

DISSOLVED CHLOROFLUOROCARBONS AS TRANSIENT TRACERS IN THE CLIVAR REPEAT HYDROGRAPHY PROGRAM

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ABSTRACT

As part of the CLIVAR Repeat Hydrography Program, a number of key hydrographic sections sampled in the 1990s as part of the World Ocean Circulation Experiment (WOCE) are being re-occupied at approximately decadal intervals. Measurements of a suite of physical and chemical properties are being made at full depth, closely spaced (nominally 30 nautical mile) CTD/rosette stations, with water samples collected at between 24 and 36 depths per station.

Key goals of the chlorofluorocarbon (CFC) studies in this program are to document the invasion of these compounds into the ocean interior on decadal timescales. These data can be used to improve our understanding of the rates and pathways of ocean circulation and mixing processes and to improve estimates of the rate of uptake of anthropogenic CO₂ in the ocean.

1. Chlorofluorocarbons as Ocean Tracers

Significant release of the chlorofluorocarbons CFC-11 (CCl₃F) and CFC-12 (CCl₂F₂) into the atmosphere began in the 1940s and atmospheric concentrations of these anthropogenic compounds increased rapidly during the following decades (Fig. 1). Atmospheric CFCs dissolve in surface seawater and are carried into the interior of the ocean where they act as passive tracers of ocean circulation and mixing processes.

There are a number of characteristics which make CFCs especially useful as time-dependent (transient) ocean tracers. These compounds are entirely anthropogenic in origin are essentially un-reactive in seawater. The concentrations of CFCs in the atmosphere as a function of location and time are well characterized and the equilibrium concentrations of these compounds in the global surface ocean can be

modelled simply from the atmospheric concentration histories and the compound's solubility in seawater (a function of temperature and salinity). Extraordinarily sensitive analytical techniques have been developed to measure these compounds in small volume seawater samples at concentrations below 1 x 10⁻¹⁵ moles kg⁻¹.

CFCs have been used as valuable time-dependent tracers in a number of studies to:

- 1) Determine the rates and pathways of ocean circulation and mixing processes.
- 2) Quantify water mass formation rates and document decadal changes therein.
- 3) Quantify biogeochemical cycling rates in the ocean interior.
- 4) Determine rates and patterns of uptake and storage of anthropogenic CO₂ in the oceans.
- 5) Evaluate global ocean model simulations and highlight the models' fidelity to oceanic uptake of anthropogenic compounds.

Measurements of dissolved CFC-11 and CFC-12 concentrations in the water column were made on a large number of hydrographic sections during the past ~25 years and were routinely included on World Ocean Circulation Experiment (WOCE) Hydrographic sections occupied in the 1990s. The WOCE program provided a high resolution global CFC data set with horizontal and vertical resolutions matching those obtained for other geochemical properties such as dissolved inorganic carbon and alkalinity.

Measured inventories of dissolved CFCs have been used in studies to obtain independent estimates of the formation rates of key water masses including Antarctic Bottom Water (AABW), Greenland Sea

Deep Water (GSDW), Labrador Sea Deep Water (LSW), and North Atlantic Deep Water (NADW). Data from repeat surveys have allowed estimates to be made of changes in the rate of formation of GSDW and LSW [1] on decadal timescales.

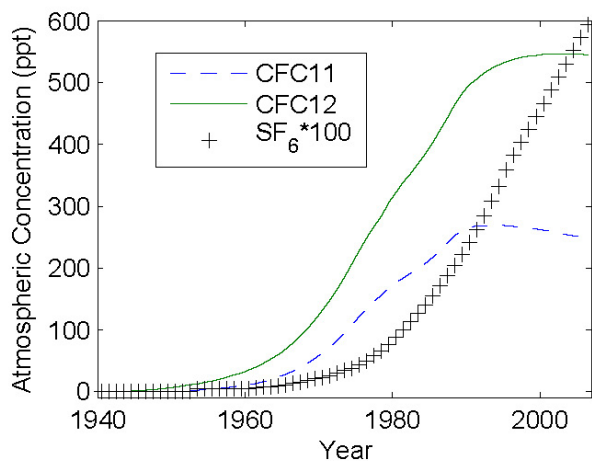


Figure 1. Concentrations, in parts per trillion (ppt), of CFC-11, CFC-12 and SF₆ in the atmosphere as a function of time. SF₆ concentrations have been multiplied by 100.

CFCs have been especially useful in helping to improve estimates of anthropogenic CO₂ uptake in the ocean. For the period from the 1960s to the mid-1990s, when the increases in CFC-12 and CO₂ in the atmosphere were quasi-linear, simple concentration-derived CFC ages have been utilized to estimate the uptake of anthropogenic CO₂ in the ocean over this time interval [2]. CFC-derived water mass ages were an essential component in the ΔC* method to estimate global anthropogenic CO₂ uptake from the WOCE dataset [3].

CFC concentration derived ages can be significantly biased due to the non-linearity of the atmospheric growth rates and mixing in the ocean interior. Recently, transit time distributions (TTDs) derived using CFCs [4] have been used in studies to better characterize the mixing-induced range in ages of the constituents comprising a watermass and have been used to improve estimates of anthropogenic CO₂ uptake and rates of geochemical processes in the ocean.

As part of the CLIVAR Repeat Hydrography Program, a number of hydrographic sections sampled in the 1990s as part of WOCE are being re-occupied [5]. The goal of this program is to repeat key full-depth hydrographic sections in the global ocean at intervals

of ~10 years in order to detect decadal-scale changes in ocean circulation, chemistry, physics and biology. Measurements of a suite of physical and chemical properties are being made at full depth, closely spaced (nominally 30 nautical mile) CTD/rosette stations, with water samples collected at between 24 and 36 depths per station. Significant differences in CFC concentrations (and CFC-derived water mass ages) have been observed during CLIVAR reoccupations of WOCE sections. The repeat CFC sections are being used to track the temporal evolution of these tracers in the ocean interior, which can be used to assess decadal changes in ventilation rates, anthropogenic CO₂ uptake and upper ocean oxygen cycling.

An example of a meridional CLIVAR CFC section made in the Atlantic Ocean is shown in Fig 2. This figure highlights the major ventilation pathways occurring on decadal time scales in this region of the Atlantic. CFCs are highest in surface waters, and there is a strong signal in the mode and immediate waters, reflecting vigorous ventilation of these waters on decadal timescales. There is a clear CFC signal in the abyssal waters reflecting ventilation via NADW from the north and AABW from the south. CFCs are detectable throughout much of the water column along this section. The extremely sensitive analytical techniques for measuring dissolved CFCs allows the ventilation pathways to be detected in regions where the corresponding anthropogenic CO₂ signal is difficult to detect directly.

The rates of growth of CFC-11 and CFC-12 in the atmosphere slowed in the 1990's and have now become negative. Although this makes age information derived directly from CFC concentrations in the upper ocean more difficult to interpret, these compounds will continue to be extremely valuable time-dependent tracers as they continue to propagate into the mid-depth and abyssal waters of the global ocean on decadal to century timescales. In contrast to the CFCs, sulfur hexafluoride (SF₆) levels in the atmosphere have continued to increase rapidly (Fig 1), making this anthropogenic compound an especially valuable new transient tracer of recently ventilated waters. Simultaneous measurements of dissolved SF₆ along with CFCs can provide additional information over the use of each tracer alone. For example, measurements of SF₆ along with CFC-12 can be used to constrain transit time distributions in the ocean interior and to help distinguish CFC (and other tracer) age changes caused by mixing from real changes in decadal-scale ventilation processes. The multiple tracer technique can also be used to correct mixing biases' effects on anthropogenic CO₂ estimates that rely on CFC ages.

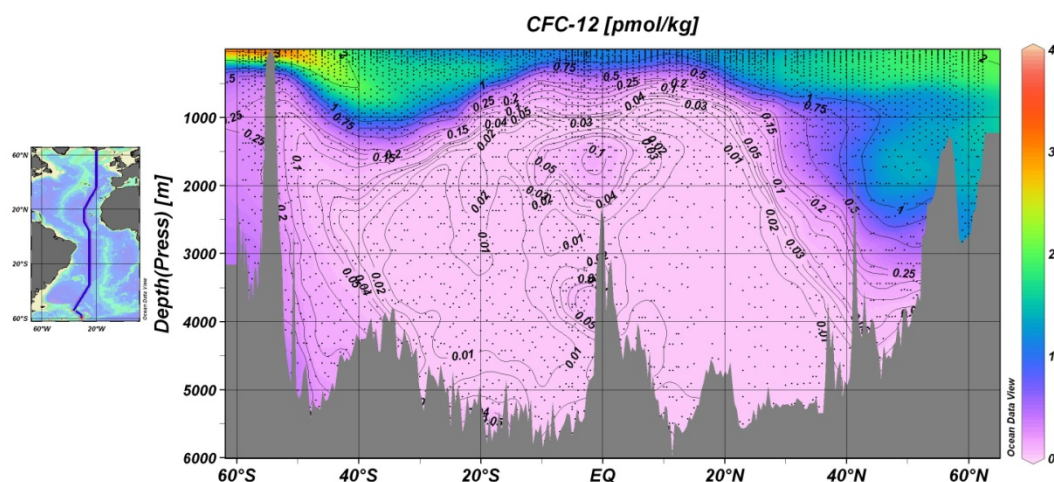


Figure 2. Concentration of dissolved CFC-12 in picomoles (10^{-12} moles) per kilogram seawater along the CLIVAR A16 section. Black dots indicate locations where samples were collected.

The addition of SF_6 to sampling programs also affords an unambiguous age tracer in the upper 400m of the water column during this and coming decades. Recent improvements in analytical techniques [6] have allowed SF_6 measurements to be made on several CLIVAR repeat sections and it is anticipated that these measurements will be included routinely in the future as part of the CLIVAR Repeat Hydrography Program.

Recent studies using CLIVAR repeat hydrography data have revealed wide-spread changes in the temperature and salinity of abyssal waters during the past several decades. In many cases these changes are strongly correlated with regions of significant CFC invasion along the sections [7]. CFCs may thus provide sensitive indicators of regions of the deep ocean where surface-derived climate change signals propagate into the ocean interior on decadal time scales.

2. REFERENCES

1. Kieke, D. & Co-Authors (2007). Changes in the pool of Labrador Sea Water in the subpolar North Atlantic. *Geophys. Res. Lett.* **34**, L06605, doi: 10.1029/2006GL028959.
2. McNeil, B. & Co-Authors (2003): Anthropogenic CO_2 uptake by the ocean based on the global chlorofluorocarbon data set. *Science* **299**(5604), 235–239.
3. Sabine, C.L. & Co-Authors (2004). The oceanic sink for anthropogenic CO_2 . *Science* **305**(5682), 367–371.
4. Waugh, D.W., Hall, T.M. & Haine, T.W.N. (2003). Relationship among tracer ages. *J. Geophys. Res. - Oceans* **108**(5), 10.1029/2002JC001325.
5. Hood, M. & Co-Authors (2010). "Ship-based Repeat Hydrography: A Strategy for a Sustained Global Program." in these proceedings (Vol. 2).
6. 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 Res. I* **55**, 1063–1074.
7. Johnson, G.C., Purkey, S.G. & Bullister, J.L. (2008). Warming and freshening in the abyssal southeastern Indian Ocean. *J. Climate* **21**, doi: 10.1175/2008JCLI2384.1, 5351–5363.