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SPARC Report on the Mystery of Carbon Tetrachloride

Q. Liang, P. A. Newman, S. Reimann

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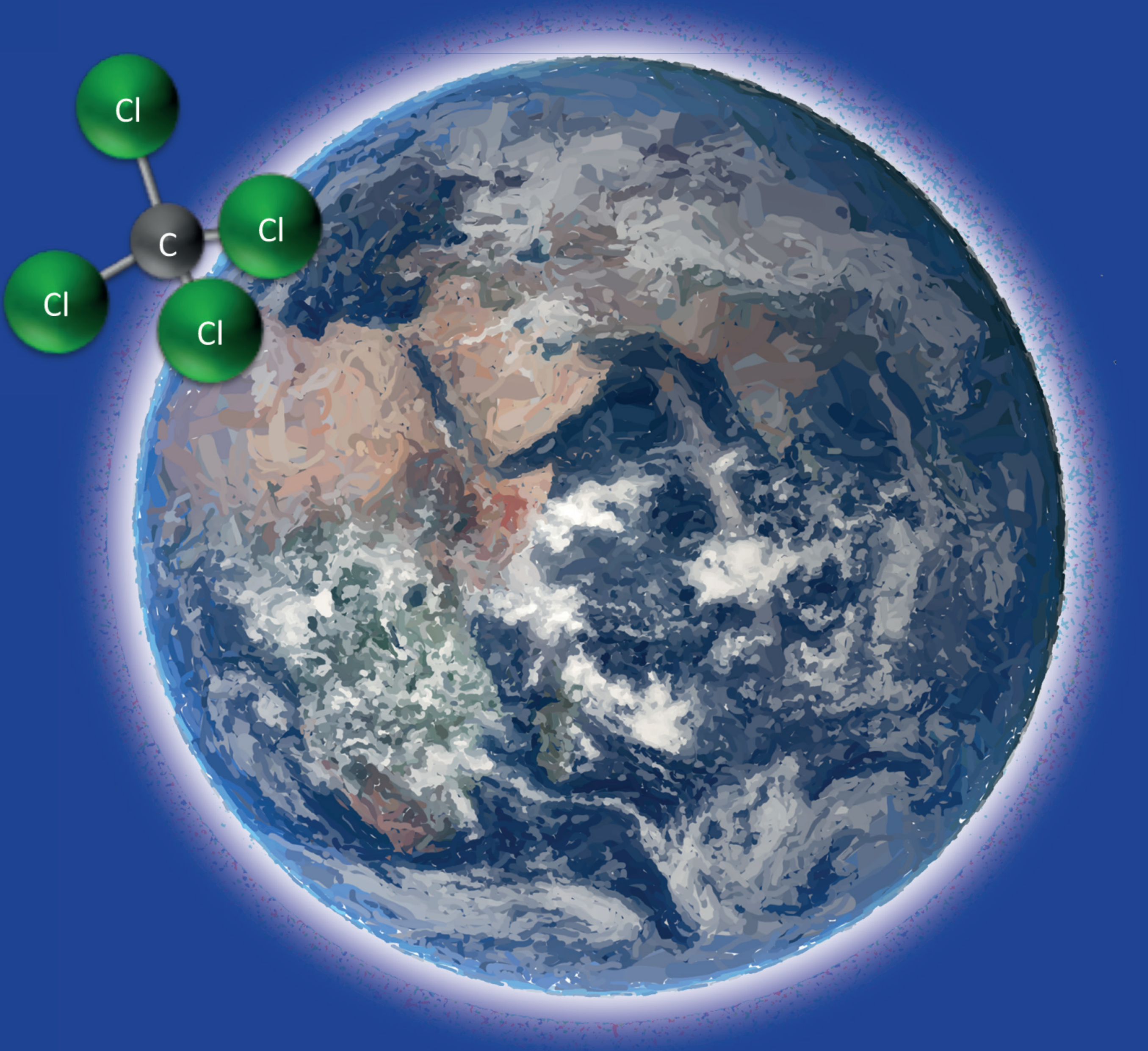

World Climate Research Programme
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STRATOSPHERE-TROPOSPHERE PROCESSES
AND THEIR ROLE IN CLIMATE

SPARC

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SPARC Report on the Mystery of Carbon Tetrachloride

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CONTENTS

PREFACE

This document describes the key findings of the "Solving the Mystery of Carbon Tetrachloride" workshop that was held in Dübendorf, Switzerland, from 4-6 October 2015. This workshop was developed under the auspices of Stratosphere-Troposphere Processes And their Role in Climate (SPARC) project, a core project of the World Climate Research Programme (WCRP).

The SPARC carbon tetrachloride (CCl_4) activity was initiated in 2014, in response to continued questions about the discrepancy between estimated emissions related to atmospheric observations and those from reported production and consumption submitted to the United Nations Environmental Programme (UNEP). This discrepancy has been highlighted in the Scientific Assessment Panel's report to the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer for both 2010 and 2014.

The "Solving the Mystery of Carbon Tetrachloride" three-day workshop included participants from 16 different countries. Attendees included scientists, technologists, engineers, industry experts, and policymakers. The workshop objectives were to:

- document the new and past research results via presentations and posters that were summarized in rapporteur reports;
- develop a key findings bullet list for the CCl_4 sub-disciplines;
- formulate research recommendations; and
- generate a draft SPARC report that will lead to a side event on CCl_4 findings at the 2016 Montreal Protocol meeting, and form the basis for an article that will appear in a scientific journal.

The first day was a meet-and-greet of all of the participants in a "Marketplace of Ideas." The second day included 22 oral presentations and 8 poster presentations (see **www.sparc-climate.org/meetings/Sparc-CCl4-workshop_October2015**). The third and final day included a broad discussion among the participants regarding how this report would be developed.

The report was crafted over the period October 2015 to June 2016, with the following timeline:

- 6 October 2015 - Outline finalised.
- 29 January 2016 - First draft circulated for review to principal writers of the report.
- 19 February 2016 - Second draft circulated for review amongst all of the workshop attendees, as well as a few additional scientists who had provided key research findings, but had been unable to attend the workshop.
- 18 March 2016 - Third draft submitted to the SPARC office for external review.
- 24 May 2016 - Fourth draft re-submitted to SPARC review editors.
- 7 June 2016 - Fifth draft re-submitted to SPARC review editors and accepted for publication.

The first and second drafts of this report were extensively edited and reviewed by all of the workshop participants. The third, fourth, and fifth drafts of the report were managed by the SPARC review editors, with the assistance of nine external referees who were independent of this report.

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ABSTRACT

The Montreal Protocol (MP) controls the production and consumption of carbon tetrachloride (CCl_4 or CTC) and other ozone-depleting substances (ODSs) for emissive uses. CCl_4 is a major ODS, accounting for about 12% of the globally averaged inorganic chlorine and bromine in the stratosphere, compared to 14% for CFC-12 in 2012.

In spite of the MP controls, there are large ongoing emissions of CCl_4 into the atmosphere. Estimates of emissions from various techniques ought to yield similar numbers. However, the recent WMO/UNEP Scientific Assessment of Ozone Depletion [WMO, 2014] estimated a 2007-2012 CCl_4 bottom-up emission of 1-4 Gg/year (1-4 kilotonnes/year), based on country-by-country reports to UNEP, and a global top-down emissions estimate of 57 Gg/year, based on atmospheric measurements. This 54 Gg/year difference has not been explained.

In order to assess the current knowledge on global CCl_4 sources and sinks, stakeholders from industrial, governmental, and the scientific communities came together at the “Solving the Mystery of Carbon Tetrachloride” workshop, which was held from 4-6 October 2015 at Empa in Dübendorf, Switzerland. During this workshop, several new findings were brought forward by the participants on CCl_4 emissions and related science.

- Anthropogenic production and consumption for feedstock and process agent uses (*e.g.*, as approved solvents) are reported to UNEP under the MP. Based on these numbers, global bottom-up emissions of 3 (0-8) Gg/year are estimated for 2007-2013 in this report. This number is also reasonably consistent with this report’s new industry-based bottom-up estimate for fugitive emissions of 2 Gg/year.
- By-product emissions from chloromethanes and perchloroethylene plants are newly proposed in this report as significant CCl_4 sources, with global emissions estimated from these plants to be 13 Gg/year in 2014.
- This report updates the anthropogenic CCl_4 emissions estimation as a maximum of ~25 Gg/year. This number is derived by combining the above fugitive and by-product emissions (2 Gg/year and 13 Gg/year, respectively) with 10 Gg/year from legacy emissions plus potential unreported inadvertent emissions from other sources.
- Ongoing atmospheric CCl_4 measurements within global networks have been exploited for assessing regional emissions. In addition to existing emissions estimates from China and Australia, the workshop prompted research on emissions in the U.S. and Europe. The sum of these four regional emissions is estimated as 21±7.5[a] Gg/year, but this is not a complete global accounting. These regional top-down emissions estimates also show that most of the CCl_4 emissions originate from chemical industrial regions, and are not linked to major population centres.
- The total CCl_4 lifetime is critical for calculating top-down global emissions. CCl_4 is destroyed in the stratosphere, oceans, and soils, complicating the total lifetime estimate. The atmospheric lifetime with respect to stratospheric loss was recently revised to 44 (36-58) years, and remains unchanged in this report. New findings from additional

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[a] The uncertainty range is a 1-σ (sigma) estimate.

measurement campaigns and reanalysis of physical parameters lead to changes in the ocean lifetime from 94 years to 210 (157-313) years, and in the soil lifetime from 195 years to 375 (288-536) years.

- These revised lifetimes lead to an increase of the total lifetime from 26 years in WMO [2014] to 33 (28-41) years. Consequently, CCl_4 is lost at a slower rate from the atmosphere. With this new total lifetime, the global top-down emissions calculation decreases from 57 (40-74) Gg/year in WMO [2014] to 40 (25-55) Gg/year. This estimate is relatively consistent with the independent gradient top-down emissions of 30 (25-35) Gg/year, based upon differences between atmospheric measurements of CCl_4 in the Northern and Southern Hemispheres. In addition, this new total lifetime implies an upper limit of 3-4 Gg/year of natural emissions, based upon newly reported observations of old air in firn snow.

These new CCl_4 emissions estimates from the workshop make considerable progress toward closing the emissions discrepancy. The new industrial bottom-up emissions estimate (15 Gg/year total) includes emissions from chloromethanes plants (13 Gg/year) and feedstock fugitive emissions (2 Gg/year). When combined with legacy emissions and unreported inadvertent emissions, this could be up to 25 Gg/year. Top-down emissions estimates are: global 40 (25-55) Gg/year, gradient 30 (25-35) Gg/year, and regional 21 (14-28) Gg/year. While the new bottom-up value is still less than the aggregated top-down values, these estimates reconcile the CCl_4 budget discrepancy when considered at the edges of their uncertainties.

1. Introduction

A. Problem Statement

Carbon tetrachloride (CCl_4 or CTC) is an anthropogenic, long-lived ozone-depleting substance (ODS), and a greenhouse gas with an estimated total lifetime (see Glossary) of 26 years, as reported in the World Meteorological Organization / United Nations Environment Programme (WMO/UNEP) Scientific Assessment of Ozone Depletion 2014 [Carpenter and Reimann, 2014]. This total lifetime has been used in the calculation of an ozone depletion potential[b] (ODP, see Glossary) of 0.72, and a 100-year global warming potential (GWP, see Glossary) of 1730 [Harris and Wuebbles, 2014]. In 2012, CCl_4 accounted for about 12% of the globally averaged inorganic chlorine and bromine in the stratosphere, compared to 20% and 14% for CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2), respectively (updated from Newman *et al*. [2007]). Further, CCl_4 emissions between 2015 and 2050 are expected to contribute 1.2 gigatonnes of CO_2-equivalent emissions to radiative forcing, while the total CFC contribution is 4.7 gigatonnes of CO_2-equivalent emissions [Harris and Wuebbles, 2014].

Because production for emissive uses of CCl_4 is globally banned under the Montreal Protocol (MP), the atmospheric concentration should decline at or near its lifetime-limited rate, as we have seen for methyl chloroform (CH_3CCl_3) over the last decade [Carpenter and Reimann, 2014]. However, CCl_4 is not decreasing in the atmosphere as rapidly as expected, given what we know about its total lifetime (based on loss processes), and the small remaining emissions that are known. Clearly, uncertainties remain in the budget (see Glossary), and this report is tasked with assessing our current understanding of sources and sinks of CCl_4 to address this “mystery”.

B. CCl_4 Discussions in the WMO/UNEP Scientific Assessments of Ozone Depletion

The atmospheric CCl_4 budget uncertainties have been highlighted in all of the Scientific Assessments of Ozone Depletion since WMO [1999] – no emissions data were available for WMO [1995] and prior reports. The following direct quotations from these Assessments after 1995 illustrate the evolving understanding of this budget discrepancy.

WMO [1999]:

- *However, if the lifetime of CCl_4 is 35 years as recommended in Table 1-1, then the industrial emission scenario provided in Simmonds et al. [1998] underestimates emissions by about 17%.*

WMO [2003]:

- *Large discrepancies existed in UNEP consumption data for past years owing to confusion over reporting procedures, and although these have been addressed by TEAP [UNEP,*

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[b] The Montreal Protocol assumes that the ODP for CCl_4 is 1.1 [UNEP, 2000].

1998], there may still be significant omissions and unrecorded sources (see Section 1.6). TEAP suggests emissions of 41(+50%, -25%) Gg from total production of 203 Gg in 1996 [UNEP, 1998], but, as discussed in Section 1.6, this is only about half of the emissions necessary to account for observed burdens and trends in that year given the updated lifetime estimate of 26 years (see Section 1.4).

WMO [2007]:

- *Overall the budget of CCl_4 remains poorly understood. Because the currently observed regional emissions, the TEAP emission estimate, and the measured interhemispheric gradient seem inconsistent with an overall lifetime of 20 years and because the uncertainty ranges for both the ocean and soil sinks allow for the possibility of only very small sinks, no change from the lifetime of 26 years given in WMO 2003 is recommended at this time.*

WMO [2011]:

- *Global emissions of CCl_4 have declined only slowly over the past decade.*
  - *These emissions, when inferred from observed global trends, were between 40 and 80 gigagrams per year (Gg/year) during 2005-2008 given a range for the global CCl_4 lifetime of 33-23 years. By contrast, CCl_4 emissions derived with a number of assumptions from data reported to the United Nations Environment Programme [UNEP] ranged from 0-30 Gg/year over this same period.*
  - *In addition, there is a large variability in CCl_4 emissions derived from data reported to UNEP that is not reflected in emissions derived from measured global mixing ratio changes. This additional discrepancy cannot be explained by scaling the lifetime or by uncertainties in the atmospheric trends. If the analysis of data reported to UNEP is correct, unknown anthropogenic sources may be partly responsible for these observed discrepancies.*

WMO [2014]: (**Figure 1**)

- *Estimated sources and sinks of CCl_4 remain inconsistent with observations of its abundance. The estimate of the total global lifetime (26 years) combined with the observed CCl_4 trend in the atmosphere (-1.1 to -1.4 ppt/year in 2011-2012) implies emissions of 57 (40-74) Gg/year, which cannot be reconciled with estimated emissions from net reported production. New evidence indicates that other poorly quantified sources, unrelated to reported production, could contribute to the currently unaccounted emissions.*

This ongoing discrepancy suggests that there may be unrecognized CCl_4 sources or a misunderstanding of its losses and, hence, its total lifetime.

C. Observed Atmospheric Levels of CCl_4

Over the past century, CCl_4 has had many uses. Its primary uses were as a feedstock (see Glossary) for the synthesis of chlorinated chemicals, and as a solvent. In addition, it also was used in relatively small amounts as a fire-extinguishing agent. Control of

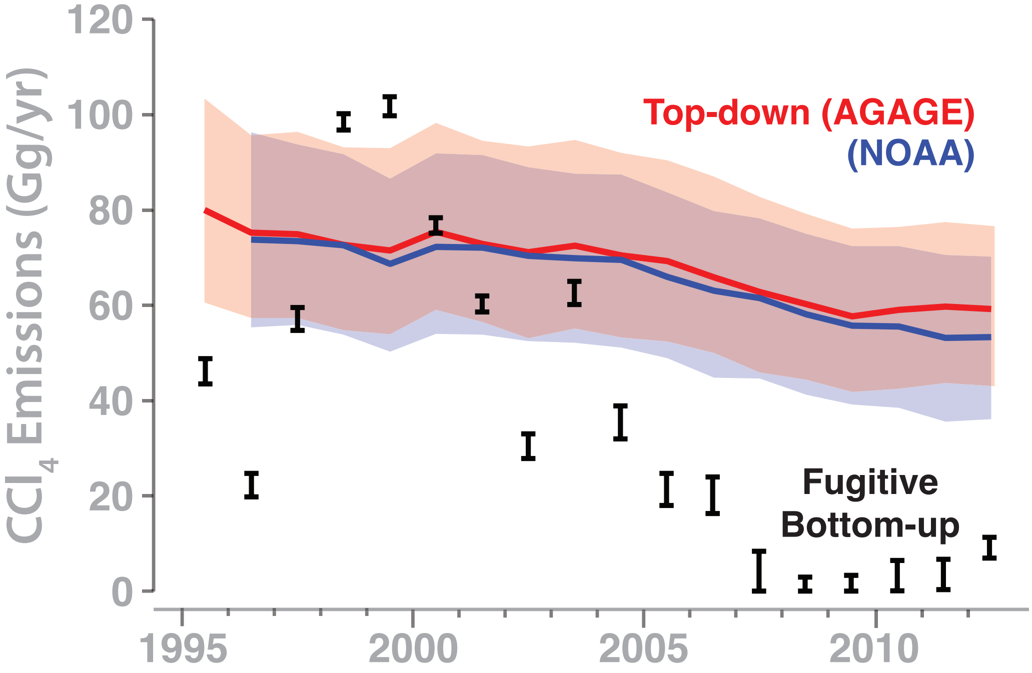

Figure 1: *CCl_4 emission calculations adapted from WMO [2014]. Top-down estimates are from Figure 1-3 [Carpenter and Reimann, 2014] and bottom-up estimates are from Figure ADM 2-1 [WMO, 2014]. Top-down emissions (see Glossary) are from atmospheric measurements (red line and shading for AGAGE-based estimates, and blue line and shading for NOAA GMD-based estimates) and fugitive bottom-up emissions (black bars). Note that emissions based on NOAA data were inadvertently plotted 4 Gg lower in Figure 1-3 in Carpenter and Reimann [2014], and are plotted correctly here. The top-down emission calculations were derived using a total lifetime of 26 years, with a range of 22-32 (1σ) years [Carpenter and Reimann, 2014]. The lower fugitive bottom-up estimate (black bars) was derived from the difference between total CCl_4 production reported to UNEP and the sum of feedstock (see Glossary) and amounts destroyed, including under-reported feedstock production estimates [Montzka and Reimann, 2011]. The upper value of the fugitive bottom-up estimate was similarly derived, but includes a 2% fugitive feedstock use emission, and 75% efficiency for reported destruction. Top-down emissions were derived using AGAGE and NOAA data and a 12-box model. The red-grey and blue-grey shadings show top-down emissions uncertainties from measurements, prior emissions, and a total lifetime range. See Section 1C for additional details on the NOAA and AGAGE observations.*

production and consumption (except for specifically sanctioned uses) that could lead to the escape of CCl_4 to the atmosphere followed after the 1987 Montreal Protocol (MP) was signed. However, CCl_4 continued to be used in contained production processes for several hydrofluorocarbons (HFCs) and pyrethroid pesticides [UNEP, 2013].

The atmospheric levels of CCl_4 peaked at ~105 ppt in around 1990 and, owing to the decline of emissions driven by the MP, these levels have continued to decline since then [Carpenter and Reimann, 2014]. **Figure 2** shows the evolution of CCl_4 to the present. CCl_4 atmospheric abundances have been monitored globally on an ongoing basis via various platforms - primarily from surface-monitoring networks, but also during airborne missions and by satellite remote sensing instruments. The longest atmospheric record is based on surface measurements at multiple sites across the globe from the Advanced Global

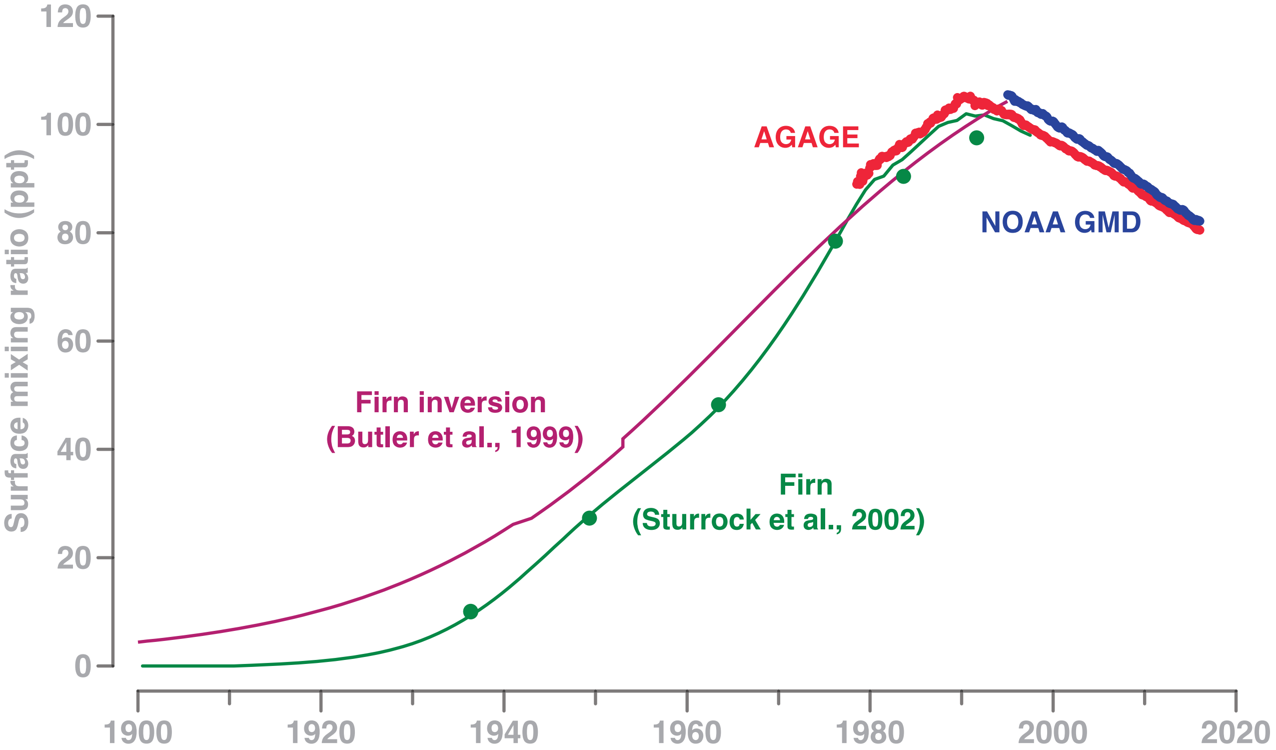

***Figure 2**: Time series of global mean surface mixing ratios of CCl_4, independently derived from measurements at multiple sites in both hemispheres by NOAA GMD (blue points) and AGAGE (red points). Southern Hemisphere CCl_4 concentrations are derived from Antarctic firn data: magenta line – inverse study that best-fits both South Pole and Siple Dome firn data [Butler et al., 1999]; green points – Law Dome (67˚S) data [Sturrock et al., 2002] and best-fit inversion (green line). The NOAA global and firn data are on the NOAA scale; the AGAGE global and CSIRO firn data are on the SIO scale, with being NOAA higher by 3-4% (2000), falling gradually to a 1-2% difference (2015). The NOAA firn data are likely higher than the CSIRO firn data by 3-4%, due to calibration differences.*

Atmospheric Gases Experiment (AGAGE, **http://agage.mit.edu**) program, which began measuring CCl_4 in the late 1970s (red line), and from the National Oceanic and Atmospheric Administration (NOAA) Global Monitoring Division (GMD) program since the mid-1990s (blue line). CCl_4 emissions can be estimated from the observations shown in **Figure 2** (as described in Section 1D below and shown as the red and blue lines in **Figure 1**). These global top-down emissions estimates (see Glossary) are sensitive to the calculated slope of the lines in **Figure 2**. Measurements of air in unconsolidated snow (firn air, see Glossary) in the polar ice caps show near zero mixing ratios of CCl_4 in the atmosphere (<5 ppt) in the early 1900s [Butler *et al*., 1999; Sturrock *et al*., 2002; Martinerie *et al*., 2009]. During the 2015 workshop, more recent samplings of firn air in polar sites were shown, in addition to those illustrated in **Figure 2**. These recent samples suggest slowly increasing atmospheric mixing ratios during the 1900s, and, therefore, insignificant natural CCl_4 emissions.

D. Loss Processes from the Atmosphere

CCl_4 sinks include: 1) stratospheric photolysis by solar radiation [Rontu Carlon *et al.*, 2010; Burkholder and Mellouki, 2013], 2) uptake in oceans [Krysell *et al.*, 1994; Yvon-Lewis and Butler, 2002; Lee, 2012; Engel and Atlas, 2013], and 3) degradation in soils [Happell and Roche, 2003; Liu, 2006; Rhew *et al.*, 2008; Mendoza *et al.*, 2011; Happell *et al.*, 2014]. The balance between emissions and losses controls the global burden in the atmosphere and its rate of change. This is mathematically represented as:

$$\frac{\partial B}{\partial t} = S - \frac{B}{\tau_{total}} \qquad (1)$$

Where B represents the global atmospheric burden, S are the global emissions, and τ_{total} is the total lifetime (see Glossary), such that the final term ($-B/\tau_{total}$) represents the total global loss rate from the atmosphere. The total lifetime is calculated by combining the lifetimes of the three degradation processes: direct loss in the atmosphere, surface losses to oceans, and surface losses to soils.

$$1/\tau_{total} = 1/\tau_{atmosphere} + 1/\tau_{ocean} + 1/\tau_{soil} \qquad (2)$$

The individual lifetimes (hereafter described as atmospheric, ocean, and soil lifetimes, see Glossary) are calculated by taking the measured distribution of CCl_4 between the atmosphere, oceans, and soils; integrating the loss due to the respective process on the global level (Gg/year); and then dividing that rate by the global atmospheric CCl_4 burden (Gg). For additional information on lifetime calculations see Plumb and Stolarski [2013]. Our understanding of the relative contributions of these processes to the total loss from the atmosphere has evolved over several decades (**Table 1**). Prior to 2002, quantitative total lifetime estimates fell between 35-50 years[c], but these only included atmospheric values (*i.e.*, degradation in the stratosphere). Although observational studies existed for ocean degradation [*e.g.*, Liss and Slater, 1974; Butler *et al.*, 1993, 1999], no global approach was published in the refereed literature at the time for estimating this ocean lifetime. In 1999 the recommended atmospheric lifetime was lowered considerably [Prinn and Zander, 1999]. This atmospheric lifetime[d] was estimated from the stratospheric lifetime calculated using the Volk *et al.* [1997] method, which made use of stratospheric CCl_4 measurements relative to CFC-11. With the then-best estimate for the CFC-11 atmospheric lifetime of 45 years, this analysis resulted in a total lifetime estimate of 35 years for CCl_4.

Yvon-Lewis and Butler [2002] estimated a global 94-year ocean lifetime. Using the previously-reported atmospheric lifetime estimate, this led to a revised 26-year total lifetime in the 2002 WMO/UNEP Scientific Assessment of Ozone Depletion [Montzka and Fraser, 2003]. This total lifetime was unchanged in the 2006 WMO/UNEP Scientific Assessment of Ozone Depletion [Clerbaux and Cunnold, 2007], although Happell and Roche [2003]

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[c] The uncertainty range here and throughout are reported as one standard deviation (1-σ) estimates.

[d] The atmospheric loss of CCl_4 occurs in the stratosphere. Throughout this report, the term “atmospheric lifetime” refers to the partial lifetime derived from the stratospheric loss (see Glossary).

proposed that soils could also contribute to CCl_4 degradation with a 90-year soil lifetime. Including soil degradation would have lowered the total lifetime to approximately 20 years. In Chapter 1 of the 2010 WMO/UNEP Scientific Assessment of Ozone Depletion [Montzka and Reimann, 2011], the total lifetime remained unchanged at 26 years, but a range of 23-33 years was estimated by considering new information about a potentially longer lifetime of CFC-11 in the stratosphere [Douglass *et al.*, 2008], and by assessing the ranges of the ocean and soil lifetimes.

In 2013, the Stratosphere-troposphere Processes And their Role in Climate (SPARC) report “Lifetimes of Stratospheric Ozone-Depleting Substances, Their Replacements, and Related Species” [SPARC, 2013] revised the CCl_4 atmospheric lifetime to 44 (36-58) years by assessing state-of-the-art models, new atmospheric observations, and revisions to recommendations of laboratory kinetics and photochemistry. The increase in the atmospheric lifetime from 35 years to 44 years was due in part to an increase in the CFC-11 reference lifetime [SPARC, 2013], and partly due to the exclusion of OH-oxidation as an important loss pathway for atmospheric CCl_4 [Burkholder and Mellouki, 2013]. In the 2014 WMO/UNEP Scientific Assessment of Ozone Depletion, the CCl_4 total lifetime was estimated as 26 years [Carpenter and Reimann, 2014], which was based on:

- an **atmospheric** lifetime of 44 (36-58) years [SPARC, 2013], derived from revised photochemistry, models, and observations that included the results of Laube *et al.* [2013] and Volk *et al.* [1997];
- an **ocean** lifetime with respect to irreversible ocean uptake of 94 (71-167) years [Yvon-Lewis and Butler, 2002]; and
- a **soil** lifetime of 195 (108-907) years [Happell and Roche, 2003; Liu, 2006; Rhew *et al.*, 2008; Montzka and Reimann, 2011].

The total lifetime was re-examined during the 2015 CCl_4 workshop in light of new information on the relative contributions of atmospheric, oceanic, and soil loss processes and is described in Section 2 below. **Table 1** shows the revised values in comparison with historical estimates.

Lifetimes (years)

Report	1986	1989	1991	1995	1999	2003	2007	2011	2014	**This report**
τ atmosphere	50	40	47	42	35[a]	35[a]	35[a]	35[a]	44[b]	**44**
τ ocean						94[c]	94[c]	94[c]	94[c]	**210**
τ soil							90[d]	90[d] -195[e]		**375**
τ total *	50	40	47	42	35	26	26	26	26	**33**

*Total lifetimes are estimated using Equation 2. The total lifetime estimate of WMO [2007] excludes the soil sink.

Table 1: *Historical overview of total lifetime (τ) estimates for CCl_4. Sources of reference for total lifetimes are WMO [1986], WMO [1989], WMO [1991], WMO [1995], WMO [1999], WMO [2003], WMO [2007], WMO [2011], and WMO [2014]. In WMO [2011], instead of summing up partial lifetimes, the total lifetime represents a best estimate. References for partial lifetimes in the atmosphere, oceans, and soils after 1999: [a] WMO [1999], [b] SPARC [2013], [c] Yvon-Lewis and Butler [2002]; [d] Happell and Roche [2003], and [e] Montzka and Reimann [2011].*

E. Emissions into the Atmosphere

Because CCl_4 depletes stratospheric ozone, its production is controlled under Article 2 Annex B Group II of the 1987 MP. Through the MP's implementation, global CCl_4 production and consumption (see Glossary) have been regulated in developed countries since January 1996, and in developing countries since January 2010. As a result, CCl_4 dispersive uses are likely to have been fully eliminated with the phase-out of production and the cessation of supply. Under Article 7, each Party provides annual data to the UNEP Ozone Secretariat on CCl_4 production, imports, exports, feedstock amounts, and amounts destroyed. These reports to UNEP do **not** include inadvertent CCl_4 production emissions resulting from processes in the manufacture of other substances (*e.g.*, chloromethanes).

Anthropogenic CCl_4 emissions resulted in a steady increase in atmospheric levels through the 1980s (**Figure 2**). Emissions peaked in the 1991-1992 period, and declined thereafter because of the MP controls on production and consumption for dispersive uses (see Glossary). Since about 2001, CCl_4 abundances have declined at an average rate slightly greater than 1% per year [Carpenter and Reimann, 2014]. Over the past decade, total UNEP-reported CCl_4 production has ranged between 150 and 205 Gg/year, although it is currently believed that only a small amount escapes into the atmosphere. Analysis based on UNEP reporting indicates that process emissions were less than 0.25 Gg/year in 2011 [Table 3-2 from UNEP, 2013]. Furthermore, **bottom-up** emissions due to feedstock usage are estimated from MP-mandated UNEP reporting on production, feedstock usage, and destruction (see Glossary). In the absence of true emission estimates based on use, release rates, bank sizes, *etc*., magnitudes of potential emissions have been derived from the difference between total production amounts and those amounts destined for destructive uses [Montzka and Reimann, 2011]. This difference has been small in recent years and was less than 4 Gg/year in 2012 [Carpenter and Reimann, 2014].

Since CCl_4 is a relatively long-lived chemical in the atmosphere and is fairly well-mixed at the Earth's surface, its global atmospheric mass and its rate of change can be reasonably well estimated from a small number of sampling sites. This globally averaged atmospheric CCl_4 time series (**Figure 2**) can be used to derive emissions into the atmosphere, provided the total global loss rate from the atmosphere is known (hereafter referred to as **top-down** calculations, see Glossary).

Using **Equation 1** and the 26-year estimated total lifetime from WMO [2014], the CCl_4 top-down emissions were calculated to be 57 (40-74) Gg/year in 2012 [Carpenter and Reimann, 2014], and slightly greater than this in the 2007-2012 period. The top-down emissions are much larger than the potential emissions suggested by UNEP data, indicating a large discrepancy in the global atmospheric CCl_4 budget (**Figure 1**).

F. SPARC Carbon Tetrachloride Activity

To address this top-down versus bottom-up discrepancy issue, an activity was formed in 2015 under the World Climate Research Programme's (WCRP) SPARC project to bring together the CCl_4 research community. This activity's overall goal was to critically evaluate the CCl_4 budget discrepancy, based on input from experts from industry and the scientific community inasmuch as possible. In support of this goal, the "Solving the Mystery of Carbon Tetrachloride" workshop was held from 4-6 October 2015 at Empa in Dübendorf, Switzerland. The workshop objectives were to:

- document the new and past research results via presentations and posters that were summarized in rapporteur reports;
- develop a key findings bullet list for the CCl_4 sub-disciplines; and
- formulate research directions that will be forwarded for discussion at the next meeting of Ozone Research Managers of the Parties to the Vienna Convention.

The following sections provide a succinct report on the Workshop. Section 2 presents new progress in the quantitative understanding of the degradation of CCl_4 in the atmosphere, oceans, and soils. Section 3 describes the observational evidence for continued substantial emissions of CCl_4, and the progress on quantifying those emissions in different regions of the globe. Section 4 describes the industrial processes that currently involve the production and use of CCl_4 and an analysis of potential emissions. Research direction suggestions are presented in Section 5.

2. Degradation in the Atmosphere, Oceans, and Soils

The total CCl_4 lifetime in the atmosphere has evolved considerably since the mid-1980s. **Figure 3** shows the historic development of our understanding of CCl_4 loss frequencies for soils (panel a, brown), the oceans (panel b, black), the whole atmosphere (panel c, blue), and combined total (panel d, red stars). Loss frequency is shown on the left axes, while the lifetime (the inverse of the loss frequency) is on the right. The total loss frequency (panel d) is the sum of the soil, ocean, and atmosphere losses. The first total lifetime estimates only included losses in the atmosphere, while subsequent studies added losses in soils and in oceans.

No new work was presented at the workshop regarding stratospheric losses. The best current estimate for the atmospheric lifetime from stratospheric losses is 44 (36-58) years [SPARC, 2013]. This loss process is constrained by laboratory measurements, stratospheric observations, and atmospheric modelling. Most CCl_4 (98%) is lost to ultraviolet radiation photolysis, with a small 2% loss to reactions with $O(^1D)$ in the lower to middle stratosphere. Atmospheric losses in the troposphere (lower atmosphere) are negligible. The 44-year lifetime and uncertainty were estimated from: 1) aircraft and balloon observations using a tracer-tracer correlation technique and the CFC-11 lifetime and uncertainty, and 2) seven different atmospheric models. The stratospheric sink is now estimated to account for a larger fraction of CCl_4 removal from the atmosphere (increased from 59% to 75% of the total), given the slower losses attributable to soils and oceans (see **Figure 3d** for 2016).

CCl_4 is degraded in oceanic sub-surface waters and possibly in surface waters. Lower concentrations are routinely observed in upwelling regions and in sub-surface waters of lower oxygen content. New results presented at the workshop estimated the partial lifetime of CCl_4 with respect to oceanic loss as 210 (157-313) years [Table 4 from Butler *et al.*, 2016]. This is considerably longer than the 94 (82-191) years from Yvon-Lewis and Butler [2002], and 81 (71-167) years from Butler *et al.* [2011]. The new estimate is based on four times as many observations, accounts for all seasons, and captures almost all major ocean basins. With these additional data, the average surface saturation anomaly of CCl_4 for the oceans used in Butler *et al.* [2016] is ~15-20% less than the average used in Yvon-Lewis and Butler [2002]. Also, the model used by Yvon-Lewis and Butler [2002] was based on the 2°x2° Comprehensive Ocean-Atmosphere Data Set (COADS) for sea surface temperatures and wind speeds, whereas Butler *et al.* [2016] is based on a different, newer data set with 1°x1° resolution. The average wind speed for the 1°x1° data set is around 5% lower than that from COADS. The most influential change, however, is the use of an updated air-sea exchange coefficient, based on a revised inventory of bomb-$^{14}CO_2$ [Naegler *et al.*, 2006; Sweeney *et al.*, 2007; Wanninkhof *et al.*, 2009]. Yvon-Lewis and Butler [2002] used the Wanninkhof [1992] relationship, which was normalized to an earlier assessment of bomb-$^{14}CO_2$. Butler *et al.* [2016] evaluated the impact of this change of wind speed parameterisation on CCl_4 flux over oceans and determined that it can account for a 45% lower flux to the oceans with the Sweeney *et al.* [2007] air-sea parameterisation, and a 58% lower flux with Wanninkhof *et al.* [2009]. Additional reductions come from the use of a simpler computational approach that differs from Yvon-Lewis and Butler [2002], which was designed for gases where *in situ* loss rates are known, and required estimates of mixed layer depth and loss during

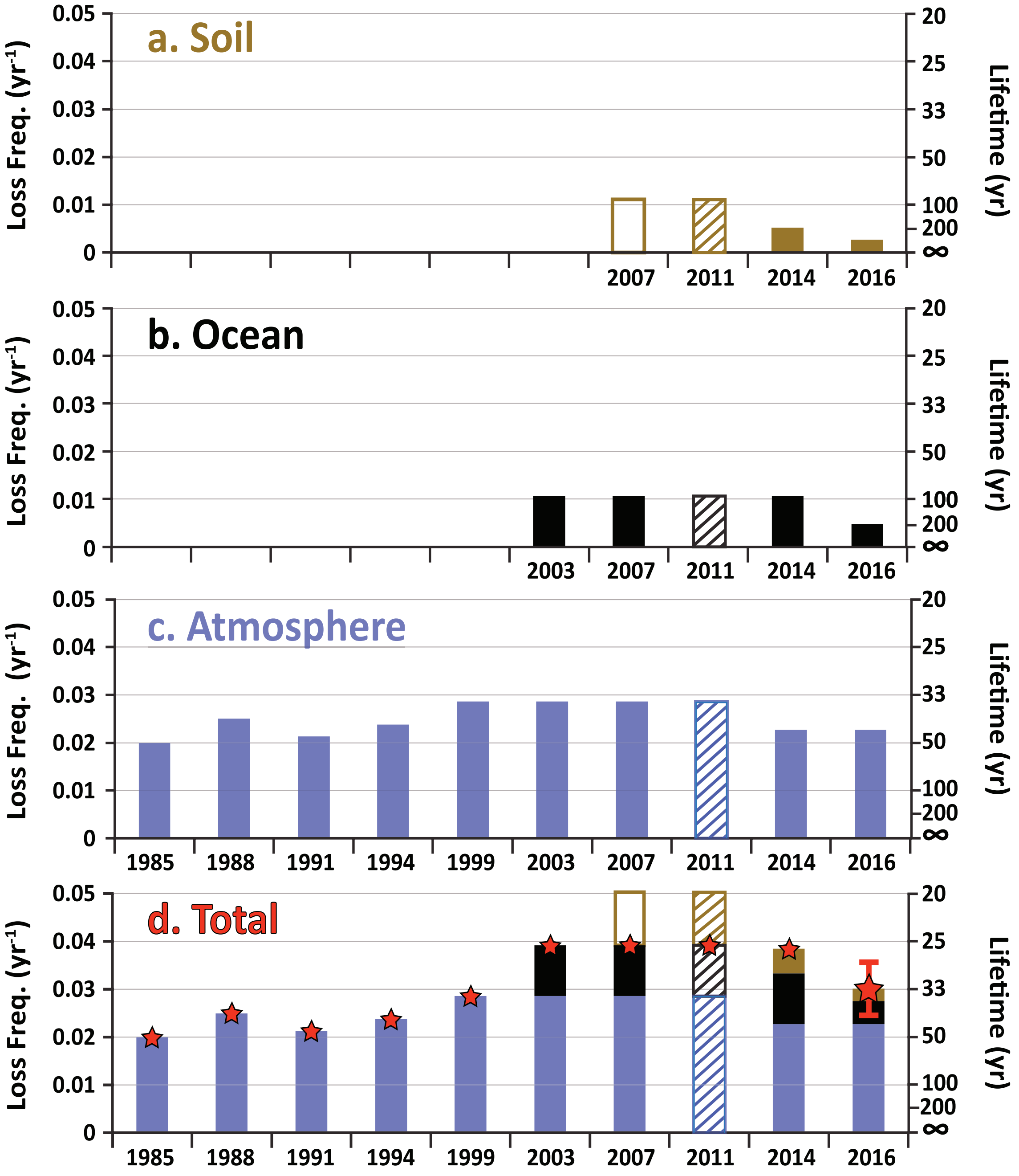

Figure 3: *The historical evolution of our understanding of CCl_4 loss frequencies (left axes) for: a) soils (brown), b) oceans (black), c) atmosphere (blue), and the d) total loss frequency (red stars) in international assessments. The total (d) is the sum of the individual loss frequencies in panels a-c. The lifetimes (right axes) are the inverse of the loss frequencies (see Equation 2). The partial lifetime for soils was not used in WMO [2007] (shown as empty box). The total lifetime in 2011 was based on a best estimate of partial lifetime combinations (shown as hatched boxes) reported in WMO [2011].*

downward mixing through the ocean thermocline. The newly revised estimate for CCl_4 uptake is based simply on measurements of the air-sea difference in partial pressure of the gas, and monthly average sea-surface temperatures and wind speeds from a global data set. This approach is more robust for CCl_4, for which there is little understanding of its mechanisms of loss, and suggests that the ocean sink is responsible for about 16% (vs. 32% previously) of the CCl_4 removed from the atmosphere.

New results presented at the workshop estimated the partial lifetime of atmospheric CCl_4 with respect to soils as 375 (288-536) years [Rhew and Happell, 2016], which is substantially longer than the earlier estimates of 195 years [Carpenter and Reimann, 2014] and 245 years from Happell *et al.* [2014]. This change is the result of newly available measurements and the application of an improved land-cover classification scheme [Happell *et al.*, 2014; Rhew and Happell, 2016]. Experiments suggest the degradation process is driven by microbial activity and is therein predominately bacterial [Mendoza *et al.*, 2011]. The updated soil sink is responsible for 9% (*vs*. 13% previously) of the CCl_4 removed from the atmosphere.

Global three-dimensional (3-D) chemical models provide sophisticated tools that can be used to integrate all sources and loss processes in the same system, and assess how each factor impacts the CCl_4 decay rate in the atmosphere with associated uncertainties. The impact of the new estimates of the uncertainties in the rates of the loss processes on atmospheric CCl_4 has been tested using the Toulouse Off-line Model of Chemistry and Transport (TOMCAT) 3-D chemical transport model [Chipperfield *et al.*, 2006]. This model was used to simulate the 1996-2014 period with assumed mean global CCl_4 emissions of 39 Gg/year, following Liang *et al.* [2014]. An ensemble of simulations was used to test the sensitivity of the modelled CCl_4 decay to variations of loss process (**Figure 4**). Following initialization in 1996, as expected, the control model run overestimates the observed CCl_4 decay. The sensitivity runs show that the largest impact on this decay rate is due to uncertainty in the ocean sink (range 157 to 313 years). While the stratospheric loss is the most important overall sink, the sensitivity simulations with an assumed uncertainty of ±10% in the CCl_4 photolysis rate [Burkholder and Mellouki, 2013] show a smaller impact. This is due in part to the compensating effect of a changed photolysis rate modifying the stratospheric CCl_4 burden (*i.e.,* the net change in the removal rate is much less), and partly due to the large uncertainty in the ocean sink. The impact of the minor soil-sink uncertainty (range 288 to 536 years) is small. **Figure 4** shows that current uncertainty in the CCl_4 sinks could account for some, but probably not all, of the emissions gap noted above.

Model transport uncertainties play a key role in the atmospheric lifetime uncertainty. SPARC 2013 multi-model analysis suggests that modelled mean circulation uncertainty is the largest contributor to the CCl_4 atmospheric lifetime uncertainty [Chipperfield and Liang, 2013]. As mentioned previously, CCl_4 is photolysed in the stratosphere. Its photolytic dissociation rate in the middle and upper stratosphere is rapid, with a short local lifetime of approximately one month at 20 hPa (~26 km). The CCl_4 atmospheric lifetime, similar to that for other long-lived ODSs that are removed mainly by photolytic destruction, is primarily the result of the long time necessary for transporting tropospheric air to this stratosphere photodissociation region. The ascent rate through this key photolytic loss region (70-20 hPa or ~18-26 km for CCl_4) is the primary factor controlling stratospheric loss [Chipperfield *et al.*, 2014]. While the model atmospheric lifetime is calculated using the atmospheric burden and globally integrated photolysis loss rates, results from SPARC [2013] and NASA Goddard Space Flight Center 2-Dimensional (2-D) model (GSFC2D) [Fleming *et al.*, 2011] simulations with different atmospheric mean circulations suggest a linear dependence of atmospheric lifetime on the difference in mean tropical age-of-air between 20 hPa (~26 km) and 70 hPa (~18 km) (**Figure 5**). Models with slower circulation have longer CCl_4 atmospheric lifetimes, while faster circulations lead to shorter lifetimes. The atmospheric circulation in the majority

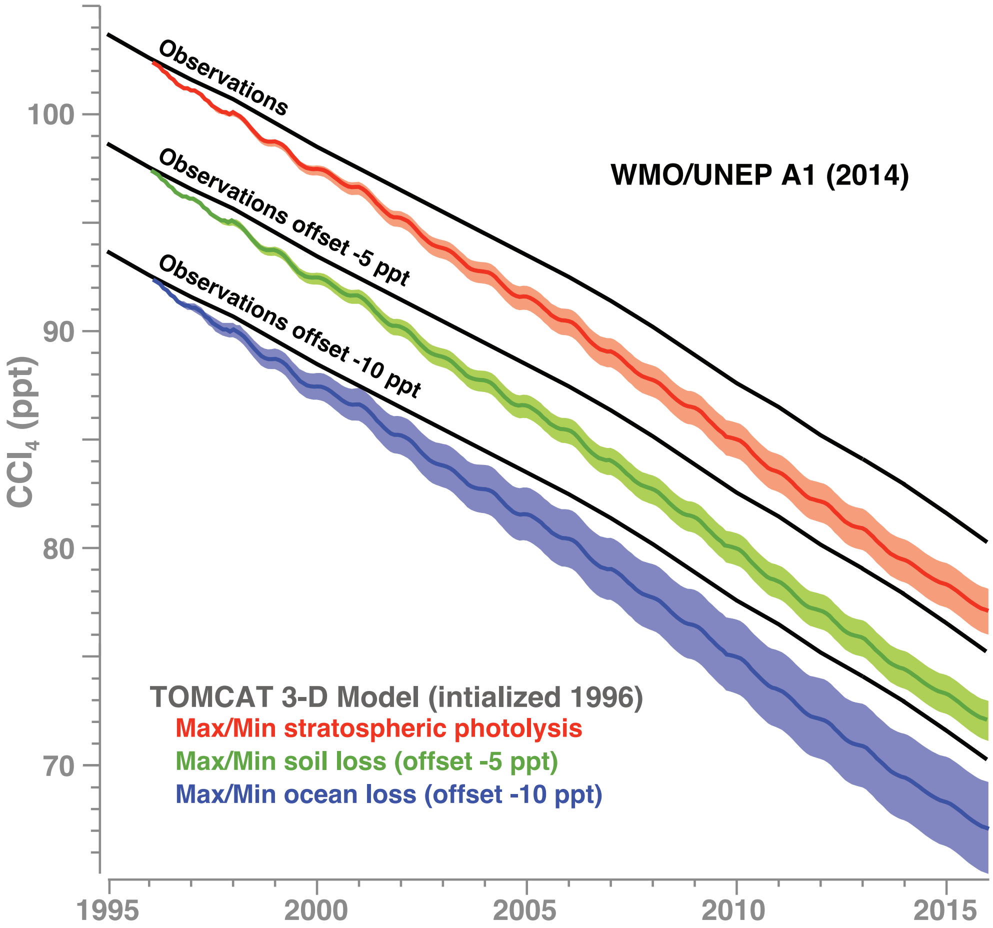

Figure 4: *Evolution of global mean surface CCl_4 (ppt) from observations extended through 2015 [Carpenter and Reimann, 2014] and a range of TOMCAT 3-D model simulations that assume different rates of CCl_4 loss by stratospheric photolysis (red), uptake by oceans (blue), and uptake by soils (green). The control run (plotted as the centre line of each shaded region) used photochemical data from JPL 2010 [Sander et al., 2011], a lifetime with respect to ocean loss of 210 years, and a lifetime with respect to soil loss of 375 years. The shaded region shows the effect of: (red) a ±10% change in stratospheric photolysis rate; (green) a soil loss variation from 288 to 536 years; and (blue) an ocean loss variation from 157 to 313 years. Note that for the comparison of the soil and ocean loss sensitivity runs, both the model and observations are offset by -5 and -10 ppt for graphical purposes only. Adapted from Chipperfield et al. [2016].*

of SPARC [2013] models through this critical tropical 70-20 hPa level is in reasonable agreement with the observed mean age-of-air. This suggests that most models reasonably estimate the CCl_4 atmospheric lifetime caused by stratospheric photolysis. However, there are large differences in the atmospheric lifetime estimates among all models (42 years to 54 years). The atmospheric lifetime difference (due to circulation differences amongst the models) is three times the difference due to the photolysis rate uncertainty (±2.5 years for ±2σ changes in photolysis absorption cross-section based on the GSFC2D calculation). Therefore, narrowing the uncertainties in modelled mean circulation in the tropical lower and middle stratosphere is crucial for reducing the CCl_4 atmospheric lifetime uncertainty.

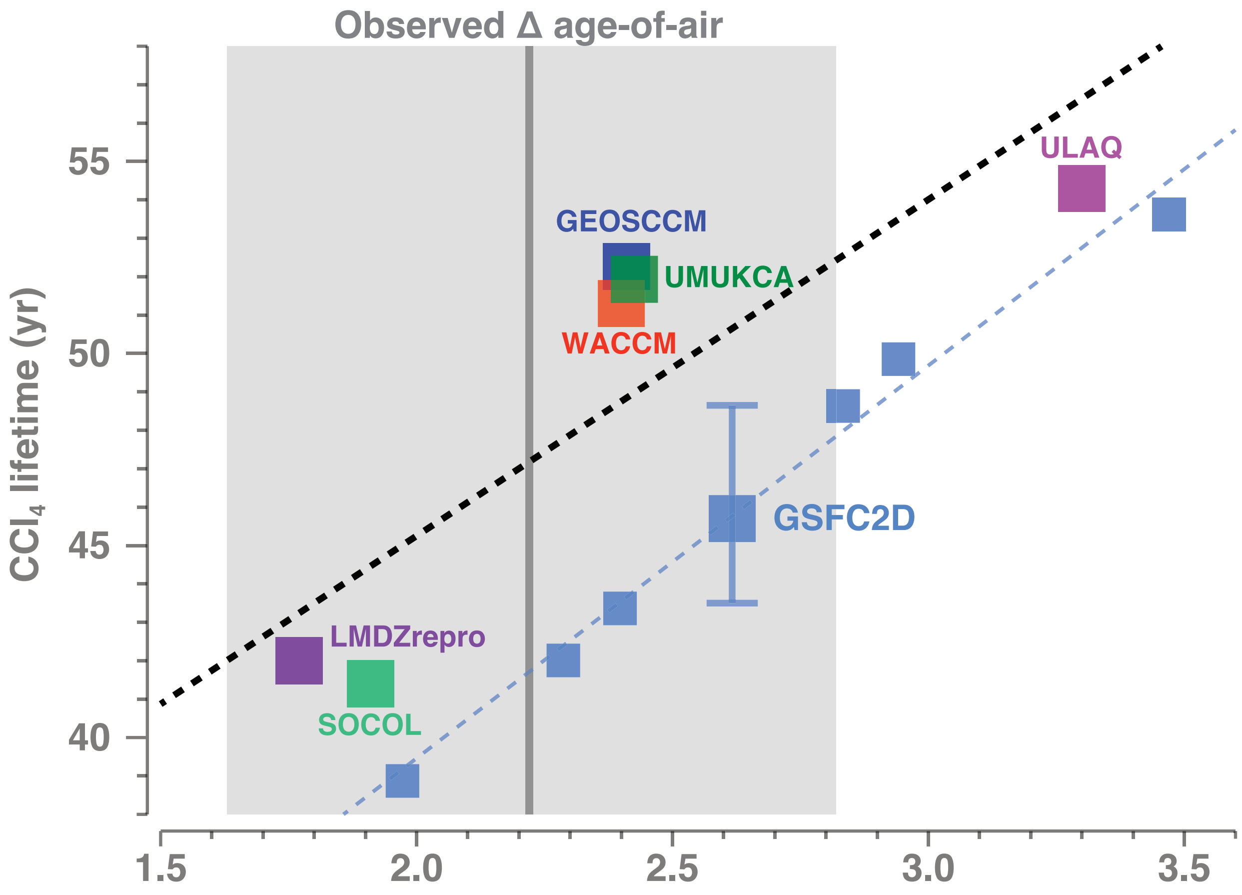

Figure 5: Correlation of modelled CCl_4 atmospheric lifetime (years) with the difference in tropical (30°S-30°N) mean age-of-air (years) between the 70- and 20-hPa levels. Results are from present-day atmosphere time-slice simulations (GEOSCCM, LMDZrepro, SOCOL, ULAQ, UMUKCA, and WACCM) conducted for the SPARC [2013] report [Chipperfield and Liang, 2013]. New model simulations also were conducted using the NASA GSFC2D model, including a baseline run (blue filled square), runs with ±2σ in photolysis cross sections from Burkholder and Mellouki [2013] (blue error bar), and runs with increased and decreased mean atmospheric circulations (small blue squares). Also shown is the observed tropical mean age difference (vertical solid line) and its 1σ uncertainty (grey shading).

In summary, based on the new information presented at the 2015 workshop regarding loss of CCl_4 to the stratosphere, oceans, and soils, a total CCl_4 lifetime of 33 (28-41) years is derived. Reducing the uncertainty of the atmospheric mean circulation strength in the tropical lower and middle stratosphere, and validating the ocean lifetime are the two most important factors to improve the CCl_4 total lifetime further.

3. Observations and Top-Down Emissions Calculations

As mentioned in Section 2C of this report, atmospheric CCl_4 concentrations have declined since 1990 because of the MP. Results from three different global air-sampling networks indicate that the mean global abundance of CCl_4 at the Earth's surface was 82.5-84.0 ppt in early 2014 and has decreased at a mean rate of 1.2-1.3 %/year over the past five years.

Atmospheric observations provide multiple lines of evidence suggesting that there are continued ongoing CCl_4 emissions. The first piece of evidence relates to the observed rate of decline of atmospheric mixing ratios in recent years. In the absence of emissions, the rate of decline is a substance's inverse lifetime (see **Equation 1**). For CCl_4, with a lifetime of 33 (28-41) years, we expect its atmospheric burden to decline, in the absence of emissions, at a rate of 3.0 (2.2-3.5) %/year. Because the observed rate of decline over the past 5 years has been substantially smaller (1.2-1.3 %/year) than the lifetime-limited rate (**Figure 2**), substantial emissions of CCl_4 have persisted. Although surface observations do not explicitly characterise the change in the entire global atmospheric burden of CCl_4, our understanding of trace-gas distributions and atmospheric processes suggests that the global decline cannot be much different than that observed at the Earth's surface over this period. Total column measurements from the Network for the Detection of Atmospheric Composition Change (NDACC, **www.ndacc.org**) stations account for this surface data shortcoming. At present, measurements are available from four stations: Jungfraujoch (46.6°N), Thule (76.5°N), Ny-Ålesund (78.9°N), and Eureka (80.1°N). In this report, we only show the CCl_4 total column measurement and its long-term trend from Jungfraujoch (**Figure 6**, updated from Rinsland *et al.* [2012]), as it has the largest number of daily samples and the smallest uncertainty in the derived trend. At Jungfraujoch the rate of decline since 1999 is -1.22 ±0.03 %/year, which is in good agreement with trends derived from the surface sampling networks.

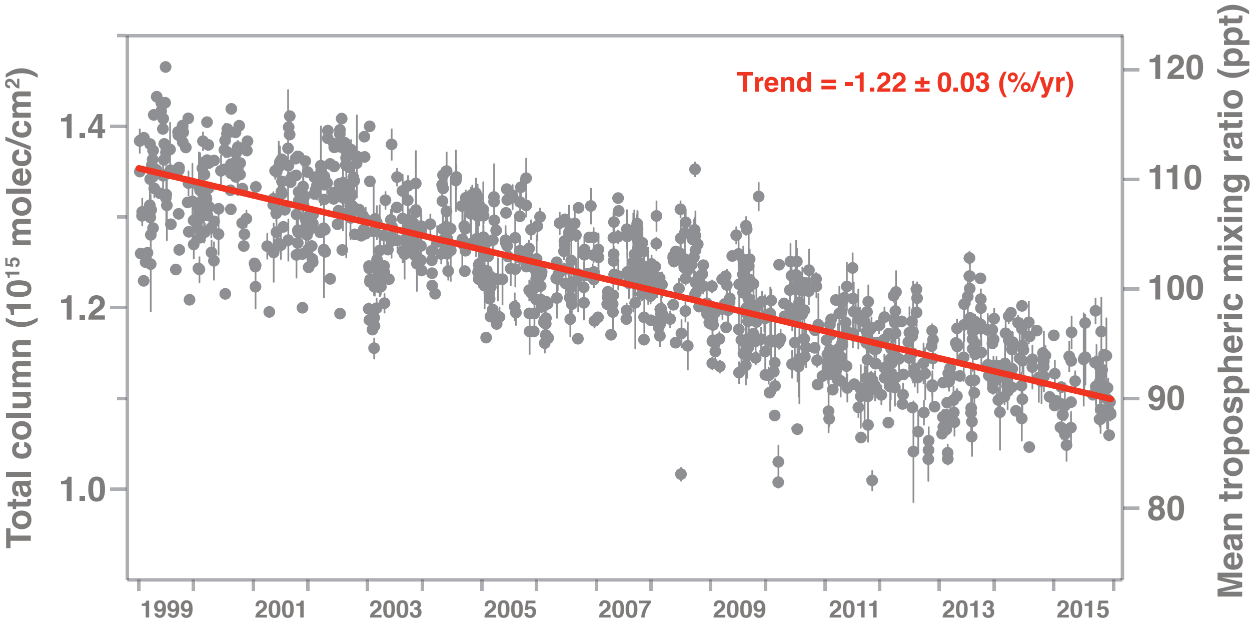

***Figure 6**: Time series of total column CCl_4 observed at Jungfraujoch, Switzerland. The long-term mean trend is shown as a thick red line. The equivalent mean tropospheric mixing ratios are shown on the right y-axis. Updated from Rinsland et al. [2012].*

Efforts have been made since the 2015 workshop to improve the CCl_4 satellite retrievals from the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) [Harrison *et al.*, 2016]. **Figure 7** shows an example of these new ACE-FTS data. These measurements will provide valuable stratospheric data for model validation in the key photolytic loss region (70-20 hPa) and additional information for deriving the CCl_4 long-term trend.

Using the new 33-year total lifetime, the observed trend, and a 2-D model of atmospheric transport and chemistry [Rigby *et al.*, 2014], we estimate global CCl_4 emissions as 40 (25-55) Gg/year. Since the instantaneous total lifetime and the steady-state total lifetime of CCl_4 are similar for the 1995-2015 period [Chipperfield and Liang, 2013], the emissions derived with the 33-year steady-state total lifetime represent the actual emissions well if the instantaneous total lifetime was used instead. The longer total lifetime derived from this workshop helps reduce the gap between calculations and bottom-up emissions estimates, but does not fully account for the difference.

The persistent hemispheric difference in CCl_4 mixing ratios measured between the Northern Hemisphere (NH) and Southern Hemisphere (SH) is a second piece of observational evidence suggesting ongoing emissions. Measured surface mixing ratios of CCl_4 in the NH are on average 1.2±0.5 ppt greater than those measured in the SH during 2010-2014 (**Figure 8**). Note that the hemispheric mean mixing ratio differences for the NOAA Network were calculated using the full set of NOAA observations, including both *in situ* and flask

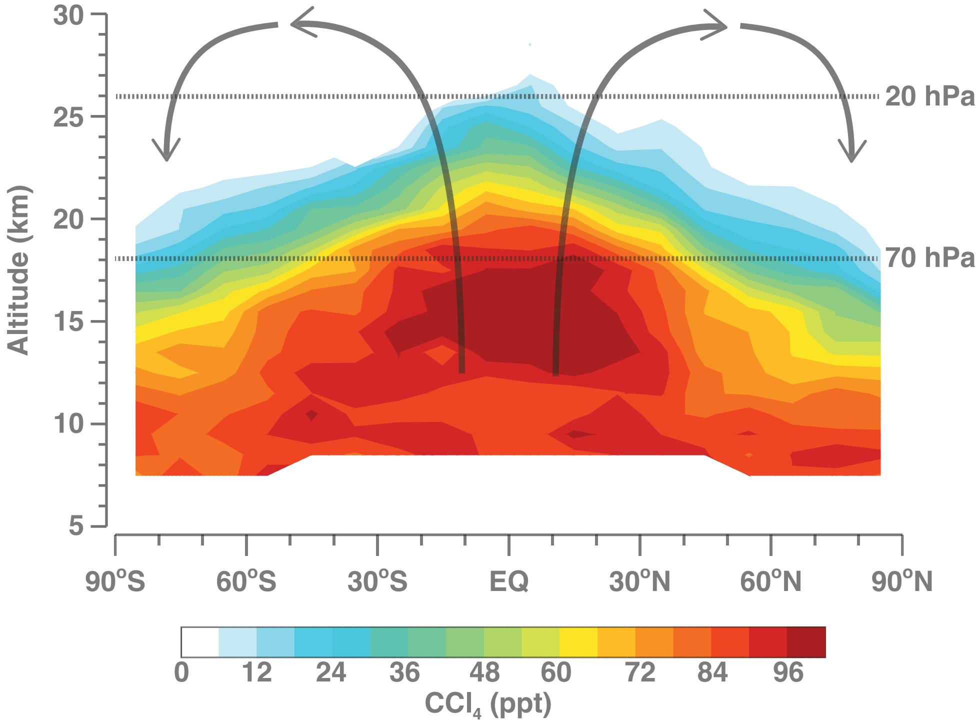

Figure 7: *An example zonal mean cross section of CCl_4 for March and April 2005, constructed from 527 ACE-FTS profiles. The grey arrows show the atmospheric mean circulation and the grey dotted lines indicate the key photolytic-loss region (70-20 hPa or ~18-26 km altitude) for CCl_4. Adapted from Harrison et al. [2016].*

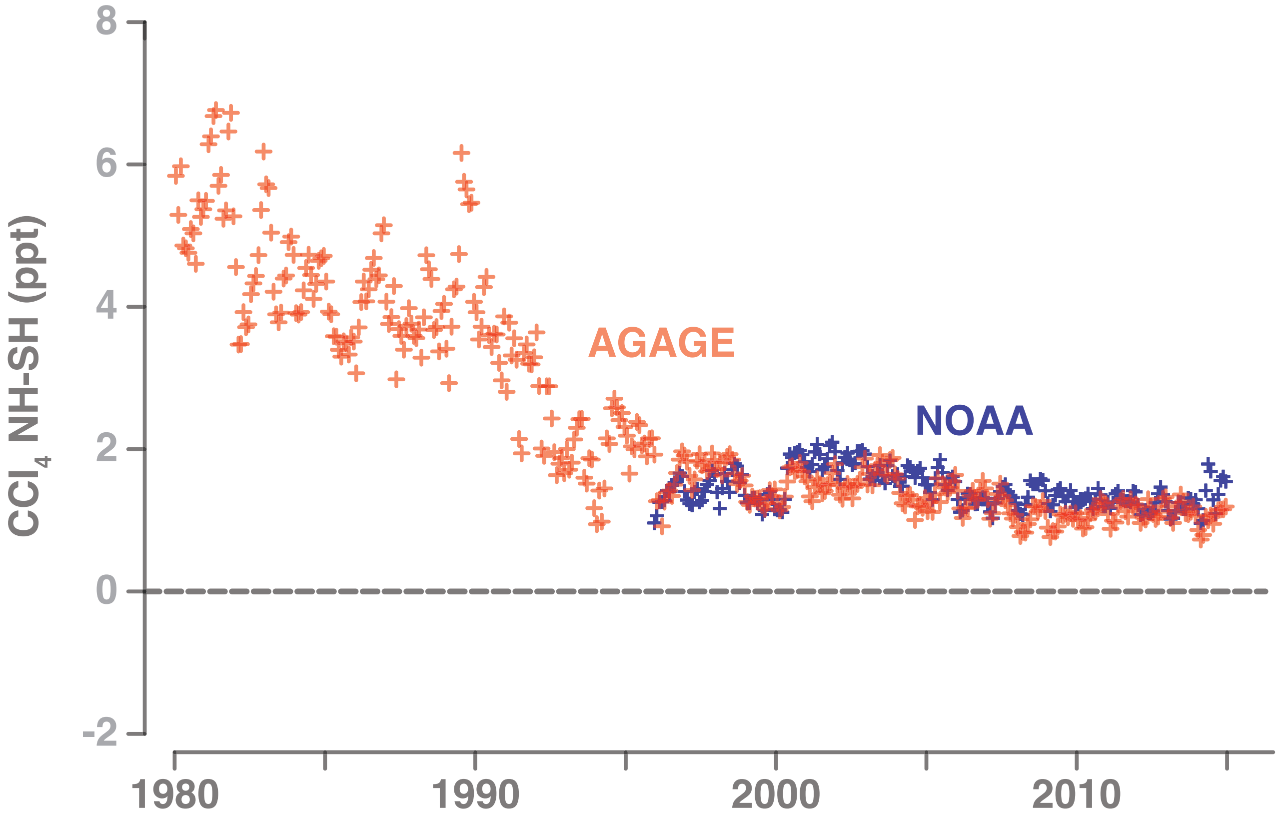

Figure 8: *Interhemispheric gradient vs. time as estimated at the surface from the NOAA (blue) and AGAGE (red) observational networks (see* ***Figure 13*** *for station locations).*

measurements. A difference in hemispheric mixing ratios of long-lived trace gases with predominant anthropogenic emissions arises because they are emitted primarily in the NH, where most people live and/or most industrial activity occurs. Given that transport of these emissions from the NH to the SH takes a year or more, the continuation of emissions sustains a difference in the hemispheric mean mixing ratios. Liang *et al.* [2014] found that there was a linear correlation between the NH-SH mixing ratio difference and annual mean global emissions; therefore, it was possible to mathematically derive global emissions using the observed differences in the NH and SH mixing ratios in a global two-box model approach, using one box for each hemisphere. The derived global emissions were a function of the NH emissions fraction and the estimated NH-SH exchange timescale. While this gradient top-down emissions estimate (see Glossary) is independent of total lifetime, it is to some extent sensitive to the relative strength of the ocean loss *vs.* the soil loss. Using an NH emissions fraction of 0.940 from Xiao *et al.* [2010], a 94-year ocean lifetime [Yvon-Lewis and Butler, 2002], and a 195-year soil lifetime [Montzka and Reimann, 2011], Liang *et al.* [2014] estimated mean global emissions of 39 (34-45) Gg/year for 2000-2012. We updated the gradient top-down emissions using the new bottom-up NH emissions fraction of 0.995 from Section 4, the new partial lifetime estimates from Section 2 ($\tau_{atmosphere}$=44 years, τ_{ocean}=210 years, τ_{soil}=375 years), and an interhemispheric exchange timescale of 1.35±0.25 years. An average NH-SH CCl_4 mixing ratio difference of 1.2±0.5 ppt suggests that the global emissions are 30±5 Gg/year during 2010-2014. The decrease in the estimated emissions, compared to Liang *et al.* [2014], are the result of both a higher NH emissions fraction and longer ocean and soil lifetimes.

One additional piece of observational evidence that points to continued CCl_4 emissions stems from enhanced mixing ratios measured in non-remote areas. Mixing ratios enhanced above the fairly narrow range of values measured in the remote atmosphere indicate the presence of sources that lie within tens to hundreds of kilometres from the monitoring sites [*e.g.*, Vollmer *et al.*, 2009]. When combined with an understanding of atmospheric transport processes and statistical "inverse" estimation techniques (regional top-down emissions estimate, see Glossary), the measured mole fraction enhancements can be used to quantify emissive fluxes. Atmospheric measurements from the AGAGE Network show that enhancements above baseline at most stations have been relatively small in recent years. There are ongoing local emissions but most of these local sources are small (**Figure 9**) [Fraser *et al.*, 2014; Graziosi *et al.*, 2016]. High-frequency (daily) flask measurements made by NOAA at sites across the U.S. show small CCl_4 mixing ratio enhancements [Hu *et al.*, 2016]. These results suggest average emissions of 0.11±0.04 Gg/year from Australia during 2009-2012 [Fraser *et al.*, 2014], 4 (2-6.5) Gg/year of CCl_4 from the U.S. during 2008-2012 [Hu *et al.*, 2016] (**Figure 10**), and 2.3±0.8 Gg/year from Western Europe during 2006-2014 [Graziosi *et al.*, 2016].

At Gosan, South Korea (**Figure 9**), and Shangdianzi, China [Vollmer *et al.*, 2009], however, significant above-baseline enhancements have been observed, with episodic enhancements as high as 30-40 ppt. These enhancements suggest CCl_4 emissions from East Asia of 15 (10-22) Gg/year (**Figure 11**) [Vollmer *et al.*, 2009].

While significant uncertainties remain in accurately deriving fluxes from these regional studies, the observations point to a minimum summed emissions estimate of 14 Gg/year from the regions studied to date (Australia, North America, East Asia, and Western Europe). Ideally, an analysis of results from non-remote sites would be expanded to include all potential emissive regions of the globe, so that a global emissions estimate could be derived

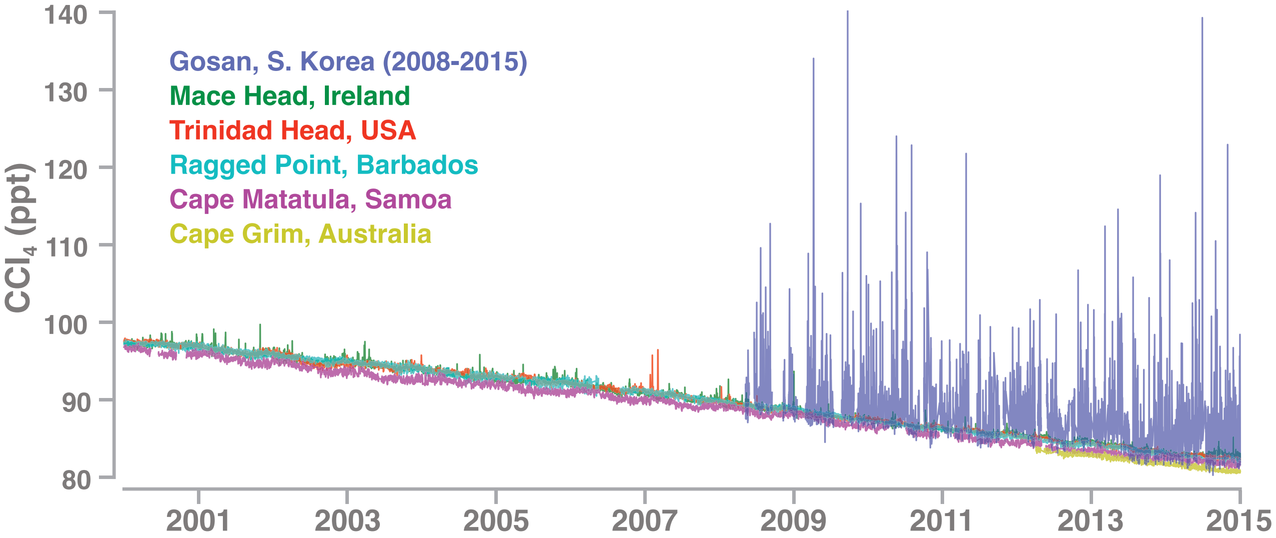

Figure 9: *Surface CCl_4 mole fraction observations at five "baseline" AGAGE stations and Gosan, South Korea. The South Korean data show that regular above-baseline mole fractions are recorded, indicating the presence of significant sources from the surrounding region.*

independently of production-based inventory approaches and the global total lifetime. At present, however, many potentially emissive regions of the globe are under-sampled.

New measurements from firn air (see Glossary) were shown at the 2015 workshop [Montzka *et al.*, 2015]. Results from the oldest air yet sampled from firn (CO_2 age = 1863) show CCl_4 mixing ratios of 3-4 ppt [Severinghaus *et al.*, 2010]. Using these new values, the same top-down technique described above, and this workshop's new 33-year total lifetime, this implies a 3-4 Gg/year upper limit on natural emissions.

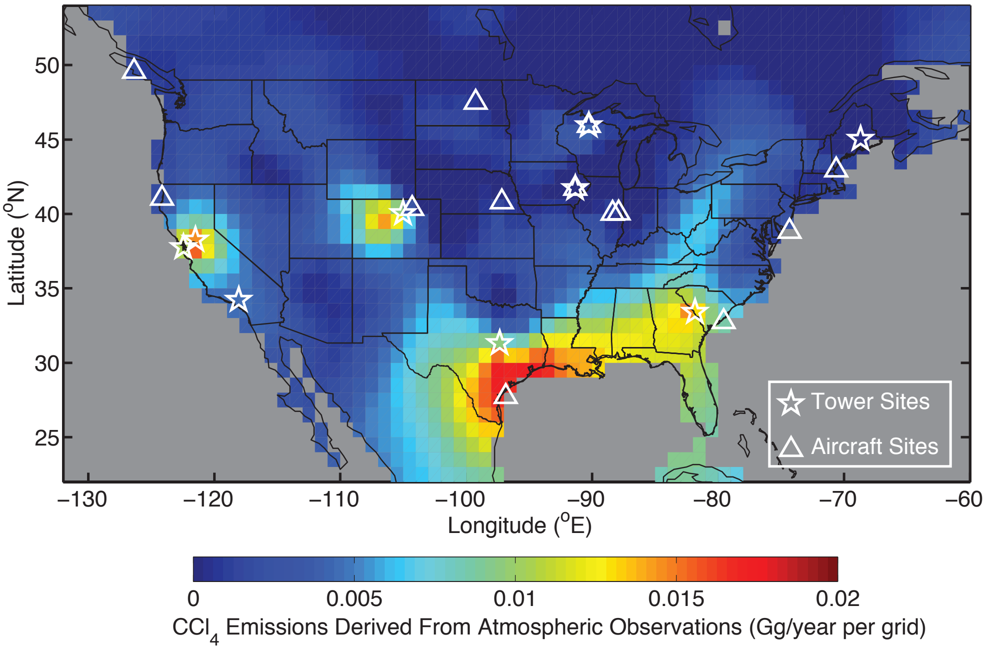

Figure 10: *Spatially resolved CCl_4 emissions over the U.S. derived from atmospheric observations during 2008-2012. The derived emission rate is indicated by the colour scale; the total mean emissions during this period were 4 (2-6.5) Gg/year. Emissions were derived from ongoing NOAA flask measurements from towers or aircraft at locations indicated by the symbols. Adapted from Hu et al. [2016].*

In summary, atmospheric observations provide strong evidence of substantial ongoing CCl_4 emissions in recent years. The ongoing emissions are estimated from multiple measurement laboratories, and stem from measurement aspects that are unique and independent. Specifically:

- **The observed global rate of decrease is 2-3 times slower than the lifetime-limited rate.** This observed rate would correspond to the lifetime-limited decay rate (zero emissions) for a chemical with a lifetime of 75 to 80 years, which is outside the possible range of our current best estimate for the total lifetime of CCl_4 (28 to 41 years). A 33-year total lifetime and a mean decline rate of 1.2-1.3 %/year imply global CCl_4 emissions of 40 (25-55) Gg/year over the past 5 years.
- **A persistent hemispheric difference of 1.2±0.5 ppt continues to be observed.** This implies substantial ongoing NH emissions, with a minimum global emissions magnitude

of 30±5 Gg/year for the 2010-2014 period.

- **Episodic enhancements above baseline atmospheric concentrations are observed in several regions of the world.** These concentration enhancements above those measured in remote areas indicate the presence of ongoing emissions from nearby regions. The continuous frequent concentration enhancements as high as 30-40 ppt at Gosan during 2008-2015 suggest significant ongoing emissions from nearby industrial source regions. The total summed emissions from North America, East Asia, Western Europe, and Australia are estimated to be 21.4±7.5 Gg/year.

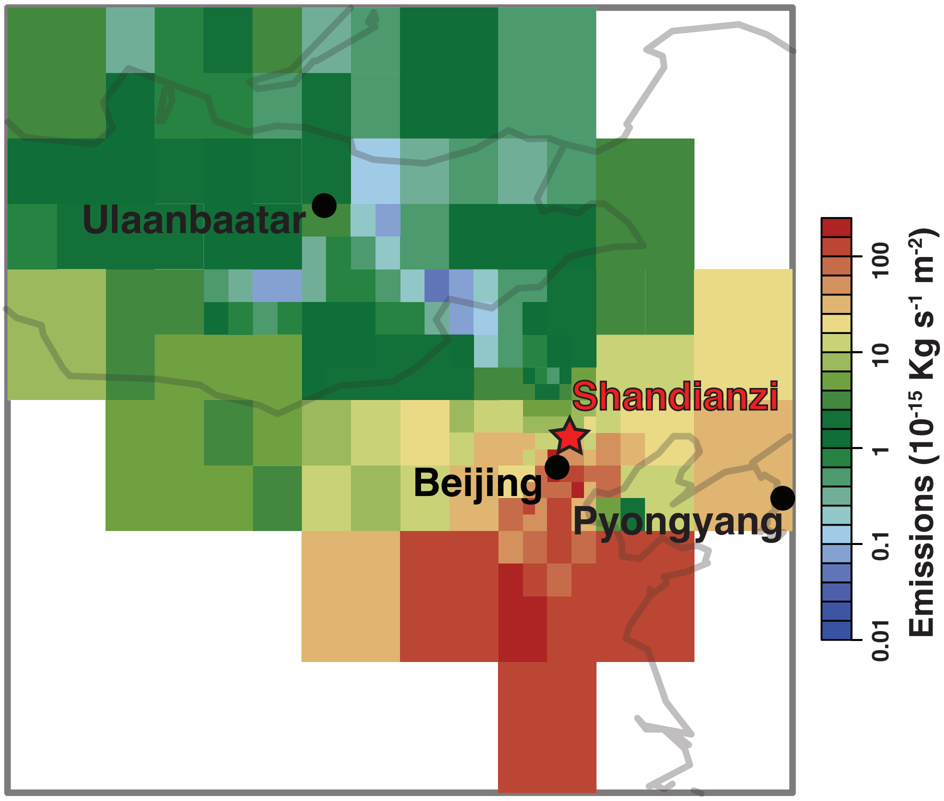

Figure 11: *Emissions of CCl_4 from East Asia derived using data from the Shangdianzi station (star), north of Beijing. Adapted from Vollmer et al. [2009].*

4. Industry Production and Emissions

CCl_4 is a co-product of the industrial production of chloromethanes, including the mono-, di- and tri- chloromethanes (CH_3Cl, CH_2Cl_2, and $CHCl_3$, hereafter referred to as "CMs") and perchloroethylene (PCE) (**Figure 12**, middle; Appendix A). During the production of CMs, hydrochlorination of methanol is used to form methyl chloride (CH_3Cl or MeCl), with subsequent chlorination to produce a series of other important chloromethanes (CH_2Cl_2 and $CHCl_3$), as well as CCl_4. In the PCE/CCl_4 process, CCl_4 and PCE are co-produced (Appendix A). In 2014 these two production routes led to a total production of 203 Gg of CCl_4. This CCl_4 was consumed by the following methods (**Figure 12**, right): (i) incineration (29 Gg); (ii) as a PCE feedstock (64 Gg); (iii) as an HFC feedstock (58 Gg); (iv) in methyl chloride production (26 Gg); (v) in divinyl acid chloride production (23 Gg); and (vi) for use as process agents and laboratory purposes (3 Gg).

CCl_4 can be emitted into the atmosphere by various processes. These emissions are grouped into four emission pathways (see Glossary) in **Figure 12** (green lines at top):

A) ***fugitive emissions*** from incineration, feedstock usage, and process agents;
B) ***unreported non-feedstock emissions*** during production of CMs and PCE;
C) ***unreported inadvertent emissions*** during the production and use of chlorine gas; and
D) ***legacy emissions*** from contaminated sites and landfills.

Deliberate and immediate emissions occur when CCl_4 is used as a solvent or from other emissive uses. This pathway presumably stopped after January 2010, with the global adoption of the control on production and consumption within the MP. However, fugitive emissions can occur when CCl_4 is used as a process agent (see Glossary) (**Figure 12 iv**), or as a feedstock for the production of HFCs and other industrial products (**Figure 12 ii-v**). Fugitive emissions also can occur during the process of handling CCl_4 as it is destroyed in chemical plants. Carpenter and Reimann [2014] estimated global fugitive emissions of 1-4 Gg/year in 2012.

Unreported non-feedstock emissions are from the inadvertent release of CCl_4 into the atmosphere when CMs and PCE are manufactured. Unreported inadvertent emissions of CCl_4 into the atmosphere occur during the production of chlorine gas in chlor-alkali plants (see Glossary), or industrial and domestic use of chlorine, *e.g.,* paper bleaching or disinfection (**Figure 12**, left side, Path C). This is due to the relative ease with which hydrocarbons are chlorinated; thus, CCl_4 may be formed in many chlorination procedures and released into the environment, atmosphere, or surface water.

Legacy emissions (*i.e.,* emissions from old industrial sites and landfills) also can be important (**Figure 12**, Path D). Fraser *et al.* [2014] estimated that unaccounted emissions (*i.e.,* legacy emissions and from chlor-alkali plants) could potentially contribute as much as 10-30 Gg/year globally. For the CCl_4 workshop, this number was revised to 5-10 Gg/year, due to an improved emissions calculation using inter-species correlations and the assumption that Australia is responsible for 1-2% of global emissions (up from 0.5-1.5%). This new 1-2% figure is based on updated ratios of Australian emissions of HFCs, hydrochlorofluorocarbons

(HCFCs), chlorofluorocarbons (CFCs), and CH_3CCl_3 to global emissions. In addition, Hu *et al.* [2016] assessed that industrial sources in the U.S. were more important than population-based diffusive sources. The non-feedstock emissions from production of CMs and PCE, and the inadvertent emissions associated with the production and use of chlorine gas, so far have not been included in the bottom-up estimates from the WMO/UNEP Scientific Assessments of Ozone Depletion [*e.g.*, WMO, 2014], and hence contribute considerably to closing the gap between bottom-up estimates and top-down calculated emissions.

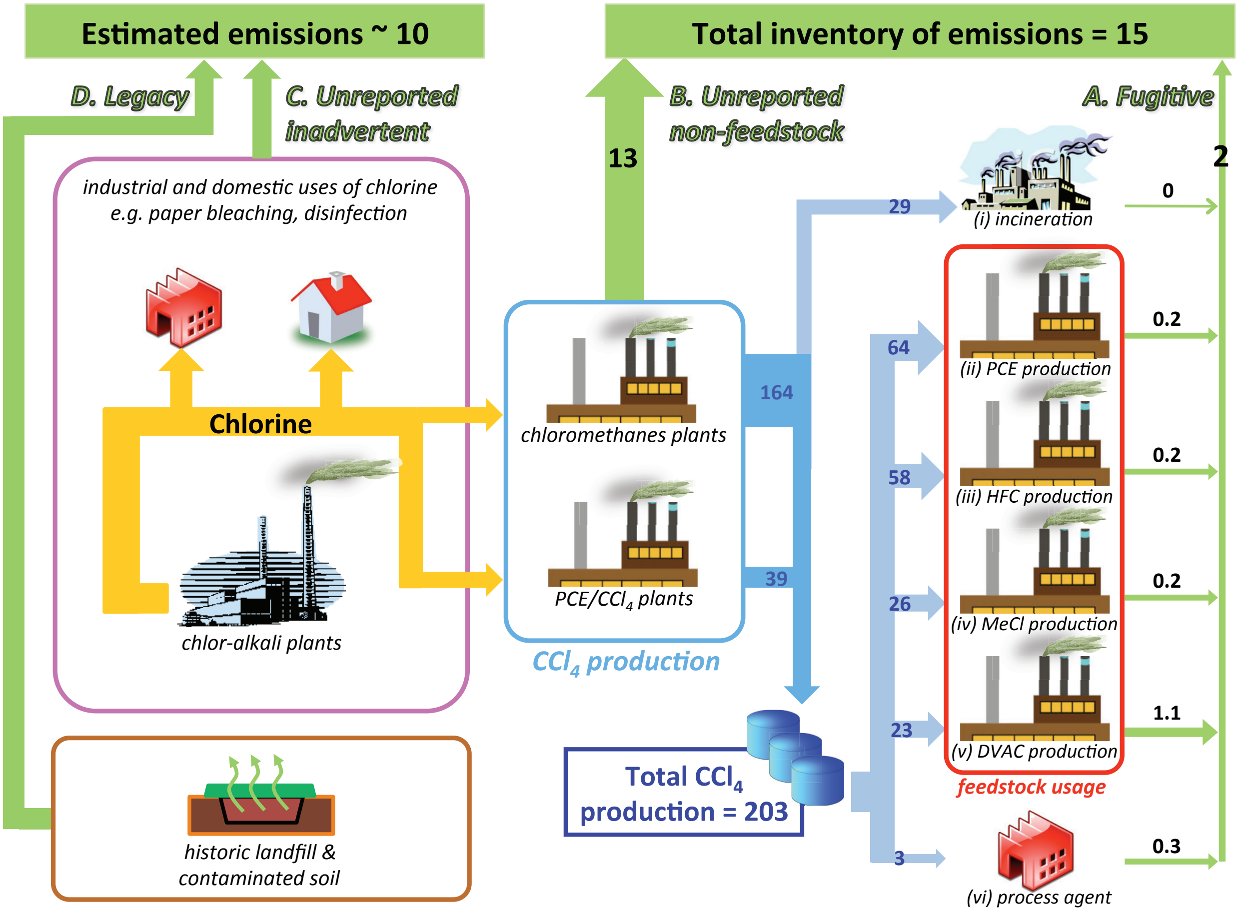

Figure 12: *Schematic of CCl_4 routes from pre-CCl_4 production of chlorine gas in chlor-alkali plants (left), and production (middle), usage (right), and emissions of CCl_4 (top) (in Gg). Production and use of chlorine gas are shown in yellow arrows. The numbers are 2014 estimates for industry production (blue box and arrows) and use (greyish blue arrows), and emissions of CCl_4 (green boxes and arrows, see* ***Table 2****). All numbers currently included in UNEP reports are shown in blue, and the ones that are not reported to UNEP are given in black. This 2014 estimate of 203 Gg is in close agreement with reports to UNEP from the Parties to the MP of 200 Gg in 2013. Feedstock uses are outlined in red: ii. PCE is perchloroethylene, iii. HFC is hydrofluorocarbon, iv. MeCl is methyl chloride, and v. DVAC is divinyl acid chloride. Estimates are courtesy of Dr. David Sherry (Nolan Sherry & Associates). More information is available in* ***Appendix A****. The global legacy emissions from decommissioned industrial sites and landfills as well as unreported inadvertent emissions from the production and use of chlorine gas are estimated based on results from Fraser et al. [2014].*

The locations of currently operating CMs and PCE production facilities are known - there are 35 CMs plants (see Glossary and Appendix A) and five PCE plants (see Glossary and Appendix A) globally (see **Table 2** and **Figure 13**). However, CCl_4 may be generated inadvertently in other processes where molecular chlorine comes into contact with a hydrocarbon, such as in the ethylene dichloride and vinyl chloride monomer production chain. The following bullets summarize the current understanding of such production and emissions, as presented at the workshop.

- CCl_4 yields from production of CMs can be minimized to ~4% CCl_4 production capacity via this route (~190 Gg) and is anticipated to increase. About 164 Gg of CCl_4 was actually produced via this route in 2014 (**Figure 12**, middle).
- PCE plants are older, but these plants can be modified to produce zero CCl_4. Overall, PCE plants are smaller production sources than CMs plants, with about 39 Gg of CCl_4 produced from the PCE route in 2014 (**Figure 12**, middle). Combining these two routes results in an estimated production of ~203 Gg for 2014. This is consistent with the 2013 UNEP-reported production of 200 Gg [UNEP, 2013].
- Because CCl_4 is used as feedstock (>95% of total production), most gets converted to other products such as HFCs, PCE, *etc.* (**Figure 12 ii-v,** red box on right). CCl_4 is still used as a process agent and in laboratory applications (**Figure 12 vi**), but in relatively small amounts (less than 3 Gg/year globally). Such uses do not necessarily mean that a significant fraction of this CCl_4 is emitted, as much may be captured, recycled, or incinerated.
- From production, total emissions of ~15 Gg from all of the above sources were estimated in 2014, shown in the **Table 2** (**Figure 12**, Paths A plus B).

Region	**Emission Sources**							**Total**
	PCE Prod.	HFC Prod.	DVAC Prod.	MeCl & other Prod.	Incineration	Process Agent/ Lab uses	CMs Prod. (at ~0.4%)	
Europe	0	0	0	0	0	0.01	2.0	**2.0**
Russia	0	0	0	0	0	0.2	0.4	**0.6**
North America	0	0	0	0	0	0.04	1.6	**1.6**
China	0.2	0.2	0.1	0.2	0	0.05	6.5	**7.3**
India	0	0	1.0	0	0	0	1.8	**2.8**
Japan	0	0	0	0	0	0	0.6	**0.6**
South Korea	0	0	0	0	0	0	0.2	**0.2**
Total	0.2	0.2	1.1	0.2	0	0.3	13.1	**15.1**

Table 2: *Estimated CCl_4 emissions during 2014 (Gg) from various production sources (see also blue ellipses in **Figure 13**). DVAC is divinyl acid chloride, which is one of the precursors to cypermethrin. Courtesy of Dr. David Sherry (Nolan Sherry & Associates).*

The chlor-alkali plants (**Figure 12**, left) are chemical production facilities that produce chlorine, hydrogen, and alkali (sodium hydroxide or potassium hydroxide) by electrolysis of a salt solution. The main technologies applied for chlor-alkali production are mercury-, diaphragm- and membrane-cell electrolysis, mainly using sodium chloride as feed, or to a lesser extent, using potassium chloride as feed. Currently, the chlor-alkali process produces 97% of the world's chlorine [Brinkmann *et al.*, 2014]. The geographic distribution of chlor-alkali processes, whether they are mercury-, diaphragm-, or membrane-cell, differs among regions globally. In 2012, global chlorine production capacity was estimated to be 76 800 Gg [Brinkmann *et al.*, 2014]. Of the world chlor-alkali capacity, more than 80% is concentrated in three regions: North America (19%), Western Europe (16%), and East Asia (48%) [Figure 1 in Brinkmann *et al.*, 2014]. Recent emission estimates using atmospheric observations over the U.S. by Hu *et al.* [2016] suggest that the majority of U.S. emissions appear to be related to industrial sources associated with chlorine production and processing. While this distribution is very similar to the distribution of chlor-alkali plants in the U.S., the results could not be used to identify the importance of these plants relative to other industry-related sources such as CMs and PCE for CCl_4 emissions. Inadvertent emissions from chlor-alkali plants have not been rigorously assessed globally. Note that CCl_4 also is used as a process agent in the chlor-alkali plants for the elimination of nitrogen trichloride (NCl_3) and the recovery of chlorine from tail gases. Worldwide, only a very small fraction of the chlor-alkali plants (nine in 2006) reported using CCl_4 as a process agent. The emissions rate from this

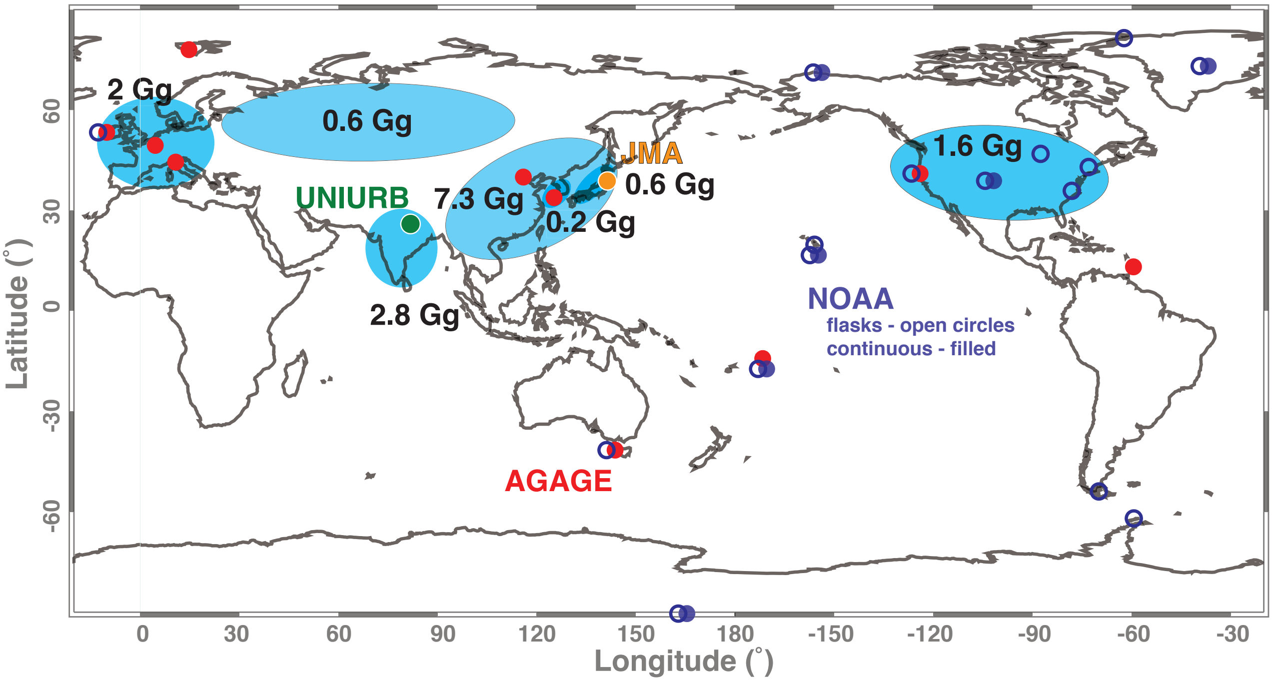

***Figure 13:** Estimated regional CCl_4 emissions (cyan ellipses in Gg) for Europe, Russia, India, East Asia (China, South Korea, Japan), and North America (see **Table 2** right column) based upon various production inventories. Also shown are some CCl_4 observing station locations: NOAA continuous (blue filled) and flasks (blue circles), AGAGE continuous (red), Japanese Meteorological Agency (JMA) continuous (orange), and U. Urbino (UNIURB) flask (green). Additional stations are shown in **Figure 10**.*

route is small: 0-30 gram CCl_4 per ton of annual Cl_2 capacity. Total fugitive emissions of CCl_4 from the use of CCl_4 as a process agent are included in **Table 2** and **Figure 12 vi** (bottom right) and are different from the unreported inadvertent emissions from chlor-alkali plants (**Figure 12**, Path C).

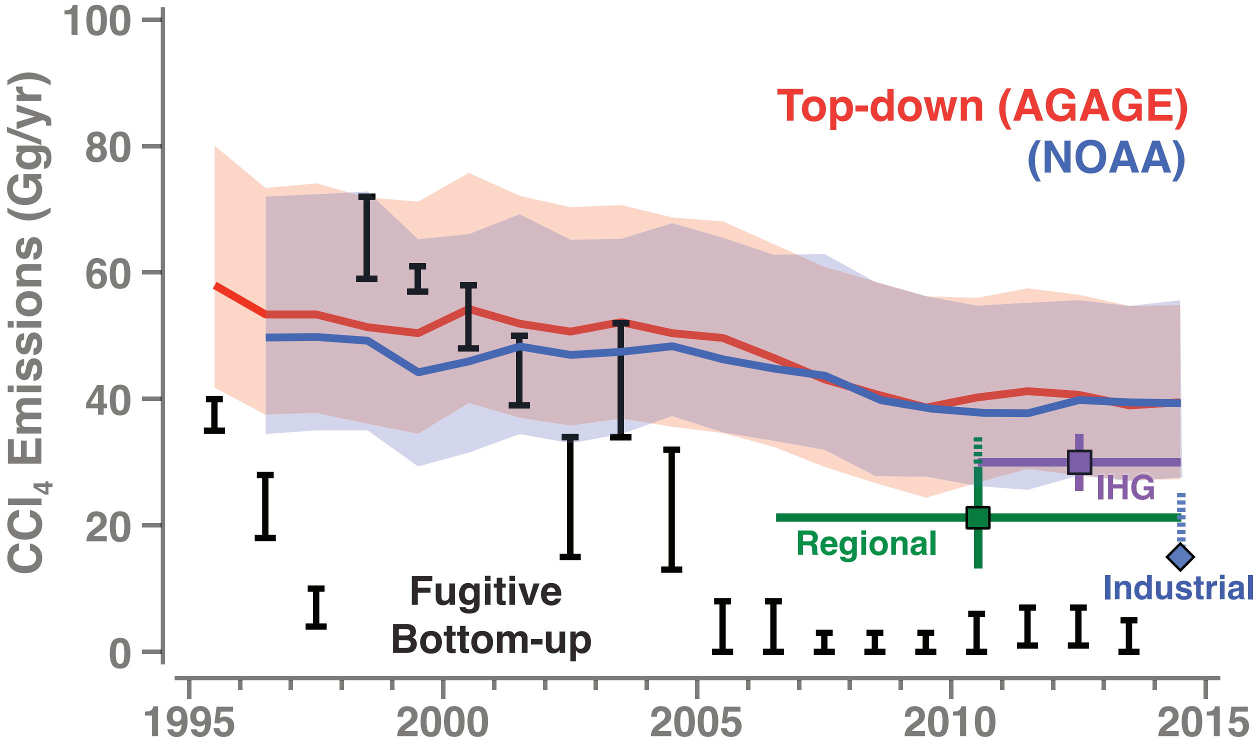

Figure 14: *Estimated annual emissions of CCl_4 based on measurements of atmospheric abundance (red shows estimates from AGAGE observations, while blue shows NOAA estimates), using the method described in Rigby et al. [2014] and used in Carpenter and Reimann [2014]. Top-down uncertainties are ±1σ. Black lines show the revised emission estimates for this report calculated from UNEP reports, as described in Montzka and Reimann [2011] and Carpenter and Reimann [2014]. The industrial point (blue diamond) is from* ***Table 2****, and the blue dotted line shows legacy emissions (see Section 4). The emission value estimated from the observed interhemispheric gradient (IHG) is the purple square, updated from Liang et al. [2014] but with new lifetimes and emissions information from this report. The derivation of the sum of the regional emissions and the related uncertainty (green square) is described in Section 3, with the green dotted line showing an estimate of regional emissions that have not been measured.*

Emissions estimates:

- Fugitive emissions are derived from reasonable feedstock emission factors (0.5-2% of use) and the assumption that post-1995 reporting of production for feedstock use (>95% of total) to the Ozone Secretariat is accurate. These emissions combined with unreported inadvertent emissions from CMs and other production still cannot explain the total CCl4 emissions derived from atmospheric observations. The 2007-2014 socalled "emissions gap" of between 10 and 40 Gg/year (**Figure 14)** is the difference between industrial bottom-up emissions (see Glossary, estimated at approximately 15 Gg/year as shown in **Figure 14** and given in **Table 2**) and measurement-based top-down emissions (now calculated at about 25-55 Gg/year, based on the new 33-year total lifetime - see **Figure 3**). This can be compared to the gap of 40-74 Gg/year calculated using the previous 26-year total lifetime in Carpenter and Reimann [2014] (**Figure 1**).

- Thus, despite a slight lowering of the magnitude of the emissions gap after applying the new total lifetime estimate of 33 years (**Figure 3**), the reporting of CCl_4 production and consumption data to UNEP is likely accurate (see Section 4), but may be incomplete with respect to estimating total global emissions. Significant unreported production and/or generation (in addition to current production for feedstock use) is likely occurring and may account for the required extra emissions (**Figure 12**, emissions from Paths B, C, and D). The existence of such major sources is consistent with the frequency and magnitude of pollution events observed in real-time surface measurements, *e.g.,* East Asia is estimated as having a 15 (10-22) Gg/year source (see Section 3).
- There is no convincing evidence that non-industrial CCl_4 emission sources can substantially account for the "emissions gap" [Fraser *et al.*, 2014; Hu *et al.*, 2016], although such sources have not been rigorously assessed globally. These non-industrial sources include waste and potable water sterilization with hypochlorite (domestic and industrial), landfills, toxic waste treatment/incineration, contaminated old industrial sites, and *in situ* atmospheric CCl_4 generation. Fraser *et al.* [2014] used a regional observation-based technique to estimate that the collective emissions from these sources (including chlor-alkali plants) are small, but together possibly account for up to 5-10 Gg/year globally.

5. Research Direction Suggestions

The 2015 workshop identified a number of research areas in which advancements could improve our understanding of the atmospheric budget of CCl_4, thereby possibly narrowing the gap between bottom-up estimates and top-down emission calculations. These are listed below in the form of research recommendations in the areas of CCl_4 emissions to, and removal from, the atmosphere. In some cases such further research, while constraining the CCl_4 budget discrepancy somewhat, are not as critical as others. Research areas in which advancements were viewed by workshop participants as having the greatest potential impact are **highlighted in bold below**.

A. With Respect to Improving Our Understanding of CCl_4 Emissions

- **Re-evaluate and improve industrial reporting of CCl_4 production and emissions**
  - o Current reporting of CCl_4 production needs to be reviewed and improved to account more accurately for all possible production processes, taking stockholdings into account, and to enable more rigorous estimates of the associated emissions.
    - Conduct quantitative reporting of CCl_4 production and emissions from production of CMs.
    - Increase monitoring of sources of CCl_4 from PCE production via MP Panels (*i.e.,* the Technology and Economic Assessment Panel (TEAP) and its Chemicals and Medical Technical Options Committee (CMTOC)).
    - Perform quantitative estimation of potential CCl_4 sources from chlor-alkali production facilities.
  - o The various facility types emitting CCl_4 within the major CCl_4 emission regions need to be specifically identified.

- **Maintain and improve CCl_4 spatial and temporal atmospheric measurement capabilities**
  - o Improve the network density for CCl_4 atmospheric measurements on a global scale to better estimate regional emissions, thereby providing a more quantitative insight into the causes of the gap between the sum of derived regional emissions and the total global "top-down" emission calculations. This will require additional measurement sites, strategically located in both under-sampled regions and in regions with significant growth in economic activity and populations, both in the local atmosphere as well as in remote areas downwind of production centres. Of particular interest are regions in:
    1. Asia, with particular focus on rapidly industrializing areas;
    2. Southern Africa; and
    3. South America.
  - o Advance the CCl_4 measurement capabilities through continued improvements in measurement precision and accuracy, and by continuing standards intercomparisons among the existing networks for both real-time and flask sampling.
  - o Improve satellite retrieval profiles for CCl_4 in the lower and middle stratosphere (10-100 hPa) and into the upper troposphere. The stratospheric measurements provide important observational constraints for atmospheric losses, and the tropospheric measurements will provide valuable information for source quantification.

  - Improve ground-based column observations of CCl_4 for trend analysis. This requires continued observations and further analysis of Fourier transform infrared spectroscopy (FTIR) observations from stations around the globe, and the comparison of these column observations to satellite and surface measurements.

- **Improve the atmospheric estimations of emissions on all scales (global, regional, point sources) through modelling analysis of pollutant transport prior to detection.** In particular, reducing the uncertainty in regional emissions estimates will require application of different modelling approaches to common observations at multiple locations.
  - Expand and continue comparisons of regionally focused inverse modelling studies for estimating emissions (*i.e.*, the regions shown in **Figure 13**).
  - Conduct and utilise observations of source-specific chemicals, together with those of CCl_4, to differentiate amongst the types of potential CCl_4 sources (*e.g.*, landfills, CMs plants, PCE plants, chlor-alkali plants, and feedstock plants).

B. With Respect to Improving Our Understanding of CCl_4 Removal from the Atmosphere

- Global 3-D model simulations include all known CCl_4 sources and sinks (atmospheric, oceanic, and soil losses). **Model simulations of the past need to be performed to critically test temporal and spatial variations in CCl_4 emissions and loss processes.** These simulations should be compared to the CCl_4 spatial distribution, trends, annual cycles, and interannual variability at the surface, in the free troposphere, and in the stratosphere.
- **Atmospheric lifetime:** The uncertainty in atmospheric lifetime is the largest contributor to the overall CCl_4 total lifetime uncertainty. **Reduction in this atmospheric lifetime uncertainty is needed to narrow the uncertainty of the atmospheric mean circulation.** This could be accomplished using models and improved remote-sensing measurements of CCl_4 and other chemicals.
- Ocean lifetime: Improve the understanding of mechanisms for the oceanic CCl_4 degradation.
  - Conduct process and incubation studies in seawater to better inform comprehensive model studies.
  - Carry out additional sampling and analysis of sub-surface oceanic distributions to characterise the mechanisms sustaining CCl_4 under saturations, including, but not limited to, low-oxygen regions.
  - Recover and evaluate historical data with respect to their potential contribution to understanding oceanic CCl_4 degradation, including those discarded due to CCl_4 degradation.
  - Investigate the role of oceanic circulation for delivering CCl_4-depleted deep ocean waters to the surface, and for improving the characterisation of Southern Ocean uptake.
- Soil lifetime: Refine estimates of the minor soil lifetime by conducting more measurements in different terrestrial biomes, especially in tropical ecosystems (*e.g.,* savannas and forests).

6. Summary

The MP has been very successful in reducing global CCl_4 emissions since the late 1980s and early 1990s. Both direct surface concentration (**Figure 2**) and total column observations (**Figure 6**) confirm that atmospheric levels of CCl_4 are currently declining at a rate slightly faster than 1% per year.

However, WMO [2014] highlighted a discrepancy of 54 (36-69) Gg/year between the low report-based CCl_4 emissions (UNEP bottom-up), and significantly higher emissions derived from CCl_4 observations (global top-down). This has exposed our incomplete understanding of the sources and sinks of this important atmospheric trace gas. This discrepancy has appeared in a number of the WMO/UNEP Scientific Assessments of Ozone Depletion and has been heavily discussed and debated in meetings of the Parties to the MP. The SPARC CCl_4 activity was formed in order to evaluate new data and to understand the gap between the top-down calculations and bottom-up emission estimates. A workshop was held from 4-6 October 2015 at Empa in Dübendorf, Switzerland. This workshop brought together science, industry, and technology experts to exchange information and coordinate research activities across disciplines to understand the CCl_4 budget, and to close the discrepancy between top-down and bottom-up CCl_4 emissions.

The findings on the magnitude loss processes of CCl_4 from the atmosphere have been re-evaluated since WMO [2014] for this report. The CCl_4 atmospheric lifetime remains unchanged from the 44 (36-58) years recommended in SPARC [2013]. However, both the soil and ocean lifetimes have been reconsidered in light of new information, and have been revised upward from 195 and 94 years, to 375 (288-536) and 210 (157-313) years, respectively. This increases the total lifetime from 26 years to our new recommendation of 33 (28-41) years. Modelling analysis conducted using multiple chemistry climate models suggests that reducing uncertainties in ocean loss rates and modelled-mean circulation strength in the tropical lower and middle stratosphere are key to further narrowing the range of the total CCl_4 lifetime in future.

This new 33-year total lifetime leads to a lowering of the calculated top-down emissions estimate based on observations. In Carpenter and Reimann [2014], the top-down calculation for the 2011-12 period was 57 (40-74) Gg/year, using the trend-based inverse approach and the 2-D model described in Rigby *et al.* [2014]. Based on this new 33-year total lifetime, we now estimate average emissions to be approximately 40 (25-55) Gg/year over the 2007-2014 period (**Figure 14**). The differences between the two surface network-derived top-down calculations also have decreased, particularly after 2007. This is due in part to the new longer total lifetime used in the top-down method, and partly to a more careful and stringent selection of observational data from the various NOAA Network instruments. Newly reported firn observations suggest an upper limit to natural sources of 3-4 Gg/year.

UNEP report-based CCl_4 bottom-up emissions are newly estimated as 3 (0-8) Gg/year over the 2007-2013 period (**Figure 14**). This estimate is based on UNEP-reported values with an approximately 0.5-2% leakage from contained feedstock production, following the technique developed in Montzka and Reimann [2011]. These bottom-up emissions differ from WMO [2014] because of revised UNEP-reported amounts used as feedstocks. This 3 Gg/year UNEP bottom-up emissions estimate is in reasonable agreement with the global industrial bottom-up fugitive emissions estimate of 2 Gg/year in this report.

An indication that industrial emissions are non-negligible also comes from the fact that regional top-down emission derivations tend to be considerably higher than bottom-up industry estimates from the same region (Section 3). The global magnitudes of possible emissions from the use of hypochlorite as bleach (domestic, industrial), chlor-alkali plants and their derivative products, *in situ* atmospheric CCl_4 generation, *etc.*, are assumed to be small, though the predominant source in the U.S. was found to have a similar distribution but much larger magnitude than sources reported from chlor-alkali plants and chlorine processing there [Hu *et al.*, 2016].

CCl_4 emissions also have been estimated from CMs and PCE production plants for this report. The analysis of these CCl_4 sources indicates a total global production of ~203 Gg in 2014 - consistent with the 2013 UNEP-reported production of 200 Gg. Leakage or non-feedstock emissions from these production sources and their regions has been separately analysed as 13 Gg/year. Combined with 2 Gg/year from usage as feedstock and process agents, this yields a global industrial bottom-up emissions estimate (see Glossary) of 15 Gg/year (**Table 2**; **Figure 14**, blue diamond). Combined with the upper-limit estimate of 10 Gg/year from legacy emissions from contaminated soils and toxic waste treatment facilities, and inadvertent emissions from chlor-alkali plants (updated from Fraser *et al.*, 2014), the current “hybrid” bottom-up emissions could be as large as 25 Gg/year (these additional emissions are noted as the dotted blue line on top of the blue triangle in **Figure 14**). However, this new estimate is still lower than the top-down calculation of 40 (25-55) Gg/year derived from the new total lifetime estimate above.

Evidence for continued emissions is derived from atmospheric measurements for three reasons. First, the observed global rate of decrease is 2-3 times slower than the rate assumed if there were no emissions. This observed rate would correspond to a total lifetime completely outside the possible range of our current best estimate for the CCl_4 total lifetime assuming zero emissions. Second, a persistent hemispheric difference of 1.2±0.5 ppt continues to be observed. This implies substantial ongoing NH emissions of 30±5 Gg/year (**Figure 14**, purple square). Third, episodic enhancements of atmospheric concentrations are observed in several regions of the world. Most observation stations do not show evidence of plumes of high CCl_4 (**Figure 9**). However, high-frequency observations at the South Korean Gosan station regularly show CCl_4 enhancements on the order of 10 ppt above background levels, with episodic enhancements as high as 30-40 ppt. Smaller enhancements also are observed in North America and Western Europe. These enhancements suggest the presence of substantial ongoing CCl_4 emissions in recent years. These observations and modelling techniques also have been used to estimate regional emissions from Australia (0.1 Gg/year), North America (4 Gg/year), East Asia (15 Gg/year), and Western Europe (2.3 Gg/year), for a total of about 21.4±7.5 Gg/year (**Figure 14,** green square).

By assuming that we can extend the emissions derivations from regions where both bottom-up and top-down emissions (see Glossary) are available (China, U.S., Western Europe, and Australia) to regions where only bottom-up emissions are available (Russia, Eastern Europe, India, *etc.*), we estimate an approximately 5 Gg/year additionally (this additional emission is noted as the dotted green line on top of the green bar in **Figure 14**). However, there is considerable uncertainty associated with estimating emissions from these unreported regions.

In summary, production levels reported to UNEP are consistent with industrial estimates presented at the workshop. The UNEP bottom-up emissions are also reasonably consistent with the industrial bottom-up fugitive emissions estimate. However, inadvertent CCl_4 emissions during CMs production and chlorine production are not currently reported. Station observations confirm that emissions likely originate from regions where CMs and chlor-alkali production plants are located. Global loss processes still have some uncertainties, and improving these will lead to some refinement of the total CCl_4 lifetime.

In closing, this SPARC activity has significantly revised our understanding of CCl_4. First, the activity recommends a new estimate of the CCl_4 total lifetime of 33 years. Second, three methods have been used to estimate CCl_4 emissions from observations. The top-down emissions calculation using a 33-year total lifetime is 40±15 Gg/year, and the hemispheric gradient method yields 30±5 Gg/year (**Figure 14**). The combination of these two observation-based estimates yields 35±16 Gg/year. The partial sum of measurement-based regional emission estimates is 21.4±7.5 Gg/year, but this is not a full global accounting. Third, one bottom-up approach based only on UNEP reports is updated here, based on new feedstock magnitudes, suggesting 0-7 Gg/year (**Figure 14**, black points). The industrial-based method, which includes fugitive emissions and unreported non-feedstock emissions, shows 15 Gg/year (**Figure 14**, blue point). If we add 0-10 Gg/year to this industrial value to account for unreported inadvertent emissions (from chlorine production and usage) and legacy emissions, we have a revised industrial-based global estimate of 20±5 Gg/year (**Figure 14**, blue dashed line). The difference between the observational (35±16 Gg/year) and the revised industrial emissions estimates (20±5 Gg/year) is 15 (0-32) Gg/year, in contrast to the 54 (36-69) Gg/year discrepancy estimated by Carpenter and Reimann [2014]. While the new bottom-up value is still less than the aggregated top-down values, these estimates reconcile the CCl_4 budget discrepancy when considered at the edges of their uncertainties.

GLOSSARY

Budget: A trace-gas budget consists of three quantities: its global sources, global sinks and total atmospheric burden. The global atmospheric burden and its trend reflect the balance (or imbalance) of emissions to the atmosphere with removal or loss from the atmosphere. If emissions exceed losses, then the global atmospheric burden increases. In the current case of CCl_4, emissions are smaller than losses, so global atmospheric levels are declining. However, the rate of CCl_4 change, estimates of emissions, and estimates of losses currently do not balance.

Chlor-alkali plants: Chemical production facilities that produce chlorine, hydrogen, and alkali (sodium hydroxide or potassium hydroxide), by electrolysis of a salt solution.

Chloromethanes (CMs) production plants: Chemical facilities that use hydrochlorination of methanol to form methyl chloride (CH_3Cl or MeCl), with subsequent chlorination to produce a series of other important chloromethanes (CH_2Cl_2 and $CHCl_3$). CCl_4 is produced as a by-product of CH_2Cl_2 and $CHCl_3$ during production of CMs.

Consumption: Is defined by the Montreal Protocol and is calculated as total production plus imports minus exports minus destroyed quantities minus feedstock uses of a controlled substance.

Dispersive uses: Uses that are not contained (*e.g.*, open-air solvent usage), ultimately leading to escape into the atmosphere.

Emission estimates, bottom-up:

i) ***UNEP bottom-up emissions:*** Emissions estimated from the annual data provided by the Parties to the UNEP Ozone Secretariat on CCl_4 production, imports, exports, feedstock amounts, and amounts destroyed. In this report, this emission lower limit was derived from the difference between total reported production and the sum of feedstock and amounts destroyed, including under-reported feedstock production estimates. The upper limit was similarly derived, but included a 2% fugitive feedstock, and 75% efficiency for reported destruction [Montzka and Reimann, 2011].
ii) ***Industrial bottom-up emissions:*** Emissions estimated from production of CMs and PCE, CCl_4 usage and transport, and destroyed amount in individual chemical facilities. Also included in this estimate are incineration, feedstock usage, and process agents (see below). This emission estimate is the sum of Paths A and B in **Figure 12**, and is described under “Emissions” below.

Emission estimates, top-down:

i) ***Global top-down emissions:*** Total global emissions derived using the observed global trend and an estimated total lifetime.
ii) ***Gradient top-down emissions:*** Total global emissions derived using the observed hemispheric difference in mixing ratios measured in the NH and SH and an estimated

interhemispheric exchange timescale.

iii) ***Regional top-down emissions:*** Regional emissions are estimated using observed enhanced mixing ratios with respect to baseline atmospheric concentrations at surface monitoring networks, modelling of atmospheric transport processes, and statistical "inverse" techniques. These regional emissions can be summed to yield a total global top-down emissions estimate.

Emissions (see **Figure 12**):

A. **Fugitive emissions:** Emissions of CCl_4 that occur from incineration, when it is used as a process agent, or as a feedstock for the production of HFCs and other industrial products.
B. **Unreported non-feedstock emissions:** Inadvertent emissions of CCl_4 into the atmosphere when CMs and PCE are manufactured.
C. **Unreported inadvertent emissions:** Emissions of CCl_4 into the atmosphere that occur during the production of chlorine gas in chlor-alkali plants, and industrial and domestic use of chlorine, *e.g.,* paper bleaching, disinfection.
D. **Legacy emissions:** Emissions of CCl_4 from old industrial or landfill sites and waste-treatment activities.

Feedstock: A compound that is used as a raw material, and undergoes chemical transformation in a process in which it is converted entirely from its original composition into another product. For example, CFCs were produced by the fluorination of a CCl_4 feedstock.

Firn air: Measurements of gases contained in air bubbles in unconsolidated snow.

Global warming potential (GWP): An index used to integrate the overall climate impact of emissions of a gas to that of emissions of an equivalent mass of CO_2.

Kharasch reaction: Named after its discoverer, the Kharasch reaction is a catalysed addition of a C_XCl_3 compound (*e.g.,* CCl_4, when X=Cl) to an alkene.

Lifetime:

i) ***Total lifetime:*** Global atmospheric burden divided by the summed global loss rate, including photochemical loss in the atmosphere, loss to the oceans, and loss to the soils.
ii) ***Atmospheric lifetime:*** Global atmospheric burden divided by loss due to atmospheric photochemistry. For CCl_4, loss in the atmosphere includes photolysis and reaction with $O(^1D)$.
iii) ***Ocean lifetime:*** Global atmospheric burden divided by the total ocean surface loss rate.
iv) ***Soil lifetime:*** Global atmospheric burden divided by the total loss rate to the land surface.

Ozone depletion potential (ODP): The integrated change in total ozone per unit mass emission of a specific ozone-depleting substance relative to the integrated change in total ozone per unit mass emission of CFC-11.

Perchloroethylene (PCE) production plants: Chemical facilities that produce PCE by reacting chlorinated hydrocarbons and chlorine at high temperature and elevated pressure. This reaction incorporates equilibrium between PCE and CCl_4, during which CCl_4 is produced as a by-product of PCE.

Process agent: A solvent that is used to facilitate the manufacturing or production of a particular chemical. Process agents are not feedstocks, and may not be destroyed in a production process. CCl_4 usage as a process agent and in associated industrial applications is specifically listed under the MP's “Decision X/14: Process Agents” and subsequent decisions on process agents.

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APPENDIX A: INDUSTRIAL BOTTOM-UP FUGITIVE EMISSIONS ESTIMATION

This appendix describes all the important processes that are involved in the production, usage, and destruction of CCl_4 (**Figure 12**). The definitions of various terms used here can be found in the Glossary.

CCl_4 Production (Figure 12, middle section):

Production of CCl_4 from chloromethanes (CMs) production (Figure 12, middle section, top panel): Production of CMs yields CCl_4. Older technology tends to produce ~6-8% CCl_4 of the total CMs, some of which will eventually form heavy products. Heavy products (also known as heavies or bottoms, specifically hexachlorobenzene and hexachlorobutadiene) are the tars that accumulate at the bottom of the distillation column needed to refine CCl_4 for chemical intermediate use. There will be some CCl_4 in these tars, but the prolonged high-temperature chlorination will produce cyclic hydrocarbons. Residual CCl_4 keeps this a tar-like dark fluid paste. Newer technology (*e.g.*, in China) generally yields about 4% CCl_4 (the default yield). In China, the CCl_4 content is used as feedstock or incinerated. Elsewhere, the CCl_4 production (over the default ratio of 4%, either because of old equipment or deliberately because CCl_4 is actively required) will be used (*e.g.,* in Kharasch reactions - reaction of a chlorinated olefin such as ethylene, styrene, or vinyl chloride monomer with a chlorinated compound such as CCl_4, HCFC-22, *etc.*), or incinerated. An average 4% on the CCl_4/CMs production number is the absolute minimum for CCl_4 generation. However, because the various producers deliberately adjust their production to satisfy CCl_4 industrial demands, a fixed percentage is not possible. Fugitive emissions from this quantity (best industry standards) will be less than 0.3%. The emissions estimate of 13 Gg is a pessimistic take (0.65%) on fugitives in the production and supply chain. [Source: multiple discussions over years with producers].

Production of CCl_4 from perchloroethylene (PCE) production (Figure 12, middle section, bottom panel): PCE and CCl_4 are co-produced in PCE/CCl_4 plants (U.S. two plants, EU three plants).The PCE/CCl_4 process made both products until the mid-1990s, when the absence of any demand and strict regulations had the companies either close completely or invest to run to 100% PCE. Residues from this process may be distilled again to use part as recycling to PCE, or sent directly to on-line thermal (reducing) oxidizers or kilns. [Source: multiple discussions over years with producers]. PCE also is produced in PCE/trichloroethylene plants (Cl_2 feedstock only, with a single plant in the U.S.), which does not involve CCl_4 production or emissions. A small amount of PCE is made from acetylene production, but this also is unlikely to create CCl_4.

CCl_4 Usage (Feedstock, Process Agent) and Destruction (Figure 12, panels on right)

i) **Incineration** does not generate CCl_4

ii) **PCE** is produced in PCE-from-CCl_4 plants (two to three such plants in China). The process for PCE-from-CCl_4 should be free of CCl_4 emissions (assumed). The process involves the co-reaction of methane, chlorine, and CCl_4 (*e.g.*, $CCl_4 + 4Cl_2 + CH_4 = C_2Cl_4 + 4HCl$). In some cases, the CCl_4 is road-shipped from third parties (producers of CMs), resulting in potential fugitive leakage during transport and storage. In China, there is no permit to operate CMs plants unless CCl_4 is demonstrably used as a chemical intermediate. In this report, it is assumed that there is some transport leakage, storage leakage, and production fugitives. Because of the limited knowledge on disposal of heavy CCl_4 tars, which may (illegally) be sold as bitumen thinner or sleeper/telegraph pole protection, a small amount has been added to the emission estimate.

iii) **Hydrofluorocarbons (HFCs)** are partly produced using CCl_4 in the Kharasch reaction (see Glossary) in relatively new plants (earliest operation started in mid-1990s, one or two in the 2000-2009 period, and about three in the last three years). These are modern products, the first two being HFC-245fa and HFC-365mfc. They are small in absolute volume, and made by large and well-practiced chemical companies. We have estimated a small default as a fugitive emissions rate. Most HFCs and some hydrofluoroolefins (HFOs) do not use CCl_4. The new bulk plant(s) in the U.S. and EU that will make the refrigerants HFO-1234yf and -1234ze will use CCl_4; the current production methods do not use CCl_4. The overall CCl_4 demand should increase by 50%+ in the coming years because HFO-1234yf, which does use CCl_4 in the new processes, with no current capacity, will replace HFC-134a, which does not use CCl_4, in automotive air-conditioning.

iv) **Methyl chloride (MeCl)**, produced from CCl_4, is made by two or three companies (China only). MeCl generally is made by the reaction of methanol with hydrogen chloride (HCl). The process is catalytic, with quite important catalyst exhaustion, and is expensive; however it must comply with regulations. MeCl does not contain CCl_4. MeCl is dehydrochlorinated from CCl_4, and the end product is MeCl and maybe some methanol. It does not carry CCl_4 traces, nor other higher CMs, because that CCl_4 would destroy upstream products. We have assumed some fugitive emissions from this production process. The other products (*e.g.*, cinnamic acid via CCl_4 + styrene) are very small.

v) **Divinyl acid chloride (DVAC)** consumes CCl_4 in a Kharasch reaction as the starting point (reacted with acrylonitrile) in a ten-stage process to make synthetic pyrethroids (ten plants in India, one plant in China). In India, the DVAC production process consumes all the CCl_4. In situations where the CCl_4 amount needed as DVAC feedstock exceeds CCl_4 produced from production of CMs, the four producers of CMs can opt to make more. Because trucks carry all of the CCl_4 from the sources to the ten producers, we included both double storage and transport fugitive emissions.

vi) **Process agent/lab** (see Glossary) is based on a pessimistic assumption that 10% of the CCl_4 (which the MP documents) will be released.

APPENDIX B: ACRONYMS AND CHEMICAL NOMENCLATURE

ACRONYMS

ACE-FTS	Atmospheric Chemistry Experiment Fourier Transform Spectrometer
AGAGE	Advanced Global Atmospheric Gases Experiment
CFC	chlorofluorocarbon
CIRES	Cooperative Institute for Research in Environmental Sciences (University of Colorado, United States)
CMs	chloromethanes, including mono-, di-, and trichloromethanes (CH_3Cl, CH_2Cl_2, and $CHCl_3$)
CMTOC	Chemicals and Medical Technical Options Committee (TEAP)
COADS	Comprehensive Ocean-Atmosphere Data Set
CSIRO	Commonwealth Scientific and Industrial Research Organisation (Australia)
CTC	carbon tetrachloride – also CCl_4
CTM	chemical transport model
DVAC	divinyl acid chloride
ESRL	Earth System Research Laboratory (NOAA)
EU	European Union
FTIR	Fourier transform infrared spectroscopy
Gg	gigagram (10^9 grams) (unit of mass)
GEOSCCM	Goddard Chemistry-Climate Model
GMD	Global Monitoring Division (NOAA)
GSFC	Goddard Space Flight Center (NASA)
GSFC2D	NASA Goddard Space Flight Center two-dimensional model

GWP	global warming potential
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
HFO	hydrofluoroolefin
hPa	hectopascal (100 Pa – also 1 millibar) (unit of pressure)
IHG	interhemispheric gradient
JMA	Japan Meteorological Agency
JPL	Jet Propulsion Laboratory (NASA)
KIT	Karlsruhe Institute of Technology (Germany)
LMDZrepro	general circulation model of the Institut Pierre-Simon Laplace Laboratory of Dynamic Meteorology (France)
MeCl	methyl chloride – also CH_3Cl
MP	Montreal Protocol
NASA	National Aeronautics and Space Administration (United States)
NDACC	Network for the Detection of Atmospheric Composition Change
NH	Northern Hemisphere
NOAA	National Oceanic and Atmospheric Administration (United States)
ODP	ozone depletion potential
ODS	ozone-depleting substance
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PCE	perchloroethylene - also tetrachloroethylene

RIVM	National Institute for Public Health and the Environment (The Netherlands)
SH	Southern Hemisphere
SIO	Scripps Institution of Oceanography (United States)
SOCOL	Solar Climate Ozone Links chemistry-climate model
SPARC	Stratosphere-troposphere Processes and Their Role in Climate (WCRP)
TEAP	Technology and Economic Assessment Panel (Montreal Protocol)
TOMCAT	Toulouse Off-line Model of Chemistry and Transport
ULAQ	University of L'Aquila climate-chemistry coupled model (Italy)
UMUKCA	Unified Model of the UK – Chemistry and Aerosol
UNEP	United Nations Environment Programme
UNIURB	University of Urbino (Italy)
U.S., USA	United States of America
WACCM	Whole-Atmosphere Community Climate Model
WCRP	World Climate Research Programme
WMO	World Meteorological Organization
2-D	two-dimensional
3-D	three-dimensional

CHEMICAL NOMENCLATURE

CCl_4	carbon tetrachloride – also CTC
C_2Cl_4	tetrachloroethylene
CFC-11	trichlorofluoromethane – also CCl_3F
CFC-12	dichlorodifluoromethane – also CCl_2F_2
CH_4	methane
CH_3Cl	monochloromethane or methyl chloride - also MeCl
CH_2Cl_2	dichloromethane or methylene chloride
$CHCl_3$	trichloromethane or chloroform
CH_3CCl_3	methyl chloroform
Cl_2	chlorine
CO_2	carbon dioxide
$^{14}CO_2$	isotopologue of carbon dioxide
HCl	hydrogen chloride
HCFC-22	chlorodifluoromethane – also $CHClF_2$
HFC-134a	1,1,1,2-tetrafluoroethane – also CH_2FCF_3
HFC-245fa	1,1,1,3,3-pentafluoropropane – also $CHF_2CH_2CF_3$
HFC-365mfc	1,1,1,3,3-pentafluorobutane – also $CH_3CF_2CH_2CF_3$
HFO-1234yf	2,3,3,3-tetrafluoropropene – also $C_3H_2F_4$
HFO-1234ze	1,3,3,3-tetrafluoropropene – also $C_3H_2F_4$
NCl_3	nitrogen trichloride
N_2O	nitrous oxide
$O(^1D)$	atomic oxygen (first excited state)

OH	hydroxyl radical

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