2021 A20 Chlorofluorocarbon (CFC), Sulfur Hexafluoride (SF6), and Nitrous Oxide (N2O)\* Measurements

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\* Note that N2O measurements are a Level 3 measurement. The concentrations were measured on the same water samples collected for the Level 1 CFC/SF6 measurements. The N2O analysis is still under development. Please contact the PI for any use of these data.

Samples for the analysis of dissolved CFC-11, CFC-12, SF6, and N2O were collected from approximately 1427 of the Niskin water samples during the expedition. When taken, water samples for tracer analysis were the first samples drawn from the 10-liter bottles. Care was taken to co-ordinate the sampling of the tracers with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. In most cases, dissolved oxygen, dissolved inorganic carbon, and pH samples were collected within several minutes of the initial opening of each bottle. To minimize contact with air, the tracer samples were collected from the Niskin bottle petcock into 250-cc ground glass syringes through plastic 3-way stopcocks. The syringes were stored in the dark in a large ice chest in the laboratory at 3.5° - 6° C until 30-45 minutes before analysis to reduce the degassing and bubble formation in the sample. At that time, they were transferred to a water bath at approximately 35° C to warm the samples prior to analysis in order to increase the stripping efficiency.

Concentrations of CFC-11, CFC-12, SF6, and N2O in air samples, seawater and gas standards were measured by shipboard electron capture gas chromatography (EC-GC). This system from the University of Washington was located in a portable laboratory on the fantail. Samples were introduced into the GC-EC via a purge and trap system. Approximately 200-ml water samples were purged with nitrogen and the compounds of interest were trapped on a Porapak Q/Carboxen 1000/Molecular Sieve 5A trap cooled by an immersion bath to -60oC. During the purging of the sample (6 minutes at 170 ml min-1 flow), the gas stream was stripped of any water vapor via a Nafion trap in line with an ascarite/magnesium perchlorate dessicant tube prior to transfer to the trap. The trap was then isolated and heated by direct resistance to 175oC. The desorbed contents of the trap were back-flushed and transferred onto the analytical pre-columns. The first precolumn was a 40-cm length of 1/8-in tubing packed with 80/100 mesh Porasil B. This precolumn was used to separate the CFC-11 from the other gases. The second pre-column was 13 cm of 1/8-in tubing packed with 80/100 mesh molecular sieve 5A. This pre-column separated the N2O from CFC-12 and SF6. Three analytical columns in three gas chromatographs with electron capture detectors were used in the analysis. CFC-11 was separated from other compounds by a long column consisting of 36 cm of Porasil B and 150 cm of Carbograph 1AC maintained at 80°C. CFC-12 and SF6 were analyzed using a column consisting of 2.33 m of molecular sieve 5A and 1.5 m of Carbograph 1AC maintained at 80°C. The analytical column for N2O was 30 cm of molecular sieve 5A in a 120°C oven. The carrier gas for this column was instrumental grade P-5 gas (95% Ar / 5% CH4) that was directed onto the second precolumn and into the third column for the N2O analyses. The detectors for the CFC-11, and for CFC-12 and SF6 were operated at 300ºC. The detector for N2O was maintained at 320 ºC.

The analytical system was calibrated frequently using a standard gas of known gas 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, precolumns, main chromatographic columns and EC detectors were similar to those used for analyzing water samples. Three 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-free gas) were injected and analyzed in a similar manner. The typical analysis time for samples was 740 sec.

For atmospheric sampling, an ~100 meter length of 3/8-in OD Dekaron tubing was run from the portable laboratory to the bow of the ship. A flow of air was drawn through this line to the main laboratory using an Air Cadet pump. The air was compressed in the pump, with the downstream pressure held at ~1.5 atm. using a back-pressure regulator. A tee allowed a flow (100 ml min-1) of the compressed air to be directed to the gas sample valves of the CFC/SF6/N2O analytical system, while the bulk flow of the air (>7 l min-1) was vented through the back-pressure regulator. Air samples were generally analyzed when the relative wind direction was within 50 degrees of the bow of the ship to reduce the possibility of shipboard contamination. The pump was run for approximately 30 minutes prior to analysis to insure that the air inlet lines and pump were thoroughly flushed. The average atmospheric concentrations determined during the cruise (from a sets of 4 or 5 measurements analyzed when possible) were 222.8 +/- 5.6 parts per trillion (ppt) for CFC-11 (n=27), 497.5 +/- 3.4 ppt for CFC-12 (N=37), 10.6 +/- 0.2 ppt for SF6 (N=19), and 307.1 +/- 12.1 parts per billion for N2O (N=18). Note that a larger aliquot was required for higher precision N2O analysis, and this higher aliquot resulted in SF6 peak areas outside the range of the calibration curve used for seawater samples.

Concentrations of the CFCs in air, seawater samples and gas standards are reported relative to the SIO98 calibration scale (Prinn et. al., 2000). Concentrations in air and standard gas are reported in units of mole fraction in dry gas, and are typically in the parts per trillion (ppt) range for CFCs and SF6 and parts per billion (ppb) for N2O. Dissolved CFC concentrations are given in units of picomoles per kilogram seawater (pmol kg-1), SF6 in femtomoles per kilogram seawater (fmol kg-1), and N2O in nanomoles per kilogram seawater (nmol kg-1). CFC 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 (UW WRS 32399) into the analytical instrument. Full-range calibration curves were run at the beginning and end of the cruise, as well as during long transits/weather delays when possible. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently (at intervals of 2 hours) to monitor short-term changes in detector sensitivity. Estimated limit of detection is 2 fmol kg-1 for CFC-11, 1 fmol kg-1 for CFC-12 and 0.01 fmol kg-1 for SF6.

The efficiency of the purging process was evaluated by re-stripping water samples and comparing the residual concentrations to initial values. These re-strip values were less than 1% for CFC-11 and essentially zero for CFC-12 and SF6. Based on the re-strips of numerous samples where the stripper blank was low and relatively constant, the mean values for N2O were approximately 5-10% during the cruise.

On this expedition, based on the analysis of 35 duplicate samples (i.e two syringe samples collected from the same Niskin), we estimate precisions (1 standard deviation) of 2.2% or 0.0031 pmol kg-1 (whichever is greater) for dissolved CFC-11, 0.58% or 0.0011 pmol kg-1 for CFC-12 measurements, 0.016 fmol kg-1 or 1.9% for SF6 (Stations 24-90), and 1.67% or 0.27 nmol kg-1 for N2O.

Analytical Difficulties

The major issue affecting the data quality was that SF6 was not being fully retained on the trap at the beginning of the cruise at the initial flow rates used for stripping (200 cc min-1). It took some time to diagnose this problem as none of the other compounds were affected. While a new trap was packed, the stripping flow was reduced to 170 cc min-1 resulting in partial retention of SF6 on the analytical trap. Peak areas for an injection of a single large gas sample loop were about 60-80 K counts during this time period. The resulting precision for SF6 was on the order of 10% based upon duplicate samples. The SF6 data are flagged as 3 during this time period, meaning they are of questionable quality. The trap was replaced after Station 23, and the SF6 peak areas for the injection of the large loop increased to 380-400K counts with the precisions reported above. SF6 data from Stations 1-23 should only be interpreted for qualitative trends.

The trap appeared to be cooling/heating unevenly for Stations 23 and 24 which affected the N2O measurements. The temperature of the trap needs to be below -45ºC or N2O can pass through the MS 5A.

Data quality for CFC-11 is affected by a compound which elutes slightly later from the trap into the detector. The chromatographic peaks for the two compounds are often fused. Post-cruise processing should result in higher reported precisions.

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, 105, 17,751-17,792