

**MONTREAL PROTOCOL  
ON SUBSTANCES THAT DEplete  
THE OZONE LAYER**



**UNEP**

**REPORT OF THE  
TECHNOLOGY AND ECONOMIC ASSESSMENT PANEL**

**AND THE  
SCIENTIFIC ASSESSMENT PANEL**

**SEPTEMBER 2016**

**VOLUME IV**

**DECISION XXVII/7 REPORT: INVESTIGATION OF CARBON  
TETRACHLORIDE DISCREPANCIES**

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## **Foreword**

### **The September 2016 TEAP/SAP Decision XXVII/7 Report: Investigation of Carbon Tetrachloride Discrepancies**

The September 2016 TEAP Report consists of four volumes:

*Volume I. TEAP Decision XXVII/4 Update Task Force Report: Additional Information on Alternatives to Ozone-depleting Substances*

*Volume II. TEAP Decision Ex. III/1 Working Group Report: Climate Benefits and Costs of Reducing Hydrofluorocarbons under the Dubai Pathway*

*Volume III. TEAP 2016 Final CUN Assessment Report*

*Volume IV. TEAP/SAP Decision XXVII/7 Report: Investigation of Carbon Tetrachloride Discrepancies*

*This is Volume IV*



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# 1 Introduction

The Montreal Protocol has been successful in reducing global carbon tetrachloride (CTC or CCl<sub>4</sub>) consumption for emissive uses, with a resulting decline of CCl<sub>4</sub> emissions [WMO, 2014]. CCl<sub>4</sub> is a major ozone-depleting substance and greenhouse gas. Observations reveal that atmospheric CCl<sub>4</sub> levels are currently declining at just over 1% per year. However, WMO [2014] also highlighted a discrepancy of 54 kilotonnes per year (kt y<sup>-1</sup>) between the lower report-based CCl<sub>4</sub> emissions estimate (UNEP-report based “bottom-up”), versus the significantly higher emissions estimate derived from atmospheric CCl<sub>4</sub> observations (global “top-down”). This discrepancy has been an issue for continuous consideration by parties to the Montreal Protocol, and has been investigated by the Scientific Assessment Panel (SAP) in various reports. TEAP has also developed estimates of emissions from consumption in emissive uses and from feedstock uses. In its Scientific Assessment of Ozone Depletion: 2014, SAP noted that this discrepancy remained unresolved.

At their Twenty-seventh Meeting, parties to the Montreal Protocol adopted Decision XXVII/7, which requested the Technology and Economic Assessment Panel (TEAP) and the Scientific Assessment Panel (SAP) “*to continue their analysis of the discrepancies between observed atmospheric concentrations and reported data on carbon tetrachloride and to report and provide an update on their findings to the Twenty-Eighth Meeting of the Parties.*” This report by TEAP and SAP responds to this decision.

## 2 Background

The addendum to the Note by the Secretariat to the Twenty-Seventh Meeting of the Parties to the Montreal Protocol (MOP-27) (UNEP/OzL.Pro.27/2/Add.1) highlighted recent work to address carbon tetrachloride emissions discrepancies. Reported emissions from CCl<sub>4</sub> sources have been inconsistent with abundance observations reported in WMO [2014], as noted above. In response to the discrepancy in emissions estimates, an activity was formed under the auspices of the World Climate Research Programme’s Stratosphere-Troposphere Processes And their Role in Climate (SPARC) project. This SPARC CCl<sub>4</sub> activity was formed in order to evaluate new data, and to understand the gap between the top-down and bottom-up emissions estimates.

A workshop held under the auspices of SPARC and entitled “Solving the mystery of carbon tetrachloride” was held in Dübendorf, Switzerland, from 4 to 6 October 2015. The workshop was attended by experts in the fields of science, industry and technology, and was hosted by the Swiss Federal Laboratories for Materials Science and Technology (Empa). The sponsors of the workshop included Empa, the National Aeronautics and Space Administration of the United States of America, SPARC, the Swiss National Science Foundation and the Ozone Secretariat. The workshop presentations were combined into written report that was peer-reviewed and published by SPARC [SPARC, 2016].

SPARC [2016] concluded that some of the discrepancy could be explained by additional emission sources unrelated to (UNEP) reported production, such as contaminated soils and industrial waste [Fraser et al., 2014], although the global significance of these sources is highly uncertain. Additional explanations include unreported emissions and revised estimates of partial lifetimes (stratosphere, ocean, or soil).

The report shows significant progress, including these main findings:

- a) New industrial estimates are in close agreement with estimates of emissions based on production (and consumption) data reported by the parties to UNEP. However, these estimated fugitive emissions (from incineration, and from feedstock, process agent and laboratory usage of CCl<sub>4</sub>), are not large enough to close the CCl<sub>4</sub> emissions discrepancy;

- b) Top-down estimates based on high-frequency, ground-based and airborne measurements indicate significant current CCl<sub>4</sub> emissions in the northern hemisphere from industrial regions;
- c) Revisions to ocean and soil lifetimes indicate that CCl<sub>4</sub> losses are slower to the oceans and soils than previously estimated. This reduces the top-down estimate, and thereby narrows the discrepancy with the bottom-up estimate;
- d) Observations based upon air trapped in snow (firn air) and ice cores have been used to construct time histories of CCl<sub>4</sub>. These data show that pre-1900 natural emissions are small.

### 3 Stratosphere-Troposphere Processes And their Role in Climate (SPARC) Project Report

SPARC [2016] used observations from the atmosphere, oceans and soils, along with modelling tools, to estimate top-down emissions. As a result of re-evaluation of losses to soils and especially to the oceans, the total CCl<sub>4</sub> lifetime has been revised upwards, from 26 to 33 years. The major uncertainty of this total lifetime was found to be the accuracy of the ocean loss estimate. This new SPARC [2016] 33-year total lifetime lowers the observations-based top-down emissions estimate to about 40 kt y<sup>-1</sup>. In addition, a persistent difference between the northern and southern hemispheres implies substantial on-going northern hemisphere emissions, yielding an independent emissions estimate of 30 kt y<sup>-1</sup>. The combination of these two observations-based estimates yields a top-down emissions estimate of 35 kt yr<sup>-1</sup>.

Regional CCl<sub>4</sub> emissions can be estimated from episodic enhancements of atmospheric concentrations at various measurement stations. Regional estimates have been made for Australia, North America, East Asia, and Western Europe. The SPARC [2016] sum of these emissions estimates is 21 kt y<sup>-1</sup>, albeit that this estimate does not include emissions from all regions of the world.

Four bottom-up CCl<sub>4</sub> emissions pathways have been identified in SPARC [2016].

- Pathway A includes CCl<sub>4</sub> emissions from incineration, feedstock usage, process agents and laboratory usage. Estimates of Pathway A have traditionally been based upon country data reporting under Article 7 to UNEP, with estimates showing emissions of 3 kt y<sup>-1</sup> over the 2007-2013 period. An independent new “industrial” emissions estimate has been performed which shows an emissions magnitude of **2 kt y<sup>-1</sup>** for Pathway A, consistent with the UNEP report-based emissions.
- Pathway B includes CCl<sub>4</sub> emissions from chloromethanes (CMs) and perchloroethylene (PCE) plants where CCl<sub>4</sub> is a co-product of the manufacturing processes. Analysis of these sources indicates a total global CCl<sub>4</sub> production of approximately 203 kt in 2014, which is consistent with the 2013 UNEP-reported CCl<sub>4</sub> production of 200 kt. Leakage or non-feedstock emissions from these production sources have been analysed as **13 kt yr<sup>-1</sup>** for Pathway B.
- Pathway C includes CCl<sub>4</sub> emissions from both the domestic and the industrial usage of chlorine, and the production of chlorine in chlor-alkali plants and their derivative products, etc. While these sources have been identified in various peer-reviewed publications, the global CCl<sub>4</sub> emissions from Pathway C have not been quantified on their own, and are currently unknown.
- Pathway D is very uncertain and includes legacy CCl<sub>4</sub> emissions from contaminated soils and toxic waste-treatment facilities.

SPARC [2016] estimated total CCl<sub>4</sub> emissions from the four bottom-up pathways to be as high as 25 kt y<sup>-1</sup>, although this estimate remains highly uncertain. While Pathways A and B have been estimated, Pathway C is unknown, and Pathway D is very uncertain, although the combined CCl<sub>4</sub> emissions from Pathways C and D have been broadly estimated to be **10 kt y<sup>-1</sup>**

<sup>1</sup>. The traditional bottom-up estimate from the UNEP reports (as used in WMO [2014]) has only included Pathway A and, therefore, is inadequate for estimating total global emissions.

The difference between the top-down  $35 \pm 16 \text{ kt y}^{-1}$  and the industrial bottom-up emissions estimates of  $20 \pm 5 \text{ kt y}^{-1}$  is about  $15 \text{ kt y}^{-1}$ , which is greatly reduced from the  $54 \text{ kt y}^{-1}$  discrepancy reported in WMO [2014]. While the SPARC [2016] bottom-up value is still less than its top-down value, these estimates reconcile the  $\text{CCl}_4$  budget discrepancy when considered at the edges of their uncertainties.

## 4 Conclusions and Recommendations

The SPARC [2016] report challenges many of the bottom-up estimates of emissions that have been used by the SAP in past reports. First, it shows that previous assessments have omitted  $\text{CCl}_4$  emissions sources from unreported additional pathways and, therefore, also that the current Article 7 data reports to UNEP are not adequate on their own for deriving bottom-up global  $\text{CCl}_4$  emissions estimates. Second, it reveals the necessity for further scientific research in order to tighten observations-derived top-down  $\text{CCl}_4$  emissions estimates, including regional emissions estimates. Third, it shows the continuing need to develop bottom-up methodologies for estimating  $\text{CCl}_4$  emissions in a consistent way.

The SAP and TEAP can continue to investigate the issue of  $\text{CCl}_4$  emissions as part of its quadrennial assessment processes. The following questions remain:

1. Can understanding of  $\text{CCl}_4$  usage efficiencies (for feedstock, process agent and laboratory usage), and resulting fugitive emissions be improved? Can the emission factors for fugitive releases be further refined? (Pathway A)
2. Can understanding of  $\text{CCl}_4$  emissions from CMs and PCE plants be improved? Can these emissions be further refined with uncertainties for these emissions? (Pathway B)
3. What are the  $\text{CCl}_4$  emissions from chlor-alkali plants and chlorine usage in domestic and industrial processes? (Pathway C)
4. What are the  $\text{CCl}_4$  emissions from landfills and contaminated sites? Can landfills and contaminated sites be studied further to estimate emissions? (Pathway D)

The SAP and the TEAP recommend the following paths forward for the consideration of parties:

- A. SPARC [2016] includes a “Research Direction Suggestions” section. Parties may request the Ozone Secretariat to forward it to the Vienna Convention’s Ozone Research Managers for consideration and evaluation for their next report.
- B. To address the above questions, a joint TEAP/SAP workshop could be held in coordination with the Ozone Secretariat in order to further evaluate the emissions pathways outlined in SPARC [2016]. This workshop could also be tasked with developing improved methodologies for estimating bottom-up  $\text{CCl}_4$  emissions.
- C. A joint TEAP/SAP working group could be established for estimating emissions of  $\text{CCl}_4$  in support of their quadrennial assessments.