

# Dissolved black carbon (DBC) concentrations and related data from water samples collected between 2011 and 2019 in the Pacific and Atlantic Oceans and from rivers in North America, South America, Africa, and Russia

**Website:** <https://www.bco-dmo.org/dataset/878750>

**Data Type:** Cruise Results, Other Field Results

**Version:** 1

**Version Date:** 2022-08-17

## Project

» [Collaborative Research: Constraining the source of oceanic dissolved black carbon using compound-specific stable carbon isotopes](#) (DBC Stable Isotopes)

Contributors	Affiliation	Role
<a href="#">Wagner, Sasha</a>	Rensselaer Polytechnic Institute (RPI)	Principal Investigator
<a href="#">Brandes, Jay</a>	Skidaway Institute of Oceanography (SIO)	Co-Principal Investigator
<a href="#">Stubbins, Aron</a>	Northeastern University	Co-Principal Investigator
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## Abstract

Pacific Ocean samples were collected from Station ALOHA (22.45°N, 158.00°W) during the Hawaii Ocean Time-series (HOT) 301 cruise aboard the R/V Ka'imikai-O-Kanaloa in April 2018. Atlantic Ocean samples were collected from Hydrostation S (31.67°N, 64.17°W) during the Bermuda Atlantic Time Series (BATS) 358 cruise aboard the R/V Atlantic Explorer in April 2019. River samples were collected from the main stem of the Amazon (Brazil), Congo (Democratic Republic of the Congo), Northern Dvina (Russia), Kolyma (Russia), and Mississippi Rivers (USA) at various time points between 2011 and 2018. Samples were analyzed for dissolved black carbon (DBC), dissolved organic carbon (DOC), and stable carbon isotopes. Data are published in Table 1 and as Supplemental Data in Wagner et al., 2019 (doi: 10.1038/s41467-019-13111-7).

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## Coverage

**Spatial Extent:** N:68.75 E:161.29 S:-4.18 W:-158

**Temporal Extent:** 2011-08-19 - 2019-04-08

## Methods & Sampling

**Sample collection:** Pacific Ocean samples were collected from Station ALOHA (22.45°N, 158.00°W) during the Hawaii Ocean Time-series (HOT) 301 cruise aboard the R/V Ka'imikai-O-Kanaloa. Samples from surface and mesopelagic depths (5, 110, 765, and 1000 m) were obtained from two casts on April 17, 2018 and the deep

water sample (3500 m) was collected on April 18, 2018. Atlantic Ocean samples were collected from Hydrostation S (31.67°N, 64.17°W) during the Bermuda Atlantic Time Series (BATS) 358 cruise aboard the R/V Atlantic Explorer. Water samples were collected along a depth profile (1, 70, 2000, and 3000 m) on April 8, 2019. All seawater samples were collected using Niskin bottles mounted to the CTD rosette. For each sample, ~10 L was passed, by gravity, through a precleaned in-line capsule filter (Whatman Polycap; 0.2 µm) into acid-cleaned Nalgene fluorinated HDPE carboys and pre-combusted glass vials and acidified to pH 2 using HCl prior to solid phase extraction and DOC analysis. River samples were collected from the main stem of the Amazon, Congo, Northern Dvina, Kolyma, and Mississippi Rivers, upstream of the river mouth where marine inputs were not observed (salinity = 0). One surface water sample was collected from the Amazon River near Óbidos (Brazil; April 20, 2018; 1.92°S, 55.53°W). The Congo River was sampled from a site upstream of the cities of Kinshasa–Brazzaville on the main stem (DR Congo; 4.18°S, 15.21°E). Five samples were collected from the Congo River between August 2011 and April 2012 to account for potential hydrologically driven variations in DBC isotopic composition in a low latitude, subtropical river. Four samples were collected from the Northern Dvina River in Arkhangelsk (64.55°N, 40.51°E) between October 2013 and May 2016 to capture isotopic variations in a high latitude river with extremely variable hydrology. One sample was collected from the Kolyma River, upstream of the city of Cherskiy (August 30, 2015; 68.75°N, 161.29°E). One sample was collected from the Belle Chase Ferry Landing on the Mississippi River, just south of New Orleans, LA (USA; February 23, 2016; 29.82°N, 90.00°W). All river samples were collected in situ using an oil-free pump equipped with a pre-cleaned, in-line capsule filter (Whatman Polycap, 0.2 µm) directly into acid-cleaned Nalgene bottles and pre-combusted glass vials. Samples were acidified to pH 2 using HCl prior to solid phase extraction and DOC analysis.

**Dissolved organic carbon analysis and solid phase extraction:** Filtered and acidified samples were analyzed for DOC, measured as non-purgable organic carbon using a Shimadzu TOC-L CPH analyzer equipped with an ASI-L autosampler. Sample DOC was quantified using a calibration curve made with a potassium hydrogen phthalate stock solution. Measurement accuracy and reproducibility was assessed by analyzing deep seawater and low carbon water reference materials obtained from the Consensus Reference Material (CRM) project (<https://hansell-lab.rsmas.miami.edu/consensus-reference-material/index.html>). Analyses of CRM were within 5% of reported values. DOC was isolated from samples via solid phase extraction (SPE; Varian Bond Elut PPL cartridges, 1 g, 6 mL; Dittmar et al., 2008) prior to DBC analysis. Briefly, SPE cartridges were conditioned with methanol, ultrapure water, and acidified water. Filtered and acidified samples were passed through the SPE cartridges by gravity. Isolated DOC was then eluted from the SPE cartridges with methanol and stored at –20 °C until DBC analysis.

**Dissolved black carbon quantification:** Sample DBC was quantified using the BPCA method, which chemically degrades condensed aromatic compounds into benzenhexacarboxylic acid (B6CA) and benzenepentacarboxylic acid (B5CA) molecular markers. BPCAs were oxidized and quantified following previously described methods (Wagner et al., 2017; Barton and Wagner, 2022). Briefly, aliquots of SPE-DOC (~0.5 mg-C equivalents) were transferred to 2 mL glass ampules and dried under a stream of argon until complete evaporation of methanol. Concentrated HNO<sub>3</sub> (0.5 mL) was added to each ampule, then ampules were flame-sealed and heated to 160 °C for 6 h. After oxidation, ampules were opened and HNO<sub>3</sub> was dried at 60 °C under a stream of argon. The BPCA-containing residue was re-dissolved in dilute H<sub>3</sub>PO<sub>4</sub> for subsequent analysis by high performance liquid chromatography (HPLC). Quantification of BPCAs was performed using a Dionex Ultimate 3000 HPLC system equipped with an autosampler, pump, and diode array detector. B6CA and B5CA were separated on an Agilent Poroshell 120 phenyl-hexyl column (4.6 × 150 mm, 2.7 µm) using an aqueous gradient of H<sub>3</sub>PO<sub>4</sub> (0.6 M; pH 1) and sodium phosphate (20 mM; pH 6) buffers. BPCAs were quantified using calibration curves for commercially available B6CA and B5CA using a 5mM BPCA-C stock solution. River samples were oxidized and analyzed in duplicate. Ocean samples were oxidized and analyzed in triplicate. The average coefficients of variation for replicate measurements of B6CA and B5CA were <5%. Sample DBC concentrations were calculated using the established power relationship between DBC (µM-C) and the sum of B6CA and B5CA (nM-BPCA) (Stubbins et al., 2015).

**Stable carbon isotopic analyses:** Riverine and oceanic SPE-DOC methanol extracts were transferred to smooth-walled tin capsules (~0.25 mg-C per capsule) and methanol evaporated to dryness in an oven set to 60 °C. Sample-containing tin capsules were folded and combusted using a Thermo Scientific Flash EA Isolink CNSOH interfaced with a Thermo Scientific Delta V Plus IRMS. The δ<sup>13</sup>C composition of each sample was calibrated against an internal lab organic matter reference material (chitin from shrimp shells), which was previously calibrated against NIST glutamic acid (RM 8573) and sucrose (RM 8542) primary isotope reference standards. The <sup>13</sup>C content is expressed in δ<sup>13</sup>C per mil (‰) notation relative to Vienna Pee Dee Belemnite (VPDB). River samples were measured in duplicate and ocean samples were measured in triplicate. The standard deviation of replicate EA-IRMS measurements was <0.1‰. Compound-specific stable carbon isotopic values for individual BPCAs were measured using a Dionex Ultimate 3000 HPLC connected to a Delta V IRMS via an LC Isolink interface following methods detailed previously (Wagner et al., 2017). Online oxidation quantitatively converts baseline-separated BPCAs to CO<sub>2</sub>. BPCA-derived CO<sub>2</sub> is then extracted from the mobile

phase and dried prior to detection by IRMS. The  $\delta^{13}\text{C}$  values for B5CA and B6CA standards were measured by EA-IRMS following the same procedure described above to calculate and correct for offsets in HPLCIRMS  $\delta^{13}\text{C}$  measurements (Wagner et al., 2017). River samples were analyzed in duplicate and ocean samples were analyzed in triplicate. Standard deviations applied to corrected sample  $\delta^{13}\text{C}$  values were propagated to account for errors associated with replicate EA-IRMS standard BPCA measurements, HPLC-IRMS standard BPCA measurements, and HPLC-IRMS sample BPCA measurements. The  $^{13}\text{C}$  content is expressed in  $\delta^{13}\text{C}$  per mil (‰) notation relative to Vienna Pee Dee Belemnite (VPDB). The error associated with corrected  $\delta^{13}\text{C}$  values was typically  $<0.5\text{‰}$ .

## Data Processing Description

### Data Processing:

All data obtained from instrumentation was processed using Microsoft Excel (version 2016 or 2019) following the methodologies described earlier.

### BCO-DMO Processing:

- renamed fields to comply with BCO-DMO naming conventions;
- converted dates to YYYY-MM-DD format;
- replaced "N.D." with "nd" (no data);
- removed directionals from Latitude and Longitude columns; converted S and West to negative values.

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## Data Files

File
<b>DBC_Stable_Isotopes.csv</b> (Comma Separated Values (.csv), 2.68 KB) MD5:885da51215257440f22e9c162acc93ad Primary data file for dataset ID 878750

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## Related Publications

Barton, R., & Wagner, S. (2022). Measuring dissolved black carbon in water via aqueous, inorganic, high-performance liquid chromatography of benzenepolycarboxylic acid (BPCA) molecular markers. PLOS ONE, 17(5), e0268059. <https://doi.org/10.1371/journal.pone.0268059>  
*Methods*

Dittmar, T., Koch, B., Hertkorn, N., & Kattner, G. (2008). A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. Limnology and Oceanography: Methods, 6(6), 230–235. doi:[10.4319/lom.2008.6.230](https://doi.org/10.4319/lom.2008.6.230)  
*Methods*

Stubbins, A., Spencer, R. G. M., Mann, P. J., Holmes, R. M., McClelland, J. W., Niggemann, J., & Dittmar, T. (2015). Utilizing colored dissolved organic matter to derive dissolved black carbon export by arctic rivers. Frontiers in Earth Science, 3. <https://doi.org/10.3389/feart.2015.00063>  
*Methods*

Wagner, S., Brandes, J., Goranov, A. I., Drake, T. W., Spencer, R. G. M., & Stubbins, A. (2017). Online quantification and compound-specific stable isotopic analysis of black carbon in environmental matrices via liquid chromatography-isotope ratio mass spectrometry. Limnology and Oceanography: Methods, 15(12), 995–1006. doi:[10.1002/lom3.10219](https://doi.org/10.1002/lom3.10219)  
*Methods*

Wagner, S., Brandes, J., Spencer, R. G. M., Ma, K., Rosengard, S. Z., Moura, J. M. S., & Stubbins, A. (2019). Isotopic composition of oceanic dissolved black carbon reveals non-riverine source. Nature Communications, 10(1). <https://doi.org/10.1038/s41467-019-13111-7>  
*Results*

## Parameters

Parameter	Description	Units
Site	General site name	unitless
Sampling_Date	Date sample was collected in fomrat YYYY-MM-DD	unitless
Latitude	Latitude	degrees North
Longitude	Longitude	degrees East
Depth	Depth of sampling (oceanic samples only)	metesr (m)
Discharge	Discharge during time of sampling (river samples only)	meters cubed per second
SPE_DOC_Recovery	Proportion of dissolved organic carbon recovered by solid phase extraction	percent
d13C_B6CA	Stable carbon isotopic composition of benzenhexacarboxylic acid	per mille
St_Dev_d13C_B6CA	Standard deviation of stable carbon isotopic values of benzenhexacarboxylic acid	per mille
d13C_B5CA	Stable carbon isotopic composition of benzenepentacarboxylic acid	per mille
St_Dev_d13C_B5CA	Standard deviation of stable carbon isotopic values of benzenepentacarboxylic acid	per mille
d13C_SPE_DOC	Stable carbon isotopic composition of dissolved organic carbon recovered by solid phase extraction	per mille
St_Dev_d13C_SPE_DOC	Standard deviation of stable carbon isotopic values of dissolved organic carbon recovered by solid phase extraction	per mille
DOC	Dissolved organic carbon concentration	micromolar C
DBC	Dissolved black carbon concentration	micromolar C

DBC_to_DOC	Proportion of dissolved organic carbon to dissolved black carbon	percent
B6CA	Concentration of benzenhexacarboxylic acid in the sample	nanomolar
B5CA	Concentration of benzenepentacarboxylic acid in the sample	nanomolar
B6CA_to_B5CA	Ratio of benzenhexacarboxylic acid to benzenepentacarboxylic acid	unitless
Salinity	Salinity	parts per thousand (ppt)
Temperature	Water temperature	degrees Celsius
O2	Dissolved oxygen concentration	micromolar O2 per kilogram

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## Instruments

<b>Dataset-specific Instrument Name</b>	Thermo Scientific Flash EA Isolink
<b>Generic Instrument Name</b>	Elemental Analyzer
<b>Dataset-specific Description</b>	Thermo Scientific Flash EA Isolink CNSOH interfaced with a Thermo Scientific Delta V Plus IRMS - To measure stable carbon isotopic values of SPE-DOC for all samples.
<b>Generic Instrument Description</b>	Instruments that quantify carbon, nitrogen and sometimes other elements by combusting the sample at very high temperature and assaying the resulting gaseous oxides. Usually used for samples including organic material.

<b>Dataset-specific Instrument Name</b>	Dionex Ultimate 3000 HPLC
<b>Generic Instrument Name</b>	High-Performance Liquid Chromatograph
<b>Dataset-specific Description</b>	Dionex Ultimate 3000 HPLC connected to a Delta V IRMS via an LC Isolink interface - To measure BPCA-specific stable carbon isotopic values of DBC for all samples.
<b>Generic Instrument Description</b>	A High-performance liquid chromatograph (HPLC) is a type of liquid chromatography used to separate compounds that are dissolved in solution. HPLC instruments consist of a reservoir of the mobile phase, a pump, an injector, a separation column, and a detector. Compounds are separated by high pressure pumping of the sample mixture onto a column packed with microspheres coated with the stationary phase. The different components in the mixture pass through the column at different rates due to differences in their partitioning behavior between the mobile liquid phase and the stationary phase.

<b>Dataset-specific Instrument Name</b>	Thermo Scientific Delta V Plus IRMS
<b>Generic Instrument Name</b>	Isotope-ratio Mass Spectrometer
<b>Dataset-specific Description</b>	Thermo Scientific Flash EA Isolink CNSOH interfaced with a Thermo Scientific Delta V Plus IRMS - To measure stable carbon isotopic values of SPE-DOC for all samples.
<b>Generic Instrument Description</b>	The Isotope-ratio Mass Spectrometer is a particular type of mass spectrometer used to measure the relative abundance of isotopes in a given sample (e.g. VG Prism II Isotope Ratio Mass-Spectrometer).

<b>Dataset-specific Instrument Name</b>	Niskin bottles mounted to the CTD rosette
<b>Generic Instrument Name</b>	Niskin bottle
<b>Generic Instrument Description</b>	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.

<b>Dataset-specific Instrument Name</b>	oil-free pump equipped with a pre-cleaned, in-line capsule filter
<b>Generic Instrument Name</b>	Pump
<b>Generic Instrument Description</b>	A pump is a device that moves fluids (liquids or gases), or sometimes slurries, by mechanical action. Pumps can be classified into three major groups according to the method they use to move the fluid: direct lift, displacement, and gravity pumps

<b>Dataset-specific Instrument Name</b>	Shimadzu TOC-L CPH
<b>Generic Instrument Name</b>	Shimadzu TOC-L Analyzer
<b>Dataset-specific Description</b>	Shimadzu TOC-L CPH analyzer equipped with an ASI-L autosampler - To measure sample DOC concentrations and SPE-DOC recoveries for all samples.
<b>Generic Instrument Description</b>	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. <a href="http://www.shimadzu.com/an/toc/lab/toc-l2.html">http://www.shimadzu.com/an/toc/lab/toc-l2.html</a>

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## Deployments

### KOK1801

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/878760">https://www.bco-dmo.org/deployment/878760</a>
<b>Platform</b>	R/V Ka`imikai-O-Kanaloa
<b>Start Date</b>	2018-04-16
<b>End Date</b>	2018-04-20
<b>Description</b>	See more at R2R: <a href="https://www.rvdata.us/search/cruise/KOK1801">https://www.rvdata.us/search/cruise/KOK1801</a>

### AE1905

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/878763">https://www.bco-dmo.org/deployment/878763</a>
<b>Platform</b>	R/V Atlantic Explorer
<b>Start Date</b>	2019-04-07
<b>End Date</b>	2019-04-14
<b>Description</b>	See more at R2R: <a href="https://www.rvdata.us/search/cruise/AE1905">https://www.rvdata.us/search/cruise/AE1905</a>

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## Project Information

### Collaborative Research: Constraining the source of oceanic dissolved black carbon using compound-specific stable carbon isotopes (DBC Stable Isotopes)

**Coverage:** Global rivers (Amazon, Congo, Mississippi, St. Lawrence, Yukon), Atlantic Ocean (BATS), Pacific Ocean (HOT)

#### NSF Award Abstract:

The char and soot remaining after fire is broadly referred to as black carbon. When char interacts with water, some of it dissolves and is carried away by rivers to the ocean. This soluble component of char is termed

"dissolved black carbon" (DBC). Recent research has revealed DBC to be a major component of the carbon cycle. Most notably, DBC is now known to make up 10% of all dissolved organic carbon that rivers carry to the sea. Once in the ocean, DBC remains there for thousands of years, storing carbon that would otherwise be in the atmosphere as carbon dioxide. As carbon dioxide contributes to the greenhouse effect, with higher carbon dioxide in the atmosphere leading to warmer global temperatures, it is important to understand where DBC in the ocean came from and how long it will stay locked away in the deep ocean. In this funded work, we set out to determine the source of the DBC in the ocean. Based upon our previous work that shows rivers export massive amounts of DBC to the coast, it has been suggested that rivers are the main source of DBC to the open ocean. However, in looking more closely at the DBC in rivers and the oceans, we found them to differ in one critical way: they have different isotopic signatures. This precludes them from having the same source, indicating that the DBC in the oceans is not from rivers. Our preliminary work only looked at a small river in Georgia, USA, and in the coastal waters offshore. In this funded project, we will take a global look at the isotopic signatures of DBC collected from large rivers such as the Amazon, Mississippi, and Yukon, and from the middle of the Atlantic and Pacific Oceans. If we find there is no overlap in the isotopes of the DBC from these major global rivers and ocean waters, we can conclude that rivers are not the main source of oceanic DBC and will need to search for new explanations of how molecules produced by fire end up in the deep ocean.

The project will enhance the career and continue the training of a first-time investigator and train undergraduate students in real world research through the Northeastern University Cooperative Program. In addition, our findings be adapted to produce learning materials for high school students in collaboration with the Science Journal for Kids.

Previous efforts to track DBC sources in natural waters have come with major limitations, preventing definitive connections to be made between oceanic DBC and its pyrogenic source. Photodegradation, a significant removal process for DBC in surface waters, drastically alters the molecular composition of DBC and erases any potential link between DBC chemical composition and its source. Bulk stable carbon isotopic measurements cannot unambiguously identify sources of DOC subcomponents, such as DBC. As such, this project aims to constrain the oceanic source of DBC by measuring compound-specific stable carbon isotopes of molecular markers (benzenepolycarboxylic acids, or BPCAs), derived exclusively from DBC. Our preliminary data show BPCA-specific isotopic values to have a sufficiently wide dynamic range between riverine and oceanic samples to test our hypotheses. In the current proposal, we aim to 1) isotopically characterize the largest quantified flux of DBC to the ocean (global rivers), 2) assess in situ oceanic variation in DBC stable carbon isotopic signatures, and 3) investigate the potential BPCA-specific fractionation effects of DBC photodegradation. In establishing a robust tracer for DBC source, we will be able to accurately constrain sources of oceanic DBC and further investigate the biogeochemical cycling of DBC across the terrestrial-marine continuum. The results of our research will also assist in answering larger research questions, specifically those regarding the fate of terrigenous DOM in the ocean, which have plagued biogeochemists for decades.

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.

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## Funding

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1756812</a>
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1756733</a>
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-2017577</a>

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