Response to Referee #1 Comments, “A comprehensive estimate for loss of atmospheric carbon tetrachloride (CCl_4) to the ocean”, by J.H. Butler et al.

1. Page 2, lines 6 and 7. The referee is correct that this is a mischaracterization of the relative uncertainty of the soil sink. We have removed the reference to the soil sink being less certain.
2. Page 2, lines 24-25, Done; changed to “we sampled daily”
3. Page 5, line 19, Done; changed to “estimated”
4. Page 6, lines 30-32, Done as requested. The statement reads as, “This is an area that requires further investigation, as there is no direct evidence to date for such pathways, microbial or otherwise, in the ocean, although there is evidence for microbial removal of CCl_4 in well oxygenated soils (e.g., Mendoza et al., 2011)”
5. Technical corrections
    a. Page 7, line 10, Text now reads “bomb and”
    b. Page 7, line 14, Text now reads “(~14%)”
    c. Page 11, line 25, Text now reads “SF_6”
    d. Table 1. (The referee refers to “Figure 4” in making this comment, but we believe the reference was to “Figure 1”, which is relevant to his or her point.) After consideration, we have decided to keep Table 1 in the text and leave the Figure 1 caption as is. The information in the caption refers only to what’s in the figure; information in the table addresses additional items such as ship names and sampling and analytical techniques, which are relevant to the data collected and can be linked to other studies.

Response to Referee #2 Comments, “A comprehensive estimate for loss of atmospheric carbon tetrachloride (CCl_4) to the ocean”, by J.H. Butler et al.

1. **Temperature trends.** The referee is correct that Huhn et al (2001) observed a temperature trend in computed CCl_4 loss at depth. However, Huhn et al. (2001) also noted that losses were not observed in waters of > 200 umol/kg. Our concern here is that there is no clear temperature dependence in surface waters, which implies a different process for removal. Surface waters are well ventilated so, a priori, we should expect no degradation. The fact that we do see a deficit suggests yet another process at work. We don’t think that the temperature trends noted by Huhn et al. (2001) are relevant to surface concentrations, especially, as we note below, since we cannot explain the observations by transport from depth. That being said, we have added a notation of the loss rates observed by Huhn in the manuscript near the end of Section 4.2 to support our point that degradation at depth cannot explain the observed undersaturations.
2. **Corrections for physical effects.**

a. **Page 3 Diffusivity temperature dependence.** The referee is correct that the change in diffusivity is about the same for the two gases (~2.7%/degree). We have added that property to Table 2.

b. **Page 3, Computations.** The referee makes a good point about the temperature dependence of the solubility of the gas, which highlights the fact that we weren't presenting it correctly in the table. Because the saturation anomaly itself is expressed as percent, we should have in the table a percent increase of solubility with temperature, not absolute units of solubility. The percent change in solubility of the two gases is about the same (3.9%/degree for CFC-11 and 4.1%/degree for CCl_4), which means that one should expect roughly the same influence of a change in temperature on the saturation anomaly of each gas. Thus, if one sees an increase in the CFC-11 saturation anomaly owing, for example, to radiative heating, CCl_4 should respond similarly.

c. **Quantitative Analysis to support statement on page 4, line 5, and corrections for physical effects page 5, line 21.** Providing a quantitative description is difficult to do without making significant assumptions about depth, extent, and timing of air injection, sea surface roughness, etc. Dissolution of bubbles favors invasion of a gas over evasion and would thus tend to sustain a positive anomaly. These effects are explained in considerable detail in Kester (1975). But, in the end, gases with similar diffusivities and changes in solubility with temperature should have similar saturation anomalies at the ocean surface if there are no other forces (e.g., production or degradation) at play. On cruises where we have measured CFC-11 and CFC-12, both long-lived in the atmosphere and conservative in surface waters, we generally see similar supersaturations and undersaturations (Lobert et al., 1995, Butler et al. 1988). The differences can be up to 2%, which we consider to be due to differences in physical properties of the two gases.

The text on Page 4 now reads as,

> "Calculated this way, a corrected saturation anomaly that is negative indicates that the gas is probably being consumed in the water, regardless of its non-corrected anomaly. In some of our studies we noted that saturations of CFC 11 and CFC 12, which also have similar physical properties (Table 2), could differ by as much as ~2% (Butler et al. 1988, Lobert et al. 1995). As a result, we consider in situ consumption of CCl_4 significant if the corrected saturation anomaly is more negative than -2%.

The text on Page 5 now reads as,

> "The correction for physical effects that we use here, i.e., subtracting the CFC-11 saturation anomaly, which more often than not is positive, makes the CCl_4 saturation anomaly more negative. Although one might expect the effects of warming and cooling to balance out on a global basis, effects such as dissolution of bubbles and mixing of

> waters tend to elevate surface saturation anomalies of all gases (e.g., Kester 1975, Bowyer and Woolf 2004). Nevertheless, the undersaturations calculated without these corrections still generally fall within 5–10%."

3. **Mixing Time scales, page 6, lines 12-14.** The average eddy diffusion coefficient through the thermocline is about 1 $cm^2\ s^{-1}$ (8.64 $m^2\ d^{-1}$). At this rate, vertical transport through the ocean thermocline, which has a scale length of hundreds of meters to reach the nadir in CCl4 concentrations, can take tens of days to move one meter. That's not nearly fast enough to sustain a 5-10% deficit of a gas in surface waters that are replenished from the atmosphere every 20-30 days. It is also consistent with the fact that Huhn et al (2001) and others suggest degradation rates in low oxygen waters of around 2-3% per year. To make this more clear, we have revised the text as follows:

> "Air–sea exchange renews gases in surface waters on the order of 20–30 days, whereas, with an eddy diffusivity of ~1 cm^2s^{-1} through the thermocline (Quay and Stuiver, 1980; Li et al, 1984), transport to depths of hundreds of meters from the ocean surface requires times of years to decades. Exceptions are apparent in areas of upwelling, where water from depth can be advected as well as mixed toward the surface in a matter of days (e.g., Tanhua and Liu 2015). Depletion of CCl_4 at depth would be in agreement with other reports suggesting a loss of CCl_4 in low oxygen waters (e.g., Lee et al, 1999), although the rate of a few percent depletion per year (e.g., Huhn et al, 2001, Min et al, 2010) at depth is still not sufficient to sustain the observed undersaturations at the surface."

4. **Newly calculated ocean sink has dropped substantially, page 7, line 20 ff**. We agree, this is a big change and it's not entirely due to the air-sea exchange coefficient. We thank the author for raising this issue, as our explanation in the text was lacking. In addressing this we've also looked carefully at other air-sea exchange studies since Sweeney et al. (2007) and Wanninkhof et al. (2009). These recent studies seem to be converging around a number very near that of Nightingale et al (2000) and Sweeney et al. (2007), which was used in the original version of this manuscript. As Wanninkhof (2014) summarizes this progress and offers a complete re-evaluation of uncertainties in estimating global fluxes, we have now chosen to use the Wanninkhof (2014) estimate, normalized to the wind speeds in our model. This increases the flux of CCl_4 to the ocean by about 15% over that of our original number based on Sweeney (2007), and reduces the uncertainty in estimates of the air-sea exchange coefficient to ±20%, down from the ±30% we had calculated in the previous version and the ±32% given in Sweeney (2007). The total atmospheric lifetime drops from our estimate of 33 y in the ACPD version of this paper down to 32 y. The text now reads as follows:

> "This updated estimate is based on four times as many observations as used in Yvon-Lewis and Butler (2002), which account for all seasons and cover almost all major ocean basins. The average saturation anomaly used in this study is 10-20% less than the average used in Yvon-Lewis and Butler [2002]. Binning the surface data in our preferred approach (rather than applying a global mean anomaly as done before) to reflect better the actual distribution over the oceans accounts for another 10-20% decrease (Table 3). The model used by Yvon-Lewis and Butler [2002] was based the 2°x2° COADS data set for sea surface temperatures and wind speeds and our new estimate is based on a different, newer data set with 1°x1° bins. The mean or median wind speed for the 1°x1° data set is ~5% lower and winds were distributed differently than in the COADS data set. The most influential change, however, is the use of an updated air-sea exchange coefficient, based on a revised inventory of bomb-$^{14}CO_2$ (Naegler et al 2006, Wanninkhof, 2014). Yvon-Lewis and Butler (2002) used the Wanninkhof (1992) relationship, which was normalized to an earlier assessment of bomb-$^{14}CO_2$. We evaluated the impact of this change on CCl_4 flux over the ocean and determined that it alone accounts for a 24% lower flux with Wanninkhof (2014; Table 2) than with Wanninkhof (1992). Additional reductions came from use of a simpler computational approach that differs from that of Yvon-Lewis and Butler (2002), which was designed for gases where in situ loss rates are known and which required estimates of mixed layer depth and loss during downward mixing through the ocean thermocline. The newly revised estimate for CCl_4 uptake provided here is based simply on the air-sea difference in partial pressure and the kinetics of air-sea exchange. It is more robust for this gas, for which there is little understanding of the loss mechanisms, and suggests that the ocean sink is responsible for about 18% (vs. 32% previously) of the CCl_4 removed from the atmosphere."

Because the ACPD version has been used already in a SPARC report (*SPARC Report on the Mystery of Carbon Tetrachloride. Q. Liang, P.A. Newman, S. Reimann (Eds.), SPARC Report No. 7, WCRP-13/2016.*), we also added text to explain the difference between our submitted version and this one and give the reasoning for overriding our earlier decision to use the Sweeney et al relationship. That text (p.8) reads as follows:

> "(Note: Our original version of this paper (doi:10.5194/acp-2016-311) preferred the Sweeney et al. (2007) relationship for computing air-sea fluxes and subsequent lifetimes. We had selected that parameterization because it was formulated similarly to Wanninkhof (1992), which had been used in the earlier calculations of the ocean sink of CCl_4 (Yvon-Lewis and Butler 2002), accounted for the change in ocean bomb-^{14}C inventory, and was centered among the distribution of wind speed relationships considered (e.g., Figure 8). We have since updated that and prefer the Wanninkhof (2014) polynomial approach, which includes a rigorous evaluation of the biases and uncertainties in estimating air-sea exchange, and takes additional studies into account.)"

5. Minor Corrections:
    a. Page 7, line 10, space between “bomb” and “and”. Done
    b. D(corrected) needs definition. Done. Text after Eq. 3 now reads as “where n_{tr} is the number of moles of air in the troposphere (1.46 x 1020), r is the fraction of atmospheric CCl4 that resides in the troposphere (0.886), and $\Delta_{corrected}$ is the difference between Δ_{CCl4} and Δ_f.”
    c. Figure 8 caption typos need fixing. Done
    d. Describe the separate studies used in the legend within the caption. Done by revising the legend to properly reference each study and with additional studies included in the plot.

Relevant Changes in the Manuscript

1. Lifetimes changed in the abstract and text, owing to use of an updated air-sea exchange relationship. (p. 6, 14,)
2. Explanation of what constitutes physical processes (p. 8, 9, 10-11)
3. Explanation of rates of subsurface mixing (p. 11)
4. Revised flux uncertainty (p.12)
5. Explanation of difference between air sea exchange coefficients in this version vs. the originally submitted version in ACPD. We felt the need to include this, as the ACPD version has already been used and cited in a SPARC report on the mystery of atmospheric CCl4 (p. 13)
6. Explanation of large difference in this estimate vs the estimate given in Yvon-Lewis and Butler (2002), (p. 13-14)

A comprehensive estimate for loss of atmospheric carbon tetrachloride (CCl_4) to the ocean

J. H. Butler[1], S. A. Yvon-Lewis[2,7], J. M. Lobert[3,7], D. B. King[4,7], S. A. Montzka[1], J. L. Bullister[5], V. Koropalov[6], J. W. Elkins[1], B. D. Hall[1], L. Hu[1,2] and Y. Liu[2,8]

[1]Global Monitoring Division, NOAA Earth System Research Laboratory, Boulder, 80305, USA
[2]Department of Oceanography, Texas A&M University, College Station, 77840, USA
[3]Entegris Inc., Franklin, 02038, USA
[4]Chemistry Department, Drexel University, Philadelphia, 19104, USA
[5]NOAA Pacific Marine and Environmental Laboratory, Seattle, 98115, USA
[6]Roshydromet, Moscow, 123242, Russia
[7]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, 80309, USA
[8]Marine Chemistry & Geochemistry, Woods Hole Oceanographic Institution, Massachusetts

Correspondence to: James H. Butler (james.h.butler@noaa.gov)

Abstract. Extensive undersaturations of carbon tetrachloride (CCl_4) in Pacific, Atlantic, and Southern Ocean surface waters indicate that atmospheric CCl_4 is consumed in large amounts by the ocean. Observations made on 16 research cruises between 1987 and 2010, ranging in latitude from 60° N to 77° S, show that negative saturations extend over most of the surface ocean. Corrected for physical effects associated with radiative heat flux, mixing, and air injection, these anomalies were commonly of the order of -5% to -10%, with no clear relationship with temperature, productivity, or other gross surface water characteristics other than being more negative in association with upwelling. The atmospheric flux required to sustain these undersaturations is ~~11~~ 12.4 (9.4~~7~~–15.4~~14~~) Gg y^{-1}, a loss rate implying a partial atmospheric lifetime with respect to the oceanic loss of ~~209~~ 183 (~~157~~147–~~313~~241) y and that ~~~16~~ 18 (~~10–21~~14-22) % of atmospheric CCl_4 is lost to the ocean. Although CCl_4 hydrolyses in seawater, published hydrolysis rates for this gas are too slow to support such large undersaturations, given our current understanding of air–sea gas exchange rates. The even larger undersaturations in intermediate depth waters associated with reduced oxygen levels, observed in this study and by other investigators, strongly suggest that CCl_4 is ubiquitously consumed at mid-depth, presumably by microbiota. Although this subsurface sink creates a gradient that drives a downward flux of CCl_4, the gradient alone is not sufficient to explain the observed surface undersaturations. Since known chemical losses are likewise insufficient to sustain the observed undersaturations, this suggests a possible biological sink for CCl_4 ~~also~~ in surface or near-surface waters of the ocean. The total atmospheric lifetime for CCl_4, based on these results and the most recent studies of soil uptake and loss in the stratosphere is now 32 (26-43) y.

1 Introduction

CCl_4 is a strong ozone-depleting gas for which production for dispersive use (e.g., fire suppression, dry cleaning, fumigation) has been banned through the Montreal Protocol (1987) and its amendments and adjustments. Although the concentration of atmospheric CCl_4 has been declining in the atmosphere since the early 1990s, its rate of decline is slower than predicted from estimates of emissions suggested by production data reported to the Ozone Secretariat (<11 Gg/yr since 2007; Carpenter and Reimann et al., 2014) and its atmospheric lifetime (e.g, Liang et al 2014, Carpenter and Reimann 2014). The dominant loss for CCl_4 is through photolysis in the upper atmosphere, which, based on the most recent evaluations, would yield an atmospheric lifetime of 44 (36–58) y (Ko et al. 2013, Laube et al. 2013, Carlon et al. 2010~~, Volk et al. 1997~~). The oceanic sink, previously calculated as 94 (82–191) y (Yvon-Lewis and Butler 2002), also removes significant amounts of CCl_4 from the atmosphere. The CCl_4 lifetime owing to uptake by soils, previously determined at 90–195 y, but recently assessed at 375 (288–536) y, is considered a lesser ~~and more uncertain~~ component (Happell et al. 2014, Rhew and Happell 2016). These additional sinks had previously brought the overall calculated lifetime of CCl_4 in the atmosphere down to 23–35y. The oceanic sink for CCl_4 determined by Yvon-Lewis and Butler (2002) and used in subsequent Scientific Assessments of Ozone Depletion (e.g., Carpenter and Reimann 2014), however, was based almost entirely on surface data from four research cruises in the Pacific Ocean from 1987–1992 (Butler et al, 1997). Considerable data exist for a deficit of CCl_4 in deeper ocean waters, particularly those associated with low oxygen (e.g. Krysell and Wallace 1994, Tanhua and Olsson 2005). This study focuses on surface data from the original four cruises and a dozen additional expeditions to enhance the earlier analysis, to examine the oceanic sink for potential sampling and analytical biases, to evaluate the potential cause of the sink, and to provide more confidence in the estimated mean rate of atmospheric CCl_4 removal by the ocean. This study also takes advantage of significant improvements in determining air–sea exchange rates, which have a substantial impact on the final estimate. Finally, we draw on hydrographic data from selected cruises to ~~underscore~~ evaluate the role of subsurface processes. With extensive surface data from numerous cruises coursing three of the world's major oceans, we provide here a more representative picture of oceanic removal of this gas from the atmosphere.

2 Sampling and Analysis

CCl_4 mole fractions in air were measured hourly in equilibrated surface water and the atmosphere on most of 16 research cruises, crossing many of the major ocean basins over a period of 23 years (1987–2010; Fig. 1, Table 1). (On four cruises, SAGA II in the West Pacific, CLIVAR-01 in the Southern Ocean, and A16N and A16S in the Atlantic, we ~~resorted to sampling~~sampled daily from surface Niskin bottles; WOCE P18 data, likewise from Niskin bottles, were used only for depth profile analyses and were not accompanied by continuous air measurements.) On the remaining cruises, air samples were collected from the ship's bow and surface samples were obtained with an underway, Weiss-type equilibrator (e.g., Johnson et al. 1997, Butler et al. 1988). Gases in all samples were separated by gas chromatography on OV-101 or similar columns, some packed, most capillary, and detected with electron capture detectors (GC-ECD) or mass spectrometers (GCMS; Hewlett Packard or Agilent 5971 or 5973). Both types of detectors and different columns were used on some cruises to evaluate potential analytical biases. To evaluate potential bias introduced by the equilibrator, surface samples from hydrocasts or bucket samples were obtained and analyzed on several occasions. Gases were extracted from these samples with a purge-and-trap technique (Bullister and Weiss 1988, Yvon-Lewis et al 2003), and subsequently analyzed by GCMS or GC-ECD. Results from these grab samples agreed well with those from underway equilibrated surface water (Fig. 2).

Full-depth water column profiles of dissolved CCl_4 concentrations, along with CFC-11 and CFC-12, were also collected on several expeditions during this period. These profiles typically consisted of measurements made on discrete water samples collected at 24–36 depths, using purge-and-trap techniques and analyzed with GC-ECD. Depth profiles of CCl_4 were obtained in some instances to identify potential zones of CCl_4 loss relative to that of CFC-11, a gas of similar physical properties, but unreactive in seawater except under virtually anoxic conditions (Bullister and Lee, 1995; Shapiro et al., 1997). However, to further understand the potential cause of the surface deficits of CCl_4, we also evaluated extensive data from World Ocean Circulation Experiment (WOCE) Repeat Section P-18 (2008), which runs from 21ºN to 70ºS in the East Pacific Ocean, and used CFC-12 as the conservative tracer. This section runs through an extensive, well developed oxygen minimum, thus allowing a close evaluation of the correlation between dissolved CCl_4 and O_2.

3 Computations

"Instantaneous" CCl_4 fluxes were estimated from the observed difference between partial pressures of CCl_4 in the atmosphere and those in the surface ocean, the air–sea exchange velocity, and the solubility and diffusivity of the gas. Influences of in situ physical effects, such as warming, cooling, and mixing (Kester 1975), on CCl_4 saturation anomalies were minimized by subtracting saturation anomalies of CFC-11 (e.g., Butler et al. 1991). The saturation anomaly (Δ_g) for a dissolved gas is expressed as the percent departure of the observed dissolved amount from equilibrium. This is computed from the difference in partial pressures:

$$\Delta_g = 100\left(\frac{p_{gw}-p_{ga}}{p_{ga}}\right)[\%]\,, \qquad (1)$$

where p_{gw} and p_{ga} are the partial pressures of the gas in water and air. If the saturation anomaly of a gas is positive, it indicates that the water is supersaturated and the net flux is from the ocean to the atmosphere. If it is negative, then the net flux of the gas is from the atmosphere to the ocean. However, the saturation anomaly alone is not sufficient for detecting or estimating in situ consumption of the gas in the water. This is because ~~of~~ physical processes, such as radiative warming and cooling of surface waters, dissolution of bubbles, or mixing of water masses, ~~that~~ can give rise to positive or, in the case of radiative cooling, negative saturation anomalies (Kester 1975). The magnitude of this effect depends upon the diffusivity of the gas, its solubility, and the temperature dependence of its solubility. In practice, the difference in saturation anomaly for similar compounds is small; saturation anomalies for CFC-11 and CFC-12 typically differ by 1–2~~3~~%. Their molecular diffusivities are not much different, nor is the temperature dependence of their solubilities, but their absolute solubility differs by a factor of 3.6 (Table 2).

Consequently, to determine if there is any consumption of a gas such as CCl$_4$ in the water, we compute its *corrected* saturation anomaly to capture that portion of the saturation anomaly that is largely free of physical influences. For CCl$_4$ ~~T~~this is done by subtracting the CFC-11 saturation anomaly from the observed CCl$_4$ saturation anomaly. CFC-11 is chosen over CFC-12, because its physical properties more closely resemble those of CCl$_4$ than do those of CFC-12, which is much less~~–~~ soluble and has a ~~smaller~~ similar percent change in solubility with temperature. Calculated this way, a corrected saturation anomaly that is negative indicates that the gas is probably being consumed in the water, regardless of its non-corrected anomaly. In some of our studies we noted that saturations of CFC-11 and CFC-12, which also have similar physical properties (Table 2), could differ by as much as ~2% (Butler et al. 1988, Lobert et al. 1995). ~~. However, because of the differences in physical properties of various gases~~ ~~, We thus~~ As a result, we consider in situ consumption ~~is more~~ of CCl$_4$ ~~probable~~ significant if the corrected saturation anomaly is ~~less~~ more negative than -2%.

The corrected saturation anomaly of CCl$_4$ should be roughly proportional to its in situ loss or production. If we assume steady-state conditions, the loss or production rate can be calculated from the flux across the surface of the water that is required to maintain the corrected saturation anomaly:

$$F_{CCl_{4,parcel}} = \frac{K_w p_{CCl_{4,a}} A}{H_{CCl_4}} \left(\frac{\Delta_{CCl_4} - \Delta_f}{100}\right), \qquad (2)$$

Here $F_{CCl_{4,parcel}}$ is the emission of CCl$_4$ across a given parcel (e.g., a 1°x1° section) of the ocean surface (mol m^{-2} d^{-1}; negative values imply uptake), K_w is the air–sea transfer velocity (m d^{-1}), H_{CCl_4} is Henry's Law constant for CCl$_4$ (m^3 atm mol^{-1}), $p_{CCl_{4,a}}$ is its partial pressure in the atmosphere, A is the area of the parcel (m^2), Δ_{CCl_4} is its measured saturation anomaly (%), and Δ_f is the saturation anomaly of CFC-11. There is some uncertainty in this kind of flux estimate, mainly associated with K_w, which varies considerably with wind speed and sea surface roughness, but also because the CFC-11 correction is only an approximation.

The rate constant for oceanic removal of atmospheric CCl$_4$ through the parcel, $k_{CCl_{4,parcel}}$, is computed as the ratio of the flux across that surface to the total amount of CCl$_4$ in the atmosphere,

$$k_{CCl_{4,parcel}} = \frac{K_W A r_{CCl_4}}{H_{CCl_4} n_{tr}} \left(\frac{\Delta_{corrected}}{100}\right), \qquad (3)$$

where n_{tr} is the number of moles of air in the troposphere (1.46 x 10^{20})~~ and~~, r is the fraction of atmospheric CCl$_4$ that resides in the troposphere (0.886), and $\Delta_{corrected}$ is the difference between Δ_{CCl4} and Δ_f. To account for spatial variations in surface ocean properties and surface wind speeds, we applied Eq. (3) to a monthly mean, 1°x1° gridded dataset of sea surface temperature (SST), salinity, and wind speed (Samuels and Cox 1988). Providing CCl$_4$ saturation anomalies on this same scale requires an extension of the available measurement data, since we have not made measurements in every 1°x1° grid cell. To do this, we considered correlations between the measured CCl$_4$ saturations and other properties in the 1°x1°

gridded dataset (e.g., temperature, wind speed, season), but found none to be significant in a global sense. Measured saturations do vary somewhat consistently over latitudes, so we used the mean saturation anomalies within latitudinal bands in the gridded data set to compute the global flux. This approach is not perfect—it does not capture unique coastal influences all that well, nor does it capture all areas of upwelling as a category, but it does accommodate the equatorial upwelling influences and those of some other fronts, which appear significant in the data. It also captures the temporal and spatial variability of wind speed and sea surface temperature. We ran additional sets of computations using the global mean and median corrected saturation anomalies~~y, the global median corrected saturation anomaly,~~ and the median saturation anomaly in 10 degree latitudinal bands to test the uncertainty associated with which averaging approach we select. Finally, we further evaluated the sensitivity of our results to these choices by alternatively considering an extreme case for the high latitude Southern Ocean, where we have little data, by selecting a saturation anomaly of -99% for that region. This last approach examines the highly unlikely possibility that circulation in the Southern Ocean could lead to extreme undersaturations and how it might influence the global flux estimates derived.

4 Results and Discussion

4.2 Explaining the Observed Undersaturations

A comparison of CCl_4 mole fractions measured in air from the ship's bow and from the equilibrator headspace shows that CCl_4 is largely undersaturated by about 5–10% in the surface ocean virtually everywhere, nearly all the time (Fig. 3, 4a). Larger undersaturations are measured in equatorial regions and, occasionally, other areas of upwelling, which is consistent with the delivery of subsurface waters undersaturated in CCl_4 with respect to CFC-11. Exceptions to this general picture are periodic, small supersaturations, often, but not always, measured in coastal waters or in rough seas. These could be evidence of periodic CCl_4 contamination from the ship or a localized anthropogenic source of CCl_4, such as riverine runoff. They could also result from an inadequate correction of physical influences on the saturation anomaly. No evidence exists for production of CCl_4 in seawater. Three of the earlier cruises, SAGA II, RITS-89 and OAXTC-92, were conducted at a time when contamination or analytical artifacts associated with these compounds was not uncommon and difficult to avoid, particularly in rough seas, owing to their widespread use and ubiquitous nature as solvents and in other common materials. Consequently, we have removed these positive values in our flux computations because including them would bias the results. Our goal is to determine an air–sea flux that best represents CCl_4 that is irreversibly removed by reactions in the ocean, which, in this instance is ~~imperfectly represented~~estimated by the corrected saturation anomaly.

These widespread undersaturations exceed those that might be expected from physical effects, such as ~~mixing or warming~~ radiative cooling of ~~water masses~~surface waters. ~~While t~~The correction~~s~~ for physical effects that we use here, i.e., subtracting the CFC-11 saturation anomaly, which more often than not is positive, ~~do~~ makes the CCl_4 saturation anomaly more negative. Alt~~T~~hough one might expect the effects of warming and cooling to balance out on a global basis, effects such as dissolution of bubbles and mixing of waters tend to elevate surface saturation anomalies of all gases (e.g., Kester 1975, Bowyer and Woolf 2004). ~~,~~ Nevertheless, t~~t~~he undersaturations calculated without these corrections still generally fall within 5–10%. Large departures from this range were usually associated with high mixing rates (e.g., upwelling) or rapid heating and were corrected somewhat, though not completely, with the algorithms applied here (e.g., Fig. 4a,b). Corrected saturation anomalies more negative than the -5 to -10% range might still be due in part to differences in the physical properties of CCl_4 and CFC-11 that are not fully corrected in our approach (e.g., Table 2). They may also be a result of differences in the atmospheric histories of CCl_4 and CFC-11, where CCl_4 has a longer and slightly differently shaped historic accumulation in the atmosphere than CFC-11, which is reflected somewhat in its concentration-depth profiles in the ocean as additional scatter in correlation plots of these gases. Finally, trace gases in surface waters may not have always equilibrated with an atmosphere identical to that observed above it. All in all, the corrections used here for physical effects largely reduce error and remove biases in the computation of atmospheric lifetime with respect to oceanic loss and thus lead to a better estimate (e.g., Butler et al. 1991). It's important to note that the corrections for physical effects are most often smaller than the gross flux of CCl_4 into the water and therefore do not change the overall picture of ~~“~~widespread undersaturation~~”~~ observed for~~of~~ CCl_4.

Plotting the corrected saturation anomalies from our cruises shows a reasonable degree of scatter, but remarkably consistent means and medians (Fig. 5; Table 3). Larger undersaturations near the equator are likely associated with increased upwelling, which brings up water more deficient in CCl_4 than CFC-11. Causes of the larger undersaturations in other areas are less clear but include, for example, a Gulf Steam ring (GasEx98), coastal waters, and larger scale ocean fronts, all of which are associated with some degree of upwelling. Yet, some areas of large, negative saturation anomalies, such as the central gyre north of Hawaii during BACPAC-99, are not so readily understood and cannot be attributed to sampling or analytical artifacts.

This relative consistency of undersaturation in surface waters during all seasons, regardless of sea surface temperature and biological regime, ~~would~~ might suggest that CCl_4 is removed not in surface waters, but at depth, with ~~the deficit~~CCl_4 being advected and mixed to ~~the surface~~deeper waters, where it is consumed~~, and ultimately to the atmosphere~~. First-order computations of the time required to mix waters between the surface and intermediate depths, however, suggest that, on average, the loss at depth cannot fully support the observed surface water deficits. Air–sea exchange renews gases in surface waters on the order of 20–30 days, whereas, with an eddy diffusivity of ~1 cm^{2}s^{-1} through the thermocline (Quay and Stuiver, 1980; Li et al, 1984), transport ~~from~~ to depths of hundreds of meters from the ocean surface requires times of years to decades. Exceptions are apparent in areas of upwelling, where water from depth ~~is~~ can be advected as well as mixed toward the surface in a matter of days (e.g., Tanhua and Liu 2015). Depletion of CCl_4 at depth would be in agreement with other reports suggesting a loss of CCl_4 in low oxygen waters (e.g., Lee et al, 1999), although the rate of a few percent depletion per year (e.g., Huhn et al, 2001, Min et al, 2010) at depth is still not sufficient to sustain the observed undersaturations at the surface. A number of depth profiles of CCl_4 along with CFCs 11 and 12 on our cruises suggest a sink for CCl_4 in intermediate waters, typically near the oxygen minimum (Fig. 6). The relationships of the relative saturations of

CCl_4 vs CFC-12 and apparent oxygen utilization (AOU) throughout the water column, where AOU is the difference between the calculated atmospheric equilibrium concentration of dissolved oxygen and the measured oxygen concentration, suggest a clear, though water-mass dependent, relationship between the ratio of CCl_4 saturation to that of CFC-12 and AOU, particularly in waters of low oxygen concentration (high AOU; Fig. 7). This invokes the possibility of CCl_4 degradation by microorganisms in oxygen-deficient waters.~~-~~ The actual mechanisms are not discernible from these data, nor is the degree of loss in waters of different oxygen content, though the loss would be consistent with anaerobic or heterotrophic metabolism. So, if exchange with deeper waters where CCl_4 is anaerobically degraded, presumably by microorganisms (e.g., Krone et al. 1991, Lee et al 1999, Tanhua et al. 1996), cannot account for widespread undersaturations in surface waters, then there must also be some mechanism for in situ removal in oxygenated surface water. With a calculated degradation time of ~2600 y, hydrolysis does not provide a removal rate that could balance air–sea exchange (e.g., Yvon-Lewis and Butler 2002, Jeffers et al. 1994), so that leaves us with invoking biological or other unknown mechanisms removing CCl_4 in well oxygenated surface waters. This is an area that requires further investigation, as there is no direct evidence to date for such pathways~~, microbial or otherwise~~ in the ocean, although there is evidence for microbial removal of CCl_4 in well oxygenated soils (e.g., Mendoza et al., 2011).

4.2 Estimating the Air–Sea Flux

4.2.1 Uncertainties

Because the observed undersaturations in surface waters appear somewhat independent of SST or surface biological activity, the major remaining variable in the distribution of the oceanic sink is the air sea exchange rate, driven largely by wind speed and not, for example, SST, as has been observed for CH_3CCl_3 and CH_3Br (e.g., Butler et al 1991, Yvon-Lewis et al., 1997). Our understanding of the dependence of air–sea exchange on wind speed has evolved substantially over time and studies over the past 15 years have been converging (Figure 8 and Wanninkhof et al. 2014). Perhaps the most influential of these is by Naegler et al. (2006), which was a re-evaluation of bomb $^{14}CO_2$ uptake that has led to substantially lower estimates of air–sea exchange (Sweeney et al. 2007;~~,~~ Wanninkhof et al. 2009; Wanninkhof, 2014). These newer studies lower the air–sea flux ~~by~~ ~~30–40%~~substantially relative to Wanninkhof (1992), which was based on earlier estimates of the ocean inventory of bomb and natural $^{14}CO_2$ (e.g., Broecker et al 1985), and which we used in previous assessments of the loss of atmospheric CCl_4 to the ocean (Yvon-Lewis and Butler, 2002). This~~ in turn~~change significantly decreases the estimated flux of CCl_4 and increases the calculated lifetime of the gas in the atmosphere with respect to loss to the ocean. To estimate overall flux uncertainties, we ~~added in quadrature the standard deviation of the mean exchange rate for CCl_4 based on the five air–sea exchange studies we've considered~~added in quadrature the value of 20% derived in Wanninkhof (2014) for uncertainty in K_w ~~(~30%; Table 2)~~ and the standard deviation of the CCl_4 flux ~~(~~(~14%; Table 4) for the four scenarios under one air–sea exchange relationship (~~Sweeney et al. 2007~~Wanninkhof, 2014). Other uncertainties are either captured within these ~~uncertainties~~ or comparatively insignificant in the calculations.

4.2.2 Air–Sea Flux and Lifetime

Propagating the rate constant for oceanic removal of atmospheric CCl_4 across the globe with consideration of parameters in Eq. 3 and the updated dependence of K_W on wind speed, our model derives a rate constant for uptake of atmospheric CCl_4 by the ocean that is highest where winds are strongest and turnover of surface waters fastest, but that is also influenced by the saturation anomaly value (Fig. 9). As noted in the Methods section, we used four approaches for estimating the overall removal of atmospheric CCl_4 by the global ocean, but our preferred approach ~~was u~~use~~d~~s ~~sing~~ the latitudinally binned, mean saturation anomalies along with the air–sea exchange relationship of ~~Sweeney~~ Wanninkhof~~et al.~~ (201~~4~~~~07~~). We note that we obtain the same results by simply using the median of all negative corrected saturation anomalies or by averaging fluxes from all approaches. (Note: Our original version of this paper (doi:10.5194/acp-2016-311) preferred the Sweeney et al. (2007) relationship for computing air-sea fluxes and subsequent lifetimes. We had selected that parameterization because it was formulated similarly to Wanninkhof (1992), which had been used in the earlier calculations of the ocean sink of CCl_4 (Yvon-Lewis and Butler 2002), accounted for the change in ocean bomb-^{14}C inventory, and was centered among the distribution of wind speed relationships considered (e.g., Figure 8). We have since updated that and prefer the Wanninkhof (2014) approach, which has all of these features, includes a rigorous evaluation of the biases and uncertainties in estimating air-sea exchange, and takes additional studies into account.)

Summing uptake across the world's oceans suggests that the oceanic sink represents a partial atmospheric lifetime of ~~209~~ 183 (~~157~~147~~–~~-~~313~~241) y, a number considerably longer than the 94 y of Yvon-Lewis and Butler (2002) used in the 2002–2014 WMO/UNEP Scientific Assessments of Ozone Depletion. ~~This reduction in estimated removal rate is largely a result of the change in our understanding of the air–sea exchange coefficient.~~ Though we have selected the latitudinally binned, global mean, corrected saturation anomaly as our best approach for interpreting the saturations, the difference among selected approaches is relatively small (Table 4). The scenario where we tested the extreme possibility of the Southern Ocean being 99% undersaturated south of 65°S changed the flux by about ~~3Gg~~ 3 Gg y^{-1} (a ~30% increase in uptake), but, given the observed undersaturations both north and south of 65°S where we obtained measurements, that scenario is unrealistic; it was run only to understand ~~extreme behaviour~~the limits of Southern Ocean influence. Barring that, and given the hemispheric asymmetries in wind speed and ocean area, the model calculates uptake by the ocean in the Southern Hemisphere that is ~~about 1.8 times~~twice that in the northern hemisphere (Table 4).

This updated estimate is based on four times as many observations than used in Yvon-Lewis and Butler (2002), which account for all seasons and cover almost all major ocean basins. The average saturation anomaly used in this study is 10-20% less than the average used in Yvon-Lewis and Butler (2002). Binning the surface data in our ~~chosen estimate~~ preferred approach (rather than applying a global mean anomaly as done before) to reflect better the actual distribution over the oceans accounts for another 10-20% decrease (Table 3). The model used by Yvon-Lewis and Butler (2002) was based the 2°x2° COADS data set for sea surface temperatures and wind speeds and our new estimate is based on a different, newer data set with 1°x1° bins. The mean or median wind speed for the 1°x1° data set is ~5% lower and winds were distributed differently than in the COADS data set. The most influential change, however, is the use of an updated air-sea exchange coefficient, based on a revised inventory of bomb-$^{14}CO_2$ (Naegler et al 2006, Wanninkhof, 2014). Yvon-Lewis and Butler (2002) used the Wanninkhof (1992) relationship, which was normalized to an earlier assessment of bomb-$^{14}CO_2$. We evaluated the impact of this change on CCl_4 flux over the ocean and determined that it alone accounts for a 24% lower flux with Wanninkhof (2014) than with Wanninkhof (1992). Additional reductions came from use of a simpler computational approach that differs from that of Yvon-Lewis and Butler (2002), which was designed for gases where in situ loss rates are known and which required estimates of mixed layer depth and loss during downward mixing through the ocean thermocline. The newly revised estimate for CCl_4 uptake provided here is based simply on the air-sea difference in partial pressure and the kinetics of air-sea exchange. It is more robust for this gas, for which there is little understanding of the loss ~~its~~ mechanisms~~ of loss~~, and suggests that the ocean sink is responsible for about 18% (vs. 32% previously) of the CCl_4 removed from the atmosphere.

5 Implications for atmospheric CCl_4

If we consider the revised oceanic sink derived here, the even weaker soil sink of 375 (288–536) y, and the partial lifetime for CCl_4 removal in the stratosphere of 44 (36–58) y, the mid-range estimate for the lifetime of CCl_4 in the atmosphere would be ~~33~~ 32 (2~~8~~6–43~~1~~) y, somewhat longer than the 26 (23–33) y used in the past four quadrennial assessments on ozone depletion and virtually identical to the 33 (28-41) years in the recent SPARC report on CCl_4 (Liang et al., 2016). ~~T~~As noted, the ocean is responsible for removing ~18~~6~~% of the CCl_4 in the atmosphere and the difference in uptake by the ocean in the two hemispheres is ~~about 3~~4±1 Gg y^{-1} for a 90 ppt atmosphere, so can account for only about 14~~0~~% of the current interhemispheric difference of 1.2 ppt in the atmosphere (Table 4). The interhemispheric difference in CCl_4 mixing ratio is still larger than can be accounted for based on known emissions. This suggests additional emissions in the northern hemisphere, as the larger oceanic sink reported here for the southern hemisphere cannot account for it. Nevertheless, the overall budget of atmospheric CCl_4 is now much closer to being balanced, owing largely to the findings presented in this paper and to the re-evaluation of the soil sink (Happell et al 2014, Rhew and Happell 2016).

Considering this new, longer lifetime for atmospheric CCl_4 and the atmospheric trends and distributions given in Carpenter and Reimann (2014), the remaining discrepancy between potential emissions, as ~~-~~suggested by data on CCl_4 production ~~for different uses~~ and destruction~~ quantities~~ reported to the UNEP Ozone Secretariat (e.g., Montzka and Reimann et al. 2011), and emissions computed from atmospheric lifetime, is now of the order of 10–20 Gg y^{-1}. While it is possible that historical natural fluxes could in part account for this additional source, no evidence exists for its presence in any significant quantity, especially given the small mole fractions measured in the oldest firn air. Butler et al. (1999) noted that the lowest firn air values were near detection limits in their samples and suggested that CCl_4, though at times not differing from zero, could have been as high as 5–10 ppt in the atmosphere before 1900; recent, unpublished firn air data we have obtained, however, suggest that it is more likely ~~around~~ between 3~~–~~ and 4 ppt in the late 19th century. Consequently, most of the emission discrepancy must arise from heretofore unquantified, anthropogenic sources, predominantly in the northern hemisphere, to be consistent with the observed rate of decline for the global mole fraction, given our understanding of the global lifetime and the mean hemispheric difference measured for atmospheric CCl_4 (e.g., Fraser et al. 2014, Liang et al 2014; Carpenter and Reimann et al., 2014). Only with an excess of northern hemispheric sources would the deficit identified in this study and its distribution be fully consistent with the observed rate of decline of CCl_4 in the atmosphere (1.2–1.4% y^{-1}), the observed interhemispheric gradient of ~1.2 ppt in recent years, and an interhemispheric exchange time of the order of 1 year (Carpenter and Reimann et al. 2014).

Acknowledgements. We thank the captains, officers, and crew of all of the ships involved during the entirety of this study and the staff who diligently assisted us over the years. Special thanks go to Debbie Mondeel, Caroline Siso, Andrew Clarke, James Johnson, David Wisegarver, and Fred Menzia of NOAA and its cooperative institutes, to Christine Harth, currently at Scripps Institution of Oceanography (SIO), and to Laurie Geller, currently at the US National Academy of Sciences. We also thank the referees, Ray Weiss of SIO, and Rik Wanninkhof of NOAA for valuable comments and discussions during review of this manuscript. This research could not have been done without the support of our various institutions and the programs through which they support science, including funds at various times from NASA's Upper Atmosphere Research Program, the US Department of Energy, NOAA's Climate Program Office, the Atmospheric and Geosciences sections of the National Science Foundation, and the National Research Council of the US National Academies of Science.

References

Bowyer, P, and Woolf, D.: Gas exchange and bubble-induced supersaturation in a wind-wave tank, J. Atmos. Oceanic Technol., 21, 1925-1935, 2004.

Broecker, W. S., Peng T.-H., Ostlund, G., and Stuiver, M.: The distribution of bomb radiocarbon in the ocean, J. Geophys. Res., 90, 6953–6970, 1985.

Bullister, J.L. and Lee, B.-S.: Chlorofluorocarbon-11 removal in anoxic marine waters, Geophys. Res. Lett., 22, 1893–1896, doi:10.1029/95GL01517, 1995.

Bullister, J. L. and Weiss, R. F.: Determination of CCl_3F and CCl_2F_2 in seawater and air, Deep Sea Res., 35, 839–854, doi:10.1016/0198-0149(88)90033-7, 1988.

Bullister, J.L. and Wisegarver, D.P.: The solubility of carbon tetrachloride in water and seawater, Deep Sea Research Part I: Oceanographic Research Papers, 45, doi:10.1016/S0967-0637(98)00017-Xt, 1285–1302, 1998.

Butler, J. H. and Rodriguez, J.M.: Methyl Bromide in the Atmosphere, in: The Methyl Bromide Issue, Bell, C.H., Price, N. and Chakrabarti, B., John Wiley & Sons, Ltd., Chichester, United Kingdom, 27–90, 1996.

Butler, J.H., Elkins, J.W., Brunson, C.M., Egan, K.B., Thompson, T.M., Conway, T.J. and Hall, B.D.: Trace gases in and over the West Pacific and East Indian oceans during the El Nino-Southern oscillation event of 1987, Air Resources Laboratory, Silver Spring, Maryland, NOAA Data Report ERL ARL-16, 1988.

Butler, J.H., Elkins, J.W., Thompson, T.M., Hall, B.D., Swanson, T.H. and Koropalov, V.: Oceanic consumption of CH_3CCl_3: Implications for tropospheric OH, J. Geophys. Res.-Atmos., 96, 22347–22355, doi:10.1029/91JD02126, 1991.

Butler, J. H., Elkins, J. W., Lobert, J. M., Montzka, S. A. and Koropolov, V.: Significant global loss of atmospheric CCl_4 to the ocean, AGU Fall Meeting, San Francisco, California, 1 December 1997, 1997.

Butler, J. H., Battle, M., Bender, M.L., Montzka, S.A., Clarke, A.D., Saltzman, E.S., Sucher, C.M., Severinghaus, J.P. and Elkins, J.W.: A record of atmospheric halocarbons during the twentieth century from polar firn air, Nature, 399, 749–755, doi:10.1038/21586, 1999.

Carlon, R.N., Papanastasiou, D. K., Fleming, E. L., Jackman, C. H., Newman, P. A. and Burkholder, J. B.: UV absorption cross sections of nitrous oxide (N2O) and carbon tetrachloride (CCl_4) between 210 and 350 K and the atmospheric implications, Atmospheric Chemistry and Physics, 10, 6137–6149, doi:10.5194/acp-10-6137-2010, 2010.

Carpenter, L.J., S. Reimann, J.B. Burkholder, C. Clerbaux, B.D. Hall, R. Hossaini, J.C. Laube, and S.A. Yvon-Lewis, Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, Chapter 1 in Scientific Assessment of Ozone Depletion: 2015, Global Ozone Research and Monitoring Project – Report No. 55, World Meteorological Organization, Geneva, Switzerland, 2014.

Fraser, P.J., Dunse B.L., Manning A.J., Walsh S., Wang R.H.J., Krummel P.B., Steele L.P., Porter L.W., Allison C., O'Doherty S., Simmonds P.G., Mühle J., Weiss R.F. and Prinn R.G.: Australian carbon tetrachloride emissions in a global context, Environmental Chemistry, 11, 77–88, 2014.

Happell, J., Y. Mendoza, and K. Goodwin (2014), A reassessment of the soil sink for atmospheric carbon tetrachloride based upon static flux chamber measurements, J. Atmos. Chem., 71(2), 113–123, doi:10.1007/s10874-014-9285-x.

Ho, D.T., Wanninkhof, R., Schlosser, P., Ullman, D.S., Hebert, D., and Sullivan, K.F.: 2011. Toward a universal relationship between wind speed and gas exchange: Gas transfer velocities measured with $^3He/SF_6$ during the Southern Ocean Gas Exchange Experiment. J. Geophys. Res. 116:C00F04 [doi:10. 1029/ 2010JC006854].

Huhn, O., Roether, W., Beining, P., Rose, H., (2001), Validity limits of carbon tetrachloride a an ocean tracer. Deep-Sea Res. 48, 2025–2049.

Jeffers, P.M., Coty, P., Luczak, S. and Wolfe, N.L.: Halocarbon hydrolysis rates-a search for ionic strength and heterogeneous effects, J. Environ. Sci. Heal. A, 29, 821–831, doi:10.1080/10934529409376074, 1994.

Johnson, J.E.: Evaluation of a seawater equilibrator for shipboard analysis of dissolved oceanic trace gases, Anal. Chim. Acta, 395, 119–132, doi:10.1016/S0003-2670(99)00361-X, 1999.

Kester, D. R.: Dissolved gases other than CO2, in: Chemical Oceanography, 2, Riley, J.P. and Skirrow, G., Academic Press, London, United Kingdom, 497–556, 1975.

Ko, P.A. Newman, S. Reimann, and S.E. Strahan (Eds), SPARC Report on the Lifetimes of Stratospheric Ozone-Depleting Substances, Their Replacements, and Related Species, SPARC Report No. 6, WCRP-15/2013.

Krone, U.E., Thauer, R.K., Hogenkamp, H.P., Steinbach, K.: Reductive formation of carbon monoxide from CCl_4 and FREONs 11, 12, and 13 catalyzed by corrinoids, Biochemistry, 30(10), 2713–9, 1991.

Krysell, M., Fogelqvist, E. and Tanhua, T.: Apparent removal of the transient tracer carbon tetrachloride from anoxic seawater, Geophys. Res. Lett., 21, 2511–2514, doi: 10.1029/94GL02336, 1994.

Laube, J. C., A. Keil, H. Bönisch, A. Engel, T. Röckmann, C. M. Volk, and W. T. Sturges (2013), Observation-based assessment of stratospheric fractional release, lifetimes, and ozone depletion potentials of ten important source gases, Atmos. Chem. Phys. 13(5), 2779–2791, doi:10.5194/acp-13-2779, 2013.

Lee, B.-S., Bullister, J.L. and Whitney, F.A.: Chlorofluorocarbon CFC-11 and carbon tetrachloride removal in Saanich Inlet, an intermittently anoxic basin, Mar. Chem., 66, 171–185, doi:10.1016/S0304-4203(99)00039-0, 1999.

Lee C.H., Lewis, T.A., Paszczynski, A., Crawford, R.L.: Identification of an extracellular agent [correction of catalyst] of carbon tetrachloride dehalogenation from Pseudomonas stutzeri strain KC as pyridine-2, 6-bis(thiocarboxylate), Biochem Biophys Res Commun., 261(3), 562–6, 1999.

Li, L-H., Peng, T-H., and Broecker, W.S. (1984), The average vertical mixing coefficient for the oceanic thermocline, Tellus 36B, 212-217.

Liang, Q., Newman, P. A., Daniel, J. S., Reimann, S., Hall, B. D., Dutton, G. and Kuijpers, L. J. M.: Constraining the carbon tetrachloride (CCl4) budget using its global trend and inter-hemispheric gradient, Geophys. Res. Lett., 41, 5307–5315, doi:10.1002/2014GL060754, 2014.

Liang, Q., Newman, P.A., Reimann S. (Eds.): SPARC Report on the Mystery of Carbon Tetrachloride. SPARC Report No. 7, WCRP-13/2016, 2016.

Liss, P.S. and Merlivat, L.: Air–sea gas exchange rates: Introduction and synthesis, in: The role of air–sea exchange in geochemical cycling/NATO ASI Series, Springer, Netherlands, 16–27 September 1985, 113–127, 1986.

Lobert, J.M., Butler, J.H., Geller, L.S., Yvon, S.A., Montzka, S.A., Myers, R.C., Clarke, A.D., and Elkins, J.W.: BLAST94: Bromine latitudinal air/sea transect 1994, Report on oceanic measurements of methyl bromide and other compounds, NOAA Tech. Memo. ERL CMDL-10, 39 pp., 1996.

Min, D.-H., Warner, M.J. and Bullister, J.L.: Estimated rates of carbon tetrachloride removal in the thermocline and deep waters of the East Sea (Sea of Japan), Mar. Chem., 21(1–4), doi: 10.1016/j.marchem.2010.03.008, 100–111, 2010

Mendoza, Y., Goodwin, K.D., and Happell, J.D.: Microbial removal of atmospheric carbon tetrachloride in bulk aerobic soils, Appl. Environ. Microbiol., 77, 5835-5841, 2011.

Mondeel, D.J., Butler, J.H., Montzka, S.A., Hall, B.D., King, D.B., Yvon-Lewis, S.A., Dutton, G.S., Thompson and T.M., Elkins, J.W.: Atmospheric Carbon Tetrachloride – A Conundrum?, American Geophysical Union, Fall Meeting 2003, San Francisco, California, 8 December 2003, A31D-0075, 2003.

Montzka, S. A., Reimann, S., Engel, A., Krüger, K., O'Doherty, S., Sturges, W.T., Blake, D., Dorf, M., Fraser, P., Froidevaux, L., Jucks, K., Kreher, K., Kurylo, M.J., Mellouki, A., Miller, J., Nielsen, O.-J., Orkin, V.L., Prinn, R.G., Rhew, R., Santee, M.L., Stohl, A. and Verdonik, D.: Ozone depleting substances (ODSs) and related chemicals, Chapter 1, in: Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project-Report No. 52, World Meteorological Organization, Geneva, Switzerland, 1.1–1.108, 2011.

Naegler, T., Ciais, P., Rodgers, K. and Levin, I.: Excess radiocarbon constraints on air-sea gas exchange and the uptake of CO2 by the oceans, Geophy. Res. Lett., 33, L11802, doi:10.1029/2005GL025408, 2006.

Nightingale, P.D., Malin, G., Law, C.S., Watson, A.J., Liss, P.S., Liddicoat, M.I., Boutin, J. and Upstill-Goddard, R.C.: In situ evaluation of air–sea gas exchange parameterizations using novel conservative and volatile tracers, Global Biogeochem. Cy., 14, 373–387, 2000.

Quay, P.D., and Stuiver, M. (1980), Vertical advection-diffusion rates in the oceanic thermocline determined from ^{14}C distributions, Radiocarbon, 22, 607-625.

Rhew, R. C. and Happell, J. D. (2016), The atmospheric partial lifetime of carbon tetrachloride with respect to the global soil sink, Geophys. Res. Lett., in print, 43, doi:10.1002/2016GL067839.

Samuels and Cox, 1988, Global Oceanographic Data Set Atlas, Climatologies, NOAA Geophysical Fluid Dynamics Laboratory/U.S. Department of Commerce. 1988. Research Data Archive at the National Center for Atmospheric Research, Computational and Information Systems Laboratory. http://rda.ucar.edu/datasets/ds279.0/. Accessed 08 OCT 1996.

Shapiro, S.D., Schlosser, P., Smethie Jr., W.M. and Stute, M.: The use of 3H and tritiogenic 3He to determine CFC degradation and vertical mixing rates in Framvaren Fjord, Norway, Mar. Chem., 59, 141–157, 1997.

Sturrock, G. A., Etheridge, D.M., Trudinger, C.M., Fraser, P.J. and Smith, A.M.: Atmospheric histories of halocarbons from analysis of Antarctic firn air: Major Montreal Protocol species, J. Geophys. Res., 107, 4765, doi:10.1029/2002JD002548, 2002.

Sweeney, C., Gloor, E., Jacobson, A.R., Key, R.M., McKinley, G., Sarmiento, J.L. and Wanninkhof, R.: Constraining global air-sea gas exchange for CO2 with recent bomb ^{14}C measurements, Global Biogeochem. Cy., 21, GB2015, doi:10.1029/2006GB002784, 2007.

Tanhua, T. and Liu, M.: Upwelling velocity and ventilation in the Mauritanian upwelling system estimated by CFC-12 and SF-6 observations, J Marine Syst, doi:10.1016/j.jmarsys.2015.07.002, 151, 57–70, 2015.

Tanhua, T. and Olsson, K.A.: Removal and bioaccumulation of anthropogenic, halogenated transient tracers in an anoxic fjord, Mar. Chem., 94, 27–41 doi:10.1016/j.marchem.2004.07.009, 2005.

Tanhua, T., Fogelqvist, E., and Basturk, O.: Reduction of volatile halocarbons in anoxic seawater, results from a study in the Black Sea, Marine Chemistry, 54, 159–170, 1996.

United Nations Environment Program: Montreal Protocol on Substances that Deplete the Ozone Layer, United Nations, Montreal, Québec, Canada, 1987.

United States Department of Energy, Carbon Dioxide Information and Analysis Center (CDIAC), World Ocean Circulation Experiment (WOCE) Repeat Section P-18, 1994: http://cdiac.ornl.gov/oceans/woce_p18s.html, Last Access 2008.

~~Volk, C. M., Elkins, J. W., Fahey, D.W., Dutton, G.S., Gilligan, J.M., Loewenstein, M., Podolske, J.R., Chan, K.R. and Gunson, M.R.: Evaluation of source gas lifetimes from stratospheric observations, J. Geophys. Res.-Atmos., 102, 25543–25564, doi:10.1029/97JD02215, 1997.~~

Wanninkhof, R.: Relationship between wind speed and gas exchange, J. Geophys. Res, 97, 7373–7382, 1992.

Wanninkhof, R., Asher, W.E., Ho, D.T., Sweeney, C. and McGillis, W.R.: Advances in quantifying air–sea gas exchange and environmental forcing, Annual Review of Marine Science, 1, 213–244, doi: 10.1146/annurev.marine.010908.163742, 2009.

Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean revisited, Limnol. Oceanogr.: Methods 12, 2014, 351–362, 2014.

WMO (World Meteorological Organization): Scientific Assesment of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project – Report No. 47, Geneva, Switzerland, 498 pp., 2003.

WMO (World Meteorological Organization): Scientific Assesment of Ozone Depletion: 2006, Global Ozone Research and Monitoring Project – Report No. 50, Geneva, Switzerland, 572 pp., 2007.

WMO (World Meteorological Organization): Scientific Assesment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project – Report No. 52, Geneva, Switzerland, 516 pp., 2011.

Yvon-Lewis, S.A. and Butler, J.H.: Effect of oceanic uptake on atmospheric lifetimes of selected trace gases, J. Geophys. Res.-Atmos., 107, 4414, doi:10.1029/2001JD001267, 2002.

Yvon-Lewis, S. A., King, D.B., Tokarczyk, R., Goodwin, K.D., Saltzman, E.S. and Butler, J.H.: Methyl bromide and methyl chloride in the Southern Ocean, J. Geophys. Res.-Oceans, 109, C02008, doi:10.1029/2003JC001809, 2004.

Table 1. Cruise details including season, ship, analytical technique used to measure CCl_4, water sampling technique, and color code for Figures 1 and 5. Gas chromatography with electron capture detection (ECGC) and gas chromatography with mass spectrometry (GCMS) are the analytical techniques.

Cruise Name	Dates	Ship	Analytical Technique	Sample Technique	Color Code
SAGA-2	1 May – 9 June 1987	R/V Akademik Korolev	ECGC	Equilibrator	Dark Gray
RITS89	6 Feb – 19 April 1989	R/V Discoverer	ECGC	Equilibrator	Light gray
SAGA-3	10 February – 12 April 1990	R/V Akademik Korolev	ECGC	Equilibrator	Blue
OAXTC	4 Aug – 21 October 1992	R/V John V. Vickers	ECGC	Equilibrator	Red
BLAST 1	28 January – 17 February 1994	R/V Discoverer	GCMS	Equilibrator	Navy
BLAST 2	18 October – 21 November 1994	R/V Polarstern	ECGC,GCMS	Equilibrator	Cyan
BLAST 3	26 February – 7 April 1996	R/V Nathaniel B. Palmer	GCMS	Equilibrator	Magenta
GasEx98	7 May – 27 July 1998	R/V Ronald H. Brown	GCMS	Equilibrator	Black
RB9906	14 September – 23 October 1999	R/V Ronald H. Brown	GCMS	Equilibrator	Purple
CLIVAR01	29 October – 13 December 2001	R/V Aurora Australis	GCMS	Surface Niskin	Maroon
A16N	4 June – 11 August 2003	R/V Ronald H. Brown	GCMS	Surface Niskin	Yellow
PHASE	22 May – 2 July 2004	R/V Wecoma	GCMS	Equilibrator	Brown
A16S	11 January – 26	R/V Ronald H. Brown	GCMS	Surface	Tan

	February 2005			Niskin	
GOMECC	10 July – 4 August 2008	R/V Ronald H. Brown	GCMS	Equilibrator	Dark Green
HalocAST-P	30 May – 27 April 2010	R/V Thomas Thompson	GCMS	Equilibrator and Surface Niskin	Orange
HalocAST-A	25 October – 26 November 2010	R/V Polarstern	GCMS	Equilibrator	Green

Table 2. Properties of CFC-11, CFC-12 and CCl_4 ~~shown as area weighted global means from our model and the Global Oceanographic Data Set Atlas, where the area-weighted global mean wind speed is 7.1 m s^{-1}, SST is~~ 18.9°C~~, and mixed layer depth is 66.5 m. The oceanic uptake rates and partial atmospheric lifetimes were calculated using the latitudinally binned median saturation anomalies (see Table 3)~~.

	CFC-11	CFC-12	CCl4
Physical Properties			
Diffusivity (D; 10^5 cm^2 s^{-1})	0.9076	0.9844	0.8465
(ΔD/D)/ΔT (% deg^{-1})	2.7	2.7	2.7
Solubility (S; m^3 atm mol^{-1})	0.1116	0.3983	0.0344
(ΔS/S)/ΔT (% deg^{-1}; 0–30°C)	3.9	3.6	4.1

	~~CFC-11~~	~~CFC-12~~	~~CCl4~~
~~Physical Properties~~			
~~Diffusivity (D; 10^5 cm^2 s^{-1})~~	~~0.9076~~	~~0.9844~~	~~0.8465~~
~~Solubility (S; m^3 atm mol^{-1})~~	~~0.1116~~	~~0.3983~~	~~0.0344~~
~~ΔS/ΔT (0–30°C)~~	~~0.0044~~	~~0.0144~~	~~0.0014~~
~~Trop. Mixing Ratio (ppt) (2012)~~	~~236.0~~	~~524.0~~	~~90.0~~
~~Calculated Properties~~			
~~**[Liss and Merlivat, 1986]**~~			
~~Gas Exchange Velocity (m d^{-1})~~	~~1.68~~	~~1.75~~	~~1.62~~
~~Ocean Uptake (Gg y^{-1}) (2012)~~	~~0.0~~	~~0.0~~	~~7.4~~
~~Partial Lifetime (y)~~	~~NA~~	~~NA~~	~~305~~
~~**[Wanninkhof, 1992]**~~			
~~Gas Exchange Velocity (m d^{-1})~~	~~3.51~~	~~3.65~~	~~3.39~~
~~Ocean Uptake (Gg y^{-1}) (2012)~~	~~0.0~~	~~0.0~~	~~15.6~~
~~Partial Lifetime (y)~~	~~NA~~	~~NA~~	~~145~~
~~**[Nightingale et al., 2000]**~~			
~~Gas Exchange Velocity (m d^{-1})~~	~~2.29~~	~~2.39~~	~~2.21~~
~~Ocean Uptake (Gg y^{-1}) (2012)~~	~~0.0~~	~~0.0~~	~~10.1~~
~~Partial Lifetime (y)~~	~~NA~~	~~NA~~	~~225~~
~~**[Sweeney et al., 2007]**~~			
~~Gas Exchange Velocity (m d^{-1})~~	~~2.43~~	~~2.53~~	~~2.34~~

~~Ocean Uptake (Gg y^{-1}) (2012)~~	~~0.0~~	~~0.0~~	~~10.8~~
~~Partial Lifetime (y)~~	~~NA~~	~~NA~~	~~210~~
~~[Wanninkhof et al., 2009]~~			
~~Gas Exchange Velocity (m d^{-1})~~	~~2.01~~	~~2.10~~	~~1.95~~
~~Ocean Uptake (Gg y^{-1}) (2012)~~	~~0.0~~	~~0.0~~	~~8.8~~
~~Partial Lifetime (y)~~	~~NA~~	~~NA~~	~~256~~

Table 3. Corrected saturation anomalies for 10 degree latitude-bins. Positive values not included (see text and Fig. 5).

Bin	**Assigned Latitude**	**mean**	**median**	**N**	**Standard Deviation**	**Standard Error**
< -65	-70	-7.40	-7.29	372	1.78	0.09
-55 to -65	-60	-4.16	-4.35	176	1.84	0.14
-45 to -55	-50	-5.40	-4.31	148	4.27	0.35
-35 to -45	-40	-7.94	-5.13	192	7.80	0.56
-25 to -35	-30	-7.31	-6.88	129	4.63	0.41
-15 to -25	-20	-7.24	-5.95	255	4.83	0.30
-5 to -15	-10	-8.20	-7.80	331	3.43	0.19
-5 to +5	0	-9.02	-8.53	723	4.71	0.18
5 to 15	10	-7.31	-6.97	722	3.64	0.14
15 to 25	20	-6.68	-5.46	539	4.92	0.21
25 to 35	30	-8.39	-6.33	530	8.00	0.35
35 to 45	40	-7.69	-6.97	656	5.46	0.21
45 to 55	50	-9.73	-6.29	880	7.32	0.25
> 55	60	-5.56	-5.06	41	2.67	0.42

Table 4. Oceanic uptake rates and partial atmospheric lifetimes with respect to ocean uptake from a 90 ppt atmosphere using the Wanninkhof (2014) air-sea exchange parameterization applied to the global median corrected saturation anomaly, global mean corrected saturation anomaly, median corrected saturation anomalies for 10° latitudinal bins, and mean corrected saturation anomalies for 10° latitudinal bins. The latitudinal bins are defined in Table 3. The variability in these results demonstrates the uncertainty associated with computational approach. The partial lifetimes are independent of atmospheric amount.

Computational Approach	**Global uptake (Gg/y)**	**NH uptake (Gg/y)**	**SH uptake (Gg/y)**	**τ_{ocean} (y)**	**$\tau_{NH,ocean}$ (y)**	**$\tau_{SH,ocean}$ (y)**
Global Median corrected Δ(%)	12.3	3.9	8.4	184	581	270
Global Mean corrected Δ(%)	14.4	4.6	9.8	157	492	231
Latitudinally binned, Median corrected Δ(%)	10.3	3.6	6.7	220	629	338
Latitudinally binned Mean corrected Δ(%)	12.4	4.4	8.0	183	514	283

~~Table 4. Calculated partial lifetimes and oceanic uptake rates from a 90 ppt atmosphere using the global median corrected saturation anomaly, global mean corrected saturation anomaly, median corrected saturation anomalies for latitude bins, and mean corrected saturation anomalies for 10° latitude bins. The latitude bins are defined in Table 2. The partial lifetimes are independent of atmospheric amount.~~

~~**Computational Approach**~~	~~**Global uptake (Gg/y)**~~	~~**NH uptake (Gg/y)**~~	~~**SH uptake (Gg/y)**~~	~~**τ_{ocean} (y)**~~	~~**$\tau_{NH,ocean}$ (y)**~~	~~**$\tau_{SH,ocean}$ (y)**~~
~~**Global MEDIAN corrected Δ(%)**~~	~~10.8~~	~~3.81~~	~~6.98~~	~~210~~	~~338~~	~~151~~
~~**Global MEAN corrected Δ(%)**~~	~~12.6~~	~~3.94~~	~~8.62~~	~~180~~	~~290~~	~~130~~
~~**Latitudinally binned**~~	~~9.0~~	~~3.12~~	~~5.83~~	~~252~~	~~365~~	~~192~~

~~MEDIAN corrected Δ(%)~~						
~~Latitudinally binned MEAN corrected Δ(%)~~	~~10.8~~	~~3.81~~	~~6.98~~	~~210~~	~~300~~	~~160~~

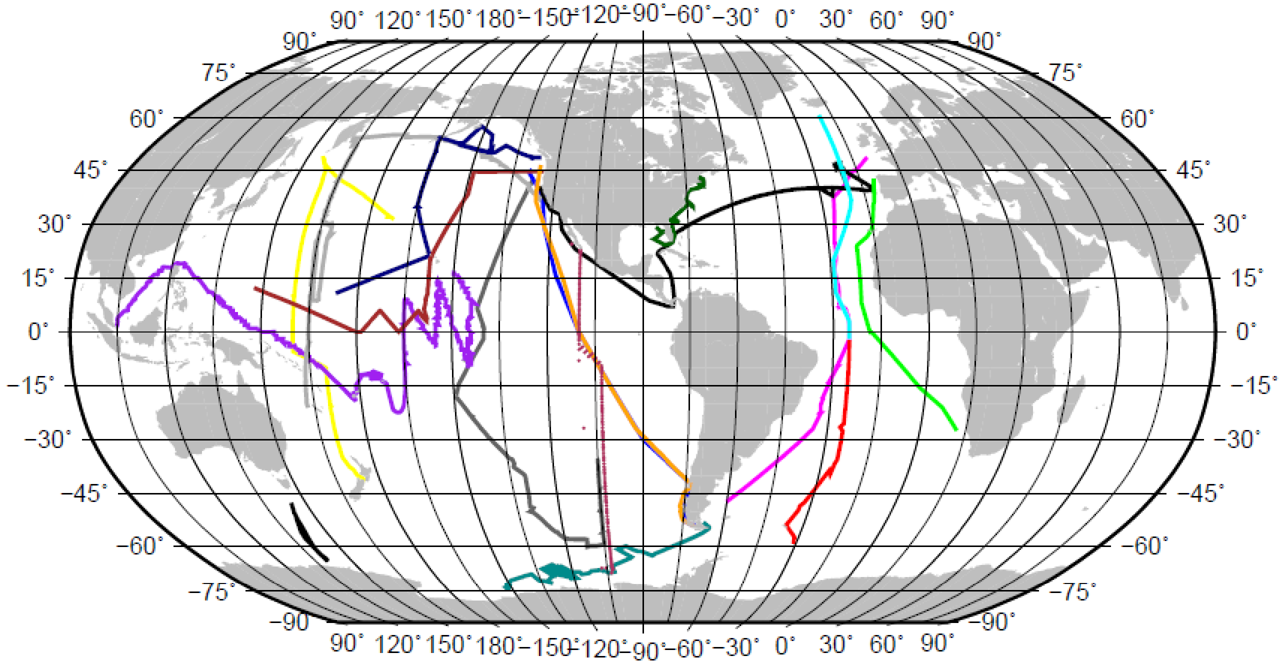


Figure 1. Research Cruises contributing to this study: SAGA-2, Leg I (1987, W Pacific; yellow), RITS89 (1989, E Pacific; orange), SAGA-3 (1990, Equatorial Pacific; lime) , OAXTC (1992 N. Pacific; light gray, part of WOCE P13), BLAST1 (1994, E Pacific; olive), BLAST2 (1994, Atlantic; cyan), BLAST3 (1996, Southern ocean; dark gray), GasEx98 (1998, N. Atlantic, Gulf of Mexico, NE Pacific; pink), RB9906 (1999, NE Pacific; cyan), CLIVAR01 SR3 (2001, Southern Ocean; brown) A16N (2003, N Atlantic; dark green), A16S (2005, S Atlantic; red), PHASE (2004, Central and North Pacific; purple), P18 (2008, Tropical and SE Pacific; dark green), GOMECC, Coastal NW Atlantic; olive), HalocAST-P (2010, E Pacific; blue, underlying BLAST 1, HalocAST-A (2009, E Atlantic; green).

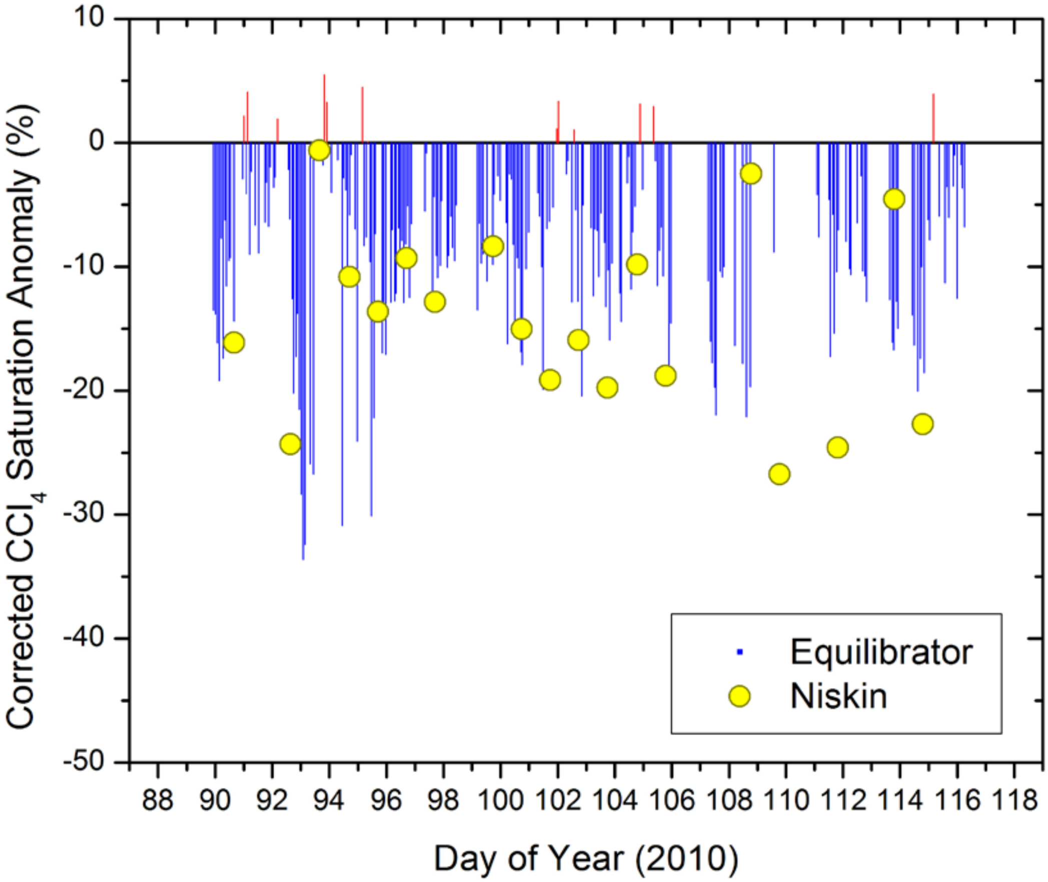
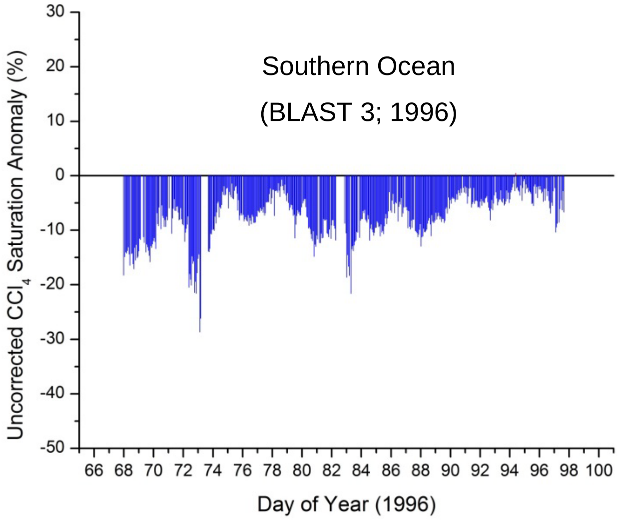
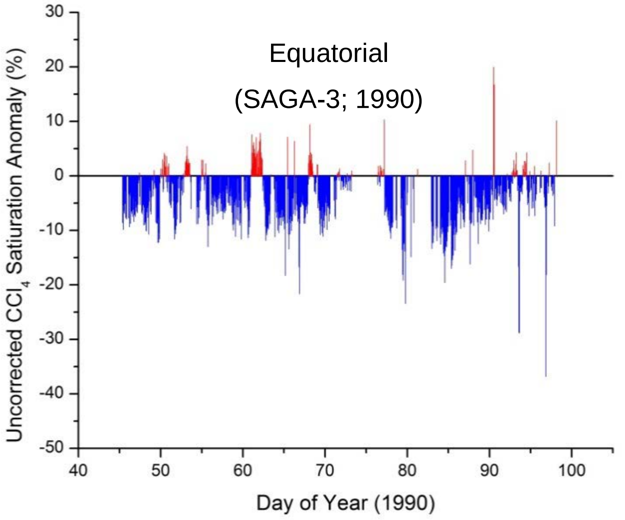
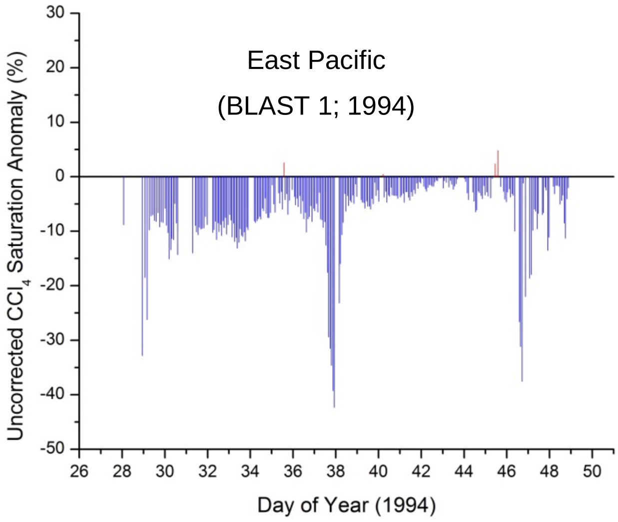
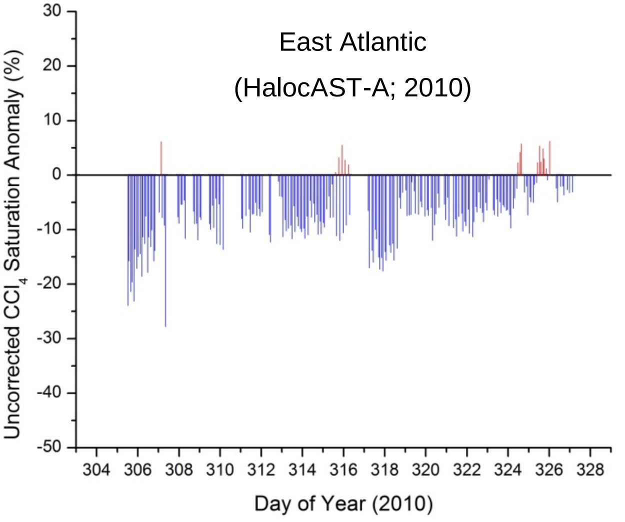


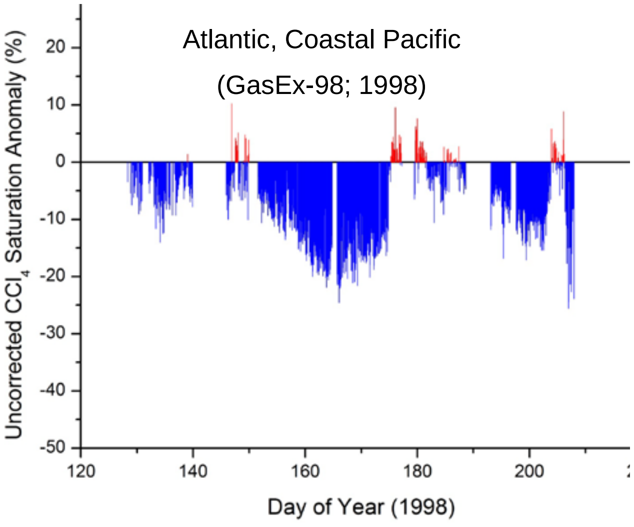
Figure 2. Corrected CCl_4 saturation anomalies determined from measurements of mole fractions in ambient air and air equilibrated with surface water in a Weiss-type equilibrator (blue bars) or extracted from near-surface grab samples (Niskin bottles; yellow points), showing no substantial bias in the equilibration technique for CCl_4 (Halocast-P, 2010; see Fig. 1, Table 1). Saturation anomalies in grab samples are calculated using solubility data from Bullister and Wisegarver, (1998). This good agreement suggests that the equilibrator does not bias results for CCl_4 and further suggests that the solubilities used to calculate saturation anomalies from discrete surface samples are correct.


Southern Ocean
(BLAST 3; 1996)
Uncorrected CCl$_4$ Saturation Anomaly (%)
30
20
10
0
-10
-20
-30
-40
-50
66 68 70 72 74 76 78 80 82 84 86 88 90 92 94 96 98 100
Day of Year (1996)


Equatorial
(SAGA-3; 1990)
Uncorrected CCl$_4$ Saturation Anomaly (%)
30
20
10
0
-10
-20
-30
-40
-50
40 50 60 70 80 90 100
Day of Year (1990)


East Pacific
(BLAST 1; 1994)
Uncorrected CCl$_4$ Saturation Anomaly (%)
30
20
10
0
-10
-20
-30
-40
-50
26 28 30 32 34 36 38 40 42 44 46 48 50
Day of Year (1994)


East Atlantic
(HalocAST-A; 2010)
Uncorrected CCl$_4$ Saturation Anomaly (%)
30
20
10
0
-10
-20
-30
-40
-50
304 306 308 310 312 314 316 318 320 322 324 326 328
Day of Year (2010)


Atlantic, Coastal Pacific
(GasEx-98; 1998)
Uncorrected CCl$_4$ Saturation Anomaly (%)
20
10
0
-10
-20
-30
-40
-50
120 140 160 180 200
Day of Year (1998)

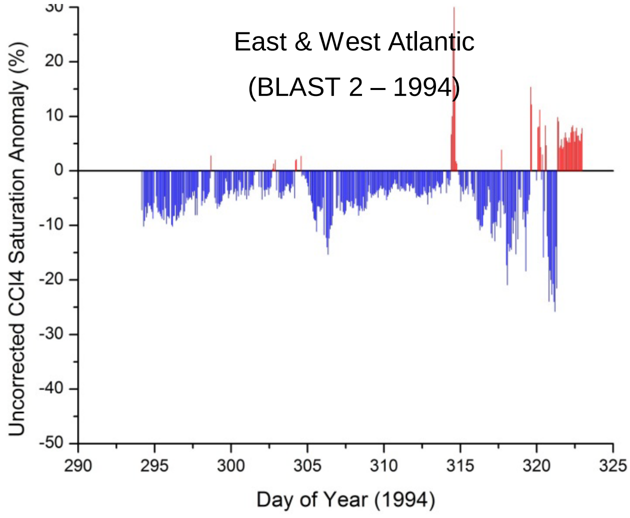

East & West Atlantic
(BLAST 2 – 1994)
Uncorrected CCl4 Saturation Anomaly (%)
30
20
10
0
-10
-20
-30
-40
-50
290 295 300 305 310 315 320 325
Day of Year (1994)

Figure 3. Regionally representative examples of observed (i.e., uncorrected) CCl_4 undersaturations from six cruises. Corrections for physical effects can alter these anomalies either direction, but largely make them more negative by 1–3%. Negative saturations are indicated with blue lines, positive with red lines.

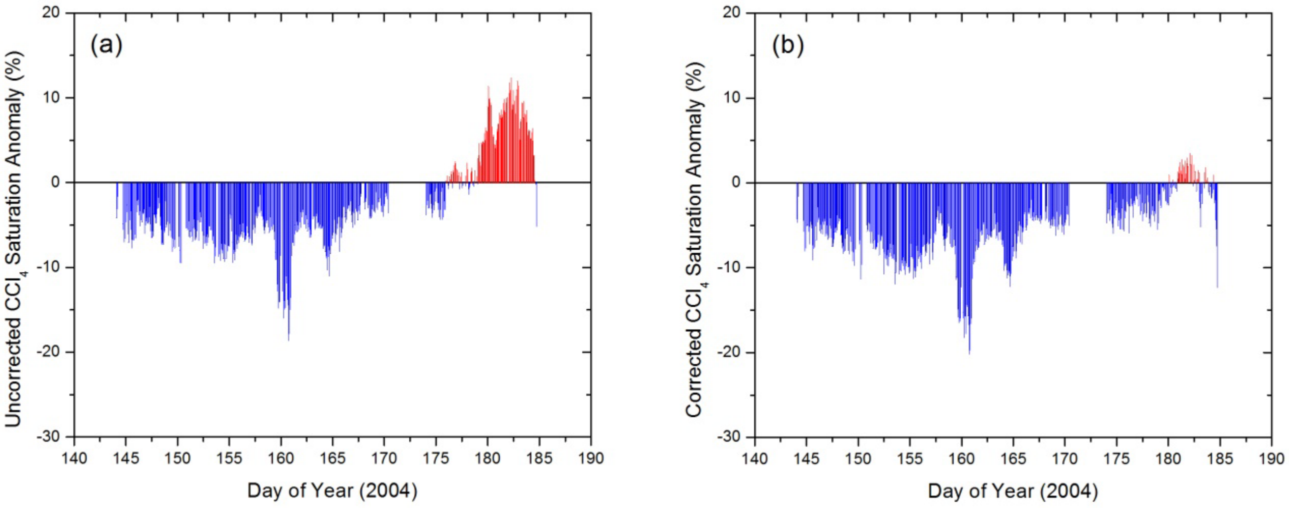


Figure 4. Observed (a) and corrected (b) CCl_4 saturation anomalies, central and NE Pacific, show the influence of physical processes on the observed values. Corrected saturation anomalies were derived by subtracting the observed anomalies of the largely unreactive gas of similar properties, CFC-11. Negative saturation anomalies are indicated with blue lines, positive with red lines.

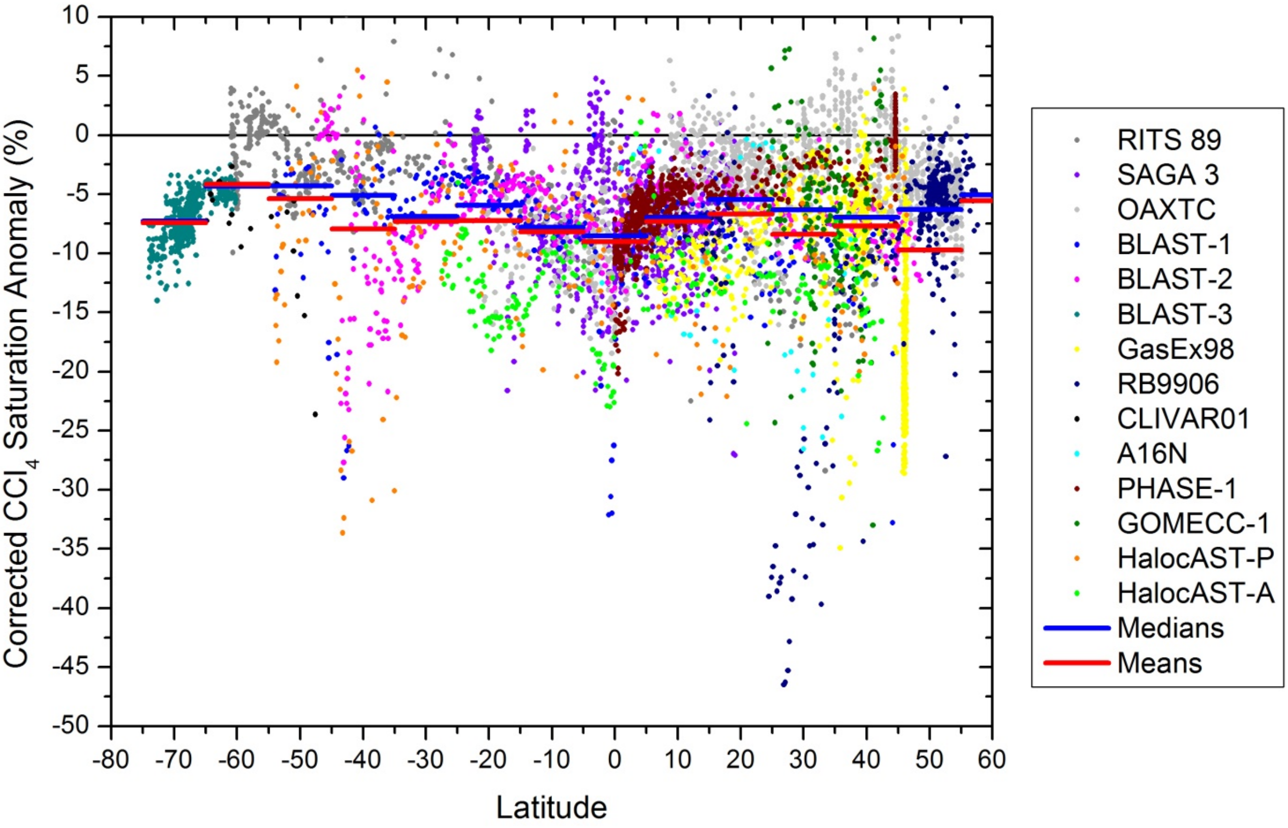


Figure 5. Zonal distribution of the corrected saturation anomaly from all cruises. Because observed positive values are likely the result of contamination, external influences, or sampling or analytical artifacts, means and medians for each 10° latitudinal band (shown as the red and blue bars) are computed from negative saturations only (See text).

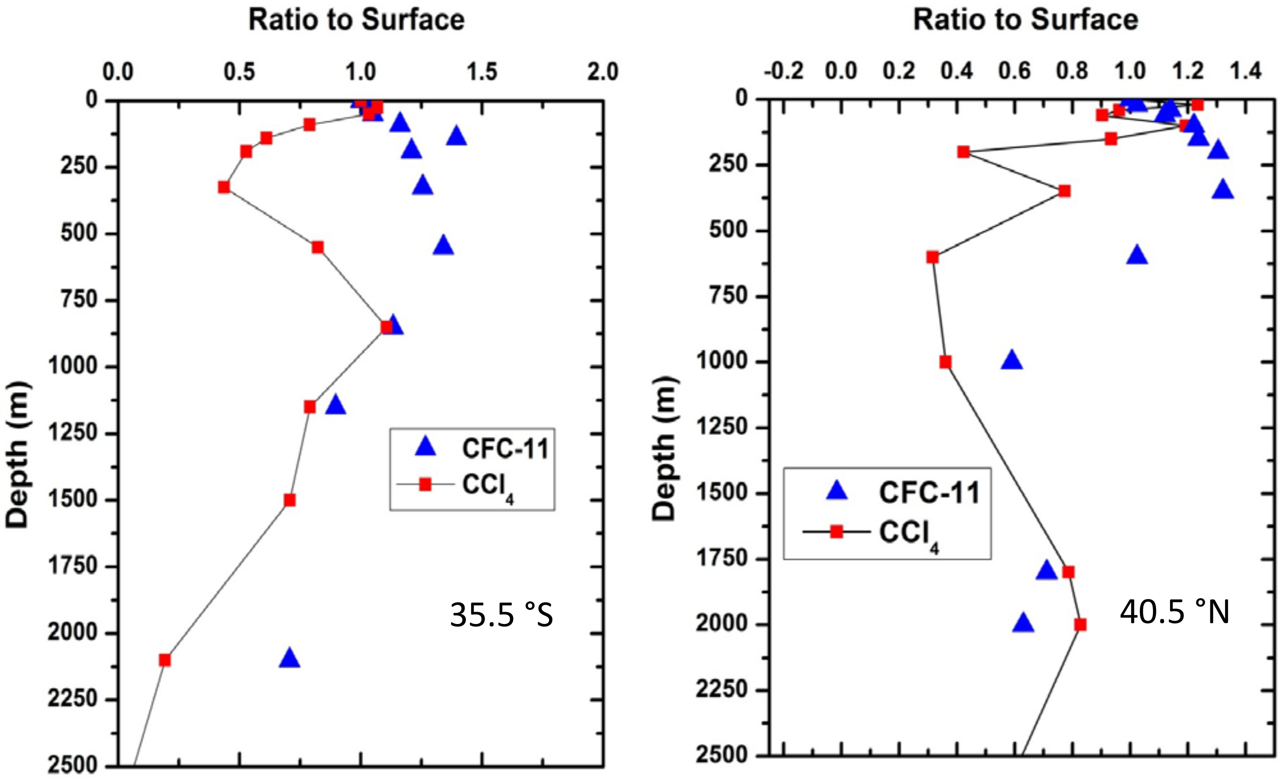


Figure 6. Depth profiles of the concentrations of CCl_4 and CFC-11, normalized to the surface value, strongly suggest consumption of CCl_4 in intermediate waters. If there were no in situ consumption and the distributions entirely a function of mixing and transport, the curves would be similar if not identical.

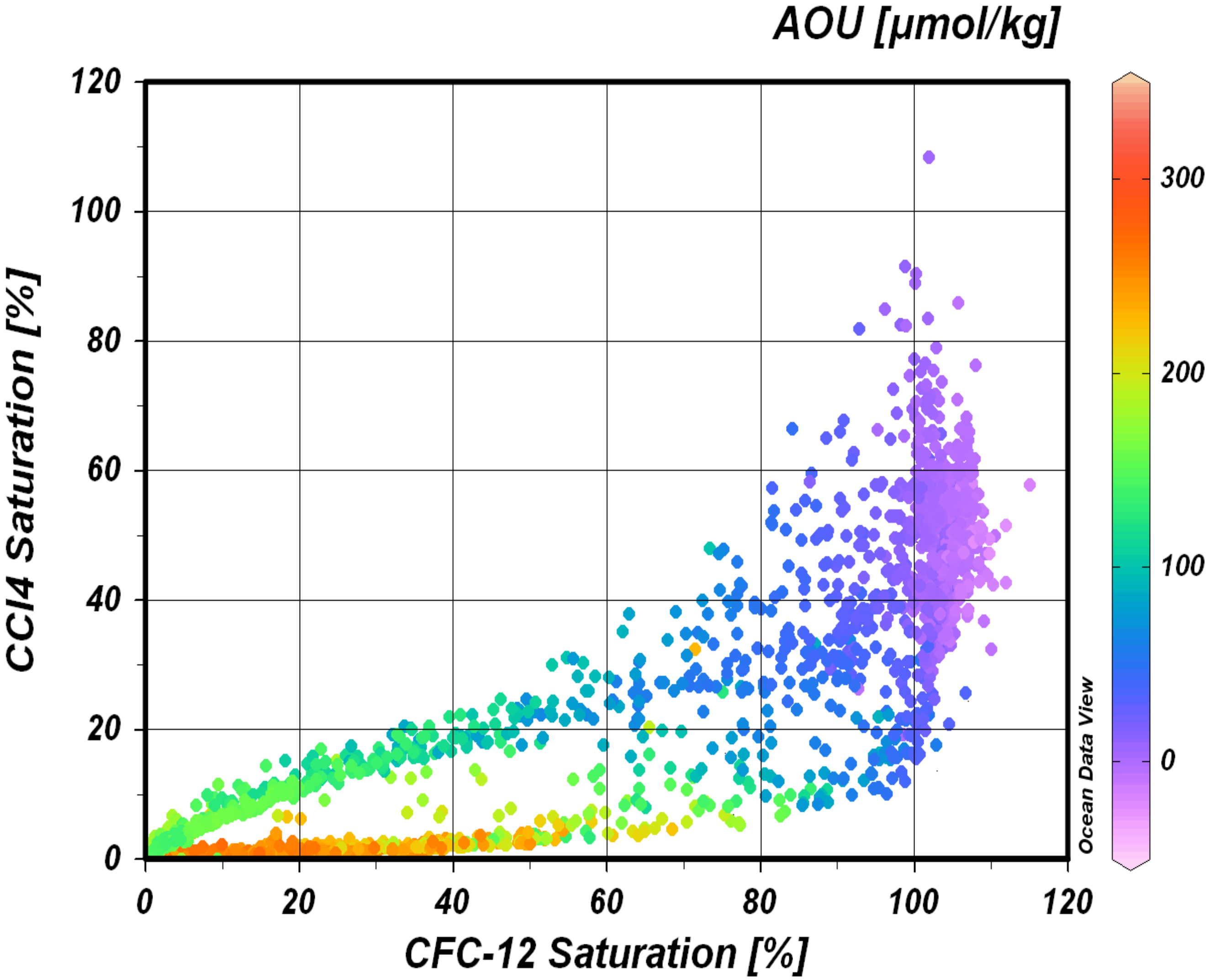
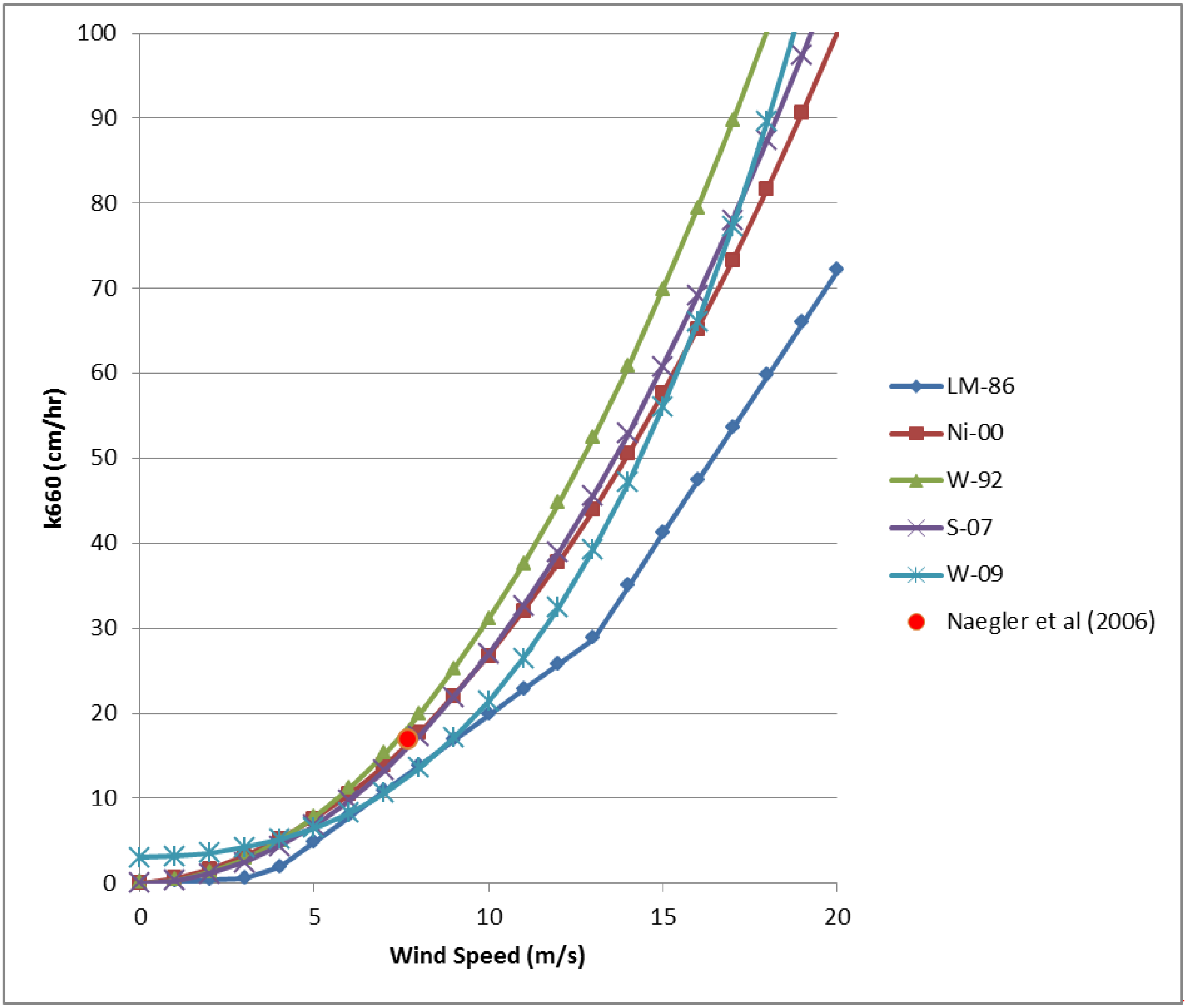


Figure 7. Measured saturations of CCl_4 and CFC-12 in sub-surface waters during the P18 cruise in the eastern Pacific as a function of Apparent Oxygen Utilization (AOU). Each point represents a single sample extracted from a Niskin bottle and analysed by electron-capture gas chromatography. Points are colored according to the AOU in each measured sample.


100
90
80
70
60
50
40
30
20
10
0
k660 (cm/hr)
0
5
10
15
20
Wind Speed (m/s)
LM-86
Ni-00
W-92
S-07
W-09
Naegler et al (2006)

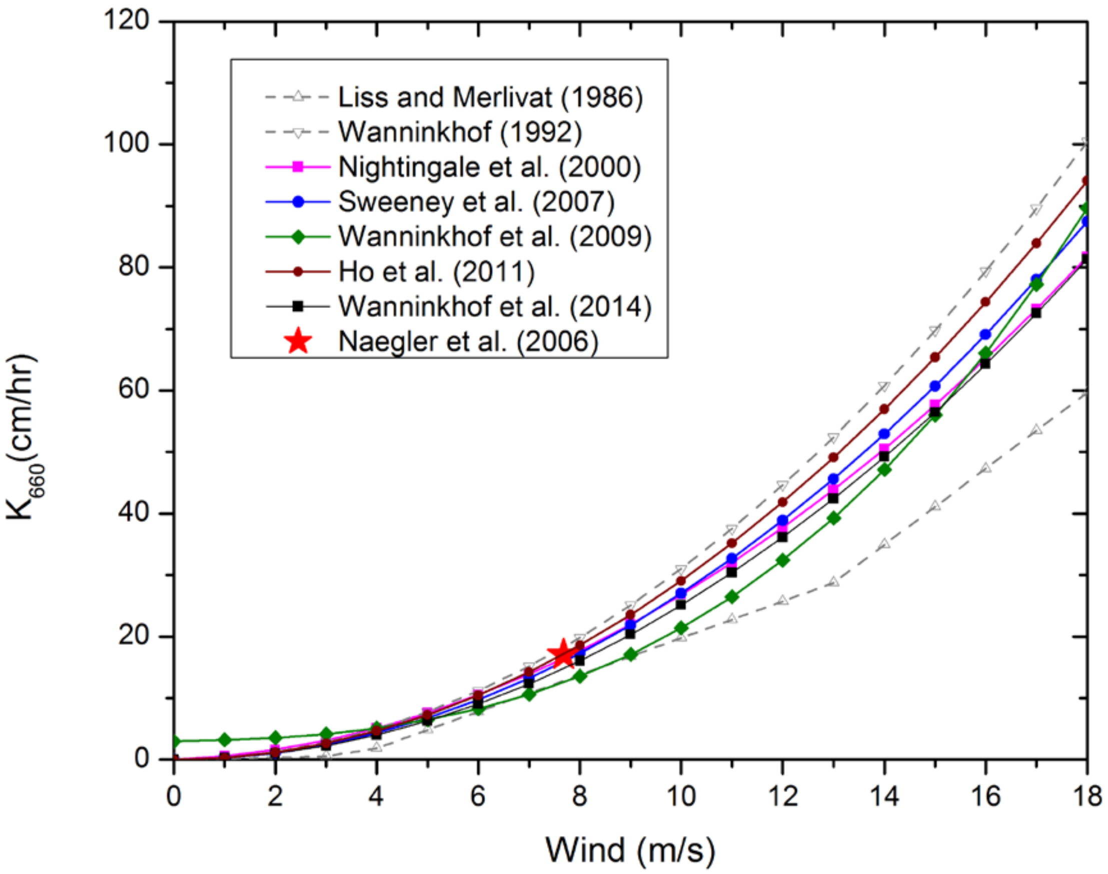


Figure 8. Various wind speed relationships for the air sea exchange velocity (~~k660~~$K_{w,660}$) determined in previous studies. Curves from each of these studies were normalized to CO$_2$, but as shown here, have been adjusted to represent CCl$_4$ according to its Schmidt number, which, a function of viscosity of the medium and diffusivity of the gas, is largely a function– of sea surface temperature.

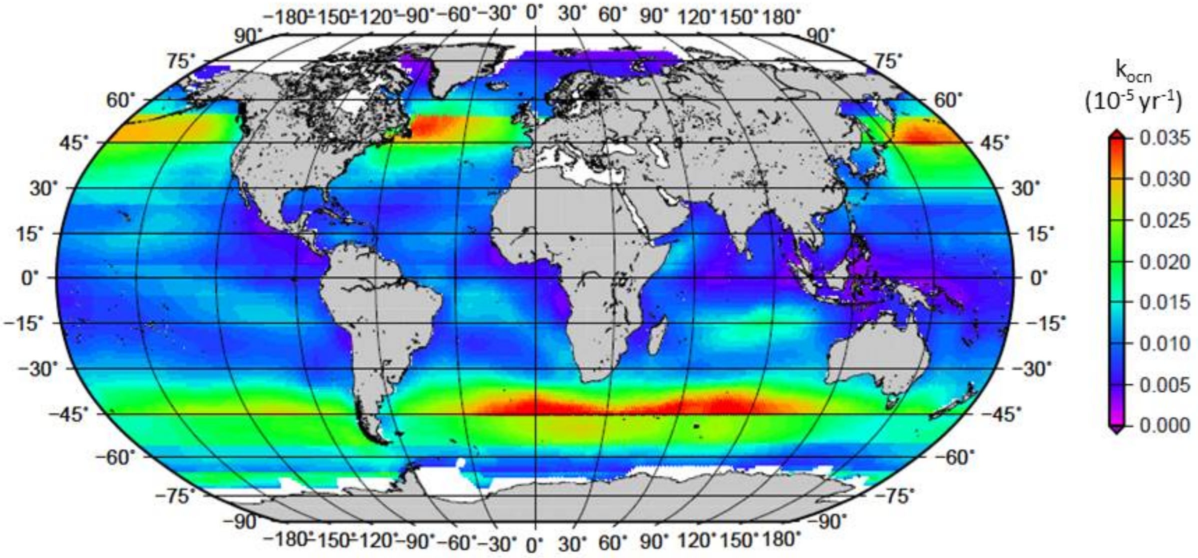


Figure 9. Global distribution of the oceanic uptake rate constant ($k_{ocn,i}$) based on the mean zonal saturation anomalies (Figure 5, Table 3) and calculated monthly air-sea exchange rates and other parameters given in Eq. 3 for 1° x 1° cells of the Global Oceanographic Data Set Atlas, Climatologies (Samuels and Cox 1988) . Because the saturation anomaly is largely similar among zonal regions of the ocean, variability in removal of CCl_4 from the atmosphere is controlled primarily by wind speed, which is highest in higher latitudes of both hemispheres.