

Concentrations of dissolved organic carbon and phenols from Polarstern cruise PS 94-ARK-XXIX/3 from August to October 2015

Website: <https://www.bco-dmo.org/dataset/767285>

Data Type: Cruise Results

Version: 1

Version Date: 2019-05-10

Project

» [Development and application of a high sensitivity, ultra low volume method to measure biomarkers of terrigenous organic matter in the open ocean](#) (Lignin phenol method development)

Contributors	Affiliation	Role
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Abstract

Concentrations of dissolved organic carbon and phenols from Polarstern cruise PS 94-ARK-XXIX/3 from August to October 2015.

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Coverage

Spatial Extent: N:89.1667 E:179.8463 S:73.2525 W:-179.9473

Temporal Extent: 2015-08-20 - 2015-10-07

Methods & Sampling

Samples were filtered straight from Niskin bottles following established protocols for trace-metal clean sampling (Sample handling protocols for GEOTRACES cruises).

Samples for DOC concentration were acidified to pH 2.5 and analyzed by high-temperature combustion on a Shimadzu TOC-L. DOC was calculated as the mean of between three and five injections using a six-point standard curve.

Lignin-derived phenols were determined following Yan and Kaiser (2018; Anal. Chem), and Yan and Kaiser (2018; Analytica Chimica Acta). Briefly, C18 extracts were redissolved in 200 μL of 1.1 mol L^{-1} argon-sparged (10 min) NaOH in a 400 μL Teflon vial (Saville Corp) and amended with containing 500 mg CuO, and amended with 10 μL of 10 mmol L^{-1} CuSO₄ and 10 μL of 0.2 mol L^{-1} ascorbic acid. Oxidation was at 150 C for 120 minutes. Following oxidation, the samples were spiked with a surrogate standard mixture of p-hydroxybenzoic acid-13C7, vanillin-13C6, and syringaldehyde-13C6 and acidified to pH \approx 2.5 with 6 mol L^{-1} sulfuric acid in the reaction vials. Clean-up of samples was performed with Waters HLB cartridges and final sample eluates were dried under ultra-high purity argon. Phenols were quantified by liquid

chromatography/electrospray ionization-tandem mass spectrometry using a five-point calibration curve bracketing the concentration range. Quantified phenols (TDLF included vanillin, acetovanillone, vanillic acid, syringaldehyde, acetosyringone, syringic acid, coumaric acid, ferulic acid, p-hydroxy-benzaldehyde, p-hydroxy-acetophenone, and p-hydroxy-benzoic acid.

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Lignin-derived phenols were determined following Yan and Kaiser (2018; Anal. Chem), and Yan and Kaiser (2018; Analytica Chimica Acta). Briefly, C18 extracts were redissolved in 200 µL of 1.1 mol L⁻¹ argon- sparged (10 min) NaOH in a 400 µL Teflon vial (Saville Corp) and amended with containing 500 mg CuO, and amended with 10µL of 10 mmolL⁻¹ CuSO₄ and 10µ L of 0.2 molL⁻¹ ascorbic acid. Oxidation was at 150 C for 120 minutes. Following oxidation, the samples were spiked with with a surrogate standard mixture of p-hydroxybenzoic acid-13C7, vanillin-13C6, and syringaldehyde-13C6 and acidified to pH ≈ 2.5 with 6 mol L⁻¹ sulfuric acid in the reaction vials. Clean-up of samples was performed with Waters HLB cartridges and final sample eluates were dried under ultra-high purity argon. Phenols were quantified by liquid chromatography/electrospray ionization-tandem mass spectrometry using a five-point calibration curve bracketing the concentration range. Quantified phenols: TDLF included vanillin, acetovanillone, vanillic acid, syringaldehyde, acetosyringone, syringic acid, coumaric acid, ferulic acid, p-hydroxy-benzaldehyde, p-hydroxy-acetophenone, and p-hydroxy-benzoic acid.

Data Processing Description

BCO-DMO Processing: modified parameter names (removed units; replaced spaces and slashes with underscores).

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Data Files

File
dissolved_phenols_PS94.csv (Comma Separated Values (.csv), 9.22 KB) MD5:944dc6ce2ae29f8e8991b07c877df5f4
Primary data file for dataset ID 767285

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Related Publications

Cutter, G., Andersson, P., Codispoti, L., Croot, P., François, R., Lohan, M. C., Obata, H. and Rutgers v. d. Loeff, M. (2010). Sampling and Sample-handling Protocols for GEOTRACES Cruises, [Miscellaneous] Version 1. <http://www.geotraces.org/libraries/documents/Intercalibration/Cookbook.pdf>

Methods

Yan, G., & Kaiser, K. (2018). A rapid and sensitive method for the analysis of lignin phenols in environmental samples using ultra-high performance liquid chromatography-electrospray ionization-tandem mass spectrometry with multiple reaction monitoring. Analytica Chimica Acta, 1023, 74-80.

doi:[10.1016/j.aca.2018.03.054](https://doi.org/10.1016/j.aca.2018.03.054)

Methods

Yan, G., & Kaiser, K. (2018). Ultralow Sample Volume Cupric Sulfate Oxidation Method for the Analysis of Dissolved Lignin. Analytical Chemistry, 90(15), 9289-9295. doi:[10.1021/acs.analchem.8b01867](https://doi.org/10.1021/acs.analchem.8b01867)

Methods

Parameters

Parameter	Description	Units
Station	Station	unitless
Cast	Cast	unitless
Bottle	Bottle	unitless
Date_Time_UTC	Date and time (UTC); format: yyyy-mm-ddTHH:MM	unitless
Latitude	Latitude north	degrees
Longitude	Longitude east (postive values = east)	degrees
Depth_water	Sample depth	meters (m)
Temp	Temperature	degrees Celsius
Salinity	Salinity	PSU
DOC	DOC	micromoles per liter (umol/L)
Phenols	Phenols	picomoles per liter (pmol/L)

Instruments

Dataset-specific Instrument Name	liquid chromatography/electrospray ionization-tandem mass spectrometry
Generic Instrument Name	Mass Spectrometer
Generic Instrument Description	General term for instruments used to measure the mass-to-charge ratio of ions; generally used to find the composition of a sample by generating a mass spectrum representing the masses of sample components.

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	Shimadzu TOC-L
Generic Instrument Name	Shimadzu TOC-L Analyzer
Generic Instrument Description	A Shimadzu TOC-L Analyzer measures DOC by high temperature combustion method. Developed by Shimadzu, the 680 degree C combustion catalytic oxidation method is now used worldwide. One of its most important features is the capacity to efficiently oxidize hard-to-decompose organic compounds, including insoluble and macromolecular organic compounds. The 680 degree C combustion catalytic oxidation method has been adopted for the TOC-L series. http://www.shimadzu.com/an/toc/lab/toc-l2.html

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Deployments

ARK-XXIX_3

Website	https://www.bco-dmo.org/deployment/767278
Platform	R/V Polarstern
Report	http://datadocs.bco-dmo.org/docs/Lignin_phenol_method_development/data_docs/BzPM_0703_2016.pdf
Start Date	2015-08-17
End Date	2015-10-15
Description	Cruise dates and cruise report were obtained from Pangaea: https://www.pangaea.de/expeditions/cr.php/Polarstern

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Project Information

Development and application of a high sensitivity, ultra low volume method to measure biomarkers of terrigenous organic matter in the open ocean (Lignin phenol method development)

Coverage: Arctic Ocean

NSF Award Abstract:

The distribution and fate of land-derived, or terrigenous, organic matter in the ocean has long been of interest to oceanographers, but that interest has grown considerably as research on the marine and global carbon cycle intensifies. Lignin is a major structural polymer found only in vascular plants, making lignin a unique tracer of terrigenous organic matter input to the marine environment. The current analytical tool for analyzing lignin, breaking it into a suite of identifiable phenolic compounds, is complex, time consuming and requires 10 to 30 liters of water. Given these limitations, applications of lignin phenols as tracers of terrestrial organic carbon in the ocean have been sparse. Through this project, the researchers aim to redesign existing chemical methodology together with modified instrumental detection for even 3 times greater sensitivity using a sample of less than 200 milliliters. Outfitting the scientific community with new methodology to sensitively trace this marker of terrigenous organic carbon will provide a clearer understanding of organic matter fluxes between and within terrestrial and oceanic reservoirs, and potentially establish lignin phenols as a robust oceanographic tracer. This project will support the development of the next generation of scientists, including an early career investigator, and graduate and undergraduate students.

Lignin phenol measurements have been used to study general distribution patterns and mechanisms of decomposition of terrigenous dissolved organic carbon (tDOC) in the global ocean. The distribution pattern of tDOC among ocean basins is generally consistent with the global pattern of riverine discharge to the ocean basins. However, large scale generalizations required and more fully resolved distributions of lignin as a tracer of tDOC are hampered by the difficulties and limitations associated with the present lignin phenol method. The main objectives of this project are to (1) develop methodology for measuring dissolved lignin in ultra-low volumes at high sensitivity in open ocean seawater and (2) apply the new method to study terrigenous tDOC processing and transport in the Eurasian Basin of the Arctic Ocean, where large Siberian rivers deliver the bulk of tDOC to the shelf areas. Results from this research will help evaluate lignin phenols as robust oceanographic tracers, useful to study physical mixing in the Arctic Ocean and potentially improve our understanding of the fate and removal of terrigenous organic carbon in the oceans. Addressing the second objective would provide well-constrained decay constants for lignin and tDOC in the Arctic Ocean and provide novel information on halocline formation. Integration of tDOC budgets, freshwater budgets, and circulation and atmospheric patterns will ultimately improve understanding of biogeochemical cycles in the Arctic Ocean and its role in global climate.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1536506

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