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On the Influence of Hydroxyl Radical Changes and Ocean Sinks on Estimated HCFC and HFC Emissions and Banks

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Key Points:

- Increasing OH suggested by Coupled Model Intercomparison Project Phase 6 models can lead to a 5%–7% underestimation in hydrochlorofluorocarbon (HCFC) and hydrofluorocarbon (HFC) emission estimations in 2005
- If there is significant ocean degradation through microbial activity, HCFC, and HFC emissions could be underestimated by up to 10%
- Our study suggests an uncertainty in the combined contribution to global warming from HCFCs and HFCs up to 15%–20% in the 2020s

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are potent greenhouse gases regulated under the Montreal Protocol and its amendments. Emission estimates generally use constant atmospheric lifetimes accounting for loss via hydroxyl radical (OH) reactions. However, chemistry-climate models suggest OH increases after 1980, implying underestimated emissions. Further, HCFCs and HFCs are soluble in seawater and could be destroyed through in situ oceanic microbial activity. These ocean sinks are largely overlooked. Using a coupled atmosphere-ocean model, we show that increases in modeled OH imply underestimated HCFC and HFC emissions by ~10% near their respective peak emissions. Our model results also suggest that oceanic processes could lead to up to an additional 10% underestimation in these halocarbon emissions in the 2020s. Ensuring global compliance to the Protocol and accurate knowledge of contributions to global warming from these gases therefore requires understanding of these processes.

Plain Language Summary Man-made hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) contribute to global warming, prompting worldwide agreement to control the production of these chemicals. It is important to estimate their emissions to ensure global compliance with the agreed phaseout. But correct emission estimation requires knowledge of different loss pathways. One major loss pathway of halocarbons is through chemical reactions with the atmospheric “scrubber” called OH. OH is difficult to measure and usually assumed to be constant with time. But some models suggest OH has increased, which implies increased emissions to match observed abundances. These halocarbons also dissolve into the oceans, where microbes may also metabolize them, but these processes are not included in current emission estimates. We show that if these halocarbons are being consumed in the oceans, this would also lead to an additional underestimation of human emissions. Confidence in the success in the Montreal Protocol and its Kigali amendment to reduce HFCs will therefore require a better understanding of both OH trends and ocean sinks, along with use of HFC and HCFC measurements.

1. Introduction

Chlorofluorocarbons (CFCs) are the main reason for the Antarctic ozone “hole” (e.g., Solomon, 1999). Under the Montreal Protocol on Substances that Deplete the Ozone Layer, the production of these molecules has been strictly regulated since the early 1990s. Hydrochlorofluorocarbons (HCFCs) were used to replace CFCs as they can react with the hydroxyl radical (OH) rapidly in the troposphere, reducing the chlorine reaching the stratosphere, and thus depleting ozone. However HCFC emissions were not globally regulated until the early 2010s, and the amount of chlorine delivered to the stratosphere from HCFCs rose by more than 60% from 1993 to 2020 (Laube & Tegtmeier, 2022). While a complete global phase-out of HCFCs is expected to happen in 2030, their use as feedstocks to manufacture other compounds remains exempted from the Montreal Protocol. In the past two decades, HCFC emissions from feedstocks are believed to have increased by five-fold (Daniel & Reimann, 2022) and leakage rates are higher than expected (Western et al., 2022), prompting discussions about narrowing feedstock exemptions (Andersen et al., 2021). HCFCs were replaced by hydrofluorocarbons (HFCs). HFCs are not ozone depleters but are potent greenhouse gases that have global warming potentials ranging from thousands to tens of thousands times that of carbon dioxide on a mass basis (Liang & Rigby, 2022). The Kigali Amendment to the Montreal Protocol to regulate HFCs entered into force in 2019. The amendment is expected to lead to a global emissions peak in the 2030s. If effective mitigation of HFCs occurs worldwide, the projected global

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warming, compared to continuing production of HFCs, will be reduced by up to 0.4°C by the end of 2100 (Velders et al., 2022).

The primary loss pathway for HCFCs and HFCs is through reaction with OH. But due to a lack of direct measurements of global-scale OH concentrations and uncertainties in the inferred OH concentration based on methyl chloroform observations (Prinn et al., 2018), current emission estimations for HCFCs and HFCs generally assume OH is seasonally-varying but annually-repeating over time. Here we consider time-varying potential trends in OH. Turner et al. (2017) found that changes in methane may be explained by an increase in OH from 1980 to 2005 and a decrease afterward. A similar decreasing trend in OH after 2005 was also found in several inversion studies (Montzka et al., 2011; Rigby et al., 2017). In contrast, while a suite of Coupled Model Intercomparison Project Phase 6 models suggest a 10% increase in OH from 1980 to 2005 similar to Turner et al. (2017), they indicate ongoing increases afterward (Stevenson et al., 2020). Recently, using methyl chloroform with 3D model inversions incorporating observed meteorology, Patra et al. (2021) also deduced a significant OH increase after 2005. We explore increasing OH trends from 1980 to 2005 and increasing or decreasing trends thereafter.

Halocarbons (mainly CFC-11 and CFC-12) have a long history of use as inert tracers to study ocean circulation (e.g., Bullister & Weiss, 1983; Ito et al., 2004; Romanou et al., 2017; Waugh, 2014). In an earlier study (Wang et al., 2021), we showed that ocean uptake can affect the inferred atmospheric residence times of CFC-11 and CFC-12, therefore affecting their emission estimates. Similarly, the ocean represents a potential loss pathway for HCFCs and HFCs since they are also soluble in seawater. However, the ocean could be a larger sink for these gases than previously thought, because certain microbes can feed on hydrogen-bearing compounds (Dworkin et al., 2006), such as methyl halides (Cox et al., 2012; Tokarczyk, Goodwin, & Saltzman et al., 2003; Tokarczyk, Saltzman, et al., 2003). Similarly, aerobic oxidation can also degrade certain HCFCs and HFCs (Chang & Criddle, 1995; DeFlaun et al., 1992; Streger et al., 1999). But due to limited measurements, ocean degradation of HCFCs and HFCs via biological processes has not been considered in previous estimations of ocean partial lifetimes (Liang & Rigby, 2022; Yvon-Lewis & Butler, 2002). Hydrolysis is another ocean degradation process for halogenated species such as methyl chloroform (Wennberg, 2004), but is considered minor for HCFCs and HFCs (Yvon-Lewis & Butler, 2002). Here we explicitly evaluate the atmospheric residence time, treating the ocean destruction and reservoir both as sinks insofar as the atmosphere (as appropriate for deriving emissions) is concerned; previous work has often used a different definition of ocean destruction only, which leads to much smaller impacts (Yvon-Lewis & Butler, 2002).

Given debate regarding feedstock emissions for HCFCs and new regulations on HFCs, it is crucial to consider uncertainties in emission estimates inferred from observed atmospheric abundance data to ensure the continued success of the Montreal Protocol and its amendments. In this study, we quantify uncertainties in emission estimations and banks due to different OH scenarios (time-varying OH trends vs. fixed OH) and ocean scenarios (only involving physical dissolution or with additional microbial ocean degradation) for three HCFCs (HCFC-141b, HCFC-142b, and HCFC-22) and three HFCs (HFC-125, HFC-134a, and HFC-23) whose seawater solubilities are provided by Li et al. (2019).

2. Data and Methods

We couple the ocean representation of the Massachusetts Institute of Technology General Circulation Model (MITgcm, Marshall, Adcroft, et al., 1997; Marshall, Hill, et al., 1997) with the atmosphere from the Advanced Global Atmospheric Gases Experiment (AGAGE) 12-box model (Rigby et al., 2013). This coupled model runs independently from the start of emissions for each species to 2050.

2.1. Ocean Representation

We use a similar MITgcm ocean configuration as Wang et al. (2021), adopting a $2.8^\circ \times 2.8^\circ$ horizontal resolution and 15 vertical layers down to 5 km depth. Despite its coarse resolution, this configuration simulates the oceanic distributions and the overall ocean burdens of CFCs reasonably well (Wang et al., 2021). The ocean is forced with monthly climatologies of wind stress and buoyancy fluxes. A detailed description of each of the forcing fields is discussed in Wang et al. (2021). Prior to the introduction of halocarbon emissions, the ocean was spun-up for 5,900 years with these climatological forcings to effectively reach a steady state. We only consider climatological forcing in this study since our earlier study showed that future climate change had a rather small impact on the

global CFC ocean burden (although it does affect the timing for the ocean to switch from a net sink to a net source (Wang et al., 2021)).

Li et al. (2019) report the Ostwald solubilities as functions of temperature and salinity for several HCFCs and HFCs. Freshwater solubilities are compared with other studies using various methods, and good agreement is achieved for most of the species except HFC-125 (Li et al., 2019). These temperature- and salinity-dependent solubilities are then fitted to a polynomial that has the format used by the MITgcm. Table S1 in Supporting Information S1 shows the fitted coefficients for HCFCs and HFCs used in this study. Figure S1 in Supporting Information S1 plots the solubility for each species as a function of temperature and salinity. These molecules are generally more soluble in colder and less salty conditions.

The Schmidt number (Sc) is used in the MITgcm to calculate the gas transfer velocity. It characterizes the ratio between the kinematic viscosity of the solution and the diffusion coefficient of the gas in the solution (Wanninkhof, 1992). We follow a similar process to obtain seawater Sc values for HCFCs and HFCs as in Wanninkhof (1992). Sc in the MITgcm is parameterized only as a function of temperature at a constant salinity of 35‰ (per mille); see Text S1, Table S2, and Figure S2 in Supporting Information S1 for details.

Several studies indicate that aerobic microbial processes in the ocean can destroy certain HCFCs and HFCs (Chang & Criddle, 1995; DeFlaun et al., 1992; Streger et al., 1999). However, ocean degradation rates can vary significantly depending upon spatial and temporal variations in biology and other properties such as oxidation state. Due to limited knowledge of the ocean degradation processes, we perform several ocean scenarios to explore various assumptions: (a) no ocean uptake (noOCN), (b) with ocean dissolution but without any degradation (OCN), and (c) with an e-folding ocean degradation timescale at 1 year (degradeOCN). We choose 1 year as the upper limit of ocean degradation losses because HCFC-22, which experiences faster decay than other species (Chang & Criddle, 1995), degrades with a timescale on the order of a year in the ocean mixed layer (detailed calculation in Text S2 in Supporting Information S1). We also present results for ocean degradation with a timescale of 5 years to illustrate the differences found between no biological degradation and a 1 year degradation timescale.

2.2. Atmosphere Representation

We use the AGAGE 12-box model as the atmospheric portion of our coupled ocean-atmosphere framework. This model has three vertical layers (surface to 500, 500–200, and above 200 hPa) and four zonally-averaged latitudinal bands (90°–30°N, 30°N–equator, equator–30°S, and 30°–90°S). It employs monthly OH concentrations and transport parameters for each box. A detailed description is provided in Rigby et al. (2013). Note that we do not consider year-to-year changes in the atmospheric transport parameters, but such interannual dynamical changes can also influence variations in inferred lifetimes and emissions (Ko et al., 2013).

Historical input emissions for HCFCs and HFCs between the 1970s and 2021 are from the posterior mean emission (later referred to as posterior emission) obtained by inverse modeling of the AGAGE measured mole fractions of each species combined with a 12-box model that assumes fixed OH and constant lifetimes from the World Meteorological Organization 2022 report (Laube & Tegtmeier, 2022; Liang & Rigby, 2022; M. Rigby et al., 2013). However, anthropogenic emissions for HCFC-22 and HFC-23 started long before the AGAGE observations began and posterior emissions are available. For these two species, we run the coupled ocean-atmosphere model starting in the 1940s with zero initial concentrations in both the ocean and atmosphere, employing a priori emissions (Miller et al., 2010) to produce reasonable tracer distributions, and then switch to the posterior emissions after the 1970s. Here we focus on the period when we switch to the posterior emission inputs. Figure S3 in Supporting Information S1 shows the model simulated atmospheric mole fractions for all the species used in this analysis using the posterior emissions compared to the AGAGE observations (Prinn et al. (2018) updated through 2021 using data from <https://agage.mit.edu/data>), and they show good agreement.

Future emissions for HFC-125 and HFC-134a are from the upper limit of the Kigali Amendment projection from Velders et al. (2022). Future emissions for HCFC-141b, HCFC-142b, and HCFC-22 are obtained from the inverse study of the projected mole fractions from Daniel and Reimann (2022) using a one-box model assuming a perfectly mixed atmosphere and constant lifetimes. HFC-23 is mainly a by-product of HCFC-22 production, and we assume future HFC-23 emissions follow the same rate of change as HCFC-22 (neglecting potential differences during leakage from banks such as refrigeration). To prevent discontinuity in the input emissions, we scale

global projected emissions from 2022–2050 to emissions in 2021, and apply this scaling to generate a smooth transition from the historical to future emissions.

Different OH scenarios are considered in order to infer HCFC and HFC atmospheric residence times and emissions. In the “fixOH” scenario, we use repeating monthly OH concentrations every year from Rigby et al. (2013). In the “varyOH” scenario, OH does not change before 1980, but it increases by 10% between 1980 and 2005 (in each box and month). Future projections of OH to 2050 vary greatly among different models (Murray et al., 2021). We therefore apply a $\pm 15\%$ change of OH between 2005 and 2050 (spanning the range from different warming scenarios (Murray et al., 2021)). Figure S4 in Supporting Information S1 summarizes different OH assumptions used in this study. Note that the absolute amount of OH concentration from inversions based on methyl chloroform can have large uncertainties (Rigby et al., 2017). These absolute uncertainties largely cancel insofar as they exist in both the “fixOH” and “varyOH” scenarios, and only the relative change in the emissions between different OH scenarios is affected.

2.3. Inferring the Atmospheric Residence Times and the Emissions

We refer to the e-folding decay timescale for each species as the atmospheric residence time in this study since the residence time involves not only atmospheric loss rates (i.e., reaction with OH) but also ocean processes (such as ocean uptake and outgassing) characterized by:

$$\tau(t) = \frac{B(t)}{L_{\text{OH}}(t) + L_{\text{OCN}}(t) + L_{\text{OTHER}}(t)} \quad (1)$$

where B is the total atmospheric burden, L_{OH} , L_{OCN} , and L_{OTHER} are the total loss rates due to OH, ocean sinks, and other photochemistry (largely stratospheric), respectively. L_{OCN} can be negative when the ocean becomes supersaturated and returns gas back to the atmosphere.

To infer global emissions, we use different residence times τ calculated from various combinations of ocean and OH scenarios, using the equation:

$$E(t) = \frac{dB(t)}{dt} + \frac{B(t)}{\tau(t)} \quad (2)$$

where the atmospheric burden B is the simulated “noOCN” and “fixOH” case, that is, what we would have “observed” in the atmosphere in the absence of time-varying OH and ocean uptake.

3. Results

3.1. Relative Magnitudes of Different Loss Pathways

We first quantify a baseline magnitude (without varying OH and neglecting ocean degradation) of each loss pathway for HCFCs and HFCs (Figure S5 in Supporting Information S1). Without considering ocean degradation, the global ocean sink and stratospheric loss through photochemistry are generally about an order of magnitude smaller than loss due to OH. However, HFC-23 has a slow reaction with OH and an atmospheric lifetime greater than 200 years (while other species considered here display decadal lifetimes), and ocean loss is comparable to OH loss for this molecule. For all species, loss rates due to ocean sinks differ between the two hemispheres. Ocean uptake in the Southern Hemisphere is twice that in the Northern Hemisphere (Figures S6 and S7 in Supporting Information S1), due in part to the larger open ocean area and enhanced upwelling of undersaturated waters driven by strong surface wind stress. Therefore, loss to the ocean in the 30°–90°S latitude band accounts for 10%–20% of the loss to OH in that region for most of the species considered here. Globally summed, loss to the ocean is less than about 5% of the total loss to OH for HCFCs and HFCs in this analysis, with the important exception of HFC-23.

3.2. Inferred Atmospheric Residence Times

Figure 1 shows the inferred atmospheric residence times for each species. Species other than HCFC-22 and HFC-23 have close to zero emissions in the 1980s, reflected in steep changes in the residence times in the first

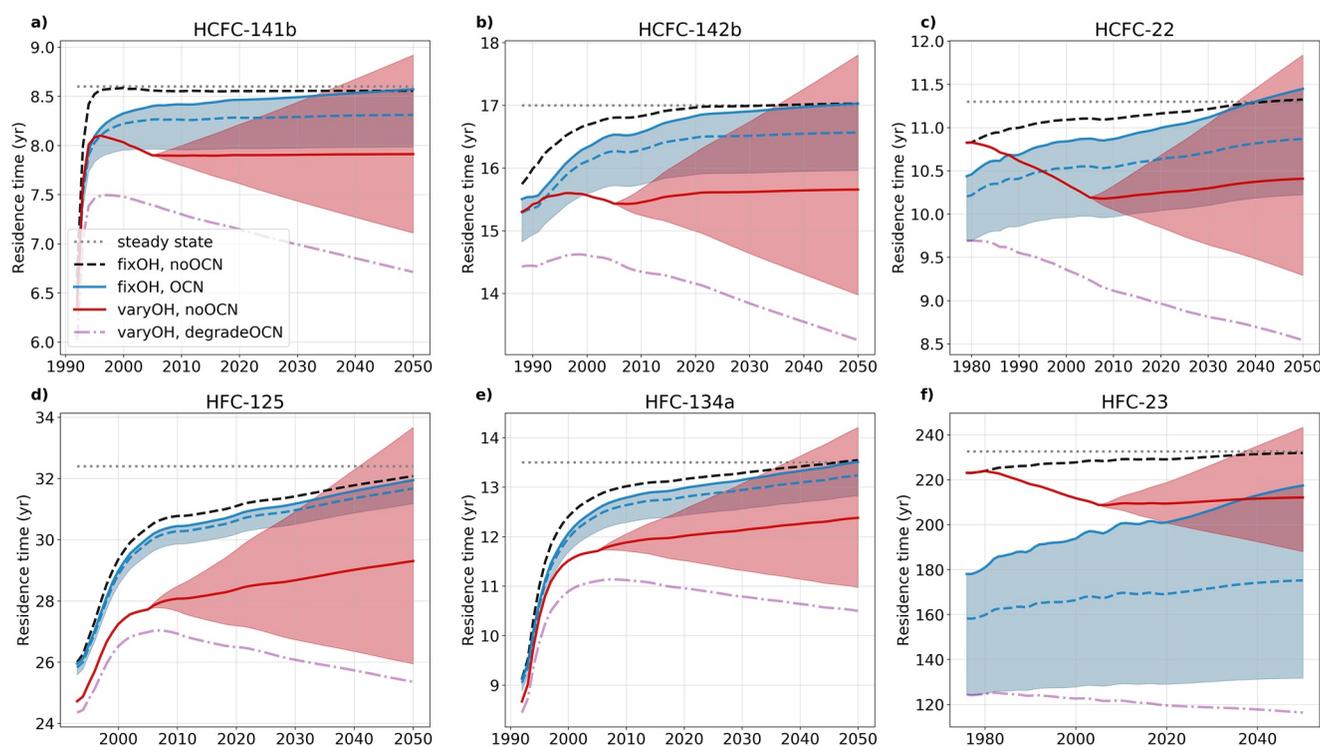


Figure 1. Global atmospheric residence times for all the species used in this study. Gray dotted lines are the steady state lifetimes calculated from the AGAGE 12-box model based on atmospheric removal rates from the WMO (2022) report. Black dashed lines are inferred from a model simulation with fixed OH over time and without ocean uptake. Blue solid lines are inferred from models with fixed OH over time but including ocean dissolution without degradation, while blue dashed lines assume a 5 years ocean degradation timescale, blue shadings denote the case for ocean degradation timescale up to 1 year. Red solid lines indicate a 10% increase in OH from 1980 to 2005 and are constant beyond 2005, and the red shadings indicate $\pm 15\%$ OH changes from 2005 to 2050. The purple dash-dotted lines combine the increasing OH (both 10% increase in 1980–2005 and 15% increase in 2005–2050) with a 1 year ocean degradation timescale to define a lower limit range.

few years. The impact of the ocean on the inferred residence times is largest in the early period, when the ocean is less saturated and has a greater ability to dissolve these gases. Overall, the ocean shortens the inferred residence times during most of the time before 2050, as the ocean is still a net sink for these species globally (although earlier ocean outgassing is occurring regionally in the tropical and coastal upwelling zones). However, an exception is HCFC-22, for which the ocean starts to become a net source of emission in the 2040s globally (Figure S5h in Supporting Information S1), and hence its residence times increase afterward. Without ocean degradation, adding the ocean shortens the inferred residence times by up to 2% before 2020 for most of the species, and 15% for HFC-23. As the ocean becomes more saturated over time, the difference in the inferred residence times with versus without the ocean shrinks.

However, if a dissolved HCFC or HFC is degraded in the ocean, the ocean will have a greater ability to uptake these gases and will be difficult to oversaturate relative to its declining trend in the atmosphere. By 2020, assuming halocarbons degrade in the ocean with a timescale of 5 years, their residence times are shortened by 2%–5% compared to the noOCN case for most species (and a 25% decrease in residence time for HFC-23). And if the ocean degradation timescale is 1 year, we obtain a 3%–10% decrease in the inferred residence times for most of the species (and a 40% decrease for HFC-23).

Increasing OH concentrations would also shorten residence times in the atmosphere. A 10% increase in the OH concentration from 1980 to 2005 leads to about an 8% decrease in the inferred residence time by 2005 for all the species in this study. After 2005, if OH increased by another 15% by 2050 as some models indicate, this would result in a 15%–20% decrease in the inferred residence time by the end of 2050 compared to the fixed OH scenario. However, if OH decreases after 2005, the inferred residence time would return to the fixed OH scenario by the end of 2040. The purple dot-dashed lines in Figure 1 show the lower limits of residence times obtained by combining both a 1 year ocean degradation timescale and an increasing OH of 25% from 1980 to 2050.

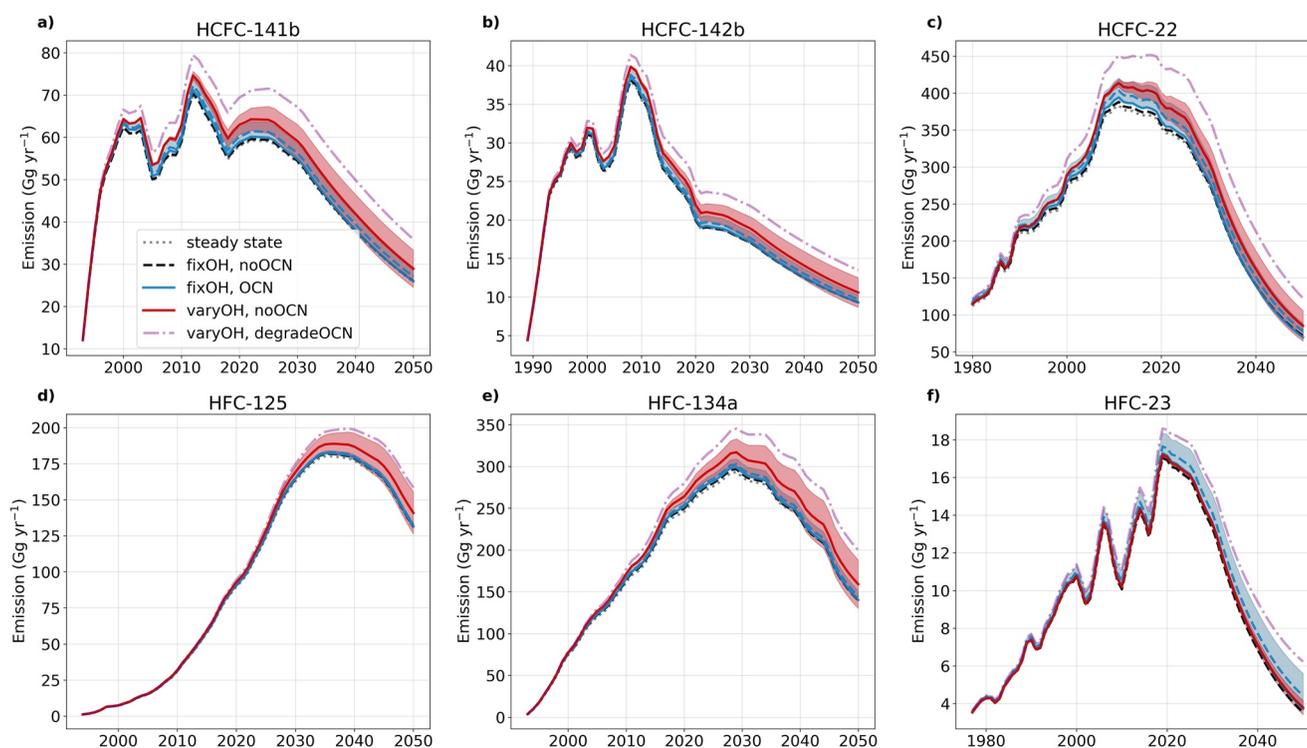


Figure 2. Inferred global emissions for all the species modeled in this study, based on the different residence times for the cases considered in Figure 1.

3.3. Inferred Global Emissions and Bank Estimations

Figure 2 shows the inferred global emissions for HCFCs and HFCs using different inferred atmospheric residence times obtained from Section 3.2 (changes in the emissions shown in Figure S8 in Supporting Information S1). Comparing cases with ocean uptake (no ocean degradation) to those without ocean uptake implies that neglect of the ocean leads to a 1%–2% underestimation in the inferred emissions for all three HCFCs and HFC-23, and less than 1% for HFC-125 and HFC-134a around 2020. If there is a 5 years ocean degradation timescale, we obtain another 2%–3% underestimation in the inferred emissions. However, if the ocean degrades these halocarbons at a 1 year timescale, an 8%–10% underestimation in the inferred emissions for HCFCs and HFC-23 is obtained, with less than 5% underestimation for HFC-125 and HFC-134a. Ocean uptake can significantly decrease the HFC-23 atmospheric residence time, but it is still above 100 years, so the relative impact on its inferred emission is not as large as the impact on its residence time.

With a 10% increase in OH concentration only from 1980 to 2005, we obtain a 5%–7% underestimation in the inferred global emissions by the end of 2005 for all three HCFCs compared to the case of the fixed OH scenario. For HFCs, there is a 1%–5% underestimation in the inferred emissions by 2005. There is a large variation in the inferred emissions after 2005 given different OH scenarios, and the corresponding variations in the emission due to different OH scenarios by the end of 2050 can be up to 40%. Considering both a 1 year ocean degradation timescale and increasing OH would imply an underestimate of the emissions, by around 10%–20% during the peak of emissions for HCFCs and HFCs.

By weighting the emissions of each species by its global warming potential compared to CO₂ (on a 100-year horizon; Burkholder & Hodnebrog, 2022), we calculate the CO₂-equivalent emissions summed from all six HCFCs and HFCs in this study (Figure 3; Figure S9 in Supporting Information S1 breaks the summed emission into different species). During the peak total emission period in the 2020s, this would underestimate the emission by 1% if one does not include the ocean uptake (and by 6% if the ocean degrades at 1 year). And if OH keeps increasing from 1980 to the 2020s, using fixed OH would underestimate the emission by another 7%. And combining ocean degradation and increase in OH could underestimate the CO₂-equivalent emission by up to 15%–20% in the 2020s.

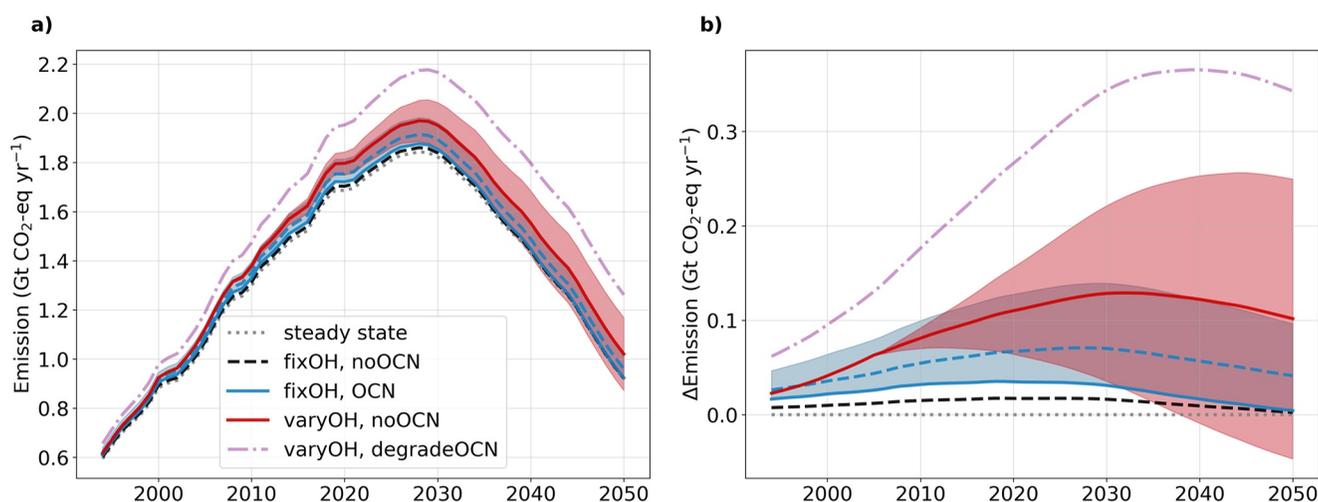


Figure 3. Summed emissions of all the hydrochlorofluorocarbons and hydrofluorocarbons in this study weighted by their global warming potentials. The absolute emissions are shown in panel (a), and the differences between the emissions inferred from transient residence times and steady state lifetimes (assuming no ocean and fixed OH) are shown in panel (b).

The estimated bank using a top-down method is the cumulative difference between the reported production and the inferred emission (calculated from Equation 2). If we assume that production has been accurately reported, then with higher inferred emissions resulting in banks depleting faster than currently expected. We quantify the resulting impact on banks by integrating the inferred emissions (from Figure 2) over time. Figure S10 in Supporting Information S1 shows the difference between HCFC and HFC banks estimates calculated from the (noOCN and fixOH) steady state residence times based on atmospheric removal rates reported in Burkholder and Hodnebrog (2022) and banks calculated from transient residence times. In the current decade, if we do not consider the ocean processes, we would overestimate the bank by 22–101 Gg for HCFC-141b, 8–40 Gg for HCFC-142b, 197–1,090 Gg for HCFC-22, 3–9 Gg for HFC-125, 40–152 Gg for HFC-134a, and 6–34 Gg for HFC-23 (the range spans no ocean degradation to a 1 year decay timescale). If we do not consider the increase in OH from 1980 to 2005, we would have overestimated the banks by 76–140 Gg for HCFC-141b, 35–63 Gg for HCFC-142b, 537–940 Gg for HCFC-22, 16–45 Gg for HFC-125, 148–340 Gg for HFC-134a, and 2–4 Gg for HFC-23 in the 2020s (the range spans continued OH increases or decreasing after 2005). Ocean uptake/loss and increasing OH would add to each other, resulting in an even larger overestimation in the global banks for these molecules (shown as the purple dash-dotted line in Figure S10 in Supporting Information S1). Alternatively, if we assume that bank estimates are accurate, higher emissions could be an indication of higher than reported production, where emissions in the year of production could be anywhere between 6% and 83%, depending on the application and gas (Lickley et al., 2022), with the remaining 17%–94% of production going into the banks. This would imply that banks are in fact higher than published estimates suggest, and the bias could be an order of magnitude (if initial releases are closer to 6%) and of the opposite sign than that shown in Figure S10 in Supporting Information S1. This wide range of uncertainty underscores the need to account for the ocean and OH lifetime effects in future bank assessments.

4. Conclusions and Discussions

In this study, we have explored the uncertainties from the ocean uptake and OH sinks for several Montreal Protocol-regulated molecules. We show that if one does not consider oceanic dissolution, and assumes no oceanic degradation, this would underestimate the emissions of HCFCs and HFCs by about 1%–2% in the current decade. This impact is rather small. Due to limited knowledge of ocean degradation rates, these species are often treated as conservative tracers within the ocean (Liang & Rigby, 2022; Yvon-Lewis & Butler, 2002). But evidence suggests certain species can be destroyed in the ocean (Chang & Criddle, 1995; DeFlaun et al., 1992; Streger et al., 1999). If there is a significant ocean degradation pathway, the emission of HCFCs and HFCs would be underestimated by up to 10% depending on how fast these species are destroyed in the ocean. Climate change can add more uncertainty in emission estimations by directly affecting HCFC and HFC solubilities, ocean circulation (Wang et al., 2021) and/or influencing the oceanic biological activity (Kirchman et al., 2009).

The main loss pathways for HCFCs and HFCs are through their reactions with OH. Models and inversions consistently suggest a 10% increase in OH from 1980 to 2005 (Stevenson et al., 2020; Turner et al., 2017), but current emission estimations for HCFCs and HFCs are based on fixed OH concentrations over time. If one assumes that OH is fixed, whereas it is actually increasing, emissions would be underestimated by 5%–7% by 2005. Future emissions estimation also depends strongly on an accurate estimation of OH concentration changes out to 2050.

The relative importance of including the ocean and OH trend for emission estimation is determined by how these processes compete. The ocean plays a significant role for HFC-23, whose reaction rate with OH is more than 20 times slower than the other modeled species, even though it is 2–5 times less soluble in seawater. For other species whose reaction rates with OH are faster: the ocean plays a more significant role for HCFC-141b and HCFC-22 due to their relatively high solubilities compared to HCFC-142b, HFC-125, and HFC-134a.

Although new production of HCFCs is now controlled, utilizing these species as feedstocks is exempted from the Montreal Protocol, based on the assumption that feedstock emissions should be small. By 2019, however, up to 8% and 33% of the global emissions of HCFC-22 and HCFC-142b appear to be from the feedstock emissions (Daniel & Reimann, 2022). The feedstock market has increased sharply in the past decade and is likely to continue increasing if there are no further actions on the feedstock exemption (Andersen et al., 2021). Inferences of banks and emissions (including feedstock emissions) depend on knowledge of residence times, for which OH trends and possible ocean degradation are important uncertainties. HCFC and HFC total emissions represent about 1.8 Gt CO₂-equivalent per year, or about 5% of total emissions of all global warming agents (IEA, 2022). Our study suggests a total uncertainty in their contribution to warming of up to 15%–20% in the current decade and draws attention to the need for additional information on oceanic degradation processes and on OH trends to better quantify the atmospheric emissions of these compounds. This will add a perspective that has been overlooked in the past to the discussion of ensuring the success of the Montreal Protocol and its following amendments.

Data Availability Statement

The coupled MITgcm-12 box model code and output, code to generate figures, and tabulated files containing the atmospheric residence times for each species under different OH and ocean scenarios are available at <https://doi.org/10.5281/zenodo.8307171> (Wang et al., 2023).

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