Concentrations of CFC-11, CFC-12, CFC-113 and SF6 in seawater from R/V Knorr KN199-04 (GT10), KN204-01 (GT11) in the subtropical northern Atlantic Ocean from 2010-2011 (U.S. GEOTRACES NAT project)

Website: https://www.bco-dmo.org/dataset/3692

Version: 3

Version Date: 2014-06-16

Project

» U.S. GEOTRACES North Atlantic Transect (GA03) (U.S. GEOTRACES NAT)

» <u>U.S. GEOTRACES North Atlantic Section: CFC and SF6 Measurements</u> (GT NAT CFC and SF6)

Program

» U.S. GEOTRACES (U.S. GEOTRACES)

Contributors	Affiliation	Role
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Dataset Description

Please note that data may not be final, pending intercalibration results and further analysis. If you are interested in following changes to US GEOTRACES data, there is an RSS feed available from the <u>GEOTRACES-NAT</u> project page.

Concentrations of CFC-11, CFC-12, CFC-113 and SF6 in seawater

CFC-11 CCl3F trichlorofluoromethane pmol/kg (10^-12 moles/kg)

CFC-12 CCl2F2 dichlorodifluoromethane pmol/kg

CFC-113 C2Cl3F3 1,1,2-trichlorotrifluloroethane pmol/kg

SF6 sulfur hexafluoride fmol/kg (10^-15 moles/kg)

Methods & Sampling

Sampling and Analytical Methodology:

Water samples for CFC and SF6 measurements were collected at all stations, including demi-stations, using the 30-liter Niskin bottle rosette. The CFC/SF6 sample was the first sample drawn from the Niskin bottle. The samples were collected in a 500 cc glass stoppered bottle through a PVC tube connected to the Niskin bottle drain valve. Bubbles were cleared from the tube with water flowing and the tube was inserted to the bottom of the 500 cc glass bottle. The glass bottle was placed in a wide mouth plastic jar that extended above the opening of the glass bottle by 4 cm. The overflow water collected in the jar, filling and overflowing the jar and covering the glass bottle opening. The flow continued for 3 overflow volumes of the glass bottle (1.5 liters) and the glass stopper was then inserted underwater preventing air from being trapped in the sample. The jar was then capped and the sample stored at room temperature until measurement, which was within 8 hours of collection. The measurements were carried out using a dual purge and trap system interfaced to a dual ECD (electron capture detector) HP6890 gas chromatograph. When a water sample is introduced into the system, it is split into two aliquots, a 20 cc aliquot for CFC measurement and a 350 cc aliquot for SF6 measurement. The aliquots are transferred to appropriately sized sparging chambers and stripped with ultra high purity nitrogen, which transports the extracted gases to cold traps (Unibeads-2s for CFCs, Carboxan-1000 for SF6) cooled to -80°C. The traps are then heated to 110°C for CFCs and 165°C for SF6 and flushed into the gas chromatograph where CFCs are separated with a Porasil-B pre-column and a Carbograph 1AC main column and SF6 is separated with a pre-column and main column of Molecular Sieve 5A. The gases are detected by the ECDs. The ECDs are calibrated by running gas standards with known concentrations of CFCs and SF6. Duplicate samples are collected and measured to provide a combined precision for sampling and measurement. The average differences from these duplicate measurements was the larger of 0.006 pmol/kg or 0.6% for CFC-11, 0.004 pmol/kg or 0.8% for CFC-12, 0.002 pmol/kg or 1.6% for CFC-113 and 0.01 fmol/kg or 1.5% for SF6.

Data Processing Description

Data Processing:

The gas chromatograph produces a peak for each compound being measured. Each chromatogram is digitally acquired on a PC and the peak areas integrated with software developed specifically for this purpose. Calibration curves relating peak area to concentration are generated using the gas standard data and this information is used to convert peak areas for the samples to concentrations. Blanks and reference standards are run about every 2 hours to provide data to correct for detector drift and blanks. After completion of the cruise, plots of the CFCs and SF6 against each other and against other hydrographic variables are prepared to determine trends in the data and identify questionable data. Questionable data are checked for possible data processing errors, sampling problems, equipment problems, etc. Mistakes are corrected and samples judged to be bad measurements are flagged as such. The WOCE flagging convention is used.

WHP Data Reporting Requirements (Rev. 2, February 1998) TABLE 4.10: Quality flag definitions for CTD data.

Flag

Value Definition

1 = Not calibrated.

2 = Acceptable measurement.

3 = Questionable measurement.

4 = Bad measurement.

5 = Not reported.

6 = Interpolated over > 2 dbar interval.

7 = Despiked.

8 Not assigned for CTD data.

9 = Not sampled.

BCO-DMO Processing/Edits

- GT11, sta-12, cast-11: corrected the press to 882.9 from submitted 874.1, which matches the depth in the bottle file. sample GEOTRC numbers added and dataset joined to the master events data.
- Data generated from original file: gt10 cfcs sf6 btl.xls contributed by H. Lee on 18 Nov. 2013.
- GT11 data revised Jan. 2013
- Data generated from original file: gt11 cfcs sf6 btl.xls contributed by Hoyle Lee on 6 Aug. 2012.
- Date column added and formatted as YYYYMMDD from MM,DD,YYYY individual columns
- Cruise Id column added
- Parameter names modified to conform to BCO-DMO conventions (blanks to underscores, etc.)

Data Files

File

CFC-SF6_GT10-11_joined.csv(Comma Separated Values (.csv), 139.27 KB)

MD5:af63b3b845e3476d5d2e078f3fed3918

Primary data file for dataset ID 3692

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Parameters

Parameter	Description	Units
cruise_id	official cruise identification	text
cruise_name	cruise alternate name	text
cruise_part	GEOTRACES Section Id	text
sta	station number	integer
cast	cast number	integer
lat_nom	latitude (South is negative)	decimal degrees
lon_nom	longitude (West is negative)	decimal degrees
date	date; UTC	YYYYMMDD
mon	integer month of year	integer
day	integer day of month	integer
year	integer year	integer
depth_w	bottom depth of water	meters
press	CTD pressure	decibars
temp	temperature	degrees celsius

sal_ctd	CTD salinity	PSS-78
sal	salinity	PSS-78
O2_ctd	CTD O2	ml/l
O2_ctd_umol_kg	OXY CTD	umol/kg
O2_bot	02	ml/l
O2_bot_umol_kg	Bottle OXY	umol/kg
NO3	NO3	umol/kg
NO2	NO2	umol/kg
PO4	PO4	umol/kg
SiO3	SIO3	umol/kg
F11	F11: CFC-11 CCl3F trichlorofluoromethane pmol/kg	pmol/kg
F11_FLAG_W	F11 FLAG. The WOCE flagging convention is used.	integer
F12	F12: CFC-12 CCl2F2 dichlorodifluoromethane pmol/kg	pmol/kg
F12_FLAG_W	F12 FLAG. The WOCE flagging convention is used.	integer
F113	F113: CFC-113 C2Cl3F3 1,1,2-trichlorotrifluloroethane pmol/kg	pmol/kg
F113_FLAG_W	F113 FLAG. The WOCE flagging convention is used.	integer
SF6	SF6: SF6 sulfur hexafluoride fmol/kg (10^-15 moles/kg)	fmol/kg
SF6_FLAG_W	SF6 FLAG: The WOCE flagging convention is used.	integer

sample_GEOTRC	Unique identifying number for US GEOTRACES samples; ranges from 5033 to 6078 for KN199-04 and from 6112 to 8148 for KN204-01. PI-supplied values were identical to those in the intermediate US GEOTRACES master file. Originally submitted as 'GEOTRACES #', this parameter name has been changed to conform to BCO-DMO's GEOTRACES naming conventions.	integer
station_GEOTRC	GEOTRACES station number; ranges from 1 through 12 for KN199-04 and 1 through 24 for KN204-01. Stations 7 and 9 were skipped on KN204-01. Some GeoFish stations are denoted as X_to_Y indicating the tow occurred between stations X and Y. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless
depth_GEOTRC_CTD	Observation/sample depth in meters, calculated from CTD pressure. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	meters
event_GEOTRC	Unique identifying number for US GEOTRACES sampling events; ranges from 2001 to 2225 for KN199-04 events and from 3001 to 3282 for KN204-01 events. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless
cast_GEOTRC	Cast identifier, numbered consecutively within a station. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless
sample_bottle_GEOTRC	Unique identification numbers given to samples taken from bottles; ranges from 1 to 24; often used synonymously with bottle number. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless
bottle_GEOTRC	Alphanumeric characters identifying bottle type (e.g., NIS representing Niskin and GF representing GOFLO) and position on a CTD rosette. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless
BTL_ISO_DateTime_UTC	Date and time (UTC) variable recorded at the bottle sampling time in ISO compliant format. Values were added from the intermediate US GEOTRACES master file (see Processing Description). This standard is based on ISO 8601:2004(E) and takes on the following form: 2009-08-30T14:05:00[.xx]Z (UTC time)	YYYY-mm- ddTHH:MM:SS.ssZ

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Dataset- specific Instrument Name	CTD Sea-Bird SBE 911plus
Generic Instrument Name	CTD Sea-Bird SBE 911plus
Dataset- specific Description	CTD/Hydrographic Measurements Program Two types of rosette/SBE9plus CTD casts (65 SIOR/30L-Niskin and 40 GT-C/15L-GoFlo) were made at 22 station locations during GEOTRACES 2011. 13 shallow and 13 deep McLane pump profiles were done at all Full and Super Stations, with an SBE19plus CTD attached to the end of the wire.
Generic Instrument Description	The Sea-Bird SBE 911 plus is a type of CTD instrument package for continuous measurement of conductivity, temperature and pressure. The SBE 911 plus includes the SBE 9plus Underwater Unit and the SBE 11plus Deck Unit (for real-time readout using conductive wire) for deployment from a vessel. The combination of the SBE 9 plus and SBE 11 plus is called a SBE 911 plus. The SBE 9 plus uses Sea-Bird's standard modular temperature and conductivity sensors (SBE 3 plus and SBE 4). The SBE 9 plus CTD can be configured with up to eight auxiliary sensors to measure other parameters including dissolved oxygen, pH, turbidity, fluorescence, light (PAR), light transmission, etc.). more information from Sea-Bird Electronics

Dataset- specific Instrument Name	Gas Chromatograph
Generic Instrument Name	Gas Chromatograph
Dataset- specific Description	Dual ECD (electron capture detector) HP6890 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	Niskin bottle
Generic Instrument Name	Niskin bottle
Dataset- specific Description	30-liter Niskin bottle rosette.
	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.

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Deployments

KN204-01

Website	https://www.bco-dmo.org/deployment/58786
Platform	R/V Knorr
Report	http://bcodata.whoi.edu/US_GEOTRACES/AtlanticSection/STS_Prelim_GT11_Doc.pdf
Start Date	2011-11-06
End Date	2011-12-11
Description	The US GEOTRACES North Atlantic cruise aboard the R/V Knorr completed the section between Lisbon and Woods Hole that began in October 2010 but was rescheduled for November-December 2011. The R/V Knorr made a brief stop in Bermuda to exchange samples and personnel before continuing across the basin. Scientists disembarked in Praia, Cape Verde, on 11 December. The cruise was identified as KN204-01A (first part before Bermuda) and KN204-01B (after the Bermuda stop). However, the official deployment name for this cruise is KN204-01 and includes both part A and B. Science activities included: ODF 30 liter rosette CTD casts, ODU Trace metal rosette CTD casts, McLane particulate pump casts, underway sampling with towed fish and sampling from the shipboard "uncontaminated" flow-through system. Full depth stations are shown in the accompanying figure (see below). Additional stations to sample for selected trace metals to a depth of 1000 m are not shown. Standard stations are shown in red (as are the ports) and "super" stations, with extra casts to provide large-volume samples for selected parameters, are shown in green. Station spacing is concentrated along the western margin to evaluate the transport of trace elements and isotopes by western boundary currents. Stations across the gyre will allow scientists to examine trace element supply by Saharan dust, while also contrasting trace element and isotope distributions in the oligotrophic gyre with conditions near biologically productive ocean margins, both in the west, to be sampled now, and within the eastern boundary upwelling system off Mauritania, sampled last year. Funding: The cruise was funded by NSF OCE awards 0926204, 0926433 and 0926659. Additional cruise information is available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/KN204-01 Other Relevant Links: ADCP data are available from the Currents ADCP group at the University of Hawaii at the links below: KN204-01A (part 1 of 2011 cruise; Woods Hole, MA to Bermuda) KN204-01B (par

KN199-04

Website	https://www.bco-dmo.org/deployment/58066
Platform	R/V Knorr
Report	http://bcodata.whoi.edu/US_GEOTRACES/AtlanticSection/Cruise_Report_for_Knorr_199_Final_v3.pdf
Start Date	2010-10-15
End Date	2010-11-04
Description	This cruise constitutes the first survey section as part of the U.S. participation in an international program named GEOTRACES. Funding: NSF OCE award 0926423 Science Objectives: To obtain state of the art trace metal and isotope measurements on a suite of samples taken on a midlatitude zonal transect of the North Atlantic. In particular, sampling targeted the oxygen minimum zone extending off the west African coast near Mauritania, the TAG hydrothermal field, and the western boundary current system along Line W. For additional information, please refer to the GEOTRACES program Web site (https://www.geotraces.org/) for overall program objectives and a summary of properties measured. Science Activities include seawater sampling via GoFLO and Niskin carousels, in situ pumping (and filtration), CTDO2 and transmissometer sensors, underway pumped sampling of surface waters, and collection of aerosols and rain. Hydrography, CTD and nutrient measurements were supported by the Ocean Data Facility (J. Swift) at Scripps Institution of Oceanography and funded through NSF Facilities. They provided an additional CTD rosette system along with nephelometer and LADCP. A trace metal clean Go-Flo Rosette and winch were provided by the group at Old Dominion University (G. Cutter) along with a towed underway pumping system. Additional cruise information is available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/KN199-04 Other Relevant Links: List of cruise participants: [PDF] Cruise track: JPEG image (from Woods Hole Oceanographic Institution, vessel operator) ADCP data are available from the Currents ADCP group at the University of Hawaii: KN199-04 ADCP

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Project Information

U.S. GEOTRACES North Atlantic Transect (GA03) (U.S. GEOTRACES NAT)

Website: https://www.geotraces.org/

Coverage: Subtropical western and eastern North Atlantic Ocean (GA03)

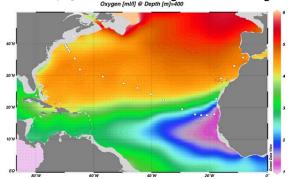
Much of this text appeared in an article published in OCB News, October 2008, by the OCB Project Office.

The first U.S. GEOTRACES Atlantic Section will be specifically centered around a sampling cruise to be carried out in the North Atlantic in 2010. Ed Boyle (MIT) and Bill Jenkins (WHOI) organized a three-day planning workshop that was held September 22-24, 2008 at the Woods Hole Oceanographic Institution. The main goal of the workshop, sponsored by the National Science Foundation and the U.S. GEOTRACES Scientific Steering Committee, was to design the implementation plan for the first U.S. GEOTRACES Atlantic Section. The primary cruise design motivation was to improve knowledge of the sources, sinks and internal cycling of Trace Elements and their Isotopes (TEIs) by studying their distributions along a section in the North Atlantic (Figure 1). The North Atlantic has the full suite of processes that affect TEIs, including strong meridional advection, boundary scavenging and source effects, aeolian deposition, and the salty Mediterranean Outflow. The North Atlantic is particularly important as it lies at the "origin" of the global Meridional Overturning Circulation.

It is well understood that many trace metals play important roles in biogeochemical processes and the carbon cycle, yet very little is known about their large-scale distributions and the regional scale processes that affect them. Recent advances in sampling and analytical techniques, along with advances in our understanding of their roles in enzymatic and catalytic processes in the open ocean provide a natural opportunity to make substantial advances in our understanding of these important elements. Moreover, we are motivated by the prospect of global change and the need to understand the present and future workings of the ocean's biogeochemistry. The GEOTRACES strategy is to measure a broad suite of TEIs to constrain the critical biogeochemical processes that influence their distributions. In addition to these "exotic" substances, more traditional properties, including

macronutrients (at micromolar and nanomolar levels), CTD, bio-optical parameters, and carbon system characteristics will be measured. The cruise starts at Line W, a repeat hydrographic section southeast of Cape Cod, extends to Bermuda and subsequently through the North Atlantic oligotrophic subtropical gyre, then transects into the African coast in the northern limb of the coastal upwelling region. From there, the cruise goes northward into the Mediterranean outflow. The station locations shown on the map are for the "fulldepth TEI" stations, and constitute approximately half of the stations to be ultimately occupied.

Figure 1. The proposed 2010 Atlantic GEOTRACES cruise track plotted on dissolved oxygen at 400 m depth. Data from the World Ocean Atlas (Levitus et al., 2005) were plotted using Ocean Data View (courtesy Reiner Schlitzer). [click on the image to view a larger version]

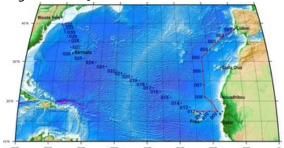


Hydrography, CTD and nutrient measurements will be supported by the Ocean Data Facility (J. Swift) at Scripps Institution of Oceanography and funded through NSF Facilities. They will be providing an additional CTD rosette system along with nephelometer and LADCP. A trace metal clean Go-Flo Rosette and winch will be provided by the group at Old Dominion University (G. Cutter) along with a towed underway pumping system.

The North Atlantic Transect cruise began in 2010 with KN199 leg 4 (station sampling) and leg 5 (underway sampling only) (Figure 2).

KN199-04 Cruise Report (PDF)

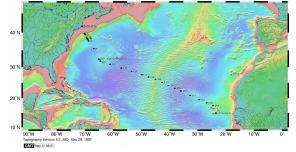
Figure 2. The red line shows the cruise track for the first leg of the US Geotraces North Atlantic Transect on the R/V Knorr in October 2010. The rest of the stations (beginning with 13) will be completed in October-December 2011 on the R/V Knorr (courtesy of Bill Jenkins, Chief Scientist, GNAT first leg). [click on the image to view a larger version]



The section completion effort resumed again in November 2011 with KN204-01A,B (Figure 3).

KN204-01A, B Cruise Report (PDF)

Figure 3. Station locations occupied on the US Geotraces North Atlantic Transect on the R/V Knorr in November 2011. [click on the image to view a larger version]



Data from the North Atlantic Transect cruises are available under the Datasets heading below, and consensus values for the SAFe and North Atlantic GEOTRACES Reference Seawater Samples are available from the GEOTRACES Program Office: <u>Standards and Reference Materials</u>

ADCP data are available from the Currents ADCP group at the University of Hawaii at the links below:

KN199-04 (leg 1 of 2010 cruise; Lisbon to Cape Verde)

KN199-05 (leg 2 of 2010 cruise; Cape Verde to Charleston, NC)

KN204-01A (part 1 of 2011 cruise; Woods Hole, MA to Bermuda)

KN204-01B (part 2 of 2011 cruise; Bermuda to Cape Verde)

U.S. GEOTRACES North Atlantic Section: CFC and SF6 Measurements (GT NAT CFC and SF6)

NSF Award Abstract:

This award is funded under the American Recovery and Reinvestment Act of 2009 (Public Law 111-5). The objectives of the GEOTRACES program are: 1) to determine the global distributions of selected trace elements and isotopes and evaluate the sources, sinks and internal cycling of these species to better understand the physical, chemical and biological processes regulating their distributions, 2) to develop an understanding of the processes involved in oceanic trace element cycles sufficiently well that the response of these cycles to global change can be predicted and their impact on the carbon cycle and climate understood, and 3) to understand the processes that control the concentrations of geochemical species used for proxies of the past environment, both in the water column and in the substrates that reflect the water column.

Understanding how the physical processes of advection, mixing, and water mass formation affect the distributions of trace elements and isotopes is critical to meeting these objectives. The evolving CFC and SF6 distributions in the ocean provide strong constraints on these processes. CFCs have been measured extensively in the global ocean for the past two and a half decades as part of several large scale oceanographic programs (e.g. SAVE, WOCE, CLIVAR) as well as many smaller programs and SF6 has become a standard measurement on the CLIVAR cruises. Measurement of CFCs and SF6 on the GEOTRACES program places the GEOTRACES data in the context of large scale ventilation patterns established by CFC/SF6 measurements on these cruises.

In this project, researchers at the Lamont-Dougherty Earth Observatory of Columbia University will measure the CFC-11, CFC-12 and SF6 distributions along the US GEOTRACES North Atlantic cruise track. They will use these data to identify the most recently ventilated cores of the North Atlantic water masses, to estimate transit times of these water masses from their source regions, and to estimate oxygen consumption rates and rates of production or decomposition of selected trace elements measured on this program using the transit time information.

Broader Impacts: In addition to providing information on ventilation and transit times for the GEOTRACES project, the CFC and SF6 data collected on this cruise will also expand the transient tracer data base for the North Atlantic Ocean. The data will be disseminated widely to the research community following NSF guidelines. Several CLIVAR cruises to the North Atlantic are planned for the 2010 - 2012 time period, and the GEOTRACES cruise will increase the coverage for CFCs and SF6. This database of the temporally evolving CFC and SF6 concentrations in the North Atlantic Ocean is used in studies of the earth's climate and the ocean's role in the earth's climate and the global CO2 cycle. It is used to validate models of ocean circulation and to quantify the uptake and storage of anthropogenic CO2 in the ocean.

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Program Information

U.S. GEOTRACES (U.S. GEOTRACES)

Website: http://www.geotraces.org/

Coverage: Global

GEOTRACES is a <u>SCOR</u> sponsored program; and funding for program infrastructure development is provided by the <u>U.S. National Science Foundation</u>.

GEOTRACES gained momentum following a special symposium, S02: Biogeochemical cycling of trace elements and isotopes in the ocean and applications to constrain contemporary marine processes (GEOSECS II), at a 2003 Goldschmidt meeting convened in Japan. The GEOSECS II acronym referred to the Geochemical Ocean Section Studies To determine full water column distributions of selected trace elements and isotopes, including their concentration, chemical speciation, and physical form, along a sufficient number of sections in each ocean basin to establish the principal relationships between these distributions and with more traditional hydrographic parameters;

- * To evaluate the sources, sinks, and internal cycling of these species and thereby characterize more completely the physical, chemical and biological processes regulating their distributions, and the sensitivity of these processes to global change; and
- * To understand the processes that control the concentrations of geochemical species used for proxies of the past environment, both in the water column and in the substrates that reflect the water column.

GEOTRACES will be global in scope, consisting of ocean sections complemented by regional process studies. Sections and process studies will combine fieldwork, laboratory experiments and modelling. Beyond realizing the scientific objectives identified above, a natural outcome of this work will be to build a community of marine scientists who understand the processes regulating trace element cycles sufficiently well to exploit this knowledge reliably in future interdisciplinary studies.

Expand "Projects" below for information about and data resulting from individual US GEOTRACES research projects.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-0928612

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