# Total phosphorus concentrations in NMR sediment pretreatment extracts from samples collected during cruises in the Arctic Ocean, California Margin, and Equatorial Pacific from 1992-1998

**Website**: https://www.bco-dmo.org/dataset/805226
**Data Type**: Cruise Results
**Version**: 1
**Version Date**: 2020-06-23

**Project**
» A new marine sediment sample preparation scheme for solution 31P NMR analysis (Marine Sediment Analysis 31P NMR)

**Program**
» Center for Dark Energy Biosphere Investigations (C-DEBI)

| Contributors | Affiliation | Role |
| --- | --- | --- |
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**Abstract**
Total phosphorus concentrations in nuclear magnetic resonance (NMR) sediment pretreatment extracts from samples collected during cruises in the Arctic Ocean, California Margin, and Equatorial Pacific from 1992-1998.

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## Table of Contents

- Coverage
- Dataset Description
  - Methods & Sampling
  - Data Processing Description
- Data Files
- Supplemental Files
- Related Publications
- Parameters
- Instruments
- Deployments
- Project Information
- Program Information
- Funding

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## Coverage

**Spatial Extent**: **N**:84.083 **E**:-125.017 **S**:-12 **W**:-174.967
**Temporal Extent**: 1992-10-30 - 1998-07-24

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## Dataset Description

Total phosphorus concentrations in nuclear magnetic resonance (NMR) sediment pretreatment extracts from samples collected during cruises in the Arctic Ocean, California Margin, and Equatorial Pacific from 1992-1998. These data were published in Defforey et al. (2017). See the related-resource page https://www.bco-dmo.org/related-resource/794727 for other datasets related to this publication. Sediment sample information for this dataset is available as a supplemental document (Sediment_Sample_Info.csv) which contains collection date, water depth, sediment depth, latitude, and longitude. Additional award information: * NSF C-DEBI subaward # 156246 to Adina Paytan * NSF C-DEBI subaward # 157598 to Delphine Defforey

**Methods & Sampling**

Location:
Arctic Ocean: P-1-94-AR P21, 84o5' N, 174o58' W
California margin: W-2-98-NC TF1, 41o5' N, 125o1' W
Equatorial Pacific: TT013-06MC, 12o00' S, 134o56' W

Methodology:

Prior to the extraction, we freeze-dried, ground and sieved sediment samples to less than 125 µm (Ruttenberg 1992). For a given sample, we weighed four sample replicates (2 g) and placed each in 250 mL HDPE bottles. Sodium dithionite (F.W. 147.12 g/mol; 7.4 g) was added to each sample split, followed by 200 mL of citrate-bicarbonate solution (pH 7.6). This step produces effervescence, so the solution should be added slowly to the sample. We shook samples for 8 h and then centrifuged them at 3,700 rpm for 15 min. We filtered the supernatants with a 0.4 µm polycarbonate filter. We took 20 mL aliquots from the filtrate for each sample split for MRP and total P analyses, and kept them refrigerated until analysis within 24 h. We added 200 mL of ultrapure water to the solid residue for each sample split as a wash step after the above reductive step, shook samples for 2 h, and then centrifuged them at 3,700 rpm for 15 min. We filtered the supernatants with 0.4 µm polycarbonate filters and set aside 20 mL of filtrate from each sample split for MRP and total P analyses. We then extracted the solid sample residues in 200 mL of sodium acetate buffer (pH 4.0) for 6 h. At the end of this extraction step, we centrifuged the bottles at 3,700 rpm for 15 min, filtered the supernatants with 0.4 µm polycarbonate filters and took a 20 mL aliquot of filtrate from each sample split for MRP and total P analyses. We added 200 mL of ultrapure water to the solid residue for each sample split as a wash step, shook samples for 2 h, and then centrifuged them at 3,700 rpm for 15 min. We filtered the supernatants with 0.4 µm polycarbonate filters and set aside 20 mL of filtrate from each sample split for MRP and total P analyses. We repeated the water rinse step, and collected aliquots for MRP and total P analyses as in the previous steps. The concentrations of TP were determined as described below.

Solid sediment sample residues following the pretreatment described above were transferred to two 50 mL centrifuge tubes (2 sample replicates combined per tube). We added 20 mL of 0.25 M NaOH + 0.05 M Na2EDTA solution to each tube, vortexed until all sediment was resuspended and then shook samples for 6 h at room temperature (Cade-Menun et al. 2005). We used a solid to solution ratio of 1:5 for this step to minimize the amount of freeze-dried material that will need to be dissolved for the 31P NMR experiments. Large amounts of salts from the NaOH-EDTA concentrated in NMR samples lead to higher viscosity and increase line broadening on NMR spectra (Cade-Menun and Liu 2013). We chose an extraction time of 6 h to improve total P recovery while limiting the degradation of natural P compounds in the sample. At the end of the extraction, samples were centrifuged at 3,700 rpm for 15 min and supernatants decanted into 50 mL centrifuge tubes. We collected a 500 µL aliquot from each sample, which we diluted with 4.5 mL of ultrapure water. These were refrigerated until analysis for total P content on the ICP-OES. The sample residues and supernatants were frozen on a slant to maximize the exposed surface area during the lyophilization step; this was done immediately after the removal of the 500 µL aliquot. Once completely frozen, the uncapped tubes containing supernatants and residues were freeze-dried over the course of 48 h. Each tube was covered with parafilm with small holes from a tack to minimize contamination. Freeze-dried supernatants from identical sample splits were combined and dissolved in 500 µL each of ultrapure water, D2O, NaOH-EDTA and 10 M NaOH prior to 31P NMR analysis. The D2O is required as signal lock in the spectrometer (Cade-Menun and Liu 2013). Sample pH was maintained at a pH > 12 to optimize peak separation (Cade-Menun 2005; Cade-Menun and Liu 2013). Sample pH was assessed with a glass electrode, and verified with pH paper to account for the alkaline error caused by the high salt content of our samples (Covington 1985).

Freeze-dried sample residues were ashed in crucibles at 550oC for 2 h and then extracted in 25 mL of 0.5 M sulfuric acid for 16 h (Olsen and Sommers 1982; Cade-Menun and Lavkulich 1997). We centrifuged samples at 3,700 rpm for 15 min, filtered supernatants with 0.4 µm polycarbonate filters, and measured P content on an ICP-OES.

Total P concentrations in sediment extracts were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES). Standards were prepared with the same solutions as those used for the extraction procedure in order to minimize matrix effects on P measurements. Sediment extracts and standards (0 µM, 3.2 µM, 32 µM and 320 µM) were diluted to lower salt content to prevent salt buildup on the nebulizer (1:20 dilution for step 1, 1:10 for steps 2 – 4). Concentration data from both wavelengths (213 nm and 214 nm) were averaged to obtain extract concentrations for each sample. The detection limit for P on this instrument for both wavelengths is 0.4 µM. The MRP concentrations were measured on a QuikChem 8000 automated ion analyzer. Standards were prepared with the same solutions used for the extraction step to minimize matrix effects on P measurements. Sediment extracts and standards (0 – 30 µM PO4) were diluted ten-fold to prevent matrix interference with color development. The detection limit for P on this instrument is 0.2 µM. We derived MUP concentrations by subtracting MRP from total P concentrations.

### Data Processing Description

Data were processed in Excel.

BCO-DMO data manager processing notes:
* Excel file Data_TP_sediments with pretreatment_v3.xlsx with four sheets (one per Step) exported to csv.  The four tables were combined into one table.  There is a column Step with values 1-4 already so there was no need to add another column to capture the original sheet names "Step #"

[ table of contents | back to top ]

## Data Files

| File |
| --- |
| **tp-sed-pre.csv** (Comma Separated Values (.csv), 166.60 KB) MD5:a10df986d9978fb4016bb5192387c490<br>Primary data file for dataset ID 805226 |

[ table of contents | back to top ]

## Supplemental Files

| File |
| --- |
| **Sediment Sample Information**<br>filename: Sediment_Sample_Info.csv (Comma Separated Values (.csv), 657 bytes) MD5:4cfcfa04b5d6f41a024f3304d1598170<br>Sediment sample information:<br>Region,Sample_ID,Latitude (decimal degrees),Longitude (decimal degrees),Water_depth (m),Sediment_Depth_Start (cm),Sediment_Depth_End (cm),Collection_Start_Date (yyyy-mm-dd),Collection_End_Date (yyyy-mm-dd)<br>Cruises: P194AR (P-1-94-AR), W9807A (W-2-98-NC), TT013 (TT013-06MC) |

[ table of contents | back to top ]

## Related Publications

Cade-Menun, B. (2005). Characterizing phosphorus in environmental and agricultural samples by 31P nuclear magnetic resonance spectroscopy. Talanta, 66(2), 359–371. doi:10.1016/j.talanta.2004.12.024
*Methods*

Cade-Menun, B., & Liu, C. W. (2013). Solution Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy of Soils from 2005 to 2013: A Review of Sample Preparation and Experimental Parameters. Soil Science Society of America Journal, 78(1), 19–37. doi:10.2136/sssaj2013.05.0187dgs
*Methods*

Cade-Menun, B. J., & Lavkulich, L. M. (1997). A comparison of methods to determine total, organic, and available phosphorus in forest soils. Communications in Soil Science and Plant Analysis, 28(9-10), 651–663. doi:10.1080/00103629709369818
*Methods*

Covington, A. K. (1985). Procedures for testing pH responsive glass electrodes at 25, 37, 65 and 85 C and determination of alkaline errors up to 1 mol dm-3 Na+, K+, Li+. Pure and Applied Chemistry, 57(6), 887–898.

doi:10.1351/pac198557060887
*Methods*

Defforey, D., Cade-Menun, B. J., & Paytan, A. (2017). A new solution 31 P NMR sample preparation scheme for marine sediments. Limnology and Oceanography: Methods, 15(4), 381–393. doi:10.1002/lom3.10166
*Results*

Olsen, S. R., & Sommers, L. E. (1982). Phosphorus. p. 403–430. In A.L. Page, R.H. Miller, and D.R. Keeney [eds.], Methods of Soil Analysis. Soil Science Society of America.
*Methods*

Ruttenberg, K. C. (1992). Development of a sequential extraction method for different forms of phosphorus in marine sediments. Limnology and Oceanography, 37(7), 1460–1482. doi:10.4319/lo.1992.37.7.1460
*Methods*

[ table of contents | back to top ]

## Parameters

| Parameter | Description | Units |
|---|---|---|
| Extract | Extract solution | unitless |
| Step | Step in the sequential extraction scheme (1-4) | unitless |
| Dilution | Sample dilution | unitless |
| Sample_ID | Sample ID, unique sample identifier | unitless |
| Analyte_Name | Element analyzed | unitless |
| Int_Corr | Intensity (corrected) | unitless |
| RSD_Corr_Int | Relative standard deviation (RSD) of corrected intensity | unitless |
| Conc_Calib | Calibrated concentration of total phosphorous | parts per million (ppm) |

[ table of contents | back to top ]

## Instruments

| | |
|---|---|
| **Dataset-specific Instrument Name** | QuikChem 8000 automated ion analyzer |
| **Generic Instrument Name** | Flow Injection Analyzer |
| **Generic Instrument Description** | An instrument that performs flow injection analysis. Flow injection analysis (FIA) is an approach to chemical analysis that is accomplished by injecting a plug of sample into a flowing carrier stream. FIA is an automated method in which a sample is injected into a continuous flow of a carrier solution that mixes with other continuously flowing solutions before reaching a detector. Precision is dramatically increased when FIA is used instead of manual injections and as a result very specific FIA systems have been developed for a wide array of analytical techniques. |

[ table of contents | back to top ]

## Deployments

**P194AR**

| | |
|---|---|
| **Website** | https://www.bco-dmo.org/deployment/794741 |
| **Platform** | USCGC Polar Sea |
| **Start Date** | 1994-07-25 |
| **End Date** | 1994-08-30 |
| **Description** | Exact dates in and out of port are not known. The start and end date listed are the start and end dates from cruise trackline and bathymetry data. The same dates are cited in several publications. |

**W9807A**

| | |
|---|---|
| **Website** | https://www.bco-dmo.org/deployment/795245 |
| **Platform** | R/V Wecoma |
| **Start Date** | 1998-07-17 |
| **End Date** | 1998-07-24 |
| **Description** | Excerpt from https://pubs.usgs.gov/of/2001/0190/intro.html W9807A (w-2-98-nc) (metadata) The most recent cruise of the STRATAFORM project took place again aboard the R/V Wecoma in July 1998. The principle investigators were Homa Lee of the USGS and Clark R. Alexander from the Skidaway Institute of Oceanography. Also participating from the USGS were Gita Dunhill and Brad Carkin. Jacques Locat and Eric Boulanger from the University of Laval, Quebec, Canada, Harold Christian from GSC, and Brian McAdoo, of Vasser College, also participated in the cruise with their own scientific agendas. Sampling centered around obtaining box cores of the study area, along with Lehigh cores, CTDs, and piezometer readings. The cruise commenced on July 17 and was completed on July 24. |

**TT013**

| | |
|---|---|
| **Website** | https://www.bco-dmo.org/deployment/57732 |
| **Platform** | R/V Thomas G. Thompson |
| **Start Date** | 1992-10-30 |
| **End Date** | 1992-12-13 |
| **Description** | Purpose: Benthic Survey, 12°N-12°S at 140°W TT013 was one of five cruises conducted in 1992 in support of the U.S. Equatorial Pacific (EqPac) Process Study. The five EqPac cruises aboard R/V Thomas G. Thompson included two repeat meridional sections (12°N - 12°S), 2 equatorial surveys, and a benthic survey (all at 140° W). The scientific objectives of this study were to observe the processes in the Equatorial Pacific controlling the fluxes of carbon and related elements between the atmosphere, euphotic zone, and deep ocean. As luck would have it, the survey window coincided with an El Nino event. A bonus for the research team.<br><br>**Methods & Sampling**<br>TT013-06MC |

[ table of contents | back to top ]

## Project Information

### A new marine sediment sample preparation scheme for solution 31P NMR analysis (Marine Sediment Analysis 31P NMR)

**Coverage**: Equatorial Pacific, California Margin, Arctic Ocean

We developed and tested a new approach to prepare marine sediment samples for solution 31P nuclear magnetic resonance spectroscopy (31P NMR). This approach addresses the effects of sample pretreatment on sedimentary P composition and increases the signal of low abundance P species in 31P NMR spectra by removing up the majority inorganic P  from sediment samples while causing minimal alteration of the chemical structure of organic P compounds. The method was tested on natural marine sediment samples from different localities (Equatorial Pacific, California Margin and Arctic Ocean) with high inorganic P content, and allowed for the detection of low abundance P forms in samples for which only an orthophosphate signal could be resolved with an NaOH-EDTA extraction alone. This new approach will allow the use of 31P NMR on samples for which low organic P concentrations previously hindered the use of this tool, and will help answer longstanding question regarding the fate of organic P in marine sediments. We developed and tested a new approach to prepare marine sediment samples for solution 31P nuclear magnetic resonance spectroscopy (31P NMR). This approach addresses the effects of sample pretreatment on sedimentary P composition and increases the signal of low abundance P species in 31P NMR spectra by removing up the majority inorganic P  from sediment samples while causing minimal alteration of the chemical structure of organic P compounds. The method was tested on natural marine sediment samples from different localities (Equatorial Pacific, California Margin and Arctic Ocean) with high inorganic P content, and allowed for the detection of low abundance P forms in samples for which only an orthophosphate signal could be resolved with an NaOH-EDTA extraction alone. This new approach will allow the use of 31P NMR on samples for which low organic P concentrations previously hindered the use of this tool, and will help answer longstanding question regarding the fate of organic P in marine sediments.

NSF C-DEBI Award #156246 to Dr. Adina Paytan

NSF C-DEBI Award #157598 to Dr. Delphine Defforey

[ table of contents | back to top ]

## Program Information

### Center for Dark Energy Biosphere Investigations (C-DEBI)

**Website**: http://www.darkenergybiosphere.org

**Coverage**: Global

The mission of the Center for Dark Energy Biosphere Investigations (C-DEBI) is to explore life beneath the seafloor and make transformative discoveries that advance science, benefit society, and inspire people of all ages and origins.

C-DEBI provides a framework for a large, multi-disciplinary group of scientists to pursue fundamental questions about life deep in the sub-surface environment of Earth. The fundamental science questions of C-DEBI involve exploration and discovery, uncovering the processes that constrain the sub-surface biosphere below the oceans, and implications to the Earth system. What type of life exists in this deep biosphere, how much, and how is it distributed and dispersed? What are the physical-chemical conditions that promote or limit life? What are the important oxidation-reduction processes and are they unique or important to humankind? How does this biosphere influence global energy and material cycles, particularly the carbon cycle? Finally, can we discern how such life evolved in geological settings beneath the ocean floor, and how this might relate to ideas about the origin of life on our planet?

C-DEBI's scientific goals are pursued with a combination of approaches:
(1) coordinate, integrate, support, and extend the research associated with four major programs—Juan de Fuca Ridge flank (JdF), South Pacific Gyre (SPG), North Pond (NP), and Dorado Outcrop (DO)—and other field sites;
(2) make substantial investments of resources to support field, laboratory, analytical, and modeling studies of the deep subseafloor ecosystems;
(3) facilitate and encourage synthesis and thematic understanding of submarine microbiological processes, through funding of scientific and technical activities, coordination and hosting of meetings and workshops, and support of (mostly junior) researchers and graduate students; and
(4) entrain, educate, inspire, and mentor an interdisciplinary community of researchers and educators, with an emphasis on undergraduate and graduate students and early-career scientists.

Note: Katrina Edwards was a former PI of C-DEBI; James Cowen is a former co-PI.

**Data Management:**
C-DEBI is committed to ensuring all the data generated are publically available and deposited in a data repository for long-term storage as stated in their Data Management Plan (PDF) and in compliance with the NSF Ocean Sciences Sample and Data Policy. The data types and products resulting from C-DEBI-supported research include a wide variety of geophysical, geological, geochemical, and biological information, in addition to education and outreach materials, technical documents, and samples. All data and information generated by C-DEBI-supported research projects are required to be made publically available either following publication of research results or within two (2) years of data generation.

To ensure preservation and dissemination of the diverse data-types generated, C-DEBI researchers are working with BCO-DMO Data Managers make data publicly available online. The partnership with BCO-DMO helps ensure that the C-DEBI data are discoverable and available for reuse. Some C-DEBI data is better served by specialized repositories (NCBI's GenBank for sequence data, for example) and, in those cases, BCO-DMO provides dataset documentation (metadata) that includes links to those external repositories.

[ table of contents | back to top ]

## Funding

| Funding Source | Award |
| --- | --- |
| NSF Division of Ocean Sciences (NSF OCE) | OCE-0939564 |

[ table of contents | back to top ]