

Evaluating Oceanic Uptake of Atmospheric CCl₄: A Combined Analysis of Model Simulations and Observations

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Key Points:

- New estimate of ocean uptake of atmospheric CCl₄ derived using an ocean biogeochemical model and global databases of CCl₄ measurements
- Best estimate of ocean CCl₄ uptake is 20.1 Gg y⁻¹ (16.6 – 22.7), with a corresponding partial atmospheric lifetime with respect to ocean uptake of 124 (110 – 150) years
- Estimated ocean CCl₄ uptake is larger than recent estimates and implies a larger missing source to the atmosphere

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Abstract

We provide new estimates of the air-sea flux of CCl_4 using simulations from a global ocean biogeochemistry model (NEMO-PlankTOM) in combination with depth-resolved CCl_4 observations from global oceanic databases. Estimates of global oceanic CCl_4 uptake are derived from a range of model analyses, including prescribed parameterizations using reported values on hydrolysis and degradation, and analyses optimised using the global observational databases. We evaluate the sensitivity of our results to uncertainties in air-sea gas exchange parameterization, estimation period, and circulation processes. Our best constrained estimate of ocean CCl_4 uptake for the period 1996-2000 is 20.1 Gg y^{-1} (range $16.6 - 22.7$), corresponding to estimates of the partial atmospheric lifetime with respect to ocean uptake of 124 (110 – 150) years. This new oceanic lifetime implies higher emissions of CCl_4 than currently estimated and therefore a larger missing atmospheric source of CCl_4 .

Plain Language Summary

Carbon tetrachloride (CCl_4) is a trace-gas emitted to the atmosphere during the industrial manufacture of refrigerants and solvents. CCl_4 is also an ozone depleting agent affecting loss of the atmosphere's protective ozone layer, and CCl_4 emissions are now controlled by the Montreal Protocol. However, recent analyses of observed atmospheric CCl_4 concentration conclude that the current rate of atmospheric decline is slower than expected, and inconsistent with recent estimates of CCl_4 emissions to and removal from the atmosphere. Estimated oceanic uptake of CCl_4 has been noted as potentially the most uncertain of the atmospheric loss processes, and here we provide new quantification of this flux. Our methodology employs a novel approach and uses a global ocean biogeochemistry model which includes representation of known physical and biogeochemical processes influencing oceanic CCl_4 uptake, together with a compiled global ocean database of CCl_4 observations. The

observational database is used to evaluate model simulations, and to derive optimised estimates of the oceanic uptake flux by minimizing the discrepancies between the model and observations. We also evaluate the sensitivity of our estimates of ocean CCl₄ uptake to known uncertainties in the model representation of processes, including air-sea gas transfer and oceanic chemical and biogeochemical loss. Our best constrained estimate of ocean CCl₄ uptake for the 1996-2000 period is 20.1 Gg y⁻¹ (range 16.6 – 22.7), which is greater than previous recent estimates, and implies a larger missing source to the atmosphere of CCl₄.

1. Introduction

1.1 Atmospheric CCl₄ and estimates of partial lifetimes

Atmospheric carbon-tetrachloride (CCl₄) is a significant ozone depleting substance [Carpenter and Reimann, 2014] used in the 20th century manufacture of refrigerants and solvents. The production of CCl₄ for emissive uses is controlled by the Montreal Protocol and subsequent amendments. Analysis of firm air samples suggests CCl₄ was very low in concentration or absent in the pre-20th century atmosphere [Butler et al. 1999]. Emission to the atmosphere commenced in the early 1920s and atmospheric concentrations increased in subsequent decades, peaking in 1991 (global average ~104 ppt) and then declining [Bullister, 2015].

The observed rate of decline in atmospheric CCl₄ in recent decades however, is not consistent with estimates of emission to, and removal from the atmosphere [Montzka et al. 2011, Carpenter and Reimann 2014]. Emissions derived from reported production are lower than “top-down” estimates based on atmospheric measurements and knowledge of CCl₄ loss processes. The 2016 SPARC Report on the Mystery of CCl₄ [Liang et al. 2016] identified a number of additional sources, including unreported inadvertent emissions and legacy emissions from contaminated sites and landfill [Fraser et al. 2014], but discrepancies still remain between bottom-up and top-down estimates.

CCl₄ is removed from the atmosphere by stratospheric photolysis [Burkholder et al., 2013], and uptake by the ocean [Krysell et al, 1994, Butler et al. 1993, 2016] and soils [Happell and Roche, 2003]. Liang et al. [2014] used available estimates of atmospheric partial lifetimes for photolysis (47 years), oceanic uptake (79 years) and soil uptake (201 years) to calculate a top-down estimate of net emission for the 2007-2012 period of 39 (34-45) Gg year⁻¹, and an associated total atmospheric lifetime of 35 (32-37) years. The 2016 SPARC Report [Liang et al. 2016] provided revised estimates of partial atmospheric lifetimes for ocean uptake (210 (157-313) years) and soil uptake (375 (288-536) years). The oceanic partial lifetime was further revised by the original authors to 183 (147–241) years [Butler et al. 2016, hereinafter B2016], yielding a total atmospheric lifetime estimate of 32 (26-43) years.

These updates have reduced, but not eliminated, the discrepancy between top-down and bottom-up estimates of CCl₄ emissions [Liang et al. 2016]. A recent atmospheric model intercomparison [Chipperfield et al. 2016] evaluated the influence of CCl₄ sources and sinks on the estimated atmospheric lifetime of CCl₄, noting that uncertainty in estimated oceanic uptake of CCl₄ is potentially the most significant influence on estimates of atmospheric CCl₄ decay, and called for an improved quantification of this flux and its associated partial atmospheric lifetime.

1.2 Oceanic CCl₄

CCl₄ is soluble in seawater [Bullister and Wisegarver, 1998], and its oceanic uptake is driven by the disequilibrium between CCl₄ partial pressures in the respective atmospheric and oceanic environments [B2016]. The distribution of CCl₄ in surface waters and the ocean interior is controlled by a combination of processes including air-sea gas exchange, circulation and water mass mixing, chemical hydrolysis [Jeffers et al. 1996], and degradation in the upper ocean (presumed to be biologically mediated) [Wallace et al. 1992, B2016].

Information on the non-conservative nature of CCl₄ in seawater has accumulated as analyses of

oceanic CCl₄ measurements have identified CCl₄ depletion (in comparison to halocarbons such as CFC-11 and CFC-12) in a range of oceanic environments. These include measurements from sub-oxic and anoxic regions [Lee et al. 1999, Tanhua et al. 1996, Krysell et al. 1994, Min et al. 2010 and references therein], oxygenated high-latitude waters [Meredith et al. 1996], and oxygenated thermocline waters in the East Sea of Japan [Min et al. 2010]. Wallace et al. [1994] analyzed measurements from the South Atlantic and noted highest depletions associated with low oxygen waters, but also throughout the thermocline.

At present there is relatively little quantitative information on oceanic CCl₄ removal processes, however various mechanisms have been proposed. Temperature-dependent chemical hydrolysis is a known loss process [Jeffers et al. 1996], however estimated loss rates are noted to be insufficient to support the observed depletions [Huhn et al. 2001]. Alternative CCl₄ depletion processes include temperature-dependent chemical reactions [Wallace et al. 1994], bacterially-mediated removal [Lee et al. 1999, Wallace et al. 1994], and scavenging associated with sinking organic matter [Wallace et al. 1994, Krysell and Wallace 1988]. Observed correlations between Apparent Oxygen Utilization (AOU) and relative CCl₄ undersaturations [e.g., B2016] suggest biologically-mediated CCl₄ loss in low-oxygen waters, though the specific mechanism remains unidentified [Yvon-Lewis and Butler 2002, Min et al. 2010 and references therein].

1.3 Aims of this Analysis

Global oceanic uptake of atmospheric CCl₄ has previously been quantified by analysis of upper ocean measurements in combination with process parameterizations [Yvon-Lewis and Butler, 2002; B2016]. Yvon-Lewis and Butler [2002] employed a 1-D mixed-layer model, which included representation of air-sea fluxes and thermocline diffusion together with presumed chemical and biological degradation (“eddy-degradation”, Johnson, 1981). This was applied to a gridded (2° x 2°) data-set of surface-ocean properties (e.g., sea surface temperature, salinity,

windspeed) to derive a global average estimate of partial lifetime with respect to ocean uptake (τ_{oc}). The recent analysis of B2016, uses CCl_4 measurements from 16 research cruises together with air-sea gas exchange parameterizations, to derive estimates of global ocean uptake and associated partial lifetime, but does not account for eddy-degradation. B2016 also employ oceanic CFC-11 measurements to account for physical influences (e.g., bubble dissolution, radiative heating and cooling) on measured CCl_4 saturation anomalies, and derive ‘corrected’ CCl_4 saturation anomalies that more accurately represent in-situ oceanic loss processes.

In this analysis we provide new estimates of the air-sea flux of CCl_4 and its associated partial atmospheric lifetime, using simulations from a global ocean biogeochemistry model (NEMO-PlankTOM) in combination with depth-resolved CCl_4 observations from global data repositories (section 2). We present estimates of ocean CCl_4 uptake derived from a range of model sensitivity analyses including: (a) parameterizations using reported literature values on hydrolysis and degradation rates; (b) model analyses optimized using data from global CCl_4 databases, and also corrected for physical influences using concurrent CFC-11 measurements; and (c) evaluation of the sensitivity of results to parameterization of air-sea gas exchange. We derive associated estimates of the atmospheric partial lifetime of CCl_4 with respect to oceanic removal, report on the uncertainties, and discuss implications for estimates of the atmospheric total lifetime of CCl_4 .

2. Methods and Model Configuration

2.1 Overview

Our methodology involves the development and optimization of model simulations of oceanic CCl_4 , with the aim of quantifying the global air-sea flux. The analysis incorporates oceanic measurements of CCl_4 and CFC-11 from global data repositories (section 2.2) in the optimization. The CCl_4 model development is presented in section 2.3. Section 2.4 outlines the

calculation of optimized estimates of oceanic CCl₄ degradation and air-sea fluxes, and section 2.5 describes sensitivity analyses exploring uncertainties in our model assumptions. Section 2.6 outlines the derivation of partial atmospheric lifetime with respect to ocean uptake. Results from our analyses are summarized in Table 1 and discussed in section 3.

2.2 Oceanic observations of CCl₄ and CFC-11

To support model evaluation and optimization, we compiled databases of oceanic CCl₄ and CFC-11 observations, incorporating measurements reported in data repositories and by individual investigators. For CCl₄, this includes measurements from the following sources, (*n* represents the number of individual measurements in each repository) : (i) GLODAPv2 (Olsen et al. 2016, *n*=43112); (ii) CARINA (Key et al. 2010, *n*=25034); (iii) PACIFICA (Suzuki et al. 2013, *n*=634); (iv) NOAA-GMD (Butler et al. 2016, *n*=3147); (v) Messias (pers. comm.) (*n*= 1693); (vi) Carpenter (pers. comm.) (*n*=1156). Measurements reported in more than one repository were only included once in the compilation. Consistency was ensured by converting all measurements to common concentration units (pmol L⁻¹) using the solubility relationships of Bullister and Wisegarver [1998]. The compiled set of CCl₄ measurements span the period 1987-2013, and the median year of observation is 1998. To enable a consistent comparison with modeled CCl₄, the compiled data were spatially gridded to the World Ocean Atlas (WOA) [2009] grid (1° × 1° × 33 depths), and aggregated to monthly timescales. This re-gridded CCl₄ database has *n*=32636 observations (1987-2013 period), and is used in the model analysis and optimization sections of 2.3, 2.4 and 2.5. We use two versions of the observational database: (i) an interannually-varying dataset spanning 1987-2013, at monthly resolution, and (ii) an annual climatology with monthly resolution constructed as an average over all years.

We also compiled a CFC-11 database combining data from GLODAPv2 ($n=315246$), CARINA ($n=86051$), NOAA-GMD [B2016] ($n=3145$), PACIFICA ($n=78244$) and M.J. Messias [pers. comm] ($n=1693$). Following regridding to the WOA [2009] grid, the number of coincident datapoints between the gridded CCl_4 and CFC-11 databases (i.e., reporting both species) is $n=28240$. This common database is employed in the sensitivity analyses and optimization of section 2.5, which use CFC-11 measurements to account for physical influences on oceanic CCl_4 .

2.3 Ocean Model Simulations

2.3.1 : Ocean Biogeochemistry Model

We employ the NEMO-PlankTOM5 ocean biogeochemistry model [Buitenhuis et al. 2013] embedded in the global ocean general circulation model NEMO v2.3 [Madec and Imbard 1996; Madec 2008]. Parameterized nutrient biogeochemistry is based on the PISCES model [Aumont and Bopp, 2006], and PlankTOM been extended to include representation of ocean ecosystem processes [Le Quere et al. 2005] and biogeochemical cycling of soluble gases [Vogt et al. 2010, Suntharalingam et al. 2012, Andrews et al. 2017, Buitenhuis et al. 2018]. For this study the model is employed at a horizontal resolution of $\sim 2^\circ$ at mid-latitudes, varying to higher latitudinal resolution of $\sim 0.2^\circ$ in equatorial and polar latitudes. The model has 31 vertical levels, with resolution varying from 10m in the upper 100m, to 500m below 2 km depth. Surface meteorological forcing uses daily values from the NCEP reanalyses [Kalnay et al. 1996], and model initialization of biogeochemical fields uses data from the World Ocean Atlas 2005 [Garcia et al. 2006] and GLODAP [Key et al. 2011], and follows the methodology of Buitenhuis et al. [2013]. Ocean model CCl_4 and CFC-11 simulations are subject to the time-varying atmospheric mixing-ratio history of Bullister [2015] (see Figure 1.1 for CCl_4) which extends the data record of Walker et al. [2000], and its 2009 update (bluemoon.ucsd.edu/pub/cfchist).

Model results are regridded to the WOA grid of section 2.2 for consistent comparison with observations.

2.3.2 CCl₄ and CFC-11 simulations

CCl₄ and CFC-11 are simulated as non-conserved tracers in the NEMO-PlankTOM5 model, following methods for soluble gases [Suntharalingam et al. 2012, Andrews et al., 2017].

Modelled CCl₄ and CFC-11 concentrations are controlled by ocean circulation and gas-exchange at the air-sea interface. CCl₄ is also subject to loss processes in the ocean interior (section 2.3.4). Equation 1 outlines the general form of the modeled CCl₄ tracer equation. Here V represents the 3-D velocity vector, D represents the ocean diffusivity tensor, and the $SMS[CCl_4]$ component accounts for local sources and sinks.

Eqn. 1:

$$\frac{\partial[CCl_4]}{\partial t} = -V \cdot \nabla[CCl_4] + \nabla \cdot (D \cdot \nabla[CCl_4]) + SMS[CCl_4]$$

Air-sea exchange of CCl₄ is included in the SMS term when Equation 1 is applied in the surface layer of the ocean model (section 2.3.3). In the ocean interior, $SMS[CCl_4]$ represents CCl₄ loss via chemical hydrolysis and biologically-mediated degradation (section 2.3.4).

2.3.3 Gas-exchange Parameterizations

Specification of the air-sea flux of CCl₄ follows standard methodology for trace-gases (e.g., Wanninkhof [2014]) where the bulk flux (F_A) for a species A , is estimated as a product of the gas-transfer velocity k , the solubility of the gas K_0 , and the partial pressure difference across the air-sea interface ($pA_{atm} - pA_{water}$).

Eqn. 2

$$F_A = k K_0 (pA_{atm} - pA_{water})$$

We employ the formulation of Sweeney et al. [2007] for the gas-transfer velocity k . This formulation optimizes the gas-exchange coefficient using the ocean ¹⁴C inventory and windspeeds from the NCEP reanalyses [Kalnay et al. 1996]; its use also enables consistency

with the NCEP wind product used for our NEMO-PlankTOM5 simulations (section 2.3.1). The parameterization of K_0 , the CCl_4 solubility in sea-water, is taken from Bullister and Wisegarver [1998].

Eqn. 3

$$k = 0.27 \langle U^2 \rangle (Sc/660)^{-0.5}$$

$\langle U^2 \rangle$ represents the square of the averaged 10m winds (U_{10}), and the Schmidt number specification (Sc) for CCl_4 uses the temperature-dependent formulation of Wanninkhof [2014]. We evaluate sensitivity of model results to uncertainties in gas-exchange formulation in sections 2.5 and 3.

2.3.4 Parameterization of CCl_4 Loss Processes

Chemical hydrolysis

Loss of CCl_4 by chemical hydrolysis is simulated using the temperature dependent formulation of Amonette et al. [2012] which updates that of Jeffers et al. [1996]. The hydrolysis rate constant is given by:

Eqn. 4

$$k_{hydrolysis} = 25.25 \times 10^{12} \times e^{(-\frac{15890}{T})} \text{ s}^{-1}$$

The contribution of this CCl_4 loss process is small in comparison to that of biologically-mediated degradation (by a factor of 10^{-6} , for our simulations), but included for completeness.

Biologically-mediated CCl_4 degradation

In-situ measurements of oceanic CCl_4 reveal under-saturation in surface waters and significant depletion in the sub-surface ocean up to depths of ~ 2000 m [B2016, Min et al. 2010]. The underlying mechanisms are currently not identified, however observed correlations between Apparent Oxygen Utilization (AOU) and CCl_4 depletion ($\Delta[\text{CCl}_4]$) (e.g., B2016, and Fig. S1 of this study) suggest mechanisms of biologically-mediated CCl_4 loss accompanying organic matter remineralization, as hypothesized in previous studies. Our analysis of correlations

between AOU and CCl₄ depletion using the compiled data of section 2.3 yields an overall correlation coefficient of $\Delta[\text{CCl}_4]/\text{AOU} \sim -27 \text{ nmol/mol}$ (i.e., $-27 \times 10^{-9} \text{ mol/mol}$) ($R^2 = 0.53$), with a range of 19 to 33 nmol/mol depending on the depth and latitudinal range considered (see Supplementary Text for specification of AOU, $\Delta[\text{CCl}_4]$ and the correlation analysis). Based on these observed predominantly linear correlations between CCl₄ depletion and AOU, our parameterization of biologically-mediated oceanic CCl₄ degradation represents CCl₄ loss as a linear function of oxygen utilization; i.e., scaled by a parameter α representing a degradation ratio of CCl₄ depletion to oxygen utilization.

Eqn. 7

$$\text{CCl}_4 \text{ Degradation Rate} = -\alpha \cdot [\text{O}_2 \text{ Utilization Rate}]$$

Here, the parameter α , represents a ratio of moles of CCl₄ degradation to moles of oxygen utilization. This follows methods adopted for biogeochemical cycling of other trace gases [e.g., Suntharalingam et al. 2012, Martinez-Rey et al. 2015], where AOU is used as a proxy for oxygen utilization associated with heterotrophic respiration in oxygenated water [Sarmiento and Gruber, 2006].

2.4 : CCl₄ Simulations and Optimization

A set of NEMO-PlankTOM CCl₄ simulations was run for the period 1920-2013, with separate prescribed values (α_{set}) for the degradation ratio. The α_{set} values used range from 0 to 90 nmol/mol, which extends beyond the range of observed correlations of $(\Delta[\text{CCl}_4])/\text{AOU}$; i.e., $\alpha_{\text{set}} = \alpha_i$ for $i = 1$ to 11; (α_i in $\{0, 0.03, 0.1, 0.3, 1, 3, 10, 20, 30, 45, 90\}$ nmol/mol). Selected results (for simulations with α_i close to observed values) for modeled global air-sea CCl₄ flux and derived partial atmospheric lifetimes are summarized in Table 1 and Figure 1.

The optimization procedure uses the set of prescribed α_{set} simulations, to derive an estimate (α_{opt}) of the global oceanic degradation parameter, by minimizing a cost-function metric

(Equation 8) dependent on the sum of squared residuals between modeled CCl_4 concentrations and the gridded oceanic observations of section 2.2. The optimization follows the methodology of Abramowitz and Stegun [1972], as employed in Buitenhuis et al. [2013, 2018]. Individual values of the cost function (CF_i) are derived using the 11 separate model simulations with prescribed α_i values. The optimized value, α_{opt} , is determined from the minimum value of the cost function CF_i across the set of degradation rates α_i .

Eqn. 8

$$\text{Cost Function: } CF = \sum_{n=1}^N \frac{([\text{Model } \text{CCl}_4]_n - [\text{Observed } \text{CCl}_4]_n)^2}{N}$$

In Equation 8, index n represents the individual oceanic observations of CCl_4 , and N the total number of observations for the period analyzed (e.g., $N = 31362$ for the period 1987 -2013).

2.5 Sensitivity Analyses

2.5.1 Correction for physical influences and model circulation errors

We also report on optimization analyses designed to minimize the influences of physical processes (e.g., bubble dissolution, warming) and ocean model circulation errors on our estimates of α_{opt} and derived air-sea fluxes. For this analysis (Case $\text{OPT}_{\text{CFC11}}$ in Table 1), the cost function optimization of CCl_4 is adjusted using CFC-11 saturation anomalies to remove the influence of physical processes, following methods of B2016 and Butler et al. [1991]. We first calculate ‘corrected’ saturation anomalies for CCl_4 (Δ_{CORR}), where CCl_4 values are adjusted by subtracting the CFC-11 saturation anomaly.

Eqn. 9

$$\Delta_{\text{CORR}} = \Delta_{\text{CCl}_4} - \Delta_{\text{CFC11}}$$

where

$$\Delta_{CCl_4} = \left(\frac{p[CCl_4]_{water} - p[CCl_4]_{air}}{p[CCl_4]_{air}} \right) \times 100\%$$

$$\Delta_{CFC11} = \left(\frac{p[CFC11]_{water} - p[CFC11]_{air}}{p[CFC11]_{air}} \right) \times 100\%$$

The values $p[X]_{water}$ and $p[X]_{air}$ denote partial pressures of X in water and air respectively.

We then derive a modified cost function (Equation 10) incorporating the corrected saturation anomalies:

Eqn 10:

$$\text{Modified Cost Function} = \sum_{n=1}^N \frac{([Model \Delta_{CORR}]_n - [Observed \Delta_{CORR}]_n)^2}{N}$$

Here, model and observed CCl_4 concentrations of equation 8 have been replaced with ‘corrected’ saturation anomaly values for model and observations, respectively.

2.5.2 Climatological vs. Long-term analysis of ocean observations

The optimization of the degradation parameter α_{opt} was derived for the two alternative observational databases of section 2.2: (i) Case $OPT_{1996-2000}$: using the observational climatology and model climatology spanning the period 1996-2000 ($n=31362$); and (ii) Case $OPT_{1987-2013}$, using the time-varying observational database with model values taken from time-varying simulations for 1987-2013 ($n=32636$). Our analysis using CFC-11 corrected saturation anomalies (section 2.5.1) is restricted to the climatological dataset due to relatively few coincident CFC-11 and CCl_4 measurements in the early stages of the 1987-2013 period. For this common dataset (CCl_4 and CFC-11 sampled together), $n=28240$. Table 1 summarizes estimates of the optimized degradation rate, α_{opt} , for all cases.

2.5.3 Sensitivity to parameterization of gas-transfer coefficient and solubility

We evaluate the sensitivity of estimated air-sea fluxes to uncertainties in the gas-exchange parameterization (Eqn. 2), and specifically to representation of the gas-transfer velocity k , and the parameterization of solubility K_0 . Sweeney et al. [2007] report an uncertainty of $\sim 32\%$ in the parameterization of the gas transfer velocity, k , for global or basin-scale applications, and Wanninkhof [2014] note a smaller uncertainty of $\sim 20\%$. Here, we evaluate sensitivity to the larger more conservative uncertainty estimate of Sweeney et al. [2007], and vary representation of k by $\pm 32\%$. Our simulations employ the temperature-dependent solubility parameterization of Bullister and Wisegarver [1998], who report a $\pm 2.5\%$ standard error for their fits of solubility curves to measurements. We assess sensitivity to the solubility parameterization by varying representation of K_0 by $\pm 2.5\%$.

The evaluation of sensitivity to these two gas-exchange related parameters is calculated by repeating the optimization process of section 2.4, but incorporating alternative values representing the $\pm 32\%$ perturbations for the gas transfer velocity k , and $\pm 2.5\%$ changes on the solubility parameter K_0 . Results for the respective assessments are reported in Table 1 and section 3.

2.6 Calculation of Partial Lifetimes

The estimate of the partial atmospheric lifetime of CCl_4 with respect to oceanic uptake, τ_{oc} , is calculated as the ratio of the global atmospheric burden (M_{CCl_4}) to the loss rate to the ocean (F_{CCl_4}); *i.e.*, $\tau_{oc} = (M_{\text{CCl}_4})/(F_{\text{CCl}_4})$ [Liang et al. 2014, Plumb et al., 2013]. Our CCl_4 model simulations span the period 1920-2013, during which CCl_4 emissions, atmospheric burden, and air-sea flux all vary with time (Figure 1). Following Chipperfield et al. [2014], we estimate the instantaneous partial atmospheric lifetime of CCl_4 with respect to oceanic uptake, $\tau_{oc}(t)$, as

Eqn. 11.

$$\tau_{oc}(t) = \frac{M_{CCl_4}(t)}{F_{CCl_4}(t)}$$

where $M_{CCl_4}(t)$ and $F_{CCl_4}(t)$ are the time-varying atmospheric burden and net air-sea flux respectively. Under assumptions of steady-state, this definition of τ_{oc} is equivalent to the time-invariant value for partial-lifetime derived by B2016. The atmospheric burden, $M_{CCl_4}(t)$, is calculated as a product of the number of moles of air in the troposphere ($n_{tr} = 1.46 \times 10^{20}$), the time-varying atmospheric mixing ratio of CCl_4 ($x_{atm}(t)$, from Bullister [2015]), and the fraction of atmospheric CCl_4 resident in the troposphere ($r_g = 0.886$, B2016).

Eqn. 12

$$M_{CCl_4}(t) = n_{tr} \times x_{atm}(t) \times r_g$$

Resulting estimates for atmospheric burden ($M_{CCl_4}(t)$) and instantaneous partial lifetime $\tau_{oc}(t)$, are presented in Figure 1 and discussed in section 3.

The calculation of total atmospheric lifetime of CCl_4 , τ_{TOT} (Equation 13), follows Liang et al. [2016], where τ_{TOT} is a function of the individual lifetimes with respect to the different CCl_4 loss processes, i.e., stratospheric photolysis (τ_{atm}), and uptake by soils (τ_{soil}), and the ocean (τ_{oc}).

Eqn. 13

$$\frac{1}{\tau_{TOT}} = \frac{1}{\tau_{atm}} + \frac{1}{\tau_{soil}} + \frac{1}{\tau_{oc}}$$

3. Results and Discussion

Table 1 summarises time-averaged model results for global air-sea CCl_4 flux, and associated partial atmospheric lifetime estimates (τ_{oc}) from a range of CCl_4 model analyses. These include simulations using prescribed values of the degradation rate α_{set} , and optimization analysis for α_{opt} and associated fluxes using oceanic CCl_4 observations. Sections B1 and B2 of Table 1 summarize evaluations of the sensitivity of optimized estimates to the CFC-11 correction (section 2.5.1), time-period (section 2.5.2), and variations in the gas-exchange parameterization

(section 2.5.3). Section B3 of Table 1 reports on the total uncertainty range for optimized estimates when accounting for all assessed sensitivities. Below, we discuss these results in turn.

3.1 Simulations with prescribed α_{set}

All model analyses of Table 1 are subject to the same atmospheric CCl_4 time-history [Bullister, 2015] shown in Figure 1a. The corresponding atmospheric burden is in Figure 1b.

Figures 1c and 1d show time-varying air-sea fluxes and partial lifetimes ($\tau_{oc}(t)$) for selected prescribed α_{set} simulations. Net air-sea fluxes for these simulations increase from 1920,

reach maximum levels in early 1990s, and decline subsequently. In the following discussion

we focus on the simulation for a prescribed α_{set} value of 20 nmol/mol for the following reasons: (a) the optimization analyses of sections 2.4 and 2.5 yield estimated α_{opt} values in

the range 19 – 22 nmol/mol (Table 1, section B); (b) the comparison of modelled average depth profiles with observations (Supplementary Figure S2), shows the closest overall match

for the simulation with $\alpha_{\text{set}} = 20$ nmol/mol. Figure 1d demonstrates the time-varying nature

of the instantaneous partial lifetime $\tau_{oc}(t)$, (Eqn. 11). For the $\alpha_{\text{set}} = 20$ nmol/mol simulation, $\tau_{oc}(t)$ increases from ~80 years in the early 1960s to values above 100 years in the 1970s,

reaching a maximum (~ 140 years) in 1992, and subsequently declining.

In subsequent discussion, we report time-averaged values (for specified periods) to enable more consistent comparison with previous studies. Air-sea fluxes for this simulation (α_{set}

=20 nmol/mol) are 18.6 Gg year⁻¹ for the period 1996-2000, and 19.0 Gg year⁻¹ for the

period 1980-2010, with associated estimates of partial oceanic lifetime of $\tau_{oc} = 134$ years and $\tau_{oc} = 129$ years respectively.

3.2 Optimized analyses and associated sensitivity assessments

We calculated the optimized degradation rate, α_{opt} , for two cases (section 2.5.2), Case OPT₁₉₉₆₋₂₀₀₀ using observational and model climatologies, and Case OPT₁₉₈₇₋₂₀₁₃ using time-varying analyses for 1987-2013. The estimated values for α_{opt} are 20.0 nmol/mol and 19.0 nmol/mol respectively, which correspond to partial atmospheric lifetime estimates of $\tau_{oc} = 131$ (118-146) years and $\tau_{oc} = 134$ (115-161) years respectively.. The reported uncertainty range corresponds to the $\pm 1 \sigma$ (68%) confidence interval on the optimized estimate, and was calculated following the methodology of Abramowitz and Stegun [1972], as described in Buitenhuis et al. [2013].

Table 1 section B1 also reports optimized estimates of α and air-sea fluxes for simulations where modeled CCl₄ is adjusted using CFC-11 (section 2.5.1) to minimize the influence of physical processes on estimation of α_{opt} and associated quantities. Case OPT_{CFC11} gives a value of $\alpha_{opt} = 22$ nmol/mol, with an associated air-sea flux of 20.1 ± 1.2 Gg year⁻¹, and a corresponding estimate for partial atmospheric lifetime of 124 (117-132) years. The CFC-11 adjustment aims to account for physical influences such as bubble dissolution which increase surface concentration levels yielding more positive saturation anomalies [B2016]. Correcting for such influences results in generally larger values of the CCl₄ deficit attributable to degradation processes, and correspondingly larger estimates for α_{opt} and air-sea flux, in comparison to the unadjusted Case OPT₁₉₉₆₋₂₀₀₀.

Sensitivity analyses on gas-transfer velocity k , and solubility K_0 , were conducted for the optimizations of Case OPT₁₉₉₆₋₂₀₀₀ and Case OPT_{CFC11} (described in 2.5.3), with results summarized in Table 1 section B2. Results are most sensitive to variation in the gas-transfer velocity k ; a variation of $\pm 32\%$ for Case OPT₁₉₉₆₋₂₀₀₀ yields changes in estimated air-sea flux

(ranging from 13.9 to 22.1 Gg yr⁻¹), and a corresponding range for partial lifetime, τ_{oc} , of 112 – 179 years. The lower and upper bounds reported here correspond to the central estimates from individual optimizations where k is reduced or increased by 32%. Similar analyses on uncertainty in k for the CFC-11 ‘corrected’ optimization Case OPT_{CFC11}, yield a range in estimated air-sea flux of 17.1 – 21.9 Gg yr⁻¹ and partial lifetime of 109 – 142 years. Assessment of sensitivity to the solubility parameter K_0 (by $\pm 2.5\%$) has a smaller impact on τ_{oc} , giving an uncertainty range of 120 – 150 years for Case OPT₁₉₉₆₋₂₀₀₀, and 115 – 132 years for Case OPT_{CFC11}.

We also evaluate the combined impact of the above sensitivity assessments on overall uncertainty in estimated fluxes and partial lifetime (section B3 of Table 1). The combined uncertainty is estimated by summing in quadrature, the individual uncertainties associated with the optimization of α , and with uncertainties in the gas-transfer coefficient k and solubility K_0 . For Case OPT₁₉₉₆₋₂₀₀₀ this gives a revised flux range of (13.0 – 23.3) Gg yr⁻¹ with a τ_{oc} range of 107-191 years. For Case OPT_{CFC11}, the revised air-sea CCl₄ flux range is 20.1 (16.6 – 22.7) Gg yr⁻¹ with a τ_{oc} range of 110 – 150 years. Given the additional constraints provided by CFC-11 measurements in accounting for physical influences on oceanic CCl₄ uptake, we report this result for Case OPT_{CFC11} as our best estimate of oceanic CCl₄ uptake and partial lifetime.

4. Conclusions

In summary, our suite of optimization analyses yields estimates for the global averaged oceanic CCl₄ degradation parameter α in the range 19 – 22.1 nmol/mol with associated global oceanic CCl₄ uptake of 17.9 – 20.1 Gg year⁻¹ (ranges reported here are the central estimates from the different optimization cases). We report as our best constrained estimate, Case OPT_{CFC11}, which uses a CFC-11 correction to reduce the influence of physical processes

on estimation of α_{opt} ; this has an oceanic CCl_4 uptake of 20.1 (16.6 – 22.7) Gg yr^{-1} and an estimate for partial lifetime τ_{oc} of 124 (110 – 150) years.

B2016 report a smaller global oceanic uptake of 12.94 (9.4-15.4) Gg yr^{-1} and associated partial lifetime of 183 (147-241) years. This estimate was derived from primarily surface CCl_4 measurements spanning the period 1987-2010. Our optimized central estimates for ocean uptake, are higher, by $\sim 7 \text{ Gg yr}^{-1}$ for Case $\text{OPT}_{\text{CFCl11}}$, and by $\sim 5.5 \text{ Gg yr}^{-1}$ for Case $\text{OPT}_{1987-2013}$. Our best constrained estimate of partial lifetime (Case $\text{OPT}_{\text{CFCl11}}$: 124 (110 – 150) years) is, accordingly, lower than that of B2016, but there is a small overlap between the uncertainty ranges of the two studies.

Factors likely responsible for the differences in our estimates from B2016 include : (a) use of both surface and water column measurements in our analysis; (b) a larger aggregated database of CCl_4 measurements in this study, including measurements from high-latitude regions not represented in B2016; (c) representation in our analysis of the influences of sub-surface degradation and 3-D oceanic circulation on surface CCl_4 ; (d) time-varying atmospheric mixing-ratios, and (e) different gas-exchange parameterizations (Sweeney et al. [2007] in this analysis and Wanninkhof [2014] for B2016, however we note that our gas-exchange sensitivity analyses encompass the differences between the two parametrizations).

We estimate corresponding values for the total atmospheric lifetime τ_{TOT} as 29.9 (24.8-38.8) years, using Equation 12 and recent estimates for τ_{atm} of 44 (36-58) years [SPARC, 2013] and τ_{soil} of 375 (288-536) years [Rhew et al. 2016]. Our reported range for τ_{TOT} corresponds to the respective lower and upper bounds of the individual partial lifetimes. Our estimate for τ_{TOT} is lower than that of B2016 (32 (26-43) years), and the SPARC 2016 report (33 (28-41) years) [Liang et al. 2016] (though each of the mean estimates is captured by the different uncertainty ranges). Our estimated τ_{TOT} is higher than that reported in the WMO Ozone

Assessment of 2014 (26 (22 -33) years), which was derived using the partial oceanic lifetime reported by Yvon-Lewis and Butler [2002] of $\tau_{oc} = 94$ years. Our results suggest a larger missing atmospheric source of CCl_4 (by approximately $5\text{-}7 \text{ Gg year}^{-1}$) than that reported by SPARC 2016 and by B2016.

Our estimates provide an advance on previous analyses through representation of water column degradation processes and 3-D circulation influences on CCl_4 , and through constraints from a larger observational database of oceanic CCl_4 and CFC-11 measurements. Limitations of our analysis include the relatively simple representation of biologically mediated degradation, which does not comprehensively account for hypothesized influences of in-situ environmental conditions (e.g., temperature, oxygen level, Wallace et al. [1994], Min et al. [2010]) on CCl_4 degradation. At present, due to limited information on these biogeochemical processes, more complex representation of oceanic CCl_4 degradation is beyond the scope of this study. Elucidating these process controls, through a combination of in-situ measurements and laboratory and model analyses, will yield more accurate estimates of oceanic CCl_4 uptake, and should be a priority for future investigations.

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The observations compiled for this analysis are available at <https://ired.uea.ac.uk/web/green-ocean/data>. The NEMO-PlankTOM model data are available at <http://opendap.uea.ac.uk:8080/opendap/hyrax/greenocean/CCl4/contents.html>.

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References

Abramowitz, M., and I. Stegun, Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables. New York: Wiley, 1972.

Amonette, J.E., P.M. Jeffers, O. Qafoku, C.K. Russell, D.R. Humphrys, T.W. Wietsma, M.J. Truex Abiotic Degradation Rates for Carbon Tetrachloride and Chloroform: Final Report. PNNL-22062; RPT-DVZ-AFRI-012, Pacific Northwest National Laboratory, Richland, WA. DOI:10.2172/1057834, 2012.

Andrews, O., E. Buitenhuis, C. Le Quéré, and P. Suntharalingam, Biogeochemical modelling of dissolved oxygen in a changing ocean, in Philosophical Transactions of the Royal Society A 375 (2102) article no. 20160328, 2017.

Aumont, O., and L. Bopp, Globalizing results from ocean in situ iron fertilization studies, Global Biogeochem. Cycles, 20, GB2017, doi:10.1029/2005GB002591, 2006.

Buitenhuis, E. et al., Combined constraints on global ocean primary production using observations and models, Global Biogeochem. Cycles, 27, 847–858, doi:10.1002/gbc.20074, 2013.

Buitenhuis, E., P. Suntharalingam and C. Le Quéré, Constraints on global oceanic emissions of N₂O from observations and models, Biogeosciences, 15, 2161-2175, <https://doi.org/10.5194/bg-15-2161-2018>, 2018.

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

Bullister, J., Atmospheric Histories (1765-2015) for CFC-11, CFC-12, CFC-113, CCl₄, SF₆ and N₂O, NDP-095, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee. doi: 10.3334/CDIAC/otg.CFC_ATM_Hist_2015, 2015.

Burkholder, J. B., and W. Mellouki (Lead Authors), E. L. Fleming, C. George, D. E. Heard, C. H. Jackman, M. J. Kurylo, V. L. Orkin, W. H. Swartz, and T. J. Wallington, Evaluation of atmospheric loss processes, Chapter 3 in SPARC Report on the Lifetimes of Stratospheric Ozone-Depleting Substances, Their Replacements, and Related Species, M. K. W. Ko, P. A. Newman, S. Reimann, and S. E. Strahan (Eds.), SPARC Report No. 6, WCRP-15/2013, www.sparc-climate.org/publications/sparc-reports/sparc-report-no6, 2013.

Butler, J. H., J. W. Elkins, T. M. Thompson, B. D. Hall, T. H. Swanson, and V. Koropalov, Oceanic consumption of CH₃CCl₃: Implications for tropospheric OH, J. Geophys. Res.-Atmos., 96, 22347–22355, doi:10.1029/91JD02126, 1991.

Butler, J. H., J. W. Elkins, T. M. Thompson, B. D. Hall, J. M. Lobert, T. H. Swanson, and V. Koropalov, A significant oceanic sink for atmospheric CCl₄, paper presented at Third Scientific Meeting, The Oceanogr. Soc., Seattle, Washington, 13-16 April, 1993.

Butler, J.H., M. Battle, M. Bender, S.A. Montzka, A.D. Clarke, E.S. Saltzman, C. Sucher, J. Severinghaus, and J.W. Elkins, A twentieth century record of atmospheric halocarbons in polar

firm air. *Nature* 399:749-765, 1999.

Butler, J.H., S. A. Yvon-Lewis, J. M. Lobert, D. B. King, S. A. Montzka, J. L. Bullister, V. Koropalov, J.W. Elkins, B. D. Hall, L. Hu, and Y. Liu, A comprehensive estimate for loss of atmospheric carbon-tetrachloride (CCl₄) to the ocean, *Atmos. Chem. Phys.*, 16, 10899–10910, doi:10.5194/acp-16-10899-2016, 2016.

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.

Chipperfield, M. P. et al., Multimodel estimates of atmospheric lifetimes of long-lived ozone-depleting substances: Present and future, *Journal of Geophysical Research: Atmospheres*, 119, pp.2555-2573. doi: 10.1002/2013JD021097, 2014.

Chipperfield, M.P., et al., Model sensitivity studies of the decrease in atmospheric carbon tetrachloride, *Atmos. Chem. Phys.*, 16, 15741–15754, 2016.

Fraser, P.J., B. L. Dunse, A. J. Manning, S. Walsh, R. Wang, J. Hsiang, P. B. Krummel, L. P. Steele, L. W. Porter, C. Allison, S. O'Doherty, P. Simmonds, J. Muehle, R. F. Weiss, R. G. Prinn, Australian carbon tetrachloride (CCl₄) emissions in a global context, *Environ. Chem.*, 11, 77–88, doi:10.1071/EN13171, 2014.

Garcia, H., and L. I. Gordon, Oxygen solubility in seawater: Better Fitting equations, *Limnology and Oceanography*, 37(6):1307-1312, doi: 10.4319/l.o.1992.37.6.1307, 1992.

Garcia, H. E., R. A. Locarnini, T. P. Boyer, and J. I. Antonov, *World Ocean Atlas 2005*, vol. 3, Dissolved Oxygen, Apparent Oxygen Utilization, and Oxygen Saturation, NOAA Atlas NESDIS, vol. 63, edited by S. Levitus, NOAA, Silver Spring, Md., 2006.

Happell, J. D., and M. P. Roche, Soils: A global sink of atmospheric carbon tetrachloride, *Geophys. Res. Lett.*, 30(2), 1088, doi:10.1029/2002GL015957, 2003.

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

Jeffers, P. M., C. Brenner, and N. L. Wolfe, Hydrolysis of carbon tetrachloride, *Environmental Toxicology and Chemistry* 15(7):1064–1065, 1996.

Johnson, J., The lifetime of carbonyl sulfide in the troposphere, *Geophys. Res. Letts.*, 8, 938-940, doi:10.1029/GL008i008p00938, 1981.

Ito, T., S. Minobe, M. C. Long and C. Deutsch, Upper ocean O₂ trends: 1958–2015, *Geophys. Res. Letts.*, 44, 9, 4214-4223, doi:10.1002/2017GL073613, 2017.

Kalnay, E., et al., The NCEP/NCAR 40-year reanalysis project, *Bulletin of the American Meteorological Society*, 77, 437–471, doi:10.1175/15200477, 1996.

Key, R., et al. *Global Ocean Data Analysis Project (GLODAP) version 1.1* (NODC Accession 0001644). Version 2.2. National Oceanographic Data Center, NOAA. Dataset. [accessed Sept. 2017], 2011.

- Krystell, M. and D.W.R. Wallace, Arctic Ocean ventilation studied with a suite of anthropogenic halocarbon tracers, *Science*, 242, 746-749, 1988.
- Krystell, M., E. Fogelqvist, and T. Tanhua, Apparent removal of the transient tracer carbon tetrachloride from anoxic seawater, *Geophys. Res. Lett.*, 21, 2511–2514, doi:10.1029/94GL02336, 1994.
- Lee, B.-S., J. L. Bullister, and F. A. Whitney, Chlorofluorocarbon CFC-11 and carbon tetrachloride removal in Saanich Inlet, an intermittently anoxic basin. *Mar. Chem.* 66, 171–185, 1999.
- Le Quéré, C. et al., Role of zooplankton dynamics for Southern Ocean phytoplankton biomass and global biogeochemical cycles, *Biogeosciences* 13, 4111-4133, doi:10.5194/bg-13-4111-2016, 2016.
- Le Quéré, C. et al., Ecosystem dynamics based on plankton functional types for global ocean biogeochemistry models, *Global Change Biology*, 11, pp. 2016-2040, 2005.
- Liang, Q., P.A. Newman, J. S. Daniel, S. Reimann, B. D. Hall, G. Dutton, and L. J. M. Kuijpers, 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., and Reimann S. (Eds.): SPARC Report on the Mystery of Carbon Tetrachloride, SPARC Report No. 7, WCRP-13/2016, 2016.
- Madec, G. and M. Imbard, A global ocean mesh to overcome the North Pole singularity, *Clim. Dynam.*, 12, 381–388. 1996.
- Madec, G., NEMO ocean engine, Note du Pole de modelisation, Institut Pierre-Simon Laplace (IPSL), Paris, No 27, 2008.
- Martinez-Rey, J., L. Bopp, M. Gehlen, A. Tagliabue, and N. Gruber, Projections of oceanic N₂O emissions in the 21st century using the IPSL Earth system model, *Biogeosciences*, 12, 4133–4148, doi:10.5194/bg-12-4133-2015, 2015.
- Meredith, M., K. A. van Scoy, A. J. Watson and R. A. Locarmini, On the use of carbon tetrachloride as a transient tracer of Weddell Sea deep and bottom waters, *Geophys. Res. Lett.*, 23, 943-2946, 1996.
- Min, D.-H., M. J. Warner, and J. L. Bullister, Estimated rates of carbon tetrachloride removal in the thermocline and deep waters of the East Sea (Sea of Japan), *Mar. Chem.*, 21, 100–111, doi:10.1016/j.marchem.2010.03.008, 2010.
- Montzka, S. A, S. Reimann, A. Engel, K. Krüger, S. J. O'Doherty, and W. T. Sturges, Ozone-Depleting Substances (ODSs) and Related Chemicals. in *Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project-Report No. 52*. World Meteorological Organization, Geneva, Switzerland, pp. 1 – 112, 2011.
- Olsen, A., et al., The Global Ocean Data Analysis Project version 2 (GLODAPv2) – an internally consistent data product for the world ocean, *Earth Syst. Sci. Data*, 8, 297–323, doi:10.5194/essd-8-297-2016, 2016.

Plumb, A. et al., The Theory of Estimating Lifetimes Using Models and Observations, Chapter 2 in Report on the Lifetimes of Stratospheric Ozone-Depleting Substances, Their Replacements, and Related Species, M. Ko, P. Newman, S. Reimann, S. Strahan (Eds.), SPARC Report No. 6, WCRP-15/2013.

Rhew, R. C. and J. D. Happell, The atmospheric partial lifetime of carbon tetrachloride with respect to the global soil sink, *Geophys. Res. Lett.*, 43, 2889–2895, doi:10.1002/2016GL067839, 2016.

Sarmiento, J. L., and N. Gruber, *Ocean Biogeochemical Dynamics*. Princeton University Press, Princeton, NJ, USA, 2006.

Suntharalingam, P., E. Buitenhuis, C. Le Quéré, F. Dentener, C. Nevison, J. H. Butler, H. W. Bange, G. and Forster, Quantifying the impact of anthropogenic nitrogen deposition on oceanic nitrous oxide, *Geophys. Res. Lett.*, 39, doi:201210.1029/2011GL050778, 2012.

Suzuki, T., et al., PACIFICA Data Synthesis Project, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, 2013.

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

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

Walker, S. J., R. F. Weiss, and P. K. Salameh, Reconstructed histories of the annual mean atmospheric mole fractions for the halocarbons CFC-11 CFC-12, CFC-113, and carbon tetrachloride. *J. Geophys. Res.*, 105:14285-14296, doi:10.1029/1999JC900273, 2000.

Wallace, D.W.R., P. Beining, and A. Putzka, Carbon tetrachloride and chlorofluorocarbons in the South Atlantic Ocean, *J. Geophys. Res.* 99, 7803–7819, 1994.

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

Vogt, M., S. M. Vallina, E. T. Buitenhuis, L. Bopp, and C. Le Quéré., Simulating dimethylsulphide seasonality with the Dynamic Green Ocean Model PlankTOM5, *J. Geophys. Res.*, 115, C06021, doi:10.1029/2009JC005529, 2010.

Yvon-Lewis, S. A. and J. H. Butler, Effect of oceanic uptake on atmospheric lifetimes of selected trace gases, *J. Geophys. Res.*, 107(D20), 4414, 2002.

Table 1: Model-derived estimates of CCl₄ air-sea fluxes and partial lifetimes with respect to ocean uptake from prescribed α simulations, optimized analyses, and sensitivity studies.

Model Analyses	CCl ₄ Degradation Parameter α (nmol/mol)	Air Sea Flux (Gg yr ⁻¹)	Partial Atm. Lifetime τ_{oc} (years)
SECTION A : FORWARD MODEL SIMULATIONS: PRESCRIBED DEGRADATION PARAMETER α			
Sensitivity Analyses on prescribed degradation parameter α (In parentheses : Estimates for 1980-2010)		Avg. Flux 1996-2000	τ_{oc}
Prescribed $\alpha_{set} = 10$ nmol/mol	$\alpha_{set} = 10$	10.8 (11.3)	229 (217)
Prescribed $\alpha_{set} = 20$ nmol/mol	$\alpha_{set} = 20$	18.6 (19.0)	134 (129)
Prescribed $\alpha_{set} = 30$ nmol/mol	$\alpha_{set} = 30$	25.4 (25.8)	98 (95)
Prescribed $\alpha_{set} = 45$ nmol/mol	$\alpha_{set} = 45$	34.3 (34.5)	73 (71)
SECTION B : OPTIMIZED RUNS^a			
Section B1 : Sensitivity Analyses for time-period and CFC-11 Correction (In parentheses : $\pm 1\sigma$ range)		Air Sea Flux (Gg yr⁻¹)	τ_{oc} (years)
Case OPT₁₉₉₆₋₂₀₀₀ : Period 1996-2000	$\alpha_{opt} = 20.0$	18.5 ± 2.3	131 (118-146)
Case OPT₁₉₈₇₋₂₀₁₃ : Period 1987-2013	$\alpha_{opt} = 19.0$	17.9 ± 3.0	134 (115-161)
Case OPT_{CFC11} : Period 1996-2000 CFC-11 Correction	$\alpha_{opt} = 22.1$	20.1 ± 1.2	124 (117-132)
Section B2 : Sensitivity Analyses on Gas-exchange parameters : Period 1996-2000		FLUX RANGE^b	τ_{oc} Range^b
Case OPT₁₉₉₆₋₂₀₀₀ with Solubility (K_0) $\pm 2.5\%$	$\alpha_{opt} = 20.0$	16.5 – 20.7	120 - 150
Case OPT₁₉₉₆₋₂₀₀₀ with gas-transfer vel. (k) $\pm 32\%$	$\alpha_{opt} = 20.0$	13.9 - 22.1	112 - 179
Case OPT_{CFC11} with Solubility (K_0) $\pm 2.5\%$	$\alpha_{opt} = 22.1$	18.8 – 21.5	115 - 132
Case OPT_{CFC11} with gas-transfer vel. (k) $\pm 32\%$	$\alpha_{opt} = 22.1$	17.1 - 21.9	109 - 142
Section B3 : Total uncertainty range (model-data optimization and gas-exchange uncertainties)			
Case OPT₁₉₉₆₋₂₀₀₀	$\alpha_{opt} = 20.0$	18.5 (13.0 – 23.3)	134 (107-191)
Case OPT_{CFC11}	$\alpha_{opt} = 22.1$	20.1 (16.6 – 22.7)	124 (110 – 150)

FOOTNOTES

a: The optimization analyses listed are derived from minimization of model-data concentration differences, as described in sections 2.4 and 2.5.

b : Lower and upper bounds of reported range are the respective optimized estimates for the –ve and +ve parameter perturbations.

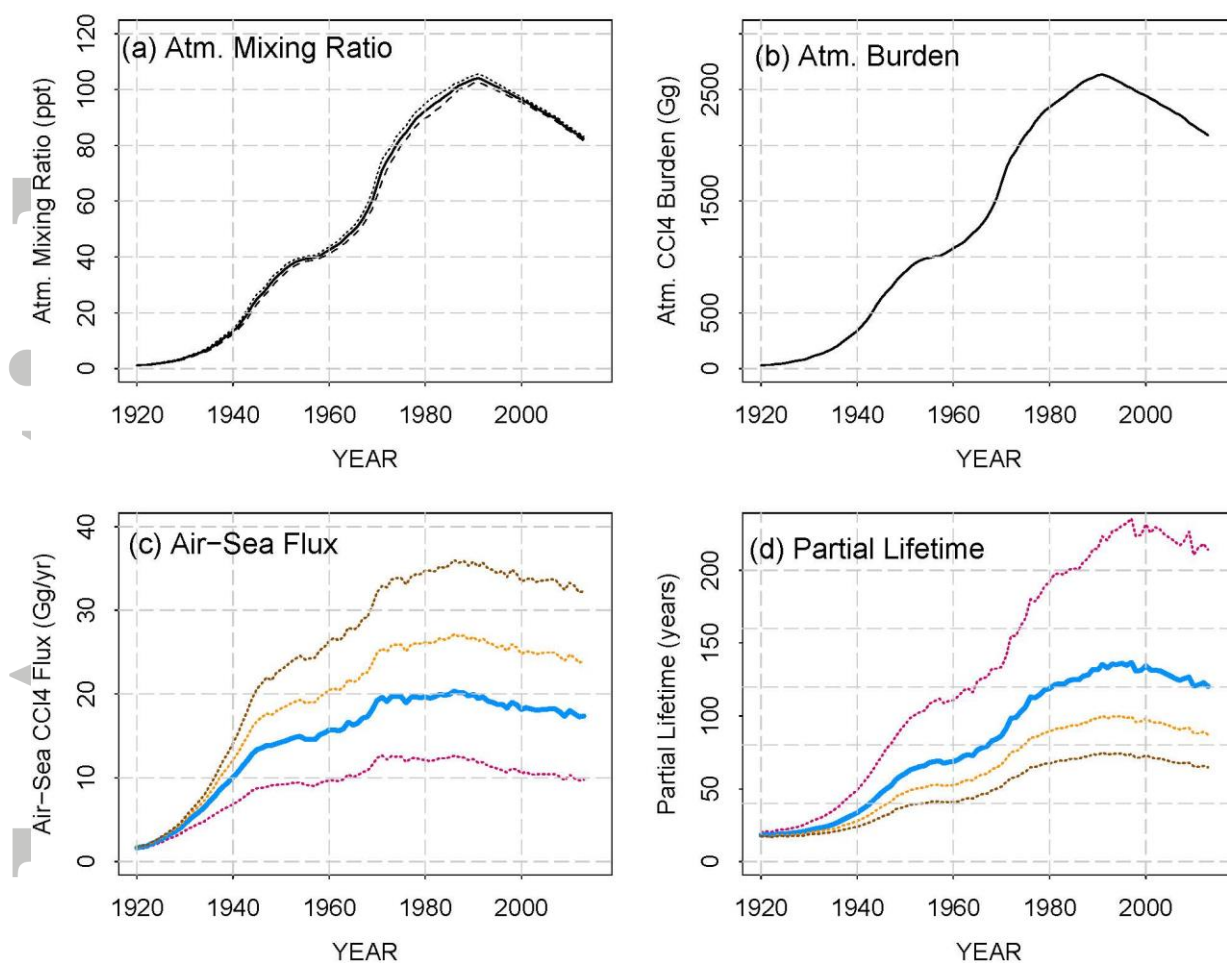


Figure 1: Time variation of CCl₄ quantities: **(a)** atmospheric CCl₄ mixing ratio (ppt), global average (solid line), Northern (dotted) and Southern Hemisphere (dashed) averages; data taken from Bullister, [2015]; **(b)** global atmospheric CCl₄ burden (see section 2.6 for calculation details); **(c)** model-derived global average air-sea CCl₄ fluxes from selected prescribed α simulations; cases shown are $\alpha_{\text{set}} = 10$ nmol/mol (magenta dotted), $\alpha_{\text{set}} = 20$ nmol/mol (blue solid), $\alpha_{\text{set}} = 30$ nmol/mol (yellow dotted), $\alpha_{\text{set}} = 45$ nmol/mol (brown dotted); **(d)** transient partial atmospheric lifetime values for selected prescribed α simulations; cases shown are $\alpha_{\text{set}} = 10$ nmol/mol (magenta dotted), $\alpha_{\text{set}} = 20$ nmol/mol (blue solid), $\alpha_{\text{set}} = 30$ nmol/mol (yellow dotted), $\alpha_{\text{set}} = 45$ nmol/mol (brown dotted).