In situ tracer injection experiment conducted with 15N-labeled ammonium in a shallow, sandy subterranean estuary in Gloucester Point, USA in August 2019.

Website: https://www.bco-dmo.org/dataset/917767
Data Type: experimental
Version: 1
Version Date: 2024-01-15

Project
» Collaborative Research: Cryptic nitrogen cycling in the anoxic subterranean estuary (Subsurface cryptic N cycle)

Contributors	Affiliation	Role
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Abstract
These data are the result of an in situ tracer injection experiment conducted with 15N-labeled ammonium to determine the fate and transport rates of ammonium within a shallow, sandy subterranean estuary in Gloucester Point, VA, USA. Replicate injections of 15N-labeled ammonium, sulfur hexaflouride, and bromide amended porewater were injected into piezometers at 50cm. Porewater was then collected overtime from the injection piezometers and tracer piezometers surrounding the injection site ranging in depth from 40-60cm. At each time point, samples were collected to analyze dissolved inorganic nitrogen (nitrate, nitrite, and ammonium) concentrations, sulfur hexaflouride, bromide, chloride. Nitrate and nitrite samples from porewater were analyzed with an isotope ratio mass spectrometer in order to assess the 15N enrichment of the nitrate in each sample resulting in a delta value (d15N) that allows for the calculation of the mole fraction of 15N-labeled nitrite and nitrate in porewater at each time point. The production or consumption over time constitutes subterranean estuary nitrogen cycling rates (e.g. nitrification, denitrification, etc.).

Table of Contents

Coverage

Location: Gloucester Point Beach subterranean estuary (37.248884N, 76.505324W) in Gloucester Point, VA, USA.
Spatial Extent: **Lat**:37.248884 **Lon**:-76.505324
Temporal Extent: 2019-08-19 - 2019-08-23

Methods & Sampling

These data were collected during August 2019 from a sandy subterranean estuary (STE) located in Gloucester Point, Virginia, USA. Porewater was collected from surface water and piezometers placed at 40, 50, and 60cm. Prior to the injection, porewater was collected from replicate 50cm piezometers and amended with 15N-labeled ammonium, sulfur hexaflouride, and bromide. The amended porewater was then reintroduced into the STE through the 50cm injection piezometers.

After injection porewater was collected overtime from both the injection piezometers and other piezometers surrounding the injection well. At each time point, porewater was collected in serum bottles prepared with potassium hydroxide and were equlibrated by shaking before being run on a gas chromatograph with electron capture detection (GC-ECD, Shimadzu) in order to determine the sulfur hexaflouride concentration. Porewater was also collected for inorganic nutrients and ions, filtered with a 0.45 µm syringe filter (Whatman GE) and were frozen (-20 °C) until analysis.

Data Processing Description

Porewater nutrient concentrations were analyzed for NOx (nitrate + nitrite), nitrite, and ammonium with a Lachat autoanalyzer ions were assessed with an ion chromatograph (ThermoFisher Scientific). The isotopic enrichment of nitrate and nitrite products were measured using a gas bench isotope ratio mass spectrometer (IRMS, Delta V Plus, Thermo Fisher Scientific, Waltham, MA) using the bacterial reduction method. A culture of Pseudomonas aureofaciens reduced NOx in collected samples to N2O. The isotopic composition of the N2O was measured with isotope-ratio mass spectrometry (IRMS) (Sigman et al., 2001).

BCO-DMO Processing Description

* Split longitude and latitude of experiment location in separate columns
* Reworked Date/Time columns

[table of contents | back to top]

Data Files

File
917767_v1_tracerdata.csv (Comma Separated Values (.csv), 9.50 KB) MD5:3ea25bd79518ba835e3f1547c5044717 Primary data file for dataset ID 917767, version 1

[table of contents | back to top]

Related Publications

Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., & Böhlke, J. K. (2001). A Bacterial Method for the Nitrogen Isotopic Analysis of Nitrate in Seawater and Freshwater. Analytical Chemistry, 73(17), 4145–4153. doi:10.1021/ac010088e
Methods

[table of contents | back to top]

Parameters

Parameter	Description	Units
Site_Name	Site name where experiment was conducted	unitless
Latitude	Latitude of experiment site location	decimal degrees
Longitude	Longitude of experiment site location	decimal degrees
Piezometer	The ID of the piezometer that was sampled written as replicate cluster-injection site or trace site-depth in cm; (e.g., 1-I-50 is the first replicate cluster, injection site, 50cm depth)	unitless
Sample_ID	The ID of the piezometer that was sampled written as replicate cluster-injection site or trace site-depth in cm-timepoint; (e.g., 1-I-50-T1 is the first replicate cluster, injection site, 50cm depth, time point 1)	unitless
Time_Point	Injection experiment time point (BKGD, T0, T1, T2, etc). BKGD means background samples, so samples that were collected prior to the start of the injection.	unitless
Date	Date of sample collection	unitless
Time	Time of sample collection	unitless
Hours_after_Injection	Hours after injectate was introduced in the subsurface	hours (hrs)
Bromide_uM	Bromide concentration in porewater in micromoles per liter (uM) measured by ion chromatograph	micromoles per liter (uM)
Chloride_mM	Chloride concentration in porewater in millimoles per liter (mM) measured by ion chromatograph	millimoles per liter (mM
SF6_ppbv	Sulfur hexaflouride concentration in porewater in parts per billion per volume (ppbv) measured by gas chromatograph-electron capture detector	parts per billion per volume (ppbv)
SF6_pM	Sulfur hexaflouride concentration in porewater in picoMolar (pM) measured by gas chromatograph-electron capture detector	picoMolar (pM)
Nox_uM	Nitrate + Nitrite concentration in porewater in micromoles per liter (uM) measured by a lachat autoanalyzer	micromoles per liter (uM)
NO2_uM	Nitrite concentration in porewater in micromoles per liter (uM) measured by a lachat autoanalyzer	micromoles per liter (uM)
NH4_uM	Ammonium concentration in porewater in micromoles per liter (uM) measured by a lachat autoanalyzer	micromoles per liter (uM)
True_d15N	Delta 15N measurement made by an isotope ratio mass spectrometer	parts per thousand (‰)
Mole_Fraction_Calc	15N Mole Fraction calculated from the d15N value	unitless

[table of contents | back to top]

Instruments

Dataset-specific Instrument Name	Ion Chromatograph, ThermoFisher Scientific; Lachat QuikChem 8000 automated ion analyzer Lachat In- struments
Generic Instrument Name	Lachat QuikChem 8000 flow injection analyzer and Ion Chromatography (IC) system
Dataset-specific Description	Ion Chromatograph, ThermoFisher Scientific; Lachat QuikChem 8000 automated ion analyzer Lachat In- struments, Milwaukee, WI, USA; detection limits for NO3−, NH4+, and PO43− are 0.20, 0.36, and 0.16 µM, respectively. Gas bench isotope ratio mass spectrometer (IRMS) Delta V Plus, Thermo Fisher Scientific, Waltham, MA.
Generic Instrument Description	The Lachat QuikChem 8000 can operate flow injection analysis and ion chromatography simultaneously and independently on the same instrument platform. Instrument includes sampler, dilutor, sampling pump, electronics unit, and data station. Analysis takes 20-60 seconds, with a sample throughput of 60-120 samples per hour. Measurements are in the range of parts per trillion to parts per hundred.

[table of contents | back to top]

Project Information

Collaborative Research: Cryptic nitrogen cycling in the anoxic subterranean estuary (Subsurface cryptic N cycle)

Coverage: Temperate (Mid-Atlantic), Sandy Beach along the York River Estuary, Gloucester Point, Virginia, USA (37.24884N/76.505324W)

NSF Award Abstract:
Nitrogen is an important nutrient that maintains high coastal ecosystem productivity. Yet excess nitrogen delivery can cause serious water quality deterioration including harmful algal blooms, fish kills, and oxygen free dead zones. Numerous nitrogen transformations regulate the balance between nitrogen delivery and nitrogen removal in coastal environments and the majority of these reactions occur in sediments where seawater passes through the subsurface and mixes with groundwater transported from uplands. This mixing zone, referred to as the subterranean estuary, is characterized by very different geochemistry than either the seawater above it or the groundwater below it. Thus, it has the potential to host a variety of unique reactions that affect nitrogen availability to the overlying water. Scientists from the College of William and Mary, Virginia Institute of Marine Science (VIMS), and the University of Connecticut (UConn) propose to examine the importance of a cryptic nitrogen cycle, a novel and potentially widespread nitrogen cycling process in the subterranean estuary. The cryptic nitrogen cycle comprises anoxic ammonium oxidation to nitrite (anoxic nitrification) coupled with anaerobic ammonium oxidation (anammox) or denitrification producing harmless dinitrogen gas. The proposed project represents highly transformative science because it has the potential to change the current paradigm detailing operation of the biogeochemical nitrogen cycle in anoxic environments. Occurrence of the cryptic nitrogen cycle would have broad implications for the nitrogen budget of terrestrial and groundwater systems and the coastal ocean. Characterization of the cryptic nitrogen cycle will allow us to better understand interactions among the nitrogen, metals, and sulfur cycles, and potential impacts of ongoing human modification of coastal environments. Educational contribution of this project focuses on graduate and undergraduate student training. Two graduate students at VIMS and UConn will receive interdisciplinary training in microbiology, molecular ecology, and biogeochemistry while several undergraduates recruited through the VIMS REU (Research Experience for Undergraduates) Program and the UConn marine science programs will also participate in the project. In addition, three summer undergraduate interns will be recruited from Hampton University, a historically Black college, and trained to enhance minority education and research in marine science. Public outreach will be achieved through popular venues such as VIMS Marine Science Day, and the VIMS After Hours Public Lecture Series at VIMS. Tobias at UConn also provides educational contributions and outreach efforts through the UConn Marine Scholars and Early College Experience programs and an exhibit at Mystic Aquarium.

A cryptic nitrogen cycle is proposed as a new process coupling anoxic nitrification to microbial nitrogen

removal pathways such as anammox and denitrification. Unlike anammox, which refers to the oxidation of ammonium by nitrite to form dinitrogen (N2) gas, anoxic nitrification occurs by oxidation of ammonium in the absence of oxygen using other common chemical oxidants such as metal oxides (namely, Fe and Mn) or sulfate, abundant in many marine and coastal systems. The thermodynamic favorability of these reactions relies on coupling nitrite formed via these oxidants with anammox or denitrification. Due to the coupling, nitrite will not accumulate or be measurable in anoxic marine systems. Thus, a cryptic N cycle responsible for nitrite production can occur as a novel N transforming process in anoxic environments, serve as a vital link to N2 production, and attenuate N loads discharging from a subterranean estuary (STE). Preliminary results from a STE in the York River Estuary located in Virginia showed substantial N2 production, representing removal of 50-75% of the fixed groundwater N, in ferruginous and sulfidic zones where neither nitrite nor nitrate were detectable. Stable isotope incubation experiments using the 15N tracer and molecular analysis of microbial communities suggest that coupled anoxic nitrification and anammox processes are the dominant N2 production pathways rather than canonical denitrification in the STE. Therefore, coupled anoxic nitrification-anammox in coastal groundwater may be a major unrecognized sink for fixed nitrogen at the land-sea interface. In addition to coastal groundwater, the cryptic N cycle has potential importance in anoxic zones and ocean basins. This proposal focuses on the STE because geochemical conditions there appear optimal for the proposed reactions to occur, and our preliminary data show strong evidence for a cryptic N cycle. The proposed work uses a combined geochemical, 15N isotope tracer and microbiological approach to evaluate environmental controls on the cryptic N cycle as well as to estimate its contribution to reduction of fixed N fluxes to the coastal ocean. Four approaches are proposed: (1) Field characterization of anoxic nitrification reactions and associated microbial communities in a subterranean estuary; (2) Laboratory incubation experiments to identify hotspots of the cryptic N cycle; (3) Controlled microcosm experiments to determine geochemical controls on anoxic nitrification; and (4) in situ assessment of anoxic nitrification to estimate the importance of the cryptic N cycle in a coastal aquifer.

[table of contents | back to top]

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1657801

[table of contents | back to top]