# Sulphur Hexafluoride (SF6) from Station/Niskin bottle sort from NOAA Ship Ronald H. Brown RB-08-02 in the Southwest Atlantic sector of the Southern Ocean near South Georgia Island in 2008 (SO\_GasEx project)

Website: https://www.bco-dmo.org/dataset/3308 Version: 16 Feb 2010 Version Date: 2010-02-16

#### Project

» <u>Southern Ocean Gas Exchange Experiment</u> (SO\_GasEx)

#### Programs

» Ocean Carbon and Biogeochemistry (OCB)

» United States Surface Ocean Lower Atmosphere Study (U.S. SOLAS)

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# **Dataset Description**

SF6 Discrete - Station/Niskin Sort Analysis of discrete samples for SF6 Samples collected from CTD casts, from underway scientific seawater line, and from submerged water pump

## Methods & Sampling

See: SO-GasEx cruise report, Section 5.3.3 ppgs 19-20

# **Operation description:**

Sampling times and locations: Sampled all CTD casts where Niskin bottles were tripped. One deep cast to 4600m, two mid-depth casts to 1500m, four shallow casts to 100m, and other casts usually to 500m. See CTD cast logs and bottle files for specific times, locations, and bottles for each cast. See event log for times and locations when sampled underway seawater line.

Overall sampling strategy: Normally collected one sample from each depth that might contain the released SF6, plus three - six samples deeper. All available depths were sampled on the first four casts and on any later cast that was shallower than 500m. If multiple Niskins were tripped at a given depth, hydrography sampled only one of these. Duplicate samples were drawn from a Niskin, normally in the mixed layer, on nearly every cast. The first Niskin of a cast that was sampled was the deepest Helium sample, and the sampling continued in order to the surface Niskin. The deeper Niskins for SF6 sampling were done next, starting at the deepest.

#### Sampling technique:

The discrete samples were collected in 550 ml borosilicate glass bottles with ground glass stoppers. A sample bottle was shaken with 30-40 ml of water; then inverted and rinsed with 10-20 ml of water. The bottle was filled from the bottom with ~800 ml of bubble free water. The stopper was put in the bottle ensuring that no gas bubble was enclosed. After all the samples were collected from a cast, a rubber band was slipped over the stopper. If the samples were not going to be analyzed within 10 hours, the glass bottles were stored in water.

#### Analytical method:

The samples were analyzed on an instrument patterned after Law et.al. [1998] and built in 1998 at AOML. About 269 ml of sample water was sucked into an evacuated chamber through a showerhead. The SF6 that entered the headspace during filling and the SF6 that remained dissolved in the water were stripped with ultra high purity nitrogen onto a Carboxen 1000 trap held at -68 C. After a little more than 3 minutes of purging, the trap was isolated and heated to 150 C. The trapped gases were swept onto a 1.5 m x 0.3 cm OD molecular sieve 5A column. The SF6 was separated from oxygen and other gases and was measured with an electron capture detector (ECD).

The detector was calibrated using six standards:

- cyl#CA2071- 5.7 pptrillion (v/v)
- cyl#CA2089- 55.1 pptr
- cyl#CA3452- 112.3 pptr
- cyl#CA2060- 166.6 pptr
- cyl#CA2056- 345.0 pptr
- cyl#CA2093- 1109.0 pptr

The custom software includes a chromatography package from WillStein Software, which is used for acquisition of the ECD output and to reintegrate peaks. The SF6 peaks were reintegrated for all blank analyses, water analyses and the analyses of 5.5 pptr standard. The larger standards had very favorable signal to noise ratios.

The pattern of analyses include initial and final groups of standards bracketing groups of water analyses. The water samples from each cast were typically split into two groups, each covering the entire water column. Within a group, the deepest water samples were analyzed before the more concentrated surface water samples.

The Typical Analyses Sequence:

- 2-3 gas blanks
- 15-20 gas standards spanning the entire range
- gas blank
- 1-2 stripper blanks
- 7-9 water analyses
- stripper blank
- 1 analysis of 166.6 pptr standard
- stripper blank
- 7-9 water analyses
- [repeat analyses of stripper blanks, 166.p pptr std, and water samples two or three times]
- stripper blank
- gas blank

- 5-15 standards

#### - 2 gas blanks

The stripping chamber was evacuated and flushed with nitrogen before the first use. If the stripping chamber was not going to used for more than 6 hours, it was rinsed with fresh water and then evacuated and flushed.

### Instrument details:

The ECD gas chromatograph is a Shimadzu Mini 2.

The custom software was written with LabView 5.1 in 1998 and revised in 2002. The reference for a description of the instrument is: Law, C.S, A.J. Watson, M.J. Liddicoat, and T. Stanton, Sulphur hexafluoride as a tracer of biogeochemical and physical processes in an open-ocean iron fertilization experiment, Deep Sea Research II, 45, 977-994, 1998.

## **Operation Log - During Cruise**

#### 5 - 6 March 2008

Attempts were made to use this discrete instrument to quantitate the amount of SF6 in water actively being bubbled in the dosing tank. All attempts resulted in peaks much larger than full scale for the ECD. The excessive amounts of SF6 were easily swept out of the instrument.

#### Station 3

one sample of a duplicate pair is stored for 23 hours before analyses - precision of duplicates was good

#### Station 5

one sample of a duplicate pair is stored for 24 hours before analyses, another sample of a different duplicate pair is stored for 52 hours. Precision of the 52-hour duplicates was poorer than normal.

#### Station 8

These samples were stored overnight before analyses as were some earlier stations and many later stations. This was the first station for which some outgassing bubbles in some samples was noticed. These tiny bubbles (<0.1 ml total volume) were not present when the bottle was sealed and did not seem to bias the SF6 results.

## Station 10

The sampling order was more discontinuous than normal to accommodate noble gas sampling. For the collection of samples from the underway system after station 10, the outflow tube of the MicroTSG in the hydro lab sink was put in the bottom of a sample bottle and left to overfill the bottle for at least 2 minutes (flow at 1.3 liter/min).

## 13 March 2008

During analysis of sample bottle 15 (stn 9, N 22) the Labview program was in its 'pause and prompt' state longer than usual. The analytical system evacuates the stripping chamber and then presents a prompt screen until a "start" button is pushed by the analyst. The analyst has to draw some of the sample through the inlet tube and solenoid valve before pushing the "start" button. If the 'pause and prompt' state is long, the chance of outside air leaking into the chamber is greater (potential higher blank).

## 15 March 2008

In an effort to have comparable results from the underway and discrete SF6 analytical systems, the single SF6 gaseous standard for the underway system (58.2 pptr) was run on the discrete system and three of the discrete standards (166.6, 55.1, and 5.7 pptr) were run on the underway system.

## 18 March 2008

Both system and stripper blanks are significantly higher. The second dosing tank is being bubbled on the afterdeck, and the lab air was enriched in SF6. No leaky fittings could be found on the analytical system despite a day of searching. After  $\sim$ 48 hrs the

blanks decreased, but remained higher than at the start of the cruise.

#### 22 March 2008

Last night was the first station (16) on the second patch. I took a sample from the underway system to quickly check the strength of ECD signal. When the sample was run, the peak went offscale. The ECD was set for 2nAmp standing current through station 14. I decreased the setting to 1 nAmp. To span the largest peak from the water analyses of station 16, I had to trap 6 regular gas loops (1.606 ml) of the most concentrated standard (1109 pptr). I am concerned about peak shape changes while trapping that many loops sequentially, so I put the second gas sample loop valve back on the system. [it was taken off during a previous experiment.] I made a large loop (~7 ml) and created new analytical methods to adequately flush the loop while and after filling it with standard or blank gas. I will have to determine the exact volume of the new gas loop back at AOML.

#### 25 March 2008

Try again to locate the source of the elevated blanks, especially the stripper blanks. Still, could not find any fitting that leaked. At the end of a day of analyses, the chamber is rinsed with fresh water to reduce the corrosion on the solenoid valves attached to the drain and vacuum connections. I stripped a sample of the fresh water on the ship and discovered that it was as concentrated as the surface 'in-patch' water (>200 fmole/liter). The chamber will continue to be rinsed with fresh water, but it will go through a couple evacuate-and-purge cycles before being left for the night. [no reduction in the blanks developed, but the procedure was continued.]

#### 25 March 2008

During analyses of sample bottles 202 (stn 25, N 3), 206 (stn 25, N 9) and 10 (stn 26, N 18) the Labview program was in its 'pause and prompt' state longer than usual.

#### 26 March 2008

During analysis of sample bottles 203 (stn 27, N 8) the Labview program was in its 'pause and prompt' state longer than usual.

#### 28 March 2008

During analysis of sample bottles 2 (stn 32, submerged pump) the Labview program was in its 'pause and prompt' state longer than usual.

#### 29 March 2008

During analyses of sample bottles 2 (stn 35, N 7) and 17 (stn 35, underway system) the Labview program was in its 'pause and prompt' state longer than usual.

#### 30 March 2008

During analysis of sample bottles 202 (stn 37, N 6) the Labview program was in its 'pause and prompt' state longer than usual. During analysis of sample bottles 206 (stn 37, N 10) there seemed to be air in the inlet line and the water level in the stripping chamber seemed lower than usual. Maybe the inlet tube was not submerged as low as it should have been [but how would the Pt wire water sensors stop the water flow automatically - splashes with gas going in?].

#### 31 March 2008

During sampling, the stopper on bottle 203 (stn 41, N 3) was removed  $\sim$ 3 minutes after sampling so some more a little more water from the niskin was gently added to the very top of the bottle and the stopper reinserted.

#### 03 April 2008

During sampling, the stopper on bottle 203 (stn 41, N 3) was removed  $\sim$ 3 minutes after sampling so some more a little more water from the niskin was gently added to the very top of the bottle and the stopper reinserted.

For Blanks and Cals See: <u>SO-GasEx Discrete SF6 Blanks and Calibration Curves</u>

#### Data Processing Log - Post Cruise

The first step in the data processing is subtracting the appropriate analytical blank from the raw peak areas: gas blank for standard and air analyses, stripper blank for the water analyses. The gas and stripper blanks were plotted and appeared to cluster around different values over separate time periods. This pattern was to be expected since there was only one analyst, who typically ran the samples from two casts together. Thus, the analytical system was used for  $\sim 1/2$  a day and then sat unused for  $\sim 1/2$  a day. Nineteen ranges of time were used for blank correction, due primarily to the variability of the stripper blanks. The same gas blank value was applied in sequentially ranges often. The applied blank values and a summary of the analytical blank results are provided below.

The analytical blanks showed no systematic trends for all but one range, so a single blank value was used for the entire range. Within one time period, the stripper blank clearly increased and then decreased. Rather than use one value, the applied blank for the water analyses was a time-weighted linear interpolation between bracketing analytical stripper blanks. For most of the water and gas analyses, the applied blank was significantly less than 1% of the sample signal.

The blank-corrected peak areas for the standard analyses were plotted versus time. The response of the ECD was fairly stable within the setting used for a patch (i.e. 2 nA standing current for patch#1; 1 nA standing current for patch#2). Three time periods were chosen for each setting. Within each time period, a least-squared regression of the standards produced a 4th degree polynomial equation relating peak area and femtomole SF6. The peak areas for the seawater analyses were not larger than for the standards; however, there were some atypical analyses (e.g. tap water after 26 March) that had peaks larger than the standards in that time period. Since the detector response was similar in the adjoining time periods to extend the standard curves for some atypical analyses. The 4th degree polynomial equations were used to convert the blank-corrected peak areas for the water analyses to aqueous concentrations (femtomole / liter).

The results of the water analyses were examined within the context of the surrounding SF6 analyses, of the titrated oxygen samples, and of the general hydrography. A quality control flag similar to the WOCE protocol were assigned to each water analysis. There were four analyses that were deemed 'bad', two of which had observations during analysis to explain the bad result. There were fifteen analyses that were deemed 'questionable', seven of which had observations to explain the poor result. The remaining 650 seawater analyses were deemed 'good', though nine analyses had observations that could have explained poor results. The assignment of a 'bad' quality control flag was conservative so that expected results would not be excluded from examination by others.

For the duplicate water samples drawn from niskin bottles, the relative precision was 3.3% for all 38 duplicate pairs and was 1.4% for the 31 duplicate pairs definitely above background SF6 concentrations (i.e. >8 fmole SF6/Liter). For the nineteen sets of multiple samples collected from the underway sea water line the average precision was 5.3%, which reflects analytical variability as well as changes in the water being sampled. A restrip of a concentrated water sample was done on nearly every day. All 27 restrips of a water sample contained 2% or less of the total SF6 extracted from a water sample, so no correction for stripping efficiency was done.

#### For Blanks and Cals See: <u>SO-GasEx Discrete SF6 Blanks and Calibration Curves</u>

#### **BCO-DMO Processing Notes**

- Generated from original file SO-GasEx08\_Disc-SF6\_Final.xls, Sheet: stn-nsk

#### **BCO-DMO Edits**

- parameter names modified to conform to BCO-DMO convention
- event, station, date, time, lon, lat inserted from CTD headers file
- blank cells changed to 'nd'

# Data Files

 File

 Disc\_SF6\_stn.csv(Comma Separated Values (.csv), 103.23 KB)

 MD5:1d6fc6c8edb128a68307948d9a51a8e6

 Primary data file for dataset ID 3308

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# **Parameters**

Parameter	Description	Units
event	Unique event number	YDAHHMM
date	Date (UTC)	YYYYMMDD
time	Time (UTC)	ННММ
lon	Station longitude in decimal degrees (West is negative)	decimal degrees
lat	Station latitude in decimal degrees (South is negative)	decimal degrees
stn_nskn	The CTD station number followed by a 0; followed by the niskin number. e.g. stn_nskn 1001 is CTD station 1; niskin 1.	integer
smpl_btl_num	Sample bottle number	integer
Helium_Flag	Helium Flag (0=yes)	integer
WOCE_QC	2 = good analysis. 3 = questionable analysis - the result does not seem to fit into the context of surrounding results whether or not any unusual conditions were observed during sampling or analysis. 4 = bad analysis - the result does not fit into the context of surrounding results and an unusual condition was observed.	integer
comments	data collection comments	text
year_day_analyzed	year day analyzed	decimal day
WS_area	WS area	integer
SF6	SF6	fmole/Liter

precision	Precision percentage: For 2 analyses percentage is difference divided by average; For >2 analyses percentage is standard deviation divided by average	percentage
station	SO-GasEx CTD Station Id	integer
niskin	niskin bottle number	integer
year_day_collected	year day collected	decimal day
pres	pressure from CTD	decibars
temp	temperature from CTD	degrees celcius
sal	salinity from CTD	dimensionless
sigma_t	sigma_t (density) from CTD	kilograms/meter^3
02	dissolved Oxygen	umol/kg
lon_collection	Collection longitude in decimal degrees (West is negative)	decimal degrees
lat_collection	Collection latitude in decimal degrees (South is negative)	decimal degrees
 DrawT_minus_C	DrawT-C	(tbd)
O2_discrete	Oxygen discrete	umol/kg
 O2_satur	Oxygen saturated	milliliters/liter

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# Instruments

Dataset- specific Instrument Name	CTD Seabird 911plus
Generic Instrument Name	CTD Sea-Bird SBE 911plus

Dataset-	Instrument Configuration File for SO-GasEx: PSA file: C:GasExacqSease.psa Date: 02/23/2008
specific	Instrument configuration file: C:GasExconssec_24_1.con Configuration report for SBE
Description	911plus/917plus CTD

**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

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# Deployments

# RB-08-02

RB-00-02	(B-08-02	
Website	https://www.bco-dmo.org/deployment/57846	
Platform	NOAA Ship Ronald H. Brown	
Report	http://bcodata.whoi.edu/SO-GasEx/SO_GasEx_Cruise_Report.pdf	
Start Date	2008-02-29	
End Date	2008-04-12	
Description	The Southern Ocean GasEx experiment was conducted aboard the NOAA ship Ronald H. Brown with 31 scientists representing 22 institutions, companies and government labs. The cruise departed Punta Arenas, Chile on 29 February, 2008 and transited approximately 5 days to the nominal study region at 50°S, 40°W in the Atlantic sector of the Southern Ocean. The scientific work concentrated on quantifying gas transfer velocities using deliberately injected tracers, measuring CO2 and DMS fluxes directly in the marine air boundary layer, and elucidating the physical, chemical, and biological processes controlling air-sea fluxes with measurements in the upper-ocean and marine air. The oceanic studies used a Lagrangian approach to study the evolution of chemical and biological properties over the course of the experiment using shipboard and autonomous drifting instruments. The first tracer patch was created and studied for approximately 6 days before the ship was diverted from the study site, 350 miles to the south, to wait near South Georgia Island for calmer seas. After more than 4 days away, we returned to the study area and managed to find some remnants of the tracer patch. After collecting one final set of water column samples and recovering the two drifting buoys deployed with the patch, we relocated to the northwest, closer to the area where the first patch was started. A second tracer patch was created and studied for approximately 15 days before we had to break off the experiment and transit to Montevideo, Uruguay for the completion of the cruise.	

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# **Project Information**

# Southern Ocean Gas Exchange Experiment (SO\_GasEx)

## Website: http://so-gasex.org/

**Coverage**: Southwest Atlantic sector of the Southern Ocean (nominally at 50°S, 40°W, near South Georgia Island)

The Southern Ocean Gas Exchange Experiment (SO-GasEx; also known as GasEx III) took place in the Southwest Atlantic sector of the Southern Ocean (nominally at 50°S, 40°W, near South Georgia Island) in austral fall of 2008 (February 29-April 12, 2008) on the <u>NOAA ship *Ronald H. Brown*</u>. SO-GasEX is funded by NOAA, NSF and NASA.

The research objectives for Southern Ocean GasEx are to answer the following questions:

- What are the gas transfer velocities at high winds?
- What is the effect of fetch on the gas transfer?
- How do other non-direct wind effects influence gas transfer?
- How do changing pCO2 and DMS levels affect the air-sea CO2 and DMS flux, respectively in the same locale?
- Are there better predictors of gas exchange in the Southern Ocean other than wind?
- What is the near surface horizontal and vertical variability in turbulence, pCO2, and other relevant biochemical and physical parameters?
- How do biological processes influence pCO2 and gas exchange?
- Do the different disparate estimates of fluxes agree, and if not why?
- With the results from Southern Ocean GasEx, can we reconcile the current discrepancy between model based CO2 flux estimates and observation based estimates?

# **Related files**

<u>SO-GasEx cruise report</u> <u>SO-GasEx Science Plan</u> <u>SO-GasEx Implementation Plan</u>

The SO-GasEx cruise report and Science and Implementation plans, may also be available at <u>the SO-GasEx</u> <u>science Web page</u>.

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# **Program Information**

## Ocean Carbon and Biogeochemistry (OCB)

Website: http://us-ocb.org/

Coverage: Global

The Ocean Carbon and Biogeochemistry (OCB) program focuses on the ocean's role as a component of the global Earth system, bringing together research in geochemistry, ocean physics, and ecology that inform on and advance our understanding of ocean biogeochemistry. The overall program goals are to promote, plan, and coordinate collaborative, multidisciplinary research opportunities within the U.S. research community and with international partners. Important OCB-related activities currently include: the Ocean Carbon and Climate Change (OCCC) and the North American Carbon Program (NACP); U.S. contributions to IMBER, SOLAS, CARBOOCEAN; and numerous U.S. single-investigator and medium-size research projects funded by U.S. federal agencies including NASA, NOAA, and NSF.

The scientific mission of OCB is to study the evolving role of the ocean in the global carbon cycle, in the face of environmental variability and change through studies of marine biogeochemical cycles and associated ecosystems.

The overarching OCB science themes include improved understanding and prediction of: 1) oceanic uptake and release of atmospheric CO2 and other greenhouse gases and 2) environmental sensitivities of biogeochemical cycles, marine ecosystems, and interactions between the two.

The OCB Research Priorities (updated January 2012) include: ocean acidification; terrestrial/coastal carbon fluxes and exchanges; climate sensitivities of and change in ecosystem structure and associated impacts on biogeochemical cycles; mesopelagic ecological and biogeochemical interactions; benthic-pelagic feedbacks on biogeochemical cycles; ocean carbon uptake and storage; and expanding low-oxygen conditions in the coastal and open oceans.

# United States Surface Ocean Lower Atmosphere Study (U.S. SOLAS)

Website: http://www.us-solas.org/

#### Coverage: Global

The Surface Ocean Lower Atmosphere Study (SOLAS) program is designed to enable researchers from different disciplines to interact and investigate the multitude of processes and interactions between the coupled ocean and atmosphere.

Oceanographers and atmospheric scientists are working together to improve understanding of the fate, transport, and feedbacks of climate relevant compounds, and also weather and hazards that are affected by processes at the surface ocean.

Oceanographers and atmospheric scientists are working together to improve understanding of the fate, transport, and feedbacks of climate relevant compounds.

Physical, chemical, and biological research near the ocean-atmosphere interface must be performed in synergy to extend our current knowledge to adequately understand and forecast changes on short and long time frames and over local and global spatial scales.

The findings obtained from SOLAS are used to improve knowledge at process scale that will lead to better quantification of fluxes of climate relevant compounds such as CO2, sulfur and nitrogen compounds, hydrocarbons and halocarbons, as well as dust, energy and momentum. This activity facilitates a fundamental understanding to assist the societal needs for climate change, environmental health, weather prediction, and national security.

The US SOLAS program is a component of the International SOLAS program where collaborations are forged with investigators around the world to examine SOLAS issues ubiquitous to the world's oceans and atmosphere.

#### <u>» International SOLAS Web site</u>

#### Science Implementation Strategy Reports

<u>US-SOLAS</u> (4 MB PDF file) <u>Other SOLAS reports</u> are available for download from the US SOLAS Web site

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# Funding

Funding Source	Award
National Oceanic and Atmospheric Administration (NOAA)	<u>unknown SO_GasEx NOAA</u>
National Aeronautics & Space Administration (NASA)	unknown SO_GasEx NASA
National Science Foundation (NSF)	unknown SO_GasEx NSF

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