

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



**UNEP**

**Chemicals Technical Options Committee  
(CTOC)  
2014 Assessment Report**



**UNEP  
REPORT OF THE  
CHEMICALS TECHNICAL OPTIONS COMMITTEE**

**2014 ASSESSMENT REPORT**

**Montreal Protocol  
On Substances that Deplete the Ozone Layer**

Report of the  
UNEP Chemicals Technical Options Committee

2014 Assessment

**ASSESSMENT REPORT**

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## **Executive Summary**

### ***Process Agents***

Nominations for process agent status were still being received as late as 2013 as Parties became aware of activities of their chemical industry sectors in which controlled substances were used.

Most of the process agent uses remained are of long standing, and the ODS are used as solvents to create unique yields (i.e. specific reactions), selectivity (i.e. specific compound) and/or resistance to harsh chemical environments, with the result that production is achieved with high efficiency. Legacy processes built around these properties make it difficult or impossible to convert in a cost effective and timely manner. Almost all of the removals of process agents from Table X/14, which at one stage included over 40 examples, have resulted from plant closures rather than substitution of other substances for the ODS process agent.

Three process agent uses have been discontinued and removed from Table A. A better standard of reporting of emissions needs to be achieved so that Table B gives a more reliable picture of emissions arising from process agent uses. This could be achieved by developing a list of Parties with approved process agent uses to the Ozone Secretariat to enable better targeting of requests for information and follow up.

#### *What is left to be achieved?*

Improved reporting on Process Agent uses and emissions.

#### *The way forward*

Assist Parties with improved tools to encourage better reporting of process agent use. Process agent uses are expected to decline as chemical plants become obsolete or products are discontinued.

### ***Feedstocks***

An extensive listing of known use of ODSs as feedstocks has been compiled. Using volumes as reported by Parties to the Ozone Secretariat, a profile of feedstock use has been generated. By following guidelines for emission calculations suggested by the IPCC for the UNFCCC, feedstock emission estimates have been generated. Data for emissions are shown for production for feedstock use. A total of 1137K metric tonnes ODSs were produced in 2013 representing about 25K ODP metric tonnes. This was an increase in production of 0.35% vs. 2012 levels and a decrease of 5.4% in ODP tonnage.

Reported volumes of feedstock uses are expected to be fairly complete with a possible exception of some small batch uses. Earlier communications concerning feedstock reporting has increased such data provided by Parties. During the past three year period during which improve data were provided to the CTOC, use of feedstocks has shown

virtually no growth.

IPCC guidelines for emission estimation do not well represent actual emissions during use of ODS as feedstock. Expert opinion suggests that the IPCC guidelines are maximal values and actual emissions may be lower at well managed facilities. Improved estimates of emissions could be achieved with improved UNFCCC guidelines or other accepted practices. Developed countries report to UNFCCC emission data for HFCs in their inventory reporting. Thus, discussions with UNFCCC may assist in developing new estimated sources of data for HFC production (which may have utilized ODSs as feedstock in their preparation). The reporting of ODS volumes for each feedstock uses by Parties through the Ozone Secretariat may enable a more complete quantification of this activity. Such reporting has not yet been established on a regular basis for developing countries.

Both governments as well as industry are making successful efforts to minimize emissions associated with ODS use in feedstock applications. An overview of such measures is provided to assist Parties to limit environmental impacts. Continued use of process permits limiting emissions along with Party oversight would likely allow for further improvements.

Concerns of use of  $\text{CH}_2\text{Cl}_2$  as feedstock could be adding to observed increases in atmospheric concentrations are addressed. Our conclusion is that such increases are not from feedstock applications but rather from direct uses.

*What is left to be achieved?*

Feedstock use is a long term activity. Accurate assessment and awareness of the extent of feedstock uses and volumes are needed annually. Improved estimation procedures would enhance quantification of environmental impacts of these practices.

*The way forward:*

Annual summaries of feedstock data submissions to the Secretariat for inclusion in CTOC Progress and/or Assessment Reports. Increase guidance from the UNFCCC on metrics that could be used for leakage estimation. Encourage Parties to license production facilities and to provide their own oversight that such emissions are below allowed levels.

### ***Solvents***

In Article 5 parties, CFC uses were completely phased out in 2012, and the phase-down of HCFC use in solvent application began. In non-Article 5 Parties, HFCs and HFEs have been used to replace the remaining HCFCs in certain application where the high cleaning performance is required. Recently HFOs are emerging in the market to replace HFCs and HFEs with middle to high GWP.

The Threshold Limit Values (TLV) of n-PB has been reset from 10ppm to 0.1ppm by American Conference of Governmental Industrial Hygienists (ACGHI). It indicates the use in solvent applications seems problematic.

The major challenge is the complete phase out of ODS solvents in Article 5 countries. Preferable alternatives have been identified and are generally available. Another hurdle to overcome is the economic impact on the small and medium size users who make up a major portion of the remaining ODS solvent market.

Regulatory changes will continue to impact on the use of solvents. In some cases, this may require solvent and/or equipment change or a new cleaning process.

*What is left to be achieved?*

Complete phase out of the use of HCFCs in solvent application

*The way forward*

The phase-out of HCFCs in Article 5 Parties is scheduled in 2035. Although solvent contribution to the Ozone layer depletion is relatively small with respect to the other applications, the transition to the alternative technologies can be undertaken as the alternatives are already available. One issue is how to support small and medium enterprises where solvent is not well-managed. These may be one of the significant emission sources of Dichloromethane.

### ***Laboratory and Analytical Uses***

There are very few identified uses of ODS in laboratory and analytical procedures in non-Article 5 countries. Some use continues in several Article 5 countries.

Advice by experts is required, together with modest financial support for alternatives that have already been identified to be trialled in Article 5 countries, alongside current procedures that involve ODS. New standard methods need to be developed.

Now, the global laboratory and analytical-use exemption is extended until 31 December 2021. TEAP is requested to report on the development and availability of laboratory and analytical procedures that can be performed without using controlled substances under the Montreal Protocol no later than 2018;

*What is left to be achieved?*

Further reduction in ODS use for Laboratory and Analytical purposes.

*The way forward*

CTOC will be vigilant in raising awareness of alternative methods. Parties can take steps to implement new standard methods (NORMS) that do not use ODS. Parties should report on successful alternatives so that this knowledge can be shared (an example was the use of butane or LPG in assessing the activity of activated carbon prepared from coconut husks).

### ***Destruction Technologies***

Since 2010, CTOC has reviewed several emerging technologies following Decision

XXI/10.

Periodic review of available destruction technologies will be necessary to provide updated technical guidelines for destruction of ozone depleting substances such as CFCs, halons and methyl bromide as well as for HFCs.

*What is left to be achieved?*

Analysis of the needs for the future destruction of unwanted ODS.

*The way forward*

Destruction of ODSs presents special challenges to A5 Parties. As the volumes are low, high unit costs make it difficult to justify installation and operation in each country. It would be helpful to identify, define and establish support projects to cover high costs and technologies associated with local destruction facilities and/or capture and transport to regional facilities. Support is also needed to help define how to deal with regulatory issues associated with transport of wastes should that be the selected option.

### ***Carbon Tetrachloride (CTC) and Dichloromethane Emissions***

TOC has reported for a number of years on the discrepancy between emissions of CTC to the atmosphere based on 'bottom up' estimates based on production and consumption and typical emission rates, and 'top down' estimates based on stratospheric concentrations of CTC and estimates of its atmospheric lifetime.

The Scientific Assessment Panel had revised the atmospheric lifetime for CTC in their OEWG report in 2012, increasing the value substantially. 'Top down' estimates thus give lower emission rates, by 10-20 Ggramme/year, to maintain the observed stratospheric concentration of CTC. Diffuse emissions could contribute 8-12 Ggramme/year, and together these figures significantly reduce the discrepancy between the two types of estimate by as much as 18-32 Ggramme/year. The gap between the two estimates of emissions has thus been reduced but not entirely closed.

CTOC has become aware that historically there may have been previously unreported or under-estimated emissions of CTC connected with the use of phosgene, for example in the production of methylene diphenyl di-isocyanate (MDI), a reactive substance that is used to make polyurethanes. It is also indicated that phosgene produced from chlorine and carbon monoxide is usually contaminated with CTC, the presence of which may not be taken into account when emissions are taken into account.

CTOC has also studied other possible emission sources. However, additional emission sources that could narrow the gap significantly could not be found.

Dichloromethane (methylene chloride) emissions to the atmosphere have been increasing since 2006. The source of the additional 300,000 tonnes emitted annually is conjectural but most of it must come from use of dichloromethane itself as solvent or cleaning agent; it is beyond reason that the source is fugitive emissions from feedstock. If that were the case, more dichloromethane would have been lost to the atmosphere than the amount used to make HFC-32 - economically disastrous as well as impossible in a

developed economy under environmental legislation.

*What is left to be achieved?*

Better understanding of the mismatch between estimates of emissions, measured stratospheric concentrations, and lifetimes.

*The way forward*

Collaboration with the Scientific Assessment Panel.

the UNEP inventory data and to further revise the atmospheric lifetime of CTC.



## **1. Process Agents**

### **1.1 Introduction**

To be accepted as a process agent use, the ODS in the specified process must meet two of the following criteria:

- i. Chemical inertness during the process.
- ii. Physical properties.
- iii. Action as a chain-transfer reagent in free radical reactions.
- iv. Control of product physical properties such as molecular weight or viscosity.
- v. Ability to increase yield.
- vi. Non-flammable/non-explosive.
- vii. Minimisation of by-product formation.

Most of the process agent uses are of long standing, and the ODS are used as solvents to create unique yields, selectivity and/or resistance to harsh chemical environments, with the result that production is achieved with high efficiency. Legacy processes built around these properties make it difficult or impossible to convert in a cost effective and timely manner, and only a few examples are known. In this regard, the process agent uses have much in common with feedstock uses that are covered in a separate section of this report. Almost all of the removals of process agents from Table X/14, which at one stage included over 40 examples, have resulted from plant closures rather than substitution of other substances for the ODS process agent.

In considering the need to continue process agent use, CTOC members were mindful that the lifetime of a chemical production plant could be as long as 50 years. If the product is important enough to warrant continued production, and the plant is maintained in good condition and not in need of renewal, then the investment required to put into operation a new process that does not use ODS is unlikely to be justified.

While each of the process agent applications is unique, there exists a suite of measures that can be applied to minimize make-up and emissions and each one needs to be considered by an operator. These measures include limiting make-up to the essential minimum, ensuring tight systems (no leaking valves and joints); evacuation and purging with recovery prior to opening equipment; closed loop transfer systems; proximity of production and use of the ODS; monitoring sensors at potential leak locations to provide alerts for prompt repair; use of absorbents such as activated charcoal on vents; and destruction of vent gases.

### **1.2 Response to Decision XXIII/7(6)**

At MOP-23 in 2011, Parties were requested to submit information to the Secretariat on make-up quantities and emissions from applications for which process agent exemptions exist. Parties were also requested by Decision XXIII/7 to report under a number of headings on existing process agent uses and to provide information to the thirty-second

meeting of the Open-ended Working Group in mid-2012. The CTOC have reviewed the fourteen process agent uses listed in Table A of Decision X/14 as amended in that 2011 decision. The data reported by Parties through 2010 to 2103 indicated that three process agent use are no longer in use and can be removed from Table A (# 10, 11 and 12)

### 1.3 Data tables

Data reported by Parties to UNEP are shown in the following tables, to which explanatory comments are appended.

**Table 1-2: Process agent emissions and make-up 2013 (MT)**

No.	ODS	Process	Country	Makeup	Emission	Note
1	CTC	Elimination of NCl <sub>3</sub> in chlor-alkali production	Colombia			1
			EU	8.1	0.001	
			USA			2
			Israel	2.4		
2	CTC	Chlorine recovery by tail gas absorption in chlor-alkali production	EU	103.4	0.274	
			Mexico			
			USA			2
3	CTC	Production of chlorinated rubber	EU	12.2	0.086	
4	CTC	Production of chloro-sulfonated polyolefin (CSM)	China	88.9	52.640	
			USA			3
5	CTC	Production of aramid polymer (PPTA)	EU	3.9	0.082	
6	CFC-11	Production of synthetic fibre sheet	USA			2
7	CFC-12	Photochemical synthesis of perfluoropolyetherperoxide precursors of Z-perfluoropolyethers and difunctional derivatives	EU	103.7	0.100	
8	CFC-113	Preparation of perfluoropolyether diols with high functionality	EU	3.41	0.095	
9	CTC	Production of cyclodime	EU	387.4	15.170	4
10	CTC	Production of chlorinated polypropene	China			5
11	CTC	Production of chlorinated ethylene vinyl acetate (CEVA)	China			5
12	CTC	Production of methyl isocyanate derivatives	China			5
13	BCM	Bromination of a styrenic polymer	USA			2
14	CFC-113	Production of high modulus polyethylene fibre	USA			2

- Note 1: There are no new data because Colombia had previously reported process agent use by Quimpac SA (formerly Prodisal SA) but this will cease when a conversion process (MLF project CUL/PAG/48/INU/66) is completed.
- Note 2: Total emissions for all process agent uses in the US are 34.50 ODP weighted MT, well below the maximum emission limit of 181 MT.
- Note 3: Chlorosulfonylated polyolefin is no longer produced in the US.
- Note 4: The emissions from CTC use in the production of cyclodime are high but the total of the emissions do not exceed anymore the applicable limit under EU legislation. Furthes step are on going to improve the situation.
- Note 5: These process agent uses have been discontinued, thus they may be removed from Table A.

**Table 1-3: Table B of Decision X/14 as amended by Decision XXIII/7 (2011 data)**

Party	Make up		Emissions	
	2013 total	Maximum	2013 total	Maximum
EU (MT)	622.10	1085.00	15.81	17.50
US (ODP-MT)			34.500	181



## **2. Feedstocks**

### **2.1 Introduction**

Feedstocks are building blocks to allow cost-effective commercial synthesis of other chemicals. Use of such compounds as carbon tetrachloride (CTC), 1,1,1-trichloroethane (TCA) (also referred to as methyl chloroform), chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and several other examples, all ozone depleting substances, as feedstocks allow incorporation of fluorine atoms into molecule structures. Products finding uses such as refrigerants, blowing agents, solvents, polymers, pharmaceuticals and agricultural chemicals are produced to benefit society. These feedstocks have been carefully selected for these uses as there are no other technologically and economically viable alternative routes available at this time. Such choices involve large investments of capital with plant lifetimes as long as 50 years when properly maintained and upgraded. As raw materials, they are converted to other products except for de minimus residues and emissions. Emissions in feedstock use consist of residual levels in the ultimate products and fugitive leaks in the production, storage and/or transport processes. Significant investments and efforts are spent to handle these feedstocks in a responsible, environmentally sensitive manner.

### **2.2 Montreal Protocol definitions**

The Montreal Protocol in Article 1, clause 5, defines Production as follows: “Production means the amount of controlled substances produced, minus the amount destroyed by technologies to be approved by the Parties and minus the amount entirely used as feedstock in the manufacture of other chemicals. The amount recycled and reused is not to be considered as Production.” The nature of feedstock was amplified in Decision VII/30 and although concern was later expressed about emissions of ODS from feedstock uses (Decision X/12) it has been argued that feedstocks are not controlled by the Montreal Protocol.

### **2.3 How the ODS feedstocks are used**

ODS can be feedstocks by being fed directly into the process as a raw material stream or as an intermediate in the synthesis of another product. Losses can occur during production, storage, transport, if necessary, and transfers. Intermediates are normally stored and used at the same site and so fugitive leaks are somewhat lower in this case. Extraordinary efforts are made to minimize such losses.

Table 2.3 shows common feedstock applications but is not necessarily exhaustive.

**Table 2.3 Common feedstock applications of ozone-depleting substances**

Feedstock ODS	Product	Further conversion	Comments
HCFC-21	HCFC-225		Product used as solvent.
CFC-113	Chlorotrifluoro-ethylene	Polymerized to poly-chlorotrifluoroethylene	Barrier film in moisture-resistant packaging.
CFC-114a	HFC-134a		The sequence for production of this refrigerant gas may begin with CFC-113, which is converted to CFC-113a and thence to CFC-114a.
CFC-113 and -113a	HFC-134a and HFC-125		Very high-volume use.
HCFC-22	Tetrafluoroethylene	Polymerized to homopolymer (PTFE) and also co-polymers	Very high-volume use. Work has been done for decades to find an alternative commercial route, but without success.
1,1,1-trichloroethane	HCFC-141b and -142b		Continues until 2030, with phaseout of HCFC-141b preceding HCFC-142b. Note alternative feedstock 1,1,-dichloroethylene (vinylidene chloride) that is not an ODS.
HCFC-142b	Vinylidene fluoride	Polymerized to poly-vinylidene fluoride or co-polymers.	Products are specialty elastomers, likely to have continuing uses and thus continuing feedstock use of 142b.
CTC	CFC-11 and CFC-12		Production and consumption of these CFCs, and thus this feedstock use, have fallen to very low levels.
CTC	Chlorocarbons	Feedstock for production of HFC-245fa and new HFOs.	HFOs have zero ODP and ultra-low GWP.
CTC with 2-chloropropene	Intermediates	Production of HFC-365mfc	
CTC with vinylidene fluoride	HFC-236fa		Production of close to 1 million pounds annually.
HCFC-123, HFC-123a, HFC-133a and Halon-1301	Production of pharmaceuticals, TFA and agrichemicals		
HCFC-123	HFC-125		
HFC-124	HFC-125		
CTC	Intermediates Production of vinyl chloride monomer (VCM)	Pyrethroid pesticides.	CCl <sub>3</sub> groups in molecules of intermediates become =CCl <sub>2</sub> groups in pyrethroids.

## 2.4 Estimated emissions of ODS

Data have been received from the Ozone Secretariat reporting production, import and export of ODS used as feedstocks for the year 2013. These also include volumes used as process agents as Parties are directed to report such consumption in a manner consistent to what is done for feedstocks. Detailed information provided by UNEP can be found in Table 2.4. Total production for feedstock uses was 1,140,794 tonnes and represents a total of 436,438 ODP tonnes. Compared with production for feedstock uses in 2012, this represents a 0.35% increase (ca. 3,977 tonnes). ODP tonnes decreased by 5.4% vs. 2012 levels.

Estimation of emissions is an inexact science. Sophistication of the operating entity can heavily influence emission amounts. Highly automated, tight and well instrumented facilities with proper procedures closely observed can have emission levels as low as 0.1% of the amount used as feedstock. On the other extreme would be batch processes of limited scale with less tight and less concern for operational excellence can have emission levels up to 5%. The largest volumes of feedstock use are at the lower end of the scale as large capacity plants have the most investment and are able to control emission levels well. In order to generate some guidance values, The IPCC guideline for HFC plants of 0.5% of feedstock was used to estimate feedstock emissions. Based on using this guidance figure, the total emissions associated with feedstock and process agent use in 2013 was approximately 5704 tonnes or 2182 ODP tonnes.

In a published paper, Newly Detected Ozone Depleting Substances in the Atmosphere, Laube et al, Nature Geosciences, the presence of CFC-113a, CFC-112, CFC-112a and HCFC-133a were reported. Sources of these compounds as pollutants were not defined. The use of CFC-113a and HCFC-133a has been included previously in reports of the CTOC as, as such, these are not new compounds. Their use is growing as they are feedstocks used in HFC production. Such HFC production, initially limited to developed countries is leveling in these regions. Their production in Article 5 countries is now growing rapidly. The atmospheric concentration of CFC-112 and CFC-112a is declining. If one were to hypothesize that all the atmospherically measured 113a and 133a were sourced from feedstock use (worst case scenario) and the accumulated production to date of associated HFCs- 134a, 125 and 143a were considered, the worst emission rate calculated would be on the order of 1.6%. This could be considered a realistic upper limit of feedstock and production emissions given these real life measurements.

The CTOC has also reviewed in detail the EU-sponsored study, the "Information Paper on Feedstock Uses of Ozone-Depleting Substances" conducted by Touchdown Consulting, December, 2012 provided by the European Union. As well as providing excellent background data including a full analysis of all previous CTOC and TEAP reports, it details best-case and worst-case (assuming all production is "small batch" with emissions of 5% of feedstock) emissions scenarios for the TEAP emissions factors when applied to feedstock production

For 2011, analysis of the European Pollutant Release and Transfer Register (E-PRTR: [www.prtr.ec.europa.ec](http://www.prtr.ec.europa.ec)) shows that the EU emissions of HCFCs was 245.9 metric tonnes of which 198.4 tonnes can be attributed to production and feedstock uses. EU Production of HCFCs in 2012 was reported (European Environment Agency) as 117,702.787 metric tonnes. In addition, the E-PRTR reports EU CTC emissions to be 167.7 tonnes (of which 110 tonnes is from a process agent use) from a production of 34020 tonnes. This means that emission levels of ca. 0.2% were achieved in this technologically advanced region where use of waste destruction capability is installed on vents. This level is much lower than the IPCC guidelines of 0.5% used in our estimate of emissions. This also serves to illustrate the effectiveness of local regulation and oversight and industrial diligence in managing and control of ODS emissions in feedstock use.

**Table 2.4 Amount of ODSs used as feedstocks in 2013**

<b>Substance</b>	<b>ODP</b>	<b>Tonnes</b>	<b>ODP Tonnes</b>
Carbon Tetrachloride	1.1	188253.8	207079.2
Methyl Bromide	0.6	4677.3	2806.4
CFC-11	1	0.0	0.0
Methyl Chloroform	0.1	107259.2	10725.9
CFC-12	1	0.0	0.0
Halon-1301	10	2085.6	20856.2
HCFC-22	0.055	483491.3	26592.0
CFC-113	0.8	113521.3	90817.0
HCFC-123	0.02	4037.1	80.7
HCFC-123a	0.06	222.4	13.3
HCFC-124	0.022	41461.3	912.1
HCFC-133a	0.06	1074.4	64.5
HCFC-141b	0.11	14740.7	1621.5
HCFC-142b	0.065	111922.9	7275.0
Halon-1211	3	0.0	0.0
HBFC-31B1	0.73	0.3	0.2
HCFC-31	0.02	0.0	0.0
HBFC-21B2	1	3.3	3.3
Bromochloromethane	0.12	496.0	59.5
HBFC-22B1	0.74	61.0	45.1
CFC-114	1	67486.2	67486.2
<b>Total</b>		1140794.3	436438.3

## 2.5 How to minimize ODS feedstock emissions

Both regulators and producers can act to assure that such emissions are kept at minimal levels. In the EU, US, China and several other countries, all new operations are required to be licensed for operation. These often defined specific maximum emission limits as well as the methodology to quantify these. Enforcement is by the Party and data for use are submitted to the Secretariat.

Producers can follow specifically defined responsible use practices defining equipment to control processes, closed loop loading and recovery, thermal destruction of vapor emissions, etc. These practices, strictly followed in continuous processes normally limit emissions to ca. 0.1%. Less responsible operation and batch processes can be as high as 5% of feed. Close cooperation between producers and regulators will continue to make these operations safe and environmentally benign.



## **3. Solvents**

### **3.1 Introduction**

In Article 5 parties, CFC uses were completely phased out in 2012, and the phase-down of HCFC use in solvent application began. In non-Article 5 Parties, the majority of ODS solvents have been replaced by not-in-kind technologies although some in-kind alternatives have been introduced advantageously in precision and electronics cleaning. Among the in-kind alternatives, HCFC-141b has been conveniently used in Article 5 countries and its use in small and medium-size customers will be expected to be replaced by not-in-kind alternatives such as chlorocarbons and hydrocarbons. Sizable amounts of HCFC-225 solvent have been used in niche applications including military and aerospace industries where no other alternatives are available in non-Article 5 Parties. The other in-kind alternatives in solvent applications include some HFC and HFE (hydrofluoroethers), which are expensive and their uses are mostly limited in non-Article 5 Parties.

The elimination of these HCFC and high GWP-HFC solvents still leaves many options available and they have found various levels of acceptance. However, no single option seems well suited to replace HCFCs and HFCs completely. HFCs and HFEs have been used to replace the remaining HCFCs in certain application where the high cleaning performance is required. Recently HFOs are emerging in the market to replace HFCs and HFEs with middle to high GWP. Their growth may be high when it is expressed by percentage, but quantities per chemical and in total are expected to remain relatively small.

The major challenge is the complete phase out of ODS solvents in Article 5 countries. Preferable alternatives have been identified and are generally available as shown in the solvent sector of Taskforce XXIV/7 and XXV/5. Another hurdle to overcome is the economic impact on the small and medium size users who make up a major portion of the remaining ODS solvent market. Some users may require economic assistance to transition away from ODS.

Regulatory changes will continue to impact on the use of solvents. In some cases, this may require solvent and/or equipment change or a new cleaning process.

### **3.2 New Solvents**

Some new HFE solvents have been introduced in the non-Article 5 market and are summarised in Table 3-2.

**Table 3-2 HFE solvents**

Code Number	HFE-64-13S1	HFE-77-12	HFE-347pc-f2
Chemical Structure	C6F13OCH3	C3HF6CH(CH3)OC3HF6	CF3CH2OCF2CHF2
Boiling Point (°C)	98	131	56
KB value	5	9.5	13
Flammability	Non-flammable	Non flammable	Non flammable
GWP (100yrs)	210	700	580
Atmospheric Lifetime (yrs)	3.8	9	7.1

Unsaturated fluorochemicals with zero ODP and ultra lower GWP are also being commercialized for the replacement of high GWP-HFC and low or moderate GWP HFE solvents.

The development of new solvents was discussed in the report of the Task Force responding to Decision XXV/5, but the major trend is the introduction of substances with unsaturated molecules and thus short atmospheric lifetimes, near zero ODP and low GWP. Such substances are expected to replace HCFCs in a number of uses and also to compete with hydrofluoro-ethers (HFEs) in the solvent sector. The main groups of new substances are unsaturated HFCs (HFOs) and unsaturated HCFCs (HCFOs). In the former category are HFO-1234yf and HFO-1234ze. A recent development is the production of HCFC-1233zd (CF<sub>3</sub>-CH=CH-Cl, *trans* isomer). This substance has boiling point 19°C and useful solvency property.

### 3.3 n-Propyl bromide

n-Propyl bromide (1-bromopropane, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br, n-PB, CAS No. 106 94 5) has been used as a solvent in a range of applications. Its boiling point, 71°C, is comparable to that of CFC-113 (48°C), hexane (69°), methyl chloroform (TCA, 74°C) and trichloroethylene (87°C). Its solvent properties are typical of those of lower molecular weight hydrocarbons and organohalogen compounds.

Due to the presence of bromine in the molecule, however, concerns have been expressed based on both the ozone-depletion and its toxicity.

SAP reported a calculation of the lifetime of n-PB as 41 days instead of formerly reported 34 days (2010 SAP Assessment Report, Table 1-4, pp38) which indicates the ODP is still very small.

On the other hand, several regulatory and health updates have occurred since the 2010 CTOC assessment report. These include the publication of the National Toxicology Program report (NTP TR 564, August 2011) and the American Conference of Governmental Industrial Hygienists (ACGIH<sup>®</sup>) reduction of the TLV<sup>®</sup> for n-propyl bromide from 10 ppm to 0.1 ppm (February 2012). ACGIH finally released 2014 editions of TLVs<sup>®</sup> and BELs book that shows 0.1ppm of TWA for nPB. Also, Japan Society for Occupational Health has set the TLV of nPB to 0.5ppm in 2013. It indicates that its use in solvent applications seems problematic.

## **4. Laboratory and Analytical Uses**

### **4.1 Introduction**

In 2007, Decision XIX/8 extended the global exemption to 31 December 2011, and then in 2009 the global exemption for all Parties was extended to 31 December 2014, with the exception of a few procedures for which it was agreed that suitable alternatives were available. This global exemption has been further extended for another 7 years to 31 December 2021 by Decision XXVI/5.1 taken in 2014. However, through Decision XXVI/5.2, the Technology and Economic Assessment Panel will be requested to report no later than 2018 on the development and availability of laboratory and analytical procedures that can be performed without using controlled substances under the Montreal Protocol.

### **4.2 The way forward to phase out the ODS use for laboratory and analytical use**

There are very few identified uses of ODS in laboratory and analytical procedures in non-Article 5 countries. Some use continues in several Article 5 countries.

In 2010 the European Commission had provided a consultancy report in which a number of alternative methods not using ODS were described. The report is too long for inclusion here but can be made available to interested Parties. The Commission also drew attention to its 'Licensing manual for ozone depleting substances' in laboratory and analytical uses (August 2011) which, although the measures it describes are specific only for the EU, contains much information that would be of interest to other Parties. The manual may be accessed at [http://circa.europa.eu/Public/irc/review\\_2037/library?l=licensing\\_manuals/manual\\_laboratories](http://circa.europa.eu/Public/irc/review_2037/library?l=licensing_manuals/manual_laboratories).

Also, ASTM International has been developing standard methods that do not use ODS. CTOC has introduced many ASTM standard that do not use ODS.

It seems to be evident that the reasons that non-ODS methods are not adopted in Article 5 countries are: (a) adherence to standard methods for which there are no non-ODS alternatives, and (b) the cost of implementing new methods, including training. As to the first of these, where purely national standards are involved, then it is within the power and capability (since skilled staff exist and methods are available in the scientific literature) of countries to adopt the necessary procedures. Only in the few cases where an international standard exists and there is no non-ODS alternative should it be necessary to persist with the use of ODS. In the second instance, The CTOC advises that costs of transition should be sustainable, although the cost of alternative substances may be higher than those of the ODS they replace.

It is possible that many Article 5 countries have incomplete knowledge of the use of CTC and TCA in their laboratories and that as a consequence reporting of solvent uses of small quantities of these ozone-depleting substances is incomplete. At the level of laboratory practice, information is needed about the use of available alternatives, and new norms

need to be adopted in many countries so that ODS are no longer employed in this way. Awareness-raising workshops and demonstration projects might assist in achieving transition away from ODS in analytical applications.

## 5. Destruction Technologies

### 5.1 Introduction

The CTOC has reviewed proposals for new technologies using information provided by the proponents. In some cases the information was subject to commercial confidentiality and so cannot be presented in detail here. The CTOC does not recommend any new technologies but a brief summary of each technology is presented.

### 5.2 Reviews on new destruction technologies

**SGL CARBON GmbH:** provided information on their porous reactor in which a mixture of air, fuel and ODS refrigerant gases is treated at high temperature for a very short time. A commercial plant is already operating in Germany. The CTOC observed that the criteria formerly established were met by this technology.

**LESNI A/S:** provided information on catalytic destruction of fluorocarbons and hydrocarbons at modest temperatures. Several commercial plants are operating in Sweden, Denmark, and the UK. The Montreal Protocol criteria are not met by this process, but commercial operation in several jurisdictions attests to the acceptability of this destruction technology.

**ASADA Corporation:** provided information on small scale plasma destruction of a range of fluorocarbons. This process is small, easily re-locatable, and meets the Montreal Protocol criteria. This may be useful for Article 5 Parties where quantities of ODS to be destroyed are small, and one-site recovery from air-conditioners and refrigerants is undertaken.

**Midwest Refrigerants LLC:** provided information on a process for reaction of ODS refrigerants with other substances at high temperatures so as to produce hydrogen chloride and hydrogen fluoride. There is a pilot plant in Florida, USA. High DRE (destruction and recovery efficiency) values and low dioxin/furan production result.

**University of Newcastle (Australia):** provided information on the thermal process for conversion of fluorocarbons to vinylidene fluoride in the presence of catalysts at high temperatures. Its commercial potential is unclear and no information was obtained about DRE or dioxin/furan production.

**SRL Plasma:** provided information on the plasma arc destruction of methyl bromide. Its DRE is over 99.6% with 2-3% of methyl bromide recovered. Brominated dioxin and furans were detected in the emissions. If the toxicology equivalent factors of those compounds are similar to those of the chlorinated congeners, this process likely meets the criterion.

**Nordiko Quarantine Systems Pty Ltd.:** provided information on the potential for the destruction of methyl bromide that has been absorbed onto activated carbon. It is difficult to evaluate this process because no information was provided about the likely efficiency of the process.

**PyroGenesis:** provided information on the steam plasma destruction of CFCs, HCFCs, halons and PFCs. The DRE is over 99.9999% when CFC12 is applied. With a reactor temperature of over 1300°C, the steam plasma hydrolysis reaction quickly and efficiently

breaks down the waste into carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O). The gas stream is then rapidly quenched to prevent any reformation of dioxins and furans. This technology is another kind of plasma arc destruction and meets the Montreal Protocol criteria.

### **5.3 Destruction Projects in Article 5 Parties**

Reverse manufacturing of ODS-containing equipment and material at a number of scales is within the capability of many countries. Difficulties that attend transboundary movements of waste mean that there is no plan (that CTOC is aware of) for a regional destruction facility but there are a number of in-country projects to link recovery of ODS with destruction. Decisions between export and in-country destruction are likely to be influenced by the cost and availability of smaller-scale destruction equipment such as some of the above examples. A number of destruction projects in Article 5 Parties were funded by MLF and implemented by UNDP.

## **6. Carbon Tetrachloride (CTC) and Dichloromethane Emissions**

### **6.1 CTC emissions**

#### **6.1.1 Introduction**

TOC has reported for a number of years on the discrepancy between emissions of CTC to the atmosphere based on ‘bottom up’ estimates based on production and consumption and typical emission rates, and ‘top down’ estimates based on stratospheric concentrations of CTC and estimates of its atmospheric lifetime.

The Scientific Assessment Panel had revised the atmospheric lifetime for CTC in their OEWG report in 2012, increasing the value substantially. ‘Top down’ estimates thus give lower emission rates, by 10-20 Ggramme/year, to maintain the observed stratospheric concentration of CTC. Diffuse emissions could contribute 8-12 Ggramme/year, and together these figures significantly reduce the discrepancy between the two types of estimate by as much as 18-32 Ggramme/year. The gap between the two estimates of emissions has thus been reduced but not entirely closed.

#### **6.1.2 Bottom up estimation**

After consideration of bulk uses of CTC, no evidence of substantial sources for release of CTC from natural sources such as oceans and volcanoes, and from pollutant releases from landfills, drinking water disinfection and contaminated groundwater was found. It was concluded that, if releases were indeed much greater than the ‘bottom up’ estimates by CTOC, then there must be other – and quite substantial – sources of CTC emissions. These could be production and consumption that had not been reported to the Ozone Secretariat, but discussions with Parties suggested that there were no such sources, at least on the scale required to ‘balance the books’.

The legacy sources such as dry cleaning and industrial solvent facilities were also studied. A new way of assessing CTC emissions from legacy sources such as chemical dumps, contaminated sites, landfills and materials being transported between venues was brought to the group’s attention by a member of the SAP, who reported persistent low concentrations of CTC in the air of Melbourne, a city of approximately 3 million people where CTC had been widely used in previous years. The idea that low concentrations of CTC in large air volumes associated with cities was taken up by other members of the group, who reported similar figures. The results are summarised in Table 6.1.2.

**Table 6.1.2.: Recent data provided by Parties to CTOC concerning concentrations of CTC in ambient air.**

Location	Concentration	Comment
Australia	0.55-0.62 µg/m <sup>3</sup> (2007-11)	Melbourne 2007-2011; leads to calculated emissions 140±35 tonnes/y
Sweden	0.00052 µg/m <sup>3</sup> (workplace) <0.0040 µg/m <sup>3</sup> (farmland)	Low concentrations in soil and water.
Canada	0.53–0.71 µg/m <sup>3</sup>	Mean values for 5-10 years of observations in a number of cities.
Thailand	0.3-0.7 µg/m <sup>3</sup>	Bangkok
United States of America	0.23 µg/m <sup>3</sup> 0.24 µg/m <sup>3</sup>	East Chicago, Fort Wayne Fort Gary
China	0.73 µg/m <sup>3</sup>	Average over 46 cities; leads to calculated emissions in 2009 of 2.2-4.1 ktonne.

While most of these results are from cities, the data from Sweden are from a rural district and they show the difference between non-industrial air and air in CTC is present, probably arising from previous uses in industry and from legacy sites. The contribution doesn't seem, however, to be enough to close the gap.

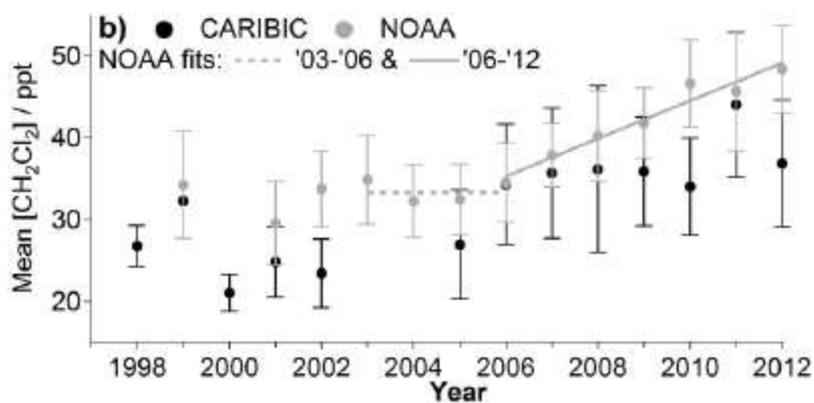
CTOC has become aware that historically there may have been previously unreported or under-estimated emissions of CTC connected with the use of phosgene, for example in the production of methylene diphenyl di-isocyanate (MDI), a reactive substance that is used to make polyurethanes. It is also indicated that phosgene produced from chlorine and carbon monoxide is usually contaminated with CTC, the presence of which may not be taken into account when emissions are taken into account.

CTOC has also studied other possible emission sources. However, additional emission sources that could narrow the gap significantly yet could not be found.

A conference is to be held in October 2015 to investigate further the discrepancy between top-down and bottom-up estimates of CTC.

## 6.2 Dichloromethane emissions

Dichloromethane (methylene chloride) emissions to the atmosphere have been increasing since 2006, having previously been almost constant. This has been demonstrated by research groups working independently and is shown in the figure below reproduced from Leedham Elvidge *et al.* 2015. The NOAA group sampled at ground level at remote locations in the Northern Hemisphere. The Caribic experiment is a sampling system carried on commercial airliners flying from Frankfurt to N and S America, S Africa and SE Asia (so that samples are retrieved from altitudes of about 10 kilometres).



The most recent estimate of global emissions of dichloromethane is  $515 \pm 22 \text{ Gg yr}^{-1}$  given in Montzka et al. (2011 WMO Assessment of Ozone) which is based on top-down estimates from Simmonds et al. (2006) from data collected between 1999 and 2003. This corresponds to the flat portion of the graphs when the ground level concentration was about 35 ppt. Atmospheric lifetimes of VSLs compounds have not changed significantly since this time and so the emissions should scale approximately to the measured concentration, indicating that the 2012 emissions were about  $800 \text{ Gg yr}^{-1}$  (800,000 tonnes/yr).

The source of the additional 300,000 tonnes emitted annually is conjectural but most of it must come from use of dichloromethane itself; it is beyond reason that the source is fugitive emissions from feedstock. If that were the case, more dichloromethane would have been lost to the atmosphere than the amount used to make HFC-32 - economically disastrous as well as impossible in a developed economy under environmental legislation. This has not stopped speculation from Hossaini *et al.* (2015) that HFC-32 production is a significant source that will increase in the future, although the scenarios used are unlikely to be realized. CTOC roughly estimates the global demand of dichloromethane in 2012 was about 1,000,000 tonnes and about 10% was used for the feedstock of HFC-32. When IPCC guideline is applied to estimate the emitted dichloromethane during the manufacturing process of HFC-32, it is calculated as 500 tonnes.

The Leedham Elvidge (2015) results "show that  $\text{CH}_2\text{Cl}_2$  emissions from the Indian subcontinent have increased two- to fourfold in a decade (1998–2008). The annual emissions from the Indian region in 2008, at  $\sim 20 \text{ Gg}$ , are similar to those estimated for the USA in 2005. Other Asian regions may also prove to be emitting large quantities of  $\text{CH}_2\text{Cl}_2$ : from a limited data set we suggest that Southeast Asia may be an important source region. However, there are few in situ data available".

Compared to the calculated global increase in dichloromethane emissions, those from the Indian subcontinent are small and, in the absence of growth in developed economies, massive growth in emissions from Southeast Asia are indicated. One could speculate about the nature of the sources but the only sure conclusion is that HFC-32 production is a very minor contributor.

Using atmospheric models, Hossaini *et al.* (2015) have shown that very short lived substances VSLs (such as dichloromethane, which has an atmospheric lifetime of 0.46

years) can reduce ozone concentrations in the lower stratosphere. Ozone is a greenhouse gas and so the result is to *reduce* radiative forcing and global warming. The authors calculate that the overall effect of all VSLS has been to *reduce* radiative forcing by  $0.02 \text{ Wm}^{-2}$ , with a contribution from chlorinated anthropogenic VSLS (among them dichloromethane) of  $-0.005 \text{ Wm}^{-2}$ . This is actually quite small and significantly less than the total from VSLS, which is dominated by the contribution from natural bromocarbons.

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