RESEARCH LETTER

Key Points:
- New estimate of ocean uptake of atmospheric CCl_4 derived using an ocean biogeochemical model and global databases of CCl_4 measurements
- Best estimate of ocean CCl_4 uptake is 20.1 Gg/year (16.6–22.7), with a corresponding partial atmospheric lifetime with respect to ocean uptake of 124 (110–150) years
- Estimated ocean CCl_4 uptake is larger than recent estimates and implies a larger missing source to the atmosphere

Supporting Information:
- Supporting Information S1
- Figure S1

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

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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 optimized 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/year (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 optimized 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 CCl_4 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 CCl_4 uptake for the 1996–2000 period is 20.1 Gg/year (range 16.6–22.7), which is greater than previous recent estimates, and implies a larger missing source to the atmosphere of CCl_4.

1. Introduction

1.1. Atmospheric CCl₄ and Estimates of Partial Lifetimes

Atmospheric carbon-tetrachloride (CCl_4) is a significant ozone-depleting substance (Carpenter et al., 2014) used in the twentieth-century manufacture of refrigerants and solvents. The production of CCl_4 for emissive uses is controlled by the Montreal Protocol and subsequent amendments. Analysis of firn air samples suggests that CCl_4 was very low in concentration or absent in the pretwentieth-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 CCl_4 in recent decades, however, is not consistent with estimates of emission to and removal from the atmosphere (Montzka et al., 2011, Carpenter et al., 2014). Emissions derived from reported production are lower than "top-down" estimates based on atmospheric measurements and knowledge of CCl_4 loss processes. The 2016 SPARC Report on the Mystery of CCl_4

(SPARC, 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.

CCl_4 is removed from the atmosphere by stratospheric photolysis (Burkholder et al., 2013), and uptake by the ocean (Butler et al., 1993, 2016; Krysell et al., 1994) and soils (Happell & 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, and an associated total atmospheric lifetime of 35 (32–37) years. The 2016 SPARC Report (SPARC, 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 CCl_4 emissions (SPARC, 2016). A recent atmospheric model intercomparison (Chipperfield et al., 2016) evaluated the influence of CCl_4 sources and sinks on the estimated atmospheric lifetime of CCl_4, noting that uncertainty in estimated oceanic uptake of CCl_4 is potentially the most significant influence on estimates of atmospheric CCl_4 decay, and called for an improved quantification of this flux and its associated partial atmospheric lifetime.

1.2. Oceanic CCl_4

CCl_4 is soluble in seawater (Bullister & Wisegarver, 1998), and its oceanic uptake is driven by the disequilibrium between CCl_4 partial pressures in the respective atmospheric and oceanic environments (B2016). The distribution of CCl_4 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., 1994; B2016).

Information on the nonconservative nature of CCl_4 in seawater has accumulated as analyses of oceanic CCl_4 measurements have identified CCl_4 depletion (in comparison to halocarbons such as CFC-11 and CFC-12) in a range of oceanic environments. These include measurements from suboxic and anoxic regions (Krysell et al., 1994; Lee et al., 1999; Min et al., 2010; Tanhua et al., 1996, 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 CCl_4 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 CCl_4 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 (Krysell & Wallace, 1988; Wallace et al., 1994). Observed correlations between Apparent Oxygen Utilization (AOU) and relative CCl_4 undersaturations (e.g., B2016) suggest biologically mediated CCl_4 loss in low-oxygen waters, although the specific mechanism remains unidentified (Min et al., 2010; Yvon-Lewis & Butler, 2002, and references therein).

1.3. Aims of This Analysis

Global oceanic uptake of atmospheric CCl_4 has previously been quantified by analysis of upper ocean measurements in combination with process parameterizations (Yvon-Lewis & 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° × 2°) data set of surface-ocean properties (e.g., sea surface temperature, salinity, wind speed) 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 CCl_4 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 CCl_4 and CFC-11

To support model evaluation and optimization, we compiled databases of oceanic CCl_4 and CFC-11 observations, incorporating measurements reported in data repositories and by individual investigators. For CCl_4, this includes measurements from the following sources (n represents the number of individual measurements in each repository): (i) GLODAPv2 (Olsen et al., 2016; $n = 43,112$), (ii) CARINA (Key et al. 2010; $n = 25,034$), (iii) PACIFICA (Suzuki et al., 2013; $n = 634$), (iv) NOAA-GMD (Butler et al., 2016; $n = 3,147$), (v) Messias (personal communications; $n = 1,693$), and (vi) Carpenter (personal communications; $n = 1,156$). 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) using the solubility relationships of Bullister and Wisegarver (1998). The compiled set of CCl_4 measurements span the period 1987–2013, and the median year of observation is 1998. To enable a consistent comparison with modeled CCl_4, the compiled data were spatially gridded to the World Ocean Atlas (2009) grid ($1° \times 1° \times 33$ depths), and aggregated to monthly time scales. This regridded CCl_4 database has $n = 32,636$ observations (1987–2013 period), and is used in the model analysis and optimization of sections 2.3–2.5. We use two versions of the observational database: (i) an interannually varying data set 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 ($n = 315,246$), CARINA ($n = 86,051$), NOAA-GMD (B2016; $n = 3,145$), PACIFICA ($n = 78,244$), and M. J. Messias (personal communications; $n = 1,693$). Following regridding to the World Ocean Atlas (2009) grid, the number of coincident data points between the gridded CCl_4 and CFC-11 databases (i.e., reporting both species) is $n = 28,240$. 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, 2008; Madec & Imbard, 1996). Parameterized nutrient biogeochemistry is based on the PISCES model (Aumont & Bopp, 2006), and PlankTOM has been extended to include representation of ocean ecosystem processes (Le Quéré et al., 2005) and biogeochemical cycling of soluble gases (Andrews et al., 2017; Buitenhuis et al., 2018; Suntharalingam et al., 2012; Vogt et al.,

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/year)	Partial Atmosphere 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)		Average flux 1996–2000	τ_{oc}
Prescribed α_{set} = 10 nmol/mol	α_{set} = 10	10.8 (11.3)	229 (217)
Prescribed α_{set} = 20 nmol/mol	α_{set} = 20	18.6 (19.0)	134 (129)
Prescribed α_{set} = 30 nmol/mol	α_{set} = 30	25.4 (25.8)	98 (95)
Prescribed α_{set} = 45 nmol/mol	α_{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: ±1σ range)		Air-sea flux (Gg/year)	τ_{oc} (years)
Case OPT$_{1996-2000}$: period 1996–2000	α_{opt} = 20.0	18.5 ± 2.3	131 (118–146)
Case OPT$_{1987-2013}$: period 1987–2013	α_{opt} = 19.0	17.9 ± 3.0	134 (115–161)
Case OPT$_{CFC11}$: period 1996–2000	α_{opt} = 22.1	20.1 ± 1.2	124 (117–132)
CFC-11 correction			
Section B2: sensitivity analyses on gas-exchange parameters: period 1996–2000		Flux range[b]	τ_{oc} range[b]
Case OPT$_{1996-2000}$ with solubility (K_0) ±2.5%	α_{opt} = 20.0	16.5–20.7	120–150
Case OPT$_{1996-2000}$ with gas-transfer velocity (k) ± −32%	α_{opt} = 20.0	13.9–22.1	112–179
Case OPT$_{CFC11}$ with solubility (K_0) ±2.5%	α_{opt} = 22.1	18.8–21.5	115–132
Case OPT$_{CFC11}$ with gas-transfer velocity (k) ±32%	α_{opt} = 22.1	17.1–21.9	109–142
Section B3: total uncertainty range (model-data optimization and gas-exchange uncertainties)			
Case OPT$_{1996-2000}$	α_{opt} = 20.0	18.5 (13.0–23.3)	134 (107–191)
Case OPT$_{CFC11}$	α_{opt} = 22.1	20.1 (16.6–22.7)	124 (110–150)

[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.

2010). For this study the model is employed at a horizontal resolution of ~2° at midlatitudes, varying to higher latitudinal resolution of ~0.2° in equatorial and polar latitudes. The model has 31 vertical levels, with resolution varying from 10 m in the upper 100 m to 500 m below 2-km depth. Surface meteorological forcing uses daily values from the National Centers for Environmental Prediction (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 (NOAA, 2011), and follows the methodology of Buitenhuis et al. (2013). Ocean model CCl₄ and CFC-11simulations are subject to the time-varying atmospheric mixing-ratio history of Bullister (2015) (see Figure 1 for CCl₄) 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 World Ocean Atlas 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 nonconserved tracers in the NEMO-PlankTOM5 model, following methods for soluble gases (Andrews et al., 2017; Suntharalingam et al., 2012). Modeled 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 [CCl₄] component accounts for local sources and sinks.

$$\frac{\partial[CCl_4]}{\partial t} = -V.\nabla[CCl_4] + \nabla.(D.\nabla[CCl_4]) + SMS[CCl_4] \tag{1}$$

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 [CCl₄] 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 ($pA_{atm} - pA_{water}$).
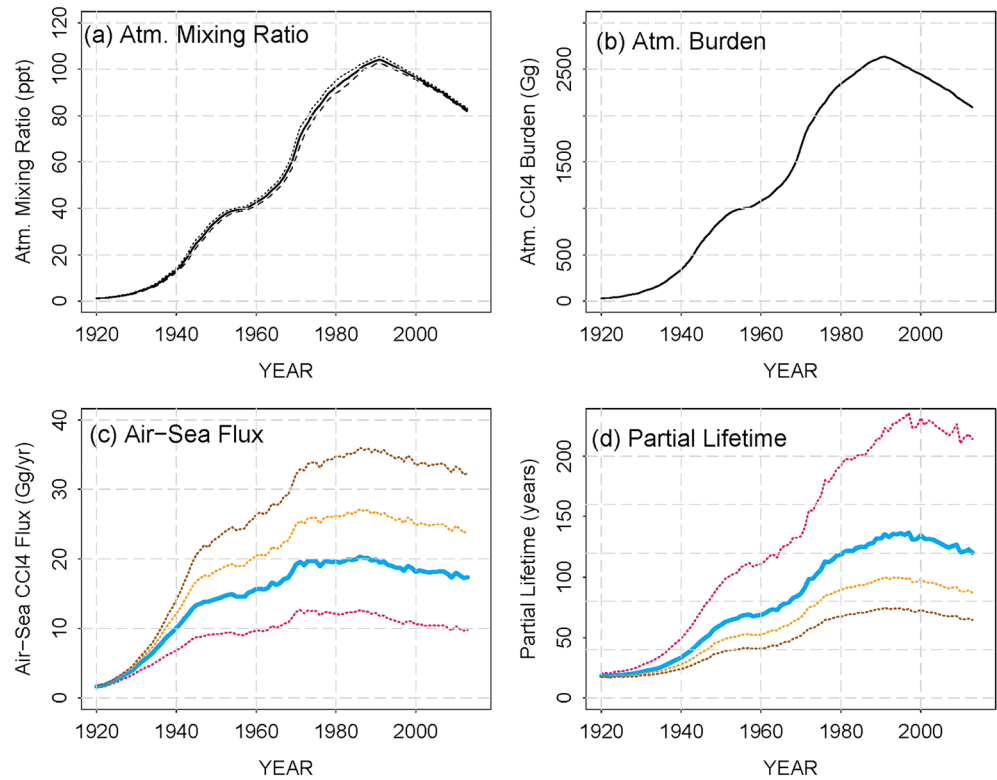
Figure 1. Time variation of CCl_4 quantities. (a) Atmospheric CCl_4 mixing ratio (ppt), global average (solid line), and northern (dotted) and southern hemisphere (dashed) averages; data are taken from Bullister (2015). (b) Global atmospheric CCl_4 burden (see section 2.6 for calculation details). (c) Model-derived global average air-sea CCl_4 fluxes from selected prescribed α simulations; cases shown are α_{set} = 10 nmol/mol (magenta dotted), α_{set} = 20 nmol/mol (blue solid), α_{set} = 30 nmol/mol (yellow dotted), and α_{set} = 45 nmol/mol (brown dotted). (d) Transient partial atmospheric lifetime values for selected prescribed α simulations; cases shown are α_{set} = 10 nmol/mol (magenta dotted), α_{set} = 20 nmol/mol (blue solid), α_{set} = 30 nmol/mol (yellow dotted), and α_{set} = 45 nmol/mol (brown dotted).

$$F_A = k \, K_0 \, (pA_{atm} - pA_{water}) \tag{2}$$

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 ^{14}C inventory and wind speeds 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 seawater, is taken from Bullister and Wisegarver (1998).

$$k = 0.27 < U^2 > (Sc/660)^{-0.5} \tag{3}$$

$<U^2>$ represents the square of the averaged 10-m 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

2.3.4.1. 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

$$k_{hydrolysis} = 25.25 \times 10^{12} \times e^{\left(-\frac{15,890}{T}\right)} \text{ s}^{-1} \tag{4}$$

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.

2.3.4.2. Biologically Mediated CCl$_4$ Degradation

In situ measurements of oceanic CCl$_4$ reveal undersaturation in surface waters and significant depletion in the subsurface ocean up to depths of ~2,000 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 (Δ [CCl$_4$]) (e.g., B2016; Figure 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 CCl$_4$ depletion using the compiled data of section 2.3 yields an overall correlation coefficient of Δ [CCl4])/AOU~-27 nmol/mol (i.e., -27×10^{-9} 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, Δ [CCl$_4$], and the correlation analysis). Based on these observed predominantly linear correlations between CCl$_4$ depletion and AOU, our parameterization of biologically mediated oceanic CCl$_4$ degradation represents CCl$_4$ loss as a linear function of oxygen utilization, for example, scaled by a parameter α representing a degradation ratio of CCl$_4$ depletion to oxygen utilization.

$$\text{CCl}_4 \text{ degradation rate} = -\alpha \, [\text{O}_2 \text{ utilization rate}] \tag{5}$$

Here the parameter α represents a ratio of moles of CCl$_4$ degradation to moles of oxygen utilization. This follows methods adopted for biogeochemical cycling of other trace gases (e.g., Martinez-Rey et al., 2015; Suntharalingam et al., 2012), where AOU is used as a proxy for oxygen utilization associated with heterotrophic respiration in oxygenated water (Sarmiento & Gruber, 2006).

2.4. CCl$_4$ Simulations and Optimization

A set of NEMO-PlankTOM CCl$_4$ 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 (Δ [CCl$_4$])/AOU, for example, $\alpha_{set} = \alpha_i$ 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 CCl$_4$ 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 (6)) 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.

$$\text{Cost function} : \text{CF} = \sum_{n=1}^{N} \frac{\left([\text{Model CCl}_4]_n - [\text{observed CCl}_4]_n\right)^2}{N}. \tag{6}$$

In equation (6), index n represents the individual oceanic observations of CCl$_4$ and N the total number of observations for the period analyzed (e.g., N = 31,362 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 OPT$_{CFC11}$ 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.

$$\Delta_{CORR} = \Delta_{CCl4} - \Delta_{CFC11} \tag{7}$$

where

$$\Delta_{CCl4} = \left(\frac{p[CCl_4]_{water} - p[CCl_4]_{air}}{p[CCl_4]_{air}} \right) \times 100\%$$

$$\Delta_{CFC11} = \left(\frac{p[CFC11]_{water} - p[CFC11]_{air}}{p[CC11]_{air}} \right) \times 100\%$$

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

We then derive a modified cost function (equation (8)) incorporating the corrected saturation anomalies:

$$\text{Modified cost function} = \Sigma_{n=1}^{N} \frac{([Model\ \Delta_{CORR}]_n - [observed\ \ \Delta_{CORR}]_n)^2}{N} \tag{8}$$

Here model and observed CCl_4 concentrations of equation (6) have been replaced with corrected saturation anomaly values for model and observations, respectively.

2.5.2. Climatological Versus 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 ($n = 31,362$) and (ii) case $OPT_{1987-2013}$, using the time-varying observational database with model values taken from time-varying simulations for 1987–2013 ($n = 32,636$). Our analysis using CFC-11-corrected saturation anomalies (section 2.5.1) is restricted to the climatological data set due to relatively few coincident CFC-11 and CCl_4 measurements in the early stages of the 1987–2013 period. For this common data set (CCl_4 and CFC-11 sampled together), $n = 28,240$. 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 (equation (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 ~32% in the parameterization of the gas transfer velocity, k, for global or basin-scale applications, and Wanninkhof (2014) notes a smaller uncertainty of ~20%. Here we evaluate sensitivity to the larger more conservative uncertainty estimate of Sweeney et al. (2007), and vary representation of k by ±32%. Our simulations employ the temperature-dependent solubility parameterization of Bullister and Wisegarver (1998), who report a ±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 ±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 ±32% perturbations for the gas transfer velocity k, and ±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_{CCl4}) to the loss rate to the ocean (F_{CCl4}), that is, $\tau_{oc} = (M_{CCl4})/(F_{CCl4})$ (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

$$\tau_{oc}(t) = \frac{M_{CCl4}(t)}{F_{CCl4}(t)} \tag{9}$$

where $M_{CCl4}(t)$ and $F_{CCl4}(t)$ 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, $M_{CCl4}(t)$, 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).

$$M_{CCl4}(t) = n_{tr} \times x_{atm}(t) \times r_g \qquad (10)$$

Resulting estimates for atmospheric burden ($M_{CCl4}(t)$) 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 (11)), follows SPARC (2016), where τ_{TOT} is a function of the individual lifetimes with respect to the different CCl_4 loss processes, that is, stratospheric photolysis (τ_{atm}), and uptake by soils (τ_{soil}), and the ocean (τ_{oc}).

$$\frac{1}{\tau_{TOT}} = \frac{1}{\tau_{atm}} + \frac{1}{\tau_{soil}} + \frac{1}{\tau_{oc}} \qquad (11)$$

3. Results and Discussion

Table 1 summarizes 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) and (b) the comparison of modeled average depth profiles with observations (Figure S2 in the supporting information), shows the closest overall match for the simulation with $\alpha_{set} = 20$ nmol/mol. Figure 1d demonstrates the time-varying nature of the instantaneous partial lifetime $\tau_{oc}(t)$ (equation (9)). For the $\alpha_{set} = 20$ 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 ($\alpha_{set} = 20$ nmol/mol) are 18.6 Gg/year for the period 1996–2000 and 19.0 Gg/year 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 $OPT_{1996-2000}$ using observational and model climatologies and case $OPT_{1987-2013}$ using time-varying analyses for 1987–2013. The estimated values for α_{opt} are 20.0 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 CCl_4 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 α_{opt} = 22 nmol/mol, with an associated air-sea flux of 20.1 ± 1.2 Gg/year, 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 CCl_4 deficit attributable to degradation processes, and correspondingly larger estimates for α_{opt} and air-sea flux, in comparison to the unadjusted case OPT$_{1996-2000}$.

Sensitivity analyses on gas-transfer velocity k, and solubility K_0, were conducted for the optimizations of case OPT$_{1996-2000}$ and case OPT$_{CFC11}$ (described in section 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 ±32% for case OPT$_{1996-2000}$ yields changes in estimated air-sea flux (ranging from 13.9 to 22.1 Gg/year), 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/year and partial lifetime of 109–142 years. Assessment of sensitivity to the solubility parameter K_0 (by ±2.5%) has a smaller impact on τ_{oc}, giving an uncertainty range of 120–150 years for case OPT$_{1996-2000}$ 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 OPT$_{1996-2000}$ this gives a revised flux range of (13.0–23.3) Gg/year with a τ_{oc} range of 107–191 years. For case OPT$_{CFC11}$, the revised air-sea CCl_4 flux range is 20.1 (16.6–22.7) Gg/year 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 CCl_4 uptake, we report this result for case OPT$_{CFC11}$ as our best estimate of oceanic CCl_4 uptake and partial lifetime.

4. Conclusions

In summary, our suite of optimization analyses yields estimates for the global averaged oceanic CCl_4 degradation parameter α in the range 19–22.1 nmol/mol with associated global oceanic CCl_4 uptake of 17.9–20.1 Gg/year (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/year 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/year 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 ~7 Gg/year for case OPT$_{CFC11}$ and by ~5.5 Gg/year for case OPT$_{1987-2013}$. Our best constrained estimate of partial lifetime (case OPT$_{CFC11}$: 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 subsurface 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 parameterizations).

We estimate corresponding values for the total atmospheric lifetime τ_{TOT} as 29.9 (24.8–38.8) years, using equation (10) and recent estimates for τ_{atm} of 44 (36–58) years (SPARC, 2016) and τ_{soil} of 375 (288–536) years (Rhew & Happell, 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; SPARC, 2016) (although 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 τ_{oc} = 94 years. Our results suggest a larger missing atmospheric source of CCl_4 (by approximately 5–7 Gg/year) 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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