, recent studies in South Texas estuaries report groundwater as a significant contributor to N and organic matter loading, thus highlighting the importance of determining the sources contributing to groundwater N [*Murgulet et al.*, 2019; *Douglas et al.*, 2020; *Lopez et al.*, 2020].

There are ~63,000 septic systems in the 18 counties of the Texas coastal zone [*TCEQ/TSSWCB*, 2018]. Portions of this region have characteristically porous and permeable soils with relatively low carbon content which is not ideal for the function of septic system drain fields. More specifically, a significant portion of the residences in the Baffin Bay, TX watershed (n = 794) use septic systems as a means of wastewater disposal (Figure 2) [*Texas A&M AgriLife Extension OSSF*, 2020]. The majority of these septic drain fields are built in sandy clay loam [*USDA*, 2021] which can be ideal for septic systems but this depends highly on sand and clay ratios. If these systems are not working efficiently and the drain field soil content is not adequate, effluent can directly percolate to groundwater. In Baffin Bay, groundwater is the primary N delivery mechanism to the bay and is orders of magnitude higher than surface input [*Lopez et al.*, 2020]. A recent study using the nitrogen isotopic composition of dissolved organic nitrogen (DON) in Baffin Bay surface water to estimate DON sources to the bay determined sewage/septic as the primary source (53 ± 4%) followed by atmospheric deposition (18 ± 13%), livestock waste (17 ± 12%), and fertilizer (12 ± 9%) [*Felix and Campbell*, 2019]. This high sewage source suggests a strong link between septic infiltration and high groundwater N loading, however there is a general lack of knowledge of how the septic systems located in the watershed are contributing to coastal N loading.

The excess N has led to eutrophication and marked water quality decline in Baffin Bay. Additionally, the N inputs (specifically DON and NH_4^+) have been associated with proliferation of brown tide blooms which have caused declines in seagrass and benthic invertebrate populations as well as decreases in water quality; all of which can be detrimental to the regional economy and the recreational and commercial fishing industries [*Buskey et al.*, 2001]. This has led state governments and stakeholders in the region to take a growing interest in decreasing N loading to the watershed. In order to develop informed mitigation strategies to decrease the harmful effects of N loading in the region, it is necessary to understand the significance of each N source contribution. This project addressed the significance of septic N loading to the Baffin Bay watershed through three objectives 1) quantifying nitrogen species and characterizing the isotopic composition of nitrogen species in groundwater directly adjacent to a septic system; 2) characterizing transport and processing of nitrogen species in groundwater; and 3) providing a first estimate of septic N load processing in the Baffin Bay Watershed using the Soil Treatment Unit Model (STUMOD).

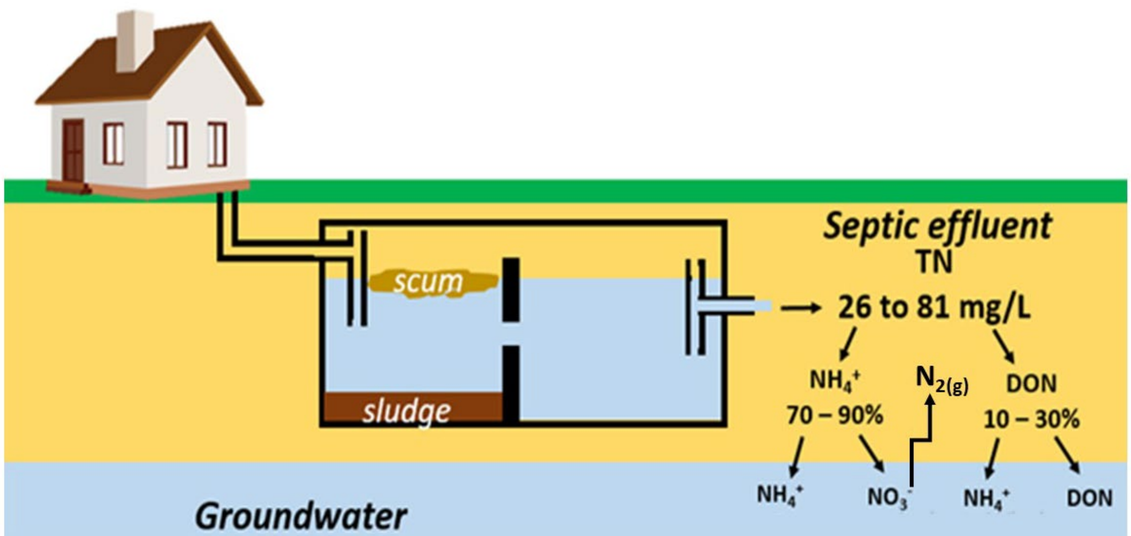

Figure 1. Diagram of a typical septic system and reported nitrogen concentrations and composition. Septic effluent total N concentration is reported to be between 26 to 81 mg/L and the majority consists of NH_4^+, and DON [*Lusk et al.*, 2017]. Ideally, in the drain field, NH_4^+ is converted to NO_3^- which is subsequently converted to N_2 via denitrification. However, in the Baffin Bay watershed it is unknown how much of the nitrogen reaches the groundwater and in what form.

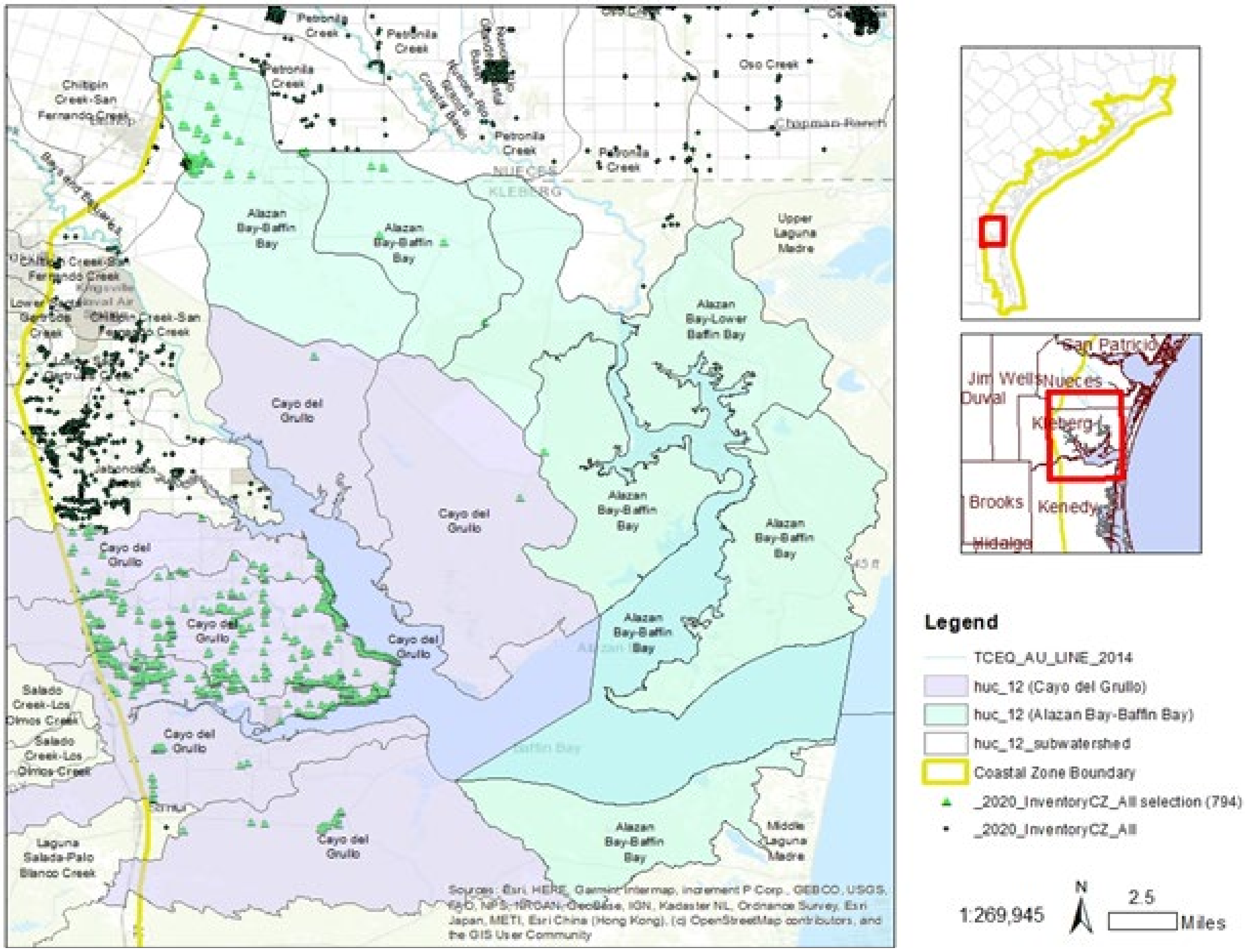

Figure 2. Map of on-Site sewage facilities in the Baffin Bay watershed. Green triangles represent the septic tanks used in the STUMOD modeling. Black dots are additional septic tanks other than those used in the STUMOD modeling. This map was created by Texas A&M AgriLife Extension OSSF Team with data collected from contract # 582-20-10160 funded by the Environmental Protection Agency (EPA) Clean Water Act (CWA) Section 319(h) funds through the Texas Commission on Environmental Quality (TCEQ), titled "Coastal Zone Act Reauthorization Amendments (CZARA) - On-Site Sewage Facilities (OSSFs) Coastal Inventory and Chocolate Bayou OSSF Inspections."

2. Methods

2.1 Sampling Site Description

Baffin Bay is a shallow (< 2-3 m) estuary located in the north-western Gulf of Mexico [*Simms et al.*, 2010]. Unlike most estuaries in the Gulf of Mexico, Baffin Bay is isolated from the open Gulf of Mexico by the 180 km long Padre Island [*Simms et al.*, 2010]. Agriculture and urban are the two major land use in the Baffin Bay watershed as a whole (NOAA Coastal Change Assessment Program). About 44% of the land use is attributed to agriculture. Baffin Bay is also adjacent to two cities (i.e. Kingsville and Alice) [*Wetz et al.*, 2017]. Although three creeks (Petronila Creek, Los Olmos Creek, and San Fernando Creek) drain into Baffin Bay, their surface discharges are variable and intermittent (from 0 m^3/s to 3.53 m^3/s) [*Simms et al.*, 2010] resulting in 65% of freshwater discharge coming from precipitation [*An and Gardner*, 2002]. Rain events can contribute 60 to 80 cm of precipitation per year and groundwater can contribute an average of 14.9 cm/d discharge to Baffin Bay [*Murgulet et al.*, 2019]. However, it is still a negative estuary with evaporation exceeding its freshwater input, leading to a hypersaline conditions with average salinities ranging from 40 to 60 ppt [*An and Gardner*, 2002]. Astronomical tidal range is less than 0.1 m [Simms et al., 2010], and tidal changes are mostly influenced by the strong and persistent winds (average wind speed between 15 to 24 km/h). As a result, the residence time of the water is about a year [*An and Gardner, 2002*].

2.2 Sampling Procedure

The sampling location includes two monitoring wells and two surface water locations along a transect radiating out from a septic drain field located at the public Riviera Fishing Pier, Riviera, TX (27.28662, -97.66412) (Figure 3).

Surface- and ground- water samples were collected in July and December 2020 at the Riviera Point site. All samples were collected in 125-mL HDPE bottles that were rinsed with acid, rinsed with type I water as specified by ASTM D1193, ISO 3696, and CLSI-CLRW standards (Resistivity of < 18 (MΩ-cm) at 25 °C and Total Organic Carbon (TOC) < 50 (ppb)), and finally triple rinsed in the water sample. Samples were placed on ice until filtered through a 0.2 µm GF/F and frozen. Groundwater samples were collected after purging three well volumes and after filed parameters stabilized.

Figure 3. Left: Baffin Bay, TX USA. Right: The blue circles are the well and surface water locations (W1: well 1; W2: well 2; S1: surface water 1; S2: surface water 2). White dashed line rectangle is the location of the septic drain field.

2.3 Dissolved Inorganic and Total Kjeldhal Nitrogen Concentrations

Dissolved inorganic nitrogen (NO_2^-, NO_3^- and NH_4^+), Total Keldjahl nitrogen and chlorine were analyzed via EPA 300.0, 300.0, 350.1, 300.0, 354.1, respectively at the National Environmental Laboratory Accreditation Program certified lab, City of Corpus Christi Water Utilities Laboratory (WUL).

2.4 Ammonium Removal Procedure Before Total Dissolved Nitrogen Conversion for Isotope Analysis

Ammonium was removed before total dissolved nitrogen (TDN) oxidation. 40 mL of each sample was added to 100 mL beakers. 5N NaOH was added to raise the pH which forces the ammonium/ammonia to volatilize. Beakers were then weighed and left uncovered in a fume hood in the dark. After 24 hours [NH_4^+] is checked via o-phthalaldehyde (OPA) fluorometric method [*Holmes et al.*, 1999]. Once the NH_4^+ was no longer detectable, the beakers were carefully weighed. The difference in weights is used to determine the new concentrations due to water loss by evaporation. Removal of NH_4^+ was done to reduce systemic errors incurred when other N species are present in the sample, i.e, there is one less measured analyte concentration needed to calculate [DON] and δ^{15}N-DON.

2.5 Isotope Analysis of Dissolved Inorganic Nitrogen

DIN (NO_2^- + NO_3^- + NH_4^+) isotopic composition was only measured in samples with DIN concentrations greater than 3 µM due to method and instrumentation limits. NH_4^+ was below the WUL detection limit so was not processed for isotope measurements. If NO_2^- accounted for more than 2% of the NO_2^- + NO_3^- concentration, it was removed using sulfamic acid so the resulting δ^{15}N represented just the δ^{15}N-NO_3^- value [*Granger and Sigman*, 2009]. Once isolated, NO_3^- was converted to N_2O via the denitrifying bacteria, *Pseudomonas aureofaciens*. The isotopic composition of NO_3^- was then determined as δ^{15}N-N_2O by injecting the N_2O into a continuous flow isotope ratio mass spectrometer (CF-IRMS) [*Sigman et al.*, 2001b]. Internationally recognized standards (USGS34, USGS32, IAEA-N3 and USGS35) were measured during sample analysis to provide a known δ^{15}N -NO_3^- reference for data corrections. Values are reported in parts per thousand, relative to atmospheric N_2 as follows:

$$\delta^{15}N\ (‰) = [(^{15}N/^{14}N_{sample}) - (^{15}N/^{14}N_{standard})] / (^{15}N/^{14}N_{sample}) * 1000 \qquad (1)$$

2.6 Isotopic Analysis of Total Dissolved Nitrogen

After NH_4^+ removal, TDN (NO_3^- + DON) of the samples was oxidized to NO_3^- using the persulfate method (Tsunogai et al., 2008). The persulfate working reagent was prepared using ultrapure High-Performance Liquid Chromatography (HPLC) Grade water. The average blank concentration (13.42 µM ± 1.3 µM) was mainly attributed to reagent water and since a relatively small amount of persulfate working reagent (0.60 mL) is added to the Baffin Bay samples coupled with the fact that Baffin Bay is a high DON environment, the overall blank effect is minimal (average 3.8%). Representative DON standards (i.e. urea, glycine, N-acetyl-D-glucosamine) were oxidized along with the Baffin Bay samples to monitor efficiency of TDN to NO_3^- from the persulfate oxidation. Resulting NO_3^- concentrations were measured via the cadmium reduction colorimetric method [*APHA*, 1992]. Urea was chosen as a standard because it is a form of DON that is a common component used in fertilizers and has been shown to contribute approximately 50% of the N utilized in many coastal regions [*Bronk*, 2002]. Glycine was chosen as a standard to represent the dissolved free amino acid (DFAA) portion of the DON pool, which has been found to comprise approximately 1.2 to 12.5% of the total DON pool [*Bronk*, 2002]. The N-acetyl-D-glucosamine was chosen as a standard because studies have shown that this biopolymer is representative of the N-acetyl amino polysaccharides (N-AAPs) and are important contributors to the semi-labile pool of DON (NAAPs can comprise ~40 to 50% of surface ocean high molecular weight dissolved organic matter (HMWDOM) [*Aluwihare et al.*, 2005]. Once the TDN in the sample was converted to the NO_3^- the isotopic composition was measured via the denitrifier method described above [*Sigman et al.*, 2001a; *Knapp et al.*, 2005, 2011]. The δ^{15}N-DON value was calculated from the measured δ^{15}N-NO_3^- and δ^{15}N-TDN by using the isotope mass balance equation:

$$\delta^{15}\text{N-TDN} = f_{NO_3^-}(\delta^{15}\text{N-NO}_3^-) + f_{DON}(\delta^{15}\text{N-DON}) \quad (2)$$

where $f_{NO_3^-}$ and f_{DON} stands for the fraction of the concentration of the respective DIN/DON contributing to the TDN concentration of the sample.

2.7 Isotope Mixing Model (DON Source Apportionment)

Nitrogen source contributions can be estimated using an isotope mixing model if the isotopic composition of the primary nitrogen sources are known and the isotopic composition of nitrogen in a sample has been measured. For this project, a four-end member isotope mixing model was developed using source signatures of four primary sources (i.e., septic/sewage, livestock waste, fertilizer, and wet atmospheric deposition) and the measured isotopic composition of DON in Baffin Bay samples (equ 3). Table 1 includes the literature δ^{15}N-DON values of DON sources and the δ^{15}N-DON values of local sources used in the mixing model [*Campbell*, 2018]. The δ^{15}N-DON value from septic/sewage is adjusted with wastewater outfall value from reference and measured δ^{15}N-DON in the well samples from the transect assuming the primary DON source in this location is the septic field. The SIAR package was used to employ the mixing model. The SIAR is an R package based on Bayesian statistical method. The Bayesian statistical method can account for variations in fractionation factors, integrate uncertainties and use prior information to guide analyses [*Moore and Semmens*, 2008; *Parnell et al.*, 2010, 2013]. The names, mean isotopic compositions and standard deviations of DON sources were entered in the R code along with the

δ^{15}N-DON value of surface water samples. SIAR provides the best estimated mean contribution of each sources and corresponding uncertainty.

$$\delta^{15}\text{N-DON}_{bay} = f_{ss}(\delta^{15}\text{N-DON}_{ss}) + f_{wad}(\delta^{15}\text{N-DON}_{wad}) + f_{fert}(\delta^{15}\text{N-DON}_{fert}) + f_{lw}(\delta^{15}\text{N-DON}_{lw}) \quad (3)$$

Where δ^{15}N-DON$_{bay}$ is of the δ^{15}N value of the bay sample, f_{ss} is the contribution of septic/sewage, δ^{15}N-DON$_{ss}$ is the δ^{15}N value of septic/sewage, f_{wad} is the contribution of wet atmospheric deposition, δ^{15}N-DON$_{wad}$ is the δ^{15}N value of wet atmospheric deposition, f_{fert} is the contribution of fertilizer, δ^{15}N-DON$_{fert}$ is the δ^{15}N value of fertilizer, f_{lw} is the contribution of livestock waste and δ^{15}N-DON$_{lw}$ is the δ^{15}N value of livestock waste.

DON Source	**Literature δ^{15}N value (‰)**	***Local δ^{15}N value (‰)**
Septic/Sewage	+12.8 to +18.6	+20.0 ± 6.8
Wet atmospheric deposition	-7.9 to +7.0	+4.4 ± 0.3
Synthetic organic fertilizer	-6 to +2	-0.6 ± 0.3
Livestock waste	+3 to +14	+3.9 ± 0.4

Table 1: δ^{15}N values of reported DON sources and local DON sources. Local livestock waste is δ^{15}N-TDN. [*Cornell et al.*, 1995; *Russell et al.*, 1998; *Curt et al.*, 2004; *Lee et al.*, 2012; *Choi et al.*, 2017; *Campbell*, 2018]. *Local value from Campbell 2018 and local septic included from this study's well samples.

Soil Treatment Unit Model (STUMOD) Parameter Selection

STUMOD uses the characteristics of soil type and the effluent nitrogen concentration from septic tanks to determine the nitrogen transfer and calculate the nitrogen concentration entering the water table. To survey the soil type in Baffin Bay, the land around Baffin Bay was divided into five sections, which is shown in Table 2. The soil type was determined using Web Soil Survey SSURGO database (https://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx) provided by United States Department of Agriculture and Natural Resources Conservation Service. The dominant soil type for each section is listed in Table 2. There were 794 septic tank systems in the adjacent Baffin Bay terrestrial region (Figure 2). Section 1-5 contains 3, 54, 9, 3 and 713 septic tanks, respectively. Most of the nitrogen in septic effluent exists as ammonium (NH_4^+) (70%) and only about 0.4% of the total nitrogen was nitrate (NO_3^-) and nitrite (NO_2^-) due to the aerobic environment [*Harrison et al.*, 2000]. The typical total nitrogen concentration in septic tanks is ~60 mg N/L, hence the 42 mg N/L was chosen as the input for NH_4^+ and 0.2 mg N/L as the NO_3^- concentration in septic tanks [*Geza et al.*, 2014; *Lusk et al.*, 2017]. Soil temperature can also influence nitrogen transformation, which was recorded each time during the sampling. The average recorded temperature was used in STUMOD. Additional ancillary parameters that are associated with soil type are provided by the STUMOD program and are listed in Table 3 in the appendix.

Name	Dominant soil type	Typical profile	No. septic tanks
Section 1	Victoria clay	0 to 15 cm: clay 15 to 94 cm: clay 94 to 127 cm: clay 123 to 203 cm: clay	3
Section 2	Victoria clay	0 to 15 cm: clay 15 to 94 cm: clay 94 to 127 cm: clay 123 to 203 cm: clay	54
Section 3	Falfurrias-Cayo complex	0 to 53 cm: fine sand 53 to 203 cm: fine sand	9
Section 4	Palobia loamy fine sand	0 to 35.5 cm: loamy fine sand 35.5 to 79 cm: sandy clay loam 79 to 203 cm: sandy clay loam	3
Section 5	Palobia-Colmena complex	0 to 35.5 cm: fine sandy loam 35.5 to 79 cm: sandy clay loam 79 to 203 cm: sandy clay loam	713

Table 2. The soil type and typical profile for each watershed section. The USDA Web Soil Survey provides interactive maps which can be referenced for this area: (https://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx)

3. Results and Discussion

3.1 Inorganic and Organic Nitrogen Concentrations and Isotopic Composition

Summer and winter sampling were performed at the transect to investigate temporal variations in the ground and surface water nitrogen dynamics (Table 2). Ammonium was below the detection limit in all well and surface water samples for both sampling sessions. This was expected for surface water as the limit of detection reported by the required NELAP certified lab was 11 µM and surface water inorganic nitrogen concentration has been reported as 3.1 µM and 6.1 µM in the summer and winter, respectively [*Felix and Campbell*, 2019]. It was unknown however, if high levels of NH_4^+ would be present in the wells adjacent to the septic system since a large portion of N in septic effluent is NH_4^+. The lack of NH_4^+ in the wells indicates NH_4^+ was processed via nitrification before it reached the groundwater. This is evident in the wells in both seasons where NO_3^-, the product of nitrification, was observed in high concentrations in Well 1 in summer and Well 2 in winter. Nitrate was not observed in the surface waters in summer but was observed in low concentrations (1.94 and 0.48 µM) during the winter. Low to below detection limit nitrate concentrations are normal in the bay suggesting a number of potential scenarios for the fate of the high NO_3^- concentrations in the groundwater. Nitrate may be processed to N_2 (denitrification) or NH_4^+ (dissimilatory nitrate reduction) before discharge to the bay, it may be quickly assimilated after discharge, or there is a diluting effect so that the high well concentrations are not represented in the bay.

Baffin Bay has unusually high DON and DOC concentrations [*Wetz et al.*, 2017] and DON was prevalent in all samples in both summer and winter. Average DON in well samples (32.1 µM) was lower than those in the surface samples (51.2 µM) indicating that while groundwater may be a very significant source of DON to the bay it is likely not its only source. However, long residence times in the bay would be conducive to build up of DON from this source [*Wetz et al.*, 2017].

To further explore nitrogen dynamics in the bay, the isotopic compositions of nitrogen species were measured. Oxygen and nitrogen isotopes ($\delta^{18}O$, $\delta^{15}N$) of well water NO_3^- signified a wastewater source (Figure 4). Specifically, the NO_3^- isotope values could represent human waste NH_4^+ that inherited the oxygen isotopic composition during processing to NO_3^- via the two step process of nitrification. The first step would incorporate one O from molecular O_2 and one O from water to produce nitrite and the final step would incorporate one more O from water to produce NO_3^- [*Granger and Wankel*, 2016]. This line of evidence strongly implies a septic source of NO_3^- to the groundwater.

DON nitrogen isotope values ($\delta^{15}N$-DON) were higher in the well waters (24.3 ± 4.4‰) than the surface waters (14.3 ± 1.1‰). The few studies reporting $\delta^{15}N$ of TDN in wastewater report a range of +12.8 to +18.6‰. The high DON in the well waters suggests a septic source and potential processing of this DON as it travels to the groundwater. For instance, assimilation and remineralization of DON would favor the use of the lighter ^{14}N isotope thus enriching the remaining DON pool with the heavier ^{15}N isotope. The $\delta^{15}N$-DON values in the surface water are within the range of those reported by a previous long term Baffin Bay surface water study [*Campbell*, 2018; *Felix and Campbell*, 2019]. The lower surface water $\delta^{15}N$-DON values in comparison to the wells suggest a mixing between the septic water DON source with other inputs to the bay that have lower $\delta^{15}N$-DON values. To investigate this further, surface water $\delta^{15}N$-DON values were used along with source $\delta^{15}N$-DON endmembers (i.e., septic/sewage, rain, fertilizer, livestock waste) to estimate potential source contribution to Baffin Bays surface waters.

	July 2020				**December 2020**			
	W1	**W2**	**S1**	**S2**	**W1**	**W2**	**S1**	**S2**
NH_4^+ (µM)	<11.09	<11.09	<11.09	<11.09	<11.09	<11.09	<11.09	<11.09
NO_3^- (µM)	62.6	††<0.81	<0.81	<0.81	0.81	62.6	1.94	0.48
NO_2^- (µM)	**521.7	<0.43	<0.43	<0.43	0.87	<0.43	<0.43	<0.43
TKN (µM)	21.4	21.4	42.9	57.1	21.4	64.3	57.1	50
DON (µM)	21.4	21.4	42.9	57.1	21.4	64.3	57.1	50
Cl^- (mM)	278.2	87.6	264.7	257.4	543.9	134.9	438.7	434.6
$\delta^{15}N$-NH_4^+ (‰)	-	-	-	-	-	-	-	-
$\delta^{15}N$-NO_3^- (‰)	15.7	††28.3	-	-	17.8	24.5	26.1	-
$\delta^{15}N$-DON (‰)	18.3	27.5	14.5	13.8	23.5	27.8	13.1	15.2
$\delta^{18}O$-NO_3^- (‰)	13.1	††16.2	-	-	15.9	12.8	16.3	-
Temp (C)	25.1	26.0	34.5	32.1	25.3	25.9	17.4	17.2
DO (mg/L)	1.32	0.58	7.42	6.71	2.4	1.17	7.17	7.02
Salinity	62.1	NA	54.5	54.8	64.8	9.0	45.1	44.0
pH	6.24	7.16	8.18	8.17	6.34	7.12	8.15	8.04

Table 3: Sample analyte concentrations, isotopic composition and ancillary YSI data. **This nitrite concentration is unusually high for this region (~1000X higher) and in subsequent tests at three independent labs outside of the NELAP certified lab, nitrite was not present in the sample, so this value is reported but not included as part of the report investigation. Since nitrite was analyzed via ion chromatography it is possible that the nitrite peak

was affected by a chloride peak in these hypersaline samples. The PIs are required by QAPP to report those values provided by a NELAP certified lab. ††While nitrate was reported under the detection limit for this sample by the NELAP certified lab, it was further checked at three independent labs to see if it had enough nitrate for isotope analysis. It did and was analyzed for isotopic composition. This is why isotope values are reported here for nitrate.

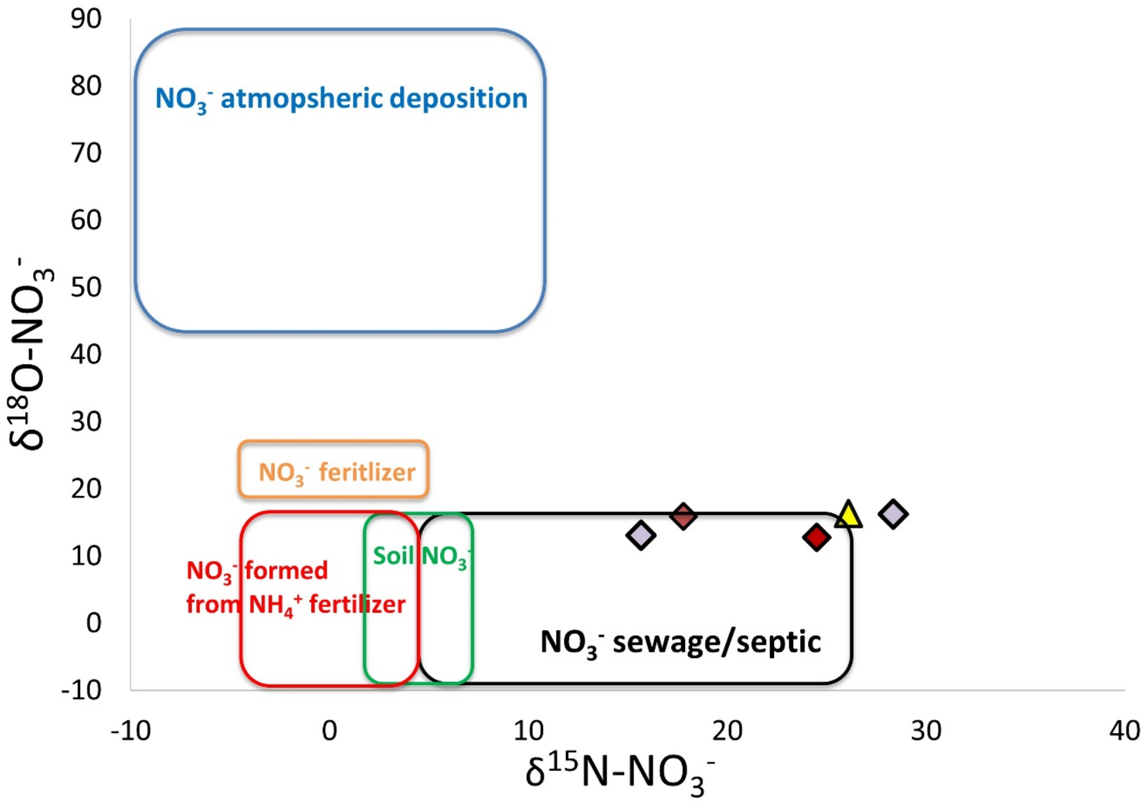

Figure 4. Dual nitrate isotope Kendall source plot. Purple diamonds are July well samples and red diamonds are December well samples. Yellow triangle is December S1 sample.

3.2 Isotope mixing model (DON source contributions)

Results from the isotope mixing model indicate average DON contributions to the bay of 16.1 ± 11.1%, 14.1 ± 9.7%, and 15.8 ± 10.8% from wet deposition, fertilizer, and livestock waste, respectively, with septic/sewage (52.8 ± 12.2%) being the primary overall DON source (Table 4, Figure 5). The high sewage/septic influence may be attributed to septic effluent discharge to groundwater and/or wastewater discharge but high DON concentrations in the well waters may indicate the former. These percent contributions are very similar to those reported by a previous surface water study in Baffin Bay conducted at six sites in Baffin Bay from March 2017 to June 2018 [*Felix and Campbell*, 2019]. This suggests that nitrogen sources have not changed in this region of the bay over the previous few years. The summer source apportionment was not significantly different from the winter (ANOVA, $p > 0.05$) suggesting the sources are relatively consistent during the year. A larger scale spatial and temporal groundwater and surface water study is underway to investigate this in more detail.

Source	Average (%)	Summer S1 (%)	Summer S2 (%)	Winter S1 (%)	Winter S2 (%)
septic/sewage	52.8 ± 12.2	55.2 ± 12.2	53.0 ± 12.4	50.3 ± 12.1	53.7. ± 12.2
wet deposition	16.1 ± 11.1	15.8 ± 11.1	16.5 ± 11.3	17.3 ± 11.6	14.9 ± 10.2
fertilizer	14.1 ± 9.7	13.6 ± 9.3	14.2 ± 9.6	15.1 ± 10.3	13.4 ± 8.9
livestock waste	15.8 ± 10.8	15.3 ± 10.6	16.3 ± 11.1	17.3 ± 11.5	14.4 ± 10.0

Table 4. DON source contributions to surface water during summer and winter sampling according to isotope mixing model results.

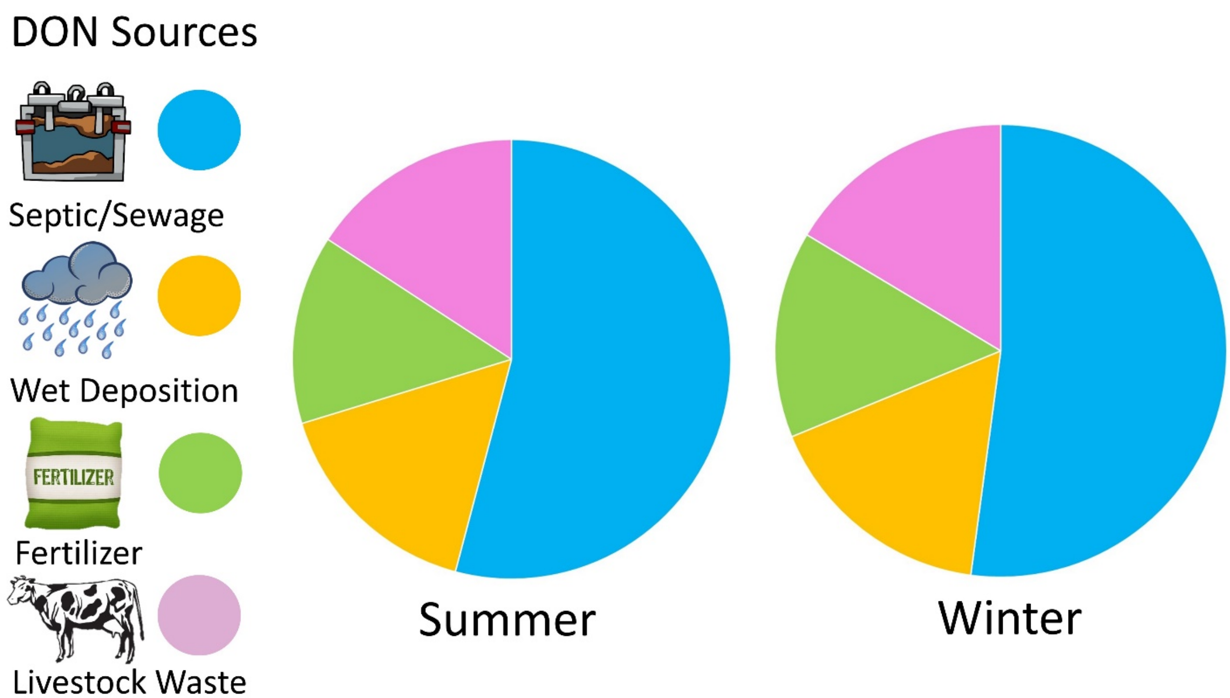

Figure 5. Pie charts representing average DON source contributions to surface water during summer and winter sampling according to isotope mixing model results.

3.3 STUMOD Analysis

The Soil Treatment Unit Model (STUMOD) was used to determine whether nitrogen from septic drain fields should be reaching the groundwater in the watershed or it should be fully processed before infiltrating the groundwater. In total, there are 57 septic tanks in the watershed that are located in clay soil types. The STUMOD results of the clay soil type shows that the NH_4^+ concentration starts decreasing once the effluent entered the soil due to nitrification, a process where nitrifier bacteria oxidize NH_4^+ to NO_2^-/NO_3^- under aerobic conditions. NH_4^+ decreases to 0 mg N/L at the depth of 21 cm (Figure 6A). NO_3^- increases until NH_4^+ is consumed. However, due to the co-existence of denitrification, where NO_3^- is reduced to N_2 by denitrifier bacteria, the rate of NO_3^- increasing is lower than the rate of NH_4^+ decreasing and NO_3^- concentration immediately decreases once NH_4^+ is depleted. This is also why the concentration of TN (in STUMOD, TN = NO_3^- + NH_4^+) keeps decreasing until it is depleted at ~42 cm.

Over 90% of the septic location soil types are loamy sand before 35.5 cm in depth and sandy clay loam after 35.5 cm. STUMOD results for this soil sequence are shown in Figure 7. ~ 35 mg N/L of NO_3^- and TN are left after infiltrating the loamy sand layer but the concentration of NH_4^+ is already depleted around the depth of 4 cm due to a higher nitrification rate in this soil type (Figure 7A). After 35.5 cm, the soil type changes to sandy clay loam and at this transition the concentration of NO_3^- equals the concentration of TN as NH_4^+ is fully processed (Figure 7B). Just like the clay soil type, the concentrations of NO_3^- and TN in sandy clay loam are soon depleted due to denitrification. The average depth to water table at this location in Baffin Bay is 168 cm, the nitrogen can be completely processed in these soil types mentioned above before reaching the water table. However, this is not the case with the sandy soil type (Figure 6B). The nitrogen has not been completely processed in sand before reaching the water table and ~ 30 mg N/L of nitrogen, which exists in the form of NO_3^-, can be released to the groundwater. An average household occupancy per capita loading rate of 4.1 kg N/yr is outlined in the EPA's Onsite Wastewater Treatment Manual [*USEPA*, 2002]. We assume that the typical total nitrogen concentration in septic effluent is around 60 mg N/L, which means an average of 68,333 L septic effluent is discharged per year. If one septic tank is built in sand, it can release 2.05 kg N (68,333 L effluent with a concentration of 30 mg N/L) in the form of NO_3^- to the groundwater per year. In Baffin Bay, 9 septic tanks are built in sand, which means that around 18.45 kg N can potentially reach Baffin Bay through groundwater. The STUMOD results also show that the clay type can quickly process nitrogen, while when the soil type is sandy, the process is slowed down increasing the chance of nutrient contamination.

The study site septic tank is in fine sandy loam soil type followed by sandy clay loam like the bulk of the septic tanks in the watershed (n = 713). According to STUMOD results, in this soil type, all nitrogen in effluent should be processed before reaching groundwater. This is clearly not the case due to the high NO_3^- and DON concentrations in the groundwaters near the septic tank. If these 713 septic systems are behaving more like those modeled in sand as evidenced by the NO_3^- present, this would suggest an additional ~1400 kg N/yr to the ground water adjacent to Baffin Bay in the form of NO_3^-. It should also be noted that depth to water table is temporally dynamic and also changes with location.

Although DON can be a significant component of septic effluent, it is a traditionally overlooked form of N. It is not modeled by STUMOD and most septic soil processing models due DON pools being complex and the historical notion that DON is primarily recalcitrant. However, DON can ultimately be mineralized to the readily bioavailable nitrogen form NH_4^+, which can also in turn be nitrified to NO_3^-. In addition, some microorganisms, like brown tide, can directly assimilate certain DON molecules thus providing a substantial direct nutrient source in Baffin Bay. With evidence of the primary source of DON being sewage, more effort into modeling processing of DON associated with septic drain fields should be considered.

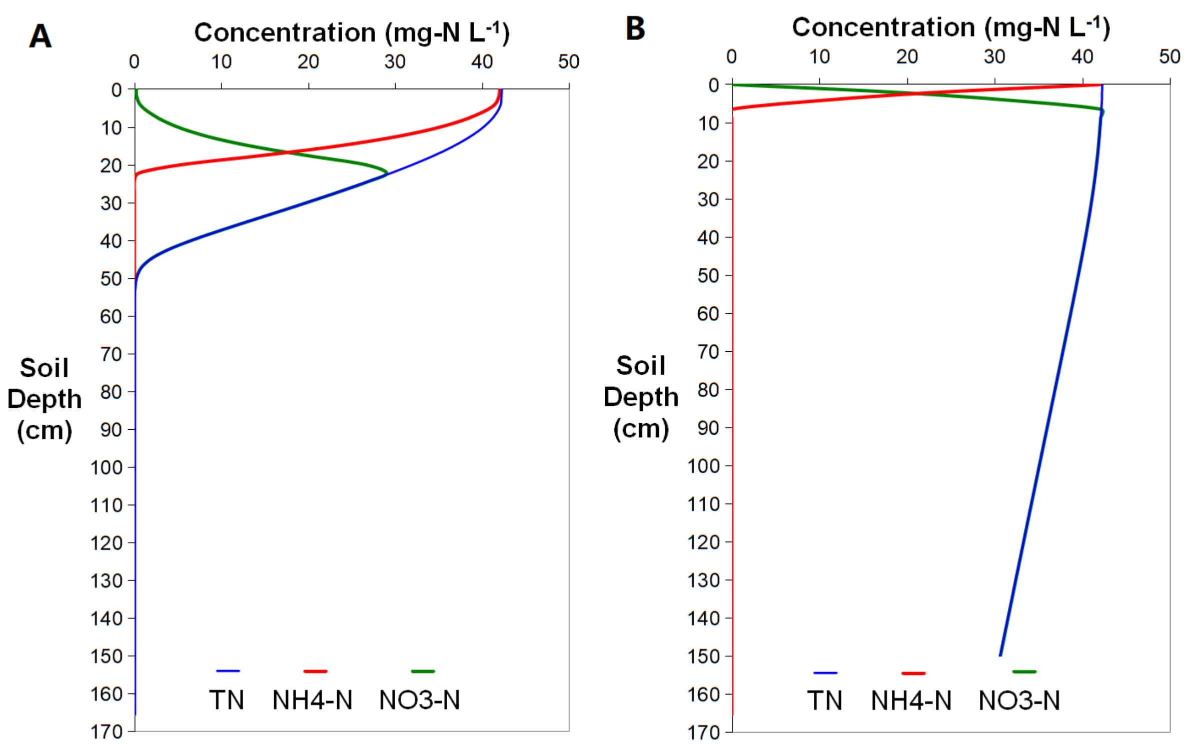

Figure 6. STUMOD results of clay soil type. B) STUMOD results of sand soil type. *TN = $NO_3^- + NH_4^+$

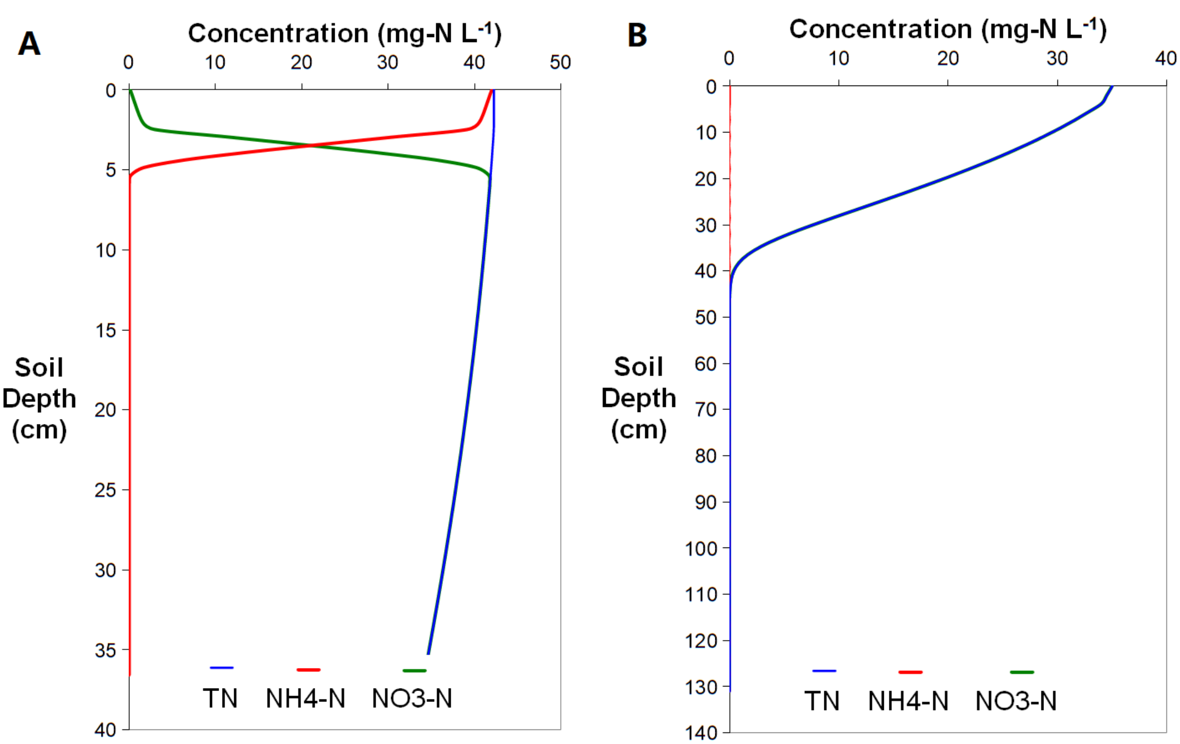

Figure 7. A) STUMOD results of loamy sand before 35.5 cm. B) STUMOD results of sandy clay loam after 35.5 cm *TN = $NO_3^- + NH_4^+$

Conclusion

The project quantified nitrogen levels and characterized the isotopic composition of nitrogen species in groundwater and surface water directly adjacent to a septic system in an effort to determine N sources and processing in the Baffin Bay watershed. It also provided a first estimate of septic N load processing in the watershed using the Soil Treatment Unit Model.

Average concentrations of ammonium (NH_4^+), nitrate (NO_3^-) and DON in the two wells sampled in this study were below detection limit, 31.5 µM, and 32.1 µM, respectively, and at the surface water sites sampled were below detection limit, 0.74 µM, and 51.8 µM, respectively (n = 4 for each). Average nitrogen and oxygen isotopic composition of nitrate ($\delta^{15}N$-, $\delta^{18}O$-NO_3^-) in the well samples and one measurable surface water sample were (21.6, 14.5‰) and (26.1, 16.3‰). The $\delta^{15}N$ and $\delta^{18}O$-NO_3^- values in the groundwater and surface waters suggest the majority of NO_3^- in both are from wastewater and is undergoing competing nitrification and denitrification processes. The average $\delta^{15}N$ values of DON in groundwater and surface water were 24.3 and 14.3‰ respectively. The SIAR isotope mixing model estimated septic/sewage as the primary source of DON (52.8 ± 12.2%) followed by atmospheric deposition (16.1 ± 11.1%), livestock waste (15.8 ± 10.8%) and fertilizer (14.1 ± 9.7%). The summer source apportionment was not significantly different from the winter suggesting the DON sources are relatively consistent during the year at the sampling location.

The Soil Treatment Unit Model (STUMOD) was used to determine whether N from septic drain fields should be reaching the groundwater in the watershed or if it should be fully processed before infiltrating the groundwater. The model suggests nitrogen in 98% of the drain fields should be processed prior to reaching the groundwater, however high NO_3^- and the associated stable isotope signature in the groundwater near the investigated site clearly indicate that this is not the case. If instead the majority of septic tanks in the watershed are functioning like those of the sandy soil types in the watershed, the 794 drain fields could be contributing ~ 1600 kg NO_3^-/yr directly to the groundwater.

Project results provide evidence that septic systems are potentially a significant source of N to the bay and may not be functioning properly. However, this study uses just one septic drain field to represent the watershed. Several more septic systems in varying soil types should be investigated to better characterize system efficacy and potential N loading. Stakeholders should encourage the local community to inspect and perform routine maintenance on septic systems in order to ensure greater nutrient processing efficiency thus preventing groundwater infiltration and subsequent discharge to the bay. The Baffin Bay Volunteer Water Quality Monitoring Group has provided valuable information about the high nutrient levels in surface waters of Baffin Bay over the last 7 years which has been accompanied by observations of high nutrient loading via groundwater discharge by the Murgulet Group at TAMU-CC. This project builds on that work by providing estimates of the significant nitrogen sources to the bay. Ultimately, this work aims to provide a foundation for stakeholders to develop informed nitrogen mitigation strategies.

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Appendix

Table 5. Parameters associated with soil types and their default values.

Parameter	Definition	Clay	Sand	loamy sand	sandy clay loam
α_c	An empirical exponent for carbon content adjustment	0			
HLR (cm/day)	Hydraulic loading rate	2			
α_1	Parameter α in Gradner's analytical equation for pressure distribution	0.025			
α_2	Parameter α in the soil water retention function	0.015	0.035	0.035	0.021
K_s (cm/day)	Saturated hydraulic conductivity	14.75	642.0	105.1	13.19
θ_1	Residual soil moisture	0.098	0.053	0.049	0.063
θ_2	Saturated soil moisture	0.459	0.375	0.390	0.384
n	Parameter n in the soil water retention function	1.260	3.180	1.747	1.330
m	Parameter m in the soil water retention function	0.206	0.686	0.427	0.248
L	Tortuosity parameter	0.5			
Kb (cm/day)	Hydraulic loading rate	0.4			
BT (cm)	Biomat thickness	2			
Co-NH4	Effluent ammonium-N concentration	42 mg N/L			
Co-NO3	Effluent nitrate-N concentration	0.2 mg N/L			

Kr-max (mg N/L/day)	Maximum nitrification rate	56
$K_{m\text{-}nit}$ (mg N/L)	Half-saturation constant for ammonium-N	5
e_2	Empirical exponent for nitrification	2.27
e_3	Empirical exponent for nitrification	1.1
f_s	Value of the soil water response function at saturation	0
f_{wp}	Value of the soil water response function at wilting point	0
s_{wp}	Relative saturation at wilting point	0.15
s_l	Relative saturation for biological process (lower limit)	0.67
s_h	Relative saturation for biological process (upper limit)	0.81
β1	Empirical coefficient for temperature function for nitrification	0.35
T_{opt} (°C)	Optimum temperature for nitrification	25

Table 4 Continued.

Parameter	Definition	Clay	Sand	loamy sand	sandy clay loam
V_{max} (mg N/L/day)	Maximum denitrification rate	2.56	2.58	2.58	2.58
$K_{m\text{-}dnt}$ (mg N/L)	Half-saturation constant for nitrate-N	5			
e_{dnt}	Empirical exponent for denitrification	3.77	2.87	2.87	2.87
s_{dn}	A threshold relative saturation (dimensionless)	0			
β2	An empirical coefficient for temperature function	0.35			
Topt (°C)	Optimum temperature for denitrification	25			
k_d (L/kg)	Adsorption isotherm	1.46	0.35	0.35	1.46
P (kg/L)	Soil bulk density	1.5			
T (°C)	Soil temperature	Recorded average soil temperature			
D (cm)	Soil depth	Soil depth in Baffin Bay			