

## **CHLOROFLUOROCARBON (CFC) AND SULFUR HEXAFLUORIDE (SF<sub>6</sub>) MEASUREMENTS AT THE HAWAII OCEAN TIME-SERIES (HOT) SITE**

PI:

John L. Bullister  
National Oceanic and Atmospheric Administration  
Pacific Marine Environmental Laboratory (NOAA-PMEL)  
7600 Sand Point Way N.E.  
Seattle, WA 98115 USA  
Telephone: [206-526-6741](tel:206-526-6741)  
e-mail: [John.L.Bullister@noaa.gov](mailto:John.L.Bullister@noaa.gov)

Analyst:

David Wisegarver  
National Oceanic and Atmospheric Administration  
Pacific Marine Environmental Laboratory (NOAA-PMEL)  
7600 Sand Point Way N.E.  
Seattle, WA 98115 USA  
Telephone: 206-526-6219  
e-mail: [David.Wisegarver@noaa.gov](mailto:David.Wisegarver@noaa.gov)

The Hawaii Ocean Time-series (HOT) site, located at ~23°N, 158°W in the North Pacific subtropical gyre, has been occupied on a regular basis since October 1988 (Karl and Lukas, 1996). Detailed, full water column vertical profiles of the concentrations of two dissolved chlorofluorocarbons (CFC-11 and CFC-12) and dissolved sulfur hexafluoride (SF<sub>6</sub>) were collected on 14 cruises to the HOT site during the period 2005 to 2011 by the NOAA-PMEL Ocean Tracer group. Vertical profiles of the concentration of dissolved carbon tetrachloride (CCl<sub>4</sub>) were collected on 5 cruises to the HOT site during the period 2009-2011 and are also included in this report, as well as nitrous oxide profiles obtained on 3 of the cruises. Over 800 water samples were collected and analyzed for dissolved CFC-11, CFC-12 and SF<sub>6</sub> ('CFC/SF<sub>6</sub>'). During the 14 trips, several methods of analysis were used in the process of developing and improving the techniques for analysis of these gases.

The first trip by the PMEL tracer group on a Hot project was HOT cruise number 166 (HOT166) in December 2004. Samples were drawn and sent by air freight to PMEL for analysis. After this initial effort, the PMEL CFC laboratory container was shipped to the University of Hawaii Marine Center and loaded onto the R/V Kilo Moana or R/V KOK so analysis could be accomplished as soon after sampling as possible. The mobile lab was then stored on site in Honolulu between HOT projects, unless required for another cruise. The primary PMEL analytical system was used on all but one of the cruises (cruise HOT202) when the system was required for several hydrographic sections in the Indian and Pacific Oceans between 2007 and 2008. After this, another system was constructed so the original system could be left in Hawaii for the duration of the project.

Seawater samples at the HOT site were collected on hydrocasts using a 24 position CTD/rosette frame equipped with specially designed 10 liter PVC bottles. The 10 liter

bottles used were based on a NOAA-PMEL bottle design, which uses a modified end-cap to minimize contact of the end-cap O-rings with the seawater sample 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-11, CFC-12 and SF<sub>6</sub> analysis were the first samples drawn from the bottles. Care was taken to coordinate the sampling of CFC/SF<sub>6</sub> with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing.

Samples were drawn from the PVC bottles by two methods each designed to minimize contact with the atmosphere. The more typical of the two methods was to draw the CFC/SF<sub>6</sub> seawater samples directly from the stopcock of the PVC bottles into 250 glass syringes through a three-way plastic stopcock at the tip of the syringe. Typical dissolved SF<sub>6</sub> concentrations in modern surface water are ~1-2 fmol kg<sup>-1</sup> seawater (1 fmol= femtomole = 10<sup>-15</sup> moles), approximately 1000 times lower than dissolved CFC-11 and CFC-12 concentrations. Because of the very low concentrations of SF<sub>6</sub>, a large (250 ml) precision glass syringe was used. To minimize the formation of bubbles in the syringes during storage, the syringes were immersed in a holding tank of clean surface seawater held at ~10°C until ~20 minutes before being analyzed, at which time, the syringe was placed in a bath of surface seawater heated to ~30°C.

The second method, used during the first few trips, was to transfer water from the PVC sampler to a nitrogen purged, 4 liter glass bottle using a 3/8" OD glass tube connected to the niskin stopcock with a short piece of Tygon tubing. All bubbles were removed from the sampling tube before placing the end of the glass tube into the bottom of the bottle, filling and overflowing with at least one liter of sample. A machined plug with O-ring seal was placed in the bottle and the screw cap tightened to give an air tight seal to the bubble free sample bottle. The large bottles were kept cool until preparation for analysis. This method was eventually abandoned as the syringe technique developed into a quicker more reliable method.

Concentrations of CFC-11, CFC-12 and SF<sub>6</sub> in air samples, seawater, and gas standards were measured by shipboard electron capture gas chromatography (EC-GC) using techniques modified from those described by Bullister and Weiss (1988), Vollmer, et al (2002) and Bullister and Wisegarver (2008). Over the 14 trips to the HOT site, the plumbing of the extraction system changed a number of times. Initially, the system was similar to that developed by Vollmer, et al (2002), using two traps, the second trap being used to re-trap f12 and sf6 before injection onto an analytical column to sharpen the SF<sub>6</sub> peak. Later the system used only one trap. There were changes to the combinations of analytical columns and precolumns, lengths, temperatures, traps and flows; eventually an additional valve was added for the analysis of nitrous oxide. The development of this system eventually led to the system described in Bullister and Wisegarver (2008) although some experimentation continued to refine techniques and to add the analysis of nitrous oxide.

For seawater analyses, water was transferred from a glass syringe to a glass-sparging chamber (volume ~200 ml) of a purge and trap system and analyzed for CFC-11, CFC-12 and SF<sub>6</sub> on board ship. On 5 cruises, CCl<sub>4</sub> was measured, in addition to the aforementioned gases, and nitrous oxide was measured on 3 cruises. The dissolved gases in the seawater sample were extracted by passing a supply of CFC/SF<sub>6</sub> free purge gas

through the sparging chamber for a period of 6 minutes at a flow rate of  $\sim 200 \text{ ml min}^{-1}$ . Water vapor and carbon dioxide were removed from the purge gas during passage through an 18 cm long, 3/8" 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" OD, 0.04" ID stainless steel tube with a 2.5 cm section packed tightly with Porapak Q (60-80 mesh), a 15 cm section packed with Carboxen 1000 and a 2.5 cm section packed with MS5A. A Neslab Cryocool CC-100 was used to cool the trap to  $\sim -70^\circ\text{C}$ . After 6 minutes of purging, the trap was isolated, and it was heated electrically to  $\sim 175^\circ\text{C}$ . The sample gases held in the trap were then injected onto a precolumn ( $\sim 60 \text{ cm}$  of 1/8" O.D. stainless steel tubing packed with 80-100 mesh Porasil B, held at  $90^\circ\text{C}$ ) for the initial separation of CFC-12, CFC-11,  $\text{SF}_6$  and  $\text{CCl}_4$  from later eluting peaks.

After the  $\text{SF}_6$  and CFC-12 (and  $\text{N}_2\text{O}$ ) had passed from the first pre-column and into the second pre-column (7.5 cm of 1/8" O.D. stainless steel tubing packed with MS5A,  $90^\circ\text{C}$ ) the first pre-column was isolated, holding CFC-11 and  $\text{CCl}_4$ . Once CFC-12 and  $\text{SF}_6$  have eluted onto the analytical column #1 (265 cm of 1/8" OD stainless steel tubing packed with MS5A + 60 cm Porasil B held at  $90^\circ\text{C}$ ), the outflow from the second pre-column was diverted to the second analytical column (90 cm 1/8" OD stainless steel tubing packed with Carbograph 1 A-C, 80-100 mesh, held at  $90^\circ\text{C}$ ). After  $\text{N}_2\text{O}$  had quantitatively transferred to the second main column, the second pre-column was backflushed to vent, and the first pre-column was put in line with the second main column. CFC-11 and if desired,  $\text{CCl}_4$  eluted onto the second main column. The gases remaining after  $\text{CCl}_4$  had passed through the first pre-column, were backflushed from the pre-column and vented. All of the columns and pre-columns were held in a Shimadzu 8AIE gas chromatograph, with electron capture detector (ECD). The effluent from the second main column was plumbed to a Shimadzu mini-2 gas chromatograph, with ECD. Due to the erratic oven temperature control, no columns were held in this gas chromatograph, so the flow went directly to the ECD.

The four liter bottles were analysed using a headspace technique. To prepare for headspace analysis, the plug was removed from the bottle and replaced by a similar plug with a Valco valve plumbed to it. Once tightened onto the bottle, a head space was created with clean nitrogen. The bottle was then placed in a temperature controlled box, and rotated for several hours, until the headspace and sample were equilibrated. At this point, the Valco valve on the bottle was plumbed into the analytical system in place of the stripper. The gas in the headspace could then be purged, trapped and run similar to a water sample, except that instead of stripping the gases from the water, the gases in the headspace were purged and swept to the trap.

The analytical system was calibrated frequently using a standard gas of known CFC/ $\text{SF}_6$  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, precolumn, 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. Air samples and system blanks (injections of loops of CFC/ $\text{SF}_6$  free gas) were injected and analyzed in a similar manner. The typical analysis time for seawater, air, standard or blank samples was  $\sim 11$  minutes. Concentrations of the CFC-11, CFC-12 and  $\text{N}_2\text{O}$  in air, seawater samples, and gas

standards are reported relative to the SIO98 calibration scale (Cunnold et al., 2000; Bullister and Tanhua, 2010). Concentrations of SF<sub>6</sub> in air, seawater samples, and gas standards are reported relative to the SIO-2005 calibration scale (Bullister and Tanhua, 2010). Concentrations in air and standard gas are reported in units of mole fraction CFC in dry gas, and are typically in the parts per trillion (ppt) range. Dissolved CFC concentrations are given in units of picomoles per kilogram seawater (pmol kg<sup>-1</sup>) and SF<sub>6</sub> concentrations in fmol kg<sup>-1</sup>. CFC/SF<sub>6</sub> concentrations in air and 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/SF<sub>6</sub> passing through the detector remained relatively constant during the cruise. Full-range calibration curves were run before and after all the samples were run. 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 this residual signal. At a flow rate of 200 cc min<sup>-1</sup> for 6 minutes, the purging efficiency for SF<sub>6</sub> and both CFC gases was > 99%. The efficiency for N<sub>2</sub>O was about 97%.

Based on the analysis of duplicate samples, we estimate precisions (1 standard deviation) of about 1% or 0.002 pmol kg<sup>-1</sup> (whichever is greater) for dissolved CFC-12 and CFC-11 measurements. The estimated precision for SF<sub>6</sub> was 2-3% or 0.02 fmol kg<sup>-1</sup>, (whichever is greater). The precision for N<sub>2</sub>O precision is estimated to be 1% or 0.08 nmol kg<sup>-1</sup> and for CCl<sub>4</sub> to be 2% or 0.002 pmol kg<sup>-1</sup>.

Overall accuracy of the measurements (a function of the absolute accuracy of the calibration gases, volumetric calibrations of the sample gas loops and purge chamber, errors in fits to the calibration curves and other factors) is estimated to be about 2% or 0.004 pmol kg<sup>-1</sup> for CFC-11 and CFC-12 and 4% or 0.04 fmol kg<sup>-1</sup> for SF<sub>6</sub>. The accuracy for N<sub>2</sub>O is estimated to be 2% or 0.16 nmol kg<sup>-1</sup>d. There were analytical problems with the CCl<sub>4</sub> analysis, including possible systematic errors, and no estimate of the absolute accuracy for CCl<sub>4</sub> can be provided.

A small number of water samples had anomalously high CFC and/or SF<sub>6</sub> concentrations relative to adjacent samples. These samples occurred sporadically during the cruise and were not clearly associated with other features in the water column (e.g., anomalous dissolved oxygen, salinity, or temperature features). This suggests that these samples were probably contaminated with CFCs/SF<sub>6</sub> during the sampling or analysis processes.

Measured concentrations for these anomalous samples are included in the data file, but are given a WOCE quality flag value of either 3 (questionable measurement) or 4 (bad measurement). A quality flag of 5 was assigned to samples which were drawn from the rosette but never analyzed due to a variety of reasons (e.g., leaking stopcock, plunger jammed in syringe barrel, etc).

Non-zero CFC concentrations (typically <0.01 pmol kg<sup>-1</sup>) are often measured in deep samples collected on the first few stations on a cruise, even where the deep water is thought to contain negligible levels of CFCs. This initial CFC ‘bottle’ blank” is thought to be due to the release of CFCs absorbed in the the walls and O-rings of the bottles

during storage before the cruise. On one occasion, the PVC bottles were filled with clean nitrogen a few days prior to sailing to reduce the levels of any CFCs absorbed in the bottle walls, but this did not have a significant effect. These initial bottle blanks typically decrease after a few stations. A comparison of the first deep cast at the ALOHA station (typically cast 3 at station 2) and the last deep cast, several days later occasionally suggested that the samples drawn at the latter cast were slightly cleaner.

The glass syringes were filled with clean seawater as soon as possible after arrival in Honolulu before a cruise, allowing them to soak for two to three days prior to the first cast. This seemed to help reduce blank concentrations in early casts, but it did not entirely eliminate the problems encountered with contaminated deep samples. Some samples from the first deep cast were flagged as questionable or bad because the CFC concentrations measured were significantly higher relative to samples taken two days later at the same depth.

#### HOT cruises with NOAA-PMEL Ocean Tracer group measurements

<b>Cruise</b>	<b>Dates</b>	<b>gases analyzed</b>	<b>Gas Standard</b>
HOT166	18-23 Dec 2004	SF <sub>6</sub> , F12, F11*	34603
HOT169	16-20 May 2005	SF <sub>6</sub> , F12, F11	34603
HOT174	6-11 Oct 2005	SF <sub>6</sub> , F12, F11	34603
HOT186	18-24 Oct 2006	SF <sub>6</sub> , F12, F11	PMEL45186
HOT188	8-12 Dec 2006	SF <sub>6</sub> , F12, F11	PMEL45186
HOT202	24-28 Jun 2008	SF <sub>6</sub> , F12, F11	PMEL45174
HOT205	9-13 Oct 2008	SF <sub>6</sub> , F12, F11	PMEL45186
HOT208	19-23 Jan 2009	SF <sub>6</sub> , F12, F11	PMEL45186
HOT212	2-6 Jul 2009	SF <sub>6</sub> , F12, F11, CCl <sub>4</sub>	PMEL45186
HOT216	2-6 Nov 2009	SF <sub>6</sub> , F12, F11	PMELWRS35063
HOT218	15-16 Feb 2010	No data**	
HOT222	7-11 Jun 2010	SF <sub>6</sub> , F12, F11, CCl <sub>4</sub> , N <sub>2</sub> O	PMELWRS35063
HOT225	2-6 Sep 2010	SF <sub>6</sub> , F12, F11, N <sub>2</sub> O	PMELWRS35063
HOT228	8-10 Jan 2011	SF <sub>6</sub> , F12, F11	PMELWRS35063
HOT230	27 Feb-3 Mar 2011	SF <sub>6</sub> , F12, F11, CCl <sub>4</sub>	PMELWRS35063
HOT248	2-6 Dec 2012	SF <sub>6</sub> , F12, F11, N <sub>2</sub> O	PMELWRS35063

\*Samples flown to Seattle for analysis

\*\*Cruise aborted after test cast.

#### References:

Bullister, J.L., and T. Tanhua (2010): Sampling and measurement of chlorofluorocarbons and sulfur hexafluoride in seawater. In The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines. E.M. Hood, C.L. Sabine, and B.M. Sloyan (eds.), IOCCP Report Number 14, ICPO Publication Series Number 134. Available online at <http://www.go-ship.org/HydroMan.html>

Bullister, J.L., and R.F. Weiss, 1988: Determination of CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub> in seawater and air. Deep-Sea Res., v. 25, pp. 839-853.

Bullister, J.L., and D.P. Wisegarver (2008): The shipboard analysis of trace levels of sulfur hexafluoride, chlorofluorocarbon-11 and chlorofluorocarbon-12 in seawater. *Deep-Sea Res. I*, 55, 1063–1074.

Karl, D. M., and R. Lukas (1996), The Hawaii Ocean Time-series (HOT) program: Background, rationale and field implementation, *Deep Sea Res., Part II*, 43, 129–156.

Prinn, R.G., R.F. Weiss, P.J. Fraser, P.G. Simmonds, D.M. Cunnold, F.N. Alyea, S. O'Doherty, P. Salameh, B.R. Miller, J. Huang, R.H.J. Wang, D.E. Hartley, C. Harth, L.P. Steele, G. Sturrock, P.M. Midgley, and A. McCulloch, 2000: A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE. *J. Geophys. Res.*, v. 105, pp. 17,751-17,792.

Vollmer, M. K. and R. F. Weiss (2002), Simultaneous determination of sulfur hexafluoride and three chlorofluorocarbons in water and air. *Mar. Chem.*, 78, 137-148.