

Concentration measurements of water column phosphate, nitrate and nitrite, dissolved organic phosphorus, methane, and ethylene from samples collected during the R/V Neil Armstrong cruise AR16 in the western North Atlantic Ocean in May 2017

Website: <https://www.bco-dmo.org/dataset/769203>

Data Type: Cruise Results

Version: 2

Version Date: 2019-07-19

Project

» [Methane, Ethylene, and Dissolved Organic Phosphorus Cycling in the Western North Atlantic Ocean](#) (PHAT)

Contributors	Affiliation	Role
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Abstract

Concentration measurements of water column phosphate, nitrate and nitrite, dissolved organic phosphorus, methane, and ethylene from samples collected during the R/V Neil Armstrong cruise AR16 in the western North Atlantic Ocean in May 2017. Seawater was collected from Niskin bottles deployed on a rosette with a CTD.

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Coverage

Spatial Extent: N:40.4025 E:-64.1875 S:29.05817 W:-71.33867

Temporal Extent: 2017-05-04 - 2017-05-20

Dataset Description

Concentration measurements of water column phosphate, nitrate and nitrite, dissolved organic phosphorus, methane, and ethylene from samples collected during the R/V Niel Armstrong cruise AR16 in the western North Atlantic Ocean in May 2017.

Acquisition Description

Sampling was conducted aboard the R/V Neil Armstrong (cruise AR16) in May 2017. Seawater was collected from Niskin bottles deployed on a rosette with a CTD.

Samples for seawater methane (CH₄) and ethylene (C₂H₄) concentration measurements were collected from the CTD rosette in 250 mL glass serum vials (pre-combusted) crimp-sealed with aluminum collars and with Teflon-lined septa. Samples were typically analyzed the same day of sampling aboard the R/V Armstrong with an Agilent 7980A gas chromatograph equipped with a flame ionization detector (FID) and a gas stripping and cryo-trap concentration method as described previously (Repeta et al. 2016). The FID was calibrated by injecting different sized loops of a gas mixture standard containing 10 ppm of CH₄ and C₂H₄ in pure nitrogen gas (Scott-Marrin, Riverside, CA, USA).

Samples for nutrient analyses were collected in acid-clean HDPE plastic bottles. Samples were shipped frozen to the Center for Microbial Oceanography: Research and Education at the University of Hawaii at Manoa where they were stored frozen until analysis.

Seawater phosphate (PO₄) concentrations were determined following the autoanalyzer colorimetric procedure of Foreman et al. (2019). Seawater nitrate+nitrite (NO_x) concentrations were determined following the autoanalyzer colorimetric procedure outlined of Foreman et al. (2016). Both PO₄ and NO_x analyses were performed on a SEAL Analytics autoanalyzer model

3 HR.

Seawater samples with low level N+N (LLN) concentrations were measured using the modified chemiluminescent method based on titanium (III) trichloride reduction of N+N to nitric oxide gas and detection with an Antek model 7090 as described by Foreman et al. (2016).

MAGIC soluble reactive phosphorus (SRP) concentrations (i.e. phosphate) were determined in seawater samples using the MAGnesium Induced Coprecipitation (MAGIC) technique as described by Karl and Tien (1992) with modifications based on Thompson-Bulldis and Karl (1998) and Cavendar-Bares et al. (2001) to increase the concentration factor of phosphate. Specifically, SRP was concentrated from 150 mL seawater samples using 0.75 mL (0.5% v/v) of 1M NaOH to precipitate Mg(OH)₂ and the Mg(OH)₂ pellets were dissolved with 5.25 mL of 0.1M HCl.

Total dissolved P (TDP) concentrations were measured by a photo-oxidation procedure in which controlled exposure to ultraviolet (UV) radiation converts organic P in seawater to phosphate which is then measured by the modified molybdenum blue method adapted for the autoanalyzer technique. The UV photo-oxidation methodology for TDP analysis is described in Foreman et al. (2019). The difference between TDP and PO₄ or TDP and SRP is calculated to estimate the concentration of dissolved organic phosphorus (DOP) in seawater.

Processing Description

nd = not determined; bdl = below detection limit.

BCO-DMO Processing:

- Re-formatted original date/time field into ISO8601 format;
- 2019-07-19: served version 2 of data (detection limits of ethylene gas were re-calculated).

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Related Publications

Cavender-Bares, K. K., Karl, D. M., & Chisholm, S. W. (2001). Nutrient gradients in the western North Atlantic Ocean: Relationship to microbial community structure and comparison to patterns in the Pacific Ocean. *Deep Sea Research Part I: Oceanographic Research Papers*, 48(11), 2373–2395. doi:[10.1016/S0967-0637\(01\)00027-9](https://doi.org/10.1016/S0967-0637(01)00027-9)

Foreman, R. K., Björkman, K. M., Carlson, C. A., Opalk, K., & Karl, D. M. (2019). Improved ultraviolet photo-oxidation system yields estimates for deep-sea dissolved organic nitrogen

and phosphorus. *Limnology and Oceanography: Methods*, 17(4), 277–291.

doi:[10.1002/lom3.10312](https://doi.org/10.1002/lom3.10312)

Foreman, R. K., Segura-Noguera, M., & Karl, D. M. (2016). Validation of Ti(III) as a reducing agent in the chemiluminescent determination of nitrate and nitrite in seawater. *Marine Chemistry*, 186, 83–89. doi:[10.1016/j.marchem.2016.08.003](https://doi.org/10.1016/j.marchem.2016.08.003)

Karl, D. M., & Tien, G. (1992). MAGIC: A sensitive and precise method for measuring dissolved phosphorus in aquatic environments. *Limnology and Oceanography*, 37(1), 105–116. doi:[10.4319/lo.1992.37.1.0105](https://doi.org/10.4319/lo.1992.37.1.0105)

Repeta, D. J., Ferrón, S., Sosa, O. A., Johnson, C. G., Repeta, L. D., Acker, M., ... Karl, D. M. (2016). Marine methane paradox explained by bacterial degradation of dissolved organic matter. *Nature Geoscience*, 9(12), 884–887. doi:[10.1038/ngeo2837](https://doi.org/10.1038/ngeo2837)

Thomson-Bulldis, A., & Karl, D. (1998). Application of a novel method for phosphorus determinations in the oligotrophic North Pacific Ocean. *Limnology and Oceanography*, 43(7), 1565–1577. doi:[10.4319/lo.1998.43.7.1565](https://doi.org/10.4319/lo.1998.43.7.1565)

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Parameters

Parameter	Description	Units
Cruise	cruise identifier	unitless
Station	station number	unitless
Cast	cast number	unitless
Latitude	latitude north (positive values = North)	decimal degrees
Longitude	longitude east (negative values = West)	decimal degrees
ISO_DateTime_UTC	date and time (UTC) formatted to ISO8601 standard; format: yyyy-mm-ddTHH:MM:SS	unitless
Depth	sample depth	meters (m)
CH4	methane	nanomoles per liter (nmol L ⁻¹)
C2H4	ethylene	nanomoles per liter (nmol L ⁻¹)
NOx	nitrate + nitrite	micromoles per liter (umol L ⁻¹)
LLN	low level nitrogen (nitrate + nitrite)	micromoles per liter (umol L ⁻¹)
PO4	phosphate	micromoles per liter (umol L ⁻¹)
SRP	soluble reactive phosphorus	micromoles per liter (umol L ⁻¹)
TDP	total dissolved phosphorus	micromoles per liter (umol L ⁻¹)

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Instruments

Dataset-specific Instrument Name	Niskin bottles
Generic Instrument Name	Niskin bottle
Generic Instrument Description	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24 or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

Dataset-specific Instrument Name	Agilent 7980A
Generic Instrument Name	Gas Chromatograph
Generic Instrument Description	Instrument separating gases, volatile substances, or substances dissolved in a volatile solvent by transporting an inert gas through a column packed with a sorbent to a detector for assay. (from SeaDataNet, BODC)

Dataset-specific Instrument Name	Antek model 7090
Generic Instrument Name	Chemiluminescence NOx Analyzer
Generic Instrument Description	The chemiluminescence method for gas analysis of oxides of nitrogen relies on the measurement of light produced by the gas-phase titration of nitric oxide and ozone. A chemiluminescence analyzer can measure the concentration of NO/NO ₂ /NO _x . One example is the Teledyne Model T200: http://www.teledyne-api.com/products/T200.asp

Dataset-specific Instrument Name	Agilent 7980A
Generic Instrument Name	Flame Ionization Detector
Generic Instrument Description	A flame ionization detector (FID) is a scientific instrument that measures the concentration of organic species in a gas stream. It is frequently used as a detector in gas chromatography. Standalone FIDs can also be used in applications such as landfill gas monitoring, fugitive emissions monitoring and internal combustion engine emissions measurement in stationary or portable instruments.

Dataset-specific Instrument Name	SEAL Analytics autoanalyzer model 3 HR
Generic Instrument Name	Seal Analytical AutoAnalyser 3HR
Generic Instrument Description	A fully automated Segmented Flow Analysis (SFA) system, ideal for water and seawater analysis. It comprises a modular system which integrates an autosampler, peristaltic pump, chemistry manifold and detector. The sample and reagents are pumped continuously through the chemistry manifold, and air bubbles are introduced at regular intervals forming reaction segments which are mixed using glass coils. The AA3 uses segmented flow analysis principles to reduce inter-sample dispersion, and can analyse up to 100 samples per hour using stable LED light sources.

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Deployments

AR16

Website	https://www.bco-dmo.org/deployment/747056
Platform	R/V Neil Armstrong
Start Date	2017-05-03
End Date	2017-05-22
Description	Redox Cycling of Phosphorus in the Western North Atlantic

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Project Information

Methane, Ethylene, and Dissolved Organic Phosphorus Cycling in the Western North Atlantic Ocean (PHAT)

Coverage: Sargasso Sea, Western North Atlantic Ocean

NSF Award Abstract: The "marine methane paradox" refers to observations of high concentrations of methane in surface waters of the ocean, even though these waters are well-oxygenated and high in sulfate, both features which generally do not favor the production of methane. This project aims to elucidate on the cause of this paradox. Based on preliminary results, the investigator identified the potential for methane production stimulated by microbial cycling of dissolved organic matter. Polysaccharides (carbonates such as starch) are a major component of high molecular weight dissolved organic matter (HMWDOM) and they can incorporate esters of methylphosphonate, which may be allowing for the production of methane in surface waters. When these HMWDOM polysaccharides were introduced to seawater samples, the researchers saw production of methane with an anomalous stable carbon isotope ratio comparable to what is seen in the paradoxical surface waters enriched in methane. By making measurements of trace gases, HMWDOM phosphonate, and stable carbon isotope measurements in the western North Atlantic Ocean, the investigator and his collaborators will reassess the preliminary data and the implications of these results for the entire oceanographic cycling of methane. Both educational and outreach efforts have been included. For the educational component, a postdoc, a graduate student, and summer undergraduate students will be work on the project, whereas for the outreach activities, the proponent plans to develop curricula on basic science and oceanography for high school students, include a high school teacher in the research cruise, and integrate results into an organic geochemistry course, the lectures of which will be publically available online. This project seeks to evaluate the possibility that the "marine methane paradox", or the super-saturation of methane in high

sulfate, well-oxygenated surface waters, is caused by microbial cycling of dissolved organic matter (DOM). There has been a great deal of preliminary evidence to support this theory. For example, samples from station ALOHA were amended with purified high molecular weight DOM (HMWDOM) polysaccharides, and methane, ethylene, and propylene productions were stimulated. HMWDOM polysaccharides incorporate esters of methylphosphonate (MPn), 2-hydroxyethylphosphonates (2-HEP), and other minor phosphonates, which are likely facilitating the production of methane, ethylene, and propylene. Carbon isotope data supports that this theory is the process behind the marine methane paradox; the $d_{13}C$ value of methane produced from HMWDOM polysaccharide enriched samples agrees well with the anomalous value associated with the super-saturated surface water. Only a small fraction of HMWDOM polysaccharides can easily explain the marine methane paradox, and this process could just as easily fully revise the current understanding of large scale methane cycling between the ocean and atmosphere. The researchers will assess the preliminary evidence and evaluate the microbial DOM cycling theory by making paired trace gas and HMWDOM phosphonate, as well as stable carbon isotope measurements in the western North Atlantic Ocean.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1634080

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