Water column, pore water, and bulk sediment geochemical data from karst subterranean estuaries of the Yucatan Peninsula and Cozumel Island, Mexico (2022-2024)

Website: https://www.bco-dmo.org/dataset/1011061
Data Type: Other Field Results
Version: 1
Version Date: 2026-11-02

Project
» Collaborative Research: Illuminating Cave Benthos in Subterranean Estuaries- Biodiversity, Ecology, and Role in Coastal Ecosystem Functioning (Karst Cave Benthos)

Contributors	Affiliation	Role
Borda, Elizabeth	Texas A&M San Antonio (TAMUSA)	Principal Investigator
Brankovits, David	Woods Hole Oceanographic Institution (WHOI)	Co-Principal Investigator
Calderón-Gutiérrez, Fernando	Texas A&M San Antonio (TAMUSA)	Scientist
Magen, Cédric	University of Maryland - College Park (UMD)	Scientist
Martínez, Alejandro	National Research Council of Italy (CNR)	Scientist
Pohlman, John	United States Geological Survey (USGS)	Scientist
Hildebrand, Anna	University of Maryland Center for Environmental Science (UMCES/CBL)	Student
Rohret, Shari	Woods Hole Oceanographic Institution (WHOI)	Student
Boze, Lee-Gray	United States Geological Survey (USGS)	Technician
Casso, Michael	United States Geological Survey (USGS)	Technician
Mann, Adrian	United States Geological Survey (USGS)	Technician
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract
An investigation of the benthic biology and biogeochemistry of caves within karst subterranean estuaries was undertaken in the state of Quintana Roo, Mexico, to establish relationships between benthic eukaryotic community diversity and elemental cycles within the sediments and in the overlying water column. This dataset focuses on the geochemical analysis of the water column, sediment pore fluids, and bulk sediments from flooded caves, open-water cave entry pools (or cenotes), and associated marine waters. The water column and pore water measurements include the following dissolved components: anions (sulfate and chloride), nutrients (nitrogen, phosphorus and silicate-based), organic carbon, inorganic carbon, methane, and carbon dioxide All species were analyzed for concentrations, and the carbon species measurements additionally include stable carbon isotope ratios. The bulk sediment measurements include the weight percent of total organic carbon, calcium carbonate, and total nitrogen, and additionally the stable carbon and nitrogen isotope ratios of the total organic carbon and total nitrogen. The dataset includes a description of the geographic region, the sampled cave system, the cave entry location, and the sampling station with the cave (if available). For each sample, the associated water mass (fresh, brackish, or saline groundwater, or seawater) and habitat (open water, cenote, cavern, cave, or sea) are provided. The dataset also includes endmembers from surface waters proximal to each cave system and the coastline. The project is a collaboration between the Woods Hole Oceanographic Institution, Texas A&M University at San Antonio, Campus Yucatan of the Universidad Nacional Autónoma de México (UNAM), and the U.S. Geological Survey (USGS). Primary funding was provided by the National Science Foundation (NSF) with additional support provided by the U.S. Geological Survey.

Table of Contents

- Coverage
- Dataset Description
  - Methods & Sampling
  - Data Processing Description
  - BCO-DMO Curation Notes
- Parameters
- Project Information
- Funding

Coverage

Location: Quintana Roo, Mexico

Methods & Sampling

Overview
Samples were collected over three campaigns (September 2022, February 2023, and February 2024) across four cave systems on the Yucatan Peninsula and Cozumel Island, Mexico. All samples were collected by certified scientific cave divers following American Academy of Underwater Sciences (AAUS) dive safety protocols. Collection, processing, and analysis followed consistent protocols across campaigns, as described in Rohret and others (2026).

1. SAMPLE COLLECTION

Water Column Samples
Water was collected from bottom waters at each station using 500-milliliter (mL) plastic syringes fitted with three-way stopcocks (closed before immersion to prevent premature water entry). Syringes were rinsed with distilled water and air-dried before use. After collection, samples were kept on ice and transported to the field laboratory, where water was filtered through a 25-millimeter (mm) PES membrane syringe filter (Whatman GD/X, 0.2-micrometer (µm) pore size) and aliquoted for nutrient, DOC, DIC, chloride, and sulfate analyses.

Dissolved gas (methane and CO2) samples were collected by headspace equilibration: 120 mL of analyte-free air was added to each ~380 mL water sample (headspace-to-water ratio ~1:3), shaken vigorously to equilibrate the gases, and ~100 mL of headspace gas was withdrawn into a dry syringe, transferred to air-tight Cali-5-Bond sampling bags, and stored at room temperature until analysis.

Porewater Samples
Porewater was collected by three methods:

Push Coring (PC): A manual push corer was used; the recovered core was extruded into discrete depth intervals at the surface, and pore fluids extracted from each interval. Associated overlying water samples (OLW) were collected directly above the sediment-water interface, representing the 0 cm interval.

PoWer-OPP configuration: Using the OctoPiPi (OPP) water sampling device (10 syringes of 60 mL, mechanically triggered to draw fluid simultaneously; described in Brankovits and Pohlman, 2020), with Rhizon pore-fluid samplers (0.22 µm filter) mounted on a fixed frame pressed into the sediment, sampling up to eight discrete depths (0–18 centimeters (cm) below the sediment-water interface); a probe at 0 cm sampled overlying water.

Octopodia configuration: The same OPP syringes without the fixed frame; Rhizon-tipped probes were connected via variable-length tubing, allowing a diver to manually place each probe at 2–4 cm depth across a ~10 meter (m) horizontal transect. Each probe collected up to 30 mL of in-situ filtered porewater.

Bulk Sediment Samples
Two collection methods were used:

Surface Scoop: Sterile 50-mL conical centrifuge tubes or 500-mL plastic jars were used to gently skim the top 1–2 cm of sediment.

Push Core: A manually inserted push corer was used; recovered sediment was extruded and subsampled into discrete 2–3 cm sections.

Both sample types were transported on ice to the field laboratory. Surface Scoop samples were allowed to settle and decanted prior to storage; Push Core sections were transferred to 250-mL plastic bags. All sediment samples were stored at –20 °C until further processing and analysis.

2. LABORATORY ANALYSES

Nutrients (nitrate, nitrite, ammonium, phosphate, silicate)
Measured using a four-channel segmented flow AA3 HR Autoanalyzer at the Nutrient Analytical Facility, Woods Hole Oceanographic Institution (WHOI). Nitrate was measured directly; where reported separately, nitrite was calculated as the difference between the combined nitrate+nitrite value and the directly measured nitrate value.

Chloride and Sulfate
Measured by ion chromatography (IC) using a Metrosep A Supp 5 150/4.0 column (Metrohm 881 Compact IC Pro) at the Environmental Geochemistry Lab, USGS Woods Hole Coastal and Marine Science Center. Salinity was calculated from the IC-determined chloride concentration, following protocols in Brankovits and others (2017).

Dissolved Organic Carbon (DOC) and δ13C-DOC
Measured by high-temperature combustion-isotope ratio mass spectrometry (HTC-IRMS) at the USGS-WHOI Dissolved Carbon Isotope Laboratory, following protocols in Brankovits and others (2017).

Dissolved Inorganic Carbon (DIC) and δ13C-DIC
Measured at the Stable Isotope Facility, University of California, Davis, using a GasBench II system interfaced to a Delta V Plus IRMS (Thermo Scientific, Bremen, Germany) according to established protocols as described by the facility: Water samples (1-4 mL) are injected into helium-filled 12 mL septum capped vials (Exetainers, Labco, High Wycombe, UK) containing 1 mL 85% phosphoric acid, which forces the equilibrium between CO_2 and H_2CO_3 to gaseous CO_2. The evolved CO_2 is purged from vials through a double-needle sampler into a helium carrier stream (20 milliliters per minute (mL/min)). The gas is sampled using a six-port rotary valve (Valco, Houston TX) with either a 100 microliter (µL), 50 µL, or 10 µL loop programmed to switch at the maximum CO_2 concentration in the helium carrier. The CO_2 is passed to the IRMS through a Poraplot Q GC column (25m x 0.32mm ID, 45 °C, 2.5 mL/min). A reference CO_2 peak is used to calculate provisional delta values of the sample CO_2 peak. Final 13C delta values are obtained after adjusting the provisional delta values for changes in linearity and instrumental drift such that correct 13C delta values for laboratory reference materials are obtained. At least two laboratory reference materials are analyzed with every 10 samples. Laboratory reference materials are lithium carbonate dissolved in degassed deionized water and a deep seawater (both calibrated against NIST 8545). Final 13C delta values, delivered to the customer, are expressed relative to the international standard V-PDB (Vienna PeeDee Belemnite). Limit of Quantitation and Long-term standard deviation for 13C-DIC by GasBench-IRMS 13C-DIC as CO_2 is approx. 150 nanomoles, while the long-term standard deviation is 0.1 ‰.

Dissolved Methane (CH_4) and CO_2, and their δ13C values
Measured at USGS Woods Hole Coastal and Marine Science Center using the Automated Sample Introduction Module (AutoSIM) coupled to the Discrete Sample Introduction Module (DSIM) and a Picarro G2201-i cavity ring-down spectrometer (CRDS), which simultaneously measures CH_4, CO_2, and their δ13C values (relative to VPDB) as described by Pohlman and others (2021). Samples were analyzed without dilution. Headspace concentrations were converted to dissolved concentrations using the method of Magen and others (2014).

Isotopic precision (1-sigma) is concentration-dependent, degrading near the instrument's limit of detection (LOD). δ13C-CH_4 requires higher CH_4 concentrations than needed for concentration measurement alone; samples below the isotope-specific LOD are reported as "b.d." (below detection) for isotopes only. The isotope-specific LOD for methane was ~12 ppm headspace (~134 nanomolar (nM) in water) for 2022–2023 samples (due to a temporary sensitivity reduction, later resolved) and ~1.5 ppm headspace (~18.7 nM in water) for 2024 samples.

Bulk Sediment — Decalcification
The freeze-dried, homogenized subsample (~5 mL) was placed in a tared 50-mL centrifuge tube; 10% HCl was added and allowed to react until effervescence ceased, with periodic stirring. Acid was removed by centrifugation/decantation and replaced repeatedly until no further effervescence occurred (indicating complete $CaCO_3$ removal). The residue was rinsed 2–3 times with Milli-Q water (centrifuged/decanted between rinses), then freeze-dried and reweighed. Weight percent $CaCO_3$ = (raw sediment mass − residue mass) / raw sediment mass. The dried residue was homogenized and subsampled into a silver Elemental Analyzer (EA) cup.

Bulk Sediment — Elemental and Isotopic Analysis
Carbon and nitrogen concentrations and their stable isotope ratios (13C/12C, 15N/14N) were measured using

a Costech ECS 4010 elemental analyzer interfaced to a Delta V Plus isotope ratio mass spectrometer (IRMS) (Thermo Scientific). Analytical precision (based on USGS40 and USGS41a reference standards): ±0.2‰ for isotope ratios, ±2% for elemental concentrations. The wt%_TOC and wt%_TN (of the whole/raw sediment) were calculated from the decalcified residue's measured elemental content, scaled by the residue-to-raw-sediment mass ratio to account for the CaCO3 removed:

wt%_TOC = (residue mass / raw sediment mass) × (mass of C measured by EA / mass of residue analyzed)

wt%_TN calculated analogously using nitrogen mass

Molar C/N ratio = (wt%_TOC / 12) / (wt%_TN / 14)

Data Processing Description

Chloride concentrations (millimolar (mM)) measured by ion chromatography were converted to milligrams per liter (mg/L) and multiplied by 0.0018066 to determine salinity (psu).

BCO-DMO Curation Notes

currently being processed

[table of contents | back to top]

Parameters

Parameters for this dataset have not yet been identified

[table of contents | back to top]

Project Information

Collaborative Research: Illuminating Cave Benthos in Subterranean Estuaries- Biodiversity, Ecology, and Role in Coastal Ecosystem Functioning (Karst Cave Benthos)

Coverage: Yucatan and Cozumel, Mexico, aquifer/anchialine caves

NSF Award Abstract:
Karst subterranean estuaries (KSEs) occur worldwide where fresh and marine-derived waters mix within coastal aquifers, creating a chemical reaction zone that alters the composition of materials transported to the sea and sustains characteristic aquatic communities. Approximately one quarter of Earth’s population depends on karst (eroded limestone) water supplies that – within coastal regions – are directly threatened by rising sea level, uncontrolled groundwater extraction, and rapid coastal development. Yet, the role of these ecosystems in coastal biogeochemical cycling and groundwater health remains unknown. While pelagic constituents of flooded caves in KSEs have been studied for decades, the living benthic (cave floor / seafloor-hosted) fauna of these caves and caverns remains understudied. The overarching goal of this project is to better understand how benthic biodiversity affects ecosystem functioning across subsurface environmental gradients between freshwater aquifers and the marine environment. Flooded coastal caves allow the team to access the KSEs and make direct observations. Results of this work benefit marine benthic ecology and biology, biogeochemistry, paleoecology and biodiversity assessments. This interdisciplinary project establishes a multinational, multi-institutional collaboration, enhance research and scholarship opportunities at a predominantly undergraduate Hispanic-serving institution in Texas and support young investigators from under-represented groups in the sciences. For outreach, the project-associated PhD student, who is an African American female, is co-authoring a semi-autobiographical children’s book about cave diving and the wonders of cave-associated organisms.

KSEs influence coastal carbon and nitrogen cycling because they buffer terrestrial material inputs with groundwater discharge into the oceans. While pelagic communities of flooded cave environments in KSEs have been studied for decades due to their adaptations, biogeography, and evolutionary origin, the living benthic fauna and their role in KSE elemental cycling remains understudied. The overall aim of this project is to establish the diversity and ecology of benthic eukaryotes across environmental gradients in extensive coastal caves flooded by the KSE in the Yucatan Peninsula and Cozumel Island (Mexico) and determine how they interact with benthic elemental cycles. This study provides a holistic characterization of KSE benthos using interdisciplinary field- and lab-based approaches including barcoding/meta-barcoding, meta-transcriptomics, ultrastructural analysis, and lab culturing that are being integrated with biogeochemical and hydrological measurements. Specifically, the investigators are characterizing (1) the drivers of spatial biodiversity patterns in coastal cave eukaryotic benthic communities across salinity/oxygen gradients, relative to organic inputs; (2) the role of benthic meiofauna (to nanobiota) communities, with emphasis on foraminifera, in ecosystem function relative to dominant biogeochemical processes that mediate organic matter transformations and nitrogen cycling; and (3) the temporal constraints of benthic meiofauna (to nanobiota) biodiversity and ecosystem resilience in response to seasonal hydrological variation associated with meteorological events.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

[table of contents | back to top]

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-2136377

[table of contents | back to top]