CFC Data Processing Quality Control Steps

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Measurement techniques and data processing for the Chlorofluorocarbons (CFCs) F-11 (trichlorofluoromethane) and F-12 (dichlorodifluoromethane) dissolved in seawater and in the atmosphere are described in detail by Bullister and Weiss (1987). This paper describes the additional data processing steps required to ensure good data quality.

1. General Data Checks

1.1 Check for Incorrectly Entered Data

- Values outside of valid range.
- Values which do not fall within a smooth trend with time (for example, pressure and temperature readings for gas measurements).
- Invalid syringe identification numbers.

1.2 Missing F-11 or F-12 Peak Areas

Check that runs with missing F-11 or F-12 peak areas (other than blanks and re-strips) actually had zero peak area. This can happen when peak areas are too small for digital integration or when retention times change suddenly and peaks are misidentified.

2. System Blanks, Standards, and Calibration Curves

2.1 Plot System Blank Areas

Plot system blank areas versus time. Look for outliers which are outside of plot's trend and which do not follow a smooth trend. Look for abrupt changes in system blank where linear interpolation of blanks should be broken, such as before switching or baking of carrier gas cleanup traps.

2.2 Plot Sensitivity

Plot sensitivity of a single large loop of standard gas *versus* time. Look for values which plot outside of range or which do not follow a smooth trend. Look for abrupt changes where linear interpolation of sensitivity should be broken, such as after changing carrier gas.

2.3 Plot Calibration Curves

Check for sensitivity values which do not fall on curve due to bad measurement or incorrectly entered data values. Determine best fitting function and note goodness of fit and intercept of sensitivity at zero.

3. Air Data

3.1 Air Measurements Sets

For each set of air measurements (usually three or four good measurements are taken at each location) look for values which differ by more than 1–2% (depending on precision of measurement) from mean of set.

3.2 Plot Air Measurements

Plot air measurements versus time or position and look for possible signs of ships-air contamination. This is normally evident from a lack of reproducible measurements or unusually high values; however, it is sometimes possible to make reproducible measurements even when the air is contaminated. Care should be taken not to eliminate high values which may be due to local sources near land.

4. Bottle Data

4.1 Stripping Blank

Plot calculated stripper blank in moles (or concentrations assuming a constant sample size) *versus* time. Look for values which are outside of range or which do not follow a smooth trend. Look for abrupt changes in stripper blank where linear interpolation of stripper blank should be broken.

4.2 Sample Volume

When applicable, plot difference in sample volume as determined from syringe barrel displacement and from buret reading on stripper versus time. Look for differences greater than 0.5% and attempt to determine which volume is more correct if the problem is not caused by incorrect data entry.

4.3 Stripper Efficiency Correction

Plot fraction CFC remaining in stripper *versus* sample analysis temperature. High CFC-concentration samples are generally stripped a second time for each station when stripper efficiency is less than 100% for either CFC. Fraction of CFC remaining in re-stripped sample is fit as a decaying exponential function of sample analysis temperature.

4.4 Sample Blank Correction

The sample blank includes bottle blank, syringe blank (mostly from nylon valve), and other blanks associated with transferring and storing sample. This blank is best determined from analyses of CFC-free water. Measured concentrations for all bottles which fall within a sigma-theta range where CFC-free water is expected are plotted *versus* time. Sample blank concentrations are fitted with a decaying exponential function of time if blank values are decreasing with time, or the median value is chosen if blank concentrations have reached a steady-state value. For cruises where CFC-free water is available along the entire cruise-track, it is possible to choose a different blank correction appropriate for each set of stations. For cruises (or parts of cruises) with no CFC-free water, the best historical values of sample blanks for similar conditions are used. It is useful to trip all the sample bottles in low or CFC free water to assess bottle blank differences and to look for contaminated bottles.

4.5 Profile Plots

Plot CFC profiles versus depth (or potential density) at each station on a split scale so that features of the surface and low-CFC deep water can be easily seen. For concentrations which appear to be incorrect, check the following:

(a) incorrect station or sample number assignment or other data entry problems.

(b) look at other hydrographic data for bottle to see if any evidence that bottle tripped at wrong depth (or leaked, *etc.*).

(c) look at adjacent stations to see if same anomaly is evident (in which case values may be correct or something systematic may be occurring with a particular bottle).

(d) these quality control steps should be done in "real time" to correct/determine problems as they occur.

4.6 F-11/F-12 Ratio

Check for F-11/F-12 ratios outside of expected ranges for CFC samples with concentrations significantly above blank levels. A ratio outside of an expected range, or which does not fall within a profile should only be used to help identify a possibly bad F-11 or F-12 value. It is possible to have reasonable F-11 and F-12 values with a ratio which appears incorrect. A seemingly incorrect ratio should never be used to discard an F-11 or F-12 value without other evidence.

4.7 Percentage Saturation

Check percentage saturation of near-surface CFC values. Like the CFC ratio, this check will help identify possible bad values or calibration problems. It has been observed that F-11 and F-12 come to equilibrium at different rates, so differences in percentage saturation between the two gases, or supersaturated or undersaturated values do not necessarily indicate a measurement problem. These values should be calculated as soon as possible to help assess data quality at sea.

4.8 Contour Sections

Generate a contour section for each CFC *versus* depth (or potential density), and distance. A method of objective mapping used to generate contour sections by computer is described by Roemmich (1983). This method generates contour sections which may be used to further identify possibly incorrect bottle data values. Contour plots done at sea can be very helpful in determining data quality and are recommended.

4.9 Replicate Measurements

Replicate samples should be run a few times per station. Comparison of these values is valuable in determining system's performance.

5. References

Bullister, J. L., and R. F. Weiss, 1987. Determination of CCl_3F and CCl_2F_2 in seawater and air. *Deep Sea Res.*, **35**(5), 839–853.

Roemmich, D., 1983. Optimal estimation of hydrographic station data and derived fields. *J. Phys. Oceanogr.*, **13**, 1544–1549.