

# Observations of CFCs and SF<sub>6</sub> as Ocean Tracers

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## Keywords

chlorofluorocarbons, sulfur hexafluoride, ocean circulation, ocean tracers, ocean biogeochemistry

## Abstract

An advantage of using chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF<sub>6</sub>) as tracers of ocean circulation is that the time-dependent source functions permit calculation of rates for ocean processes. These compounds are also sensitive indicators highlighting interior ocean regions where surface-derived anomalies can be transported on timescales of decades. Significant applications for CFCs have been for the deep limb of the Atlantic meridional overturning circulation, upper ocean ventilation, and biogeochemical rates, including apparent oxygen utilization rates and anthropogenic CO<sub>2</sub> inventories. Although CFCs have started to decrease in the atmosphere, SF<sub>6</sub> continues to increase. There are benefits to measuring both CFCs and SF<sub>6</sub>: A large global CFC data set exists; CFCs are still increasing in older waters; SF<sub>6</sub> expands estimates of age; and calculations of anthropogenic CO<sub>2</sub> inventory are enhanced. Thus, the outlook for using CFCs as tracers for oceanic processes, and in particular in concert with SF<sub>6</sub>, remains very positive.

## INTRODUCTION

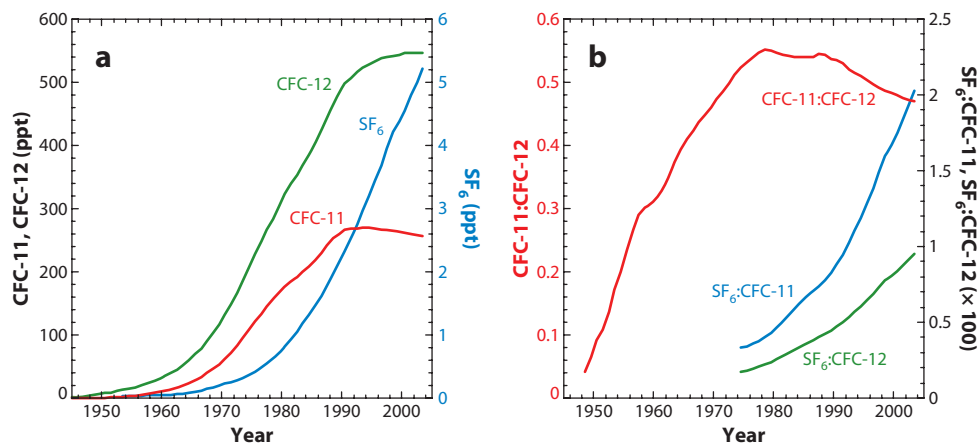
Advantages to using tracers such as the chlorofluorocarbons (CFCs) and sulfur hexafluoride ( $\text{SF}_6$ ) for ocean processes are that they give the added dimension of time, their time histories are fairly well known, they are an integrating quantity, and they provide an independent test for models. Timescale information can be used to estimate rates for physically and biogeochemically important processes. Examples include the Atlantic meridional overturning rate and apparent oxygen utilization rates, as well as the calculation of anthropogenic  $\text{CO}_2$  inventories, and the rate at which  $\text{CO}_2$  is moved into the interior oceans, which can limit the oceanic uptake of  $\text{CO}_2$  (Sarmiento et al. 1982).

The CFCs are gases that are synthetic halogenated methanes. The chemical structures of the major CFCs and those used for ocean sciences are  $\text{CCl}_3\text{F}$  for CFC-11,  $\text{CCl}_2\text{F}_2$  for CFC-12, and  $\text{CCl}_2\text{FCClF}_2$  for CFC-113. In the 1930s and after, CFCs were introduced as industrial coolants in refrigerators, aerosol spray propellants, foaming agents, cleaning agents, etc.  $\text{SF}_6$  is also a synthetic compound; it has been used in the electrical industry since the 1960s.

Lovelock (1971) published the first measurements of CFC-11 and  $\text{SF}_6$  in the troposphere. Molina & Rowland (1974) cautioned that chlorine from the CFCs could destroy the beneficial stratospheric ozone layer. It was later recognized that CFCs are greenhouse gases (Ramanathan 1988), and  $\text{SF}_6$  is a potent greenhouse gas. The Montreal Protocol on Substances that Deplete the Ozone Layer was signed in 1987 by 196 nation-states. Its purpose was to phase out the use of halogenated hydrocarbons, including the CFCs. The Montreal Protocol has been effective in slowing rates of increase of the atmospheric content of CFCs (**Figure 1**). However, because CFCs have long lifetimes, they will remain in the atmosphere in decreasing quantities throughout this century.

## ANALYTICAL BACKGROUND

To apply CFCs and  $\text{SF}_6$  to processes of ocean circulation and biogeochemistry, it is necessary to know their atmospheric time histories, be able to make precise and contamination-free shipboard



**Figure 1**

Northern Hemisphere atmospheric time histories of CFC-11, CFC-12, and  $\text{SF}_6$  in ppt (*a*) and as ratios (*b*). Data taken from Walker et al. 2000, Geller et al. 1997, Maiss & Brenninkmeijer 1998, <http://bluemoon.ucsd.edu/pub/cfchist/> (ALE/GAUGE/AGAGE network), and [http://cdiac.ornl.gov/oceans/new\\_atmCFC.html](http://cdiac.ornl.gov/oceans/new_atmCFC.html).

measurements, know their solubilities, determine if they are stable compounds in the ocean, and estimate their surface saturations. Natural sources of CFCs (Jordan et al. 2000) and SF<sub>6</sub> (Harnisch & Eisenhauer 1998) in the oceans are usually insignificant. In 1995, Plahn et al. (1999) observed unusual CFC-12 concentrations, 8- to 40-fold higher than normal, in Persian Gulf water outflow, which they attributed to materials used during and after the Gulf War.

## Atmospheric Time Histories

The CFCs and SF<sub>6</sub> have long residence times and are well mixed in the atmosphere. As a consequence, there is only a small difference between mixing ratios in the Northern and Southern hemispheres. The atmospheric mixing ratio of CFC-12 is approximately twice that of CFC-11, and CFC-11 is approximately twice that of CFC-113. The atmospheric mixing ratios of the CFCs increased exponentially through the 1970s and increased linearly after that. Once the Montreal Protocol was in effect, the growth of all the CFCs slowed markedly. Furthermore, CFC-11 and CFC-12 reached a maximum in approximately 1990 and 2000, respectively, CFC-113 reached a maximum in the early 1990s. SF<sub>6</sub> continues to increase, though its content is approximately 100 times lower than CFC-12 in the atmosphere.

Atmospheric time histories of the CFCs were reconstructed by Prinn et al. (2000) and Walker et al. (2000). Prior to 1979, such reconstructions depend on knowing the atmospheric lifetimes of the compounds, were constructed using production and release data from the Chemical Manufacturers Association, and have uncertainties of a few percent. Since 1979, atmospheric data have come from direct measurements from sampling stations set up around the world. The direct measurements are also checked against the production and release data, and they have uncertainties of 1–2%. Similarly, atmospheric time histories of SF<sub>6</sub> were reconstructed by Maiss & Brenninkmeijer (1998) using production estimates dating back to 1953, and direct measurements since that date. The present Advanced Global Atmospheric Gases Experiment network of direct measurements shows five stations located worldwide where atmospheric compounds, including the CFCs and SF<sub>6</sub>, are measured. Monthly averages are provided for each station, and data can be obtained from <http://agage.eas.gatech.edu/data.htm>.

## Shipboard Measurements

In addition to entering the atmosphere, the CFCs and SF<sub>6</sub> have been entering the oceans for the past few decades. The three CFC compounds have been measured in the ocean, with CFC-11 and CFC-12 being the most commonly measured. Concentrations of the CFCs and SF<sub>6</sub> in seawater are quite low: CFC concentrations are at most 10<sup>-12</sup> mol l<sup>-1</sup>, and SF<sub>6</sub> 10<sup>-15</sup> mol l<sup>-1</sup>. In addition, the solubility of SF<sub>6</sub> is approximately 100 times lower than that of CFC-12. Thus, measurements of CFCs, and particularly of SF<sub>6</sub>, in the oceans are difficult due to their low concentrations, and the possibility of contamination by the compounds in the atmosphere.

The pioneers of demonstrating the potential for measuring CFC-11 and/or CFC-12 in seawater on board ship were Hammer et al. (1978) and Hahne et al. (1978). These were followed by measurements of vertical distributions in the northeast Pacific, published by Gammon et al. (1981). Their technique was modified by Bullister & Weiss (1988) who significantly improved accuracy and precision, and theirs is basically the technique being used today. Wisegarver & Gammon (1988) published the first seawater analysis of CFC-113. For the CFCs, samples are collected using 100-cc glass syringes, injected into an extraction system and are then analyzed using a gas chromatograph. Calibration is done by measuring known quantities of gas standards for the CFCs.

Concentrations in seawater are reported relative to a scale set up by the group at Scripps Institution of Oceanography.

Pioneering measurements of SF<sub>6</sub> in the oceans were made by Watson & Liddicoat (1985). Since then, SF<sub>6</sub> has been used for some time in air-sea gas exchange experiments (Wanninkhof et al. 1985) and as a deliberate tracer for studying ocean mixing processes (e.g., Ledwell et al. 1986, 1993, 2000). However, a few years ago, the use of SF<sub>6</sub> as a deliberate tracer was discontinued and another compound, SF<sub>5</sub>CF<sub>3</sub>, is now being used (Ho et al. 2008). Because it is no longer used as a deliberate tracer, this allows the use of SF<sub>6</sub> as a global transient tracer in the oceans with the CFCs.

Using measurements from 1994, Law & Watson (2001) were the first to use SF<sub>6</sub> as a transient tracer in the ocean, and they used ratios of SF<sub>6</sub>/CFCs to estimate ventilation ages. Tanhua et al. (2004) used measurements from 1998 in the Southern Ocean to firmly establish the value of SF<sub>6</sub> as a transient tracer. In 2005, Bullister et al. (2006) made measurements of SF<sub>6</sub> and CFCs from the same seawater sample at the Hawaii Ocean Time Series site. Bullister & Wisegarver (2008) developed an analytical system for fast and simultaneous measurement of SF<sub>6</sub> with CFC-11 and CFC-12 (**Figure 2**). The technique allows SF<sub>6</sub> to be measured on the same small-volume seawater samples as were CFC-11 and CFC-12, and there is improved sensitivity for dissolved CFC-11 and CFC-12 relative to earlier systems. It is estimated that the current analytical sensitivity of SF<sub>6</sub> measurements will provide temporal information for water mass ventilation dating back 25 years.

Present analytical uncertainty for CFC-11, CFC-12, and SF<sub>6</sub> is usually less than 3%. When using tracer data, there will be errors related to spatial (Robbins 1997) and temporal resolution. Recent work shows that in regions of high eddy activity, a discrete tracer measurement may be biased by eddy variability (Peacock et al. 2005, Waugh & Abraham 2008; see below).

## Solubilities

Solubility measurements have been made in the laboratory: CFC-11 and CFC-12 by Warner & Weiss (1985), CFC-113 by Bu & Warner (1995), and SF<sub>6</sub> by Wanninkhof et al. (1991) and Bullister et al. (2002). These authors have expressed the solubility, *F*, as a function of temperature, *T*, and salinity, *S*, at a total pressure of 1 atm:

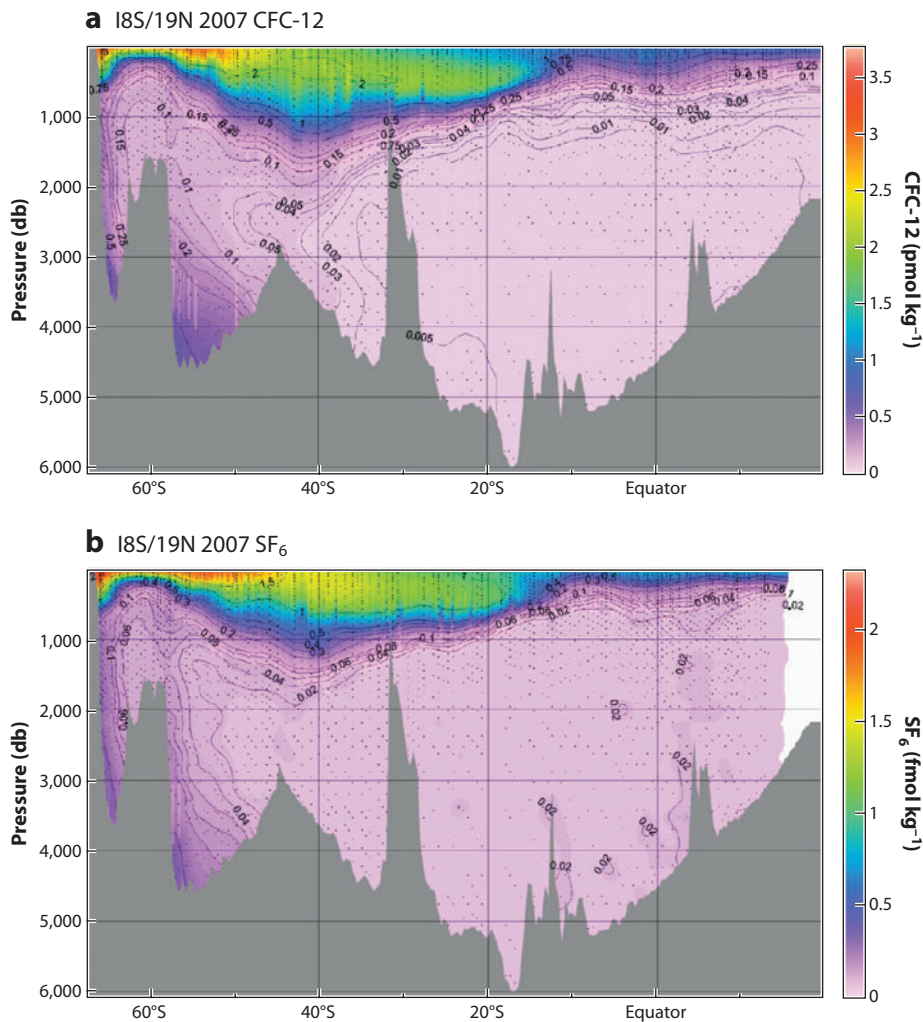
$$\ln F = a_1 + a_2(100/T) + a_3 \ln(T/100) + a_4(T/100)^2 + S[b_1 + b_2(T/100) + b_3(T/100)^2]$$

Accuracy of the laboratory measurements is approximately 1.5–2.0%, and precision is 0.7%. Over the range of oceanic conditions, the effect of temperature on solubility is much larger than that of salinity. Solubilities of the CFCs increase with decreasing temperature at approximately 1% per degree Celsius.

Although the atmospheric mixing ratio of CFC-12 is approximately twice that of CFC-11, CFC-11 is more soluble in seawater. As a consequence, the concentrations of CFC-11 in seawater are approximately twice those of CFC-12. Concentrations of CFC-113 are considerably lower than either CFC-11 or CFC-12. Concentrations of SF<sub>6</sub> are orders of magnitude lower than CFC-12.

## Stability of CFCs and SF<sub>6</sub> in the Open Ocean

In the oxygenated open ocean, the compounds CFC-11, CFC-12, and SF<sub>6</sub> are stable. CFC-11 and CFC-12 have been shown to be unstable in anoxic marine waters (Bullister & Lee 1995, Shapiro et al. 1997). At temperatures lower than 19°C, CFC-113 appears to be stable. However, at higher temperatures, CFC-113 is unstable, based on comparisons with profiles of CFC-11 and CFC-12.



**Figure 2**

(a) Section of dissolved CFC-12 along 90°E (the I8 S/I9N hydrographic sections) in the South Indian Ocean collected February–April 2007. (b) Dissolved SF<sub>6</sub> along the same section shown in (a). Black dots indicate sampling stations. Figure adapted from Bullister & Wisegarver (2008).

For this reason, the compound will not be discussed further. Based on laboratory experiments, SF<sub>6</sub> does not adsorb onto particles and it is inert in seawater (Ledwell & Watson 1991).

### Saturations at the Ocean Surface

Entry of CFCs and SF<sub>6</sub> into the oceans is similar to the air-sea exchange of other gases (e.g., Wanninkhof et al. 2009). There is a correlation between gas exchange rate and wind speed. The direction of the flux is controlled by the difference in concentration between the air and ocean. Because the atmospheric mixing ratios of these compounds greatly exceed concentrations in the oceans, the flux is into the oceans, and predominantly into regions with cold sea surface temperatures in the high latitudes.

The concentrations of CFCs and SF<sub>6</sub> dissolved in the surface layer of the ocean are dependent upon solubilities, atmospheric concentrations, and other physical factors affecting the gas saturations, including seasonality, upwelling, entrainment due to mixing, ice cover, etc. (e.g., Haine & Richards 1995). It takes days up to a few weeks after a change in temperature or salinity for oceanic surface mixed layers to come to equilibrium with the present atmosphere, and equilibration time increases with depth of the surface mixed layer. Although the surface waters of the world's oceans are close to equilibrium with the present day atmospheric concentration of CFCs, there are exceptions. During times of rapid warming, as in spring, the surface waters will be a few percent supersaturated with the gas (Warner 1988). Similarly, at times of rapid cooling, the surface waters will be a few percent undersaturated with the gas. There are also undersaturations within a few degrees of the equator due to upwelling of less saturated waters. At the outcrops for thermocline waters, nonequilibration with the atmosphere is considerably less of a problem than for high-latitude water masses with deep winter mixed layers (e.g., Doney & Jenkins 1988, Wallace & Lazier 1988, Schlosser et al. 1991, Rhein 1991, Trumbore et al. 1991, Warner et al. 1996). Warner (1988) and Fine et al. (2001) have found that at their outcrops, waters that subduct into the thermocline are usually within a few percent of equilibration with the present atmosphere. Their analyses even include some late winter cruises.

A limitation in assessing the state of equilibration is the lack of late winter surface ocean tracer data. In high latitudes where there are deep convective mixed layers, there are likely to be undersaturations. Undersaturations of as much as 60% were observed in the Labrador Sea in winter (Wallace & Lazier 1988; Rhein et al. 2002). In austral Winter 2005 in the southeast Pacific formation region of Antarctic intermediate water (AAIW), Hartin et al. (2010) also observed on average 60% undersaturations. While poleward of the Subantarctic front (SAF) and within the core of AAIW, CFC-12 is 85% saturated relative to the present atmosphere. Once AAIW subducts under the SAF, average CFC-12 saturations decrease dramatically to less than 60%, due to mixing along the front with older CFC-depleted waters. At the Subantarctic mode water formation region, Hartin et al. (2010) observed CFC-12 saturations to be surprisingly high, on average at 94% with respect to the 2005 atmosphere. Undersaturations in the high-latitude water mass source regions need to be taken into account when using CFCs for oceanic processes, in particular, for partial pressure CFC ages and for estimates of formation rates (see below).

In a recent study of the Antarctic shelf waters using a regional general circulation model (GCM), Rodehacke et al. (2010) found an increase in CFC surface saturations of 0.1–0.9% per year. The increase is caused by the once increasing atmospheric source, ice suppression of air-sea gas exchange, and mixing with water of different compositions. These increasing saturations introduce a systematic error of at most 10% into estimating CFC inventory for the year 2000, if the temporal evolution of surface saturation is not considered; whereas, they point out that in ice-free regions the air-sea flux of gas mostly depends on the sea surface temperature.

## TRACER AGES

One of the main advantages of using CFCs and SF<sub>6</sub> as tracers of ocean circulation is that the time-dependent source function permits calculation of rates for ocean processes. A tracer-derived age is the elapsed time since a subsurface water mass was last in contact with the atmosphere. Several estimates of age can be calculated, from the partial pressure of an individual compound, from the ratio of the partial pressure of CFCs to each other or SF<sub>6</sub>, and from transit time distributions (TTDs).



## Partial Pressure and Ratio Ages

The pCFC (Fine et al. 1988, Doney & Bullister 1992) or pSF<sub>6</sub> age is defined as the measured seawater concentration (C) divided by the solubility function (see above):

$$\text{pCFC} = C/F(T, S)$$

The partial pressure is adjusted for what the percent equilibration with the atmosphere is thought to be at the water mass source region. The computed partial pressure is then compared to the atmospheric history (**Figure 1**) to determine a corresponding date, which is subtracted from the date the seawater sample was collected. The difference in dates gives an average age for the water parcel.

The age can also be calculated using the ratio of two CFC partial pressures (e.g., Weiss et al. 1985) or the ratio of the SF<sub>6</sub> partial pressure to a CFC partial pressure. In this case, no assumptions are needed about percent equilibrium at the time of water mass formation. Since the ratio of atmospheric CFC-11/CFC-12 has remained unchanged since the mid-1970s and is now decreasing, this somewhat restricts the application of the age calculated from the ratio of CFC-11 and CFC-12 partial pressures to waters dating back before 1975 (**Figure 1**). However, for waters formed in the past three decades, the ratio of SF<sub>6</sub> partial pressure to a CFC partial pressure will give a distinct age (**Figure 1**). Partial pressure ratios give the ages of the tracer-bearing components.

**Caveats for using partial pressure and ratio ages.** Errors in tracer ages arising from seawater concentrations, atmospheric source functions, and solubilities are discussed above. The main source of errors in partial pressure and ratio ages is introduced when there is mixing of more than one water mass component. Because of nonlinearities in the source functions and solubilities, neither age mixes linearly in multicomponent systems over the entire concentration range observed in the ocean (e.g., Doney et al. 1997, Pickart et al. 1989, Rhein 1994).

A variety of approaches has been applied to estimate the effects of mixing on CFC ages (e.g., Rhein 1994, Beining & Roether 1996, Doney et al. 1997, Karstensen & Tomczak 1998, Sonnerup 2001, Mecking et al. 2004). The approach of Rhein (1994), looking at the DWBC, is discussed below. Beining & Roether (1996) estimated that in regions of extensive mixing, pCFC ages increase at a rate of approximately 5–10% per decade.

Partial pressure and ratio ages are appropriate for putting timescales on some processes. For thermocline ventilation, where equilibrated water is subducted and mixed isopycnally along extensively outcropping density surfaces, water subducted within a given year mixes with water subducted in previous years. In this situation, a water mass is a mixture of water parcels that have left the surface over a multiyear period. The average age of this water mass can be represented by the pCFC age (Doney et al. 1997). Furthermore, over a couple of decades, CFC-11 and CFC-12 can be approximated as being linear between the late 1960s and 1990, and SF<sub>6</sub> as being linear between 1980 and the present. Over these periods, pCFC ages of less than 20 years are in excellent agreement with model-generated ideal ages (Sonnerup et al. 1999), and these usually apply to upper ocean waters.

However, the atmospheric source functions have been nonlinear for much of the input history (**Figure 1**). Mecking et al. (2004) found that depending on the curvature of the atmospheric time histories, nonlinearities can cause pCFC ages to be younger or older than the true average age of water mass end-members. As an example, in the thermocline, CFC-11 ages are biased younger than CFC-12 ages because the relative rate of increase in the atmosphere of CFC-11 was higher (Sonnerup 2001; see also discussion below and Sonnerup et al. 2008). Furthermore, Sonnerup (2001) finds CFC ratio ages are younger than model-generated ideal and partial pressure ages.

In regions where surface waters are converted to deep and bottom waters, which then spread into a background of near-blank level tracer water, a tracer ratio is conserved. The corresponding ratio age represents that of the youngest component of the mixture. However, when there is mixing into a background of elevated concentrations, mixing biases can occur due to nonlinearities in the atmospheric CFC-11/CFC-12 ratio history. As for the pCFC ages, the CFC-11/CFC-12 ratio of the mixture can be biased toward the end-member with the higher or lower CFC concentration, depending on the atmospheric curvature of the ratio (Mecking et al. 2004).

In most high-latitude intermediate and deep-water source regions, the age clock is not reset to zero, due to entrainment of older water during convective formation. Thus, water masses will start out with an age of at least a few years (rather than zero); that is, water masses are not completely renewed during formation. This age in the formation region has been called a relic age. It can be estimated from observations of the tracers at the water mass formation regions, as was done by Fine et al. (2002) for North Atlantic deep water (NADW) (**Figure 3**). The relic age can then be subtracted from the downstream tracer ages to calculate an effective spreading rate from water mass formation regions.

### Transit Time Distributions

There are many areas of the ocean where mixing can lead to substantial biases in partial pressure and ratio ages. In these areas, the history of parcels in a water mass can be described statistically in terms of an age distribution: Kida (1983) applied the concept to the stratosphere, and Beining & Roether (1996) to the ocean. The TTD method employs a rigorous mathematical framework to characterize transport in fluids due to large-scale advection and diffusion (e.g., Hall & Plumb 1994, Holzer & Hall 2000, Khatiwala et al. 2001, Haine & Hall 2002, Waugh et al. 2004, Peacock & Maltrud 2006). Applying TTDs assumes that a water mass consists of many different ages or transit times. The method allows identification of regions where the age can be well defined as an elapsed time, and it gives information on the mixing history of the water masses. At an interior ocean location, a TTD is assumed to be an inverse Gaussian function, with the mean age ( $\Gamma$ ) equal to the width of the TTD ( $D$ ). Waugh et al. (2004) showed that TTDs with  $\Gamma = D$  are consistent with simultaneous observations of several different transient tracers (e.g., CFC-11, CFC-12 or  $\text{SF}_6$ ). Steinfeldt et al. (2009) employ a variable ratio of  $D/\Gamma$  in using TTDs to estimate anthropogenic carbon in the North Atlantic. Using multiple tracers with different source functions and time histories enhances TTD analysis (e.g., Waugh et al. 2002).

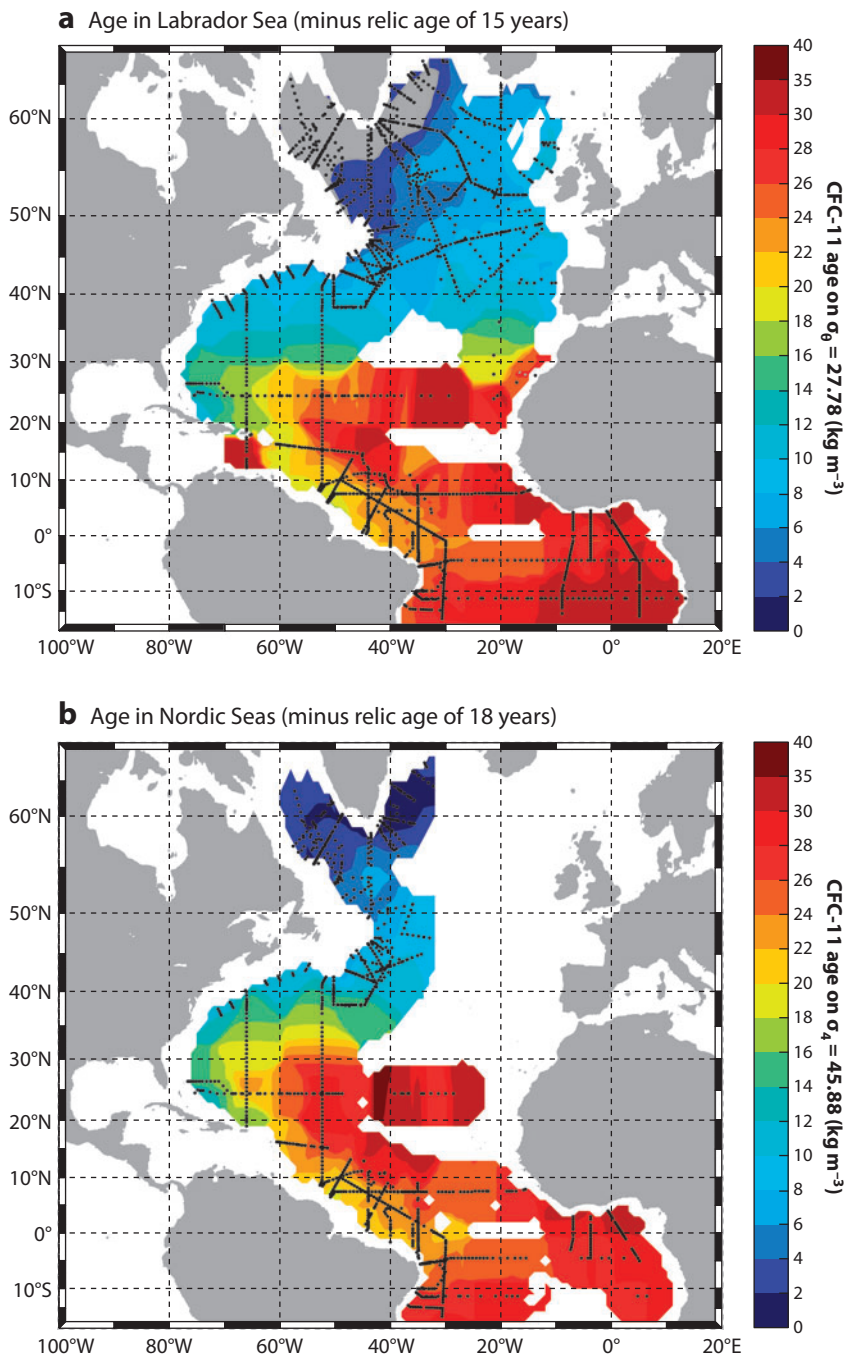
## CHLOROFLUOROCARBONS FOR OCEAN SCIENCE

There are several reasons that CFCs are still useful for oceanographic applications, even though industrial uses of the CFCs have been phased out and their content in the atmosphere is decreasing. First, there is a rich history of three decades of global ocean observations of CFCs to compare with new observations. Second, in some parts of the oceans, CFCs are still increasing. Third, CFCs are being routinely measured in concert with  $\text{SF}_6$ , and the ratios give additional timescale information.

### Global Distribution of Chlorofluorocarbons

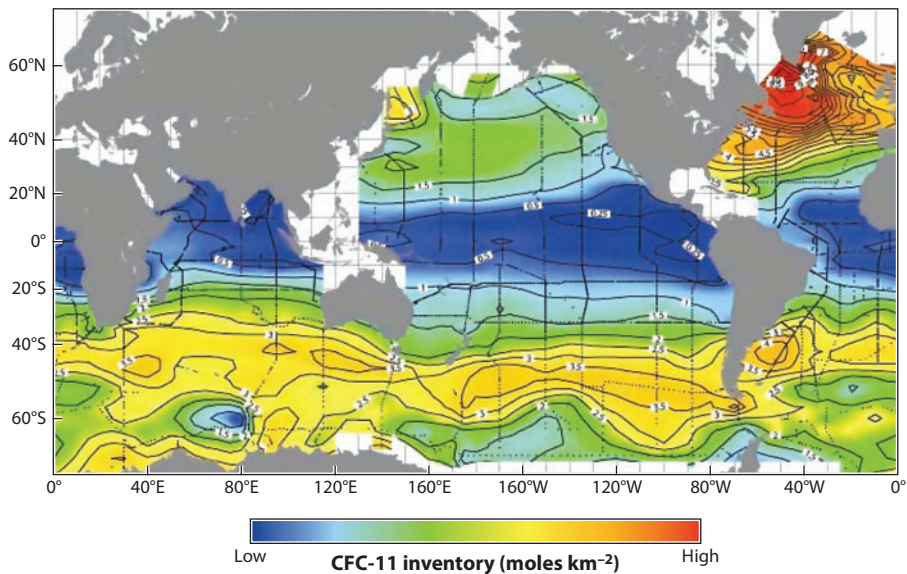
Measurement of CFC-11 and CFC-12 became routine as part of the large programs Transient Tracers in the Oceans (1980s), World Ocean Circulation Experiment (WOCE; 1990s), and Climate Variability (CLIVAR) and  $\text{CO}_2$  Repeat Hydrography (2000s). In addition, these





**Figure 3**

Maps of effective pCFC-11 ages with relic ages subtracted for (a) Upper Labrador Sea Water on  $\sigma_\theta = 27.78 \text{ kg m}^{-3}$  and (b) Overflow Water on  $\sigma_4 = 45.88 \text{ kg m}^{-3}$ , except north of  $55^\circ\text{N}$  and west of  $30^\circ\text{W}$ , where the bottom value is used if  $\sigma_\theta$  is greater than  $27.88$ . Data used were collected during the 1990s. Black dots indicate station locations. Unit of contour is 2 years. Figure adapted from Fine et al. (2002).



**Figure 4**

Map of vertically integrated CFC-11 in  $\text{mol km}^{-2}$ . Highest values are in red, lowest in blue. The + symbol shows station locations. Figure adapted from Willey et al. (2004).

measurements have been used over the past few decades in process studies (e.g., Smethie et al. 1988; Schlosser et al. 1991; Fine et al. 1988, 1994; Gordon & Fine 1996; Rhein et al. 2010; Hartin et al. 2010).

A small amount,  $5.5 \pm 1.2 \times 10^8$  mol, or 1% of atmospheric CFC-11, was taken up by the oceans by the mid-1990s (Willey et al. 2004). The map of total water column inventory of CFC-11 in the oceans (**Figure 4**) is based on data collected primarily in the 1990s as part of WOCE. The highest inventories are observed in and downstream from the locations of NADW formation. However, more than 60% of the inventory is in the Southern Hemisphere. The second-highest inventories are observed in a ring around the Southern Hemisphere equatorward of the Antarctic Circumpolar Current. This is where thick volumes of mode and intermediate waters are formed. These waters ventilate and carry heat, freshwater, and  $\text{CO}_2$  into the Southern Hemisphere subtropical gyres (Fine 1993, Fine et al. 2001). Note there is a similarity between the map of CFC-11 inventory and that of anthropogenic  $\text{CO}_2$  inventory, in part due to the use of CFCs in the calculation of anthropogenic  $\text{CO}_2$  (Sabine et al. 2004). About 82% of the CFCs in the ocean reside in the upper ocean above 1,000 m, and another 10% resides between 1,000–2,000 m. This 92% of the inventory includes cold, high-latitude waters near the source regions.

### Atlantic Meridional Overturning Circulation: Deep Limb

A significant application for the CFCs has been their use for the deep limb of the Atlantic meridional overturning circulation (AMOC). The CFCs describe pathways from the NADW source regions, effective spreading rates, and rates of formation of NADW components—including variability in these rates.

Measurements of the transient tracer tritium showed the fast response of the Deep Western Boundary Current (DWBC) in transporting NADW from its source regions into the subtropics

(Jenkins & Rhines 1980). As part of the Transient Tracers in the Oceans program more than a decade later, a plume of elevated CFCs at 1,500 m first revealed the branching of the DWBC along the equator (Weiss et al. 1985), with a timescale of approximately 23 years from the Labrador Sea. At the equator, Upper NADW had undergone a fivefold dilution by mixing with CFC-free waters. Subsequent occupations across the DWBC in the subtropical and tropical North Atlantic showed the DWBC to be present into the tropics (Fine & Molinari 1988, Molinari et al. 1992, Smethie 1993, Rhein et al. 1995). Observations of CFCs over time in the interior western North Atlantic basins helped to focus on the importance of deep recirculation gyres in ventilating the interior out to the mid-Atlantic Ridge and delaying equatorward transport (e.g., Rhein 1994, Smethie et al. 2000).

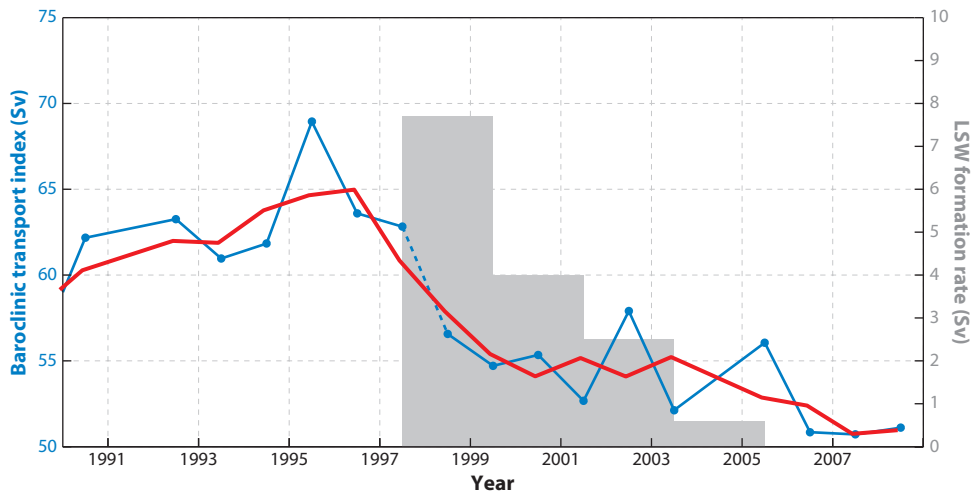
- Effective equatorward spreading rates of the NADW components have been estimated based on changing CFC concentrations (e.g., Molinari et al. 1998) and use of relic ages (Fine et al. 2002). These studies showed, for example, the surprisingly long timescale of approximately 10 years for transport of Labrador Sea Water (LSW) from its source to the subtropics (**Figure 3**), as compared with rates of 1–2 years that could be deduced from direct current measurements (e.g., Lee et al. 1996, Johns et al. 1993).
- In a model study, Rhein (1994) invoked mixing to explain the small 1–2 cm s<sup>-1</sup> CFC-derived DWBC transports, as compared with direct velocity measurements about five to ten times higher. Similar to float data, the CFC data show that a typical water parcel spends considerable time in large-scale, deep recirculations and in eddies (e.g., Lozier 1997) rather than being transported equatorward in a direct pathway.
- Recent float observations show the importance of transport of LSW from the subpolar gyre into the subtropics by interior pathways, including on the western flank of the mid-Atlantic Ridge (Bower & von Appen 2008, Bower et al. 2009). Although it is clear from the elevated inventories of CFCs that the DWBC continues to be a pathway into the subtropics, interior CFC inventories support the importance of interior pathways that are related to the role of eddies and winds (Lozier 2010).

Inventories of the CFCs have been used to quantify rates of formation for Southern Ocean deep and bottom waters (Orsi et al. 1999, 2002) and NADW components (Smethie & Fine 2001). The formation rate is the flux of water into a water mass, leading to an increase in water mass volume. The method relates the rate of formation ( $R$ ) to the inventory ( $I$ ) of a CFC within a layer as

$$I = \int R(t)C(\theta, S, t)dt$$

where  $C$  is the source water concentration as a function of potential temperature ( $\theta$ ), salinity ( $S$ ), and time ( $t$ ). Actual integration of the equation is approximated as a summation, where the formation rate is varied until the estimated inventory matches that calculated from the data. The approximation gives a rate of formation from the 1970s, when the major input of CFCs to the oceans occurred, to the time of observations. LeBel et al. (2008) estimated a total formation rate for NADW, over the period of the 1970s to 1998, of  $19.6 \pm 4.0$  Sv (for rates for water mass components, see LeBel et al. 2008). Largest contributions to errors in the calculation are from assumptions of a constant rate of formation and constant saturation for the water mass at its source. It is interesting that tracer-derived rates compare well to mean estimates from current moorings of DWBC transport of  $22.5 \pm 2.3$  Sv at Line W 39°N (e.g., Toole 2009) and of  $18.7 \pm 5.6$  Sv at 26.5°N Cunningham et al. (2007).

Estimates of LSW formation rates vary widely, and particularly those from observations. Some of the differences are not surprising, because there is no consistent definition of LSW or even formation rate, and some estimates do not include formation outside the Labrador Sea



**Figure 5**

Baroclinic mass transport (*blue line*) between Bermuda and the Labrador Sea relative to 2,000 m, following Curry & McCartney (2001) for the same period, with 3-year low-pass filtered data added as a red line. Gray bars show the biennial formation rate (Sv) of Labrador Sea Water (LSW) corresponding to the scale at right. Data prior to 1998 published by Curry & McCartney (2001). Figure updated by Kieke et al. (2007) and slightly different due to the inclusion of more hydrographic data from the Labrador Sea. Drawn from Rhein et al. (2010).

(Haine et al. 2008). There is a time-series dating back to 1991 of CFC-12 inventory in the Labrador Sea (Azetsu-Scott et al. 2003; Kieke et al. 2006, 2007; Rhein et al. 2010).

A recent application of the CFC inventory method has been to study variations in water mass formation rates over time. From changes in the CFC inventory in the subpolar North Atlantic, Rhein et al. (2002, 2010) and Kieke et al. (2006, 2007) estimate variable rates of formation for LSW over the period 1997–2005. Kieke et al. (2006, 2007) show formation of Upper LSW increased, and Rhein et al. (2010) show a decrease in formation of classical LSW between 1997 and 2005 (**Figure 5**). The decrease in classical LSW formation is accompanied by a decrease in subpolar gyre transport index (Curry & McCartney 2001, Kieke et al. 2007, Rhein et al. 2010) and a decrease in strength of the subpolar gyre from altimeter analysis (Hakkinen & Rhines 2004, Hakkinen et al. 2008).

Also looking at variability in NADW components, Tanhua et al. (2008) found temporal switching of Denmark Strait overflow water (DSOW) components (also found by Rudels et al. 2003). Their study is based on percentage of water masses at Denmark Strait Sill in 1997, 1999, and 2002 from multiparameter (nutrients, oxygen, CFCs, SF<sub>6</sub>) analysis. For example, they find a striking difference in the high abundance of Arctic Intermediate water in 1999 and accompanying low levels of modified Atlantic water. Tanhua et al. conclude that as a result of the switching, the volume of the overflow can stay relatively constant, whereas at the same time the properties of the overflow may change significantly, which would effect the entrainment downstream of the Denmark Strait and the circulation. The notion of a relatively constant strength of the Denmark Strait overflow over decadal timescales is supported by observations (Dickson et al. 2008) and models. As CFC-12 concentrations will continue to increase for some time in NADW, studies related to the AMOC, including estimates of formation rates, remain a significant use for CFC observations.

## Upper Ocean Ventilation Over the Decade Between WOCE and CLIVAR

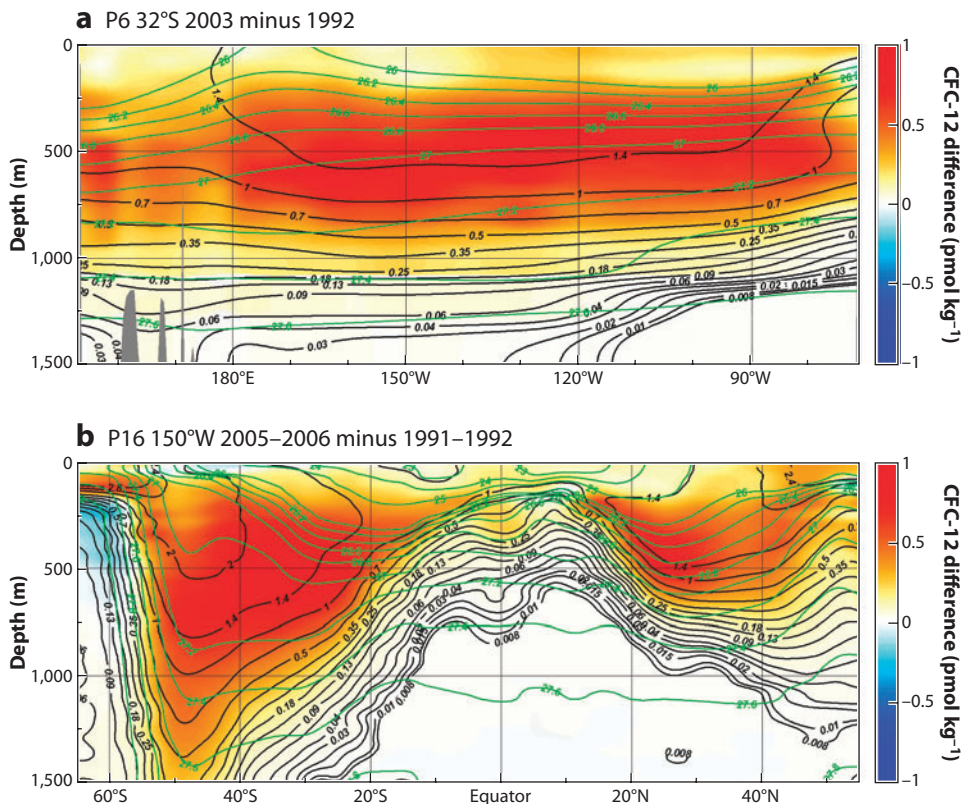
Ventilation can be broadly defined as the penetration and sinking of waters from the surface ocean into the interior. A water mass is said to be ventilated if it has been in contact with the atmosphere with gas exchange occurring. Ventilation characteristics are imprinted on individual water masses through heat and freshwater exchange, both as climatic averages and as anomalies. Recently, ventilated waters carry a signature of relatively high gas concentrations: CFCs, SF<sub>6</sub>, oxygen, CO<sub>2</sub>, etc. For example, by looking at differences in CFC concentrations in the upper ocean, there is an opportunity to directly observe ocean ventilation and to estimate subduction and formation rates (e.g., Fine 1993; Fine et al. 1994, 2001, 2008; Warner et al. 1996; Mecking et al. 2004; O'Connor et al. 2002, 2005; Sonnerup et al. 2008; Hartin et al. 2010).

Before examining differences in CFCs, it is worthwhile to look at how representative a discrete measurement is, and how much is it aliased by natural ocean variability. If detection of anthropogenic change is considered a signal-to-noise problem, then natural background variability needs to be removed from evolving oceanic properties. Anthropogenic inventories (CFCs, CO<sub>2</sub>) are highest in large well-ventilated regions (**Figure 4**; see above), yet there is considerable natural variability in regions that are associated with strong gradients in tracer quantities and other properties. These regions coincide with high eddy kinetic energy (EKE), and Rossby waves. Rodgers et al. (2009) looked at the effect of Rossby waves (an intrinsic part of natural variability) on seasonal to intra-annual variations in dissolved inorganic carbon and oxygen. Waugh & Abraham (2008) and Bryan et al. (2008) used a model to assess context changes in CFC concentrations and CFC ages expected from noise due to internal ocean variability. The largest noise is found in regions of strong gradients (i.e., across the Gulf Stream) and in regions of high EKE (i.e., Southern Ocean), whereas noise is low in subtropical gyres. The focus for the comparison presented below is on subtropical gyres.

Differences in CFC concentrations over time highlight regions where atmospheric constituents, such as CO<sub>2</sub> and climate anomalies, penetrate into the oceans and provide data for calculating the timescales of these penetrations. A comparison is presented between the WOCE decade of the 1990s and the CLIVAR decade of the 2000s. Sections are chosen to represent the subtropical gyres. **Figures 6** and **7** are prepared by gridding and subtracting in Ocean Data View (<http://odv.awi.de>). Over most of the sections, data are plentiful, and errors related to data resolution will be little more than the square root times the measurement error—when compared with sampling errors at locations of high EKE. In the nearly 15 years between the WOCE (1990s) and CLIVAR (2000s) surveys, CFC concentration differences in the Pacific show the large-scale downward and equatorward penetration of the CFCs from high-latitude source regions of both hemispheres (**Figure 6**). In general, increases in CFC concentration are largest in subtropical gyre thermocline and intermediate waters.

There are larger increases in CFC-12 concentrations in the South Pacific, and the subtropical gyre reaches deeper (**Figure 6**) due to a combination of the greater strength of Subantarctic mode water (SAMW) and Antarctic intermediate water (AAIW) formation compared with the strength of their North Pacific counterparts (e.g., Fine et al. 2001). In the South, CFC-12 increases the equivalent of  $\sim 1$  pmol kg<sup>-1</sup> over 15 years. The biggest change occurs between 26.8–27.2 neutral density ( $\gamma$ ) corresponding to SAMW/AAIW. Starting in the mid-1990s, there was an increase in southern subtropical gyre circulation related to the Southern annular mode (SAM) (Roemmich et al. 2007). Increasing CFCs on deep surfaces is consistent with decadal intensification of wind stress curl with an increase in the SAM and affects all three connected Southern Hemisphere subtropical gyres (e.g., Ridgway & Dunn 2007, Speich et al. 2007). This characteristic of larger CFC concentration increases in Southern Hemisphere subtropical gyres since the time of WOCE





**Figure 6**

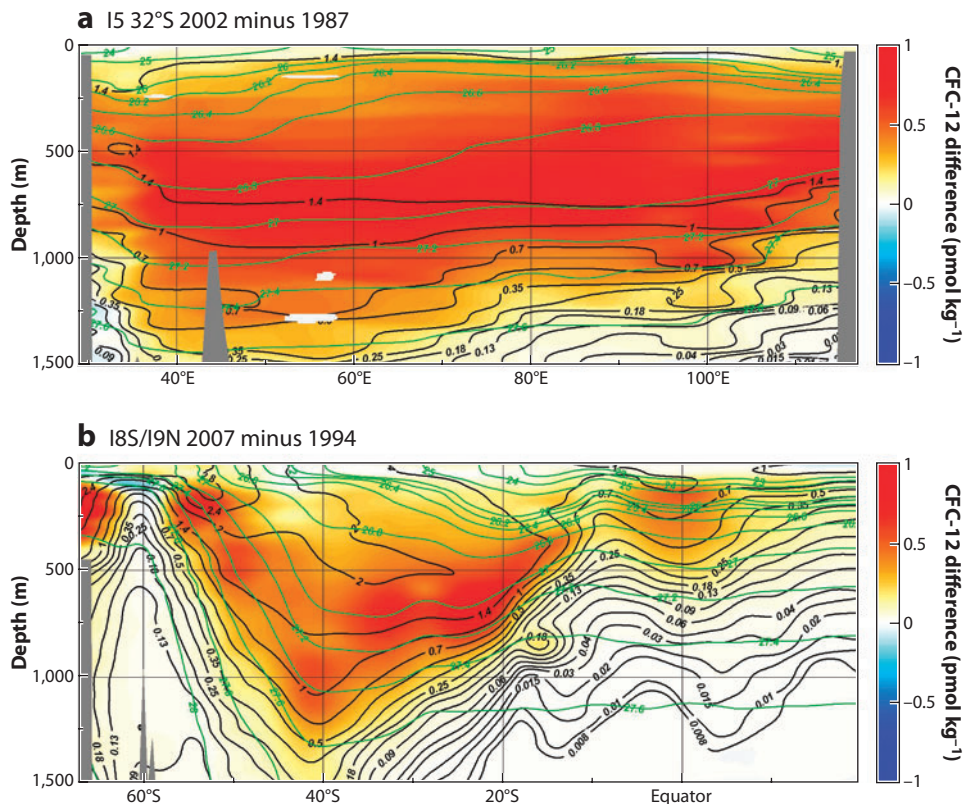
(*a*) Section of dissolved CFC-12 along 32°S (the P6 hydrographic sections) in the South Pacific Ocean from CLIVAR repeat hydrography and CO<sub>2</sub> program August–September 2003 in black contours, and in color shading difference from WOCE section P6 May–July 1992. (*b*) Section of dissolved CFC-12 along 150°W (the P16 sections) January–February 2005 and February–March 2006 in black contours, and in color shading difference from February–April 1991, July–October 1991, and October–November 1992. (*a, b*) Green contours indicate neutral density. Data were plotted using Ocean Data View. Abbreviations: CLIVAR, Climate Variability; WOCE, World Ocean Circulation Experiment.

is also observed in the Indian Ocean and Atlantic (not shown in **Figure 6**) and is observed in oxygen concentrations.

In the Indian Ocean, there is the largest north-south difference in CFC-12 concentrations due to the absence of a mid- and high-latitude North Indian Ocean (e.g., Fine et al. 2008). As in the South Pacific, in the South Indian Ocean, CFC-12 increases the equivalent of  $\sim 1$  pmol kg<sup>-1</sup> over 15 years (**Figure 7**). Again the biggest changes are 26.8–27.2  $\gamma$ , and the changes are widespread. Furthermore, an observed increase in thermocline oxygen reverses what had been considered a global trend in upper-ocean oxygen concentrations (McDonagh et al. 2005).

In the North Pacific, several studies have used CFCs and SF<sub>6</sub> to assess whether changing oxygen concentrations are related to changes in ocean ventilation. In the North Pacific, CFC-12 increases the equivalent of  $\sim 0.67$  pmol kg<sup>-1</sup> over 15 years, which is significantly less than in the Southern Hemisphere (**Figure 6**). The major change is along 26.6  $\sigma_{\theta}$  ( $\gamma$  is a little shallower), where Mecking et al. (2006, 2008) found decreasing apparent oxygen utilization (AOU); the AOU decrease reversed a previously reported trend here also. Periodic changes in the outcrop position





**Figure 7**

(a) Section of dissolved CFC-12 along 32°S (the I5 hydrographic sections) in the South Indian Ocean from CLIVAR March–April 2002 in black contours, and in color shading difference from WOCE section I5 November–December 1987. (b) Section of dissolved CFC-12 along 90°E (the I8S/I9N sections) collected from February–May 2007 in black contours, and in color shading difference from December 1994–March 1995. (a, b) Green contours indicate neutral density. Data were plotted using Ocean Data View. Abbreviations: CLIVAR, Climate Variability; WOCE, World Ocean Circulation Experiment.

of  $26.6 \sigma_{\theta}$ , including a complete cessation of the outcropping of this isopycnal (as it is the densest one to outcrop in the open North Pacific in climatological data), may play a more important role than circulation changes for producing AOI variations in the North Pacific Ocean (Emerson et al. 2004, Mecking et al. 2006).

Another study in the North Pacific by Sonnerup et al. (2008) used a model to quantify the impacts of mixing on the pCFC ages and to determine if there were changes in thermocline ventilation. They were looking at a time when the atmospheric source function for CFC-12 was increasing but not linearly (see above). Sonnerup et al. found a 6–10 year mixing-induced increase in pCFC-12 ages, based on pSF<sub>6</sub> ages at stations along 150°W between 52°N and 14°S over the years from 1991 to 2006. They conclude that there is no overall net change in ventilation timescales between 1991 and 2006.

Thus, when looking at the limited time period over the decade between WOCE and CLIVAR in the North Pacific, Mecking et al. (2006, 2008) found variations in densities ventilated. Although in the North Pacific subtropical gyre, CFCs in thermocline and intermediate layers increase, the

increase is substantially less than in the Southern Hemisphere subtropical gyres. A larger increase in Southern Hemisphere ventilation on lower thermocline and intermediate-level isopycnals is consistent with SAM variability. Thus, as is the case for temperature and salinity, CFC changes at thermocline and intermediate levels are linked to decadal changes in atmospheric forcing, and there is no consistent pattern of an anthropogenic warming signal in the short record available. However, effects of anthropogenic warming on SAM variability have not been evaluated. It is important to note that the above discussion applies to a comparison of data from only two decades. When looking over longer timescales, the North Pacific subarctic gyre at the least appears to be an exception, in that oxygen has been decreasing over the past 50 years. Keeling et al. (2010) summarize observations from both the eastern and western subarctic gyres that show declines in oxygen of  $7 \mu\text{mol kg}^{-1}$  per decade superimposed on a bi decadal oscillation (Aleutian Low and 18.6-year nodal tide). They attribute the decreasing oxygen concentrations to changes in ventilation and subduction rather than to oxygen utilization (Emerson et al. 2004; Deutsch et al. 2006; Mecking et al. 2006, 2008), and also to increased stratification, freshening, warming, shoaling of the mixed layer in the region of Ocean Station P since the 1950s (Whitney et al. 2007).

### Biogeochemical Applications

Transient tracer ages have been used for some time to estimate rates of biogeochemical processes. These include rates of apparent oxygen utilization (see above; Warner et al. 1996, Sonnerup et al. 1999, Abell et al. 2000, Mecking et al. 2004), denitrification (Howell et al. 1997), and organic matter remineralization (Abell et al. 2000). One of the most utilized biogeochemical applications for CFCs and  $\text{SF}_6$  has been for estimating anthropogenic  $\text{CO}_2$  inventories (e.g., Gruber et al. 1996; Sabine et al. 2004; Waugh et al. 2004, 2006; Hall et al. 2004; Steinfeldt & Rhein 2004; Friis et al. 2005; Terenzi et al. 2007; Tanhua et al. 2007, 2009; Steinfeldt et al. 2009; Alvarez et al. 2009; Vazquez-Rodriguez et al. 2009).

When dissolved inorganic carbon is directly measured in the ocean, its anthropogenic carbon content cannot be distinguished from natural carbon. Some of the methods developed to estimate the inventory of anthropogenic dissolved inorganic carbon ( $C_{\text{ant}}$ ) in the oceans use CFCs and  $\text{SF}_6$  partial pressure and TTD derived ages. Although the methods may yield differences in the distribution of  $C_{\text{ant}}$  and its total amount, they provide a fairly consistent picture of anthropogenic  $\text{CO}_2$  in the oceans (Schneider et al. 2010). Readers are referred to recent reviews of air-sea flux of anthropogenic  $\text{CO}_2$  (Gruber et al. 2009) and of oceanic storage of anthropogenic  $\text{CO}_2$  (Sabine & Tanhua 2010) for thorough discussions of the strengths and weaknesses of the different methods.

### CONCLUSIONS AND OUTLOOK

The tracers CFC-11, CFC-12, and  $\text{SF}_6$  are now measured at sea with relatively good precision and accuracy. These compounds are stable in the oceans, and their atmospheric time histories are well known. An advantage of using CFCs and  $\text{SF}_6$  as tracers of ocean circulation is that the time-dependent source functions permit calculation of rates for ocean processes from partial pressure ages, ratio ages, and TTDs. CFCs and  $\text{SF}_6$  are sensitive indicators highlighting interior ocean regions where surface derived anomalies can be transported on timescales of decades.

A comparison of CFC data from the 1990s with that from the 2000s reveals that in the Southern Hemisphere subtropical gyres, a larger increase (than in the North) in ventilation on lower thermocline and intermediate-level isopycnals is consistent with decadal varying SAM. Possible effects of anthropogenic warming on atmospheric variability have not been considered. Over these timescales in the North Pacific, there are indications of variability in the densities at which lower

thermocline layers are ventilated with CFCs and oxygen from earlier studies (Mecking et al. 2006, 2008). However, on timescales of the past 50 years in the North Pacific, other studies have shown decreasing oxygen concentrations.

A significant application for the CFCs has been for the deep limb of the AMOC, where they are used to describe pathways from the NADW source regions, effective spreading rates, and rates of formation of NADW components. Inventories of the CFCs have been used to quantify rates of formation for Southern Ocean deep and bottom waters (Orsi et al. 1999, 2002), and NADW components (Smethie & Fine 2001). LeBel et al. (2008) estimate a total formation rate for NADW over the period of the 1970s to 1998 of  $19.6 \pm 4.0$  Sv.

A recent application of the CFC inventory method for estimating water mass formation rates has been to study temporal variability in NADW rates. Kieke et al. (2006, 2007) and Rhein et al. (2010) show a decrease in formation of Classical LSW between 1997 and 2005, while there was formation of Upper LSW. Also looking at temporal variability in NADW, Tanhua et al. (2008) found that the water mass components that contribute to DSOW can vary over time (as found by Rudels et al. 2003). Tanhua et al. conclude that, although there is switching of components, the volume of DSOW can stay relatively constant. In the short CFC record, there is no consistent pattern of a global anthropogenic signal of reduced NADW formation rates.

CFCs and SF<sub>6</sub> concentrations, inventories, and ages will continue to be highly useful for applications discussed herein, such as AMOC, upper ocean ventilation, and biogeochemical rates including apparent oxygen utilization rates and anthropogenic CO<sub>2</sub> inventory. Other applications of CFC and SF<sub>6</sub> data include calibration for ARGO sensors (Wong et al. 2003). Tracer data such as maps, timescales, and inventories provide targets for model calibration and validation. Also, repeated observations of the tracers can provide constraints on models of ocean ventilation.

Whereas the atmospheric content of the CFCs has started to decrease, SF<sub>6</sub> continues to increase. The use of SF<sub>6</sub> for timescale information is less ambiguous. There are some benefits to measuring both CFCs and SF<sub>6</sub>. SF<sub>6</sub> expands the partial pressure, ratio, and TTD estimates of age or elapsed time. SF<sub>6</sub> measurements also provide a means to separate observed CFC age changes that are due to mixing from actual variability due to ventilation changes (e.g., Sonnerup et al. 2008). Furthermore, calculations of anthropogenic CO<sub>2</sub> inventory are enhanced in the recently ventilated waters and by using an additional tracer.

Finally, there is an existing large global data set of CFCs. The use of CFCs with SF<sub>6</sub>, in particular, ratio and TTD ages, continues to offer a powerful tool for calculating ages and rate information. In fact, CFCs are still increasing in some water masses, and this will continue to be the case in older waters away from the source regions. Thus, the outlook for using CFCs as tracers for oceanic processes and, in particular, in concert with SF<sub>6</sub> remains very positive.

## DISCLOSURE STATEMENT

The author's laboratory measures CFCs and SF<sub>6</sub> in the oceans. She has received funding from U.S. government agencies to measure and analyze tracer data in the past three years.

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## Errata

An online log of corrections to *Annual Review of Marine Science* articles may be found at <http://marine.annualreviews.org/errata.shtml>