

Abstract

In the urban coastal environments of Honolulu, Hawai'i, water high in inorganic nutrients often becomes further enriched by human activity. This water seeps into the ocean by mode of submarine groundwater discharge (SGD). We hypothesize that SGD influences greenhouse gas (GHG) production in coastal systems at a measurable rate and is overlooked as a significant source of methane emissions. Marshes and wetlands are the largest contributors to methane production due to methanogenic bacteria metabolizing large amounts of organic matter, but this phenomenon is less studied in coastal systems with SGD because these systems are not usually oxygen-limited. Our research seeks to quantify methane production in areas with low salinity and high nutrients by collecting water and sediment samples from coastal areas near SGD and creating closed systems where methane and other greenhouse gasses can accumulate. The GHG rates of production will be measured with respect to the water and sediment samples' proximity to the SGD so we can quantify the magnitude of GHG on SGD in coastal systems.

Introduction

- Methane is a potent greenhouse gas (GHG) that is often produced in low-oxygen, high-nutrient aquatic systems
- Methanogens are archaeobacteria that use organic matter to undergo anaerobic metabolic processes^{1,3-5}
- Methane emissions from coastal wetlands account for 60% of all methane emitted into Earth's atmosphere^{1,2}; these emissions are on the rise due to human activity and climate change
- Phenomenon has mostly been studied in freshwater systems and coastal wetlands
- Processes are thought to be out-competed in typical coastal systems²
- Submarine groundwater discharge (SGD) is a vector for nutrients to move from land, into underground aquifers, and into the ocean⁶
- Literature of SGD's effect on GHG production is sparse, but it has been suggested that the influx of nutrients into coastal systems is correlated to the amount of GHG being produced in the benthos when compared to surface water GHG concentrations⁷⁻⁹
- Impact of SGD on coastal biogeochemistry and its relation to microbial methane production is a novel area of research
- Could reveal more about the nutrients in the sea floor, the structure of the microbial communities relative to the SGD, and GHG production by methanogens in areas with SGD¹
- Maunalua Bay, O'ahu reef flats experience widespread degradation due to urbanization resulting in high amounts of nutrients and groundwater seepage¹⁰
- SGD and GHG emissions are changing marine ecosystems by creating an influx of nutrients, altering the natural biogeochemistry, and ultimately affecting the organisms that call them home
- Probable that SGD and GHG also have synergistic effects on microbial communities

Goals and Hypotheses

Goals:

1. Quantify inorganic nutrients including nitrate, phosphate, and ammonia flowing into coastal ecosystems via SGD
2. Measure the change in nutrients as the plume moves away from the SGD seep and into the open ocean at low tide
3. Quantify GHG rate of production in coastal systems with SGD to connect what is understood about the behavior of methanogens in the presence of high nutrients to a coastal system with an SGD source

Hypotheses:

1. The rate of methanogenesis can be quantified in coastal ecosystems in the presence of SGD
2. GHG production will increase in proximity to SGD
3. A higher nitrate concentration will correlate to a larger amount of N₂O being produced relative to the SGD seep



Fig 1 shows sediment and water samples of a known mass and volume in GHG incubation bottles in which 6 samples were taken from each of the two sites



Fig 2 is an image taken from the nitrate concentration determination and Fig 3 from the phosphate determination by visible light spectrophotometer where color intensity corresponds to nutrient concentration

Methods and Materials

Sediment and water samples were taken from each of the two sites, Wailupe and Black Point, to observe the change in GHG emissions spatially across urban Maunalua Bay, O'ahu. They were transferred into gas incubation bottles (Fig 2) to create a closed system in which methanogens could undergo metabolism in an anaerobic environment. GHG samples were taken at an initial time, and once a week for the two weeks following. Water column samples were also taken from across the reef to quantify GHG in the water column, rather than the benthos. The samples were kept in pre-evacuated exetainers and sent on a Gas Chromatograph (GC) for analyzing CH₄ and N₂O samples. The rate of CH₄ production of incubation samples can be seen in Fig 4 and Fig 5. Nutrient concentrations of NO₃⁻, PO₄³⁻, and NH₄⁺ were determined by spectrophotometry (Fig 2-3) from samples taken from the SGD seep, offshore, and two distances in between at both sites. Nutrient concentrations were plotted against salinity (Fig 4) to determine

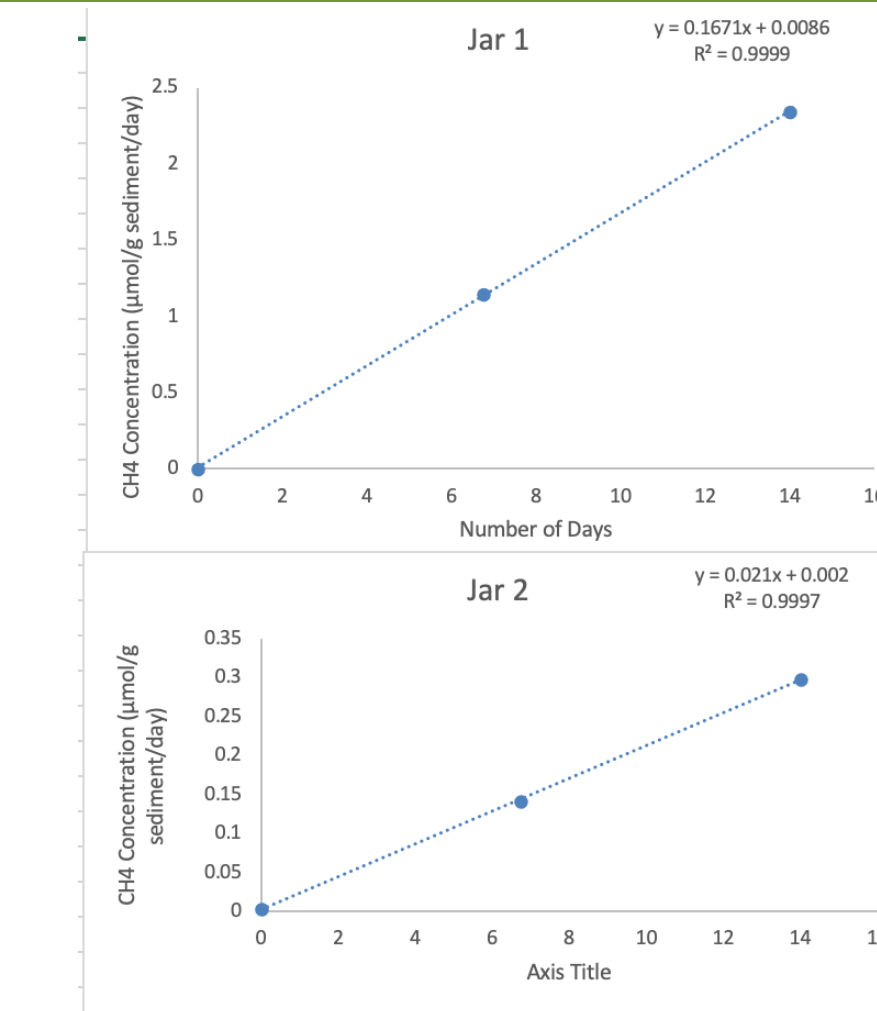


Fig 4 and Fig 5 show the increase in methane concentration over the sampling period of two weeks

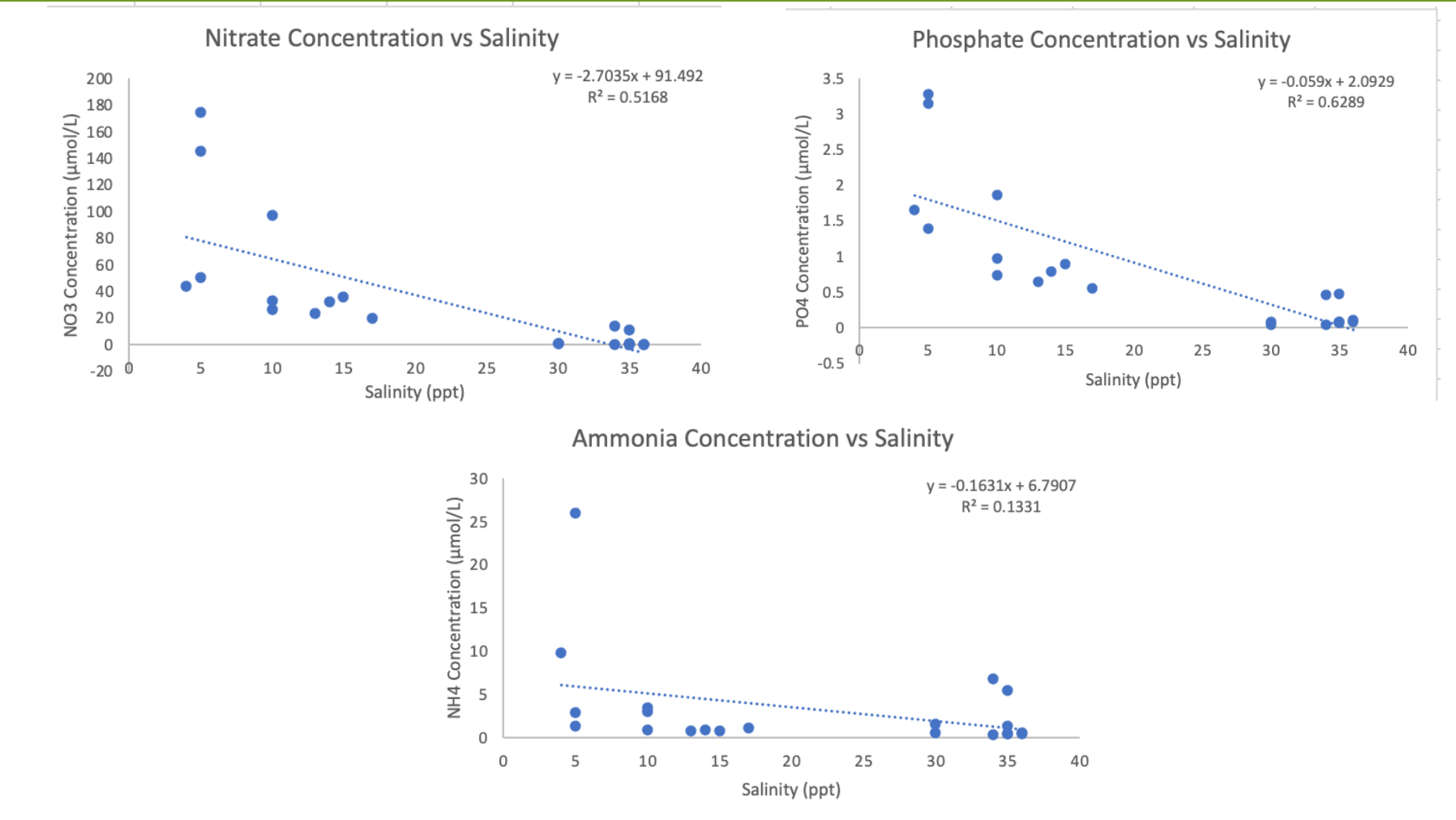


Fig 6 -8 plot nitrate, phosphate, and ammonia concentrations against salinity

Results

Fig 4 is the plot of a sample taken from the SGD at Black point where the methane concentration was calculated to be $2.22 \times 10^{-3} \mu\text{mol/g sediment/day}$ compared to the sample shown in Fig 5 collected from offshore which had a calculated concentration of $5.03 \times 10^{-5} \mu\text{mol/g sediment/day}$. Fig 6 and Fig 7 show that nutrients increase as salinity decreases (near SGD) for nitrate and phosphate, but this is not consistent for ammonia concentrations (Fig 8).

Expected Results

Distance from SGD Seep	Nitrous Oxide Concentration	Methane Concentration	Inorganic Nutrient Concentration (Nitrates, Phosphates, Ammonia)
From SGD	↑↑	↑	↑↑
Offshore	↓	↓	↓

↑↑ indicates a large increase relative to average concentrations at the site
 ↑ indicates an increase relative to average concentrations at the site
 ↓ indicates a decrease relative to the SGD seep

Conclusion

- Addresses how human presence has increased nutrients flowing into the ocean through industrial wastewater, sewage and septic tanks, agricultural fertilizers, and pesticides, which all collect in SGD¹¹
- SGD flowing into a location is unique due to surrounding land use, biogeochemical processes in surrounding aquifers and estuaries, and precipitation rates¹²
- SGD is a way to measure how activities and processes on land translate to those of the sea¹²
- Using SGD to quantify GHG can fill knowledge gaps about nutrient cycling in near shore ecosystems
- The global carbon budget is greatly impacted by rising GHG emissions, so identifying causes and the mechanisms by which these emissions change ecosystems is essential for understanding the connection between human land use in coastal areas as the chemical composition and biogeochemistry are affecting organisms in real time
- Future directions: continue sampling/data analysis regarding the effect increased nitrogenous nutrients have on the presence of N₂O near SGD
- Compare CH₄ to N₂O concentrations relative to spatial variables like salinity, nutrient content, and temperature across the reef

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