Submarine Groundwater Discharge as a Potential Hidden Pathway for Eelgrass Decline in San Juan County

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ABSTRACT

Understanding recent eelgrass declines in San Juan County is of vital importance, as these eelgrass communities represent incredible ecological and economic value. The alarming magnitude of these losses and the unlikelihood of natural recolonization are additional reasons to continue exploring factors that may have contributed to decline. This project addressed one of the least studied vehicles for coastal pollution as a potential contributor to eelgrass loss: submarine groundwater discharge (SGD). SGD can introduce potent pollutants such as nutrients and herbicides directly to nearshore ecosystems. The goal of this project was to determine whether SGD is affecting eelgrass health in San Juan Island National Historical Park sites by adding excess nitrogen or phosphorous to waters at these sites. While no phosphate loading was detected, elevated nitrogen concentrations were observed both in seawater samples, at approximately 1 mg/L, as well as in SGD samples at 1-2 mg/L nitrogen. Roche Harbor, on the north side of the island showed the highest concentrations at 2.1 mg/L. Considering the harmful effects of nitrogen loading on eelgrass, it seems that SGD may have a negative effect on local eelgrass habitats.

INTRODUCTION

Eelgrass (*Zostera marina*) habitats are diverse, productive, and economically and ecologically important. Eelgrass beds provide critical habitat for a diverse range of finfish, shellfish, crustaceans, and birds, especially as “nursery” areas for juveniles and stopover feeding grounds for migratory birds. Eelgrass stands structure loose sediment, preventing erosion. They serve as a substrate for algae and diatoms, or epiphytes, which are a food source for small invertebrates. The plants themselves are primary producers and are grazed upon by many birds and marine species. (Kenworthy et al., 2004). Because of their crucial role in nearshore ecosystems, some anthropogenic disturbances to eelgrass beds have been studied, including nutrient loading, dredging, shoreline construction, trampling, logging, boating and mooring, shellfish harvesting, and herbicide runoff. (Dumbauld and Wyllie-Echeverria, 2003).

Seagrass populations, including eelgrass, are in decline worldwide, and rates of loss are accelerating. (Waycott, et al., 2009). Westcott Bay and Garrison Bay in San Juan County, Washington, have experienced losses of over 35 acres as of 2003 (Wyllie-Echeverria et al, 2003) and have not recovered since. It is not clear what has caused the decline, but it is clear that the problem and possible explanations for it should be examined. Considering the importance of eelgrass beds as habitat for many species, loss of this significance has the potential to threaten the health of entire regional ecosystems and economies.

Nutrient loading is a significant threat to eelgrass stands directly, due to toxic effects of excess nitrates and ammonium, or indirectly, from the resulting eutrophication and phytoplankton blooms, which increase turbidity. (Moore and Wetzel, 2000). Limited light availability negatively affects eelgrass photosynthesis, growth, survival, and even community structure. Nutrient loading may also increase epiphyte growth on seagrass shoots, which could further reduce light availability for photosynthesis. (Moore and Wetzel, 2000).

Nutrients may be introduced to nearshore eelgrass habitat via submarine groundwater discharge (SGD), defined as a discharging flow of groundwater out across the sea floor. SGD can be a significant mechanism of transport for a variety of materials into coastal zones, including nutrients, organic pollutants such as herbicides and pesticides, and other toxic substances. SGD has been shown to contribute nutrient enrichment in coastal zones and has been linked to resulting algal blooms and environmental degradation. (Burnett, et al., 2006; Moore, 2010).

Thus, substances introduced into San Juan coastal ecosystems via SGD can represent a significant potential threat to eelgrass habitat. Considering recent eelgrass disappearances in Westcott and Garrison Bays on San Juan Island and the cascade of potential repercussions, it is vital to further investigate SGD in the San Juan Islands and how this phenomenon may be affecting local eelgrass populations.

Several methods can be used to locations of SGD and quantify rate of discharge, including seepage meters, piezometers, naturally occurring geochemical tracers, water balance calculations, (Burnett, et al., 2006) or *in situ* conductivity measurements (Stieglitz et al., 2008), as were used in this experiment. For the purposes of this project, it was more helpful to observe nearshore conditions in order to infer that SGD may be occurring. For example, since groundwater in the San Juan Archipelago is likely to be cold and fresh, drops in conductivity or temperature near shore may indicate sites of discharge. Small, localized algal blooms may be another clue, since SGD can carry nutrients, as described previously.

This project was an effort to investigate the effects of SGD on eelgrass beds in San Juan National Historical Park sites. The park is part of the National Park Service's Vital Signs Program, which monitors the condition of natural resources in national parks. However, the San Juan division of the program primarily focuses on terrestrial resources and does not include any subtidal marine monitoring. Our results can set a precedent for local marine monitoring and encourage the inclusion of this kind of data in the NPS Vital Signs Program.

Water and sediment samples were obtained on a weekly basis at two sites on San Juan Island, one site of former eelgrass beds now devoid of eelgrass, and one with eelgrass stands present, in order to assess nutrient and herbicide levels at these sites. Possible sites of SGD were tentatively identified at these sites by visual observation and conductivity changes, and samples were taken at suspected discharge sites. Samples of submarine groundwater discharge were also taken, although at different locations on the island. This research examines the potential role of SGD, an oft overlooked factor in addressing coastal environmental problems, in recent eelgrass declines. Thus, results may provide important insight about how the further decline of these critical habitats can be prevented before they disappear altogether.

METHODS

Sample Locations

The two sample sites that were chosen were Garrison Bay at English Camp and 4th of July Beach at American Camp, on the north and south sides of San Juan Island respectively. These sites were chosen because the shallows of American Camp are largely covered with eelgrass stands, while Garrison Bay, which once had a flourishing eelgrass population, is now barren. Both sites exhibit signs of possible submarine groundwater discharge. Testing both of these sites will allow comparison of nutrient and herbicide levels in areas with and without eelgrass, and may thus provide some insight as to what factors are related to eelgrass decline.

Figure 1: English Camp and American Camp on San Juan Island.

Figure 2: Sampling sites at English Camp/Garrison Bay.

Figure 3: Sampling locations at Fourth of July Beach at American Camp.

Three sample locations and a control location were selected at English Camp, and two were chosen at American Camp. English Camp (EC) sampling locations are denoted by letters A, B and C, while the control location is site D. EC A was chosen due to the presence of green algae, which could indicate eutrophication due to nutrient loading. EC B and C also appeared somewhat eutrophic, while D lacked signs of eutrophication. American Camp (AC) sampling locations are A and B. AC B was chosen at a location with visible discharge and algal blooming, while AC A was chosen for its clean appearance.

Samples of submarine groundwater discharge were collected on the west side of the island near Lime Kiln and at Roche Harbor on the north side of the island. No duplicates were taken for these samples.

Figure 4: Lime Kiln and Roche Harbor sample sites on San Juan Island.

Sample Collection

Grab samples of seawater for nutrient analysis were taken in small (125 mL) plastic bottles both from shore and at the surface some distance away from shore by kayak at each location. The term “grab” samples refers to samples taken at a particular location at a particular time, rather than a composite sample across locations or over time. Duplicates were periodically taken for each sample to ensure validity of sample data.

Transects

We sampled along normal shore transects 150 ft in length at two locations at each beach: EC C and D, and AC A and B. 1 m by 1 m quadrats were placed at intervals of 30 m (50 ft) from shore depending on depth and eelgrass presence. Eelgrass stem density was recorded and sediment samples were taken at each quadrat.

Nitrogen Analysis

Nutrient samples were treated with 1M HCl dropwise until the pH reached approximately 3-4 in order to preserve samples. All glassware was acid washed before use.

Total nitrogen content was determined using the general procedure outlined by EPA Method 353.1: Nitrate-Nitrite (Colorimetric, Automated, Hydrazine Reduction A standard solution of concentration 100 mg/L NO_3^- N was prepared by dissolving 0.7218 g anhydrous KNO_3 in 100 mL of deionized water. The solution was further diluted with MilliQ water in volumetric glassware to prepare six standards of different concentrations of NO_3^-: 0.125 mg/L, 0.25 mg/L, 1.0 mg/L, 2.0 mg/L, and 3.0 mg/L. 30 mL of each standard solution were transferred to small beakers. 1 mL of borate buffer solution (61.8 g of boric acid and 8.0 g NaOH with water up to 1000 mL) and 3 drops of 6 M NaOH were added to each.

5 mL of each solution were transferred to glass test tubes. 0.725 mL NaOH reagent (made from 25 g NaOH and 237.5 mL DI water) and 0.420 mL reducing reagent were added to each test tube. The reducing reagent was prepared fresh daily by separately dissolving 2.7 g hydrazine sulfate in 100 mL DI water (Solution A), 0.25 g $CuSO_4 \cdot 5H_2O$ in 100 mL DI water (Solution B), and 5.3 g $ZnSO_4 \cdot 7H_2O$ in 100 mL DI water (Solution C). Just prior to use 27.4 mL DI water, 10 mL of solution A, 1.5 mL of solution B and 1.1 mL solution C were mixed to make the reducing reagent. After the NaOH and reducing reagents were added to the test tubes, the reactions were allowed to proceed for approximately 5 minutes, after which 0.725 mL of color reagent was added (147.5 mL DI water, 50 mL orthophosphoric acid, 5 g sulfanilamide, and 0.25 g N-1-napthylethyldiamine dihydrochloride). The solutions were swirled to mix and allowed to develop for at least 30 minutes. Finally, a few milliliters of each standard were transferred to a plastic cuvette and absorbance readings were taken at 535 nm with a Shimadzu UV-1601 spectrophotometer. This data was used to construct a six-point standard curve with an R^2 value of 0.98 in order to analyze the seawater samples.

For sample analysis, 10 mL of digestion reagent (20.1 g potassium persulfate and 3.0 g sodium hydroxide in 1000 mL DI water) was added to 20 mL of seawater. The samples were digested on a hot plate to the point of steaming for approximately 30 minutes. The volume in each beaker was marked, and the solutions were boiled on a hot plate for 30 minutes, adding DI water to the mark to maintain the initial volume and concentration. The solutions were allowed to cool to room temperature. The borate buffer and 6 N NaOH were added in the same amounts and all subsequent steps were followed for the samples as for the standards.

Orthophosphate analysis

Orthophosphate analysis followed the general procedure outline by EPA method 600/4-79-020 for Chemical Analysis of Water and Wastes (EPA). All glassware was washed in a bath of dilute HCl followed by three rinses of DI water to remove interferents before use. A standard curve was constructed using solutions of known phosphate concentrations. A solution of 5.0 mg/L phosphate was diluted with deionized water to concentrations of 0.1, 0.2 0.4, 0.6, 0.8, and 1.0 mg/L phosphate. One Permachem PhosVer 3 Phosphate Reagent pillow was added to 10 mL of each solution. Then, a few milliliters of each standard solution were transferred to a plastic cuvette, and absorbance readings were taken at 880 nm. This data was used to construct a six-point standard curve with an R^2 of 0.95.

Seawater samples were analyzed using a similar procedure. 20 mL of sample was digested with 10 mL of digestion solution on a hot plate for 30 minutes, made up to 30 mL with DI water, and allowed to cool to room temperature. Two 10 mL aliquots were separated into small beakers. 1 mL borate buffer solution and 3 drops of 6 N NaOH were added to each and swirled to mix, followed by one PhosVer reagent pillow. Color was allowed to develop for 20-30 minutes and absorbance was measured at 880 nm.

GIS Methods

A map was created using ArcGIS online to store data for this project. Layers were created for water quality data, nutrient data, and herbicide data for each sampling date. The map can be accessed at the following URL: http://bit.ly/1sDV8PD

RESULTS

Total Nitrogen

Samples at English Camp and American Camp were taken in duplicate over three sampling dates as described above. Friday Harbor Lab seawater results represent a single sample taken in duplicate on June 30. Submarine groundwater discharge samples represent single samples without duplicates taken on July 25 and thus have no error associated with results. Nitrogen concentrations for both sample groups are as follow

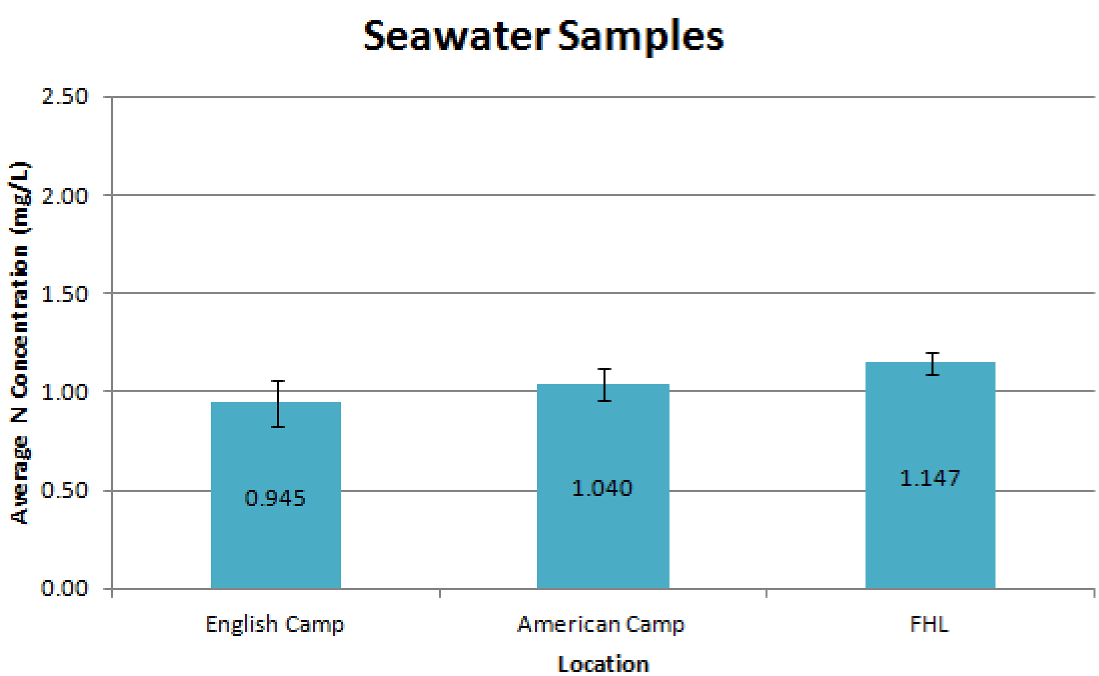

Chart 1: Total N in seawater samples.

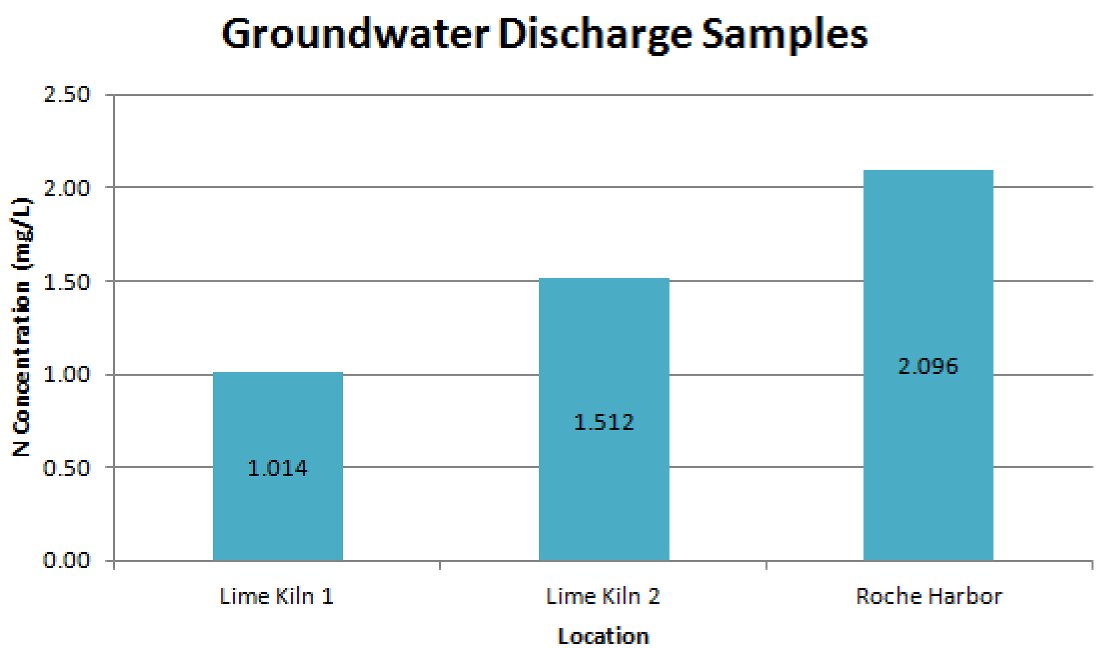

Chart 2: Total N in SGD samples.

Orthophosphate

Orthophosphate analysis followed the same sampling regime as described for nitrogen analysis. Orthophosphate concentrations for each sample are show below.

Seawater samples:

Site	Avg. conc. PO_4^{2-} (mg/L)
English Camp	Non-detect
American Camp	Non-detect
FHL	Non-detect

Table 1: Orthophosphate concentrations in seawater samples.

Submarine groundwater discharge samples:

Site	Conc. PO_4^{2-} (mg/L)
Lime Kiln 1	Non-detect
Lime Kiln 2	0.004
Roche Harbor	Non-detect

Table 2: Orthophosphate concentrations in SGD samples.

DISCUSSION

Submarine groundwater discharge represents a potential vehicle for nutrient pollution. In this study, we found that nitrogen concentrations in seawater samples at English Camp, American Camp, and Friday Harbor Laboratories were approximately 1 ppm. Total nitrogen concentrations in seawater are typically less than 1 ppm (Sverdrup et al.), so these concentrations are elevated and indicate some degree of nitrogen loading. In contrast, SGD samples range from approximately 1 ppm to over 2 ppm. This result of 2.096 ppm for Roche Harbor is double the ambient concentration of the seawater samples and conclusively points to nitrogen loading in this area. There are several factors that may be contributing to nitrogen loading near Roche Harbor, which are a resort community and the most commercially developed area on the island. Perhaps most enlightening is the reliance on septic tanks by the Roche Harbor community (Simonson, 2014), as well as elaborate gardens in the area (Roche Harbor). Thus, nitrogen from these sources may be seeping into coastal groundwater aquifers and entering subtidal waters via submarine groundwater discharge.

Since results indicate nitrogen loading, it is possible that phosphate concentrations would also be higher than usual concentrations of less than 0.1 ppm (Stanford). However, no phosphate or low concentrations of 0.004 mg/L were detected in all samples. There are two possible reasons for this. Firstly, phosphorous is removed from nitrogen faster than groundwater (Moore, 2010). This is due to its ability to complex with aqueous calcium in groundwater to form calcium phosphate ($Ca_3(PO_4)_2$), which is highly insoluble in water (Ksp = 1×10^{-26}) (CSU Dominguez Hills). San Juan Island has large deposits of limestone, the largest of which is located at the north side of the island at Roche Harbor (UW). These limestone deposits would be a source of dissolved calcium in groundwater with which phosphate can complex. Secondly, in high carbonate systems such as San Juan Island, waters are more likely to be P-limited than N-limited due to this removal of soluble phosphate by carbonate in sediment (Littler, et al., 1991). Therefore, we may assume that phosphorous is first being precipitated from groundwater by carbonate, and that since San Juan waters are likely P-limited, that any leftover soluble phosphorous is consumed as soon as it enters the environment. Finally, nutrients are subject to seasonal cycling and variability; although no phosphate was detected during this short sampling period of late June through early July, this does not mean that phosphate is never present or that it cannot be affecting nearshore ecosystems.

GIS is a useful tool for visualizing the various types of data for each aspect of this project and elucidating geographical and in the data. The ArcGIS map for this project includes layers containing nutrient data, water quality data, herbicide data, and land use, to name a few examples. These layers can also be shared and used in a variety of contexts, such as for the National Park Service's Vital Signs Program, which currently lacks subtidal marine monitoring in the San Juan Island National Historical Parks.

While it appears that phosphate loading is not currently occurring, nitrogen loading is. However, further evidence is required in order to link this trend with eelgrass health. Firstly, it would be useful to test samples of SGD at the sites where we primarily sampled, English Camp and American Camp. We would then be able to more clearly make the connection between nutrients concentrations in the discharge and concentrations in the eelgrass habitats at these sites. We might also more thoroughly quantify eutrophication and algae coverage as a way to evaluate the potential threat to eelgrass. These results would be further supported by continuing sample collection during winter and collecting more replicates for each sample. Tentative plans are in place to collect samples across a wider time span and broader geographical range.

Further work may also include collection and analysis of additional SGD and seawater samples. Additionally, it is important to continue with the herbicide analysis portion of this project. No such data has yet been collected in the San Juan region, so this data will be important in establishing a general idea of local herbicide contamination. The likelihood of recolonization of areas of eelgrass disappearance is another question driving the investigation of herbicide pollution. Eelgrass can only recolonize locations where they have been extirpated by two pathways: transplantation or natural seed dispersal. Gao et al. showed that the impacts of the herbicide atrazine are highest on eelgrass seedlings (2011). This brings to mind two questions: are herbicides present in these areas, and if so, could they be contributing to a hostile environment that may be preventing seedling survival and recolonization? Additional steps in the project may include mesocosm experiments in which eelgrass seedlings are treated with different concentrations and mixtures of herbicides.

CONCLUSION

Understanding recent eelgrass declines is a priority of much importance, as eelgrass communities represent incredible ecological and economic value. The alarming magnitude of these losses, as well as the unlikelihood of natural recolonization, are further reasons to continue exploring factors that may have contributed to decline. This project aimed to address one often underlooked vehicle for coastal pollution: submarine groundwater discharge. SGD can introduce potent pollutants such as nutrients and herbicides, to nearshore ecosystems, including eelgrass beds. Thus, this summer was an effort to determine whether SGD could be affecting eelgrass health in San Juan Island National Historical Park sites by adding excess nitrogen or phosphorous to waters at these sites. While the carbonaceous geology of the island likely prevents phosphorous loading, nitrogen loading was observed both in SGD and seawater samples, especially at the north side of the island at Roche Harbor, with 2 mg/L nitrogen. Considering the harmful effects of nitrogen loading on eelgrass, primarily decreased light availability due to increased epiphyte, phytoplankton, and macroalgae growth (Moore 2000), it is reasonable to conclude that SGD could, indeed, be having a negative impact on local eelgrass communities. Further work, as mentioned above, will include sampling across a wider time span and geographical reach. Additionally, herbicide concentrations at the two primary sample sites, English Camp and American Camp, will be analyzed in order to investigate another potential factor contributing to eelgrass decline through SGD.

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