Nitrous oxide (N2O) and transient tracer (chlorofluorocarbons, sulfur hexafluoride) concentrations from samples collected on three GO-SHIP cruises in the tropical Pacific Ocean during 2015-2016

Website: https://www.bco-dmo.org/dataset/944886
Data Type: Cruise Results
Version: 1
Version Date: 2024-12-10

Project
» Equatorial transport of nitrous oxide from the eastern tropical Pacific Ocean (Equatorial N2O)

Contributors	Affiliation	Role
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Abstract
Nitrous oxide (N2O) and transient tracer (chlorofluorocarbons, sulfur hexafluoride) concentrations were determined in water samples collected on three Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP) cruises to investigate the transport, production, and efflux of N2O across the tropical Pacific Ocean. The three GO-SHIP cruises were 1) P16N in April – May 2015 aboard the R/V Ronald H. Brown, 2) P15S in April – June 2016 aboard the R/V Investigator, and 3) P18 in Nov – Dec 2016 aboard the R/V Ronald H. Brown from rosettes of either 24 or 36 – 10-liter (L) Niskin bottles equipped with Seabird SBE9plus CTDs. Samples for dissolved chlorofluorocarbons (CFC–11, CFC-12), sulfur hexafluoride (SF6), and N2O were collected following the method described in Bullister et al. (2008).

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Coverage

Location: Tropical Pacific Ocean
Spatial Extent: **N**:22.999 **E**:-102.997 **S**:-22.999 **W**:-170.059
Temporal Extent: 2015-04-11 - 2016-12-21

Methods & Sampling

Water samples were collected in bottles designed with a modified end-cap to minimize the contact of the water sample with the end-cap O-rings after closing. Stainless steel springs covered with a nylon powder coat were substituted for the internal elastic tubing provided with standard Niskin bottles. When taken, water samples collected for dissolved CFC/SF6/N2O analyses were the first samples drawn from the bottles. To minimize contact with air, the CFC/SF6/N2O samples were drawn directly through the stopcocks of the bottles into 250-milliliter (ml) precision glass syringes equipped with three-way plastic stopcocks. The syringes were immersed

in a holding tank of clean surface seawater held at ~10 degrees Celsius (°C) until 20 minutes before being analyzed. At that time, the syringe was placed in a bath of surface seawater heated to 32°C.

Concentrations of CFC/SF6/N2O in seawater and gas standards were measured by shipboard electron capture detector gas chromatography (ECD-GC) using techniques modified from those described by Bullister and Wisegarver (2008), as outlined below. For seawater analyses, water was transferred from a glass syringe to a glass-sparging chamber (volume 200 ml). The dissolved gases in the seawater sample were extracted by passing a supply of CFC/SF6/N2O-free N2 through the sparging chamber for a period of 6 minutes at 150 milliliters per minute (ml min-1). Water vapor was removed from the purge gas during passage through a Nafion drier. Carbon dioxide was removed with an 18-centimeter (cm) long, 3/8-inch diameter glass tube packed with Ascarite and a small amount of magnesium perchlorate desiccant. The sample gases were concentrated on a cold-trap consisting of a 1/16-inch OD stainless steel tube with a 2.5 cm section packed tightly with Porapak Q, a 15 cm section packed with Carboxen 1000 and a 2.5 cm section packed with MolSieve 5 angstrom (Å). A Neslab Cryocool CC-100 was used to cool the trap to -65°C. After 6 minutes of purging, the trap was isolated, and heated electrically to 170°C. The sample gases held in the trap were then injected onto a precolumn (~61 cm of 1/8-inch OD stainless steel tubing packed with Porasil B, held at 80°C) for the initial separation of CFC-12, CFC-11, SF6 from later eluting peaks.

After the SF6 and CFC-12 had passed from the pre-column and into the second pre-column (26 cm of 1/8-inch OD stainless steel tubing packed with MolSieve 5Å, 160°C) and into the analytical column #1 (174 cm of 1/8-inch OD stainless steel tubing packed with MolSieve 5Å and 60 cm Porasil C held at 80°C), the outflow from the first pre-column was diverted to the second analytical column (180 cm 1/8-inch OD stainless steel tubing packed with Porasil B held at 80°C). The gases remaining after CFC- 11 had passed through the first pre-column, were backflushed from the precolumn and vented. After CFC-12 had passed through the second pre-column, a flow of Argon:Methane (95:5) was used to divert the N2O to a third analytical column (30 cm of MolSieve 5Å, 150°C). Column #3 and the second pre-column were held in a Shimadzu GC8AIE gas chromatograph with an electron capture detector (ECD) held at 330°C. Columns #1, and the first pre-column were in another Shimadzu GC8AIE gas chromatograph with ECD. The column #2 was also in a Shimadzu GC8AIE gas chromatograph with the ECD held at 330°C.

The analytical system was calibrated frequently using a standard gas of known CFC/SF6/N2O composition. Gas sample loops of known volume were thoroughly flushed with standard gas and injected into the system. The temperature and pressure was recorded so that the amount of gas injected could be calculated. The procedures used to transfer the standard gas to the trap, pre-columns, main chromatographic column, and ECD were similar to those used for analyzing water samples. Four sizes of gas sample loops were used. Multiple injections of these loop volumes could be made to allow the system to be calibrated over a relatively wide range of concentrations. System blanks (injections of loops of CFC/SF6/N2O-free gas) were injected and analyzed in a similar manner. The typical analysis time for seawater, standard or blank samples was ~12 minutes. Concentrations of CFC-11, CFC-12, and N2O in seawater samples and gas standards are reported relative to the SIO98 calibration scale (Prinn et al., 2000). Concentrations of SF6 in seawater samples and gas standards are reported relative to the SIO-2005 calibration scale (Bullister and Tanhua, 2010). Dissolved CFC concentrations are given in units of picomoles per kilogram seawater (pmol kg-1), SF6 concentrations in femtomoles per kilogram (fmol kg-1), and N2O concentrations in nanomoles per kilogram (nmol kg-1). CFC/SF6/N2O concentrations in seawater samples were determined by fitting their chromatographic peak areas to multi-point calibration curves, generated by injecting multiple sample loops of gas from a working standard into the analytical instrument. The response of the detector to the range of moles of CFC/SF6/N2O passing through the detector remained relatively constant during the cruise. Full-range calibration curves were run at several times during the cruise and partial curves were run as frequently as possible, usually while sampling. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently (at intervals of 90 minutes) to monitor short-term changes in detector sensitivity.

The purging efficiency was estimated by re-purging a high-concentration water sample and measuring the residual signal. At a flow rate of 150 ml min-1 for 6 minutes, the purging efficiency for SF6 and both CFC gases was >99%. The efficiency for N2O was typically about 96%.

Data Processing Description

Data acquisition and processing of temperature/condutivity/depth was done using manufacturer's software (Seabird Scientific, Inc.).

Data acquisition and processing of CFC/SF6/N2O was done using custom software (GCWerks, Inc.).

Quality flags are assigned using the Ocean Data View quality flag scheme (https://odv.awi.de/fileadmin/user_upload/odv/docs/ODV_quality_flag_sets.pdf) where:

Good = 0;
Unknown = 1;
Questionable = 4;
Bad = 8.

BCO-DMO Processing Description

- Imported original files "P16N_BCO-DMO.csv", "P15S_BCO-DMO.csv", and "P18_BCO-DMO.csv" into the BCO-DMO system.
- Marked the following as missing data identifers: "-9,-9.0,-9.00,-9.000,-9.0000,-999,-999.0". Missing data values are empty/blank in the final CSV file.
- Concatenated the three data files into one single data file.
- Renamed fields to comply with BCO-DMO naming conventions.
- Created date/time UTC column in ISO 8601 format; removed the original date/time fields.
- Converted longitude values from a 0-360 scale to minus 180 to 180. (negative values = West)
- Saved the final data file as "944886_v1_N2O_and_transient_tracers.csv".

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Data Files

File	
944886_v1_N2O_and_transient_tracers.csv	(Comma Separated Values (.csv), 724.19 KB) MD5:c0d3192bca8993918916eed6bbdd193a
Primary data file for dataset ID 944886, version 1	

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Related Publications

Bullister, J. L., & Tanhua, T. (2010). Sampling and Measurement of Chlorofluorocarbon and Sulfur Hexafluoride in Seawater. In, The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. Version 1. GO-SHIP. https://doi.org/10.25607/OBP-1343
Methods

Bullister, J. L., & Wisegarver, D. P. (2008). The shipboard analysis of trace levels of sulfur hexafluoride, chlorofluorocarbon-11 and chlorofluorocarbon-12 in seawater. Deep Sea Research Part I: Oceanographic Research Papers, 55(8), 1063–1074. doi:10.1016/j.dsr.2008.03.014
Methods

Prinn, R. G., Weiss, R. F., Fraser, P. J., Simmonds, P. G., Cunnold, D. M., Alyea, F. N., O'Doherty, S., Salameh, P., Miller, B. R., Huang, J., Wang, R. H. J., Hartley, D. E., Harth, C., Steele, L. P., Sturrock, G., Midgley, P. M., & McCulloch, A. (2000). A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. Journal of Geophysical Research: Atmospheres, 105(D14), 17751–17792. Portico. https://doi.org/10.1029/2000jd900141
Methods

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Parameters

Parameter	Description	Units

Cruise	GO-SHIP cruise ID	unitless
Station	station number	unitless
ISO_DateTime_UTC	Date and time (UTC) when sample was taken in ISO 8601 format	unitless
Longitude_360	longitude sample was taken in degrees East (0-360)	decimal degrees
Longitude	Longitude in degrees East (-180 to 180); negative values = West direction	decimal degrees
Latitude	Latitude in degrees North; negative values = South direction	decimal degrees
Bot_Depth	depth of the seafloor	meters (m)
Pressure	pressure at the depth sample was taken	decibars (db)
SAMPNO	sample number	unitless
SAMPNO_QF	sample number quality flag	unitless
TEMPERATURE	temperature	degrees Celsius
CFC11	CFC-11 concentration	picomoles per kilogram (pmol/kg)
CFC11_QF	CFC-11 concentration quality flag	unitless
CFC12	CFC-12 concentration	picomoles per kilogram (pmol/kg)
CFC12_QF	CFC-12 concentration quality flag	unitless
SF6	SF6 concentration	femptomoles per kilogram (fmol/kg)
SF6_QF	SF6 concentration quality flag	unitless
CTD_SALINITY	salinity [PSS-78] from Seabird SBE9plus	unitless

CTD_SALINITY_QF	salinity from Seabird SBE9plus quality flag	unitless
N2O	N2O concentration	nanomoles per kilogram (nmol/kg)
N2O_QF	N2O concentration quality flag	unitless

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Instruments

Dataset-specific Instrument Name	Seabird SBE9plus CTD
Generic Instrument Name	CTD Sea-Bird
Dataset-specific Description	Temperature, conductivity, depth were measured using Seabird SBE9plus CTDs.
Generic Instrument Description	Conductivity, Temperature, Depth (CTD) sensor package from SeaBird Electronics, no specific unit identified. This instrument designation is used when specific make and model are not known. See also other SeaBird instruments listed under CTD. More information from Sea-Bird Electronics.

Dataset-specific Instrument Name	Niskin bottles
Generic Instrument Name	Niskin bottle
Dataset-specific Description	Seawater samples were collected using ~10L Niskin bottles.
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 GC8AIE
Generic Instrument Name	Shimadzu GC-8AIE gas chromatograph
Dataset-specific Description	CFC/SF6/N2O concentrations were measured using Shimadzu GC8AIEs.
Generic Instrument Description	A gas chromatograph that separates and analyses gas mixtures in water or air for dedicated applications. The instrument includes a single column injector, one pressure regulator, capillary column, Electron Capture Detector (ECD) and analogue output. The column oven has a two-stage overheat prevention for protection of columns. The injection port is on-column type whereby the solution is directly injected into the head of a glass column. The constant-current ECD maintains a constant current flow in the detector. The isothermal temperature ramp program holds the column oven at a set temperature throughout the analysis.

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Deployments

RB1503_leg1

Website	https://www.bco-dmo.org/deployment/787503
Platform	NOAA Ship Ronald H. Brown
Report	http://dx.doi.org/10.7942/C2WC7C
Start Date	2015-04-10
End Date	2015-05-13
Description	2015 P16N, Climate Variability and Predictability (CLIVAR), R/V Ronald H Brown, RB1503, leg 1. Cruise aboard the National Oceanic and Atmospheric Administration (NOAA) vessel the Ronald H. Brown (the Brown) acting under the auspices of the Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP). Expocode: 33RO20150525. The Cruise Report and additional data from the cruise are available from CCHDO: Cross, J. and Siedlecki, S. (2015). Hydrographic Cruise 33RO20150410, exchange version. Accessed from CCHDO https://cchdo.ucsd.edu/cruise/33RO20150410. Access date 2021-05-21. CCHDO cruise DOI: 10.7942/C2WC7C Cruise information is also available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/RB1503

RB1606_leg1

Website	https://www.bco-dmo.org/deployment/821809
Platform	NOAA Ship Ronald H. Brown
Report	http://dx.doi.org/10.7942/C21T0F
Start Date	2016-11-19
End Date	2016-12-24
Description	P18 US GO-SHIP Reoccupation Leg 1 (2016/2017). Leg 1 of the 2016/2017 occupation of the P18 hydrographic section aboard the National Oceanic and Atmospheric Administration (NOAA) vessel the Ronald H. Brown acting under the auspices of the Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP). The Cruise Report and additional data from the cruise are available from CCHDO: Sonnerup, R., Carter, B., Purkey, S., and Bourbonnais, A. (2017) . Hydrographic Cruise: 33RO20161119, exchange version. Accessed from CCHDO https://cchdo.ucsd.edu/cruise/33RO20161119. Access date 2021-05-21. CCHDO cruise DOI: 10.7942/C21T0F

IN2016_V03

Website	https://www.bco-dmo.org/deployment/945014
Platform	R/V Investigator
Report	https://cchdo.ucsd.edu/data/12704/096U20160426_do.pdf
Start Date	2016-04-26
End Date	2016-06-22
Description	2016 P15S GO-SHIP cruise. EXPOCODE: 096U20160426 The Cruise Report and additional data from the cruise are available from CCHDO: https://cchdo.ucsd.edu/cruise/096U20160426

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Project Information

Equatorial transport of nitrous oxide from the eastern tropical Pacific Ocean (Equatorial N2O)

Coverage: Equatorial Pacific Ocean

NSF Award Abstract:
Nitrous oxide (N2O) is a powerful greenhouse gas, ~300 times stronger than carbon dioxide and is also implicated in the destruction of the ozone layer. Thus, it is important to understand the magnitude and sources of N2O to the atmosphere in order to predict future climate impacts. The ocean is a significant source of N2O to the atmosphere, but its overall contribution is uncertain. A significant amount of the marine N2O delivered to the atmosphere comes from the eastern tropical Pacific (ETP). This region is host to some of the lowest oxygen concentrations in the entire ocean, which is favorable to a massive production of N2O. Previous estimates of the amount of N2O diffusing out of the ETP to the atmosphere considered only the area directly over the high N2O region of the ETP. However, there are strong subsurface currents that flow away from the ETP, westward along the equator, and N2O carried away in these equatorial currents has been overlooked when determining the contribution of the ETP to marine emissions of N2O. This proposed work will use new, high-quality N2O data collected on 3 Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP) cruises through the tropical Pacific to investigate N2O cycling across the entire tropical Pacific Ocean. Low oxygen regions, like the ETP, are predicted to expand in the future, potentially leading to an increase in N2O production, underscoring the importance of understanding N2O cycling in this region. This project will support mentoring up to two undergraduate summer interns.

Recent advances in analytical capabilities within the NOAA/PMEL Trace Gas group, and their application to three Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP) repeat hydrography cruises through

the tropical Pacific, have facilitated the collection of nitrous oxide measurements of unprecedented quality and coverage of the region, together with complementary hydrographic parameters. We propose to use this new, high-quality GO-SHIP N2O data in concert with the stable isotopic composition of nitrous oxide, tracers of ventilation rates, and current velocities to investigate the transport, production, and efflux of nitrous oxide in the tropical Pacific Ocean. Using both observation data and idealized modeling, the research will (i) estimate the magnitude of the physical transport of N2O to/from the ETP, and losses to the atmosphere, and (ii) differentiate the sources of N2O in equatorial currents between advection from the ETP and in situ production. The work proposed here will lead to a more nuanced understanding of N2O production, transport, and fate in the tropical Pacific.

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
NSF Division of Ocean Sciences (NSF OCE)	OCE-2048518

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