

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



**UNEP**

**Report of the  
Technology and Economic Assessment Panel  
April 2001**



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REPORT OF THE  
TECHNOLOGY AND ECONOMIC  
ASSESSMENT PANEL  
APRIL 2001**

**Montreal Protocol On Substances that Deplete the Ozone Layer**  
UNEP Technology and Economic Assessment Panel  
April 2001 Report

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**UNEP Report of the  
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# 1 Introduction

Subsequent Meetings of the Parties to the Montreal Protocol have taken a number of decisions, which request actions by the UNEP Technology and Economic Assessment Panel (TEAP). Responses of the TEAP to several of the 1999 and 2000 requests, as well as responses to requests made in earlier Meetings of the Parties, are presented in this April 2001 report.

The April 2001 TEAP report provides the responses from TEAP on the following decisions:

*Decision VII/34 “Essential Use nominations for Parties not operating under Article 5 for controlled substances”*

In accordance with Decision VII/34(5) the essential use nominations are dealt with in Chapter 2 of this report. It concerns the essential use applications for ODSs for the year 2002 and beyond. This part of the report is of a similar set-up as the Essential Use chapters in the April 1999 and April 2000 TEAP reports.

*Decision XII/2 “Measures to facilitate the transition to chlorofluorocarbon-free metered dose inhalers”*

Decision XII/2 elaborates on many issues related to measures to facilitate the transition in MDIs. It mentions that all Parties should develop a national or regional strategy based on economically and technically feasible alternatives or substitutes (and submit the text of any such strategy to the Secretariat), and to report annually on progress made on their transition. The Decision then requests the Technology and Economic Assessment Panel (a) to summarise and review by 15 May each year the information submitted to the Secretariat, (b) to modify as necessary the handbook for Essential Use Nominations, to take account of the requirements in this Decision, and (c) to consider and report to the next Meeting of the Parties on issues related to the campaign production of chlorofluorocarbons for CFC-based metered-dose inhalers. The Handbook has been updated and is issued as a separate report (see also Chapter 3). Issues related to the campaign production are dealt with in Chapter 4.

*Decision X/19 “Exemption for Laboratory and Analytical Uses”*

This decision requests the TEAP to report annually on the development and availability of laboratory and analytical procedures that can be performed without using the controlled substances in Annexes A and B of the Protocol. Chapter 5 contains the third response of TEAP to this decision. It should

be noted that, in Decision XI/15, a number of uses were removed from the global exemption.

*Decision X/7*      *“Halon-management strategies”*

This decision requests the Parties not operating under Article 5 to submit their strategies to the Ozone Secretariat by the end of July 2000. The TEAP was requested to update its assessment of the future need for halon for critical uses, in light of these strategies, and was furthermore requested to report on these matters to the Twelfth Meeting of the Parties. However, the deadline of 31 July 2000 made reporting to the Twelfth Meeting impossible. A report on Halon-management strategies can therefore be found in chapter 6 in this April 2001 report.

*Decision XI/19*      *“Assessment of new substances”*

Decision XI/19 mentions that it should be noted that “many new chemicals are brought into the market by the chemical industry so that criteria for assessing the potential ODP of these chemicals will be useful”. Parties requested the SAP and the TEAP (a) to develop criteria to assess the ODP of new chemicals, and (b) to develop a guidance paper on mechanisms to facilitate public private sector co-operation in the evaluation of the potential ODP of new chemicals in a manner that satisfies the criteria to be set by the Panels, and to report to the Thirteenth meeting. An update paper which elaborates on the TEAP part of the work is given in Chapter 7 of this April 2001 progress report.

*Decision IX/6*      *“Critical-use exemptions for methyl bromide”*

In Decision IX/6 the Parties elaborated on criteria and procedures in assessing a critical methyl bromide use and gave three criteria that must be satisfied if production and consumption, if any, of methyl bromide for critical uses should be permitted. In the decision, the TEAP is requested to review nominations and make recommendations based on criteria established in the decision. In chapter 8 a first elaboration of the TEAP on this issue can be found.

*Decision X/8*      *“New Substances with Ozone-Depleting Potential”*

In Decision VII/34 (c) the TEAP was requested to report on progress and developments in the control of substances each year. Decision IX/24 requests the TEAP to report to each ordinary Meeting of the Parties on any new substances with a certain Ozone Depletion Potential. A short Solvents TOC report on nPB was given in the April 2000 report. Decision X/8 requests the Technology and Economic Assessment Panel and the Science Assessment Panel, taking into account, as

appropriate, assessments carried out under Decision IX/24, to collaborate in undertaking further assessments: “To determine whether substances such as “n-propyl-bromide (nPB)”, with a very short atmospheric life time of less than a month, pose a threat to the ozone layer”. This April 2001 report contains information on the upper bound limits to the geographical dependent emission of nPB in the near future, which can be used by the Science Assessment Panel for further evaluation (published as a separate report in this April 2001 progress report).

*Decision X/14 “Process agents”*

In Decision X/14 the report of the TEAP and the Process Agent Task Force in response to Decision VII/10 was noted with appreciation. Decision X/14 also mentions that all Parties should report to the Ozone Secretariat by 30 September 2000 and each year thereafter on their use of controlled substances as process agents, the levels of emissions etc. and, in reporting annual data, provide information on the quantities of controlled substances produced or imported by them for process agent applications. Paragraph 8 of this decision requests the TEAP and the Executive Committee to report to the Meeting of the Parties in 2001 on the progress made in reducing emissions of controlled substances from process agent uses and on the implementation and development of emission reduction techniques and alternative processes not using ozone depleting substances and to review tables A and B of the present Decision (X/14). TEAP established a new Process Agent Task Force, the report of which can be found as a separate report in this April 2001 progress report.

*Decision VII/34 “Progress and Development in the Control of Substances”*

In Decision VII/34 (c) the TEAP was requested to report on progress and developments in the control of substances each year. This request was renewed in Decision X/17 “...to keep the Parties to the Montreal Protocol informed of any important new developments on a year-to-year basis. Progress reports of different TOCs (Aerosols, Foams, Methyl Bromide, Refrigeration and Solvents) can be found in Chapter 9 of this report.

*Decision VII/34 “Background and Contact Information for TEAP Members and TOCs”*

TEAP reported on progress towards improved geographical balance and other structural adjustments in past progress reports. Chapter 10 of this 2001 report presents further information on the operation of the TEAP and its TOCs, including some restructuring decisions taken. It also includes contact details of the TEAP members and membership lists of the different TOCs. It also gives background information of the TEAP members (Decision VII/34, paragraph (e)(iv)).

This report has also been transferred to the TEAP Internet Site (<http://www.teap.org>).

## **2 Essential Use Nominations**

### **2.1 Review of Essential Use Nominations for MDIs**

Decision IV/25 of the 4<sup>th</sup> Meeting and subsequent Decisions V/18, VII/28, VIII/9, VIII/10 and now XII/2 have set the criteria and the process for the assessment of essential use nominations for metered dose inhalers (MDIs).

#### ***2.1.1 Review of Nominations***

The review by the Aerosols, Sterilants, Miscellaneous Uses and CTC Technical Options Committee (ATOC) was conducted as follows:

- Three members of the ATOC independently reviewed each nomination.
- Members prepared preliminary reports, which were forwarded to the Co-chair. The committee considered the results of these assessments and drafted this report.
- For nominations where some divergence of view was expressed, additional expertise or information was sought.

Concurrent with the evaluation undertaken by the ATOC, copies of all nominations were provided to the Technology and Economic Assessment Panel (TEAP). The TEAP were able to consult with other appropriate individuals or organisations in order to assist in the review and to prepare the TEAP recommendations to the Parties.

#### ***2.1.2 Committee Evaluation and Recommendations***

Nominations were assessed against the guidelines for essential use contained within the *Handbook on Essential Use Nominations* (TEAP, 1997). Further information was requested where nominations were found to be incomplete.

The TEAP and its ATOC recommended in its April 2000 Report that additional information would facilitate the assessment of nominations under Decision IV/25. With the assistance of the Ozone Secretariat, in November 2000 the TEAP and its ATOC contacted nominating Parties and respectfully requested supplemental information for essential use nominations being submitted in 2001.

The ATOC reviewed all of the submitted nominations for a production exemption. Production in this context includes import of ozone depleting substances for the purposes of manufacture.

In 2001 the following Parties nominated essential use production exemptions for MDIs (asthma and COPD). Canada did not nominate for an essential use exemption but did submit a Reporting Accounting Framework for the year 2000).

Country	2001	2002	2003	2004
Australia	(1)	(1)		
European Community			✓	
Hungary		✓	✓	
Japan		✓		
Russian Federation		✓	✓	✓
USA		(2)	✓	

(1) Requested reduction in quantity for a nomination previously approved by Parties in 2000.

(2) Requested supplemental quantity for 2002 for a nomination previously approved by the Parties in 2000.

### 2.1.3 Observations

TEAP and its ATOC contacted nominating Parties and respectfully requested the following supplemental information for essential use nominations submitted in 2001:

- Progress with implementation of national or regional transition strategies;
- Availability of alternatives including trends in availability;
- Information regarding any MDI products approved in 1999 and 2000;
- Information about the proportion of the nominated quantity intended for use in MDIs for export, and information about the essential status of MDI products in those markets.

The EC and the USA specifically addressed this request for information in their nominations, which facilitated ATOC's assessment of these aspects of the nominations. These efforts to respond at short notice to this additional request are appreciated.

The EC and the USA also reported that no new CFC containing MDIs were approved in 2000.

### 2.1.4 Future Considerations

In response to Decision XII/2, "*Measures to facilitate the transition to chlorofluorocarbon-free metered-dose inhalers*", TEAP and its ATOC have made changes to the Handbook for Essential Use Nominations. These take account of the new requirements in this decision and aim to provide guidance to Parties and to assist in the preparation of nominations.

As transition progresses, certain scenarios may impact on the essential use process, for example:



- Some Parties may have very small and static annual CFC requirements for CFC MDI production, and few changes from year to year in their nomination;
- Campaign production may be needed to satisfy future requirements for CFCs and consequently, different approaches are likely to be taken to stockpile management;
- The need for transfers of authorisations.

Parties may wish to note the above scenarios and the need for the essential use process to flexibly accommodate and take account of these and other situations.

### **2.1.5 Recommendations for Parties' Essential Use Nominations**

Quantities are expressed in metric tonnes.

#### **Australia**

ODS/Year	2001	2002
<b>Quantity</b>	11 tonnes	11 tonnes

Requested reduction in quantity for nomination previously approved by Parties in 2000.

**Specific Usage:** MDIs for asthma and COPD

**Recommendation:** Note reduction from previously approved quantities

**Comments:** Australia is to be commended on its success in reducing CFC use. The country reduced its initial nomination for 2001 and 2002 from 74.95 tonnes to 11 tonnes for each year. This reduction resulted from reduced exports and its internal transition strategy. The committee notes the submission of the accounting framework data for 2000 and notes the size of the stockpile, which is reasonable for the level of actual use at about 15 months supply.

## European Community

<b>ODS/Year</b>	<b>2003</b>
<b>Quantity</b>	2579 tonnes

**Specific Usage:** MDIs for asthma and COPD

**Recommendation:** Recommend Exemption

**Comments:** The committee notes that actual use in 2000 more closely matches the amounts nominated. The EC is to be commended for continuing reductions in amounts nominated and in actual use. Previous nominations from the EC had projected no need for CFCs for domestic use by 2003, however the 2003 nomination includes over 1200 tonnes for domestic use. This relates to the disparate pace of transition within Member States. The ATOC notes the submission of the accounting framework data for 2000. While the stockpile has increased by about 200 tonnes since last year, it still represents less than one-year's supply.

## Hungary

<b>ODS/Year</b>	<b>2002</b>	<b>2003</b>
<b>Quantity</b>	1.75 tonnes	1.75 tonnes

**Specific Usage:** MDIs for asthma and COPD

**Recommendation:** Recommend Exemption

**Comments:** There has already been a substantial fall in the amount of CFC approved in 2000 and 2001 (1.75 tonnes each) compared to 1999 (9.23 tonnes) and this nomination for 2002 and 2003 remains small. The ATOC notes the submission of the accounting framework data, and that the stockpile at the end of 2000 is small.

## Japan

<b>ODS/Year</b>	<b>2002</b>
<b>Quantity</b>	45 tonnes

**Specific Usage:** MDIs for asthma and COPD

**Recommendation:** Recommend Exemption

**Comments:** Nominated volumes and amounts used have decreased over previous years and the nominated volume for 2002 (45 tonnes) amounts to 53% of that volume estimated to have been used for year 2000. The accounting framework shows that for 2000 Japan was authorised 98.2 tonnes but only used 9.7 tonnes. In 2000 almost 90% (75 tonnes) was taken from stockpiles which were reduced from 259.9 tonnes to 184.9 tonnes. This being equal to more than two years consumption. Much of Japan's future requirements could be met from this stockpile, but the request for 45 tonnes is reasonable and may not actually be used. The continued reduction in CFC volumes used over an extended number of years in Japan is to be commended.

## Russian Federation

<b>ODS/Year</b>	<b>2002</b>	<b>2003</b>	<b>2004</b>
<b>Quantity</b>	495 tonnes	465 tonnes	455 tonnes

**Specific Usage:** MDIs for asthma and COPD

**Recommendation:** Recommend Exemption only for MDIs for asthma and COPD for 2002 and 2003. Quantities to be approved are subject to clarification of the volumes intended for MDI production.

**Comments:** The ATOC welcomes the nomination of the Russian Federation. The Russian Federation is to be congratulated for its decision to cease domestic CFC production in December 2000. While the committee considers the request for MDI use to be essential, the specific volumes required for the MDI use versus non-essential medical uses are not clear. As the Russian Federation has not provided nominations in recent years, there is no data from a Reporting Accounting Framework.

## United States

ODS/Year	2002	2003
Quantity	550 tonnes (1)	3270 tonnes

(1) Supplemental volume requested

**Specific Usage:** MDIs for asthma and COPD

**Recommendation:** Recommend Exemption

**Comments:** In 2001, the USA nominated 3270 tonnes for the year 2003, and a supplemental volume of 550 tonnes for the year 2002 (in addition to the previously approved volume of 2900 tonnes). The decline in CFC tonnages requested between 2002 and 2003 is small and the pace of transition in the USA is slower than in most nominating Parties. The nomination attributes this to an increasing prevalence of asthma and COPD and to increased usage of MDIs. Poor penetration of some newer non-CFC containing inhalers into the market is noted. Since the nomination was received a second HFC albuterol MDI has been approved; official action should be able to accelerate transition. The ATOC notes the submission of the accounting framework data, and that the stockpile is reducing and represents approximately 9 months use.

### **2.1.6 Review of Previously Authorised Quantities of Ozone-depleting Substances for Essential Uses (Decision VII/28 (2a))**

Under Decision VII/28 (2a), Parties decided that:

*“(a) The Technology and Economic Assessment Panel will review, annually, the quantity of controlled substances authorised and submit a report to the Meeting of the Parties in that year;”*

The ATOC reviewed the essential use nominations for MDIs for asthma and COPD for 2002 and 2003 and concluded that CFC MDIs remain essential for patient health until an adequate range of technically and economically feasible alternatives are available.

New CFC-free product launches are likely to increase further over the next two years. As most nominations are received 2 years in advance, Parties may wish to continue to monitor and manage their own CFC acquisition and usage under authorised essential use quantities, and adjust their nominated quantities annually on an “as needed” basis. This year Australia requested a reduction in the nominated quantities for 2001 and 2002 to 11 tonnes compared with 74.95 tonnes previously approved by the Parties in 2000. The ATOC will continue to monitor the changing market situation.

## 2.2 **Nomination by Poland for Solvents Used in the Maintenance of Oxygen Systems of Torpedoes**

In 1997, Poland exercised its option under the Emergency Exemption (Decision VIII/9, paragraph 10). Import of 1,700 kilograms of CFC-113 for this use was authorised by the Secretariat after consultation with TEAP and its STOC.

In 1998, Poland applied for 1,700 kg of CFC-113 for use in each of the years 1999-2003.

In February 1998, the STOC requested additional information such as: which substrate alloys for components and assemblies, which types of coatings applied, the types of non-metallic components used and the type of grease to be removed as well as its liquefying temperature, and the approximate thickness of grease layer. It also mentioned details of the grease-removing process and working conditions such as ventilation arising from the use of recycled CFC-113, which alternative processes or substances had been evaluated and which were the technical reasons for their rejection, the types of tests carried out and the criteria used for qualification.

TEAP considered this nomination. It documented in its April 1998 report that the STOC did not receive the information requested in February 1998 and, therefore, it was unable to recommend this nomination for continued use. After considering the special circumstances, Parties approved the essential use.

In December 1998, TEAP Co-chairs asked the Head of the Ozone Protection Unit in Warsaw and the Head of the Polish Delegation, of the Ministry of Environmental Protection, to organise a joint meeting with representatives of the Polish Navy, the manufacturers of the torpedoes and a team of STOC members. Kazakhstan was suggested as the venue.

The STOC team and the Head of the Ozone Protection Unit in Warsaw agreed that apart from the meeting in Kazakhstan (20-24 March 2000), it was necessary to schedule a follow-up meeting without the participation of key players on this issue from Kazakhstan. This meeting was held at the Polish Navy Headquarters in Gdansk on 27 March 2000.

The objectives of this meeting were:

- To discuss any outstanding issues which needed clarification following the Almaty meetings.
- To provide further information to the Navy to assist in their efforts to phase out CFC-113 in torpedo maintenance.

The main outcome of the meeting was the manufacturer's commitment to evaluate further technical options and the Navy's commitment to perform and evaluate the unique flammability and compatibility tests on alternative non-ozone depleting options suggested by the STOC.

The Navy also agreed to provide 6 months status updates on the evaluation of alternatives by the manufacturer, on their in-house evaluation and submit these to the STOC through the Polish Ozone Layer Protection Unit. Furthermore, the Polish Navy would look into the possibility of utilising recycled CFC-113.

The STOC agreed to provide relevant information to the Navy on the practice of other naval and aircraft facilities on the qualification of alternatives for oxygen system maintenance.

### ***2.2.1 Essential Use Nomination forwarded by Poland, February 2001***

Taking into consideration the commitment of the torpedo manufacturer on evaluation of alternatives and the Navy's in-house evaluation and its submission to the STOC through the Polish Ozone Layer Protection Unit, TEAP recommended the nomination for 0.85 MT for 2001 only.

In February 2001, Poland has exercised its options under the Emergency Exemption (Decision VIII/g, paragraph (10)) for the import of 0.85 MT of CFC-113 for the year 2002.

This issue has been discussed intensively within the STOC and the most significant points raised by the STOC were:

- a) why can recycled CFC-113 not be used;
- b) why can the emission of CFC-113 not be contained in a close-loop processing of torpedo system parts during maintenance.

The response from the Ozone Protection Unit in Poland to the first question indicated that the manufacturer insists that only not-recycled, newly produced CFC-113 guarantees this for use on critical parts of the system.

To the second question, the Ozone Protection Unit emphasised that the Polish Navy does not have the installation for recovery of CFC-113. Establishment of such installation is not considered as technically and economically feasible.

Even if recycled or reclaimed CFC-113 would be imported the manufacturer does not accept its use for the critical parts of the torpedoes. In addition, recycled or reclaimed CFC-113 needs a certification from the torpedo manufacturer otherwise the Polish Navy loses warranty.

The Head of the Polish Ozone Protection Unit and the STOC team presented a joint paper at the Military Workshop jointly organised by UNEP, the US EPA and the US DoD (6-9 February 2001, Brussels).

#### *Situation Analysis:*

- The Polish Ozone Protection Cell has provided a 6 month status report on the evaluation of alternatives suggested by the STOC. These alternatives have

failed to meet the requirements of the unique oxygen impact test (at a pressure of 200 bar oxygen) for the type of greases (chloro-fluorinated types) used.

- In all non-Article 5(1) countries only fluorinated types of greases are used and evaluated at 150 bar oxygen pressure.
- The CFC-113 is not only used for removing of greases used during maintenance but also as carrier for re-application of the grease for protection of the parts during storage. Protective coating such as phosphating coupled with paints is the current practice in non-Article 5(1) countries. The Head of the Polish Ozone Protection Unit and the Polish Navy have shown a strong interest in this proposal. Such a step, if adopted, will completely eliminate CFC-113 use for torpedo maintenance.

TEAP recommends this nomination for the year 2002.

### **2.3 Essential Use Nomination for Halons by the Russian Federation**

An essential use exemption nomination for the production of halon 1211, 1301 and 2402 was received from the Russian Federation. However, the Halons Technical Options Committee was informed at its annual meeting in Washington, DC, that the Russian Federation was withdrawing the nomination. The committee was further informed that the Russian Federation intended to satisfy its critical uses for the halons aforementioned either from internal stocks in the case of halon 2402 and/or from imports of halon 1211 and 1301. Therefore HTOC did not evaluate the essential use nomination further.

Furthermore the Ministry of Natural Resources of the Russian Federation informed UNEP, that all halon production in the Russian Federation had ceased as of 20 December 2000. The letter also stated that the ODS needed for 2002-2004 would be met by legal imports from abroad.





## **3 History and Purpose of the Handbook on Essential Use Nominations**

### **3.1 Introduction**

The adjustments adopted at Copenhagen by the Fourth Meeting of the Parties to the Montreal Protocol mandated a phase-out of production and consumption of CFCs, carbon tetrachloride, 1,1,1-trichloroethane and other fully halogenated controlled substances by 1 January 1996, while allowing Parties to authorise production for uses decided to be essential. Decision IV/25 of the Fourth Meeting set the criteria and the procedure for assessing an essential use nomination and requested each Party to nominate uses to the Secretariat, at least nine months prior to the Sixth Meeting of the Parties to the Protocol to be held in 1994. This decision also requested the Technical Options Committees to consider and make recommendations on the nominations.

Decision V/18 of the Parties to the Montreal Protocol calls upon the Technology and Economic Assessment Panel to  
*“assemble and distribute a handbook on essential use[s] nominations including copies of relevant decisions, nomination instructions, summaries of past recommendations, and copies of nominations to illustrate possible formats and levels of technical detail.”*

A new "Handbook on Essential Use Nominations" has been assembled in 2001, as a response to Decision XII/2, and has been published separately from this report. It is intended to assist the Parties in the preparation of essential use nominations. This handbook augments and updates the earlier July 1994 Handbook.

### **3.2 Content and Structure**

The Handbook describes the nomination process for essential use exemptions as it has evolved through Articles of the Protocol and Decisions of the Parties; the procedures followed under the Protocol; and the experience of the Panel and its Technical Options Committees in managing the process to date. The Handbook contains three sections: (1) review of the essential use process, (2) instructions for the completion of essential use nominations, and (3) appendices. The appendices contain provisions of the Montreal Protocol, decisions of the Parties to the Protocol and an essential use nomination form.

### **3.3 Handbook Updates**

The Panel may revise and update the Handbook again in future as circumstances require. Parties may consult the Ozone Secretariat for updated handbooks to ensure use of the latest version.



## **4 Response to Decision XII/2**

### **4.1 Introduction**

#### ***4.1.1 Terms of Reference***

Decision XII/2 of the Twelfth Meeting of the Parties requested the Technology and Economic Assessment Panel (TEAP) to consider and report to the Thirteenth Meeting on issues related to the campaign production of chlorofluorocarbons (CFCs) for chlorofluorocarbon metered-dose inhalers (CFC MDIs). With the assistance of the Ozone Secretariat, the TEAP and its ATOC contacted nominating Parties, some Article 5(1) Parties and other interested parties, and invited them to provide any relevant information in relation to campaign production issues. Information that was provided assisted the TEAP and its ATOC in responding to Decision XII/2.

#### ***4.1.2 Definitions***

For the purposes of this response the following definitions were used:

- *Just-in-time Supply* – The supply of the quantity of CFC required by a MDI manufacturer to assure continuous production.
- *Periodic Campaign Production* – The operation of a CFC production plant during a defined time period to produce a specific quantity of pharmaceutical-grade CFCs for future use, after which the facility is switched over to produce another product(s) or shut-down until further production of the desired CFCs is required.
- *Final Campaign Production* – The operation of a CFC production plant for a period of time to produce a specific quantity of pharmaceutical-grade CFCs for future use after which the facility is irreversibly modified to produce a different product or dismantled.
- *Pharmaceutical-grade CFCs* – CFCs produced under Good Manufacturing Practices with sufficient purity so that they are acceptable to health regulatory authorities for use in human inhalation products. These regulations vary between countries.

### **4.2 CFC production for CFC MDI manufacture - current situation**

#### ***4.2.1 Non-Article 5(1) Countries***

At the present time, four CFC production facilities, all situated in the European Union, produce and supply CFC-11 and CFC-12 to pharmaceutical companies that manufacture CFC MDIs. Another unit in the USA produces CFC-114 but does not produce CFC-11 or CFC-12. These facilities also export to Article 5(1) countries to meet their basic domestic needs including pharmaceutical use. This enables the

costs of operating the facility to be spread across a larger quantity of CFC production.

The quantities of CFCs consumed in Article 5(1) countries will reduce as a result of the Montreal Protocol (50% reduction from 1<sup>st</sup> January 2005). The quantities of CFCs being used to manufacture CFC MDIs are decreasing with time as a result of the transition away from CFC MDIs. CFC producers are evaluating the economic viability of their individual production facilities, and some may close as CFC requirements continue to decline.

#### **4.2.2 Article 5(1) Countries**

CFC MDIs used in Article 5(1) countries originate from three sources:

- Local CFC MDI manufacture;
- Importation of CFC MDIs manufactured in other Article 5(1) countries;
- Importation of CFC MDIs manufactured in non-Article 5(1) countries.

In the first two cases, the CFCs are produced in Article 5(1) countries under the Montreal Protocol consumption allowances and supplied to local CFC MDI manufacturers or exported to CFC MDI manufacturers in other Article 5(1) countries. While non-Article 5(1) CFC producers supply CFCs to Article 5(1) countries for basic domestic needs, which are used to manufacture CFC MDIs, no CFCs produced in Article 5(1) countries are approved for the manufacture of CFC MDIs in non-Article 5(1) countries. In the third case, the CFCs required for the manufacture of CFC MDIs for export to Article 5(1) countries are included in the requests made by the CFC MDI manufacturer to its national competent authority under the Montreal Protocol essential use process.

### **4.3 Future Requirements for CFCs for the Manufacture of CFC MDIs**

#### **4.3.1 Non-Article 5(1) countries**

The transition away from CFC MDIs is well underway but is subject to a large number of uncertainties including differing national regulations, rates of approvals and penetration into the market. While the quantities of CFCs requested by non-Article 5(1) Parties for the manufacture of CFC MDIs has been reduced substantially over the past five years, it has proven to be extremely difficult to predict future requirements for CFCs.

#### **4.3.2 Article 5(1) countries**

The production of CFC MDIs will decline as countries develop and implement strategies to transition away from CFC MDIs to new products and technologies. In the majority of cases, CFCs will be supplied by producers in Article 5(1) countries. If the manufacture of CFC MDIs should increase substantially then the CFC production limit for an Article 5(1) CFC producer under the Montreal Protocol may be reached. It is likely that non-Article 5(1) MDI manufacturers will fully

switch at some point to exporting HFC MDIs rather than either, moving their CFC MDI manufacture to an Article 5(1) country or, continuing to export CFC MDIs.

Due to the adverse public health consequences of underestimation of the volumes of CFCs required in both non-Article 5(1) and Article 5(1), any attempt at this stage to project future CFC requirements will result in considerable over-estimation.

#### **4.4 Source of CFC Requirements**

There are a number of potential options for sourcing the CFC requirements for CFC MDI manufacture. These are as follows:

##### ***4.4.1 Current stockpiles***

Data reported to UNEP indicate that the stockpile of CFCs in the year 2000 held by CFC MDI manufacturers was approximately 5,300 tonnes and is reducing in overall tonnage from year to year. It is assumed that the CFC MDI manufacturing companies will wish to continue to retain approximately one year's supply of CFCs until near to the time that they stop CFC MDI production.

##### ***4.4.2 Future production of CFCs for CFC MDI manufacture***

Production of CFCs for CFC MDIs can be from a number of different sources.

###### ***4.4.2.1 Article 5(1) CFC production***

As noted above, CFC production facilities in Article 5(1) countries will continue to produce CFCs for the manufacture of CFC MDIs in accordance with the Article 5(1) phase-down schedule. TEAP has noted previously that CFC MDI manufacturers situated in non-Article 5(1) countries could potentially evaluate sources of CFC production in Article 5(1) countries. Mexico has noted the availability of pharmaceutical quality CFCs from its production facility. The necessary manufacturing and quality assurance processes to qualify a new source of CFCs are complex and could potentially take more than 2 years. Although such a process might be possible, it may not be viable or cost-effective and may not be possible with decreasing CFC production in Article 5(1) countries.

###### ***4.4.2.2 Non-Article 5(1) CFC production***

In theory, there are a number of approaches that could meet CFC production requirements for MDIs until production ceases in non-Article 5(1) countries. These approaches are not mutually exclusive.

*Continue just-in-time supply* – Continued production is subject to local government approval and dependent on how long it remains economically feasible. This approach assures that only the amount of CFCs that is actually required to manufacture MDIs will be produced, however this approach will eventually cease to be feasible as production decreases.

*Periodic Campaign Production* – This approach involves intermittent use of a production facility. Due to inefficiencies in CFC production involved in start up and shut down of production, the facility will produce CFCs that will not be of pharmaceutical-grade quality during the start and finish of such a campaign. These CFCs will either have to be destroyed or exported to Article 5(1) countries to meet their basic domestic needs, both of which can present difficulties. The destruction of the CFCs is expensive and the latter option may become difficult if the CFC producer is no longer supplying to Article 5(1) countries. Furthermore, intermittent operation of a CFC plant will increase costs and cause operational difficulties (see Box 1 for one example).

*Final Campaign Production* – This approach requires that at a given point in time a stock is built up to meet the total projected CFC requirements for all future production of CFC MDIs. This approach has a number of drawbacks.

- The adverse public health consequences of underestimation of the volumes of CFCs required will mean that any attempt at this stage to make projections of the volumes required for in a Final Campaign could result in considerable over-production.
- Currently ATOC understands that there is only 6,000 tonnes of storage capacity, which is already being utilised to hold strategic stockpiles. It is unlikely that this would be sufficient to safely store the necessary quantity of additional CFCs required if a Final Campaign were to take place in the near future. Extensive work to increase storage capacity would involve refurbishment of storage containers and possibly new facilities. The effort, costs and time involved in such a program would be substantial.
- The available storage capacity will determine the quantity of pharmaceutical-grade CFCs which can be produced in any Final Campaign. Much of the current capacity is either in tanks owned and operated by CFC producers, or facilities owned and operated by pharmaceutical companies. In general the tanks are under close and regular supervision, ensuring that they are maintained and operated to high standards of containment. The larger and the earlier the Final Campaign the greater the challenge to maintain the necessary quality standards.
- Although the satisfactory storage of pharmaceutical-grade CFCs for extended periods, e.g. 3-5 years under controlled conditions appears possible, it is not clear that quantities stored in less controlled circumstances would remain of pharmaceutical grade (see Box 2). If it was not possible to use some or all of the CFCs that were stored, the manufacture of CFC MDIs could be disrupted for both non-Article 5(1) and Article 5(1) countries and patient health compromised.

*Box 1: Production of pharmaceutical-grade CFCs over a year-end to supply MDI manufacturers at the beginning of a year*

CFC producers have brought to the attention of the ATOC a problem concerning licences for the production of pharmaceutical-grade CFCs which can interrupt just in time supply of pharmaceutical grade CFCs to MDI manufacturers at the end of each year.

Some Parties grant licences to MDI manufacturers early in the year for which the Parties have approved an essential use allowance. The MDI manufacturers then request CFC supply from the CFC manufacturers. Production and supply then must take place in that year. This leads to surges in demand for and production of CFCs resulting from the necessity of having the approved documentation on hand to abide by national regulations. A CFC manufacturing facility may not always be able to work effectively to produce pharmaceutical grade CFCs within an annual regulatory schedule. However manufacturing for the basic domestic needs of Article 5(1) countries has to date allowed the CFC production schedule to be managed effectively by smoothing out some of these surges. As CFC production reduces for both MDIs and basic domestic needs, economic factors may lead CFC manufacturers towards increasingly infrequent Periodic Campaign Production, which may not fit into an annual licensing schedule.

As many Parties have approved essential use allowances for two-years in advance, consideration may need to be given to regulatory licensing schedules to ensure these fit with an effective, technically and economically feasible CFC production schedule for pharmaceutical grade CFCs.

*Box 2: Long term storage of CFCs*

Stockpiles of CFCs are currently being held by a number of pharmaceutical companies, and some of these companies have been using some stockpiled material. The material from the stockpiles for use has generally met specification and been suitable for use. However, there have been a number of exceptions to this, which longer-term storage could only exacerbate. Problems include:

*Odour* – This is one of the most persistent of storage problems for pharmaceutical CFCs, particularly for CFC-12, which can develop a strong odour on storage. This makes it unsuitable for use in MDIs. There have been instances where substantial quantities of CFC-12 have ‘gone off’ in this way. It is sometimes possible to remove such odour by ‘polishing’ it out with adsorbents, but the approach is not reliable, and material ‘reworked’ in this way may not be acceptable in countries with exacting pharmaceutical standards.

*Related impurities* – CFCs are chemically stable, and are unlikely to undergo significant chemical change on storage. In recent years, analytical methods (Gas Chromatography) have been developed to a very high level and are currently ‘state of the art’. There have been previous instances of CFC stockpiles effectively becoming out of specification on impurity content during storage. This has been attributed to the improvements in analytical techniques over the duration of the storage period and not to any change in the material.

## 4.5 Conclusions

Due to these considerations, ATOC believes that the best approach would be to continue just-in-time supply for as long as possible. Given the uncertainties, for example potential early closure of a CFC manufacturing facility, a final campaign could be needed to supply the remaining projected requirements. However, it should not be conducted until the end of the transition can be seen with greater clarity. The later into the eventual phaseout any Final Campaign is done, the more the concerns over the integrity of CFC storage, the volume of storage capacity needed, and the over-estimation of the amounts required would then be minimised.

If it is decided in the future that a final campaign is needed, then the Parties may wish to consider with sufficient anticipation:

- CFC requirements for CFC MDI manufacture for the period to be covered by the campaign;
- Approval of the nominations for the required period by a Meeting of the Parties;
- Authorisation by the Parties and the Government, in which the production facility is located, to produce the CFCs in a single final production campaign.

Other issues that will also require consideration by CFC producers and MDI manufacturers include:

- The definition of the ownership of the stockpiled CFCs;
- The location(s) of the stockpiled CFCs;
- The time over which the stockpile will be maintained;
- Responsibility for destruction of surplus CFCs.

In summary, Parties may wish to consider the following:

- Continue just-in-time supply for as long as possible;
- Any Final Campaign Production should be done preferably as late as possible into the transition;
- Should a Final Campaign be needed in the future, and recognising that this could not be implemented quickly, the Parties may wish to consider changes to the legal framework of the Montreal Protocol to facilitate Final Campaign Production.



## **5 Laboratory and Analytical Uses**

There are no changes from last year to report to the Parties. To assist the 2002 Assessment, Parties are requested to provide any new information on alternatives that have been identified and are now available or analytical methods that do not require the use of ozone depleting substances to the Secretariat. Any new developments will be reported in the 2002 Assessment.



## **6 Response to Decision X/7**

### **6.1 Decision X/7**

Decision X/7 requested all Parties to develop and submit to the Ozone Secretariat a national or regional strategy for the management of halons, including emissions reduction and the ultimate elimination of their use.

The Decision further requested the Technology and Economic Assessment Panel to update its assessment of the future need for halon for critical uses in light of these strategies.

As of February 2001, the HTOC had received halon management strategies from 10 Parties not operating under Article 5(1), namely Australia, Canada, Czech Republic, Hungary, Japan, New Zealand Norway, Poland, Slovakia, USA and from the European Union representing an additional 15 Parties not operating under Article 5(1). Also, 11 halon management strategies were received from Parties operating under Article 5(1), (Colombia, Ecuador, Guyana, Jordan, Republic of Korea, Kuwait, Maldives, Niger, Oman, Uruguay, South Africa), some in the form of their country plans for halon.

### **6.2 Overview of National Halon Management Strategies**

The term "critical uses" when used in the context of this response means uses defined as critical by the Parties in their different strategies.

Basically there were two general approaches taken to define critical uses. Some Parties have chosen to define a list of critical uses and thus make all installations not on the list obsolete. Other Parties have chosen to let the market decide which uses are viewed as critical based upon supply and demand. In these cases, the price mechanism decides which of the applications are considered critical uses.

Only three strategies from Parties/regions not operating under Article 5(1) provided estimates on their halon inventories, the amount of halon installed in critical uses, and the amount of halon stockpiled either in centralised or in distributed storage facilities. These estimates indicated that those Parties/regions might eventually have a surplus of both halon 1301 and halon 1211 that could be destroyed or used to meet the needs of other Parties. One strategy reported that the Party had already destroyed a significant quantity of halon 1211.

The other halon management strategies from Parties not operating under Article 5(1) did not quantify the installed base, stockpile, or the amounts required for critical uses in the future.

One halon management strategy outlined a market-based approach intended to maintain supply and demand in balance. The Party believes that this approach will prove effective in satisfying their future needs for critical uses as it supports the flow of halon from less critical to more critical applications over time.

In the halon management strategies submitted by Parties operating under Article 5(1), most provided an estimate of the quantities of halons in their installed bases and their needs for critical uses. Some strategies indicated that Parties were counting on the availability of the halons from Parties not operating under Article 5(1) to meet the continuing needs of their critical uses over the next decade.

### **6.3 Assessment of Future Need for Halons**

Based on the quantitative information provided by 3 Parties and 1 region, it appears that in these countries/regions there is a surplus of both halon 1211 and halon 1301 in excess of the requirements for present and future critical uses. However, the information provided contained significant uncertainties regarding the quantities of stored or installed halons, the rate at which they are currently consumed, and the quantities that will be required to meet future uses. Two Parties also reported a surplus of halon 2402.

With regard to earlier assessments of the HTOC on availability of halons for critical uses, the supplied data appears to confirm the HTOC estimate of a surplus of halon 1211 in many of the countries of Parties not operating under Article 5(1). Parties therefore may wish to consider developing measures to collect and store surplus halon 1211 and proceed with the destruction of excess material.

Regarding halon 1301, the information supplied by these Parties/regions indicates a larger regional surplus of halon 1301 than HTOC estimated in its earlier assessments. However, as explained previously, the estimates provided by these Parties also contain significant uncertainties. Parties may therefore wish to consider developing measures to collect and store surplus halon 1301 while continuing to assess future needs for it. Also, to avoid a future need for any party to apply for an essential use production exemption, Parties may wish to consider not destroying the stored halons before all Parties, including Parties operating under Article 5(1), have confirmed that they have sufficient halon 1301 to meet the future needs of their critical uses.

### **6.4 Market Situation for Halons at Present**

The Committee polled its members about the situation concerning the availability, the price, and the forecast demand for halons in the immediate future. It became clear that, at present, the halon market in Europe has nearly collapsed owing to a large surplus of halon 1211 and halon 1301 being made available. The market in Japan has also become rather unstable because many users are concerned about the prospect that a regulation requiring mandatory decommissioning might be set in place. Users are generally afraid of having too much halon in their possession if tighter use restrictions are likely to be put in place. This would then result in a high cost to them for the destruction of these halons.

The situation in Europe and Japan was seen by the HTOC as resulting from the new EC-Regulation 2037/2000 coming into force. The regulation mandates that all but certain specified critical uses have to be decommissioned not later than 31 December 2003. The Committee is concerned about the consequences of this

situation. As indicated in the earlier reports, HTOC maintains that efforts to recover halon 1211 and/or halon 1301 will only be successful if governments finance the collection and destruction of surplus halons. Unless great care is exercised in the development of programs, procedures, and regulations, there is a very real possibility that many owners will simply vent halon at a time when the ozone layer is most fragile.

## **6.5 Concluding Observations**

If a Party's halon management strategy identifies a potential surplus of halons, that Party should also explore mechanisms for collecting the surplus, the safe storage of the collected material and, if appropriate, the timetable for its destruction. Such timetables should include a review of the availability of specialised destruction facilities and should take into account the current slow process of halon destruction. In addition, a halon management strategy should take into consideration how these operations will be funded and which agency or organisation will be responsible for the collection and disposal process. Lack of clearly established mechanisms and funding may result in larger emissions of halons during the process of early decommissioning.

Before destruction schemes are implemented, a review process should be established to determine whether or not changes in the risk situation for critical uses, or the availability of fire protection solutions, have affected the original estimates for critical uses. In addition, halon management strategies should take into account changes in the international situation, especially changing demands for their critical needs from Parties operating under Article 5(1).

For the past several years the HTOC has used a computer program to estimate the size of the halon "bank" and the annual transfer of halon from less critical to more critical applications. The computer program uses historic production data and estimated recovery and emission factors for halons. It is based on a steady state flow of halon fire protection equipment reaching the end of its useful life, when the halon is then recovered, recycled and reused for more critical and essential uses. However, two events have recently taken place that has drastically changed this pattern. Firstly, the US Military established its own halon bank and has built a reserve adequate for the expected life of critical equipment. This decision has resulted in a much larger than expected flow of halon from existing installations into a single bank. Secondly, the newly adopted EC-regulation that mandates the decommissioning of all but critical halon system within the next 3 years has resulted in a collapse of the market for recovered and recycled halons in Europe.

These two factors have introduced volatility into the market that has made it virtually impossible to continue to use a model that relies on historic trends. The HTOC must therefore regretfully abandon use of the model for future predictions, and the Parties may now wish to rely upon figures provided in the different halon management strategies to predict future supply for critical and essential uses.

Finally, the HTOC maintains its opinion that adequate stocks of halon will be available to meet the needs of critical uses for the foreseeable future provided

governments take the necessary responsibility to manage these assets. In addition, these provisions help avoid the need for a future production exemption to meet the essential needs of these critical uses.

## 7 Procedure Recommended by TEAP for Evaluation of New ODP Substances<sup>1</sup>

Decision XI/20 (Procedure for new substances) recalls decisions IX/24 and X/8 on control of new ozone-depleting substances and requests full consideration to ways to expedite the procedure for adding new substances and their associated control measures to the Protocol and for removing them therefrom.

Decision XI/19 (Assessment of new substances) requests the Scientific Assessment Panel and the Technology and Economic Assessment Panel to develop criteria to assess the potential ODP of new chemicals and to develop a guidance paper on mechanisms to facilitate public-private sector co-operation in the evaluation of the potential ODP of new chemicals in a manner that satisfies the criteria to be set by the Panels.

TEAP and its nPB Task Force have made substantial progress in developing methodologies to estimate potential future sales of newly introduced ozone-depleting substances and in predicting the geographical distribution of emissions. TEAP and its Technical Options Committees are working to generalise these methodologies to all sectors where new ozone-depleting substances may be used and where such geographical distribution details are needed to calculate their ODP.

TEAP plans to meet with members of the SAP at the July 2001 meeting of the Open-Ended Working Group to further elaborate evaluation of the potential ODP of new chemicals in a manner that satisfies the criteria to be set by the Panels. As a starting point for those discussions and mindful of the administrative advantage of a process not requiring frequent Amendment of the Protocol, the TEAP is considering the following assessment process:

1. Require developers of new substances with likely ODPs (substances containing chlorine or bromine and with certain other physical and chemical properties, to be decided after consulting SAP and chemical researchers) to disclose to the Ozone Secretariat their likely ODPs based on standard scientific modelling.
2. Prohibit (phaseout immediately) all such substances with a modelled ODP greater than a specific threshold to be determined by Parties.
3. Request TEAP and SAP to review substances nominated by Parties. The TEAP review could investigate potential uses and determine any

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<sup>1</sup> The definition of what constitutes a 'new ODP substance' under the Montreal Protocol still requires clarification. It is clear that a newly engineered molecule would classify as a 'new substance' under any interpretation. However, the first commercial use of an existing chemical with a potential ODP would also represent a threat to the ozone layer. Liaison with the chemical industry should be pursued to agree a precise definition so that all appropriate chemicals are captured within this procedure.

environmental, health, or economic advantages or disadvantages of the new substance.

4. Use the Protocol Adjustment mechanism to authorise use following review by the SAP and TEAP.



## **8 Consideration of Critical Use Exemption Nominations for Methyl Bromide**

Parties may wish to request TEAP to prepare for nominations for Critical Use Exemptions for methyl bromide under Decision IX/6. Early preparation would help to ensure consistency in nominations and will simplify review.

At the Ninth Meeting of the Parties, in Decision IX/6, the Parties introduced a “Critical-Use Exemption” from control of methyl bromide uses post-phaseout (1 January 2005 for non-Article 5(1) Parties and 2015 for Article 5(1) Parties).

The criteria for the Critical Use Exemption are similar to those established for the Essential Use Exemption (Decision IV/25) applicable to other ODS, but adjusted to take into account the special circumstances associated with the agricultural uses of methyl bromide.

Methyl bromide uses controlled under the Protocol are mainly for soil fumigation in the production of certain high value crops, postharvest fumigation of dry foodstuffs (e.g. grains, dried fruit) and, under particular circumstances, for some pest control in buildings and transportation. Uses of methyl bromide for quarantine and pre-shipment (QPS) applications are already exempt from control under Article 2H of the Protocol.

Now is the time to prepare for nominations for critical uses of methyl bromide in the event that an alternative for a specific use is not likely to be available by 1 January 2005. When the 1 January 2005 phase-out of methyl bromide was agreed by the Parties at the Ninth Meeting of the Parties in 1997, seven growing seasons in the northern hemisphere (six in the southern hemisphere) were available for development of alternatives prior to phase-out in non-Article 5(1) countries. Now only three or four seasons remain. Use of methyl bromide in the agricultural sector is often scheduled on a seasonal basis, imposing substantial restrictions on the time taken for testing and development. Because of widely differing agricultural situations (e.g. climate, soil type, pests, markets, crop variety) often trials must be carried out to adapt alternatives to local situations and particular alternatives may only be suitable in restricted circumstances.

A Party may wish to consider submitting to the Ozone Secretariat a nomination for a Critical Use Exemption for 2005 by 31 January 2003, for a decision as early as the 2003 Meeting of the Parties (see desirable Timetable A below). A 2003 decision by the Parties would allow farmers 12-15 months to plan agricultural practices for the 2005 growing season. A Party may (still) wish to submit a nomination to the Ozone Secretariat by 31 January 2004 but the applicant would have only 2-3 months notification by the Parties prior to 1 January 2005 on whether or not to grant an exemption for the use of methyl bromide after that date (see desirable Timetable B below). This may have the consequence that proper planning of agricultural practices is not possible if the nomination is not approved.

National governments will need time to review applications from farmers and other users of methyl bromide prior to submitting nominations, and those

applicants will need time for preparation of the application and gathering supporting data, including fulfilment of clause (b)(iii) of Decision IX/6. This states *inter alia*:

“It is demonstrated that an appropriate effort is being made to evaluate, commercialise and secure national regulatory approval of alternatives and substitutes.....Non-Article 5(1) Parties must demonstrate that research programmes are in place to develop and deploy alternatives and substitutes.....”

A desirable timetable for 2005 Critical Use Exemptions might be:

*Timetable A*

When decisions are desirable 12-15 months prior to the 2005 growing season:

October 2001	Parties request TEAP/MBTOC to prepare guidance
May 2002	TEAP issues guidance on Critical Use Exemptions
June 2002	Methyl bromide users apply to national governments
January 2003	National governments submit nominations to Secretariat
May 2003	TEAP and MBTOC make recommendation to Parties
July- December 2003	Parties decide (at the 15th Meeting of the Parties).

*Timetable B*

When decisions can be made just a few months prior to the 2005 growing season:

June 2003	Methyl bromide users apply to national governments
January 2004	National governments submit nominations to Secretariat
May 2004	TEAP and MBTOC make recommendation to Parties
July- December 2004	Parties decide (at the 16th Meeting of the Parties).

Note: An applicant may choose to submit a nomination for the year 2005 to the Ozone Secretariat by January 2004. However, if the Meeting of the Parties were held in July 2004, the applicant would have only 5 months notification prior to January 2005, and if the Meeting of the Parties were held in December, the applicant would have less than one month notice.

Mindful of this timeline, Parties may wish to request the TEAP to prepare for nominations for Critical Use Exemptions for methyl bromide. Early preparation would help to ensure consistency in nominations and will simplify review. TEAP will assist in this process as decided by the Parties.

With instructions from the Parties at the OEWG Meeting and the following Meeting of the Parties, TEAP will assist in developing nomination procedures, including:

- Consultations and workshops;
- Development of a simple submission and assessment process; and

- Co-ordination with national authorities over processes for preparation of nominations.

TEAP may consider, if Parties so wish, to include nomination procedures in an additional chapter of the Essential Uses Handbook.



## 9 Progress Reports

### 9.1 Aerosols, Sterilants, Miscellaneous uses and Carbon Tetrachloride Technical Options Committee (ATOC)

This section covers new developments since the TEAP Report April 2000 related to: aerosol products (other than metered dose inhalers, MDIs), metered dose inhalers and sterilants.

#### 9.1.1 *Aerosol products (other than MDIs)*

There are no technical barriers for the transition to alternatives for aerosol products other than MDIs. However, some consumption of CFCs in aerosols still remains in Article 5(1) Parties and CEIT. The main uses for CFCs in these countries have been identified as:

- Non-MDI medical aerosols such as local anaesthetics, throat sprays, nasal sprays, wound sprays, vaginal products and traditional Chinese medicine;
- Industrial / technical aerosols such as electronics cleaners, spinnerette sprays, anti-spatter sprays and tyre inflators;
- Personal products filled in small volume cans.

The main change that has occurred in the sector since the publication of the 2000 Report is the closure of CFC production facilities in the Russian Federation effective December 2000. The Russian Federation reported to the Montreal Protocol Secretariat that several hundred tonnes of CFCs were needed for the continued production of non-MDI medical aerosols. These products can either be reformulated to use non-CFC propellants or replaced by not in kind substitutes.

In China around 2000 metric tonnes of CFCs are still used for the production of medical aerosols, which include traditional Chinese medicine. The use of aerosols is increasing and new products with CFCs continue to be developed, local efforts to begin the reformulation of these products have been reported.

The situation in other countries remains similar to that which was reported last year. In some cases better economic conditions might have contributed to local increases in the use of CFCs in aerosols, which partially offset the reductions that have occurred in the Russian Federation. The remaining usage of CFCs in aerosols is small, distributed in many countries and difficult to identify. Specific actions from governments and their ozone departments will be needed to achieve final phase-out.

The reformulation of the non-MDI medical aerosol products and industrial/technical aerosols may require technical assistance. In the case of medical aerosols approval by national health authorities will be required. In both cases, more expensive products result if the new products have to use HFCs.

## **9.1.2 Metered dose inhalers**

### **9.1.2.1 Trends in CFC consumption**

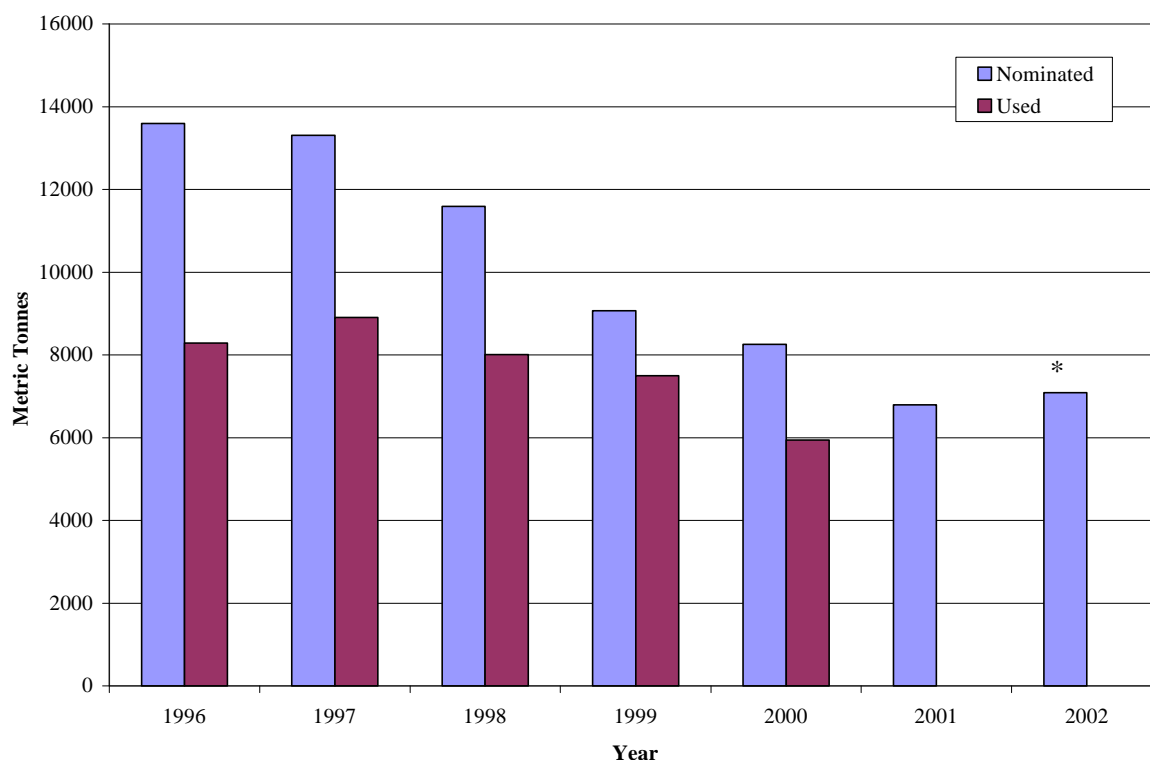
The following trends in CFC use for MDIs have been drawn from Reporting Accounting Frameworks submitted by non-Article 5(1) countries manufacturing CFC based MDIs as essential uses (see also Figure 1).

Total CFC use for non-Article 5(1) countries manufacturing MDIs has fallen by about 30% from 8,290 tonnes in 1996 to an estimated 5,948 tonnes in 2000. ATOC estimates that a total of 7,500-8,000 tonnes of CFCs were used world-wide for the manufacture of MDIs in 2000, including an estimated 1,500 tonnes used in Article 5(1) countries for the local manufacture of CFC based MDIs.

The overall trend is for a reduction in CFC used for the production of MDIs in most non-Article 5(1) regions of the world. For example, Australia (60 percent), Canada (91 percent), European Community (36 percent), Hungary (92 percent) Japan (40 percent) and Poland (67 percent) have all achieved significant reductions in consumption of CFCs from 1996 to 2000. There is no consistent trend yet for the United States, with CFC use variously increasing and decreasing from year to year between 1996 and 2000, with an overall increase in that period (5 percent).

In some cases trends may reflect regional changes in production, such as relocating some of the CFC-MDI manufacturing from Canada and the European Community to USA, or other factors. However, overall there is a clear global downward trend in CFC use, at the same time as prevalence in asthma and COPD has been increasing.

These reductions reflect the fact that alternatives continue to be introduced around the world. For example, of the estimated 450 million MDIs manufactured worldwide in 2000 approximately 350 million were CFC MDIs and 100 million HFC MDIs (up from an estimated 70 million in 1999). However it would appear that the reduction in CFC use for MDIs and the transition to alternatives is slower than was originally anticipated.



**Figure 1: Total amounts of CFCs nominated/exempted and used for essential uses for MDIs 1996-2002**

\* Year 2002 data include a nomination from the Russian Federation where previous years have not.

#### 9.1.2.2 Availability of Alternatives

**HFC MDIs** – HFC MDIs continue to be introduced and commercialised around the world.

- At least one HFC MDI has been launched in at least 57 countries around the world;
- In all of these countries there is at least one short-acting beta agonist formulation available;
- In 34 countries, at least one inhaled corticosteroid formulation is available;
- At least one HFC MDI has now been launched in each of 27 Article 5(1) countries.

Brand by brand based transition has proceeded relatively quickly where the substituted products were withdrawn. The transition in some non-Article 5(1) countries (e.g. Germany) is likely to be virtually complete by the end of 2002. The recent approval of a second salbutamol HFC MDI in the USA may help expedite the US transition. One domestic manufacturer in India has now marketed both beta agonist and inhaled corticosteroid HFC MDIs.

**Dry powder inhalers** – The introduction of new dry powder inhalers (DPIs) using existing technologies is continuing around the world. ATOC estimates that total annual DPI use is of the order of 100 million inhalers. Data indicate that in established European markets the overall usage of DPIs continues to increase. In

other markets such as the USA and Japan, additional DPIs have become available in the past year and more DPIs are in the regulatory review process. Overall, the acceptance of DPIs appears to be increasing in asthma and COPD patients. In a number of countries, new medications have been introduced first as a DPI followed by the HFC MDI version.

*Novel Delivery Systems* – A number of sophisticated pulmonary delivery systems that do not use propellants are in development. These take the form of novel DPIs or liquid-based systems. While commercial availability of these is still in the future, it is expected that some may serve as alternatives to CFC MDIs when used to deliver asthma/COPD drugs. However, many of these novel systems are being developed to deliver drugs into the systemic circulation via the lungs (e.g. insulin for diabetes), and will therefore not be considered as substitutes for existing CFC MDIs for asthma and COPD.

### 9.1.2.3 *Experiences in transition*

The rate of introduction of HFC MDIs has varied from country to country and experience of the effects of transition has therefore similarly varied. Even when new products have been introduced the rate of uptake of use of new products has varied. This has occurred for a number of reasons of varying importance, some of which are addressed as follows.

*Economic considerations* – Irrespective of the system of health care delivery, economic barriers to the introduction of HFC MDIs appears to be as relevant in Article 5(1) countries as in non-Article 5(1) countries. Brand by brand transition has generally occurred at equivalent prices but funders of health care, whether governments, private insurers, or managed care organisations have continued to favour lower cost, often locally produced or generic CFC MDIs.

*Health professional considerations* – Despite widespread educational initiatives, transition does not appear to be an important issue amongst most doctors and other health professionals, many of whom have taken a passive approach to transition.

*Method of introduction of new products* – The introduction of an HFC MDI does not by itself lead to use, even when considerable marketing initiatives are utilised. Experience in several countries shows that transition can be enhanced by brand by brand transition as well as by phase-out by class. In the UK for example one manufacturer introduced a CFC free salbutamol (albuterol) but use only increased when that manufacturers pre-existing branded CFC containing product was voluntarily withdrawn from sale. Similar experience occurred in Germany where final transition of a class was successfully effected by government legislation that banned CFC use in beta-2-agonist metered dose inhalers.

*Patient factors* – The level of the patient concern engendered by this issue reflects the rate of transition. In the UK where transition has been occurring at a modest but steady pace, calls to an asthma patient telephone helpline on this issue accounted for only 2 percent of total calls. In Germany there was a much higher peak of enquiries reflecting a more sudden rate of changeover. Overall patient



concerns have been minor and no significant medical consequences of transition have been identified so far.

*Reformulation difficulties* – It needs to be appreciated that although transition is progressing well, reformulation is still problematic for some drug molecules.

Reviewing all possible methods of transition (e.g. drug by drug, brand by brand, category by category, targets and timetables) it is clear that action by patient organisations, health professional organisations and the pharmaceutical industry will not alone complete transition. Parties may wish to observe that official action (e.g. targets and timetables) is essential to effect final transition. This will involve consideration of the economic factors involved.

#### 9.1.2.4 *Strategic Reserves*

Based on the data submitted by individual nominating Parties under the Reporting Accounting Frameworks, the amount of CFCs held in reserve is approximately 12 months supply. The ATOC believes this is reasonable based on the uncertainties of CFC supply. However, under Decision XII/2 the ATOC was specifically requested to evaluate the issue of campaign production for which storage issues are relevant. The response to this Decision can be found elsewhere in this TEAP report (chapter 4).

#### 9.1.2.5 *Article 5(1) country and CEIT considerations*

The 1998 ATOC Assessment Report addressed a series of issues regarding CFC phase-out and MDI availability in Article 5(1) countries and CEIT (Section 3:9; pages 59-63). The first conclusion stated at that time remains of paramount importance today, namely the maintenance of adequate supplies of the full range of necessary inhaled medications.

Phase-out of overall CFC usage is mandated by the year 2010 under the Montreal Protocol. Facilitation of phase-out under the Multilateral Fund has concentrated entirely on CFC uses other than in inhalers for asthma and COPD, and how transition is likely to occur in Article 5(1) countries and CEIT needs to be further addressed. Continued availability of inhaled therapy depends either upon local production of CFC or HFC MDIs or import of similar finished products. Current availability of HFC MDIs may be, in addition to imports, the result of production by a local manufacturer (for example as in India), or by a multinational company with a production site in that country (for example as in Brazil). It is possible that production of HFC MDIs could in future also result from a local producer working with a multinational company or under a licensing arrangement. The cost implications of transition to CFC-free alternatives may vary according to the proportion of MDIs imported or produced by each of these methods. CFC-free alternatives may cost more than those previously produced by local manufacturers. Parties may wish to consider this and develop strategies to ensure continued supply of necessary medication at an affordable price for all patients with asthma and COPD.

Demand for the continued availability of low cost CFC MDIs in Article 5(1) countries and CEIT is unlikely to be met by production of CFC MDIs in non-Article 5(1) countries; partially because of the decreasing availability of pharmaceutical grade CFCs but more because the unit costs of such CFC containing MDIs will become proportionately greater as the majority of MDIs become CFC free and multinational manufacturers switch production facilities. An overall picture of the situation in each Article 5(1) Party and each CEIT is currently difficult to ascertain because information available from those countries on the breakdown of CFC consumption does not always account for the amount of CFC used for MDI manufacture.

A smooth transition and continued availability of essential medications may need to involve further work with other agencies such as WHO, national health departments, NGOs and other organisations (for example the Global Initiative for Asthma (GINA), Global Initiative on Obstructive Lung Diseases (GOLD), and the International Union against Tuberculosis and Lung Diseases (IUATLD)).

The inevitable transition from CFC to HFC MDIs this decade necessitates all developing countries to develop transition strategies and to address these issues now.

### **9.1.3      *Sterilants***

The situation in this sector remains much the same as was reported in 2000. Use of CFC-12/ethylene oxide (EO) mixtures (12/88) has been eliminated in most non-Article 5(1) Parties as there are no technical barriers to the phase-out of CFCs in sterilisation. Use of CFC-12 in Article 5(1) Parties and in some CEIT is estimated to be less than 1,500 tonnes. Estimated use of substitute HCFC replacement is less than 100 ODP tonnes worldwide. Although HCFC replacements are virtual drop-in substitutes for CFC/EO, some users in Article 5(1) Parties and East Europe view this option as significantly more expensive than the traditional mixtures of CFC/EO and EO/CO<sub>2</sub>. The development of non-flammable mixtures of EO with HFCs have been reported.

## **9.2      Foams Technical Options Committee (FTOC)**

### **9.2.1      *General***

This update is the second foam sector review published since the 1998 Report of the Flexible and Rigid Foams Technical Options Committee. It builds on the update provided by the Technical Options Committee early last year (published in the Report of the Technology and Economic Assessment Panel in April 2000) and provides important new information that has emerged since then. The purpose of these updates is to highlight changes in technology that have occurred in the last year rather than to offer a comprehensive review of the current technologies available. Such a comprehensive review will be the subject of the 2002 Report of the Flexible and Rigid Foams Technical Committee which is currently in preparation.

The key conclusions from this update report are as follows:

- Developing countries are making substantial CFC phase-out progress;
- The financial constraints of SMEs remain key factors in many transition strategies both in developing and developed countries;
- Regional discrepancies in the availability and timing of alternatives are requiring adjustments to transition strategies in parallel market segments;
- The timing of availability of liquid<sup>2</sup> HFCs remains a key factor in transitional strategies;
- Lack of availability of HCFCs following the phase-out in the foam sector in developed countries could become a significant transitional issue in developing countries;
- Insulation foams continue to grow in use ahead of alternative insulation materials because of their excellent insulation efficiency and structural integrity. Increased concerns over climate change will drive this growth further;
- HFCs continue to offer foams with the best thermal efficiencies in most instances. This favours the selection of HFC-blown foams in space-limited and other demanding applications;
- Hydrocarbon-based technologies are making substantial in-roads into several additional market segments, including the North American boardstock sector. Product and process optimisation is assisting HCs to compete thermally in several applications. The main challenge facing HCs is that of increasing fire code requirements and safety concerns in the construction sector.

### **9.2.2 Technology Status**

This section covers the technology status in the polyurethane, extruded polystyrene and phenolic foam sectors.

#### **9.2.2.1 Polyurethane**

##### *Flexible Foams*

**Slabstock Foams - Continuous:** The use of ODS technologies in this sector has been driven historically by the need to generate lower density and hardness combinations. Typically the cut-off point for the use of auxiliary blowing agents is at around 23 kgm<sup>-3</sup>. Almost all foams affected by the ODS phase-out are TDI-based and the prime initial auxiliary blowing agent replacement was

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<sup>2</sup> In previous FTOC reports, the word 'liquid' when referred to HFCs has been taken to mean both HFC-245fa and HFC-365mfc. For consistency of understanding this terminology will continue to be used in both this Update and in the full 2002 Foam Technical Options Committee Report. However, in doing so, the FTOC wishes to draw the attention of the reader to the fact that HFC-245fa boils at 15<sup>o</sup>C and may require either pressurised blending facilities or cooling equipment for other blend components.

methylene chloride. However, increasing regulatory scrutiny around the world is forcing wider consideration of other alternatives. CO<sub>2</sub> (LCD)<sup>3</sup> has emerged as a strong contender and continues to grow at the expense of other ODS replacement technologies. However, CO<sub>2</sub> (LCD) has its limitations. At equi-molar replacement levels, the foam will be softer and the heat sink will be less than for CFC-11. In addition, the technology is rather sensitive to the use of fillers and the amount of CFC-11 that can be replaced in a given formulation is limited (less than or equal to 15 php). Although these limitations can be overcome, learning curves in the adoption of CO<sub>2</sub> (LCD) technology can be upwards of two years. Variable pressure technology is another option for this sector but the economics only begin to work at production levels above 7,000 tonnes per year. Reliance on methylene chloride can also be mitigated to some extent by the use of low index additives.

***Slabstock Foams – Discontinuous:*** At the current level of development, CO<sub>2</sub> (LCD) technologies are not suited for discontinuous flexible slabstock processes and, with increasing pressures on methylene chloride as an option, variable pressure technologies are beginning to emerge. There are currently four main suppliers and their approaches vary. As yet, it is not clear which of the methods will provide the most effective production solution, but in all cases investments are upwards of \$300,000 taking this option out of the reach of many SME operators. The Foams Technical Options Committee therefore has concern about the future transition step for this sector and a solution is required to prevent the extended use of CFC-based technologies.

***Moulded Foams:*** CO<sub>2</sub> (water) is still the most widely used replacement and has set the benchmark for other systems. However, CO<sub>2</sub> (LCD) and CO<sub>2</sub> (GCD) have been of particular value in reaching a wider range of hardness/density properties, closer to those previously achieved with CFCs. A growing use of such foams is as acoustic insulation in the automotive sector. Although limited, there still appears to be some continuing use of HCFC-141b in the short-term. However, there is now little, if any, technical justification for this.

***Integral Skin Rigid Foams:*** This sector includes cabinets for electronic equipment, as well as several other minor non-insulating uses. CO<sub>2</sub> (water) systems have again been the first option explored but thinner skins have caused many to look at other options. Hydrocarbons provide an excellent skin but have investment constraints. Accordingly, some are still using HCFC-141b in this product sector. Liquid HFCs such as HFC-245fa and HFC365mfc/227ea are also under investigation and show promise, particularly in terms of skin quality.

Commonly, products made with CFCs in developing countries are of much lower density than equivalent products in developed countries. When transitions are enacted, based on developed country technologies, therefore, they are often

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<sup>3</sup> Carbon dioxide or CO<sub>2</sub> as a blowing agent in foam can be chemically generated from the reaction between water and isocyanate but also added as an auxiliary blowing agent in liquid or gas form. The different options are hereafter referred to as CO<sub>2</sub> (water), CO<sub>2</sub> (LCD) and CO<sub>2</sub> (GCD).

accompanied by a significant density increase, which increases costs and thereby presents an additional barrier to transition.

***Integral Skin Flexible Foams:*** This sector includes shoe soles, steering wheels (and other internal and external car parts), bicycle saddles, furniture fitments and leisure equipment. The currently available technical options are CO<sub>2</sub> (water), HCFC-141b, HFC-134a and hydrocarbons. With respect to the latter, both pentane and n-hexane have been used. For higher density mouldings, it is possible to use low level pentane and hexane pre-mixes which can be transported safely. Investment for the handling of these systems at the point of use can be reduced, thereby bringing the option within the financial range of small producers that could otherwise not afford the investment required for bulk hydrocarbon use. Nevertheless, CO<sub>2</sub> (water) continues to be the benchmark and the use of in-mould coatings, although not universally accepted, is increasingly overcoming some of the earlier problems with skin quality – even for the highly demanding automotive sector (e.g. in Australia). Liquid HFCs continue to be assessed and some of the recent work with HFC-245fa by Honeywell and HFC-365mfc by Solvay may well offer further alternatives to this sector, since both materials have better solubility than HFC-134a. In principle, such blowing agents are always being used to control skin quality rather than to reduce density per se.

HCFC-141b has not been allowable as an alternative in the United States since 1996 and has recently been phased-out under the new European Regulation (2037/2000).

#### *Rigid Foams*

The use of blowing agent blends in the rigid foam sector is gaining broader acceptance. Combinations of liquid HFCs with CO<sub>2</sub> (water) are emerging for some of the more challenging sectors, while HFC/hydrocarbon blends are being considered for others. Blends of different hydrocarbons are also being successfully introduced to further optimise the larger sectors such as appliance foam, boardstock and the various panel technologies.

***Appliance Foam – Domestic Refrigerators and Freezers:*** Energy efficiency continues to be the dominant issue in this field. In the United States, relative energy efficiency of different insulation combinations has been the focus of several studies and more recently, these have been related to cost-effectiveness criteria which support the use of higher cost blowing agents such as HFC-245fa (co-blown with CO<sub>2</sub> (water)) where improved performance justifies it. Significant improvements have also been reported recently in the use of HFC-134a and, commercially, this blowing agent is gaining popularity as a potential next generation blowing agent.

The split between the preferred North American approach and that adopted in the rest of the world remains as stark as ever, with the use of cyclo-pentane/iso-pentane blends becoming ever more dominant in Europe (estimated 60% of market currently) and elsewhere. In addition, there is some use of cyclopentane/iso-butane blends. Pure cyclo-pentane also remains an option technically but is less cost-effective than these other hydrocarbon blends.

The North American situation is claimed by some to be unique because of differences in product design and energy performance requirements. Life-cycle studies are cited as a justification for persistence with HFCs and, in areas of carbon intensive power generation, the argument remains quite compelling. However, the consideration by at least one producer of long-term supply of hydrocarbon blown refrigerators from Mexico sheds some doubt on whether future energy standards will preclude hydrocarbons. Nonetheless, modification of existing designs using more energy efficient components (if available) and the modification of existing foaming facilities are both considered as cost prohibitive in the North American context. Recent draft publications by the Insurance Underwriters Association have been cited to this effect. Safety requirements appear to be considerably higher than those specified in Europe. In addition, several US appliance plants are situated in VOC non-attainment areas and hydrocarbons may not be an option. HFCs are not classified as VOCs in the US, whereas all hydrocarbon options are. For the transition out of HCFC-141b in 2003, three out of the five major North American producers will use HFC-245fa-based systems. One will continue the use of HFC-134a for most of its production but is undecided about the remaining portion. The plans of the other operation remain unclear at this time. A true test of technical options in North America will arise as and when new manufacturing facilities are constructed. Under these circumstances, handling requirements for hydrocarbons could be built in at the outset at more modest cost.

In Japan, all producers but one have moved to hydrocarbon technologies based on cyclopentane rather than blends. The remaining producer is using HCFC-141b for existing models and is investigating alternatives for new models.

Replacement options under the Multilateral Fund continue to be strongly directed towards permanent solutions in the appliance sector, in line with the preference expressed by the Executive Committee. Excellent progress has been made with hydrocarbons in three of the key centres of population in China, India and Brazil. China is estimated to have already achieved a 70% phase-out of previous CFC use with work on the remaining 30% in progress. 60% of the market has switched to hydrocarbons (mainly cyclo/iso blends) and 10% has moved to HCFCs. This latter option is recognised as necessary for the smaller producers, who may move to HFCs in a second transition step.

In contrast, some other developing countries are having more difficulty stimulating transition, either because of size, regulatory constraints or because of domestic economic circumstances and resulting priorities.

***Appliance Foam – Commercial Refrigeration:*** This sector covers supermarket display cabinets, vending machines and other food and drink storage facilities. It is distinguished from such sectors as ‘walk-in’ coolers and cold stores by the fact that these applications do not need to meet building code requirements.

A common global trend is the increasing inclusion of the commercial refrigeration sector in future energy efficiency targets. This is tending to drive manufacturers to more energy efficient solutions and the relatively minor on-going use of CO<sub>2</sub> (water) foams in some vending machine designs may come under further threat. However, the fact that there is significantly more design flexibility in the

commercial refrigeration sector means that there is not quite the same focus on thermal efficiency 'per unit of thickness' as there is in the domestic refrigeration sector. In addition, the moulding process can provide the opportunity to use hydrocarbons for some manufacturers, although not all are convinced that they should follow this route and are waiting for the emergence of liquid HFC solutions.

However, one area creating particular discussion in the vending machine sector is Coca Cola's announcement at the 2000 Sydney Olympics that all of its drink dispensers would be CFC, HCFC and HFC free by 2004. This announcement was closely followed by similar statements from Lever and Fosters Beer. The challenge left facing the engineers of these companies is how to interpret the foam-blowing dimension of these statements. Some assessment of hydrocarbon technologies is on-going in North America in a bid to meet the Coca Cola energy and environmental mandate.

There seems to be little further penetration of vacuum panels in this sector except where there are exceptional thermal requirements (e.g. combined heating and cooling units). Indeed, Sharp has reduced the content of its only commercially available vacuum panel-containing refrigerator from three panels to one in order to make it more cost-competitive. Nonetheless, work continues to assess more cost-effective means of producing vacuum panels and the forthcoming 2002 Technical Options Committee report will investigate progress in more detail.

**Water Heaters:** Again, this area of application is being increasingly impacted by emerging energy standards both in Europe and the United States. In Germany several producers moved initially to CO<sub>2</sub> (water) technology but have now switched to hydrocarbons to ensure the ability to reach a 2003 reduction target in energy usage of 30%. Those still using HCFCs are viewing either hydrocarbons or HFCs as their forward options. Several of the larger global producers are against moving to hydrocarbons on the basis of flammability risks in the factory, particularly where there are substantial product range commitments. However, significant research work continues in North America and initial feedback is more positive concerning hydrocarbons. As with other areas where hydrocarbons and HFCs are under consideration, it is unlikely that there will be only one final solution and both HFCs and HFC/CO<sub>2</sub> (water) are expected to play a role.

**Flexible-faced laminate (boardstock):** Virtually all of the boardstock manufacturers in the United States have decided to change from HCFC-141b to hydrocarbon based technologies. It is not precisely clear whether any dual-strategy<sup>4</sup> options will be retained or whether some niche producers will focus on HFC-245fa. Much will depend on the finalisation of fire testing programmes (especially ASTM E-84 and FM4450) and the results of further field trials. However, in any event, this announcement through PIMA (the Polyiso-cyanurate Insulation Manufacturers' Association) is a landmark step in the phase-out of HCFC-141b use. It is clear that the producers believe they can live with the usually marginal

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<sup>4</sup> A 'dual strategy' in this context relates to having some plants running with HFCs and others with hydrocarbons

loss of insulating efficiency that may result. This view is strengthened by the efforts being made to standardise building codes under the 'International Building Code' initiative. However, this harmonisation of regional codes may also stimulate wholesale improvements in energy efficiency standards in future as concerns over CO<sub>2</sub> emissions increase.

In Japan, most manufacturers are still using HCFC-141b as their prime blowing agent but are looking to either HFCs or hydrocarbons for the next transition. It is not yet clear whether all current fire tests can be met with hydrocarbon-based products and this is likely to be the determining factor on technology.

In Europe, the ramifications of the harmonisation of fire standards (Euroclassification) continue to be assessed and the polyurethane sector is moving increasingly to the use of higher index polyisocyanurate formulations, including, in some cases, the incorporation of aromatic polyester polyols. Most production is with pentane but HCFCs and later HFCs are likely to be required for some fire standards.

The use of HFCs is also coming under renewed discussion as the European Union seeks to develop its Climate Change policy under the European Climate Change Programme (ECCP) process. HFCs have long been identified as significant part of the blowing agent solution for this sector, with both liquid HFCs and blends with HFC-227ea being considered. In addition, blends of HFC-365mfc or HFC-245fa with hydrocarbons are still under review for applications where flammability concerns are less of an issue but where optimum energy performance is required.

***Composite (sandwich) Panels - continuous:*** This market is growing rapidly in Europe and has already reached a level above that of flexible-faced laminate. The ability to dismantle and re-use such panels is a particular benefit for end-of-life management. In blowing agent technology terms, isopentane /CO<sub>2</sub> (water) co-blown predominate. These systems allow low levels of hydrocarbon to be used (1.5 – 2 parts by weight) and thereby permit achievement of current German B2 fire standards and, in some cases, even B1. For areas where very stringent fire tests apply, HCFC-141b continues to be used and this may lead to the uptake of HFCs in due course.

The co-blown isopentane /CO<sub>2</sub> (water) systems have been pioneered in Germany and Holland with France, Spain and Italy following close behind. In the US, a mix of blowing agents are used including HCFC-141b and HCFC-22. HCFC-142b/22 could be a technical option where regulation permits. Hydrocarbon is also an option for Class II applications such as garage door panels. Although continuous production exists in the United States, it should be noted that this only equates to 5% of the parallel market size in Europe. While there is no new information on this market in Japan, it has been noted that China is modifying its fire codes to allow for the wider use of composite panels in construction applications.

From a machinery cost perspective, it is estimated that a line specified for hydrocarbon adds 15- 30% to the overall cost depending on precise configuration and location. This is not viewed as prohibitive by investors when investing in new



equipment and many companies are taking the precautionary step at the outset to avoid a more costly upgrade later.

**Composite (sandwich) Panels – discontinuous:** For discontinuous panel producers the situation is rather more difficult. The costs of upgrade to hydrocarbon are substantial (up to \$0.5 million) and are often beyond the financial reach of smaller businesses, particularly those not supported by outside funding. Nonetheless, several bigger producers have been able to make the transition successfully.

For the majority, HCFC-141b remains the preferred blowing agent in the short-term with the expectation of eventually switching to liquid HFCs. For those applications which are less sensitive to insulation performance and dimensional stability (e.g. doors), the manufacturers are also looking to CO<sub>2</sub> (water) systems and HFC-134a. Liquid HFC/HFC-227ea blends may also have a part to play.

In developing countries, where MF funding has been available, there has been a greater move towards hydrocarbon.

**Spray foam:** There is some interest in the use of hydrocarbons in spray foam systems. However, following the approval of hydrocarbons under SNAP last year, progress in the uptake of this technology has been slowed because of industry consolidations and continued health and safety concerns. Current efforts are being focused on individual Systems Houses<sup>5</sup> rather than the Sprayed Polyurethane Foam Alliance (SPFA) to develop commercially viable foam systems and provide appropriate hydrocarbon blowing agent handling guidance for the industry. There are clear liability issues related to this work and the allocation of this liability between blowing agent suppliers, systems houses and contractors is continues to be a serious source of discussion. Nonetheless, some progress has been made on the training of Systems House staff and in the development of appropriate equipment. It may be that usage at low enough levels (1.5 – 2 pbw of hydrocarbon) could be part of a wider co-blowing option. However, technology of this type is yet to emerge commercially.

The potential for the use of both HFC-245fa and HFC-365mfc has also been under review in the last year. In particular, HFC-245fa has taken a considerable step forward by the emergence of new formulations which are effectively HFC-245fa/CO<sub>2</sub> (water) co-blowing combinations. The particular advantage of these formulations is that they reduce the vapour pressure of the systems sufficiently to potentially allow their handling within existing equipment. There will also be operational savings as a result of the lower usage levels of the blowing agent.

In Europe, blends of HFC-365mfc and HFC-227ea, in addition to HFC-245fa are potentially available for evaluation in spray foam applications. The limited

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<sup>5</sup> A 'Systems House' provides formulated chemical systems (typically polyols and isocyanates) to smaller consumers of foam chemicals

flammability of HFC-365mfc needs special care – particularly in view of the fact that the mixture of HFC-365mfc and HFC-227ea is not an azeotrope.

Pure CO<sub>2</sub> (water) systems have not been ruled out in either of the major markets and new technology developments are bringing the performance of these systems closer to that of other alternatives. However, there may be fire performance issues as well as density and thermal penalties to be considered.

In all cases, the key concern is that technology options have neither been optimised or extensively field trialled at this stage. This fact is causing the industry extreme concerns because of the rapidly advancing phase-out dates for HCFC-141b. Most estimates suggest that a minimum of 3-4 years will be required to take promising candidates to widespread commercialisation.

**One component foam:** These systems are intended primarily for gap filling and are widely used throughout the construction industry. There has been a significant debate about the ability to use hydrocarbons such as butane/propane mixes or dimethylethers in these systems. However, the factory (can filling) process has caused some fires. This phenomenon may be related to charge size, but the industry is now strongly defending the option of using HFCs in future formulations. Since this is essentially an emissive application, there is concern that the widespread use of HFC-134a could have a significant impact on Greenhouse Gas emission targets (already a reality in Germany). Accordingly, HFC-152a is also being considered because of its lower relative GWP. Although HFC-152a is flammable, it can be blended in such a way as to avoid this problem. In the meantime, safety concerns are resulting in the continued use of HCFCs (particularly HCFC-22) where other technologies have not yet been proven.

**PU Block – continuous:** Hydrocarbons have historically been difficult to use in these applications because of exotherm concerns. However, more recently, modified formulations have begun to provide options and it is thought that most continuous block foam production will eventually move to hydrocarbon. Nonetheless, current manufacture is still substantially based around HCFC-141b and may need to move to HFCs in areas where product fire performance is a key issue – for example in polyisocyanurate (PIR) materials for the chemical process sector.

**PU Block – discontinuous:** In the discontinuous block foam sector, there is increased expectation that the market will eventually move towards hydrocarbons. Some estimates suggest that market penetration could be greater than 50% ultimately. However, as with panel manufacture, the move to hydrocarbons will need to progress with the investment cycle since the cost of retrofitting existing equipment is likely to be prohibitive. A new discontinuous plant would be expected to cost in the region of \$400,000 for a pentane-capable plant.

The balance of block foam manufacture is likely to switch to liquid HFCs or co-blown systems with CO<sub>2</sub> (water). However, the extent to which CO<sub>2</sub> (water) can be relied upon will be limited by overall exotherm control and dimensional stability constraints.

***Pipe-in-pipe:*** This application is primarily directed at serving the district heating market, particularly in the more centralised economies in Northern and Eastern Europe. The approach is now, however, finding wider acceptance in other parts of the world as the use of small to medium combined heat and power (CHP) units increases because of their higher efficiency and reduced greenhouse gas emissions.

In this sector, the switch to hydrocarbon technology in Europe took place relatively early because the products have high added value, thereby negating the impact of conversion costs. The main preference is for blends of linear hydrocarbons with cyclopentane. Interest in hydrocarbon based foam systems is also beginning to be seen in North America. In Switzerland, HCFCs continue to be used a little and there is an expectation that there will be a later switch to either HFC-245fa or HFC-365mfc. This trend is primarily driven by the size of the local producers who cannot afford hydrocarbon investments. However, bearing in mind the longevity of district heating systems and the lack of obvious emission mechanisms, this use of HFCs is perceived to present little concern in a global climate change context.

***Refrigerated transport:*** The refrigerated transport sector splits into three prime sub-sectors:

- Fixed road transport bodies;
- Containers and other demountable units;
- Tankers and other shaped vessels.

For the flat sided units, requirements can be met by either pre-fabricated panels, cut block foams or injected/spray systems. The latter is the only real option for tankers and other shaped units.

One of the key constraints on all refrigerated transport is insulation thickness. This is constrained both by the maximum allowable width on the road (or rail) and the minimum internal dimensions required to accommodate standard pallet widths. Of course, this restriction only truly affects the sides of a container and, in most cases, does not impact the ends, roof or floor to the same extent. However, the tendency in the industry has been to maximise thermal efficiency wherever possible and this, in turn, has led to the use of the most efficient insulation materials throughout. On this basis, HCFCs have been the choice of many truck body producers in the last five years, even in environmentally sensitive areas.

More recently some producers of truck bodies have been willing to consider hydrocarbons and take the consequences of a higher energy consumption. However, this is not an option for the container (reefer) sector because the power availability on ships is strictly limited. The majority of global reefer construction is now based in China. This segment will likely consider HFCs in future.

***Picnic coolers/thermoware:*** In developed countries, many of the major producers of picnic boxes and other thermoware have been investigating CO<sub>2</sub> (water) systems. Early adhesion problems appear to have been overcome and those still using HCFCs are likely to switch within the next 2-3 years. This, however, is not the case in developing countries where CFC-11 transitions are typically still

moving to HCFC-141b, at least in part because of the lack of availability of appropriate CO<sub>2</sub> (water) blown systems.

Even the larger producers are reluctant to consider complete conversion to hydrocarbons because of the other non-related operations being carried out in their factories. Nonetheless, one manufacturer in the Philippines has converted to hydrocarbons and this may extend to others in due course. U.S. interest in hydrocarbon is limited but growing, especially for the thermally sensitive product applications. In Italy, one producer is using HFC-134a, and HFC-134a/CO<sub>2</sub> (water) systems may demonstrate wider potential. The only other likely technology in the field will probably be based on liquid HFCs. However, HFC-245fa has too low a boiling point and HFC-365mfc too high a boiling point and both have a lower blowing efficiency. Some blend of the two may therefore prove to be most effective.

#### 9.2.2.2 *Extruded Polystyrene*

The divide between European and North American technologies and markets is becoming increasingly clear as national and European-wide regulations on HCFC phase-out are implemented.

In Europe CO<sub>2</sub> and CO<sub>2</sub>/alcohol systems continue to gain market share generally, except in some markets where traditionally heavy focus is put on thermal conductivity performance. Technological limitations on thickness (i.e. currently no greater than 120 mm) still exist either in actual production or in post-production performance vis-à-vis dimensional stability. HFC-134a, in particular, is the alternative blowing agent preferably selected for those markets and applications where high thermal insulation performance is demanded. Its low polymer solubility is offset by blending either with HFC- 152a or an organic solvent. The XPS industry in Europe has committed to study plant emission reduction potential via recapture and recovery technology for HFCs used in its processes as part of its 'responsible use' justification.

In North America, the XPS industry has not yet identified a way to transition from HCFCs owing to the particular challenges of the North American market. The market and subsequently the manufacturing processes have evolved around lower density products emphasising thermal performance over structural. The preponderance of thin (12 mm) and wide (1200 mm) products, like sheathing, present severe process constraints that are not present in Europe. In some cases the required fire performance within the existing building codes in use across the USA cannot be met at high densities because of the higher fuel loadings. This prevents the adoption of either of the CO<sub>2</sub> or HFC-134a technologies currently making progress in Europe without significant modification. Local producers are working to solve these problems but anticipate that they will need the full ten years available to them under the current regulatory framework to achieve successful transition.

In Japan, there is some hydrocarbon use in XPS. Typically iso-butane is used in conjunction with methyl chloride or ethyl chloride to produce a Grade 1 product with relatively poor insulating properties, suggesting that the hydrocarbon diffuses

out of the foam before use. However, more recently, one manufacturer has announced that it will be able to make a Grade 3 product with a thermal conductivity of lower than 0.028 W/mK. This implies the retention of the blowing agent and immediately raises concerns over the release of blowing agent in a fire as the thermoplastic melts. However, the manufacturers have assured that they can pass JIS standard (JIS A-9511), apparently the only standard for insulation materials in construction applications. However, this standard may have multiple test criteria. Further clarification is being sought on the fire classification structure in Japan.

#### 9.2.2.3 *Phenolic Foam*

The two major markets for phenolic foam materials continue to be in Europe and Japan. The European market is expected to be boosted by the adoption of harmonised fire standards across the EU over the next five years. This will be particularly the case for internal lining materials. However, the effect is less clear for fabricated pipe insulation until the appropriate test configurations and reference scenarios are finalised.

In Japan, one chemical company commercialised its 10 million m<sup>2</sup> continuous laminator in October 2000. In contrast with its European counterparts, the plant will produce a low density hydrocarbon blown system. This again reflects the unusual standard and building code structure in Japan and will be the subject of further coverage in the 2002 Full Report.

In discontinuous block foam manufacturing processes, the combination of process safety and product fire requirements makes phenolic foam is more reliant on liquid HFC formulations than other sectors of the foam industry. Indeed, limited production of foams based on HFC-365mfc is already underway and technical evaluation of HFC-245fa has begun. For the production of pipe sections in particular, consideration is being given to methods of reducing blowing agent wastage during fabrication.

As noted from the Japanese experience, continuous laminate production (boardstock) has greater opportunities for control of blowing agent releases and safety is viewed as something which can be engineered. However, HFCs are still likely to dominate in Europe because of the more stringent requirements of the harmonised fire standards and the need to optimise energy saving.

There is growing interest in sandwich panels using phenolic foam cores, based on the fire performance of the material. However, the presence of a metallic skin is likely to make the selection of blowing agent less sensitive and, for continuous production at least, an engineered solution could emerge for the use of hydrocarbon blowing agents.

#### 9.2.3 *Transitional Status*

A more comprehensive quantitative analysis of ODS use in the foam sector is planned as part of the 2002 Full Report. Accordingly, this section only deals with qualitative issues affecting transition

### 9.2.3.1 *Liquid HFC availability*

The time-lines for the introduction of commercial production of liquid HFCs continue to be focused on the second half of 2002. Both Solvay and Honeywell are already supplying larger scale sample quantities from pilot plant facilities (Solvay produced 300 tonnes of HFC-365mfc from its pilot plant in 2000 and Honeywell now has capacity to produce HFC-245fa of approximately 450 tonnes per year).

Despite this recent availability of semi-commercial quantities of both of these liquid HFCs, some smaller users and systems houses continue to comment that there is now insufficient time to meet the phase-out dates for HCFC-141b, especially in certain sectors of the US foam industry. Because patent issues limit the availability of HFC-365mfc in the US, some have expressed concern that their lack of access to this product will prevent them from developing “truly liquid” systems. However, Honeywell’s efforts to introduce HFC-245fa/CO<sub>2</sub> (water) are viewed by some as beneficial.

HFC-365mfc has been registered as a new chemical in North America, but only currently for solvent uses. However, this means that distribution channels will exist for the chemical as and when the current patent constraints ease (post 2010). In Europe, there is more focus on HFC-365mfc to assist in the transition in the foam sector by 2004. However, the stronger presence of hydrocarbons in the region and the marginal flammability of HFC-365mfc are tending to drive the blowing agent into applications where tailored blends are seen to have particular advantages.

In Japan, Central Glass has also announced that it will produce HFC-245fa for foam applications amongst others. A plant is expected to be on-stream by the middle of 2003.

### 9.2.3.2 *On-going availability of HCFCs for developing countries*

The drop in demand for HCFCs in developed countries will inevitably have a considerable effect on the on-going availability of HCFCs for foam uses. However, plants for the production of HCFCs fall into two categories:

- Dedicated HCFC-141b production units;
- ‘Swing’ plants which can adjust the balance between HCFC-141b and HCFC-142b production.

It is expected that several of the dedicated HCFC-141b plants in developed countries will close after 2004. However, HCFC-142b is required as a feedstock for PvDF manufacture and will be manufactured on an on-going basis. This allows not only for the on-going availability of HCFC-142b but, in the case of ‘swing’ plants, could offer opportunities for the on-going production of HCFC-141b. In addition to this, there are now several dedicated HCFC-141b production units in developing countries (e.g. currently three in China).

Much now depends on how the usage pattern for HCFC-141b will look in developing countries once the CFC phase-out programme is complete. The

Executive Committee of the Multilateral Fund is in the process of commissioning a report to study the likely requirement for HCFC-based technologies in the foam sector, bearing in mind the economics of alternatives and the current rules of the Fund (see the next section).

#### *9.2.3.3 Other issues affecting ODS phase-out in MLF Projects*

The funding of foam projects under the Multilateral Fund continues amidst concern over the cost of non-HCFC technologies for small-scale operations. An attempt to limit the long-term use of HCFCs in developing countries by the European Union was unsuccessful but it is likely that pressure will continue on this subject unless the report commissioned by the Executive Committee of the Multilateral Fund concludes otherwise. Additionally, a Notice of Proposed Rulemaking issued by the US EPA in July last year listed HCFCs as 'unacceptable' blowing agents. This was in stark contrast to the position adopted by the USA historically in international negotiations. It has been stressed since that the proposal was intended as a reflection of the specific alternatives available in the USA and that the position has not changed in respect of the international use of HCFCs. Nonetheless, this classification proposal is now under review and is expected to be dropped, or modified as clearer technical evidence emerges and the Notice is finalised to address technical/economic issues raised through public comment.

The continuing uncertainty over the acceptability of HCFCs as medium-term substitutes in some sectors is causing concern for enterprises who view that they may be forced into further transitions out of HCFCs prematurely. However, phase-out pressures at country level are now forcing decisions and HCFCs are being seen as the most cost-effective solution for the Fund. Announcements such as those cited earlier from Coca Cola, Lever and Fosters Beer are equally causing some confusion with the potential drive to a non-halogenated solution limiting transition options.

#### *9.2.4 Regulatory Activities in Developed Countries*

The US EPA Notice of Proposed Rulemaking is one of several important developments in the regulatory field in the last year. While this continues to be the subject of review prior to finalisation later in 2001, it is not expected that SNAP will approve any significant transitions from HCFC-141b to other HCFCs except, perhaps, in some specialist areas.

The European Regulation (2037/2000) came into force in October 2000, slightly after some of the original 'effective dates' had passed. However, integral skin and polyethylene foam phase-outs were enacted prior to the end of 2000. The regulation continues to enforce the phase-out of varying end-uses in the period from 2002 to 2004 although the Management Committee (made up of regulatory experts from Member States) retains the option to extend deadlines for specific sectors if no technically and economically acceptable alternatives have emerged by the prescribed phase-out date.

There are basically four different regulatory structures being applied to HCFC phase-out currently:

- (1) ODP cap on all HCFC uses with no end-use consideration (e.g. Australia)
- (2) ODP cap on all HCFC uses with end-use monitoring and voluntary action
- (3) ODP cap on all HCFC uses with end-use control (e.g. Europe)
- (4) Planned phase-out of selected ODSs based on their relative ODPs (e.g. USA, Japan)

At present, both Canada and Australia are looking at moving from model (1) to model (2) in order to obtain a better understanding of HCFC phase-out issues. However, Canada is likely to wait on the decisions of the United States before reaching a final conclusion in view of the significant border implications.

### **9.2.5      *Recovery and Destruction***

As attention moves from the Montreal Protocol to the Kyoto Protocol, the focus is switching towards minimising emissions. Several regulators have therefore sought to re-introduce emissions control legislation into their ODS regulations – particularly at end-of-life.

In Japan, it will become a legal requirement in April 2001 for suppliers of appliances to take back old units from the general public. As part of this requirement, manufacturers will be expected to make provision to recover and appropriately dispose of all ODSs remaining in the systems at their return. Several appliance-dismantling units are now in place in readiness for this new law but few are clear as to how much the provision will be used, particularly in view of the fact that a levy will be charged for each appliance returned.

Within the new European Regulation there is a requirement to recover blowing agents from foam at the end-of-life 'if practicable' to do so. The definition of 'practicability' is still under review and the current wording also makes the coverage of this requirement ambiguous. Nonetheless, considerable work is continuing on recovery and disposal technologies involving both the re-use of shredded foam (with blowing agent extracted) and the grinding of foam to a powder. Concern over the need for a common expression of recovery results has been raised by several technology providers and the Foam TOC may need to address this issue as an appendix to the 2002 Report.

In order to establish an emissions baseline, a further project has been initiated in Denmark to assess the rate of release of blowing agent from shredded foam without specific blowing agent extraction. This will provide an insight into the impact of foams already in land-fill sites.



## 9.3 Methyl Bromide Technical Options Committee (MBTOC)

### 9.3.1 *Executive Summary*

Methyl bromide (MB) is used as a fumigant to control pests, mainly as a preplant treatment for soil. Lesser amounts are used for disinfestation of durable and perishable commodities, including for quarantine and pre-shipment (QPS) reasons, and for control of pests in buildings and transport.

This update presents developments in methyl bromide and alternatives that have been reported subsequent to those detailed in the April 2000 Report of TEAP.

This year is the first for non-Article 5(1) countries where methyl bromide controls and requirements under the Protocol cannot be easily met by transitional strategies. It can be expected that there will be strong incentives to adopt non-MB alternatives, induced by lack of supply and increase in MB price. It has been reported to MBTOC that supplies of MB for non-QPS uses are difficult or impossible to obtain in at least some MB-using countries. It is highly likely that supplies of methyl bromide will become increasingly sparse as the year progresses.

Non-Article 5(1) countries have significantly surpassed the reductions required in 1999 under the Protocol. Reported non-Article 5(1) production of controlled MB (i.e. not including production for feedstock and QPS) was reduced from 65,596 tonnes in 1991 (baseline) to 48,039 tonnes in 1999, a reduction of 27%. Equivalent production in 1998 was reported as 60,375 tonnes. Non-Article 5(1) consumption was reduced from 55,923 tonnes in 1991 to about 35,553 tonnes in 1999, representing a reduction of about 36%.

Regulatory processes regarding registration remain major constraints to adoption of some MB alternatives, both in terms of time and cost. This is particularly so where direct treatment of foodstuffs is involved. Because of the small market for alternative chemicals there is often insufficient profit to be made in an MB replacement to justify the expense of developing the required registration data. Despite this, there are some important chemically-based alternatives in process of registration at least for the larger markets. Formulations of phosphine in CO<sub>2</sub> or N<sub>2</sub> are now in increasing use and sulfuryl fluoride is at an advanced stage of registration for some foodstuffs in USA. Mixtures of chloropicrin with 1,3-dichloropropene or other materials have been registered as soil fumigants or are in process in several major MB-using countries.

The EU has introduced a number of controls on MB that are more stringent than those currently agreed under the Protocol. In particular, a new EC-wide regulation mandates an accelerated phaseout relative to the Montreal Protocol timetable consisting of a 60% cut in production and consumption, based on 1991 levels, from January 2001 in EU Member States. The controls also cap, from January 2001, the amount of MB to be supplied for QPS at 1996-1998 levels. For soil treatments, the regulation mandates that the soil is covered with virtually impermeable film (VIF) before fumigation to minimise MB release, or any other techniques ensuring at least the same level of environmental protection.

Field and demonstration trials are in place in both Article 5(1) and non-Article 5(1) countries to test the major alternative procedures over most of the range of crops at present grown with the assistance of MB. These are mainly tomatoes, cucurbits, strawberries (runners and fruit), cut flowers, flower bulbs and tobacco. For all of these crops there are now procedures that have been successfully trialled under full scale conditions that result in product yields similar to those with MB. Further development of application methods for alternatives to improve consistency of treatment delivery will assist their implementation on a wider scale.

There remain problems in identifying MB alternatives for a few special crops, including control of replant problems of some vines and tree crops (e.g. stone fruit, apples, citrus) where the ability of MB to penetrate 60 cm or more into soils is important for effective control of some pathogens.

Soilless culture allows crops and seedlings to be grown without MB, thus avoiding some current uses of MB. The process is in increasing use in non-Article 5(1) countries and some Article 5(1) countries, particularly for tobacco seedling and cut flower production. One impediment to more widespread use in Article 5(1) countries is the perceived need to import the required substrates. There is a continuing need to identify locally available substrates.

Progress in MB alternatives for durable commodities has been mainly in research, development and implementation of existing processes, not development of new processes. Where time for treatment is not a major constraint, there is a range of systems that can substitute for methyl bromide (MBTOC 1998). There are still some applications where the speed of treatment offered by methyl bromide is important. This is particularly so in some pre-shipment and import applications where logistic constraints do not favour use of alternatives, notably phosphine, that require substantially longer treatment times for full effectiveness.

Recapture systems for methyl bromide may be useful in QPS treatments to minimise emissions. Several types of recapture system are now in commercial use. In current installations using activated carbon, the captured MB is decomposed either on site or after transport on the carbon to a central location. An on-site system of recapture/decomposition, developed in Australia, is based on decomposing the recaptured methyl bromide using aqueous thiosulphate solution.

### **9.3.2 Introduction**

Methyl bromide (MB) is used as a fumigant to control pests, mainly as a preplant treatment for soil. Lesser amounts are used for disinfestation of durable and perishable commodities, including for quarantine and pre-shipment (QPS) reasons, and for control of pests in buildings and transport.

This update presents developments in methyl bromide and alternatives that have been reported subsequent to those detailed in the April 2000 TEAP Report.

### 9.3.3 *Production and Consumption*

Controls on methyl bromide agreed at the Ninth Meeting of the Parties require non-Article 5(1) Parties to reduce their production and consumption to 50% of their 1991 production and consumption baseline in 2001, with a further reduction to 30% of these amounts in 2003, both with exemptions from control for QPS uses. The production of MB for basic domestic needs of Article 5(1) Parties will be capped in 2005 at 80% of the average of 1995-98 baseline levels, with exemptions from control for QPS uses.

The latest year for which production and consumption estimates are available is 1999. Figures given here are subject to amendment as some reports are not yet finalised. Data reported by Parties to the Ozone Secretariat shows that previous estimates of MB production by MBTOC were too low. According to Ozone Secretariat data, global manufacture of MB for all uses was reported to be 75,203 tonnes in 1998; MBTOC had previously estimated it to be about 71,400 tonnes. Ozone Secretariat data suggests that global MB manufacture for all uses in 1999 was about 65,428 tonnes, reflecting the controls implemented in non-Article 5(1) countries. Most MB production occurs in the USA and Israel.

Non-Article 5(1) countries have significantly surpassed the reductions required in 1999 under the Protocol (25% reduction from 1991 baseline values). Reported non-Article 5(1) production of controlled MB (i.e. not including production for feedstock and QPS) was reduced from 65,559 tonnes in 1991 (baseline) to 48,039 tonnes in 1999, a reduction of 27%. Equivalent production in 1998 was reported as 60,375 tonnes. Non-Article 5(1) consumption was reduced from 55,923 tonnes in 1991 to about 35,553 tonnes in 1999, representing a reduction of about 37%.

This year, 2001, is the first for non-Article 5(1) countries where methyl bromide controls and requirements under the Protocol cannot be easily met by transitional strategies. It can be expected that there will be strong incentive to adopt non-MB alternatives, induced by lack of supply and increase in MB price. It has been reported to MBTOC members that supplies of MB for non-QPS uses are difficult to obtain in at least some MB-using countries. It is highly likely that supplies of methyl bromide will become increasingly sparse as the year progresses.

Scarcity and levies of various kinds have increased the price of MB substantially, at least in non-Article 5(1) countries. For example, estimates (J. Sansone pers. com.) for methyl bromide prices in west coast USA are \$US2.5-2.9 (1995), \$ 2.8-3.3 (1996), \$3.1-3.9 (1997), \$3.7-4.4 (1998), \$4.4-6.6 (1999), \$6.6-8.8 (2000) with \$8.8-11 per kilo estimated in 2001.

MB was on average 38% more expensive in the EU in 1998 compared with prices paid in 1991 (see table below) (Batchelor and Ohm 1999). Since about 75% of the MB was imported from countries outside the European Union, it is possible that some of this increase in price was due to declining foreign exchange rates against the US dollar during this period and therefore not due solely to the demand-supply of MB in the market.

Percentage change in the cost of methyl bromide charged by importers for methyl bromide sold in the EC in 1998 compared with 1991 (European Commission 1999).

Country	Change in cost ('98/'91)
Spain	25 – 110% increase
Portugal	28% increase
Greece	24% decrease to 70% increase
France	7 – 20% increase
Italy	77 – 114% increase
Belgium	16% increase
Germany	45% increase
Netherlands	24% decrease
Overall, average price has increased 38% in 1998 compared to 1991	

The prices recorded in Italy were the highest within the EC and showed an increase of 77-114% over this 7 year period.

Details of methyl bromide consumption for QPS purposes will be collected by MBTOC in 2001. This use is exempt from control under Article 2H of the Protocol. However, this remains one of the largest emissive uses of an ODS not controlled under the Protocol. The estimated use of MB for QPS in 1996 (TEAP 1999) of 15,000 tonnes corresponds to an emission of 6,570 ODP-tonnes at an ODP of 0.6 and an average emission to usage ratio of 0.73 (MBTOC 1998). According to the data reported by Parties so far, production for QPS purposes rose from 7,998 tonnes in 1998 to 11,410 tonnes in 1999.

Destruction of 980 tonnes was reported to the Ozone Secretariat in 1999.

Article 5(1) Parties reported production of 2,382 tonnes in 1999, with 700 tonnes of this for QPS purposes. 1995 production was reported as 596 tonnes. Much of this increase resulted from a joint venture established in 1995 between Israel's Dead Sea Bromine Group and Lianyungang Seawater Chemical Industry Plant in China (SEPA-UNEP 1999). Recently, Linhai Jianxin Chemical Co. has also established commercial MB fumigant production in China (Yongfu Zhou pers.com).

### 9.3.4 Methyl bromide regulations and policy

Regulatory processes regarding registration remain major constraints to adoption of chemical alternatives to MB, both in terms of time and cost. This is particularly so where direct treatment of foodstuffs is involved. Registration for use on foodstuffs requires development of an extensive data package including costly long term feeding studies. Because of the small market for alternative chemicals there is often insufficient profit to be made in MB replacements to justify the expense of developing the required registration data. Despite this, as noted below, there are some important chemically-based alternatives in process of registration at least for the larger markets.

The EC in its Regulation (EC) No 2037/2000 on substances that deplete the ozone layer has introduced a number of controls on MB that are more stringent than those currently agreed under the Protocol. In particular, there is an accelerated phaseout

relative to the Montreal Protocol timetable consisting of a 60% cut in production and consumption based on 1991 levels from January 2001 and a 75% cut from January 2003 leading to phase-out in 2005. EU Member States are obliged to report to the European Commission annually the volumes of methyl bromide used for QPS and progress being made in evaluating and adopting alternatives. It also caps, from January 2001, the amount of MB that can be used for QPS. Any Member States still using MB for QPS are also obliged to report to the European Commission annually the volumes of MB used for this purpose and on progress being made in evaluating and adopting alternatives. For soil treatments, the regulation mandates that the soil is covered with virtually impermeable film (VIF) before fumigation to minimise MB release, or any other techniques ensuring at least the same level of environmental protection.

In USA, and Canada, domestic regulations (Environmental Protection Agency, 2000; Department of the Environment, 2000) are now in place to align their methyl bromide phaseout with that of the Montreal Protocol, replacing more rapid schedules under the US Clean Air Act and the Canadian Environmental Protection Act. In the USA, the regulations are silent on any exemptions for QPS use. A regulation that will delineate a process for exempting quantities of methyl bromide used in the U.S. for quarantine and pre-shipment from the reduction steps in the phaseout schedule is expected to be available during 2001.

In Japan, the registrations of existing substitutes for MB have been extended to cover many more pests and diseases as a result of extensive tests, partly sponsored by the government. There has been Japanese government funding for field and demonstration trials to encourage farmers to take up alternatives.

### **9.3.5 *Progress in development and use of alternatives***

In the discussion below, the term ‘alternative’ is used in the sense defined in the MBTOC 1998 Assessment. Applicability and expectations for alternatives differ widely in different technical and economic situations.

#### **9.3.5.1 *Alternatives for soil treatments***

Field and demonstration trials are in place in both Article 5(1) and non-Article 5(1) countries to test the major alternative procedures over most of the range of crops at present grown with the assistance of MB. These are mainly tomatoes, cucurbits, strawberries (runners and fruit), cut flowers, flower bulbs and tobacco. As noted previously (MBTOC 1998) there are many production systems in use for these crops that are not reliant on MB, but there are others where MB treatment of soil for their production has become established practice in particular regions and markets. For all of these crops there are now procedures that have been successfully trialled under full scale conditions that result in pest control and product yields similar to those with MB. Raising awareness of alternatives for farmers and further development of application methods for alternatives to improve consistency of treatment delivery will assist their implementation on a wider scale.

There remain problems in identifying MB alternatives for control of replant problems of some vines and tree crops (e.g. stone fruit, apples, citrus) where the ability of MB to penetrate 60 cm or more into soils is important for effective control of some pathogens. None of the existing alternative fumigants appear to provide the same depth of control as methyl bromide. Currently, MB has been identified as the only treatment to assist replant of ginseng in China and for suppression of soilborne virus of cucurbits and peppers in Japan. Progress is being made with alternative replant treatments for vines and tree crops (e.g. Trout and Ajwa 2000, McKenry 2000, Schneider et al. 2000), but a single trial may take several years to conduct in order to assess final fruit yield. Initial vigour is not necessarily an indication of productivity (Stirling et al. 1995).

Growing crops and seedlings in soilless culture presents a way of avoiding some current uses of MB. The process is in increasing use in non-Article 5(1) countries and some Article 5(1) countries, particularly for tobacco seedling production on float trays and hydroponic production of cut flowers. One impediment to more widespread use in Article 5(1) countries is the perceived need to import the required substrates. There is a continuing need to identify locally available substrates. Increasingly materials such as rice hulls, pumice and coconut fibre are being used but further attention is needed to this problem to assist MB replacement.

#### *Transitional strategies*

Phaseout schedules have been met in some countries, e.g. Australia and USA, not by direct adoption of alternatives, but by substitution of part of the MB dosage by other materials, particularly chloropicrin. In southern Europe, mixtures of MB/chloropicrin and other products mixed with chloropicrin are being used as replacements for MB. This strategy allows time for development of alternatives while reducing MB use. MB/chloropicrin mixtures (50:50 or 30:70) have been found to be particularly effective, giving superior control of fungi and nematodes compared with MB alone though some MB is needed for control of weeds if they are not controlled by other means.

The schedule of controls for MB under Article 2H are such that non-Article 5(1) countries will only be able to use this strategy for about three more agricultural seasons to meet consumption targets. Thereafter current users of MB will be forced to adopt MB-free alternatives. Nevertheless the experience gained using high proportions of chloropicrin (e.g. 50:50) has led to improved application technology for application of chloropicrin mixtures with other materials such as 1,3-dichloropropene.

Barrier films (VIF, virtually impermeable films) are increasingly being used with MB. Unlike polyethylene-based films or tarps, these films are relatively impermeable to MB. As a result they contain the MB gas better in the treated soil, leading to higher retained concentrations for a given dosage together with longer effective exposures. With skilled application of the VIF, MB dosage can be reduced substantially while leading to the same level of control of pathogens, pests and weeds as obtained with polyethylene films.

New types of barrier or VIF films continue to enable rate reduction in methyl bromide of up to 50%, where high rates (e.g. 50 g m<sup>-3</sup>) were formerly used and still maintain effective control of weeds and pests. These new films have better handling qualities and are becoming relatively cheaper (approx. 1.5 to 2.0 times the cost of standard polyethylene) compared to VIF films produced several years ago, and there are efforts being made to reduce their cost still further.

#### *Chemical alternatives*

1,3-dichloropropene (Telone®) and mixtures with other materials.

Research internationally continues to show that mixtures of 1,3-dichloropropene/chloropicrin are one of the more promising immediate fumigant alternatives to MB, although metham sodium and dazomet, alone or in conjunction with chloropicrin, are being used in countries where 1,3-dichloropropene has not been registered (e.g. see papers in MBAO 2000). Present regulations on 1,3-dichloropropene on area quotas, buffer zones and personal protective equipment can be very restrictive. These restrictions are currently under review in USA and there is research to refine the regulations on use of this material (Houtman 2000). New emulsifiable (EC) formulations of 1,3-dichloropropene and chloropicrin are providing results equivalent or better than that provided with methyl bromide and offer potential for treatments of soils in protected environments (greenhouses) where user safety issues are preventing use of other fumigant alternatives.

In the last year, trials evaluating new combinations of fumigant products produced results equivalent to MB. For instance, in the USA, drip application of EC 1,3-dichloropropene and chloropicrin has proven to be an excellent alternative for strawberries in California. The development of a coulter plough application rig allows the use of the 1,3-dichloropropene /chloropicrin combination in the sandy soils of Florida.

In Canada, fumigation with a 1,3-dichloropropene/chloropicrin mixture (Telone® C-17) provided excellent control of viable seeds (>80%) and weed species (>90%) in soils of Nova Scotia strawberry nurseries. Combination treatments, such as with 1,3-dichloropropene and metham sodium increased weed control an additional 5-10%, reducing the high cost of manual and mechanical weed control (Jensen, 2001)

Chloropicrin alone is an irritant with an offensive odour. However, it is said chloropicrin odour is mitigated by mixture with 1,3-dichloropropene. In Japan, a mixture containing chloropicrin (40%) and 1,3-dichloropropene (52%) is registered under the trade name of Soilean®. Other mixtures of these compounds are under development.

Registration or re-registration of 1,3-dichloropropene, and mixtures with chloropicrin, for soil use are being actively sought in several MB-using countries. 1,3-dichloropropene was recently reregistered in USA (Houtman, 2000).

## Furfural

Furfural as an aqueous emulsion has been shown to have good nematicidal and weed control properties. These are enhanced by addition of mustard oil or various natural isothiocyanates (Rodriguez-Kabana 2000a).

## MITC (methyl isothiocyanate) generators

Metham sodium is often considered as an alternative to MB, in addition to its uses where MB is not normally used. Its effectiveness is improved if applied under tarping as with MB. This is now increasingly used in trials on comparative effectiveness compared with MB. Slow release of MITC from soil means that longer plant back times (up to 8 weeks) may be required (Porter et al, 2000), especially in cool climates.

Metham sodium in combination with chloropicrin under plastic is as effective as MB for open field strawberry fruit production. Presently the products cannot be mixed. However, machinery has been developed which allows injection of the two products without contact during application.

## Methyl iodide and other iodinated compounds

Methyl iodide, a potential 'drop in' replacement for MB, is receiving more interest now a commercial partner has been found (Allan and Schiller 2000). Registration is being projected for USA and Japan within two to three years. The product is still likely to be expensive relative to current MB prices and the availability of iodine could be restrictive.

Recent trials on the efficacy of methyl iodide, in conjunction with chloropicrin, showed similar performance to a MB/chloropicrin mixture for production of strawberries and tomatoes (Allan and Schiller 2000). Because of its water solubility, it can be applied through a drip irrigation system (Sims and Stranghellini 2000).

Plantpro45®, an iodinated mixture, has shown promise as a MB replacement in laboratory trials and in field experiments with tomatoes, giving similar yields to MB with control of several pathogens and nematodes (Adams et al. 2000).

## Nematicides

Fostiazate (Nematorin ace®) is promoted for farmers in Japan to control nematodes. Applications of chloropicrin following fostiazate or fostiazate following dazomet are under development. These approaches are very effective in controlling nematodes that survive single fumigant applications.

Enzone (sodium tetrathiocarbonate), a carbon disulphide generator, is registered in France and Spain. It is effective against nematode and insect pests (Quenin, in press).



Avermectin was trialled under a UNIDO demonstration project in China (MP/CPR/97/125). It was found to be very effective against nematodes in protected cultivation systems for vegetables and strawberries. It has a number of advantages as a nematicide compared with MB. These include low toxicity and cost, no waiting time before planting after application and it can be applied under cold conditions effectively. However it has no effect on soil pathogens and weeds, which need to be managed by other means. Worldwide it lacks registration as a nematicide and needs further studies to determine if its use is acceptable.

#### Propargyl bromide

Propargyl bromide is showing some promise as a direct MB replacement, though at higher dosages than MB (Dungan et al., 2000). It is active against nematodes, weed seeds and pathogens in soil and has similar physical properties to MB. Relatively high rates of application and tarping may be required for full effectiveness (Rodriguez-Kabana 2000b). Trials with propargyl bromide on tomatoes gave good control of nutsedge and the nematode, *Meloidogyne incognita*, with good yield of fruit (Noling et al. 2000).

#### Potassium azide

A liquid formulation of potassium azide was found to be highly nematicidal with reasonable activity against weeds in greenhouse trials (Rodriguez-Kabana 2000c).

#### Sulfuryl fluoride

Preliminary results show sulfuryl fluoride is effective against root knot nematodes in protected cultivation (Cao et al, unpublished data).

### *Biological and non-chemical alternatives*

#### Cultural processes

New production methods, floatation trays, substrates and plug plants continue to gain greater acceptance as alternatives to MB for certain crops, which in the past have been produced in soil, notably tobacco seedlings, cut flowers, and strawberry runners. In northern and central Europe, and in Canada, crops grown in glasshouses and plastic houses, utilising substrates and hydroponics, are producing crops of high quality and yields that are competitive with crops grown in soils treated with methyl bromide. In southern Europe, lower labour costs and climate have enabled methods, such as solarisation and grafting, to continue to gain acceptance. Float trays and hydroponic production are in increasing use in Article 5(1) countries for tobacco seedlings and cut flower production respectively.

Non-chemical techniques and integrated pest management are gaining greater acceptance as suitable sustainable options for soil disinfestation without methyl bromide. For instance the use of biofumigant crops in the rotation has been adopted by 10% of strawberry runner growers in Australia, composts adopted on some strawberry farms in North Carolina and trap crops, biofumigants and solarisation have been used successfully in many Mediterranean countries.

## Flooding

In some regions of Japan, flooding is used to control soil-borne diseases and nematodes in the production of eggplant, tomatoes, strawberries and cucumbers (A. Tateya, pers. com.).

Crop rotation, in Japan, between root crops (e.g. sweet potato, taro or burdock) and rice efficiently controls nematodes in the soil through the flooding of the paddies during the rice phase.

## Steam

Steam treatments have long been recognised as alternatives to MB in protected cropping and nursery systems. However cost, lack of suitable equipment and length of time for treatment has tended to prevent its use in open field systems. Increased efficiency of newly developed steam generators has seen an increase in the use of steaming for protected cropping systems. However, cost is still preventing broad scale adoption in open fields. A machine for treatment of open fields with steam has recently been introduced (Wilke Recycling Systems, UK). Steam is also used for field treatments in the USA by a large grower of ornamentals (Yoder Brothers).

## Solarisation

Solarisation has been accepted as a stand alone process for soil disinfestation in many regions of the world, where hot climates can be expected reliably and where crop production can tolerate the 4 to 6 week treatment time.

In those parts of Japan with sufficient sunshine and temperatures, solarisation is widely adopted by farmers. It is not feasible where water is limited or the soil is very porous, as it relies on water saturation for effectiveness. Water is applied through irrigation lines placed below the vinyl sheeting used in the solarisation process.

### *Case studies*

A recent publication by UNEP DTIE (Batchelor 2000) presents case studies from 13 different regions in the world where IPM treatments of soil have been applied successfully and offer techniques to use instead of methyl bromide. The techniques include solarisation, substrates, organics, grafting and biological controls. As markets are increasingly demanding pesticide free produce, farmers and researchers worldwide should consider development of more sustainable options as part of the search for and implementation of methyl bromide alternatives.

#### *9.3.5.2 Alternatives for durable foodstuffs and structures*

Progress in MB alternatives in this category of use has been mainly in research, development and implementation of existing processes, not development of new processes. Where time for treatment is not a major constraint, there is a range of systems that can substitute for methyl bromide (MBTOC 1998). There are still

some applications where the speed of treatment offered by methyl bromide is important. This is particularly so in some pre-shipment and import applications where logistic constraints do not favour use of alternatives, notably phosphine, that require substantially longer treatment times for full effectiveness.

Use of high concentrations of phosphine fumigant potentially can reduce treatment times to a few days without compromising effectiveness, but treatments of less than 3 days exposure do not appear possible if all stages of major grain pests are to be eliminated. Rapid supply of high concentrations of phosphine has been made possible by recent developments in phosphine supply systems by generators (e.g. Waterford and Asher, in press) or as compressed gas (e.g. Bridgeman et al., in press). A significant concern is the emergence of substantial levels of pest resistance to phosphine. Control of resistant strains may require reversion to MB in the absence of other alternatives.

In the port of Hamburg, Germany, phosphine is typically used to disinfest imported cocoa beans. In event of failure of this treatment permission is given to use MB. The failures may be from resistance, low commodity temperatures or short exposure times.

Phosphine has replaced MB in treatment for almost all the Californian walnut crop in long term storage facilities, a use previously thought not possible because of potential for taint on the nuts. Disinfestation of early season walnuts destined for immediate shipment to meet premium markets is currently carried out with MB under vacuum. In trials to date vacuum fumigation with sulphuryl fluoride was found to be as fast and effective as MB treatment under vacuum and, subject to registration, could replace MB for this application (Zettler and Leesch 2000). The application was identified by MBTOC (1998) as one of the few treatments of durables lacking alternatives.

Registration continues to be a major difficulty facing potential chemical alternatives to MB. A number of these alternatives are being progressed through the required reviews and data collection. Registration is currently being sought for sulphuryl fluoride, and carbonyl sulphide for fumigation of foodstuffs. Either of these fumigants has potential to replace significant portions of remaining MB use on durables.

Registration in USA has been granted for use in structures and on durable foodstuffs for a formulation, Eco<sub>2</sub>fume®, of phosphine mixed with CO<sub>2</sub> in cylinders. Its registration is being sought in the EU. Another formulation of phosphine, as a compressed gas in nitrogen, is in use for fumigation of imported durables into Germany, using a high dosage/ short exposure strategy (2 to 3 days at 4 g m<sup>-3</sup>).

The application of heat is now commercially in practice in Germany for the control of insects in stored product and also cockroaches in empty flour mills or other factories. Heat is generated either from burners outside a premise and ducted in by use of large diameter hoses or from several explosion protected electrical heaters which are distributed within a premise. This technique is also well established for the disinfestation of insects in wood in roofs, formerly carried out with MB.

Guidelines for non-MB control of pests in Danish flour mills have recently been published (Asthon and Lange 2000).

### *Case studies*

A recent publication by UNEP DTIE (Batchelor 2000) presents 5 case studies of the implementation of non-MB strategies for disinfestation of commodities or structures, or for the avoidance of the need for MB fumigation. Processes include nitrogen treatments, hermetic storage, diatomaceous earth use, heat treatments and Integrated Pest Management systems.

#### Vacuum treatment and hermetic storage

Hermetic storage systems for storage of grain are available commercially. These flexible sealed systems use natural metabolic processes to remove the oxygen within the store to create an inert storage atmosphere that controls insects and other pests, thus avoiding the need for fumigation. Whilst the process is relatively slow it appears quite promising for long-term (over 6 months) storage.

Simple systems that use vacuum within a storage structure to eliminate pests are under development (Navarro et al., in press). These utilise a fully sealed, flexible storage. After loading, a small vacuum pump is used to reduce the pressure within the structure to less than 30 mmHg. This results in insufficient oxygen concentration in the store for long term survival of insects and similar pests. This very simple process appears suitable for many situations including areas of Article 5(1) countries with limited infrastructure.

#### Ethyl formate

Ethyl formate is one of the few candidate replacements for MB that can match MB's speed of treatment (Damcevski and Annis, in press). Successful field trials have been carried out on disinfestation of wheat, barley, canola and oats and of milling plant and machinery (Annis and Graver 2000). It is registered as a fumigant for dried fruit in some countries and is an approved food additive.

#### Propylene oxide

Propylene oxide is under re-evaluation as a fumigant for durable foodstuffs, particularly nuts in store. It is currently registered as a sterilant on nutmeats, cocoa and spices in USA. A rapid fumigant is needed to disinfest walnuts ex USA from codling moth to meet European import requirements. In addition to propylene oxide, methyl iodide, carbonyl sulphide and sulphuryl fluoride are under evaluation (Zettler and Leesch 2000).

#### CO<sub>2</sub>

Machinery capable of disinfesting milled rice in an in-line process using high pressure CO<sub>2</sub> has been developed in Japan (Nakakita et al., in press). The process can give more rapid disinfestation than MB, but its complexity and cost is likely to restrict its use.

CO<sub>2</sub> at atmospheric pressure was demonstrated as a replacement for MB in the export fumigation of dried figs from Turkey using gastight flexible systems to contain the CO<sub>2</sub> gas (Ferizli and Emekci 2000). Carbon dioxide fumigation in warehouses and silo bins is now approved as a disinfection procedure in Japan.

#### Sulfuryl Fluoride

In the USA, work on sulfuryl fluoride is proceeding swiftly to establish a use pattern on food and for food processing facilities, with registration expected by 2002. Research shows this material to be efficacious against most stored product pests, without impacting taste. This material looks to be a good replacement of MB for dried fruits and nuts and in flour and grain mills. Whilst there is concern regarding elimination of the egg stage, tests have shown that by varying concentration, exposure time and temperature, effective doses for all life stages can be implemented.

#### 9.3.5.3 Alternatives for timber, wood and wooden materials

Most treatment of timber, wood and wooden materials such as furniture or wooden packing material with MB probably falls under the QPS exemption from control. Work continues aimed at finding a more suitable and non-ODS alternative to MB for these materials.

#### Vapour heat treatment

Pine wood nematode, *Bursaphelenchus xylophilus*, infesting wooden packages for export to China from Japan, are treated by vapour heat (56C for 30 minutes) (F. Kawakami, pers.com).

#### Methyl isothiocyanate (30% MITC in CO<sub>2</sub>)

In laboratory tests pine wood nematodes infesting red pine lumber (15cm×15cm×30cm) were killed completely by MITC fumigation with 40g m<sup>-3</sup> for 24 hours or 20g m<sup>-3</sup> for 48 hours at 15C, at 25% loading (Soma et al., in press). MITC is available in cylinders in Japan as a compressed gas. Large scale tests with this process are planned in Japan in 2001 (F. Kawakami, pers. com.).

No effect was observed on the nematode by sulfuryl fluoride fumigation at 40g m<sup>-3</sup> for 24 hours at 15C or 20g m<sup>-3</sup> for 48 hours at 15C, respectively (Soma et al., in press).

Forest insect pests (wood borers, bark beetles, ambrosia beetles, longicorn beetles, weevils) were killed by MITC fumigation at 40-60g m<sup>-3</sup> for 24 hours at 15C (Naito et al., 1999). The fumigant was registered for forest insect pests in December 2000 in Japan. Tests under sheets with import logs as a quarantine treatment are planned using with the schedule, 40g m<sup>-3</sup> at 15C for 24 hours, in Japan in 2001.

## Sulfuryl fluoride

Fumigation of flour mills using sulfuryl fluoride has been carried out in Germany and UK during the last 18 months on basis of experimental permits. Sulfuryl fluoride is now in regular use for disinfestation of timber in church roofs in Germany (C. R. Watson, pers. com.).

### Sulfuryl fluoride /MITC mixtures

In laboratory tests forest insect pests were killed by a mixture of sulfuryl fluoride at  $20\text{g m}^{-3}$  and MITC at  $20\text{g m}^{-3}$  for 24 hours at 15C. Further tests are planned. MITC is unsuitable for warehouse and ship fumigation because of its high sorption on fumigation facilities and its nasty odour (F. Kawakami, pers. com.).

### *Sulfuryl fluoride/methyl bromide mixtures*

Forest insect pests, except for ambrosia beetle, were killed by a mixture of sulfuryl fluoride at  $30\text{g m}^{-3}$  and methyl bromide at  $15\text{g m}^{-3}$  for 24 hours at 15C. The methyl bromide dosage was one-thirds or two-thirds less with the gas mixture than when used alone ( $32.5\text{g m}^{-3}$  or  $48.5\text{g m}^{-3}$ , depending on ambient temperature) (Soma et al., 1999).

#### 9.3.5.4 *Alternatives for perishable commodities*

Almost all MB treatments of perishable commodities, principally fruit and vegetables and cut flowers, are carried out as QPS treatments.

To date, few alternatives have actually replaced MB. This is primarily because the potential alternatives may be effective at controlling pests but cause unacceptable damage to the commodity, or, once proven effective, there are delays caused by the regulatory processes and bilateral negotiations that are needed to establish a new quarantine treatment.

## Phosphine

Until recently, phosphine was not considered as a potential MB replacement for treatment of perishable commodities. Recent developments in the supply of phosphine as a fumigant have made its use much more attractive and potentially feasible. These include formulations in gas cylinders such as Eco<sub>2</sub>fume® and phosphine generators to replace in situ generation of the gas from metal phosphide formulations. The gas can be supplied quickly and free of damaging contaminants such as ammonia.

In Australia, Eco<sub>2</sub>fume® has been shown to disinfest oranges from larvae of *Bactrocera tryoni*, pears from *Epiphyas postvittana* and apples from larvae of *Cydia pomonella* without injuring the produce (Williams and Ryan, in press). In Japan (F. Kawakami, pers. com.) mites *Tetranychus urticae*, *T. kanzawai* and *Eotetranychus sexmaculatus* were controlled at 15C by phosphine from a generator on Japanese apples, pears and grapes without damage to the fruit.

### **9.3.6      *Recapture systems for methyl bromide***

Decision XI/13(7) urges Parties to adopt recovery and recycling technology, where technically and economically feasible, to reduce emissions of methyl bromide when used for QPS, until alternatives to methyl bromide for quarantine and pre-shipment uses are available. Recapture technology also presents a transitional strategy to reduce emissions while alternatives are developed for non-QPS MB applications.

There are now available both activated carbon and zeolite-based MB recapture systems. The carbon systems are not well suited to recycling because of the low purity of the raw recaptured material. In current installations the captured MB is decomposed either on site or after transport on the carbon to a central location.

An on-site system of recapture/decomposition has been developed in Australia (Nordiko 2001). This system uses activated carbon to capture the MB after a fumigation. The sorbed MB is decomposed by immersing the carbon in aqueous thiosulphate solution, giving methylated thiosulphate and bromide ion products. The resulting solution can be disposed of as industrial waste and the carbon can be dried and reused. The process has been demonstrated on a modified 40' container for timber fumigation and a clip-on unit has been produced that allows fumigation of a container with MB and subsequent recapture.

A version of this system is being installed for MB recapture at Hobart, Australia on fumigation chambers treating export apples with MB.

A large scale recapture plant is undergoing commissioning at Watsonville, California on a fumigation system for export strawberries. This operates using activated charcoal contained in a sealable and removable canister. After absorbing methyl bromide, the canister is sealed and transported to a disposal centre where the carbon is burnt under controlled conditions, destroying the sorbed gas.

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## 9.4 Refrigeration, A/C and Heat Pumps Technical Options Committee (RTOC)

### 9.4.1 *Executive Summary*

As a non-ODP refrigerant, HFC-134a currently fulfils an important role in almost all refrigeration and air conditioning sectors, from domestic refrigeration to large size chillers, and particularly in mobile air conditioning. The application of HFC blends is also growing. The use of hydrocarbons, especially R-600a, is steadily increasing in domestic and commercial refrigeration. In commercial refrigeration systems, the use of secondary loop systems with propane, hydrocarbon blends, and ammonia is also growing. Intensive work is going on in the field of carbon dioxide cycles for the sub-sectors mobile air conditioning, commercial and transport refrigeration and unitary air conditioning.

HC-600a and HFC-134a continue to be the dominant alternative refrigerants to replace CFC-12 in domestic refrigeration new equipment. In commercial refrigeration, the use of hydrocarbons in stand-alone equipment has started, particularly in Europe. Here the “distributed system” –a system with the compressor close to the rest of the refrigeration system-- drastically limits the length of refrigerant pipes applied and consequently leads to a substantial reduction of the refrigerant charge applied. In the ship-subsectors HCFC-22 is still the main refrigerant used and its substitution in new ships shows a very slow start. Other fluids such as ammonia, which is one of the promising alternatives for this application, have so far not gained much importance due to the high initial costs. In unitary air conditioning during the past three years, developed country manufacturers have continued to commercialise non-ODP technologies, mostly HFC based products. The dominant HFC refrigerants being employed are the blends R-407C and R-410A. HCFC-22 remains the most commonly used refrigerant in positive displacement chillers. Manufacturers have introduced new equipment employing HFCs including R-134a (particularly for water-cooled chillers), R-407C (particularly for air-cooled chillers), and less commonly R-404A, R-717 (ammonia), and R-1270 (propylene). Following the CFC phase-out, the principal refrigerants used in centrifugal water chillers have been HCFC-123 and HFC-134a. New products continue to be offered for both of these refrigerants. For existing centrifugal chillers, the replacement or retrofit of chillers using CFC-11, CFC-12, or R-500 continues to be a slow process.

In vehicle air conditioning, HFC-134a is the only refrigerant used in new equipment. Substantial activities are underway to develop alternatives to HFC-134a air conditioning systems for vehicles, in particular the trans-critical carbon dioxide cycle and the hydrocarbon (secondary loop) system. Both the carbon dioxide systems and the secondary loop systems are assumed to have energy efficiencies comparable to HFC-134a.

Refrigerant conservation has seen an accelerated development during recent years, mainly due to the completion of recovery, recycling and reclaim schemes in a number of countries. The primary options for limiting (any refrigerant) emissions are the use of alternative refrigerants and refrigeration technologies, reduced

refrigerant charge, improved containment, and recovery with recycling and/or destruction.

There is increasing emphasis in all sectors upon the importance of achieving high system energy efficiency to minimise the indirect global warming from energy related CO<sub>2</sub> emissions.

Experience in different countries where certain policies have now been implemented for a certain period would be useful to analyse at present in order to evaluate the most effective means to limit refrigerant emissions.

#### **9.4.2 Introduction**

Refrigeration, air conditioning and heat pumps include a number of distinct applications such as domestic, commercial and transport refrigeration, unitary air conditioning, chillers, and vehicle air conditioning. The following is an update of the development and progress made in several refrigeration and air conditioning sectors.

#### **9.4.3 Refrigerants**

Where it concerns non-ODP refrigerants, HFC-134a currently fulfils an important role in almost all refrigeration and air conditioning sectors, from domestic refrigeration to large size chillers, and particularly in mobile air conditioning. Next to HFC-134a, blends of HFCs such as R-404A, and to a lesser extent R-507 and R-407C are applied in the majority of commercial refrigeration equipment, and the blend R-410A is applied in transport refrigeration. HFC blends such as R-407C and R-410A are important replacement candidates for unitary air conditioning, as well as in chillers, however, less commonly in the latter.

The use of hydrocarbons, especially R-600a, is steadily increasing in domestic and commercial refrigeration. In commercial refrigeration also propane and hydrocarbon blends are applied, however, together with secondary loops. Limits to the charges applied are dependent on national regulations. Propylene is applied in some supermarkets in Germany with indirect systems, with refrigerant charges up to 30 kg. Propane is also applied in some unitary air conditioning products and in some transport refrigeration equipment, particularly in Europe. In some water cooled chillers, the use of hydrocarbons, such as propylene, is expanding from a small base. Hydrocarbons are also being applied in retrofits of vehicle air conditioning equipment in places where local regulations permit their use in these systems.

Ammonia has its traditional share in several sectors, particularly ones with large size equipment. Its application is growing, not so much as an alternative to HFCs, but as an efficient low GWP alternative to HCFCs (and CFCs). It is increasingly being applied in smaller equipment, together with the use of secondary loops, however, the minimum capacity (50 kW) sets limits to its use at the lower end.

Research and development has been initiated into the use of CO<sub>2</sub> systems with the trans-critical vapour compression cycle. Intensive work is going on in this field for

the sub-sectors mobile air conditioning, commercial and transport refrigeration and unitary air conditioning, each of them having specific requirements. If R&D prove to be successful, CO<sub>2</sub> systems may be commercialised in 4-7 years, particularly in vehicle air conditioning. Possible dates for other sectors are less certain; however, these systems may appear on the commercial refrigeration market in the short term.

#### **9.4.4 Domestic Refrigeration**

More than 80,000,000 domestic refrigerators and freezers are produced annually for food storage use in dwelling units and other non-commercial areas throughout the world. Life style and food supply infrastructure differences drive widely varying consumer preferences among different global regions.

HC-600a and HFC-134a continue to be the dominant alternative refrigerant candidates to replace CFC-12 in domestic refrigeration new equipment. Other alternative candidates have only regional niche appeal, primarily driven by established chemical production capability. Long term new equipment options will likely be limited to these two refrigerants. HC-600a is currently being used in about 50% of the refrigerators being produced in Europe. Both refrigerants, HFC-134a and HC-600a, have demonstrated mass production capability for safe, efficient, reliable and economic use. The application of HC-600a or HFC-134a provides approximately equal efficiency. Refrigerant selection is a strategic decision; comprehensive refrigerant selection criteria include safety, environmental, functional and performance requirements, export market opportunities and regulatory differences. Either alternative refrigerant may be the “right answer” for a specific set of conditions. Other design parameters introduce more efficiency variation opportunities than is presented by the refrigerant choice.

Conversion of refrigerant choice for new production of domestic refrigerators from the historic use of CFC-12 refrigerant to ozone-safe alternatives continues to occur in advance of the Montreal Protocol requirements. Conversion in all non-Article 5(1), several Article 5(1) and CEIT countries is complete. National transition schedules in remaining Article 5(1) and CEIT countries are influenced by national regulatory initiatives and the availability of capital resources, including those obtained through the Multilateral Fund. The RTOC is in the process of assessing the transition status. Preliminary information suggests significant progress in completed transitions and in commitments to transition schedules. Notable among interactive national initiatives are efforts to reduce greenhouse gas emissions in compliance with the Kyoto Protocol. The Kyoto Protocol also has increased consideration of energy efficiency initiatives to influence the secondary effects of greenhouse emissions from power generation and distribution in addition to direct product emission prescriptive regulations.

Practice of mature domestic refrigeration technology should provide products that require less than one-half of the electrical energy of the product being replaced. Improvements in compressor efficiency, heat exchange efficiency, insulation efficiency and construction techniques are the main contributors. As previously stated, either HC-600a or HFC-134a can provide comparable energy efficiency. Energy efficiency, however, may not be comparable with other refrigerant

alternatives. For example, blends of HC-290 and HC-600a have been selected by a small number of manufacturers in order to avoid capital costs required to modify compressor-manufacturing tooling. This blend is generally less energy efficient than HC-600a, and also HFC-134a; previous applications of the blend have been a temporary step toward final transition to HC-600a.

In contrast to new equipment manufacture, progress has been limited on elimination of ozone depleting substance use for service of domestic refrigeration equipment. A large number of the existing refrigerators are several years old and still contain CFC-12. CFC-12 is normally used to service these refrigerators. The typical 20+ year equipment life creates a long-term demand for CFC-12. Particularly in many developing countries the premium value of capital goods versus labour expense exacerbates this situation by promoting component rebuilding which extends the demand for CFC-12. Production and trade constraints are limiting the global supply and increasing the cost of CFC-12. Increased CFC-12 cost promotes demand reduction. Technology opportunities to achieve this reduction include refrigerant recovery and recycling as well as field retrofit for conversion to alternative refrigerants. TOC assessment of available technology and progress achieved to date in progress. Regulatory initiatives to promote progress are also being addressed.

#### **9.4.5 Commercial Refrigeration**

The types of equipment applied in commercial refrigeration are very different, where it concerns their size, the logistics of the specific refrigeration circuit, and the refrigerant charges applied, and these parameters very much depend on country specific conditions. Commercial refrigeration consists of four main types of equipment:

Stand-alone equipment covers many different types including vending machines, ice machines, etc. in summary, all kinds of small equipment that is installed in stores or public areas in many developing as well as in the developed countries. 10 to 12 million pieces of this equipment are in use globally. Refrigerant charges vary from 200 g up to 1 kg. The usual refrigerant applied is HFC-134a, which has largely replaced CFC-12. In some European countries one has started applying hydrocarbons --in principle only HC-600a-- with charges up to 150 g, sometimes up to 800 g, dependent on national regulations. However, HFC-134a is the current dominant option for stand-alone equipment.

Condensing units are typically installed in specialised shops. The refrigerant charge varies between 1 and 5 kg. The number of equipment in use globally is estimated at about 2.5 million. The refrigerant choice is depending on the application temperature level. For medium temperature HFC-134a and sometimes R-407C are the preferred options, for low temperature it is R-404A. Due to safety concerns, HCs are not a wide spread option for equipment where refrigerant charges are applied in the order of 1 to 5 kg.

Centralised systems can be found in supermarkets, where the estimated number is 120,000 globally; these systems have a wide range of refrigerating capacities. The refrigerant charge varies from 100 kg to about 1,500 kg. The refrigerating system

is installed in machinery rooms and the refrigerant circulates from this machinery room to the display cases installed in the sales area.

A relatively new concept, called "*distributed system*", drastically limits the length of refrigerant pipes applied because the compressors are installed in sound-proof boxes inside or nearby the sales area, and consequently leads to a substantial reduction of the refrigerant charge applied.

As already stated above, the choice of refrigerants varies substantially and is very much dependent on regional and national regulations. CFC-12 is still being used in Article 5(1) countries, and HCFC-22 is still the main refrigerant in use in the USA. In Europe, HCFC-22 has been banned for new equipment in this sector as of 1 January 2001; here R-404A has become the preferred choice. In Japan CFC-12 or R-502 has been replaced by R-134a but also by R-407C.

Particularly in Europe, a lot of technical work has been done to develop indirect systems in order to limit the refrigerant charge or to allow the use of ammonia or hydrocarbons. European supermarket and cold storage companies are evaluating these different options, but the initial investment is still the most important factor in the decision-making process, which may work out prohibitive on this type of systems. Of course, the energy consumption is also an important factor on the evaluation process. Namely, the use of an indirect system will imply higher energy consumption, especially at a low cooling temperature, whereas at medium cooling temperature the increase in energy consumption will be moderate. However, to achieve the same energy consumption at this medium (refrigeration) temperature level, it would need a more complex and more expensive design.

In the past, commercial refrigeration showed typical annual leakages of 15-30%, and even higher. Adequate designs for containment, leakage monitoring, and minimal losses during servicing will reduce the annual leakage to 3-15%. The application of distributed systems or secondary loops, both with a significant charge reduction, may yield annual leakage percentages in the order of 2-5%.

#### **9.4.6      *Transport Refrigeration***

The transport refrigeration sector contains the sub-sectors reeferships, intermodal refrigerated containers, road transport, refrigeration and air conditioning on merchant marine ships and air conditioning in railcars.

In these different sub-sectors HFCs have generally taken over in new systems and they are also going to substitute HCFC-22 via refrigerant mixtures such as R-407C, R-404A and R507. R-410A has not gained much importance up to now.

In the ship-subsectors HCFC-22 is still the main refrigerant used and its substitution in new ships shows a very slow start. Other fluids such as ammonia have so far not gained much importance; particularly ammonia seemed to be a possible candidate but due to the high initial costs it is not considered a favourable solution to date. Where it concerns intermodal refrigerated containers, retrofitting of old systems to HFC or HCFC mixtures was common, however, a new direction was taken due to the decision of the Danish government to phase out HFCs by the

year 2006. This was the reason that research and development was initiated into the use of CO<sub>2</sub> systems with the trans-critical vapour compression cycle; intensive work is going on in this field. As far as commercialisation of the system is concerned, no data are yet available.

Where it concerns road transport and its continuing use of HCFC-22, the market share of systems with R-404A is growing. Moreover, for a smaller amount of refrigerated road transport systems R-410A has been selected. Where it concerns the air-conditioning systems in railcars, R-134a is the leading candidate for future systems; however, the application of air-cycle based systems in high speed trains has been started in the year 2000, particularly in Germany. Here, the air-cycle seems to be an attractive solution for the future, however for other reasons than for substituting ODSs. In all transport sub-sectors flammable hydrocarbons have not gained any importance as refrigerants and this applies to sea, road and railway transport.

In future, decisions such as an HFC-phase-down, or announcements stating that HFCs are no long-term solution, or that other fluids than HFCs are more sustainable, may have the consequence that an early transition from (CFCs and) HCFCs to HFCs could be delayed. This is due to the fact that engineers in the field question the influence of policy based regulations on the future role of HFCs in this sector.

#### **9.4.7 Unitary Air Conditioning**

Since the 1998 Assessment there has been continued progress in the development of alternative technologies needed to replace ODSs in unitary air conditioning and heat pump systems. During the past three years, manufacturers in the developed countries have continued to commercialise non-ODP technologies, mostly HFC based products. The dominant HFC refrigerants being employed are the blends R-407C and R-410A.

Japan has made the greatest progress in the conversion with significant portions of its residential and commercial markets being converted to R-410A and R-407C. In Europe, R-407C has been the dominant replacement for HCFC-22. Europe has also seen some penetration of R-290 (propane) and R-410A into commercialised products.

In the US a number of manufacturers have introduced non-ODP unitary systems however, currently less than 5% of the unitary market is using non-ODP refrigerants. It is anticipated that there will be a significant shift toward the non-ODP technologies in 2006, which will coincide with the implementation of new minimum efficiency standards.

The search for other alternative refrigerants has continued to move forward. The development of non-HFC technologies also received a boost from the announcement of the Coca-Cola, McDonald's, Lever and Foster Beer companies when they announced plans to phase out the use of HCFCs and HFCs by 2004.

Furthermore, there has been a significant increase in research on system designs using CO<sub>2</sub>. Research centres in Europe, the US and Japan all have extensive research programs to develop efficient and cost effective CO<sub>2</sub> systems. The greatest challenges in developing air-to-air CO<sub>2</sub> systems have been low operating efficiencies, high operating pressures and the availability of components designed for CO<sub>2</sub> systems. There is optimism that technology developments will lead to solutions to these issues.

Overall, significant progress is being made in the development and implementation of non-ODP technologies in the developed countries. It is anticipated that the currently available technologies will enable a smooth transition to non-ODP substances here. Significant work is still needed to ensure that cost effective technologies are in place to support this transition in the Article 5(1) countries.

#### **9.4.8 Chillers**

The vapour compression cycle remains the predominant type; most systems are driven by electric motors but engine and turbine drives also are available. Absorption chillers with steam, natural gas, or waste heat as an energy source also are offered. The market for absorption chillers is greatest in Asia (Japan and China, as examples) but remains much smaller than for vapour compression chillers elsewhere in the world. The production of small gas-fired absorption chillers (3-18 kW capacity) exceeds 10,000 units per year but this represents a very small fraction of a market mainly served by air-to-air air-conditioners and heat pumps.

HCFC-22 remains the most commonly used refrigerant in positive displacement chillers (7.0 kW up to over 700 kW) employing reciprocating, screw, or scroll compressors. This refrigerant is scheduled for phase-out in new products by 2010 in most countries. However, a number of national regulations, particularly in the European Union member states (EC regulation 2037/2000), mandate the phase-out of HCFC-22 in new systems even earlier. In response, manufacturers have introduced new equipment employing HFCs including R-134a (particularly for water-cooled chillers), R-407C (particularly for air-cooled chillers), R-410A, and less commonly R-404A, R-717 (ammonia), and R-1270 (propylene). For existing positive displacement chillers, HCFC-22 sometimes is replaced by HFC-134a, causing a significant reduction in capacity for the same compressor displacement, or R-407C, with a reduction in energy efficiency.

Following the CFC phase-out, the principal refrigerants used in centrifugal water chillers have been HCFC-123 and HFC-134a. New products continue to be offered for both of these refrigerants. There is a clear trend to improve the energy efficiency of these chillers, particularly in the United States where new ASHRAE energy efficiency standards have been introduced. Although subject to phase-out after 2020 under the Montreal Protocol, HCFC-123 remains the most efficient refrigerant for water chillers. Studies have shown that continued use of HCFC-123 in chillers would have indiscernible impact on stratospheric ozone while offering significant advantages in efficiency, thereby lowering greenhouse gas emissions from power generation.



For existing centrifugal chillers, the replacement or retrofit of chillers using CFC-11, CFC-12, or R-500 continues to be a slow process. Thousands of chillers continue to operate with these CFC refrigerants as a result of good maintenance (low leakage rates), recovery of refrigerant when units are serviced, stocks of old refrigerant reclaimed from units taken out of service, and owners' desire to defer chiller retrofit or replacement costs.

New chillers of both types – positive displacement and centrifugal – are being designed to have negligible refrigerant emissions during their operating life. Studies have shown that refrigerant releases throughout the life-cycle of chillers can be held to less than 0.5% per year as contrasted to losses sometimes exceeding 30% per year as recently as thirty years ago. Regulations are being put in place around the world to require service personnel to minimise refrigerant emissions during their activities and to require refrigerant to be reclaimed or destroyed when units are taken out of service. These measures, together with increased energy efficiency, are substantially reducing the environmental impact of new water chilling equipment.

#### **9.4.9 Vehicle Air Conditioning**

HFC-134a replaced CFC-12 in virtually all vehicle air conditioners produced in the developed countries after 1994. It is predicted that in the period 2000-2010, 70-80% of all new vehicles produced globally will have HFC-134a air conditioners. It is technically and economically feasible to significantly reduce emissions of HFC-134a refrigerants. This includes recovery and recycling, the use of high quality components with low leakage rates, and by minimising the refrigerant charge, as well as the use of different systems using alternative refrigerants. Efficiency improvements and smaller AC units can further reduce the energy related carbon dioxide emissions.

Manufacturers are working to increase the energy efficiency, and reduce the emissions of HFC-134a systems. Refrigerant charges are also being reduced to levels below 0.8 kg per vehicle, with lowest charges currently applied in Japan and in Europe. This will show demonstrable progress during the period 2001-2003, which implies that improved HFC-134a systems can be introduced faster and at lower incremental cost than alternative systems. This is also related to the introduction of hybrid vehicles where an electricity driven hermetic refrigeration cycle using HFC-134a would virtually phase out emissions during the useful life of the equipment.

However, substantial activities are underway to develop alternatives to HFC-134a air conditioning systems for vehicles, in particular the trans-critical carbon dioxide cycle and the hydrocarbon (secondary loop) system. The carbon dioxide systems are assumed to have energy efficiencies comparable to HFC-134a. However, their high operating pressures require substantial new engineering, component reliability testing, technician training etc. It is estimated that the first CO<sub>2</sub> systems could be commercialised in 4-7 years. Where it concerns secondary loop systems with a flammable refrigerant in the refrigeration cycle, it is also estimated that the energy efficiency of these systems can be brought to a level comparable of that of HFC-

134a. Where it concerns new engineering, reliability testing etc., the introduction of secondary loop systems would require fewer technical innovation than would be the case for carbon dioxide systems, which implies that these systems could be implemented in 3-5 years.

#### **9.4.10 Refrigerant Conservation**

Refrigerant conservation has seen an accelerated development during recent years, mainly due to the completion of recovery, recycling and reclaim schemes in a number of countries. This particularly applies to the non-Article 5(1) countries but much progress is also made through the development of Refrigerant Management Plans in CEIT and Article 5(1) countries.

The other aspect of refrigerant conservation, i.e., the limitation of emissions through better leaktightness and leak detection, will be increasingly applied, but it needs much more attention than to date. In Article 5(1) and CEIT countries, an important priority is to improve the maintenance of systems in the proper operating condition, including tightening up systems by finding and repairing leaks, and recovering refrigerant when opening the system. In order to be effective, conservation technologies must be matched by technician training and, in some cases, the adaptation of technology. This has been declared to be an important element in many projects that were approved by the Multilateral Fund for Article 5(1) and by the Global Environment Facility for CEIT, as well as for CIS countries, including the Russian Federation. In addition, strong government incentives may be necessary to ensure that conservation occurs. This should be the case in Article 5(1) countries where CFCs are still available at a relatively low price (compared to their alternatives) but it may also be the case in the developed countries in order to increase conservation for the CFC alternatives such as HCFCs and HFCs.

The primary options for limiting (any refrigerant) emissions are the use of alternative refrigerants and refrigeration technologies, reduced refrigerant charge, improved containment, and recovery with recycling and/or destruction. Experience in different countries where certain policies have now been implemented for a certain period can be analysed at present in order to evaluate the most effective means to limit refrigerant emissions. This then relates to policies and standards to minimise all refrigerant emissions – including HFCs – in many developed countries.

### **9.5 Solvents Technical Options Committee (STOC)**

#### **9.5.1 STOC Sub-Committee on 1-Bromopropane (nPB)**

Decision X/8 requests the Technology and Economic Assessment Panel and the Science Assessment Panel to determine whether substances with short atmospheric life-times pose a threat to the ozone layer. One such substance is n-propyl bromide (nPB). The Solvents, Coatings and Adhesives Technical Options Committee (STOC) formed a Sub-Committee on nPB soon after the 20th Meeting of the OEWG discussed draft Decision X/8. The Sub-Committee's task was to formulate

and finalise a draft report, including necessary data and methodology. The final draft was to be submitted to the TEAP. The TEAP then created a Task Force on nPB, which consisted of all the members of the STOC Sub-Committee on nPB with the addition of several TEAP members.<sup>6</sup>

### **9.5.2      *Essential Use Nomination***

The Government of Poland submitted an Essential Use Nomination for 850 kg of CFC-113 for the years 2002 and 2003. The STOC has submitted its report on this nomination to the TEAP, confirming that the nomination meets the Essential Use criteria (see section 2.2).

### **9.5.3      *STOC Membership Issues***

Diminishing sponsorship of STOC members by developed country industries and under-representation by Article 5(1) and CEIT experts are making it difficult for the STOC to complete its work. Ways must be found to support, also by the use of financial means, those members from non-Article 5(1) countries expected to be leaders of a Chapter as well as those expected to provide strong inputs to the subject matter (the diminishing support and sponsorship also applies to non-Article 5(1) country members of other TOCs, see section 10.1).

### **9.5.4      *Status of US Space Program***

NASA and the Titan IV program representatives provided the following information during the recent STOC meeting in Brussels (30 January - 1 February 2001).

#### **9.5.4.1      *Progress Report on NASA–Thiokol Reusable Solid Rocket Motor ODS Elimination***

Of the 176,353 kg essential use exemption allowance, approved in 1996, one-third (53,319 kg) was used by December 2000. The US estimates an additional 7,257 kg will be used in 2001. Additional flights scheduled and a delay in Space Shuttle replacement may necessitate additional quantities at some point in the future.

If ODS replacement technologies perform well in the firing of a test motor on May 24, 2001, one third of the remaining essential uses will be eliminated. Replacement technologies to be tested in further firings on May 16, 2002 may eliminate a further one third of the remainder. Although significant progress has been made on Class 1 ODS use elimination, certain processes of a critical nature continue to require the use of ODSs.

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<sup>6</sup> The TEAP points out the following: The TEAP Task Force on nPB began its work in early 2001, based its work on the STOC Sub-Committee draft report and submitted its report to TEAP in April 2001 (which is included in this TEAP report).

STOC notes that the significant amount of research conducted to find alternatives for critical space-related uses of ODS solvents have produced important scientific understanding that enabled alternatives to be identified and implemented in other solvent use areas, such as:

- Advances in the overall knowledge of materials and processes that apply to the functions performed by solvents;
- Improved bonding and adhesives technologies, resulting in more robust systems;
- Better ability to deal with a wide variety of chemical and compound program issues
  - Supplier obsolescence and discontinued products
  - Increasingly stringent worker safety issues
  - Employee preferences and ergonomic considerations
- Increased hardware life due to less aggressive refurbishment processes
  - Aqueous cleaning of metal components
  - Elimination of repetitive grit blasting operations

The remaining technical challenges prevent complete elimination of ODS from reusable solid rocket motor applications:

- Selecting or formulating of a non-n-propyl bromide based solvent for the activation of insulating rubber;
- Selecting or formulating of a solvent that will clean and prepare flexible bearing (natural rubber) vulcanisation surfaces without affecting post-vulcanisation processes (assembly, installation, etc.);
- Selecting or formulating of a solvent that will clean and prepare nozzle phenolic bone surfaces for use with new generation adhesive systems;
- Confirming acceptable performance in full-scale static tests with verifiable post-test inspections before incorporating into flight hardware;
- Managing remaining TCA stockpiles and EUE allowances for unanticipated setbacks or unacceptable performance.

#### **9.5.5      *Status on Progress Report – US Titan IV Programme***

The progress on Phase II of the methyl chloroform elimination has been presented. The Titan IV class 1 ODS elimination progress since 1996 has been reviewed covering:

EUE Applications:

- Tackifier for breather cloth;
- Tackifier for insulator case bond;
- Surface preparation for propellant-insulator bond;

- Propellant mix dispersion.

Non-EUE Applications:

- Thermal protection system;
- Core and mold plate release agents;
- Forward insulator assembly.

Under each item, the past practices, replacement and reduction has been reported.

#### ODS Challenge – Graphite Fiber Case Winding

Whilst tremendous progress has been made on Class 1 ODS use elimination, the essential use quantities already granted are required until all the ODS-free graphite fibre rocket motor segments have satisfied environmental, safety, and performance requirements.

On the above programs, the STOC notes that a significant amount of research conducted to find alternatives for critical space-related uses of ODS solvents have produced the important scientific understanding that enabled alternatives to be identified and implemented in other solvent use areas.

### **9.5.6 New Developments**

#### *9.5.6.1 Phase-out of HCFC-141b and HCFC-225*

The European Union has scheduled the phaseout by the end of 2005 of all HCFCs and HFCs used for solvent applications. This will be particularly challenging because solvent users will also be implementing more stringent regulations for the three main chloro-carbons, viz., methylene chloride, perchloroethylene and trichloroethylene. The STOC will endeavour to catalogue suitable alternatives and substitutes to ozone-depleting solvents where methylene chloride, perchloroethylene or trichloroethylene are currently used.

#### *9.5.6.2 Aqueous Cleaning and Degreasing Methods*

United Technologies and United Airlines in the USA have converted to aqueous methods for all operations that previously used chlorocarbons. The water consumption of advanced aqueous cleaning is now less than 5% of that required 4-5 years ago (a 95% reduction). Both technical and economic considerations were the driving force behind this changeover. Most of the European airlines have been using aqueous methods instead of vapour cleaning/ degreasing. Introduction of new aqueous alkaline cleaners with low pH is likely to increase the use of aqueous methods. The 2002 STOC report will provide complete details on the latest aqueous cleaning systems.



## 10 Technology and Economics Assessment Panel (TEAP)

### 10.1 TEAP Operation

Tables 10.1 and 10.2 present an overview of the 2001 composition of the TEAP and its TOCs.

*Table 10.1: Country representation in TEAP as of April 2001*

<b>Total Membership</b>	<b>Article 5(1) and CEIT</b>	<b>Non-Article 5(1)</b>	<b>% Article-5(1) and CEIT</b>
23	12	11	52

TEAP now has 23 members from 18 countries (Australia, Brazil, Canada, China, Egypt, Germany, Hungary, India, Japan, Kenya, Mauritius, Mexico, Netherlands, Poland, Switzerland, United Kingdom, United States and Venezuela) including 12 from CEIT and Article 5(1) countries (52%). The 2000-2001 TOCs have 164 members from 47 countries<sup>1</sup> including 30% from CEIT and Article 5(1) countries; 2000-2001 Task Forces had 26 members from 14 countries<sup>2</sup> (40% from CEIT and Article 5(1) countries).

During 1999-2001 there has been ongoing collaboration between the TEAP and the Intergovernmental Panel on Climate Change. TEAP and TOC members were Lead Authors of the IPCC Third Assessment Report, Working Group III, Chapter 3, Appendix: "Options to Reduce Global Warming Contributions from Substitutes for Ozone Depleting Substances." Lead Authors from the TEAP included Dr. Stephen O. Andersen (USA), Dr. Suely Carvalho (Brazil), Dr. Yuichi Fujimoto (Japan), Dr. Barbara Kucnerowicz-Polak (Poland) and Dr. Lambert Kuijpers (Netherlands). A Lead Author from the Refrigeration, Air Conditioning and Heat Pumps Technical Options Committee was Dr. Sukumar Devotta (India). The above Lead Authors were involved in several review rounds; the total IPCC Third Assessment Report, the Technical Summaries and the Summaries for Policy Makers (SPM) for each of the Working Group reports, including that of Working Group III, were endorsed and the reports will have been published by mid-2001.

In 2000, Dr. Jonathan Banks replaced Dr. Thomas Batchelor and Dr. Rodrigo Rodriguez-Kabana as co-chair of the Methyl Bromide Technical Options Committee. In 2001 TEAP is seeking a replacement for Dr. David Okioga (Methyl Bromide TOC) and Dr. Lalitha Singh (Rigid and Flexible Foams TOC).

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<sup>1</sup> Argentina, Australia, Belgium, Brazil, Canada, Chile, China, Colombia, Cyprus, Denmark, Egypt, Finland, France, Germany, Hungary, India, Indonesia, Israel, Italy, Japan, Jordan, Kenya, Korea, Malaysia, Mauritius, Mexico, Morocco, Netherlands, New Zealand, Norway, Pakistan, Philippines, Poland, Russia, Singapore, South Africa, Spain, Sweden, Switzerland, Tanzania, Thailand, Tunisia, Uganda, UK, USA, Venezuela and Vietnam

<sup>2</sup> Australia, Brazil, Canada, China, Cyprus, Egypt, France, Germany, India, Japan, Jordan, Netherlands, USA and Venezuela

TEAP is also seeking additional members with appropriate expertise, particularly in economics and in issues of CEIT and Article 5(1) countries. Nominations including curriculum vitae should be submitted by national governments to the Ozone Secretariat.

*Table 10.2: Country representation in TOCs as of April 2001 (including Co-chairs who serve as TEAP members)*

<b>Body</b>	<b>Total Membership</b>	<b>Article 5(1) and CEIT</b>	<b>Non-Article 5(1)</b>	<b>% Article 5(1) and CEIT</b>
ATOC	33	10	23	30
FTOC	24	5	19	21
HTOC	17	6	11	35
MBTOC	32	11	21	34
RTOC	34	10	24	29
STOC	24	7	17	29
<b>Total</b>	<b>164</b>	<b>49</b>	<b>115</b>	<b>30</b>

Since 1988 many Parties have made substantial in-kind and financial contributions to the operation of the TEAP and its TOCs, Working Groups and Task Forces. The principal financial contributors include Australia, Canada, Denmark, Finland, Germany, Japan, Netherlands, Norway, Sweden, Switzerland, United Kingdom, and the United States.

Diminishing sponsorship of members, particularly from developed countries, in most of the TOCs is causing difficulties in completing different work assignments in an adequate manner. Industries in non-Article 5(1) and even in Article 5(1) countries that now successfully employ non-ozone-depleting technologies (and are therefore no longer seeking alternatives) gain less from participation, and hence are reluctant to fund the travel and other expenses for an employee to serve on TEAP and its TOCs. Furthermore, allowing their employee to devote time to TEAP and TOC assignments, is not among the companies' top priorities.

The Montreal Protocol has reached a stage in the phase-out process where Parties frequently require additional technical information not anticipated by the TEAP. Some requests require additional travel, report preparation, and miscellaneous expenses that cannot be met by the organisations who employ members of TEAP and its TOCs and Task Forces. Accordingly, TEAP requests an annual budget of up to US\$125,000 to offset unanticipated direct expenses necessary to undertake special projects such as Task Force Reports and for unanticipated contingencies. The TEAP proposes that the funds be subject to the following restrictions:

- 1) to be used only by Task Forces or unanticipated direct expenses and only when other avenues of funding are not available;
- 2) to be used exclusively for travel and subsistence, organisation of meetings, and report preparation (and not for consultancies) and,
- 3) to be authorised by consensus of TEAP Co-Chairs and the Ozone Secretariat through budget redeployment funds rather than additional funds.

TOCs typically spend US\$35,000-100,000 depending on whether the time of chairs is an in-kind contribution or a sponsored contribution.



## 10.2 TEAP Members

The following contains the background information for all TEAP members:

**Dr. Radhey S. Agarwal**

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Radhey S. Agarwal, Co-chair of the Refrigeration, Air-conditioning, and Heat Pumps Technical Options Committee, is the Deputy Director (Faculty) and Professor of Mechanical Engineering at the Indian Institute of Technology (IIT Delhi), Delhi, India. IIT Delhi makes in-kind contribution for wages. Costs of travel, communication, and other expenses related to participation in the TEAP and its TOCs are paid by the Ozone Secretariat.

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Paul K. Ashford, Co-chair of the Rigid and Flexible Foams Technical Options Committee is the principal consultant of Caleb Management Services. He has over nearly 20 years direct experience of foam related technical issues and is active in several studies concerning future policy for the foam sector. His funding for TEAP activities, which includes professional fees, is provided under contract by the Department of Trade and Industry in the UK. Other related non-TEAP work is covered under separate contracts from relevant commissioning organisations including international agencies (e.g. UNEP DTIE), governments and trade associations.

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Jonathan Banks, Co-chair of the Methyl Bromide Technical Options Committee, is a private consultant. He currently has contracts with Environment Australia and the Australian Quarantine Inspection Service related to methyl bromide and use of alternatives. He has a post-retirement fellowship with CSIRO Stored Grain Research Laboratory, a government/industry funded research laboratory engaged in finding improved ways of protecting stored grain, including developing and commercialising alternatives to methyl bromide. His funding for TEAP and MBTOC activities is through an Epson Australia Fellowship, a competitive fellowship administered by Environment Australia.

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Jorge Corona is in charge of foreign relations of the Environmental Commission of Camara Nacional de la Industria de Transformacion (CANACINTRA), National Chamber of Industries, Mexico City. Communications, wages and miscellaneous expenses are covered personally. Travel expenses are paid by the Ozone Secretariat. From 1997, communications and other expenses are being covered by the Ozone Secretariat. During recent years, Jorge Corona has worked for UNEP and UNDP on a consultancy basis.

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Lambert Kuijpers, Co-chair of the Technology and Economic Assessment Panel and Co-chair of the Refrigeration, Air-conditioning and Heat Pumps Technical Options Committee, is based in Eindhoven, The Netherlands. In 1998 and 1999 he was supported by a number of European countries (through the UNEP Ozone Secretariat) and the European Commission and this was entirely taken over by the European Commission in 2000. This applies to his activities related to the TEAP and the TOC Refrigeration, which includes in-kind contributions for wages and travel expenses. They also fund administrative costs on an annual budget basis. In addition to activities at the Department "Technology for Sustainable Development" at the Technical University Eindhoven, other activities include consultancy to governmental and non-governmental organisations, such as the World Bank and UNEP DTIE. Dr. Kuijpers is also an advisor to the Re/genT Company, Netherlands (R&D of components and equipment for refrigeration, air-conditioning and heating).

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K. Madhava Sarma has recently retired after nine years as Executive Secretary, Ozone Secretariat, UNEP. Earlier, he was a senior official in the Ministry of Environment and Forests, Government of India and held various senior positions in state government. He is doing honorary work for UNEP and the Government of India. The Ozone Secretariat pays for his travel, and other actual expenses in connection with his work for the TEAP.

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Gary Taylor, Co-chair of the Halon Technical Options Committee (HTOC), member of the TEAP and Co-chair of the PATF is a principal in the consulting firm Taylor/Wagner Inc. Funding for participation by Mr. Taylor on the HTOC is provided by the Halon Alternatives Research Corporation (HARC). HARC is a not-for-profit corporation established under the United States Co-operative Research and Development Act. Additional funding was provided by HARC to Taylor/Wagner Inc. to develop, maintain and operate the TEAP Web Site. Funding for administration and the participation of Mr. Taylor on the Process Agents Task Force (PATF) was provided by the Chlorine Institute and EuroChlor, both are broadly based trade associations.

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Ashley Woodcock, Co-chair Aerosol Products Technical Options Committee, is a Consultant Respiratory Physician at the NorthWest Lung Centre, Wythenshawe Hospital, Manchester, UK. Prof. Woodcock is a full-time practising physician and Professor of Respiratory Medicine at the University of Manchester. The NorthWest Lung Centre carries out drug trials of CFC-free MDIs and DPIs for pharmaceutical companies (for which Prof. Woodcock is the principal investigator). Prof. Woodcock has received support for his travel to educational meetings and occasionally consults for several pharmaceutical companies. Wythenshawe Hospital makes in-kind contributions of wages and communication and the UK Department of Health sponsors travel expenses in relation to Prof. Woodcock's Montreal Protocol activities.

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Brian Ellis has been a member of the Solvents, Coatings and Adhesives Technical Options Committee since its foundation in 1989 and has been leader of the Electronics Chapter until 2001. Until his official retirement in 1998, he was General Director of Protonique SA (now liquidated) in Switzerland but is still Chairman of Protonique Limited in the UK. His activity in the STOC is funded by the government of Switzerland, including partial professional fees. He is also a Senior Solvents Sector Consultant to the Secretariat of the Multilateral Fund and a member of the Executive Team of the Professional Network for Engineering for a Sustainable Future, organised by the Institution of Electrical Engineers.

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Asad Khan is a Programme Coordinator at IICT. He has over 30 years of direct experience in the area of process technology development and commercialization for chemical sector. His funding for STOC activities, which includes travel expenses and daily subsistence allowances, are provided by UNEP's Ozone Secretariat.

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Professor Ian Rae is Technical Director of the Australian Academy of Technological Sciences and Engineering, and holds an Honorary Professorial Fellowship in History and Philosophy of Science at the University of Melbourne, Australia. A chemist by training, he was formerly dean of science and deputy vice-chancellor (vice president) at Australian universities. He is chair of Australia's National Advisory Body on Scheduled Wastes and of the Scheduled Wastes Management group, and adviser to the Director, National Industrial Chemical Notification and Assessment Scheme. Funding for his participation in the PATF has been provided by the Commonwealth Government Department, Environment Australia.

### 10.3 2001 Technology and Economic Assessment Panel (TEAP)

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



**UNEP**

**11 Report of the Process Agents Task Force  
April 2001**



**UNEP  
REPORT OF THE  
PROCESS AGENTS  
TASK FORCE  
APRIL 2001**

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April 2001**

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## Summary and Conclusions

In 1997 the PATF and the TEAP reported that it was technically feasible to further reduce the relatively small emissions from process agent use in non-Article 5(1) countries and that it was technically and economically feasible to substantially reduce the emissions of ODS process agents in CEIT and Article 5(1) countries. This 2001 PATF report has been prepared in response to the request of the TEAP contained in Decision X/14. The Multilateral Fund Secretariat is preparing a separate 2001 Report to Parties that describes the current process agent use in Article 5(1) countries and also reports progress in financing the incremental costs of reducing and eliminating those emissions.

### **1. ODS process agents are locally used but benefits are globally important**

ODS process agents are reported to be used by fewer than 10 Parties to produce intermediate and final products that are globally marketed for uses important to health, safety, environmental protection and economic prosperity.

### **2. Process agents support health, safety, and economic prosperity**

Products and processes depending on ODS process agents include human and animal drugs, pesticides, corrosion inhibitors, water purification, plastic armour used to protect humans and to contain ballistic debris from equipment failure, asbestos-free brake and clutch plates, and chlorine.

### **3. Most Parties have yet to report process agent use and emissions**

Most Parties have yet to report process agent uses and emissions. Decision X/14 requested all Parties to report to the Secretariat by 30 September 2000 and each year thereafter on their use of controlled substances as process agents, the levels of emissions from those uses and the containment technologies used by them to minimise emissions of controlled substances. The Ozone Secretariat received only 17 reports, 4 from non-Article 5(1), 3 from CEIT, and 10 from Article 5(1). Most lacked sufficient detail to allow for meaningful evaluation.

The Ozone Secretariat has drawn our attention to paragraph 36 of the Report of the 25th meeting of the ImpCom, 9 December 2000, as follows:

"One representative expressed the view that the reporting requirement on process agents set out in decision X/14 was not sufficiently clear, leading to problems with the drafting of data form 6 and its eventual approval. It was agreed that the Secretariat would identify the Parties which would be affected by the reporting requirement and invite them to discuss which data should be provided and how the form should be designed. It would then report back to the Committee with a review to a recommendation being made to the Meeting of the Parties."

#### **4. Precise accounting is difficult to achieve**

Precise accounting of actual emissions is much more difficult than Parties may recognise because estimates are based on engineering calculations using process assumptions, because chemical process yields vary over time, and because equipment failure and leaks result in unmonitored emissions.

#### **5. Unofficial reports confirm reduced emissions in non-Article 5(1) countries**

The PATF estimates that 4000-5000 tonnes of ODSs are used annually in process agent applications in non-Article 5(1) countries. Plant specific annual emissions are estimated as less than 250 tonnes – less than 7% of make-up quantities. This has been achieved by capture and recycle or destruction, or chemical transformation of the ODS.

From an examination of the literature and the case studies of the identified processes the following conclusions are offered:

- In most cases emissions from use of ODS as process agents in non-Article 5(1) countries are similar to the insignificant quantities emitted from the use of ODS as feedstock.
- Depending on the difficulties of the process under investigation there is a diversity of progress, ranging as follows:
  - phase-out achieved or achievable
  - expected phase-out within the next few years subject to solution of final technical issues
  - a few processes facing extreme difficulty to find an alternative
- Realising that these results have been achieved over a period of 5 to 6 years, together with measures to significantly reduce emissions where ODS process agents are still in use, there has been remarkable progress and further progress is expected.
- Care should be taken that ODS are not inadvertently produced in significant quantities by the substitution of an alternative process agent or by the use of an alternative process.

The expectation, is that in the coming 10 years a substantial part of the use of ODS as process agents will be virtually phased out in non-Article 5(1) countries. Adequate technical and financial assistance will facilitate the implementation of ODS free process technologies in Article 5(1) countries.

#### **6. PATF recommendations for Necessary Changes to Table A and B (Decision X/14)**

##### **1) Table A:**

In 1997, the PATF documented process agent uses numbered 1-12 and 19-24 found in Table A of Decision X/14. Despite efforts of the Ozone Secretariat,

TEAP and the PATF, no documentation of uses 13, 17a, 17b, 17c and 25 has been received. Parties may wish to consider appropriate modifications to the list of authorised process agent uses found in Table A of Decision X/14. In addition one Party has supplied information to the Ozone Secretariat, the TEAP and the PATF regarding the use of CTC in the manufacture of Cyclodime. Parties may therefore wish to consider adding the use of CTC in the manufacture of Cyclodime to Table A.

As well, Parties may wish to consider those processes “Not Yet Submitted to the Ozone Secretariat” as shown in Table 2.1 of Chapter 2 of this report of the PATF. It appears that some Article 5(1) countries have been confused by the wording of Decision X/14 as to whether they should submit information to the Executive Committee of the Multilateral Fund or the Ozone Secretariat.

## 2) Table B:

i) Parties may wish to restructure Table B to require annual reporting of each ODS process agent use and estimated emissions but may not wish to prescribe limits to either use or emissions. The technical justification for this change is that society may require increases in the quantity of products depending on process agents, that business rationalisation may shift the location of process agent use, and that emissions of process agents are a relatively insignificant contribution to ozone depletion.

ii) Parties may also wish to consider that “Make-Up” quantity include the total quantity of ODS from both stockpile and new production plus estimated ODS produced in-situ. Neglect of in-situ ODS production creates the false impression that a process has no impact on the ozone layer.

iii) Parties may wish to not require reporting of estimated emissions. The economic and administrative justification for CEIT and Article 5(1) countries is that accurate reporting of emissions for each process will require expensive training, equipment, and operating expenses that could better be spent in financing the incremental cost of phasing out ozone depleting substances. Reporting in non-Article 5(1) countries is an administrative burden that is increasingly difficult to justify as ozone staffs are down-sized. Periodic reporting by TEAP could be fully adequate.

iv) If Parties reject the option to not report emissions (iii above), then Parties may wish to estimate “Emissions” using procedures outlined in appropriate ISO Standards, using reporting guidelines established by some Parties (e.g. US-EPA), or other appropriate national instructions. The technical justification is that Parties need standardised instructions to report emissions.

## **Dissenting opinion**

This report has been developed at meetings held in Washington and Beijing and by correspondence before, between and after these meetings. The report has been

agreed upon by all members of the PATF, except one. One member, Mr. Arvind Kapoor has offered the following dissenting opinion to this report:

**Dissenting opinion by Arvind Kapoor**

1. At paragraph 5 of the Summary and Conclusions I differ with the conclusion: “Unofficial reports confirm reduced emissions in non-Article 5(1) countries ”.

No data on actual make up quantity and emissions of ODS in non-Article 5(1) countries was tabled, collated or discussed between the PATF members nor has any such data been published in this PATF report. The basis for PATF’s estimate of 4,000-5,000 MT of ODS as make up quantity per year for non-Article 5(1) countries is without any support. Further, in paragraph 4 of the Conclusions, it is stated that the ODS emissions in non-Article 5(1) countries are based only on engineering calculations and are not actuals.

Vide Decision X/14, Parties allowed non-Article 5(1) countries a total ODS usage of 4,501 MT per annum for process agents applications until 2001. In the TEAP April 1997 Report -Volume II, at paragraph 2.2 on page 89, it was estimated that the make up quantity of ODS for process agent applications in 1995 in non-Article 5(1) countries was 3,498.5 MT; TEAP further projected that this would reduce to 1,940 MT by the year 2000. Comparing these figures with that of the estimate of make up quantity of 4,000-5,000 MT of ODS per year mentioned in this PATF report does not signify a reduction in the use of ODS as process agents in non-Article 5(1) countries.

Even the current ODS emissions of less than 250 MT per year in non-Article 5(1) countries as mentioned in this PATF report have not reduced as shown in the Table below. This table also compares the figures of ODS make up quantities for process agent applications in non-Article 5(1) countries.

**TABLE: ESTIMATES OF MAKE UP QUANTITIES AND EMISSIONS OF ODS PROCESS AGENT USES IN NON-ARTICLE 5(1) COUNTRIES.**

	Reference	Year	Make-up quantity (MT)	Emissions (MT)	Emissions, as percentage of make-up quantity (%)
1.	TEAP April 1997 Report, Vol. II, page 89	1995	3489.5	1087.9	31.1
2.	Table B, Decision X/14 of Meeting of Parties at Cairo (see page 7 of this report)	1998 to 2001	4501.0	220.9	4.9
3.	TEAP April 1997 Report, Vol. II, page 89.	2000	1940	79.4	4.1
4.	Estimates as per 2001 PATF Report at para 2.4 (see page 17 of this report)	2000	4000-5000	<250.0*	<7.0

\* Calculated as 7% of make-up quantity range of 4,000-5,000 MT, this figure should be 280 – 350 MT.

It is thus clear that both the ODS make up quantity as well as their emissions from process agent applications in non-Article 5(1) countries do not currently show any reduction.

2. With reference to following portions of the report:

- a. the last bullet on page xii under paragraph 5;
- b. paragraph 3 on page 40 under paragraph 4.4;
- c. the bullet under Conclusions in paragraph 4.5 on page 40; and
- d. sub-item ii) on page xiii of paragraph 6(2).

I see no justification in clubbing two entirely different scenarios emerging from the use of non-ODS alternative process agents and alternative aqueous chlorination processes of hydrocarbon substrates such as natural rubber, synthetic rubber, polyolefins or paraffins as done in the portions of this report cited above.

In the case of use of a chemical substance as a non-ODS process agent, there is possibility of such process agent itself transforming into its next ODS homologue, if reaction conditions are conducive for such a chemical conversion. The ODS production in such cases could be substantial and it cannot be termed as inadvertent production. During such chemical reactions, care needs to be exercised to prevent use of such a non-ODS chemical substitute which can result in production of the next ODS homologue in that chemical series, as recommended in this report.

However, the use of the alternative aqueous processes as a substitute of ODS as process agent is a totally different situation. In this case, any likely in-situ and inadvertent ODS production in trace quantity can only occur if there are reaction conditions favourable for the same. No scientific evidence has been tabled to substantiate whether such inadvertent ODS production actually occurs in any or all such aqueous chlorination processes. Even in the event if such a minuscule inadvertent ODS production does take place during the use of aqueous process for the end product, then it is neither significant nor intentional. Further, such inadvertent ODS production is exempted under Decision IV/12 of the Protocol. The scenario utilising aqueous process as an alternative process is, thus, quite different from the use of alternative non-ODS process agents.

Let us assume for the sake of argument, that the inadvertent and in-situ CTC production does take place in Chlorinated Rubber manufacture by an aqueous process which is of the order of a maximum of 150 ppm of the product. Even if this process were to be adopted by all countries, then for an assumed total production of about 10,000 MT per annum of Chlorinated Rubber (which could be about double the current chlorinated rubber production in Article 5(1) Countries), the in-situ and inadvertent CTC production resulting from this process would be below 1.5 MT per annum, which is insignificant. This report states at third paragraph under heading 4.4 on page 49 that:

“If the process is conducted on a very large scale, then even “slight” can result in substantial annual ODS emissions”. This is by no means borne out by the above example.

In fact, in the case of Chlorinated Rubber production by an aqueous process recently developed in India, the inadvertent CTC production in that process is not measurable being minuscule.

In view of the foregoing any reference to need for care in adopting alternative processes through aqueous chlorination processes is not justified in any part of this report.

3. Mandate paragraph given to TEAP by the Parties, vide paragraph 8 of Decision X/14.

This report does not fully deal with the mandate of the Parties in as much as that it does not cover the progress made in implementation and development of emission reduction techniques and alternative processes not using ODSs subsequent to the 1997 PATF report.

Due to TEAP’s assumption as stated in the last paragraph on page 9 limited to non-Article 5(1) countries and does not update the situation in Article 5(1) countries. However, some disjointed references concerning Article 5(1) countries are included in this report. This report, is therefore, not representative of the complete picture in Article 5(1) countries relating to identification of any additional process agent applications utilising ODSs and progress made in developing alternative non-ODS processes for identified process agent applications since the 1997 PATF report.

As such, in my view, this report is not comprehensive and falls short of the mandate of the Parties.

### **Response by Gary Taylor, Co-chair PATF**

Many of the points objected to by Mr. Kapoor were debated at length at the final meeting of the PATF held in Beijing. Mr. Kapoor was unable to attend the Beijing meeting because it took place at the same time as the ExCom meeting in March 2001 in Montreal. Mr. Kapoor is a principal of Rishiroop Rubber International and his company has requested assistance from the Multilateral Fund in conversion of their chlorinated rubber facility from a CTC based process to an aqueous process. It was his decision to attend the ExCom meeting in Montreal rather than the PATF meeting in Beijing.

With regard to the three specific points made by Mr. Kapoor in his dissent, the following are offered for consideration:

1. Since the last report of the PATF, Parties have identified several processes in addition to those found in the 1997 PATF report. However, the Ozone Secretariat has not been supplied with any data by Parties regarding make-up or emissions since Decision X/14. In the absence of “official” data, the PATF members



reported on reductions in use of ODS process agents in processes reported in the 1997 PATF report that are employed by their respective companies in non-Article 5(1) countries. Significant reductions have occurred. Please refer to 4.2.9 and 4.2.10 of the report. In both cases significant production has now been switched to non-ODS processes, with only certain grades of product still being produced using ODS based technologies. The statement “Unofficial reports confirm reduced emissions in non-Article 5(1) countries” is a valid statement.

2. All members of the PATF, except Mr. Kapoor, have concluded that the possibility of small amounts of inadvertent production of CTC exists in the aqueous chlorination process. The report places this in context. Parties are especially referred to the final paragraph of 4.2.3. Parties may also wish to note that 1.5 MT of annual CTC emissions from the aqueous process, as estimated by Mr. Kapoor for a 10,000 MT/year of chlorinated rubber production, is over 150% of the annual CTC emissions from the German facility that actually produces 10,000 MT/year of chlorinated rubber.

3. The PATF would have preferred to eliminate Chapter 5 of the report, as a report on process agent use in Article 5(1) countries is being prepared by the Secretariat of the Multilateral Fund. However, Chapter 5 provides the only reference to the processes identified in Chapters 2 and 4, as #27 to #38.



# 1 Introduction and Definitions

## 1.1 Background

Pursuant to Decision X/14 of the Parties, the Technology and Economic Assessment Panel (TEAP) reconstituted the Process Agents Task Force (PATF). The PATF has endeavoured to further develop and improve upon the previous work undertaken in 1997.

This report was developed during meetings held in Ouagadougou, Washington and Beijing. During the Beijing meeting a joint session was held with members of a Process Agents Task Group established by SEPA. The meeting was a useful opportunity for PATF members to gain insight into the typical issues facing Article 5(1) users of process agents and to share the new technologies that have been employed to significantly reduce emissions in the non-Article 5(1) countries.

## 1.2 Decisions

The following Decisions of the Parties to the Montreal Protocol have been used as the basis for the work of the Process Agents Task Force (PATF):

### **Decision I/12B: Clarification of terms and conditions: Controlled substances produced**

The *First Meeting of the Parties* decided in *Dec.I/12B*:

- (a) to agree to the following clarification of the definition of “controlled substances produced” in Article 1, paragraph 5:

“Controlled substance produced” as used in Article 1, paragraph 5 is the calculated level of controlled substances manufactured by a Party. This excludes the calculated level of controlled substances entirely used as a feedstock in the manufacture of other chemicals. Excluded also from the term “controlled substances produced” is the calculated level of controlled substances derived from used controlled substances through recycling or recovery processes;
- (b) each Party should establish accounting procedures to implement this definition.

## **Decision IV/12: Clarification of the definition of controlled substances**

The *Fourth Meeting of the Parties* decided in *Dec.IV/12*:

1. that insignificant quantities of controlled substances originating from inadvertent or coincidental production during a manufacturing process, from unreacted feedstock, or from their use as process agents which are present in chemical substances as trace impurities, or that are emitted during product manufacture or handling, shall be considered not to be covered by the definition of a controlled substance contained in paragraph 4 of Article 1 of the Montreal Protocol;
2. to urge Parties to take steps to minimise emissions of such substances, including such steps as avoidance of the creation of such emissions, reduction of emissions using practicable control technologies or process changes, containment or destruction;
3. to request the Technology and Economic Assessment Panel:
  - (a) to give an estimate of the total emissions resulting from trace impurities, emission during product manufacture and handling losses;
  - (b) to submit its findings to the Open-ended Working Group of the Parties to the Montreal Protocol not later than 31 March 1994.

## **Decision VI/10: Use of controlled substances as process agents**

The *Sixth Meeting of the Parties* decided in *Dec.VI/10*, taking into account:

That some Parties may have interpreted use of controlled substances in some applications where they are used as process agents as feedstock application;

That other Parties have interpreted similar applications as use and thereby subject to phase-out;

That the Technology and Economic Assessment Panel has been unable to recommend exemption, under the essential use criteria, to Parties submitting applications of such uses nominated in 1994; and

The pressing requirement for elaboration of the issue and the need for appropriate action by all Parties;

1. To request the Technology and Economic Assessment Panel:
  - (a) To identify uses of controlled substances as chemical process agents;

- (b) To estimate emissions of controlled substances when used as process agents and the ultimate fate of such emissions and to evaluate emissions associated with the different control technologies and other process conditions under which chemical process agents are used;
  - (c) To evaluate alternative process agents or technologies or products available to replace controlled substances in such uses; and
  - (d) To submit its findings to the Open-ended Working Group of the Parties to the Montreal Protocol not later than March 1995, and to request the Open-ended Working Group to formulate recommendations, if any, for the consideration of the Parties at their Seventh Meeting;
2. That Parties, for an interim period of 1996 only, treat chemical process agents in a manner similar to feedstock, as recommended by the Technology and Economic Assessment Panel, and take a final decision on such treatment at their Seventh Meeting.

**Decision VII/10: Continued uses of controlled substances as chemical process agents after 1996**

The *Seventh Meeting of the Parties* decided in *Dec.VII/10*, recognising the need to restrict emissions of ozone-depleting substances from process-agent applications,

1. To continue to treat process agents in a manner similar to feedstocks only for 1996 and 1997;
2. To decide in 1997, following recommendations by the Technology and Economic Assessment Panel and its relevant subgroups, on modalities and criteria for a continued use of controlled substances as process agents, and on restricting their emissions, for 1998 and beyond.

**Decision VII/30: Export and import of controlled substances to be used as feedstock**

The Seventh Meeting of the Parties decided in *Dec.VII/30*:

1. That the amount of controlled substances produced and exported for the purpose of being entirely used as feedstock in the manufacture of other chemicals in importing countries should not be the subject of the calculation of “production” or “consumption” in exporting countries. Importers shall, prior to export, provide exporters with a commitment that the controlled substances imported shall be used for this purpose. In addition, importing countries shall report to the Secretariat on the volumes of controlled substances imported for these purposes;

2. That the amount of controlled substances entirely used as feedstock in the manufacture of other chemicals should not be the subject of calculation of “consumption” in importing countries.

#### **Decision X/14: Process agents**

The Tenth Meeting of the Parties decided in Dec. X/14:

Noting with appreciation the report of the Technology and Economic Assessment Panel and the Process Agent Task Force in response to decision VII/10,

Noting the findings of the Technology and Economic Assessment Panel that emissions from the use of ozone-depleting substances as process agents in non-Article 5 Parties are comparable in quantity to the insignificant emissions of controlled substances from feedstock uses, and that yet further reductions in use and emissions are expected by 2000,

Noting also the Technology and Economic Assessment Panel's findings that emissions from the use of controlled substances as process agents in countries operating under Article 5, paragraph 1, are already significant and will continue to grow if no action is taken,

Recognising the usefulness of having the controlled substances produced and used as process agents clearly delineated within the Montreal Protocol,

1. That, for the purposes of this decision, the term "process agents" should be understood to mean the use of controlled substances for the applications listed in table A below;
2. For non-Article 5 Parties, to treat process agents in a manner similar to feedstock for 1998 and until 31 December 2001;
3. That quantities of controlled substances produced or imported for the purpose of being used as process agents in plants and installations in operation before 1 January 1999, should not be taken into account in the calculation of production and consumption from 1 January 2002 onwards, provided that:
  - (a) In the case of non-Article 5 Parties, the emissions of controlled substances from these processes have been reduced to insignificant levels as defined for the purposes of this decision in table B below;
  - (b) In the case of Article 5 Parties, the emissions of controlled substances from process-agent use have been reduced to levels agreed by the Executive Committee to be reasonably achievable in a cost-effective manner without undue abandonment of infrastructure. In so deciding, the Executive Committee may consider a range of options as set out in paragraph 5 below;
4. That all Parties should:
  - (a) Report to the Secretariat by 30 September 2000 and each year thereafter on their use of controlled substances as process agents, the levels of emissions from those uses and the containment technologies used by them to minimise emissions of controlled substances. Those non-Article 5 Parties

which have still not reported data for inclusion in tables A and B are urged to do so as soon as possible and in any case before the nineteenth meeting of the Open Ended Working Group;

- (b) In reporting annual data to the Secretariat for 2000 and each year thereafter, provide information on the quantities of controlled substances produced or imported by them for process-agent applications;
5. That the incremental costs of a range of cost-effective measures, including, for example, process conversions, plant closures, emissions control technologies and industrial rationalisation, to reduce emissions of controlled substances from process-agent uses in Article 5 Parties to the levels referred to in paragraph 3 (b) above should be eligible for funding in accordance with the rules and guidelines of the Executive Committee of the Multilateral Fund;
6. That the Executive Committee of the Multilateral Fund should, as a matter of priority, strive to develop funding guidelines and begin to consider initial project proposals during 1999;
7. That Parties should not install or commission new plant using controlled substances as process agents after 30 June 1999, unless the Meeting of the Parties has decided that the use in question meets the criteria for essential uses under decision IV/25;
8. To request the Technology and Economic Assessment Panel and the Executive Committee to report to the Meeting of the Parties in 2001 on the progress made in reducing emissions of controlled substances from process-agent uses and on the implementation and development of emissions-reduction techniques and alternative processes not using ozone-depleting substances and to review tables A and B of the present decision and make recommendations for any necessary changes.

Table A: List of uses of controlled substances as process agents

No.	Substance	Process agent application
1	Carbon tetrachloride (CTC)	Elimination of NCl <sub>3</sub> in the production of chlorine and caustic
2	CTC	Recovery of chlorine in tail gas from production of chlorine
3	CTC	Manufacture of chlorinated rubber
4	CTC	Manufacture of endosulphan (insecticide)
5	CTC	Manufacture of isobutyl acetophenone (ibuprofen – analgesic)
6	CTC	Manufacture of 1-1, Bis (4-chlorophenyl) 2,2,2-trichloroethanol (dicofol insecticide)
7	CTC	Manufacture of chlorosulphonated polyolefin (CSM)
8	CTC	Manufacture of poly-phenylene-terephthal-amide
9	CFC-113	Manufacture of fluoropolymer resins
10	CFC-11	Manufacture of fine synthetic polyolefin fibre sheet
11	CTC	Manufacture of styrene butadiene rubber
12	CTC	Manufacture of chlorinated paraffin
13	CFC-113	Manufacture of vinorelbine (pharmaceutical product)
14	CFC-12	Photochemical synthesis of perfluoropolyetherpolyperoxide precursors of Z-perfluoropolyethers and difunctional derivatives
15	CFC-113	Reduction of perfluoropolyetherpolyperoxide intermediate for production of perfluoropolyether diesters
16	CFC-113	Preparation of perfluoropolyether diols with high functionality
17	CTC	Production of pharmaceuticals – ketotifen, anticol and disulfiram
18	CTC	Production of tralomethrine (insecticide)
19	CTC	Bromohexine hydrochloride
20	CTC	Diclofenac sodium
21	CTC	Cloxacilin
22	CTC	Phenyl glycine
23	CTC	Isosorbid mononitrate
24	CTC	Omeprazol
25	CFC-12	Manufacture of vaccine bottles

*Note:* Parties may propose additions to this list by sending details to the Secretariat, which will forward them to the Technology and Economic Assessment Panel. The Panel will then investigate the proposed change and make a recommendation to the Meeting of Parties whether or not the proposed use should be added to the list by decision of the Parties.



*Table B: Emission limits for process agent uses*  
(All figures are in metric tonnes per year)

<b>Country/region</b>	<b>Make-up or consumption</b>	<b>Maximum emissions</b>
European Community	1000	17
United States of America	2300	181
Canada	13	0
Japan	300	5
Hungary	15	0
Poland	68	0.5
Russian Federation	800	17
Australia	0	0
Czech Republic	0	0
Estonia	0	0
Lithuania	0	0
Slovakia	0	0
New Zealand	0	0
Norway	0	0
Iceland	0	0
Switzerland	5	0.4
<b>TOTAL</b>	<b>4501</b>	<b>220.9 (4.9%)</b>

**- end of Decisions -**

### **1.3 Definitions**

In order to clarify uses of controlled substances as process agents the PATF recommends that Parties consider the following definitions:

**Feedstock:** A controlled substance that undergoes transformation in a process in which it is converted from its original composition except for insignificant trace emissions as allowed by Decision IV/12.

**Process Agent:** A controlled substance, that because of its unique chemical and/or physical properties, facilitates an intended chemical reaction and/or inhibits an unintended chemical reaction.

Controlled substances are typically used in chemical processes as process agents for at least two of the following unique chemical and/or physical properties:

- 1.) Chemically inert during a chemical reaction
- 2.) Physical properties, e.g.

- boiling point

- vapour pressure
- specific solvency
- 3.) To act as a chain transfer agent
- 4.) To control the desired physical properties of a process, e.g.,
  - molecular weight
  - viscosity
- 5.) To increase plant yield
- 6.) Non-flammable/non-explosive
- 7.) To minimise undesirable by-product formation

**Note 1:** Refrigeration, solvent cleaning, sterilisation, aerosol propellants and fire-fighting are not process agents according to this definition.

**Note 2:** Parties need not consider use of ODS's for foam blowing, tobacco puffing, caffeine extraction, or fumigation because these uses are already covered in other Decisions and/or by Technical Options Committee Reports.

Where the term “Process Agent” is used in this report it refers to the use of a controlled substance used as a process agent.

The Montreal Protocol defines “consumption” as:

$$\text{Consumption} = \text{production} + \text{imports} - \text{exports}$$

Parties should be aware that if process agent applications are considered differently than feedstock applications the quantities of controlled substances required do not always fit this definition of consumption as consumption may not equal emissions.

In the case of ODS use as process agents, the supply is utilised to replenish process inventory lost as the result of transformation, destruction and emissions to the atmosphere from the process and/or trace quantities slowly emitted from the product.

Therefore the supply required for replenishment of lost inventory is referred to as “make-up” and defined as follows:

**Make up quantity:** The quantity of controlled substance per year, needed to continue the manufacture of products in a plant, due to transformation, destruction and inadvertent losses (i.e. emissions and residual amounts in final product).

#### **1.4        *Information required by the TEAP***

The critical information required of the PATF by the TEAP is to:

Report on the progress made in reducing emissions of controlled substances from process-agent uses and on the implementation and development of emissions-reduction techniques and alternative processes not using ozone-depleting substances and to review tables A and B of the Decision X/14 and make recommendations for any necessary changes.

The TEAP assumes that the review by the PATF and the TEAP should be limited to non-Article 5(1) countries to avoid conflict with the instructions to the Executive Committee of the Multilateral Fund found in Decision X/14.



## 2 Process Agent Use and Emissions

### 2.1 Summary of processes included in Decision X/14 or subsequently submitted to the Ozone Secretariat

Included in Decision X/14	Process	Process Agent	Case Study	Application	Reason used	Product use	Used in Article 5(1)	Used in non-Article 5(1)
1 - Yes	Chlor-alkali	CTC	CS-1*	Elimination of $\text{NCl}_3$	Safety and quality of product	Chlorine is a universal chemical used for more than 60 % of all chemical synthesis.	Unknown	Yes
2 - Yes	Chlor-alkali	CTC	CS-2*	Chlorine recovery by tail gas absorption	Safety, Yield	Chlorine is a universal chemical used for more than 60 % of all chemical synthesis.	Unknown	Yes
3 - Yes	Chlorinated Rubber	CTC	CS-3*	Chemical inert solvent for high quality product	Inert solvent	Heavy duty anti-corrosives and adhesives	Yes	Yes
4 - Yes	Endosulfan production	CTC	CS-4*	Solvent	Inert solvent	Biodegradable insecticide	Yes	Unlikely
5 - Yes	Ibuprofen production	CTC	CS-5*	Solvent for Friedel-Crafts synthesis	Inert solvent	Anti-inflammatory drug	Yes	Unlikely
6 - Yes	Dicofol	CTC	CS-6*	Solvent	Inert solvent	Broad spectrum acaricide	Yes	Unlikely
7 - Yes	Chloro sulfonated Polyolefin	CTC	CS-7a* & CS-7b*	Chlorination agent	Safety, yield		Yes	Yes
8 - Yes	Aramid Polymer PPTA	CTC	CS-8*	Chlorination specific solvent	Safety and quality of product	Asbestos replacement, public and military safety products	Unknown	Yes
9 - Yes	Fluoropolymer Resins	CFC-113	CS-9*	Specific solvent	Specific dispersant, chemical inert	Extreme temperature electrical insulation, insert coatings	Unknown	Yes
10 - Yes	Synthetic fibre sheet	CFC-11	CS-10*	Spinning agent	Quality, safety, yield	Protective wrappings, very strong sheets	No	Yes

**2.1 Summary of processes included in Decision X/14 or subsequently submitted to the Ozone Secretariat**

<b>Included in Decision X/14</b>	<b>Process</b>	<b>Process Agent</b>	<b>Case Study</b>	<b>Application</b>	<b>Reason used</b>	<b>Product use</b>	<b>Used in Article 5(1)</b>	<b>Used in non-Article 5(1)</b>
11 - Yes	SBR	CTC	No	Solvent	Chain transfer agent	Synthetic rubber, strong and resistant to extreme temperatures and climate	Yes	Unknown
12 - Yes	Chlorinated Paraffin	CTC	CS-12*	Solvent	Inert solvent	Lubricant additive, flame retardant for plastics, plasticizer in rubber paints	Yes	Unknown
13 - Yes	Manufacture of Vinobrelina	CFC-113	No	Unknown	Unknown	Pharmaceutical	Unknown	Unknown
14 - Yes	Photochemical synthesis of perfluoro-polyetherpolyperoxide precursors of Z-perfluoropolyethers and difunctional derivatives	CFC-12	CS-14*				Unknown	Yes
15 - Yes	Reduction of perfluoropolyetherpolyperoxide intermediate for production of perfluoropolyether diesters	CFC-113	CS-15*				Unknown	Yes
16 - Yes	Preparation of perfluoropolyether diols with high functionality	CFC-113	CS-16*				Unknown	Yes
17a - Yes	Production of ketotifen	CTC	No	Unknown	Unknown	Pharmaceutical	Likely	Likely
17b - Yes	Production of anticol	CTC	No	Unknown	Unknown	Pharmaceutical	Likely	Likely

**2.1 Summary of processes included in Decision X/14 or subsequently submitted to the Ozone Secretariat**

<b>Included in Decision X/14</b>	<b>Process</b>	<b>Process Agent</b>	<b>Case Study</b>	<b>Application</b>	<b>Reason used</b>	<b>Product use</b>	<b>Used in Article 5(1)</b>	<b>Used in non-Article 5(1)</b>
17c - Yes	Production of disulfiram	CTC	No	Unknown	Unknown	Pharmaceutical	Likely	Likely
18 - Yes	Production of tralomethrine	CTC	No	Unknown	Unknown	Insecticide	Unknown	Unknown
19 - Yes	Bromohexine hydrochloride	CTC	CS-19*	Unknown	Unknown	Pharmaceutical	Yes	Unknown
20 - Yes	Diclofenac sodium	CTC	CS-20*	Solvent	Yield	Pharmaceutical	Yes	Unknown
21 - Yes	Cloxacillin	CTC	No - see Chapter 5a	Unknown	Unknown	Pharmaceutical	Yes	Unknown
22 - Yes	Phenyl glycine	CTC	CS-22*	Solvent	Unknown	Pharmaceutical	Yes	Unknown
23 - Yes	Isosorbid mononitrate	CTC	No - see Chapter 5a	Unknown	Unknown	Pharmaceutical	Yes	Unknown
24 - Yes	Omeprazol	CTC	No - see Chapter 5a	Unknown	Unknown	Pharmaceutical	Yes	Unknown
25 - Yes	Manufacture of vaccine bottles	CFC-12	No	Unknown	Unknown	Pharmaceutical	Unknown	Unknown
26 - Submitted to Ozone Secretariat	Manufacture of Cyclodime	CTC	CS-26*	Solvent	Inert Solvent	Extreme and adverse temperatures in aeronautic hydraulic system components	Unknown	Yes

\* Case Studies can be found at: [http://www.teap.org/html/process\\_agents\\_reports.html](http://www.teap.org/html/process_agents_reports.html)

**2.2 Summary of processes not yet included in Decision X/14 - information supplied to PATF**

<b>Included in Decision X/14</b>	<b>Process</b>	<b>Process Agent</b>	<b>Case Study</b>	<b>Application</b>	<b>Reason used</b>	<b>Product use</b>	<b>Used in Article 5(1)</b>	<b>Used in non-Article 5(1)</b>
27 - Not yet submitted to Ozone Secretariat	Chlorophenesin	CTC	No- see Chapter 5a	Unknown	Unknown	Pharmaceutical	Yes	Unknown

28 – Not yet submitted to Ozone Secretariat	Manufacture of Chlorinated Polypropene	CTC	No – see Chapter 5b	Solvent	Yield, quality of product	Coating materials, adhesives, silk screen inks	Yes	Unknown
29 – Not yet submitted to Ozone Secretariat	Manufacture of Chlorinated EVA	CTC	No – see Chapter 5b	Solvent	Yield, quality of product	Coating materials, silk screen inks	Yes	Unknown
30 – Not yet submitted to Ozone Secretariat	Manufacture of methyl Isocyanate derivatives	CTC	No – see Chapter 5b	Solvent	Inert solvent, yield, quality, safety	Pesticide	Yes	Unknown
31 – Not yet submitted to Ozone Secretariat	Manufacture of 3-PhenoxyBenzyldehyde	CTC	No – see Chapter 5b	Solvent	Inert solvent, yield, quality, safety	Pesticide	Yes	Unknown
32 – Not yet submitted to Ozone Secretariat	Manufacture of 2-chloro-5-methylpyridin	CTC	No – see Chapter 5b	Solvent	Inert solvent, yield, quality, safety	Intermediate for Imidacloprid	Yes	Unknown
33 – Not yet Submitted to Ozone Secretariat	Manufacture of Imidacloprid; 1-(6-chloro-3-pyridylmetyl)-N-nitroimidazoleneamine-2	CTC	No – see Chapter 5b	Solvent	Inert solvent, yield, quality, safety	Pesticide	Yes	Unknown
34 – Not yet submitted to Ozone Secretariat	Manufacture of Bupropfenzin; 2-tert-butylimino-3-isopropyl-5-phenylperhydro-1,3,5-thiadiazin-4-one	CTC	No- see Chapter 5b	Solvent	Inert solvent, yield, quality, safety	Pesticide	Yes	Unknown
35 – Not yet submitted to Ozone Secretariat	Manufacture of Oxadiazon; 2-tert-butyl-4-(2,4-dichloro-5-isopropoxyphenyl-1,3,4-oxadiazolan-5-one	CTC	No – see Chapter 5b	Solvent	Inert solvent, yield, quality, safety	Herbicide	Yes	Unknown
36 – Not yet submitted to Ozone Secretariat	Manufacture of Chloridized N-methylaniline	CTC	No – see Chapter 5b	Solvent	Inert solvent, yield, quality, safety	Intermediate for Bupropfenzin	Yes	Unknown
37 – Not yet submitted to Ozone Secretariat	Manufacture of Mefenacet; D-(1,3-benzothiozole-2-oxy)-N-methylacetanilide	CTC	No – see Chapter 5b	Solvent	Inert solvent, yield, quality, safety	Pesticide	Yes	Unknown



38 – Not yet submitted to Ozone Secretariat	Manufacture of 1,3-dichloro-benzothiazole	CTC	No – see Chapter 5b	Solvent	Inert solvent, yield, quality, safety	Intermediate for Mefenacet	Yes	Unknown
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### **2.3 ODS used as process agents**

The preceding tables have shown that the most common process agent used is CTC, one process used CFC-11, one uses CFC-12 and four use CFC-113. The widest use of CTC as a process agent is in the field of chlorine production. Other uses vary and consist of manufacture of polymers, chlorinated (intermediate) products, pharmaceuticals, pesticides and other agricultural chemicals.

Some process agent uses listed have no known or feasible alternatives at present. However, this knowledge is not static; much progress has been made and will continue in finding solutions or alternatives that reduce or eliminate use of ODS's.

### **2.4 Emissions of process agents in non-Article 5(1) countries**

Precise accounting of emissions is not technically and administratively feasible because estimates are based on engineering calculations using process assumptions, because chemical process yields vary over time, and because equipment failure and leaks result in unmonitored emissions.

Most Parties have failed to report process agent uses and emissions. Decision X/14 requested all Parties to report to the Secretariat by 30 September 2000 and each year thereafter on their use of controlled substances as process agents, the levels of emissions from those uses and the containment technologies used by them to minimise emissions of controlled substances. The Ozone Secretariat received only 17 reports, 4 from non-Article 5(1), 3 from CEIT, and 10 from Article 5(1). Most lacked sufficient detail to allow for meaningful evaluation.

The Ozone Secretariat has drawn our attention to paragraph 36 of the Report of the 25th meeting of the ImpCom, 9 December 2000, as follows:

"One representative expressed the view that the reporting requirement on process agents set out in decision X/14 was not sufficiently clear, leading to problems with the drafting of data form 6 and its eventual approval. It was agreed that the Secretariat would identify the Parties which would be affected by the reporting requirement and invite them to discuss which data should be provided and how the form should be designed. It would then report back to the Committee with a review to a recommendation being made to the Meeting of the Parties."

The PATF received unofficial reports from industry association and process agent users and government authorities confirming that ODS emissions from process agent application in non-Article 5(1) countries have decreased since the 1997 TEAP report.

The PATF estimates that 4000-5000 tonnes of ODSs are used annually in process agent applications in non-Article 5(1) countries. Plant specific annual emissions are estimated as less than 250 tonnes – less than 7% of make-up quantities. This has been achieved by capture and recycle or destruction, or chemical transformation of the ODS.

## **3 Regulations and Guidelines for Minimising and Monitoring Emissions**

### ***3.1 Introduction***

This chapter provides an overview of approaches currently in use to minimise and monitor emissions of ozone-depleting substances in process agent applications. As indicated by the Case Studies in Appendix C, all process agent industries operating in non-Article 5(1) countries are subject to specific domestic emission regulations or negotiated government-industry targets which have resulted in the elimination or significant reduction of ODS emissions. In addition to pressure for elimination because of its ozone depletion potential, CTC use in non-Article 5(1) countries has historically been subject to rigorous regulatory control because it is highly toxic.

In the Article 5(1) countries emission standards for CTC and other ODS vary from stringent to non-existent. Widespread knowledge of the health and safety issues of CTC has resulted in reduced emissions, contributing to the goal of the Montreal Protocol. No information is available from CEIT countries.

### ***3.2 Governmental approaches***

The unique legal and industrial circumstances of individual non-Article 5(1) countries have resulted in a broad array of successful approaches for minimising emissions from process agent applications. One Scandinavian country has allowed ODS use only with payment of monetary penalties. Other countries in the EU and North America have adopted more traditional command-and-control measures or negotiated limits established in collaboration with the affected industry or facility. In general, the PATF identified four levels of regulatory approaches used in non-Article 5(1) that have resulted in the very low ODS emissions observed in process agent applications. Although there is a descending order of administrative hierarchy, each of these types of regulations are equally effective. Due the high toxicity of CTC, health and safety standards have often been a driving force behind the rapid emission achievements observed in non-Article 5(1) countries.

#### **3.2.1 Supra-national and regional approaches**

For example the European Union issues regulations and directives that are applicable in the member states. EU regulations have the force of law; directives mandate more general guidelines and requirements. Member states are required to change national laws and regulations to implement directives but they are free to tailor programs to meet their needs as long as the programs provide compliance with the EU regulations.

#### **3.2.2 National approaches**

In many countries national legislation on air, water and waste provide legal authority to meet standards on emission controls and monitoring/reporting requirements for toxic and hazardous chemicals.

### 3.2.3 Sub-national approaches

In order to implement national regulatory programs or through prefecture, departmental, provincial or state legislation, specific sub-national regulations are developed. Often these regulations are more stringent than nationally-set regulations.

Local authorities have a delegated or mandated authority to issue licenses, permits and other controls which limit emissions.

### 3.3 *Voluntary standards to reduce emissions*

In some countries and for some applications, voluntary efforts by industry have led to significant reductions in emissions. For example, in Japan the goal of industry has been to voluntarily eliminate all use of ODS as process agents. Industry and trade associations have generated “codes of good practice” as support for members in meeting voluntary standards. Technical directives and guidelines based on proven techniques have facilitated moving process agent applications toward lower emissions. Individual companies using non-toxic ODSs have also initiated corporate policies to minimise ODS emissions. Some Article 5(1) process agent users also rely on corporate policies, that may be more stringent than applicable regulatory standards, to minimise ODS emissions in the absence of regulatory standards.

### 3.4 *Regulatory review*

#### 3.4.1 Introduction

This section provides an overview of approaches currently in use in Article 5(1) and non-Article 5(1) countries to monitor and minimise emissions of ozone-depleting substances in process agent applications. Differences in national, regional and local standards complicate efforts to compare standards or to estimate the overall burden placed on process agent facilities located in different countries or within a specific country. However, as indicated by the Case Studies that can be downloaded from [http://www.teap.org/html/process\\_agents\\_reports.html](http://www.teap.org/html/process_agents_reports.html), all non-Article 5(1) countries must currently meet specific regulations to minimise emissions of ODSs used in process agent applications. In the Article 5(1) countries emission standards for CTC and other ODS vary from stringent to non-existent. Similar to the non-Article 5(1) countries, widespread knowledge of the health and safety issues pertaining to CTC has resulted in some lowering of emissions, and thereby contributes to the goals of the Montreal Protocol. The PATF also considered institutional/regulatory barriers to emission reductions.

#### 3.4.2 Types of Standards

##### 3.4.2.1 Regulatory

A number of countries currently restrict ODS emissions in process agent applications through the use of licensing, industry- or chemical-specific control standards or use bans. Mandatory reduction strategies were identified that control

direct emissions to air, water, waste and to limit occupational exposures. Specific emission or concentration limits and technical control requirements (e.g. maximum achievable control technologies) are commonly imposed on process agent applications. Ambient release standards and general emission concentration limits are generally linked to the toxicity of the ODS rather than the Ozone Depletion Potential (ODP). Some countries vary emission standards depending on whether production processes are continuous or batch. One country has, however, banned emissions of ODS including uses in process agent applications.

In addition to ambient emission controls, some countries regulate equipment leaks or mandate leak detection and repair programs that include such control mechanisms as mandated leak detection and repair programs, periodic monitoring, visual inspections, and instrument monitoring.

Reporting and record keeping requirements are mandated in a number of countries to support the enforcement of emission reduction strategies. In some countries penalties can be applied to both an individual offender within a corporation and the corporation as an entity. Compliance orders outlining activities and a schedule for compliance are other common means of enforcement.

#### 3.4.2.2 Voluntary and industry set standards to reduce emissions

Several facilities with licensing or other partnerships with non-Article 5(1) based companies reported implementation of corporate-dictated ODS emission initiatives.

Some non-article 5(1) governments have developed ordinances or guidelines in lieu of or to supplement regulatory requirements. One country reported negotiated but non-binding agreements with process agent sources in order to identify specific control commitments. One country also reported the use of economic incentives such as grants or tax concessions to reduce the burden of environmental regulation and encourage environmentally friendly actions

#### 3.4.3 Institutional/Regulatory impediments to emission reduction

For pharmaceutical and agricultural chemical products, some countries require additional regulatory review for any formulary change.



## 4 Alternatives to the Use of Controlled Substances as Process Agents

### 4.1 *The nature of process agents*

Alternatives for process agents can often be devised if the reasons for the use of the process agents are analysed carefully and due consideration is given to their chemical and physical properties, their toxicology, the environmental consequences of their release or emission, and the costs associated with their use or with modifications to plant or processes that might be needed to introduce alternatives.

No rigorous definition of process agent has been established by the Parties, but the PATF has provided an operational definition in section 1.3 of this report. In decision X/14, clause 1, the Parties agreed that process agents were those uses of controlled substances listed in table A of the decision. Table A of decision X/14 is shown in Section 1.2 of this report.

The process agent is generally present during the chemical reaction as a solvent, although examples are accepted in which the process agent participates in the chemical reaction but is recovered unchanged at the end of the reaction. This would be the case, for example, when a process agent is used as a chain transfer agent, in a polymerisation process, when the role of the process agent is to terminate a growing polymer chain and initiate the growth of a subsequent chain. The overall effect is to produce more short or intermediate-length polymer chains at the expense of fewer long chains.

The use of a process agent as a solvent is not necessarily a simple matter. The essential requirements are that one or more of the reactants, and possibly the products, should dissolve in the solvent, and that the solvent should remain unchanged while the chemical reaction takes place. These requirements are frequently in opposition: more polar substances have greater solvent power but they are more chemically reactive, too. For example, carbon tetrachloride (CTC) is not a particularly powerful solvent, but since it does not react with chlorine it is often the solvent of choice when chlorine chemistry is involved or when chlorine has to be absorbed from a gas stream. Chloroform, trichloromethane, is a more powerful solvent than carbon tetrachloride but it reacts with chlorine (as well as with many other chemical substances to which CTC is un-reactive) and so is less often employed in chemical industry.

Some specialised considerations of solvent properties may also apply, as when a re-crystallisation needs to be performed. The product, in such a case, will need to dissolve in the hot solvent but be precipitated as the solution cools. The success of a subsequent materials handling step, for example filtration, will depend on the physical form of this precipitate, and this can often be optimised by choice of the appropriate solvent for re-crystallisation.

Examples are also known where the operation to be performed is not a chemical reaction but a physical one, such as fibre spinning, and here the viscosity of the solution will be an important factor. This will depend on the concentration of the

solution that can be achieved (and thus on solvent power) as well as on specific solute-solvent interactions which determine viscosity.

In some cases, the preferred solvent is chosen over solvents with similar solvent power or chemical properties on the basis of its melting or boiling point. To take an example from outside the field of ODS, toluene (liquid range  $-95^{\circ}$  to  $111^{\circ}\text{C}$ ) may be preferred to the similar hydrocarbon, benzene (liquid range  $6^{\circ}$  to  $80^{\circ}\text{C}$ ). By conducting the chemical reaction in solvent with appropriate boiling point, the reaction temperature may be maintained close to the boiling point of that solvent (in the case of CTC,  $76^{\circ}\text{C}$ ), although pressures higher than atmospheric may be required to maintain a low-boiling solvent in liquid state.

Finally, consideration in choice of a solvent would be given to the removal of the solvent from the product, especially where traces of retained solvent would constitute a hazard to human health or the environment. A well-known advantage of the use of carbon dioxide (used under high pressure to maintain the liquid or super-critical state) is that traces of residual "solvent" remaining in foodstuffs such as decaffeinated coffee do not constitute a hazard. Substantial efforts must be made, however, to remove the residues of solvents such as CTC from industrial products such as the aramid resins which are discussed below.

**4.2 Alternatives to the use of ODS (Available Case Studies can be found at: [http://www.teap.org/html/process\\_agents\\_reports.html](http://www.teap.org/html/process_agents_reports.html))**

**4.2.1 Chlor-Alkali production**

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-1
Application	Elimination of $\text{NCl}_3$
Reason Used	Safety and quality of product
Product use	Chlorine is a universal chemical used for more than 60% of all chemical synthesis
Identified alternatives	No general alternatives. Some plant specific alternatives.

CTC is the traditional and efficient agent to extract nitrogen trichloride ( $\text{NCl}_3$ ) from liquid chlorine.  $\text{NCl}_3$  is a highly explosive substance inadvertently produced in chlor-alkali plants when the electrolysed salt contains nitrogenous impurities. Both sea salt and mined salt contain such impurities, although there is more in salt from the latter source. The nitrogen is at the ammonia (rather than nitrate) oxidation level, often in the form of protein material, and exposure to chlorine converts it to nitrogen trichloride. While some uses of chlorine can tolerate the presence of small proportions of nitrogen trichloride, when the focus of the operation is the production of liquid chlorine then  $\text{NCl}_3$  can build up to a dangerous concentration.



The obvious ODS free solution is the use of very pure salt but this is an extremely rare commodity. Transportation of salt of required purity to an existing plant site is often not technically or economically feasible. Strategies for dealing with the  $\text{NCl}_3$  problem must be taken on a case by case basis, as plant design and equipment, presence of nitrogen derivatives, and purity requirements for chlorine are very different from one facility to another. For a particular plant, one technique might be a suitable solution, only a partial one, or cannot be safely used at all.

The strategies available to the industry include:

- selection of a non-ODS process agent
- elimination of the nitrogen derivatives from the salt solution before electrolysis
- destruction of  $\text{NCl}_3$
- dilution of  $\text{NCl}_3$  in liquid chlorine

The first of these has not been fruitful because no alternative process agent having the unique set of required properties has been identified by the industry. It has been suggested that chloroform might be a suitable replacement for CTC, since it is a good solvent for  $\text{NCl}_3$ , but it is converted to CTC by reaction with chlorine and so offers no advantage over starting with CTC itself. A complete set of technical requirements is not available to the PATF at this time, so the extent to which suitable alternative process agents have been sought cannot be evaluated.

Similarly, no method is available for economically removing nitrogenous impurities from the salt.

Nitrogen trichloride is rapidly destroyed by heating above approximately  $50^\circ\text{C}$ , and this is the usual technique for destroying it either in the chlorine stream or in the CTC extract. The first method is employed where chlorine is used at the site of generation, with only minimal storage in liquid form. Re-vaporisation of chlorine by heating the liquid, suffices to destroy the  $\text{NCl}_3$ . The second method is the one in which CTC is traditionally employed as solvent to extract  $\text{NCl}_3$  from the chlorine.

As mentioned above, some uses can tolerate small proportions of  $\text{NCl}_3$  in the chlorine gas, and it is presumably destroyed in subsequent processing or acts in the same way as chlorine to perform a chlorination reaction on some organic substrate.

#### 4.2.2 Recovery of chlorine in gas from production of chlorine

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-2
Application	Chlorine recovery by gas absorption
Reason Used	Safety, yield
Product use	Chlorine is a universal chemical used for more than 60% of all chemical synthesis
Identified alternatives	Plant specific alternatives only

CTC has been the solvent of choice for the tail gas recovery process. Strict requirements for stability in the presence of chlorine, corrosivity, acceptable toxicity, mutual solubility with chlorine, and vapour pressure have excluded the use of alternate substances. The absorption/stripping tail gas process allows for essentially complete recovery of all of the chlorine as liquid product. Other technologies do exist for partial recovery of the tail gas chlorine or for conversion of the tail gas to a different product.

The most obvious substitute for the CTC gas process is to install additional liquefaction equipment. Additional drying steps using sulphuric acid may be necessary to prevent excessive corrosion in this case. Equipment to perform a neutralisation step with an alkali (or other treatment) must then also follow due to the practical limits to which chlorine can be recovered through liquefaction alone. The product from this neutralisation step must then be disposed of in an appropriate manner.

In addition to this technological approach, there are several chemical reactions that can be used to sequester chlorine from the tail gases. One is to absorb the chlorine in sodium hydroxide, leading to formation of the marketable product sodium hypochlorite. Another is to react the tail gas chlorine with hydrogen to form gaseous hydrogen chloride, which is then absorbed in water to form hydrochloric acid. This requires specialised equipment at a substantial cost, and also adds additional safety risk from the standpoint of explosion potential. Both of the "chemical" approaches involve the production of co-products, small in volume compared to the major product chlorine, but nonetheless requiring separate marketing or disposal.

#### 4.2.3 Chlorinated Rubber

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-3
Application	Chemical inert solvent for high quality product
Reason Used	Inert solvent
Product use	Heavy duty anti-corrosives and adhesives
Identified alternatives	Aqueous process – see 4.4

Some details of the CTC based process used in Germany to produce chlorinated rubber (CR) are given in Case Study CS-3. These substances are used in surface coatings and solvent based inks. An important criterion which drives the choice of CTC is its role in determining the quality of the product, but a number of different processes are used for the production of chlorinated rubber so the search for alternatives has explored many possibilities. Two main lines of investigation can be distinguished:

- CTC use is maintained in the process but the emissions have been virtually eliminated.
- a water based process has been developed after 5 years of research and development.

The reduction of more than 99% of CTC emissions from CR production in the non-Article 5(1) countries, in less than 5 years, shows that CR can be produced in an environmentally responsible manner.

A Case Study (CS-3a) describing an aqueous process for the production of chlorinated rubber will be provided at:

[http://www.teap.org/html/process\\_agents\\_reports.html](http://www.teap.org/html/process_agents_reports.html) in the near future. The aqueous process does not require the use of CTC as a process agent, however there is some possibility of inadvertent production of CTC from the aqueous process. For a plant operating in an Article 5(1) country it is likely that the aqueous process would result in much lower emissions than the CTC based process. In an Article 5(1) country it would be very difficult to achieve the type of process control and facility maintenance achieved at the German plant or for an Article 5(1) government to provide the degree of compliance monitoring undertaken by the German government. These important factors have resulted in the extremely low emissions of CTC achieved by the German facility.

#### 4.2.4 Endosulfan production

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-4
Application	Solvent
Reason Used	Inert solvent
Product use	Biodegradable insecticide
Identified alternatives	Yes – aromatic solvent

The insecticide Endosulfan, which is widely used by cotton growers, is produced in two stages, the second of which involves the reaction of thionyl chloride ( $\text{SOCl}_2$ ) with the two  $-\text{CH}_2\text{OH}$  groups of the initial adduct, forming a new seven-membered ring. The initial patent in this area does not describe the use of a solvent during this second stage, but while some plants operate in this way (probably using excess thionyl chloride as a solvent which is recovered when the reaction has taken place) others use CTC as solvent, recovering it at the conclusion of the reaction and recycling it in the process. There are few specific chemical requirements for such a solvent and so CTC should be easily replaced in this process and several companies have made such a substitution. Thus, one company uses ethylene dichloride (EDC) while another reports successful use of an aromatic solvent, but in the latter case flammability of the selected solvent may be an issue. The adoption of the alternatives requires only a small change in the production process (see Case Study CS-4).

#### 4.2.5 Ibuprofen production

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-5
Application	Solvent for Friedel-Crafts synthesis
Reason Used	Inert solvent
Product use	Anti-inflammatory drug
Identified alternatives	Yes

The initial step in production of the anti-inflammatory drug Ibuprofen (see Case Study CS-5 available at: [http://www.teap.org/html/process\\_agents\\_reports.html](http://www.teap.org/html/process_agents_reports.html)) involves the Friedel Crafts acylation of isobutyl benzene with acetyl chloride in the presence of aluminium chloride and a suitable solvent, and in the initial patent CTC was used for this purpose. As above, however, a range of solvents might be employed and it is reported that ethylenedichloride (EDC) is an acceptable substitute for CTC.

#### 4.2.6 Dicofol production

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-6
Application	Solvent
Reason Used	Inert solvent
Product use	Broad spectrum acaricide
Identified alternatives	Yes

Mites and ticks are controlled with the acaricide Dicofol, the molecule of which is closely related to DDT and Dicofol is in fact prepared from that substance. CTC is used as a solvent in two of the three stages of that process. In the second stage, the reaction involves chlorination and so a non-reactive solvent is required, but in the third stage the CTC is used as a water-immiscible solvent to extract the Dicofol product. It is reported that dichloroethane (ethylene dichloride) is an acceptable substitute for CTC, although certain technical changes are required in both stages, (see Case Study CS-6).

#### 4.2.7 Chlorosulfonated Polyolefin (CSM)

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-7a and CS-7b
Application	Chlorination agents
Reason Used	Safety, yield
Product use	High tech coatings, protective materials
Identified alternatives	No viable alternative as yet for majority of products. Non-ODS for limited application.

These flexible materials find use mainly because of their oil and grease resistance and general durability. In North America, no viable alternative to the use of CTC has been found for the full range of products and processes of commercial significance. Of the many investigated possibilities chloroform seemed promising, but it leads to a 40% reduction of production capacity and to inadvertent formation of large quantities of CTC. The reaction conditions are particularly harsh, involving reaction of the polyolefin with chlorine and sulphur dioxide at moderately elevated temperature.

The processes employed are described in Case Studies CS-7a and CS-7b. In China, the possibility of using chlorobenzene as a process agent was investigated, but this option was abandoned for the following reasons:

- energy consumption is much higher than when using CTC due to the higher boiling point of chlorobenzene
- chemical stability of the solvent to chlorine and sulphur dioxide is lower than that of the CTC process
- plant safety was compromised by the flammability, explosivity and toxicity of chlorobenzene

#### 4.2.8 Aramid polymer (PPTA)

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-8
Application	Chlorination specific solvent
Reason Used	Quality, safety, waste reduction
Product use	Asbestos replacement, public and military safety products
Identified alternatives	No viable alternative as yet

Fibres produced from these substances are light weight and have high tensile strength, good flame resistance and good chemical stability. They may be used in protective helmets, cladding for chemical storage and transport containers, non-asbestos brake linings, and bullet-proof vests. The polymer is formed by reaction of two monomers, paraphenylenediamine and terephthaloyl dichloride (TDC), as described in Case Study CS-8. The second of these monomers is formed in a preliminary stage which involves chlorination of p-xylene, in CTC, followed by fusion of the chlorination product, hexachloro-p-xylene with terephthalic acid.

A commercial non-ODS process for the production of the raw material TDC is known. This is however based on a different chemical reaction and the process is carried out with the use of phosgene as a raw material. Such use is only technically and commercially viable when phosgene is already available on the site or, where new plant is required, it may be used for more than one product. A research and development program to find an ODS free alternative to the existing production process is showing promising progress.

#### 4.2.9 Fluoropolymer resins

Included in Decision X/14	Yes
Process agent	CFC-113
Case Study	CS-9
Application	Specific solvent
Reason Used	Specific dispersant, chemical inert
Product use	Extreme temperature electrical insulation, inert coatings
Identified alternatives	Alternative for portion of products. Continuing program.

This family of polymers are commonly used in non-stick cookware and high-performance electrical insulation, see Case Study CS-9. In North America, close to fifty potential process agents for use in polymer production have been explored over the past eight years as part of a research and development program. Much of the product line was converted away from CFC-113 ( $\text{CF}_3\text{-CCl}_3$ ) during 1997 and 1998. However, there are still specific critical use applications for which non-ODS process agents have yet to be found. Efforts are continuing to find an acceptable process agent or suitable processing conditions for these products.

In Japan, a plant for manufacture of fluoropolymer resins has been converted to a non-ODS process utilising a proprietary technology, but the facility does not produce the full range of products.

#### 4.2.10 Fine synthetic fibre sheet

Included in Decision X/14	Yes
Process agent	CFC-11
Case Study	CS-10
Application	Spinning agent
Reason Used	Quality, safety, yield
Product use	Protective wrapping, very strong sheets
Identified alternatives	Conversion to non-ODS process agent underway.

Sheets derived from synthetic fibres such as high density polyethylene are widely used in protective clothing, sterilisable packaging, and air filtration. The fibres are formed by extrusion in a spin cell of solutions of the polymer in a low-boiling solvent which vaporises as the fibrous mass is formed and may then be recovered for recycling, see Case Study CS-10. No simple, safe, drop-in candidate has been identified to replace CFC-11 in the existing facilities, despite a continuing (more than twelve years) program that has examined over one hundred and twenty possible process agents. A non-ODS process agent has been developed, but it requires completely new spinning and recovery facilities to use it. The first two new commercial facilities were started in 1995, and a third in 2000. Process safety management is key to the safe operation of these facilities. Continued safety analysis has shown that process safety can be significantly improved with the addition of new solution mixing technology. This technology will be retrofitted on the first two facilities at considerable expense and down time over the next three years. In addition, a new fourth generation facility is being constructed with operation scheduled for 2002. This fourth generation technology will form the basis for future capacity expansions. Confirmation of this fourth generation technology is needed to allow full conversion from CFC-11 operations.

#### 4.2.11 SBR

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Chain transfer agent
Product use	High tech coatings, protective materials
Identified alternatives	Yes - mercaptans

CTC is used as a chain transfer agent in the manufacture of this type of synthetic rubber that is strong and resistant to extreme temperatures and climate. No CTC is used to manufacture this product in China.

#### 4.2.12 Chlorinated paraffins

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-12
Application	Solvent
Reason Used	Inert solvent
Product use	Lubricant additive, flame retardant for plastics, plasticizer in rubber paints.
Identified alternatives	Yes

These substances, with chain lengths between 10 and 26 carbons and chlorine content of 28-70% are produced by chlorination of respective paraffin fractions derived from petroleum refining. They are used variously as high pressure lubricants, as plasticizers and as flame retardants, depending on their physical properties. The lower members of the family are bio-accumulative and are generally being phased-out in developed countries. Chlorination may be undertaken in the absence of a solvent provided the product is liquid at reaction temperatures, but the highly chlorinated materials are solids, making it necessary to use a solvent such as CTC to reduce the viscosity of the reaction mixture. Aqueous processes are probably available as well.

#### 4.2.13 Vinorelbine

Included in Decision X/14	Yes
Process agent	CFC-113
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Pharmaceutical
Identified alternatives	Yes

This is an anticancer drug (antineoplastic) manufactured by modification of a natural product from the vinca alkaloid family and known as nor-5 $\beta$ -anhydrovinblastine. The original publications do not mention CFC-113, but instead report the use of m-chloroperbenzoic acid in dichloromethane followed by trifluoroacetic anhydride in the same solvent. It is possible that in manufacture CTC has been found to be more satisfactory from a chemical point of view than dichloromethane. Production quantities of such a drug are likely to be very small when compared to basic chemicals like chlorine or chlorinated rubbers.



4.2.14 Photochemical synthesis of perfluoropolyetherpolyperoxide precursors of Z-perfluoropolyethers and difunctional derivatives

Included in Decision X/14	Yes
Process agent	CFC-12
Case Study	CS-14
Application	
Reason Used	
Product use	
Identified alternatives	

4.2.15 Reduction of perfluoropolyetherpolyperoxide intermediate for production of perfluoropolyether diesters

Included in Decision X/14	Yes
Process agent	CFC-113
Case Study	CS-15
Application	
Reason Used	
Product use	
Identified alternatives	

4.2.16 Preparation of perfluoropolyether diols with high functionality

Included in Decision X/14	Yes
Process agent	CFC-113
Case Study	C-16
Application	
Reason Used	
Product use	
Identified alternatives	

4.2.17a Ketotifin

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Antihistamine
Identified alternatives	Likely

This substance is an antihistamine which is structurally similar to the tricyclic antidepressants. The first stage in its synthesis involves reaction of a CTC solution of an alkene (-CH=CH-) with N-bromosuccinimide and benzoyl peroxide, to form a dibromo-compound (-CHBr-CHBr-) which is further modified in subsequent

stages. None of these later stages involves the use of CTC. Investigations should easily identify a suitable replacement solvent.

#### 4.2.17b Anticol

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Possible pharmaceutical
Identified alternatives	Unknown

No information was provided or located on this substance, which appears to be used as a pharmaceutical.

#### 4.2.17c Disulfuram

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Pharmaceutical
Identified alternatives	Yes

This substance is taken to sensitise users against alcohol consumption. Nothing in the chemical literature suggests the use of CTC as reported to the PATF. In the first of two stages in its production, diethylamine is reacted with carbon disulphide in aqueous alkali, and then this product is oxidised with sodium hypochlorite, again in aqueous solution, in the second stage.

#### 4.2.18 Tralomethrine

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Insecticide
Identified alternatives	Unknown

This substance is a synthetic pyrethrin, which like all members of this chemical family is an ester formed from a cyclopropane carboxylic acid and an aromatic alcohol. No further details are available.

#### 4.2.19 Bromohexine hydrochloride

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-18
Application	No information provided
Reason Used	No information provided
Product use	Pharmaceutical - expectorant
Identified alternatives	Likely

The molecule of this substance, which is used as an expectorant, is constructed by joining two major portions at a central nitrogen atom. The original patent describes how one portion is elaborated through conversion of a  $-CH_3$  group to  $-CH_2Br$ . This bromination is effected by a selective brominating agent and, although no solvent is mentioned in the patent, it is likely that CTC is involved since it is commonly employed in such reactions. As in other cases previously discussed, however, it should be easy to find a replacement solvent.

#### 4.2.20 Diclofenac sodium

Included in Decision X/14	Yes
Process agent	CTC
Case Study	CS-20
Application	Solvent
Reason Used	Yield
Product use	Pharmaceutical – anti-inflammatory
Identified alternatives	Yes

This anti-inflammatory drug has been synthesised in a number of ways, but the most elegant (and presumably commercially advantageous) method involves the use of oxalyl chloride ( $Cl-CO-CO-Cl$ ) and a Friedel Crafts reaction catalysed by aluminium chloride. The original patent describes the use of “tetrachloroethane” as solvent for this stage of the synthesis, and it is possible that this is a misprint for tetrachloromethane - CTC. The reaction is conducted under mild conditions, so there would be no need to take advantage of the higher boiling point of the tetrachloroethane, but its greater solvent power may have been the reason for its use if indeed it was the solvent involved. In the scheme shown in Case Study CS-20, CTC is used (in conjunction with perchloroethylene) in the very first step, the chlorination of phenol. The choice of solvent affects the selectivity of the reaction so that 2,6-dichlorophenol is favoured over the alternative product, 2,4-dichlorophenol.

#### 4.2.21 Cloxacillin

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Pharmaceutical - antibiotic
Identified alternatives	Likely

This is a semi-synthetic penicillin formed by reaction of the natural penicillanic acid and an acid chloride, which is then formed from a synthetic acid. The formation of the acid chloride involves reaction of the acid with thionyl chloride (SOCl<sub>2</sub>), and the original patent describes this reaction as being carried out in excess thionyl chloride, which thus plays the role of solvent as well as reactant. CTC could be used as solvent in this reaction, but finding a substitute for CTC should be possible.

#### 4.2.22 Phenyl glycine

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	No information provided
Product use	Pharmaceutical
Identified alternatives	Unknown

The solvent CTC is known to be used in two successful chemical reactions which use this amino-acid (C-phenyl glycine). In the first reaction, HCl in dry CTC is used to form the hydrochloride salt, which is then reacted with thionyl chloride to convert the -COOH group to the acid chloride. This product, being similarly insoluble in CTC, is washed with CTC to effect purification.

#### 4.2.23 Isosorbid mononitrate

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Pharmaceutical – vasodilator
Identified alternatives	Yes

This is a vasodilating drug, similar in its effects to the nitro-glycerine (glyceryl trinitrate) that is used by angina sufferers. The dinitrate, and presumably the mononitrate, may be prepared from sorbitol by reaction with a typical nitric-and-

sulphuric acid nitrating mixture. The published chemistry provides no indication of the use of CTC.

#### 4.2.24 Omeprazole

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	No information provided
Product use	Pharmaceutical – anti-ulcer drug
Identified alternatives	Likely

This anti-ulcer drug is produced by joining together two building blocks. One of these is primed for the coupling step by reacting it with thionyl chloride ( $\text{SOCl}_2$ ) to convert a  $-\text{CH}_2\text{OH}$  group into a  $-\text{CH}_2\text{Cl}$  group. The literature descriptions of this step do not mention the use of a solvent, but CTC would be an appropriate choice, as it is for other reactions (see above) involving thionyl chloride. But, as before, suitable replacement solvents could be found at the expense of a little research and possibly minor adjustments to plant.

#### 4.2.25 Manufacture of vaccine bottles

Included in Decision X/14	Yes
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Vaccine bottles
Identified alternatives	Likely

No information was provided or located that would justify the use of CTC for this purpose.

#### 4.2.26 Manufacture of Cyclodime

Included in Decision X/14	Submitted to Ozone Secretariat
Process agent	CTC
Case Study	CS-26
Application	Inert solvent
Reason Used	Chemically and photochemically inert, product yield and quality
Product use	Formation of hydraulic components used in extreme and adverse temperatures including aeronautics and aerospace
Identified alternatives	

Cyclodime is a synthesis intermediate used for the manufacture of polymers raw materials. The polymers produced are used for technical applications (such as hydraulic systems) in the aerospace, aeronautics, automotive and appliance industries.

The materials are dissolved in CTC and then reacted under powerful light radiation in order to produce the crude Cyclodime by a photochemical reaction in CTC used as a solvent.

The use of CTC is at present essential in this process due to stability and as it is the only suitable solvent known to not decompose under the aggressive photochemical reaction. Evaluation of other solvents under process conditions, such as non-fully halogenated compounds has led to the resulting polymer raw material being unsatisfactory for the production of the final polymers, primarily due to the breakdown of the solvent during the photochemical reaction and the formation of free radicals.

#### 4.2.27 Chlorophenesin

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5a Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	No information provided
Reason Used	No information provided
Product use	Pharmaceutical
Identified alternatives	Unknown

#### 4.2.28 Chlorinated polypropene

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Yield, quality of product
Product use	Coating materials, adhesives, painting inks
Identified alternatives	Unknown

#### 4.2.29 Chlorinated EVA

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Yield, quality of product
Product use	Coating materials, painting inks
Identified alternatives	Unknown

#### 4.2.30 Manufacture of methyl isocyanate derivatives

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Pesticide
Identified alternatives	Unknown

#### 4.2.31 Manufacture of 3-phenoxy benzaldehyde

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Pesticide
Identified alternatives	Unknown

#### 4.2.32 Manufacture of 2-chloro-5-methylpyridine

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Intermediate for Imidacloprid
Identified alternatives	Unknown

#### 4.2.33 Imidacloprid

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Pesticide
Identified alternatives	Unknown

#### 4.2.34 Buprofenzin

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Pesticide
Identified alternatives	Unknown

#### 4.2.35 Oxadiazon

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Herbicide
Identified alternatives	Unknown

#### 4.2.36 Chloradized N-methylaniline

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Intermediate for Buprofenzin
Identified alternatives	Unknown



#### 4.2.37 Mefenacet

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Pesticide
Identified alternatives	Unknown

#### 4.2.38 1,3-Dichlorobenzothiazole

Included in Decision X/14	No – information provided directly to PATF – see Chapter 5b Not yet submitted to Ozone Secretariat
Process agent	CTC
Case Study	No
Application	Solvent
Reason Used	Inert solvent, yield, quality, safety
Product use	Intermediate for Mefenacet
Identified alternatives	Unknown

### 4.3 *Submissions lacking documentation*

Detailed process descriptions and explanations of why an ODS was used as a process agent were lacking for a number of the uses found in Table A of Decision X/14 or subsequently provided to the Ozone Secretariat and/or PATF. For many of the undocumented CTC uses, examination of the research and patent literature raised the possibility that CTC was being used as a result of developments in process chemistry, which pointed to advantages derived from CTC use, or from commercial considerations such as patent protection. However, the literature did not permit clarification of these matters.

### 4.4 *Care in adopting alternatives*

Care is required when changing an ODS based process to avoid changes that would result in the inadvertent production of the same or another ODS or a Persistent Organic Pollutant (POP).

In some cases the replacement process agent, although not itself an ODS might transform to an ODS during the chemical process. An example would be the substitution of chloroform for CTC in the production of chlorine. In this case it would be expected that the chloroform would be transformed to CTC. In such a case it is unclear what obligations or remedies would be provided by the Montreal Protocol to discourage emissions resulting from such emissions of “inadvertently produced” CTC.

Another situation that deserves consideration occurs when an ODS might be produced, albeit to only a slight extent, in the alternative process. If the process is conducted on a very large scale, then even “slight” can result in substantial annual ODS emissions. The most likely cases where there is a probability that this would occur are processes involving chlorination of hydrocarbon substrates, such as natural rubber, synthetic rubber, poly-olefins or paraffin. In such processes CTC is a likely minor by-product. Aqueous chlorination processes are not immune to this problem. Again, it is unclear what obligations or remedies would be provided by the Montreal Protocol to discourage emissions resulting from such emissions of “inadvertently produced” CTC.

#### **4.5 Conclusions**

From an examination of the literature and the case studies of the identified processes the following conclusions are offered:

- In most cases emissions from use of ODS as process agents in non-Article 5(1) countries are similar to the insignificant quantities emitted from the use of ODS as feedstock.
- Depending on the difficulties of the process under investigation there is a diversity of progress, ranging as follows:
  - phase-out achieved or achievable
  - expected phase-out within the next few years subject to solution of final technical issues
  - a few processes facing extreme difficulty to find an alternative
- Realising that these results have been achieved over a period of 5 to 6 years, together with measures to significantly reduce emissions where ODS process agents are still in use, there has been remarkable progress and further progress is expected.
- Care should be taken that ODS are not inadvertently produced by the substitution of an alternative process agent or by the use of an alternative process.

The expectation, is that in the coming 10 years, a substantial part of the use of ODS as process agents will be virtually phased out in non-Article 5(1) countries. Adequate technical and financial assistance will facilitate the implementation of ODS free process technologies in Article 5(1) countries.

## 5 Overview of ODS Use in Chemical Processes in Article 5(1) Countries

### 5.1 *Emissions of ODS from chemical process industries in Article 5(1) countries*

#### 5.1.1 Use of controlled substances in chemical processes

In Article 5(1) countries, carbon tetrachloride (CTC) is the main ODS which finds extensive use in chemical processes as an inert solvent medium in carrying out chemical reactions.

No data came to light on the use of any other ODS e.g. methyl bromide in bromine based processes in Article 5(1) countries. All references in this chapter, therefore, relate to the usage of CTC.

#### 5.1.2 Industries using CTC in chemical processes

The chemical industries using CTC, excluding those using it as feedstock, in Article 5(1) countries are as follows:

- Chlorosulphonated Polyethylene (CSM)
- Chlorinated Rubber (CR)
- Chlorinated Paraffin (solid, 70% content grade)
- Pharmaceuticals
- Agricultural chemicals
- Chlor-Alkali
- Styrene Butadiene Rubber (SBR)

The survey revealed that CTC is also being used as a chain transfer agent in the emulsion polymerisation process of SBR in South Korea. A more detailed investigation is needed, including that in other Article 5(1) countries, to further check possible use of CTC for this application.

#### 5.1.3 CTC usage in chemical processes

In Article 5(1) countries, CTC is widely used as a process agent. In the identified chemical applications, CTC is not transformed chemically, as in the case of feedstock use, except to the extent of an unintended transformation/conversion in trace or insignificant quantity. Use of CTC in the aforesaid chemical industries is generally by means of batch operation/process. The quantity of CTC used in the production cycle (i.e. inventory contained within the process equipment) in such operations is large and the bulk of it is recovered and recycled in the system, yet annual loss is significant relative to non-Article 5(1) countries.

A major source of CTC emissions is from CSM and from Chlorinated Rubber production facilities operating in China and India. According to the information available, there exist two plants for CSM production in China. For chlorinated rubber production, there exist eight plants in China and four plants in India.

The amount of CTC use and of its emissions in pharmaceutical and agricultural chemical industries comes next in order of magnitude to that of CSM and CR production facilities.

In the pharmaceutical sector, CTC is being used in India for the following products:

- Bromohexine hydrochloride
- Cloxacilin
- Chlorophenesin
- Diclofenac sodium
- Ibuprofen
- Isosorbid mononitrate
- Omeprazol.
- Phenyl glycine

Case Study CS-5 on the status of CTC usage in the production of Ibuprofen in India can be found at: [http://www.teap.org/html/process\\_agents\\_reports.html](http://www.teap.org/html/process_agents_reports.html). The manufacture of Ibuprofen is the largest amongst the above pharmaceutical products.

In the agricultural chemicals sector, CTC use in India is in the manufacture of the following products :

- Endosulfan (insecticide)
- Dicofol (an acaricide)

Case studies on the status of CTC usage in the production of Endosulfan and Dicofol in India, CS-4 and CS-6 are also available at : [http://www.teap.org/html/process\\_agents\\_reports.html](http://www.teap.org/html/process_agents_reports.html).

## ***5.2 Changing pattern of CTC usage in chemical process applications in India***

At the time of preparation of the India Country Programme in 1993, the main source of emission of CTC was identified to be from the production of pharmaceutical product, Ibuprofen. There are, at least, 14 producers of Ibuprofen in India and a number of them have phased out use of CTC and converted their processes using non-ODS solvents. As a result, CTC emissions from Ibuprofen production has already been reduced.

Currently, other uses of CTC for production of Chlorinated Rubber, Endosulfan and Dicofol are the main sources of emissions of CTC in India.

## ***5.3 ODS use in chemical processes in China***

### ***5.3.1 Background***

China has recently completed its Country Program Update, which left phaseout of ODS process agent applications as a future action plan to be developed. However,

there had been little study made of ODS process agent applications within China and detailed data on its consumption was not available. In order to make clear the main uses and the quantities of the ODS used as process agents in China to provide a sound basis for developing strategy for control, replacement and finally phase-out of the ODS process agents, a preliminary four-week survey was conducted in late December 1999 on a national basis.

Followed that, a project to develop the action plan for phasing out process agent applications in China was put into practice at the end of 2000 with financial supports from the MP Multilateral Funds. At the first stage of the work, a full field survey has been carried out to collect detailed information and conduct analysis on the consumption of ODS process agents and the development of emissions-reduction techniques and alternative process that does not use ozone-depleting substances. Currently the field survey is still going and expected to finish by April, 2001.

Therefore, the data and information presented in this report are essentially based on the results from:

- 1) The preliminary survey on the ODS process agent applications in China conducted in late December 1999.
- 2) The partly completed full survey currently carried out in China.

#### 5.3.2 Review on the 25 Process Agent Applications

Process agent applications generally involve the use of ODS as a reaction or dissolving medium in the production of specified products. In China, carbon tetrachloride (CTC) is the main ODS which use in chemical processes as an inert solvent in carrying out chemical reactions. For the 25 applications of ODS process agents outlined in Decision X/14, review of the China's situation based on the 1999 preliminary survey is shown in Table 1. Of the applied processes, major uses of CTC are generally in the production of chlorinated rubber (CR), chlorosulphonated polyethylene (CSM) and chlorinated paraffin (70% solid grade, CP-70). For the question-marked processes, the situation is still unknown and need to be further verified.

## Review on the 25 applications of ODS as process agents in China

ODS applications as process agents (as listed in Table A of Decision X/14)			China's situation	
No.	ODS	Process agent application	Status	Description
1	CTC	Elimination of NCl <sub>3</sub> in production of chlorine and caustic	Not applicable	No ODS used
2	CTC	Recovery of chlorine in tail gas from chlorine production	Not applicable	No ODS used
3	CTC	Manufacture of chlorinated rubber	Major use	
4	CTC	Manufacture of endosulphan (insecticide)	?	
5	CTC	Manufacture of isobutyl acetophenone (ibuprofen)	Not applicable	No ODS used
6	CTC	Manufacture of dicofol (insecticide)	Not applicable	No ODS used
7	CTC	Manufacture of chlorosulphonated polyolefin (CSM)	Major use	
8	CTC	Manufacture of poly-phenylene-terephthalamide	Not applicable	No production
9	CFC-113	Manufacture of fluoropolymer resins	Not applicable	No ODS used
10	CFC-11	Manufacture of fine synthetic polyolefin fibre sheet	?	
11	CTC	Manufacture of styrene butadiene rubber (SBR)	Not applicable	No ODS used
12	CTC	Manufacture of chlorinated paraffin	Major use	
13	CFC-113	Manufacture of vinorelbine (pharmaceutical product)	Not applicable	No ODS used
14	CFC-12	Photochemical synthesis of perfluoropolyetherpolyperoxide precursors of Z-perfluoropolyethers and difunctional derivatives	?	
15	CFC-113	Reduction of perfluoropolyetherpolyperoxide intermediate for production of perfluoropolyether diesters	Not applicable	
16	CFC-113	Preparation of perfluoropolyether diols with high functionality	Not applicable	
17	CTC	Production of pharmaceuticals – ketotifen, anticol and disulfiram	?	
18	CTC	Production of tralomethrine (insecticide)	Not applicable	No production
19	CTC	Bromohexine hydrochloride	?	
20	CTC	Diclofenac sodium	Not applicable	No ODS used
21	CTC	Cloxacilin	Not applicable	No production
22	CTC	Phenyl glycine	?	
23	CTC	Isosorbid mononitrate	?	
24	CTC	Omeprazol	?	
25	CFC-12	Manufacture of vaccine bottles	?	

### 5.3.3 New Applications of CTC as a Process Agent

Based on the result from 1999 preliminary survey, a number of additional applications of CTC, which were not included in Decision X/14, might exist in China as follows:

- CTC application in manufacture of chlorinated polypropene.
- CTC application in manufacture of Methyl Isocyanate derivatives such as Furandam.

These new applications were verified in the current survey. Besides, some other new processes that use CTC as a process agent are also being found during this survey. The following Table summarises the new applications of CTC that have been currently identified in China. Most of the new applications are concerned with the manufacture of agro-chemicals such as C3 to C11 processes.

#### Verified new applications of CTC as a process agent in China

Case No.	New applications of CTC as process agents	Product Use
C1	Manufacture of Chlorinated Polypropene (CPP)	Coating Materials, Adhesives, Painting Inks.
C2	Manufacture of Chlorinated Ethylene-Vinyl Acetate (CEVA)	Coating Materials, Painting Inks.
C3	Manufacture of 3-Phenoxybenzyldehyde	Agro-chemicals (Pesticide)
C4	Manufacture of 2-chloro-5-methylpyridin	Intermediate for Imidacloprid
C5	Manufacture of Imidacloprid; 1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolene amine-2;	Agro-chemicals (Pesticide)
C6	Manufacture of Buprofenzin; 2-tert-butylimino-3-isopropyl-5-phenylperhydro-1,3,5-thiadiazin-4-one	Agro-chemicals (Pesticide)
C7	Manufacture of Oxadiazon; 2-tert-butyl-4-(2,4-dichloro-5-iso-propoxyphenyl)-1,3,4-oxadiazolan-5-one	Agro-chemicals (Herbicide)
C8	Manufacture of Methyl Isocyanate derivatives (Furandam)	Pesticide
C9	Manufacture of Chloridized N-methylaniline	Intermediate for Buprofenzin
C10	Manufacture of Mefenacet; D-(1,3-benzothiazole-2-oxy)-N-methylacetanilide	Pesticide
C11	Manufacture of 1,3-dichloro-benzothiazole	Intermediate for Mefenacet

### 5.3.4 Progress on emission-reduction techniques in China

Since 1995, great efforts have been made in some manufactures to reduce CTC emissions in their production. The emission-reduction techniques or measures, which have been taken, are as follows:

- Modifying the production facilities;
- Changing the process technology to enhance CTC recovery;
- Exacting the technologic conditions and process operations.





**Glossary**

ATM	Atmospheric pressure
BAP	Best available technology
BEP	Best environmental practices
CAER	Community awareness and emergency response
CAS	Carbon adsorption system or carbon adsorption stripper
CCS	Compression and condensation system
CFC-11	Trichloromonofluoromethane
CFC-113	Trichlorotrifluoroethane
CR	Chlorinated rubber
CSM	Chlorosulphonated polyolefins
CTC	Carbon tetrachloride
DCS	Distributed control system
DCE	Dichloroethane
ECO	Ecological
ECTFE	Ethylenechlorotrifluoroethylene
EDC	Ethylenedichloride
eop	End of pipe
ETFE	Ethylenetetrafluoroethylene
EU	European Union
FMEA	Failure mode and effect analysis
H&V	Heating and ventilation
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
HP	High pressure
IR	Infrared
LEL	Lower explosive limit
LP	Low pressure
MACT	Maximum achievable control technology
MT	Metric tonne
NPDES	Non-point discharge elimination system
ODS	Ozone depleting substance
PA	Process agent
PATF	Process Agents Task Force
PAWG	Process Agents Working Group
PFC	Perfluorocarbon
ppb	Parts per billion
ppm	Parts per million
PPD	Para-phenylenediamine
PPTA	Polyparaphenyleneterephthalamide
R&D	Research and development
SBR	Styrene butadiene rubber
SS	Stainless steel
TEAP	Technology and Economic Assessment Panel
TCA	Trichloroethane
TDC	Terephthaloyl dichloride
TFE	Tetrafluoroethylene
TLV	Threshold limit value
UV	Ultraviolet



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



**UNEP**

**12 Report on the Geographical Market Potential and  
Estimated Emissions of n-Propyl Bromide**

**April 2001**



This is the report of the Technology and Economic Assessment Panel (TEAP) Task Force on “The Geographical Market Potential and Estimated Emissions of n-Propyl Bromide(nPB).” The nPB Task Force includes the three Co-Chairs of the TEAP, (one a Co-Chair of the Refrigeration and Air Conditioning Technical Options Committee (TOC), the two Co-Chairs of the Solvents Coatings and Adhesives TOC, a Co-Chair of the Halons TOC, a Co-Chair of the Aerosol Products TOC and select members of the Solvents TOC.

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# UNEP Report on the Geographical Market Potential and Estimated Emissions of n-Propyl Bromide April 2001

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# 1 Introduction

Decision IX/24 (Montreal 1997) requests the Technology and Economic Assessment Panel to report on any new substance estimated to have a significant ozone-depleting potential, including an evaluation of the current and potential use of each substance (see Appendix 1). In its April 1999 Report (UNEP, 1999b), TEAP predicted significant production of n-propyl bromide (nPB) and recommended: "... that the Parties consider appropriate action to prevent or limit further depletion of the ozone layer due to this substance." In Decision XI/19 TEAP and the Science Assessment Panel (SAP) were asked to develop criteria to assess the potential ODP of new chemical substances. In May 2000 the Science Assessment Panel published its report: "Assessing the Impacts of Short-Lived Compounds on Stratospheric Ozone" (UNEP 2000a and 2000b) which emphasised the need for geographic estimates of nPB emissions in order to estimate the risk to the ozone layer. In 1998 the Solvent, Coatings, and Adhesives Technical Options Committee came to the conclusion that nPB could be safely used only under limited circumstances where emissions and worker exposure could minimise the effects of potential toxicity and ozone depletion. In March 2001, the Multilateral Fund Executive Committee approved the release funds to China on the understanding that nPB would not be made available for export and that any annual production quota would be imposed on nPB to meet the requirement for solvent use only.

TEAP formed a Task Force to estimate the geographical distribution as input to the Science Assessment Panel in estimating the ODP and risk of ozone depletion of n-propyl bromide.<sup>7</sup>

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<sup>7</sup> See also Decision XI/17 (5b) on short-lived substances and XI/20 on the procedure for evaluating new substances.

## Executive summary

1. nPB is aggressively marketed for applications traditionally using ozone-depleting and non-ozone-depleting substances. nPB is used as a solvent, a feedstock and as a carrier and intermediate for pharmaceutical and other industries. Recommended human exposure limits for pure nPB solvents are currently comparable to toxic chlorinated solvents and nPB solvents with isomer *iso*- propyl bromide contamination are even more toxic.

- Some nPB manufacturers have recommended responsible use practices that limit emissions and minimise human exposure. However, this message may not reach customers if solvent blends are mixed locally and distributed through small- and medium-sized enterprises (SMEs) or the informal sector. Many other suppliers not advocating responsible use advertise nPB as a “drop-in” replacement for existing solvents, encouraging use in old, emissive, equipment. Some samples of nPB solvents produced in China are contaminated with a highly toxic isomer, *iso*- propyl bromide.
- Parties may wish to consider the advantage of cautioning the use of nPB solvents in all countries pending completion of toxicity testing and determination of the ODP. Furthermore, Parties may wish to suspend MLF financing of nPB projects and environmental authorities and companies may wish to reconsider the financial viability of nPB investments and use.
- No-clean, aqueous, and hydrocarbon solvents are environmentally superior to nPB and other halocarbon solvents. Trichloroethylene (TCE) and methylene chloride have technical and economic advantages over nPB and are comparatively toxic. Trichloroethylene and methylene chloride are not ozone-depleting, cheaper to produce, technically equal or superior in almost all applications where nPB can be used, more chemical stable, contribute less to photochemical smog, and emissions are more easily controlled. Trichloroethylene is a substitute for nPB in solvent cleaning applications and methylene chloride is a substitute for nPB in adhesive applications.

2. The Task Force estimates that current annual use and emissions<sup>8</sup> of nPB as a solvent and ingredient are approximately 5,000 to 10,000 metric tonnes.

3. The TEAP Task Force estimated the “upper bound” and “most likely” global emissions of nPB used as solvent or ingredient and apportioned the “upper bound” emissions to specific geographical regions as requested by the Scientific Assessment Panel.

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<sup>8</sup> Production, sales, consumption and emissions on nPB used as a solvent or ingredient are substantially equal in the long run, although nPB held in inventory or contained in solvent equipment may be emitted up to several years after production. The majority of all halogenated solvents end up as emissions into the atmosphere, with the exception of very small quantities that may be incinerated or otherwise destroyed.

- The Task Force estimates that the “most likely” use and emissions in 2010 at 40,000 metric tonnes plus or minus 20,000 metric tonnes, depending on the results of pending toxicity testing and price trends of nPB and the solvents it may replace. The estimate of 20,000 metric tonnes is based on replacement of ozone-depleting solvents in CEIT and Article 5(1) countries and no replacement in any country of chlorinated solvents not controlled by the Montreal Protocol. The estimate of 60,000 metric tonnes is based on the extrapolation of nPB use as a solvent and ingredient based on a 5,000 metric tonne base year and a typical “S-Shaped” curve .
- The Task Force estimates the “upper bound” global emissions at 250,000 metric tonnes plus or minus 25,000 metric if nPB were to replace other solvents in applications where nPB is technically comparable in cleaning and ingredient performance. It is unlikely that this level of use and emissions will be experienced.
- If the Science Assessment Panel determines that upper bound emissions will cause significant ozone depletion, Parties may wish to further refine sales estimates based on more extensive market research and globally reported data on nPB solvent and ingredient use. TEAP and its TOCs will continue to improve methodology for predicting future markets. Parties may wish to request reporting of global nPB solvent and ingredient use.

4. It is challenging to estimate future market demand for new chemical substances. TEAP Task Force estimates are premised on a number of assumptions and necessarily employ expert judgement and calculations using standard analytical techniques. An Excel Spreadsheet documenting Task Force calculations is posted at TEAP.org. Analytical techniques, assumptions and uncertainties are explained in the text. The Task Force estimates assume:

- Free access to markets;
- Regulatory authorities do not impose additional control;
- Toxicity concerns do not dampen sales; and
- The price of nPB will be at least as low as it is today.

5. The ultimate use and emissions of nPB will depend on the results of ongoing toxicity testing and environmental regulation. The results of second-generation reproductive toxicity testing are expected to be announced within weeks. Parties may wish to consider the market and regulatory response to the announcement when considering possible controls under the Montreal Protocol and the SAP will want to consult with TEAP and its nPB task force before calculating geographic ODPs.

- nPB has been classified by the European Commission and the U.S. EPA as a Volatile Organic Compound and can pollute water and soil.
- There is a growing concern of nPB neurotoxicity, developmental and reproductive toxicity. Some nPB manufacturers and vendors have recently reduced the recommended exposure limits. One company recommends 10

ppm, three companies recommend 25 ppm, one company 50 ppm, and seven companies recommend 100 ppm. 10-25 ppm is comparable to high and medium-toxicity chlorinated solvents respectively. The U.S. Occupational Safety and Health Administration (OSHA) has nominated nPB and its isomer *iso*-propyl bromide for testing by the National Toxicology Program, which has since selected both substances for testing.

6. Contrary to previous industry claims, there is no physical resource limit on nPB production.

- nPB manufacture is a simple process requiring just two compounds. It can be produced economically in both Article 5(1) countries and non-Article 5(1) with access to bromine-rich brine, salt deposits, or seawater.
- The Task Force estimates that up to 300,000 metric tonnes/annum can be produced from existing and planned bromine production facilities and more if demand justified investment in additional plant capacity.

7. The market price of nPB has recently dropped considerably.

- The current bulk nPB price is typically USD 3 to 5/kg – more expensive than chlorinated solvents but less expensive than some CFC-113, HCFC, HFC and HFE solvents. Economies-of-scale in nPB production may further reduce prices, but the Task Force was unable to estimate how low the price may fall.

8. The geographical distribution is summarised in Appendix 2 and the full calculations, using the stated methodology, are available in a separate set of spreadsheets that can be downloaded from [TEAP.org](http://TEAP.org).

- Large countries or regions with a potentially important use of nPB are split into sub-regions. Article 5(1), CEIT and other non-Article 5(1) countries are treated separately.
- Each region and sub-region is shown with latitudes and longitudes.

### 3 Analytical technique to estimate geographical nPB solvent emissions

#### 3.1 *Traditional Methods of Estimating Demand for Alternatives to Controlled Substances*

Archie McCulloch (1994; 1995; 1999a; 2000), Mack McFarland (2000), and others have successfully extrapolated the demand for solvent cleaning but have been less successful in estimating the portion of that solvent cleaning that would be satisfied by each available alternative. Projections have overestimated the portion of ODS that would be replaced by halocarbon alternatives and underestimated the portion replaced with hydrocarbons, aqueous, and no-clean options.

The demand for chlorinated solvents in developed countries is static (trichloroethylene) or falling (perchloroethylene and methylene chloride) (McCulloch and Midgley, 1996). Of the older halocarbon substitutes, only HCFC-141b has significant solvent sales but these have in fact fallen, from 16,000 to 11,000 metric tonnes/year (AFEAS, 2000). Existing cleaning with controlled substances in CEIT and Article 5(1) countries and replacement technology in developed countries will be replaced by nPB only if it confers a clear advantage in terms of cost, performance, safety and environmental considerations.

The market demand for a new substance is a combination of demand to replace existing substances plus a portion of the new demand resulting from economic growth. Growth in sales follows an S-shaped curve: relatively slow but accelerating initial growth, followed by a period in which growth is sustained at a constant absolute rate, and a final period of decelerating growth to a constant rate of growth reflecting saturated substitution and only a portion of sales to expanding markets due to economic growth. Continuous compound growth has been shown to be reliable for short-term prediction but very poor over longer time intervals (McCulloch, 1999a; 2000 and Fehlberg and Ulloa-Fehlberg, 1994). However, extrapolations of relative share based on Gross Domestic Product (GDP) have been shown to be an excellent means of subdividing demand between geographical areas (McCulloch and Midgley, 1996).

### 3.2 TEAP Task Force Method of Estimating “Upper Bound” Emissions nPB

The TEAP Task Force developed a hybrid analytical technique presented on the following charts (see Figs. 1 to 5) to estimate the “upper bound” consumption in each geographic location:

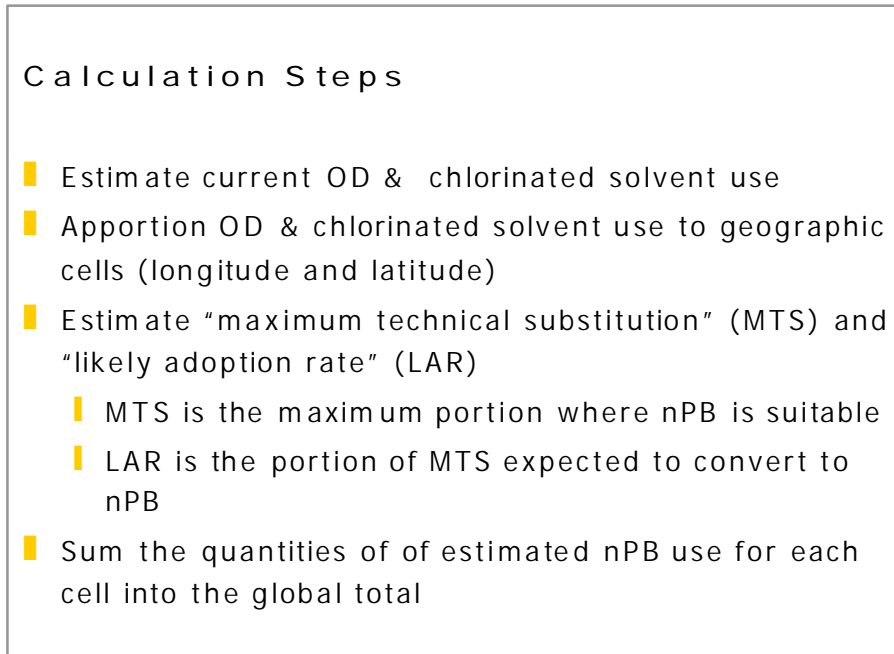


Figure 1 Steps taken to calculate the substitution of nPB for ozone-depleting and chlorinated solvents.

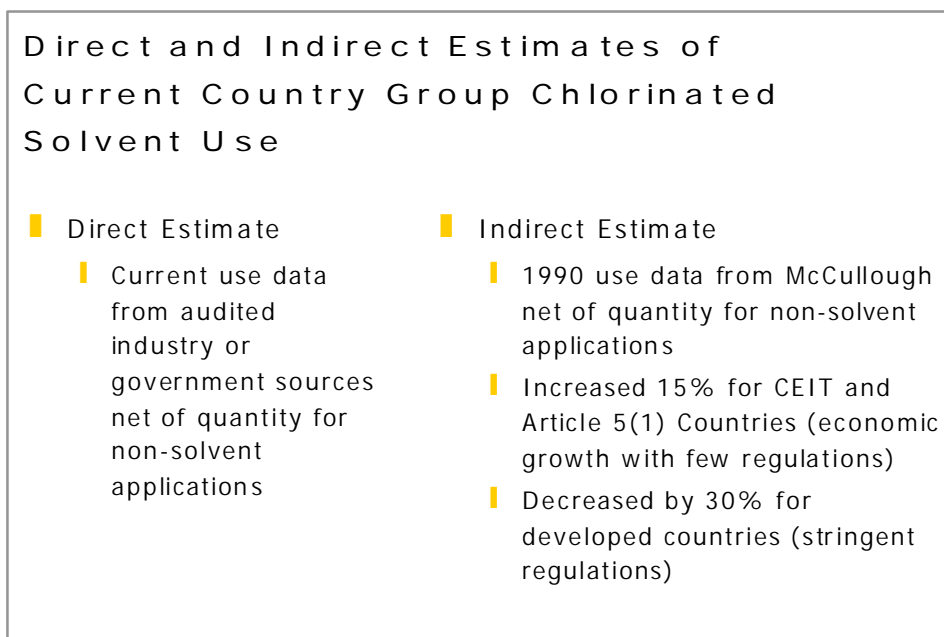


Figure 2 Current use determination for each country.

### Calculation of nPB for Each Geographical Cell

- Cell-nPB = CSU times MTS times LAR
  - CSU (tonnes used as solvent)
  - MTS (maximum technical substitution)
  - LAR (likely adoption rate)
- Where CSU = TCU minus NSCU
  - TCU (total tonnes used)
  - NSCU (non-solvent use tonnes)

Figure 3 nPB substitution in each geographical cell for each solvent.

### Methodology for Apportioning Chlorinated Solvent to Geographical Cells

- Small country use treated as one cell
- Large country use apportioned:
  - In China to 12 regions on a basis of government statistics
  - In India to 32 states on a basis of GDP, population and industrial activity
  - In Russia to 9 regions on a basis of population density and industrial activity
  - In USA to 50 states on a basis of GDP

Figure 4 Apportioning of solvent use to countries

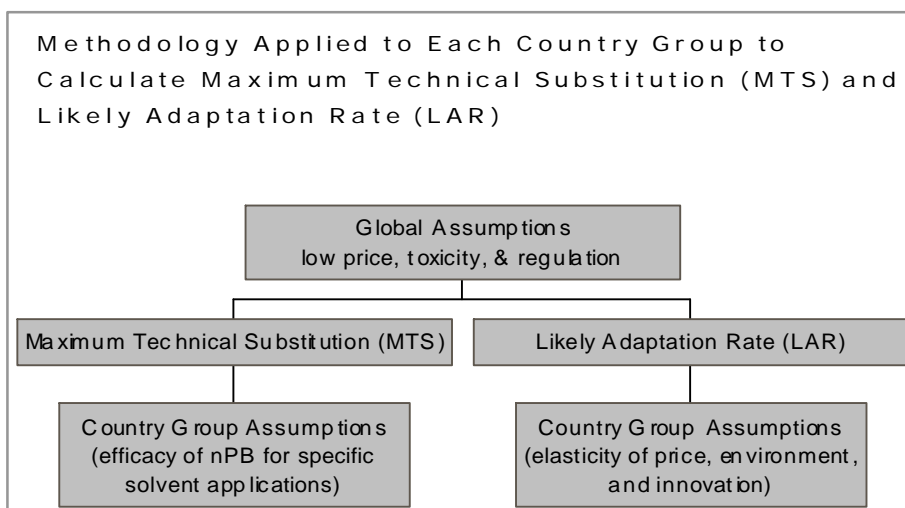


Figure 5 Overall methodology for calculating “upper bound emissions”

TEAP used the analytical technique presented on the above charts (see Figs. 1 to 5) to estimate the “upper bound” consumption in each geographic location using the following sequential procedure:

1. Estimate current OD and chlorinated solvent use for each country, where available.
2. For spatially large countries, apportion national chlorinated solvent use to geographical cells on a basis of gross domestic product.
3. Estimate the “Maximum Technical Substitution” (MTS) which is the portion of each solvent that is technically suitable for replacement by nPB on a basis of solvency, materials compatibility and other technical factors (see Section 5).
4. Estimate the “Likely Adaptation Rate (LAR) which is the portion of the MTS that will be replaced in a specific group of countries on a basis of price, environmental and innovation factors (the elasticity of replacement). This calculation reflects the five assumptions (see Section 4).
5. Multiply the quantity of chlorinated solvent used in each geographical cell or geographically compact country times the substitution factor.

The rates used for each solvent type and geographical region are shown in Appendix 2, Tables 14 (MTS and LAR) and 15 (overall).

It should be noted that the input data for carbon tetrachloride is derived from data supplied by Country Plans and subsequent reporting. Feedstock use is therefore already discounted. India is a special case, because about half of the CTC reported is used as process agents, for which nPB cannot be substituted. For this reason, the percentage shown in Appendix 2, Table 14, for India is half that of other Article 5(1) countries. China is another special case, because all the reported CTC is used as solvents and it is estimated that 100 percent can be technically replaced (MTS).



### 3.3 TEAP Task Force Methods of Estimating “Most Likely” Emissions nPB

The Task Force estimates that the most likely use and emissions in 2010 will be 40,000 metric tonnes plus or minus 20,000 metric tonnes, depending on the results of pending toxicity testing and price trends of nPB and the solvents it may replace.

The estimate of 20,000 metric tonnes is based on replacement of ozone-depleting solvents in CEIT and Article 5(1) countries and no replacement of chlorinated solvents not controlled by the Montreal Protocol.<sup>9</sup>

The estimate of 60,000 metric tonnes is based on the extrapolation of nPB use as a solvent and ingredient based on a 5,000 metric tonne base year and a typical “S” curve. The nPB market growth may follow the S-shaped curve with a relatively slow but accelerating initial growth followed by a period in which growth is sustained at a constant rate and final period of decelerating growth to a constant saturated market.<sup>10</sup> The market growth is estimated for 2000-2010 as follows:

Year	Rate of Market Increase (Percent)	Projected Consumption (Metric Tonnes per year)
2000	Base Year	5,000
2001	27%	6350
2002	28%	8,128
2003	29%	10,485
2004	30%	13,630
2005	30%	17,719
2006	30%	23,035
2007	28%	29,485
2008	26%	37,152
2009	24%	46,068
2010	20%	55,282

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<sup>9</sup> McCulloch 2001.

<sup>10</sup> Calculated by Task Force Members Dr. Mohinder Malik and Dr. Ahmad Gaber.

#### **4 Assumptions necessary to estimate geographical emissions**

A number of assumptions are necessary to estimate “upper bound” nPB emissions. Notwithstanding the difficulty of data derived from many sources using different methods of estimation, the Task Force is confident in its findings.

The upper bound estimate of emissions assumes that

- 1) there will be no national, regional or international restrictions affecting the development of the market for nPB,
- 2) the time weighted average (TWA) exposure level of nPB in all countries will be 50 – 100 ppm (higher than for some chlorinated solvents),
- 3) brominated solvents substitute for chlorinated solvents on a tonne-for-tonne basis,
- 4) the market for total solvents will be constant and
- 5) the nPB is marketed at a price not more than two to three times that of chlorinated solvents.

Based on these assumptions, the Task Force has estimated rates of substitution of nPB for OD and chlorinated solvents presented in the spreadsheets (filename, appendix210.xls). Details of the estimates for each country, group of countries or region are explained in the individual regional worksheets and are summarised briefly in Appendix 2.

For each geographical region, the Task Force first estimated the total OD and chlorinated solvent use. The Task Force then estimated the portion of total OD and chlorinated solvent use that could be technically and economically replaced with nPB. Geographically compact countries, states or regions are assigned a single representative latitude and longitude while large countries or countries spread over many degrees are assigned a range of latitudes and longitudes. The estimated emissions are given in Appendix 2.

Because solvent operations have little seasonal variation in emissions, annual emissions are simply divided by twelve to obtain the monthly emissions. This is the same methodology employed by McCulloch (1999b).

## 5 Physical and chemical properties of n-propyl bromide

n-propyl bromide (synonyms 1-bromopropane, 1-BP, *normal*-propyl bromide, nPB) is a colourless or pale liquid with a heavy sweetish smell. It is used mainly as a solvent, as a carrier and as an intermediate for the pharmaceutical industry. It may also be used as feedstock for some other substances.

nPB, in its pure form, is limited as a cleaning solvent because it is somewhat reactive and unstable. It must therefore be blended with stabilisers, inhibitors, and co-solvents to produce optimised solvents. Most commercial solvent blends contain between 85 to 99 percent nPB.

Comparison of the Physical Characteristics and Permitted Exposure Limits (PEL) of nPB, 1,1,1 –Trichloroethane and Trichloroethylene (TCE)

	Unit	NPB	1,1,1-TCA	TCE
Boiling Point	°C	70.8	74.1	86.7
Specific Gravity, 25° C		1.353	1.32	1.5
Viscosity, 25° C,	cps	0.49	0.795	0.592
Surface Tension, 20° C	dynes/cm	25.9	25.56	28.8
Vapour Pressure, 20° C	mm Hg	110.8	121.62	67.67
Specific Heat, 25° C		0.27	0.345	0.288
Latent Heat of vaporisation	cal/gm	58.8	7.74	8.19
Solubility in Water,	%	0.24	0.1495	0.1099
Flammability limits,	%	4-7.8	7.5-12.5	8-10.5
Kauri Butanol Value		125	124	130
ODP		*	0.1	negligible
US OSHA PEL	ppm	10-100**	350	100

\* ODP unknown

\*\* No official PEL, manufacturers' recommendations are 10 – 100 ppm

## 6 Manufacture of nPB

nPB is synthesised by reacting n-propyl alcohol with hydrogen bromide to form a mixture of nPB and water, with the water being subsequently removed. The n-propyl alcohol is a low-cost by-product of the petrochemical industry and is abundantly available from the major petroleum companies in various degrees of purity.

Commercial nPB may contain various impurities, including its isomer, *iso*-propyl bromide. Because of the toxicity of the isomer (see Appendix 4), some environmental and health authorities recommend that *iso*PB be limited to 0.1 percent of the total weight in commercial solvents.

nPB solvents are widely distributed in developing and developed countries. At least 47 companies claim to produce nPB (UNEP 1999a) in eight non-Art 5(1) Parties and four Art 5(1) Parties. However, some of these companies may not be actual manufacturers but may be nPB refiners, blenders, packagers or feedstock producers. The Task Force believes that molecular nPB is manufactured in, at least, China, France, India, Israel, Japan, Netherlands, United Kingdom and USA. There are at least 17 multi-national companies known to blend or package nPB solvent blends (see Lists B & C). Vendors advertise nPB solvents and/or cleaning equipment suitable for nPB in Austria (1), Australia (3), Argentina (1), Belgium (3), Brazil (3), China (3), Colombia (1), Hong Kong (2), India (2), Japan (6), Malaysia (1), Mexico (1), Philippines (1), Singapore (1), Switzerland (1), Thailand (1), Turkey (2), United Kingdom (8), USA (31) and Venezuela (at least 1). This list does not include vendors, blenders, or producers who sell directly to the user or into other countries, for example a French vendor selling nPB solvents into Spain and Italy (Rollet 2000).<sup>11</sup>

In March 2000, the Executive Committee of the Multilateral Fund approved a grant of US\$52 million for the China Solvents Sector Plan. China agreed to eliminate its total non-exempt solvent uses of CFC-113, TCA, and CTC in accordance to the schedule set in the Sector Plan which requires elimination of CFC-113 by 2006, TCA by 2010, and CTC by 2004 (UNEP 2000c). Although the China Solvents Sector Plan allows flexibility in meeting the goals, China has expressed an interest in using nPB to replace a portion of their solvent use. In March 2001, the Executive Committee approved the release funds to China on the understanding that nPB would not be made available for export and that an any annual production quota would be imposed on nPB to meet the requirement for solvent use only.<sup>12</sup>

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<sup>11</sup> These non-exhaustive lists are two years old and the market evolution has been considerable.

<sup>12</sup> China: Report and request for second payment on the implementation of the 2000/2001 annual programme under the China solvent sector plan (UNDP) (UNEP/OzL.Pro/ExCom/33/24/China) states that

Having considered the recommendation of the Sub-Committee on Project Review (UNEP/OzL.Pro/ExCom/33/17, paras. 81 and 82), the Executive Committee in Decision 33/46

## 6.1 *Estimated nPB Production and Emissions*

There are well-established databases for CFCs, HCFCs, HFC-134a, methyl chloroform and for the chlorinated solvents that are not ODS (trichloroethylene, perchloroethylene and methylene chloride). (AFEAS, 2000; McCulloch, et al., 1994; McCulloch and Midgley, 1996; Midgley and McCulloch, 1995; 1997; 1999). TEAP provides additional information for countries that are not included in the industrial data collection system (UNEP, 2000). The UNEP and industrial databases are consistent to within a few percent for the same geographical areas. However, there is no comparable global database for nPB production.<sup>13</sup>

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approved the release of funds for the annual work programme at the level indicated in Annex V to the 33<sup>rd</sup> Executive Committee meeting report, in accordance with China's agreement with the Executive Committee on the solvent sector plan, on the understanding that:

- (a) N-propyl bromide produced by China would not be made available for export;
- (b) An annual production quota would be imposed on n-propyl bromide to meet the requirement for solvent use only;
- (c) China would control the sale of n-propyl bromide only to enterprises involved in the conversion projects under the China Solvent Sector Plan;
- (d) The Import and Export Office of China would monitor and ensure that no n-propyl bromide was exported by China;
- (e) The implementing agency of the China Solvent Sector Plan, UNDP, would include in its annual audit plan verification that no n-propyl bromide was exported;
- (f) No further financial assistance would be sought from the Multilateral Fund for the final conversion to zero ODP alternatives.

<sup>13</sup>The Brominated Solvents Consortium (BSOC) estimated global sales and emissions of nPB for solvent and adhesive applications at 4839 metric tonnes in 2000, 3152 metric tonnes in 2001, and 3736 metric tonnes in 2002. Members of the BSOC are Albemarle Corporation, Great Lakes Chemical Corporation, and Bromine Compounds Ltd. The Task Force estimates that these companies accounted for about half of nPB global production in 2000. Each BSOC company separately estimated global production for each year--mindful of relevant technical, regulatory and commercial factors--and submitted these confidential estimates to BSOC. These annual company estimates were then averaged by BSOC to arrive at initial estimates that were then provided to BSOC members for reconsideration. Each company then provided its revised estimates to BSOC and averaged to the estimates presented here.

## 7 Economic considerations and market penetration

The Task Force has confirmed that there is no physical resource limit on the quantity of nPB that can be manufactured. There are economic and practical constraints in expanding production beyond existing capacity and other markets for bromine may effect the market price.

### 7.1 Production cost and market prices

The current market price of nPB-based solvents, produced in relatively small quantities, is typically about USD 5.00/kg but is as low as USD 3.00/kg in at least one South American Article 5(1) country. Based on the current bulk selling price of n-propanol (about USD 0.50/kg) and bromine (about USD 1.25/kg (ChemExpo 1999)), the Task Force estimates that, with sufficient economies of scale, a bulk selling price of nPB solvents could drop to USD 1.75 – 2.25/kg. The price could be further reduced in countries with government-owned manufacturing facilities that have access to government subsidies and avoid taxes or with financing from the Multilateral Fund. However, another source (USGS 2000) quotes a bulk selling price of USD 0.87/kg for pure bromine. At this price, the cost of producing nPB could become comparable to that of the chlorinated solvents. Current market prices for bulk quantities of competitive halogenated solvents and blends:

Solvent	Bulk Price Range USD/kg	ODP <sup>14</sup>
Perchloroethylene <sup>15</sup>	0.70 – 1.90	~0
Carbon tetrachloride	0.75 – 1.25	1.10
Methylene chloride <sup>16</sup>	0.80 – 1.25	~0
Trichloroethylene <sup>17</sup>	1.00 – 1.35	~0
1,1,1-trichloroethane <sup>18</sup>	1.25 – 2.00	0.15
<b>nPB</b> (estimated lowest price with economy of scale)	<b>1.75 – 2.25</b>	TBD <sup>19</sup>
<b>nPB</b> (current market price)	<b>3.00 – 5.00</b>	TBD
HCFC-141b	2.50 – 3.50	0.11
CFC-113	3.00 – 10.00	0.8
HFC-43-10 mee	25.00 – 35.00	None
HCFC-225	25.00 – 35.00	0.025to 0.033
HFE-7100-7200	30.00 – 35.00	None

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<sup>14</sup> The Ozone Depleting Potential as adopted under the Montreal Protocol. “~0” indicate that the compounds have negligible potential to deplete the ozone layer. TBD = to be determined

<sup>15</sup> Synonyms: Tetrachloroethylene, tetrachloroethene

<sup>16</sup> Synonym: Dichloromethane

<sup>17</sup> Synonym: Trichloroethene

<sup>18</sup> Synonym: Methyl Chloroform

<sup>19</sup> The Montreal Protocol Science Assessment Panel will use estimates from this report to calculate region-specific ODPs.

Based on the above assumptions, the TEAP Task Force therefore estimates that nPB might be more commercially viable, price competitive, alternative in markets where either ozone depleting or non-ozone-depleting solvents are marketed. Significant market penetration has already occurred, in some applications, as a replacement for methylene chloride (Mertens 1999, OSHA 1999 and Protonique 1999).

## **7.2 Replacement of chlorinated solvents by nPB**

Some nPB manufacturers do not recommend using nPB in inferior equipment with high emission rates, however, many users ignore safety warnings that are not mandated and enforced under national regulation.

If available solvents had comparable technical performance and health and safety requirements, price alone would determine their use. However, nPB is already replacing chlorinated solvents despite the current higher price of nPB. For example, in the USA, nPB replaced methylene chloride in adhesives applications at a time when nPB was more than eight times more expensive than the methylene chloride it replaced. Adhesive manufacturers paid the premium solvent price because solvent ingredients are only a minor cost in adhesives. Also, they were willing to pay more because it was believed that nPB was less toxic with the advantage that, in some markets, adhesives manufacturers could avoid labelling products as toxic and adhesives users could avoid reporting toxic emissions. Similarly, when CFC-113 was marketed as a cleaning solvent at over 15 times the price of some of the solvents it replaced, it rapidly gained market share because of its lower toxicity, non-flammability and minimum regulatory restrictions.

For cleaning applications, trichloroethylene is the most widely used halogenated solvent. Today, nPB is typically two to four times more expensive than trichloroethylene and with expanded nPB production the price of nPB may become less than 50 percent more expensive.

nPB is substantially less expensive than HCFC-225, HFCs, HFEs, and some other commercial solvents. However, these are “niche” solvents with technical properties that may not be satisfied by nPB. The Task Force estimates that nPB is suitable for about half to one-third of the applications of these solvents. nPB is a very attractive substitute for HCFC-141b used as a cleaning solvent, despite different toxicity, because the solvency and compatibility of nPB and HCFC-141b are comparable and the prices are competitive. If nPB is not controlled, it will gain market share from HCFC-141b. HCFC-141b, ODP of 0.11, is scheduled for phaseout under the Montreal Protocol.

Many large companies in countries worldwide and many smaller users in developed countries have used various forms of aqueous cleaning as effective and economical alternatives for halogenated solvents in many applications. However, halogenated solvents will continue to be used by small- and medium-sized enterprises (SMEs) where aqueous techniques are less economical.

In some applications where performance of aqueous techniques has been less than ideal, companies could revert to halogenated solvents if they are considered environmentally acceptable.

In some Article 5(1) countries considerable quantities of carbon tetrachloride (CTC) are used as cleaning solvents for metals (frequently cold cleaning) and for dry cleaning textiles. If nPB is determined to be less toxic than other chlorocarbon solvents, it will be attractive for metal cleaning as the supply of CTC is phased out under the Montreal Protocol. The price differential will favour chlorinated solvents. At this time, nPB is unlikely to be considered as a substitute for CTC in dry cleaning applications (Clark 2000). In some Article 5(1) countries, reliable supplies of good quality water are unavailable at low cost, making aqueous cleaning less attractive.

The Task Force estimates that nPB will replace no more than 35-50% of the CFC-113 market in CEIT and Article 5(1) countries, mainly for materials compatibility reasons. A large percentage of the 1,1,1-trichloroethane market may be penetrated by nPB because it has similar performance characteristics and a close price differential.

The penetration of nPB in applications using chlorinated solvents in Article 5(1) countries will depend on price and toxicity. The Task Force estimates that nPB will penetrate no more than 10 percent of the Article 5(1) market before the chronic toxicity is determined.

If occupational exposure limits for nPB were 2 – 4 times higher than exposure limits of methylene chloride, nPB would replace a substantial portion of methylene chloride solvent use even if nPB had a significantly higher price. High rates of market penetration will require U.S. EPA SNAP listing, a favourable AEL, and market confidence.<sup>20</sup>

The consumption of CTC in China is currently small, less than 1,000 metric tonnes per annum, as a solvent for metal and dry cleaning. nPB is therefore more likely to be used as a substitute for CFC-113 and 1,1,1-trichloroethane and is under consideration by both industry and the government (Hu 2000).

Many of the 48 completed (to August 2000) solvent projects financed by the Multilateral Fund use trichloroethylene as a substitute for OD-solvents despite the very high incremental capital costs of the machinery employed. If nPB were not controlled under the Montreal Protocol, were qualified for funding under the Multilateral Fund and Global Environment Facility rules, and were determined to have acceptable toxicity, a simple low-cost retrofit of existing equipment would be technically feasible (UNEP 1998). The small increase in incremental operating costs due to the higher solvent price would be partially or wholly offset by the lower emissions from the retrofitted equipment. It is therefore believed that there is a very substantial future market for nPB in developing countries, provided that the toxicology is acceptable.

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<sup>20</sup> The U.S. EPA SNAP listing has a global effect because it is considered by many to be a reliable measure of environmental acceptability.



## 8 Applications for nPB solvents

nPB and its solvent blends have been proposed for many applications, including most of the ones where chlorinated solvents are used:

- vapour degreasing
- cold cleaning of metal and plastics parts
- spray cleaning
- de-fluxing
- precision cleaning
- optical cleaning
- field cleaning with aerosol or other sprays
- carrier for oils and greases
- carrier for flame retardants
- evaporative solvent for inks, coatings and adhesives
- diluent for HC solvents to reduce flammability

There are a few applications currently using chlorocarbon solvents that are unlikely to switch to nPB:

- dry cleaning of textiles (Clark 2000) (one nPB manufacturer does propose it for this (DSBG 2000 ff))
- process agent for rubber manufacture
- feedstock for pharmaceutical and other applications
- paint stripping
- some extractions (HSIA 2000)
- polycarbonate plastic manufacture (HSIA 2000)

De-fluxing in the electronics industry cannot be done with nPB-based solvents in at least half of the applications because many assemblies contain components using plastics that are incompatible with nPB (e.g., polystyrene and polycarbonate). nPB blends are, however, a very good solvent for thick film hybrid assemblies, provided that under-component access problems are resolved (Ellis 2000). Other problems with nPB in the electronics industry include reactivity with silver or silvered contacts and compatibility with new organic surface protection finishes. For these reasons, nPB cannot be considered as a “drop-in” defluxer for CFC-113 azeotropes for about half these applications.

There may also be a few restrictions in the precision cleaning sector, especially with perfluorocarbon lubricants, polymeric assemblies and parts made from amphoteric metals. Perchloroethylene is widely accepted for motion picture film cleaning and nPB can not readily be substituted in the land gate process.

Metal degreasing with nPB-based solvents is technically comparable with the results obtained from chlorinated solvents. In vapour degreasing equipment, the quality is generally very good to excellent.

nPB can replace methylene chloride as an adhesives solvent (methylene chloride replaced 1,1,1-trichloroethane after the 1996 phase-out). The Task Force estimates that nPB may replace flammable oxygenated and aromatic compounds, such as acetone, methyl ketone, toluol, and xylol in adhesives because no flameproofing would be needed in manufacturing plants and facilities where adhesives are used.

Manufacturers of nPB solvents advocating responsible use propose nPB as a replacement for 1,1,1-trichlorethane only in modern equipment designed to minimise emissions. Other vendors (Amity 2000, Tetra 2000, Tulstar 2000, Lord 2000) promote nPB as a “drop-in” replacement for chlorinated solvents not controlled by the Montreal Protocol using existing equipment.

A large number of manufacturers in both Article 5(1) and non-Article 5(1) countries are packaging nPB blends in spray cans, mostly aerosols with liquid petroleum gas, HFC-134a or carbon dioxide propellants. These are used for a number of applications such as field cleaning of electrical, electronic and mechanical equipment, maintenance of information technology equipment, contact lubrication, carrier for penetrating oils etc. (Poly 2000, Tulstar 2000).

nPB is also reported to be used for some non-solvent applications, but the Task Force was unable to document these uses.

## 9 Data and analytical uncertainty

The TEAP Task Force developed its analytical forecasting method mindful of data presentation and accuracy required by the Science Assessment Panel. The Task Force worked within its limited budget using the talents of its volunteer members and completed the study on time.

The Task Force is confident that production and emissions will not exceed the upper bound estimate. Furthermore, TEAP and its Task Force can present more reliable estimates if the Science Assessment Panel determines that emissions corresponding to upper-bound estimates pose a significant threat to stratospheric ozone depletion.

The data supporting the Task Force findings are from a number of sources including international and governmental organisations, manufacturing and trade associations, and commercial statistics. The latest available data from a variety of sources are used in these calculations.

A major source of data (McCulloch 1999b) lists the 1990 consumption of chlorocarbon solvents by country. Between 1990 and 2000, there have been increasing precautionary measures resulting in lower emissions of chlorocarbon solvents in some developed countries (partially from increasing toxicological and environmental concerns) and conversion from 1,1,1-trichloroethane to trichloroethylene (from the ODS phase-out). In some other developed countries and in developing ones, there has been an average increase in consumption of chlorocarbon solvents over this period.

Errors in estimation due to data problems are probably not very significant on a global scale, but there may be considerable errors for individual countries.

Extrapolation beyond 2010 is less accurate with a best estimate of 1 – 3% annual growth in Article 5(1) and CEIT countries and 0.3 – 1% annual reduction in non-Article 5(1) countries. Appendix 2, Chart 1 and Table 15 (p. 30) show the minimum, maximum and mean effects of this extrapolation, by latitude.

The Task Force believes that the upper bound estimates are accurate within an overall global or regional uncertainty of a  $\pm 25$  percentile and that individual country/state estimates are accurate to a  $\pm 50$  percentile. The estimates would be more accurate if chlorinated solvent emissions were reported for each relevant geographic location. The spreadsheet cells are empty for countries where data was not available.

## **10 Conclusion**

The Task Force estimates that current annual use and emissions of nPB as a solvent and ingredient are approximately 5,000 to 10,000 metric tonnes. The TEAP Task Force estimated the “upper bound” global emissions of a complete market shift at 250,000 metric tonnes plus or minus 25,000 metric tonnes if nPB were to replace other solvents in applications where nPB is technically equal or better in cleaning and ingredient performance. It is unlikely that this level of use and emissions will be experienced. The Task Force also estimated the “most likely” global emissions in 2010 at 40,000 metric tonnes plus or minus 20,000 metric tonnes based on current use extrapolation following the standard new substance market integration.

If the Science Assessment Panel determines that upper bound emissions will cause significant ozone depletion, Parties will want to further refine sales estimates based on more extensive market research and globally reported data on nPB solvent and ingredient use. TEAP and its TOCs will continue to improve methodology for predicting future markets. Parties may wish to request reporting of global nPB solvent and ingredient use.

## 11 References

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## **Appendix 1:        Decision IX/24:**

Control of new substances with ozone-depleting potential

The Ninth Meeting of the Parties decided in Dec. IX/24:

1. That any Party may bring to the attention of the Secretariat the existence of new substances which it believes have the potential to deplete the ozone layer and have the likelihood of substantial production, but which are not listed as controlled substances under Article 2 of the Protocol;
2. To request the Secretariat to forward such information forthwith to the Scientific Assessment Panel and the Technology and Economic Assessment Panel;
3. To request the Scientific Assessment Panel to carry out an assessment of the ozone-depleting potential of any such substances of which it is aware either as a result of information provided by Parties, or otherwise, to pass that information to the Technology and Economic Assessment Panel as soon as possible and to report to the next ordinary Meeting of the Parties. To request the Technology and Economic Assessment Panel to report to each ordinary Meeting of the Parties on any such new substances of which it is aware either as a result of information provided by Parties, or otherwise, and for which the Scientific Assessment Panel has estimated to have a significant ozone-depleting potential. The report shall include an evaluation of the extent of use or potential use of each substance and if necessary the potential alternatives and shall make recommendations on actions which the Parties should consider taking;
4. To request Parties to discourage the development and promotion of new substances with a significant potential to deplete the ozone layer, technologies to use such substances and use of such substances in various applications.



## Appendix 2: “Upper bound” emission estimates by region

This appendix gives a summary of the calculations, copied from the spreadsheet workbook newapp210.xls. The world is divided into 11 “regions”, for which each is given a separate worksheet. The worksheets are consolidated in Table 1. For the sake of clarity in this printed document, the method of calculation cannot be shown here but can be seen in the workbook.

<b>Global Calculations (summary) Provisional predictions of "Upper Bound" nPB use</b>			
			Metric tonnes
			Output
Country(ies)	Class	Source	nPB “Upper Bound”
W. Europe	A2	Data from W. Europe worksheet	40810
Japan	A2	Data from Japan worksheet	35219
USA	A2	Data from USA worksheet	103428
Can-Aus	A2	Data from Australia/Canada worksheet	4910
Other A2	A2	Data from other A2 worksheet	815
Russia	CEIT	Data from Russia worksheet	5436
Other CEIT	CEIT	Data from other CEIT worksheet	6227
China	A5(1)	Data from China worksheet	16353
India	A5(1)	Data from India worksheet	4876
Other A5(1)	A5(1)	Data from other A5(1) worksheet	40476
Non-signatory	NS	Data from non-signatory regions worksheet	1295
<b>Totals</b>			<b>259,846</b>
Version 7.1 03.04.01			

Appendix 2 Table 1: Global consolidation of the results in Tables 2 – 13

<b>W. Europe Calculations (basic)</b>							Metric tonnes
Country	Class	Lat. Min	Lat. Max	Long. Min	Long. Max	Year CC	nPB Upper Bound
Andorra	A2	43N	43N	1E	1E		0
Austria	A2	46N	49N	10E	17E	1999	818
Belgium	A2	49N	52N	2E	6E	1999	2010
Finland	A2	60N	70N	21E	32E	1999	856
France	A2	43N	51N	5W	7E	1999	9675
Denmark	A2	55N	57N	8E	13E	1999	792
Germany	A2	47N	55N	6E	15E	1999	2895
Greece	A2	35N	42N	20E	27E	1999	713
Ireland	A2	52N	55N	6W	10W	1999	848
Italy	A2	37N	47N	7E	18E	1999	7035
Liechtenstein	A2	47N	47N	9E	9E		0
Luxembourg	A2	50N	50N	6E	6E		0
Monaco	A2	44N	44N	8E	8E		0
Netherlands	A2	52N	54N	4E	7E	1999	1065
Norway	A2	58N	71N	5E	30E	1999	517
Portugal	A2	37N	42N	7W	9W	1999	930
Spain	A2	36N	43E	3E	9W	1999	4125
Sweden	A2	56N	69N	11E	24E	1999	1595
Switzerland	A2	46N	47N	6E	11E	1999	923
United Kingdom	A2	50N	58N	2E	8W	1999	6015
<b>Totals</b>							<b>40810</b>

Appendix 2 Table 2 Data for Western Europe (shaded areas indicate that no chlorocarbon data is available)

<b>Japan Calculations (basic)</b>							Metric tonnes
Country	Class	Lat. Min	Lat. Max	Long. Min	Long. Max	Year CC	nPB Upper Bound
Japan	A2	31N	46N	130E	145E	1990	35219
<b>Totals</b>							<b>35219</b>

Appendix 2 Table 3 Data for Japan

<b>USA Calculations (basic)</b>							Metric tonnes nPB Upper Bound
Country	Class	Lat. Min	Lat. Max	Long. Min	Long. Max	Year CC	
Alabama	A2	27N	35N	85W	88W	1999	1221
Alaska (w/o Aleutian)	A2	60N	71N	141W	165W	1999	135
Arizona	A2	31N	37N	109W	115W	1999	1472
Arkansas	A2	33N	37N	91W	94W	1999	605
California	A2	33N	42N	114W	124W	1999	14493
Colorado	A2	37N	41N	102W	109W	1999	1539
Connecticut	A2	41N	42N	72W	74W	1999	1656
Delaware	A2	39N	40N	75W	76W	1999	233
District of Columbia	A2	39N	39N	75W	75W	1999	233
Florida	A2	25N	27N	80W	88W	1999	5267
Georgia	A2	27N	35N	81W	85W	1999	2967
Hawaii	A2	19N	22N	155W	160W	1999	322
Idaho	A2	42N	49N	111W	117W	1999	200
Illinois	A2	37N	43N	87W	91W	1999	5446
Indiana	A2	38N	42N	85W	88W	1999	2031
Iowa	A2	41N	43N	91W	96W	1999	909
Kansas	A2	37N	40N	95W	102W	1999	788
Kentucky	A2	37N	39N	82W	89W	1999	1180
Louisiana	A2	29N	31N	89W	94W	1999	1515
Maine	A2	43N	47N	68W	71W	1999	214
Maryland	A2	38N	39N	75W	78W	1999	1922
Massachusetts	A2	41N	43N	70W	73W	1999	2850
Michigan	A2	42N	47N	83W	90W	1999	3648
Minnesota	A2	43N	49N	90W	97W	1999	1861
Mississippi	A2	30N	35N	88W	91W	1999	603
Missouri	A2	36N	41N	89W	95W	1999	1898
Montana	A2	45N	49N	104W	116W	1999	62
Nebraska	A2	40N	43N	96W	104W	1999	471
Nevada	A2	35N	42N	114W	120W	1999	590
New Hampshire	A2	43N	45N	71W	72W	1999	323
New Jersey	A2	39N	41N	74W	75W	1999	3944
New Mexico	A2	32N	37N	103W	109W	1999	422
New York	A2	41N	45N	73W	80W	1999	9224
North Carolina	A2	34N	37N	76W	84W	1999	2821
North Dakota	A2	46N	49N	97W	194W	1999	15
Ohio	A2	39N	42N	82W	85W	1999	4352
Oklahoma (no panhandle)	A2	34N	37N	95W	100W	1999	856
Oregon	A2	42N	46N	117W	124W	1999	1156
Pennsylvania	A2	40N	42N	75W	81W	1999	4621
Puerto Rico	A2	18N	18N	66W	67W	1999	0
Rhode Island	A2	41N	42N	71W	72W	1999	181
South Carolina	A2	28N	35N	79W	83W	1999	1085
South Dakota	A2	43N	46N	97W	104W	1999	76
Tennessee	A2	35N	37N	82W	90W	1999	1828
Texas	A2	26N	37N	94W	106W	1999	8534
Utah	A2	37N	42N	109W	114W	1999	563
Vermont	A2	43N	45N	72W	73W	1999	7
Virgin Islands	A2					1999	0
Virginia	A2	37N	39N	76W	83W	1999	2716
Washington	A2	46N	49N	117W	124W	1999	2177
West Virginia	A2	37N	40N	78W	83W	1999	325
Wisconsin	A2	43N	47N	88W	93W	1999	1832
Wyoming	A2	41N	45N	104W	111W	1999	40
<b>Total</b>							<b>103428</b>

Appendix 2 Table 4 Data for USA

<b>Australia/Canada Calculations (basic)</b>							Metric tonnes nPB Upper Bound
Country	Class	Lat. Min	Lat. Max	Long. Min	Long. Max	Year CC	
Australia	A2	11S	39S	113E	154E	1990	948
Canada	A2	45N	80N	55W	141W	1990	3962
<b>Totals</b>							<b>4910</b>

Appendix 2 Table 5 Data for Australia and Canada

<b>Other A2 Calculations (basic)</b>							Metric tonnes nPB Upper Bound
Country	Class	Lat. Min	Lat. Max	Long. Min	Long. Max	Year CC	
Greenland	A2	60N	85N	10W	70W		0
Iceland	A2	64N	67N	14W	24W		0
Israel	A2	29N	33N	34E	35E	1990	383
New Zealand	A2	34S	46S	167E	178E	1990	121
South Africa	A2	22S	35S	16E	32E	1990	312
<b>Totals</b>							<b>815</b>

Appendix 2 Table 6 Data for other non-Article 5(1) countries

<b>Russia Calculations (basic)</b>							Metric tonnes nPB Upper Bound
Region	Class	Lat. Min	Lat. Max	Long. Min	Long. Max	Year CC	
W. Russia	CEIT	50 N	70 N	30 E	40 E	2000	2169
Mid Euro Russia	CEIT	50 N	60 N	40 E	60 E	2000	814
N Euro Russia	CEIT	60 N	70 N	40 E	60 E	2000	1
S Euro Russia	CEIT	42 N	50 N	40 E	50 E	2000	544
Siberia	CEIT	60 N	75 N	60 E	170 E	2000	1
SW Asia Russia	CEIT	52 N	60 N	60 E	80 E	2000	814
S Asia Russia	CEIT	50 N	60 N	80 E	120 E	2000	546
SE Asia Russia	CEIT	42 N	55 N	120E	141 E	2000	492
E Asia Russia	CEIT	55 N	60 N	120 E	138 E	2000	55
<b>Totals</b>							<b>5436</b>

Appendix 2 Table 7 Data for Russia (N.B. The input data from which this table was derived is may be too low: see the Russia worksheet in the spreadsheet workbook for details).

<b>Other CEIT Calculations (basic)</b>							Metric tonnes nPB Upper Bound
Country	Class	Lat. Min	Lat. Max	Long. Min	Long. Max	Year CC	
Albania	CEIT	40N	42N	20E	21E		0
Armenia	CEIT	39N	41N	43E	47E	1990	36
Azerbaijan	CEIT	39N	42N	45E	50E	1990	131
Bosnia & Herzegovina	CEIT	42N	45N	16E	19E		0
Bulgaria	CEIT	42N	44N	22E	29E		0
Byelorussia (Belarus)	CEIT	53N	56N	23E	32E	1990	608
Croatia	CEIT	42N	47N	14E	20E		78
Czech Republic	CEIT	47N	51N	12E	22E		0
Estonia	CEIT	57N	59N	23E	28E	1990	4
Georgia	CEIT	41N	44N	40E	47E	1990	170
Hungary	CEIT	46N	48N	16E	23E		0
Kazakhstan	CEIT	42N	55N	47E	90E	1990	729
Kyrgyzstan	CEIT	39N	43N	70E	80E	1990	12
Latvia	CEIT	56N	58N	21E	27E	1990	89
Lithuania	CEIT	54N	57N	21E	26E	1990	143
Macedonia	CEIT	41N	43N	21E	23E		0
Moldavia	CEIT	46N	48N	28E	29E	1990	93
Montenegro	CEIT	42N	43N	19E	20E		0
Poland	CEIT	49N	55N	14E	24E	1990	423
Romania	CEIT	43N	48N	21E	29E	1990	96
Slovakia	CEIT	47N	50N	17E	23E		0
Slovenia	CEIT	45N	47N	14E	17E		0
Turkmenistan	CEIT	35N	43N	53E	66E		0
Ukraine	CEIT	45N	52N	22E	40E	1990	2964
Uzbekistan	CEIT	37N	45N	56E	72E	1990	465
Yugoslavia	CEIT	41N	46N	18E	23E	1990	188
<b>Totals</b>							<b>6227</b>

Appendix 2 Table 9 Data for other CEIT and E. European countries (Reliable data is not available for many countries listed in this table).

<b>China Calculations (basic)</b>							Metric tonnes nPB Upper Bound
Area	Class	Lat. Min	Lat. Max	Long. Min	Long. Max	Year CC	
Haikou, Nanning, Kunming	A5(1)	20N	25N	101E	110E	2000	164
Shenzhen, Guangzhou	A5(1)	20N	25N	111E	120E	2000	3925
Lhasa	A5(1)	26N	30N	91E	100E	2000	0
Guiyang, Chongqing	A5(1)	26N	30N	101E	110E	2000	491
Fuzhou, Changsha, Nanchang, Hangzou	A5(1)	26N	30N	111E	120E	2000	2453
Chengdu, Xi'an	A5(1)	31N	35N	101E	110E	2000	1635
Wuhan, Hefei, Nanjing, Zhengzhou	A5(1)	31N	35N	111E	120E	2000	2780
Shanghai	A5(1)	31N	35N	121E	130E	2000	1799
Xi'ning, Lanzhou, Yinchuan	A5(1)	36N	40N	101E	110E	2000	327
Jinan, Taiyuan, Tianjing, Huhehaote, Beijing	A5(1)	36N	40N	111E	120E	2000	1635
Wulumuqi	A5(1)	41N	45N	88E	100E	2000	0
Shengyang, Changchun, Haerbin	A5(1)	41N	46N	121E	130E	2000	1145
<b>Totals</b>							<b>16353</b>

Appendix 2 Table 10 Data for China (These data do not include consumption in Hong Kong, Macao or Taiwan. Chlorocarbon data is from imports only. Local production is unknown, but finite.)

<b>India Calculations (basic)</b>							Metric tonnes nPB Upper Bound
Area	Class	Lat. Min	Lat. Max	Long. Min	Long. Max	Year CC	
Andhra Pradesh	A5(1)	13N	20N	77E	85E	1990	620
Andaman & Nicobar Islands	A5(1)	7N	13N	92E	93E	1990	0
Arunchal Pradesh	A5(1)	26N	29N	92E	99E	1990	1
Assam	A5(1)	24N	28N	90E	97E	1990	0
Bihar	A5(1)	22N	27N	83E	88E	1990	35
Chandigarh	A5(1)	31N		77E		1990	0
Dadra & Najar Haveli	A5(1)	20N		73E		1990	0
Daman & Diu	A5(1)	20N	21N	71E	73E	1990	0
Delhi	A5(1)	29N		71E		1990	149
Goa	A5(1)	14N	16N	74E	75E	1990	0
Gujrat	A5(1)	21N	24N	68E	76E	1990	483
Haryana	A5(1)	27N	31N	75E	77E	1990	315
Himachal Pradesh	A5(1)	30N	33N	76E	79E	1990	0
Jammu & Kashmir	A5(1)	32N	37N	72E	89E	1990	0
Karnataka	A5(1)	12N	18N	74E	78E	1990	569
Kerala	A5(1)	8N	13N	75E	77E	1990	33
Lakshadweep	A5(1)	8N	12N	72E	73E	1990	0
Madhya Pradesh	A5(1)	17N	27N	74E	84E	1990	116
Maharastra	A5(1)	16N	22N	74E	81E	1990	1135
Manipur	A5(1)	24N	26N	93E	95E	1990	1
Meghalaya	A5(1)	25N	26N	90E	93E	1990	0
Mizoram	A5(1)	22N	24N	92E	93E	1990	0
Nagaland	A5(1)	25N	27N	93E	96E	1990	0
Orrissa	A5(1)	18N	22N	81E	88E	1990	19
Pondicherry	A5(1)	12N		80E		1990	0
Punjab	A5(1)	29N	32N	73E	77E	1990	107
Rajastan	A5(1)	23N	30N	69E	79E	1990	35
Sikkim	A5(1)	27N	28N	69E	79E	1990	0
Tripura	A5(1)	23N	24N	88E	89E	1990	0
Tamilnadu	A5(1)	8N	13N	76E	80E	1990	619
Uttarpradesh	A5(1)	24N	31N	77E	85E	1990	132
West Bengal	A5(1)	21N	29N	86E	90E	1990	508
<b>Totals</b>							<b>4876</b>

Appendix 2 Table 11 Data for India

Other A5 Calculations (basic)							Metric tonnes
Area	Class	Lat. Min	Lat. Max	Long. Min	Long. Max	Year CC	nPB Upper Bound
Afghanistan	A5(1)	30N	37N	62E	71E		0
Algeria (inhabited)	A5(1)	32N	38N	3W	8E	1990	486
Angola	A5(1)	7S	17S	13E	22E	1990	16
Antigua and Barbuda	A5(1)	17N	17N	62W	62W	1990	0
Argentina (industrial)	A5(1)	22S	35S	56W	67W	1998	2999
Argentina (non-industrial)	A5(1)	35S	55S	66W	71W		0
Bahamas	A5(1)	22N	27N	71W	79W		0
Bahrain	A5(1)	26N	26N	51E	51E	1990	158
Bangladesh	A5(1)	21N	26N	89E	92E	1990	313
Barbados	A5(1)	14N	14N	60W	60W		0
Belize	A5(1)	16N	19N	88W	89W		0
Benin	A5(1)	6S	12N	1E	4E		0
Bhutan	A5(1)	27N	28N	89E	92E		0
Bolivia	A5(1)	10S	22S	57W	70W		0
Botswana	A5(1)	18S	26S	20E	29E		0
Brazil	A5(1)	5N	33S	35W	74W	1990	3990
Brunei Darussalam	A5(1)	5N	5N	115E	115E	1990	4
Burkina Faso	A5(1)	10N	15N	5W	2E		0
Burundi	A5(1)	2S	4S	29E	31E		1
Cambodia	A5(1)	10S	15S	102E	107E		0
Cameroon	A5(1)	2N	11N	9E	16E	1990	186
Cape Verde	A5(1)	16N	16N	25W	25W		0
Central African Republic	A5(1)	3N	11N	15E	26E		0
Chad	A5(1)	7N	24N	14E	24E		0
Chile	A5(1)	17S	55S	68W	71W	1990	119
Colombia	A5(1)	4S	12N	67W	79W	1990	566
Comoros	A5(1)	12S	12S	44E	44E		0
Congo	A5(1)	5S	4N	11E	19E		0
Congo (Dem. Rep.)	A5(1)	10S	5N	18E	29E		60
Costa Rica	A5(1)	8N	11N	83W	85W	1990	48
Cuba	A5(1)	20N	23N	74W	85W	1990	263
Cyprus	A5(1)	34N	36N	32E	34E		0
Djibouti	A5(1)	11N	12N	42E	43E		0
Dominica	A5(1)	15N	15N	61W	61W		0
Dominican Republic	A5(1)	18N	19N	69W	72W	1990	60
Ecuador	A5(1)	5S	1N	75W	81W	1990	21
Egypt	A5(1)	22N	31N	25E	36E	1990	735
El Salvador	A5(1)	13N	14N	88W	90W	1990	26
Equatorial Guinea	A5(1)	1N	2N	9E	11E		0
Ethiopia	A5(1)	4N	17N	33E	46E	1990	41
Fiji	A5(1)	19S	19S	175E	175E		2
Gabon	A5(1)	4S	2N	9E	14E	1990	15
Gambia	A5(1)	13N	13N	14W	16W		0
Ghana	A5(1)	5N	11N	1E	3W	1990	43
Granada	A5(1)	12N	12N	62W	62W		1
Guatemala	A5(1)	14N	18N	89W	92W	1990	101
Guiyana	A5(1)	2N	6N	52W	54W		0
Guinea	A5(1)	7N	12N	8W	15W		0
Guinea-Bissau	A5(1)	11N	12N	14W	16W		0
Haiti	A5(1)	18N	20N	72W	74W		0
Honduras	A5(1)	13N	16N	84W	89W	1990	38
Hong Kong	A5(1)	22N	22N	114E	114E	1990	1031
Indonesia	A5(1)	11S	6N	95E	141E	1990	2286
Iran	A5(1)	25N	40N	45E	63E	1990	6617
Iraq	A5(1)	29N	36N	39E	48E	1990	752
Ivory Coast	A5(1)	5N	11N	3W	8W	1990	129



Other A5 Calculations (basic)							Metric tonnes
Area	Class	Lat. Min	Lat. Max	Long. Min	Long. Max	Year CC	nPB Upper Bound
Jamaica	A5(1)	17N	17N	76W	78W	1990	20
Jordan	A5(1)	29N	33N	35E	39E		16
Kenya	A5(1)	5S	5N	34E	41E	1990	18
Kiribati	A5(1)	1S	1S	174E	174E		0
Kuwait	A5(1)	28N	30N	46E	47E	1990	355
Laos	A5(1)	14N	22N	100E	107E		0
Lebanon	A5(1)	33N	35N	35E	36E		0
Lesotho	A5(1)	29S	30S	27E	29E		0
Liberia	A5(1)	4N	8N	8W	12W		0
Libya (inhabited)	A5(1)	25N	33N	10E	25E	1990	563
Madagascar	A5(1)	12S	26S	43E	50E		0
Malawi	A5(1)	9S	17S	33E	36E		0
Malaysia	A5(1)	1N	7N	100E	119E	1990	670
Maldives	A5(1)	5N	5N	70E	70E		0
Mali	A5(1)	10N	25N	4E	12W		0
Malta	A5(1)	36N	36N	14E	14E		15
Martinique	A5(1)	15N	15N	61W	61W	1990	3
Mauritania	A5(1)	15N	27N	6W	16W		0
Mauritius	A5(1)	20S	20S	58E	58E		11
Mexico	A5(1)	15N	33N	82W	117W	1990	3903
Mongolia	A5(1)	42N	147N	88E	120E		0
Morocco (inhabited)	A5(1)	30N	36N	1W	13W	1990	181
Mozambique	A5(1)	11S	27S	30E	41E		0
Myanmar	A5(1)	15N	28N	92E	101E	1990	305
Namibia	A5(1)	17S	29S	12E	21E		0
Nauru	A5(1)	3S	3S	170E	170E		0
Nepal	A5(1)	27N	30N	80E	88E		0
Nicaragua	A5(1)	11N	15N	84W	87W		0
Niger	A5(1)	12N	23N	0	16E		0
Nigeria	A5(1)	4N	14N	3E	15E	1990	577
North Korea	A5(1)	37N	43N	125E	130E		735
Oman	A5(1)	16N	25N	52E	60E	1990	108
Pakistan	A5(1)	24N	37N	61E	79E	1990	1047
Panama	A5(1)	7N	10N	77W	83W	1990	24
Papua New Guinea	A5(1)	3S	10S	140E	153E		0
Paraguay	A5(1)	19S	27S	54W	63W		0
Peru	A5(1)	0S	18S	69W	81W	1990	141
Philippines	A5(1)	6N	18N	119E	126E	1990	1220
Puerto Rico	A5(1)	18N	18N	66W	67W		0
Qatar	A5(1)	24N	26N	51E	52E	1990	62
Rwanda	A5(1)	2S	3S	29E	31E		0
St Christopher and Nevis	A5(1)	17N	17N	63W	63W		0
Saint Lucia	A5(1)	14N	14N	61W	61W		0
St Vincent and the Grenadines	A5(1)	13N	13N	61W	61W		0
San Marino	A5(1)	44N	44N	13E	13E		0
São Tomé e Príncipe	A5(1)	1N	1N	7E	7E		0
Saudi Arabia	A5(1)	16N	32N	35E	56E	1990	1199
Senegal	A5(1)	12N	16N	12W	17W	1990	32
Seychelles	A5(1)	4S	4S	55E	55E		0
Sierra Leone	A5(1)	7N	10N	11W	13W		0
Singapore	A5(1)	1N	1N	104E	104E	1990	478
Solomon Islands	A5(1)	8S	11S	156E	162E		0
Somalia	A5(1)	2S	13N	42E	52E		0
South Korea	A5(1)	35N	38N	126E	129E	1990	2758
Sri Lanka	A5(1)	8N	10N	80E	82E	1990	86
Sudan	A5(1)	4N	22N	22E	37E	1990	195

<b>Other A5 Calculations (basic)</b>							Metric tonnes
Area	Class	Lat. Min	Lat. Max	Long. Min	Long. Max	Year CC	nPB Upper Bound
Surinam	A5(1)	2N	6N	54W	57W		0
Swaziland	A5(1)	26S	27S	31E	32E		0
Syria	A5(1)	32N	37N	36E	42E	1990	164
Tanzania	A5(1)	1S	11S	30E	40E		11
Thailand	A5(1)	12N	21N	97E	106E	1990	1569
Togo	A5(1)	6N	11N	0	2E		0
Tonga	A5(1)	20S	20S	173W	173W		0
Trinidad and Tobago	A5(1)	10N	11N	61W	62W		4
Tunisia (inhabited)	A5(1)	33N	37N	7E	12E	1990	16
Turkey	A5(1)	36N	42N	26E	45E	1990	1400
Tuvalu	A5(1)	8S	8S	177E	177E		0
Uganda	A5(1)	1S	4N	30E	35E		0
United Arab Emirates	A5(1)	23N	26N	51E	56E	1990	458
Uruguay	A5(1)	30S	35S	53W	58W	1990	8
Vanuata	A5(1)	15S	17S	166E	169E		0
Venezuela	A5(1)	1N	12N	60W	73W	1990	840
Vietnam	A5(1)	9N	23N	102E	109E	1990	83
Western Samoa	A5(1)	15S	15S	177W	177W		0
Yemen	A5(1)	13N	19N	42E	53E	1990	50
Zambia	A5(1)	8S	18S	22E	34E		0
Zimbabwe	A5(1)	16S	22S	26E	33E		39
<b>Totals</b>							<b>40476</b>

Appendix 2 Table 12 Data for Other Article 5(1) countries

<b>Non-signatory Regions Calculations (basic)</b>							Metric tonnes
Area	Class	Lat. Min	Lat. Max	Long. Min	Long. Max	Year CC	nPB Upper Bound
Taiwan	NS	22N	25N	120E	122E	1990	1295
<b>Totals</b>							<b>1295</b>

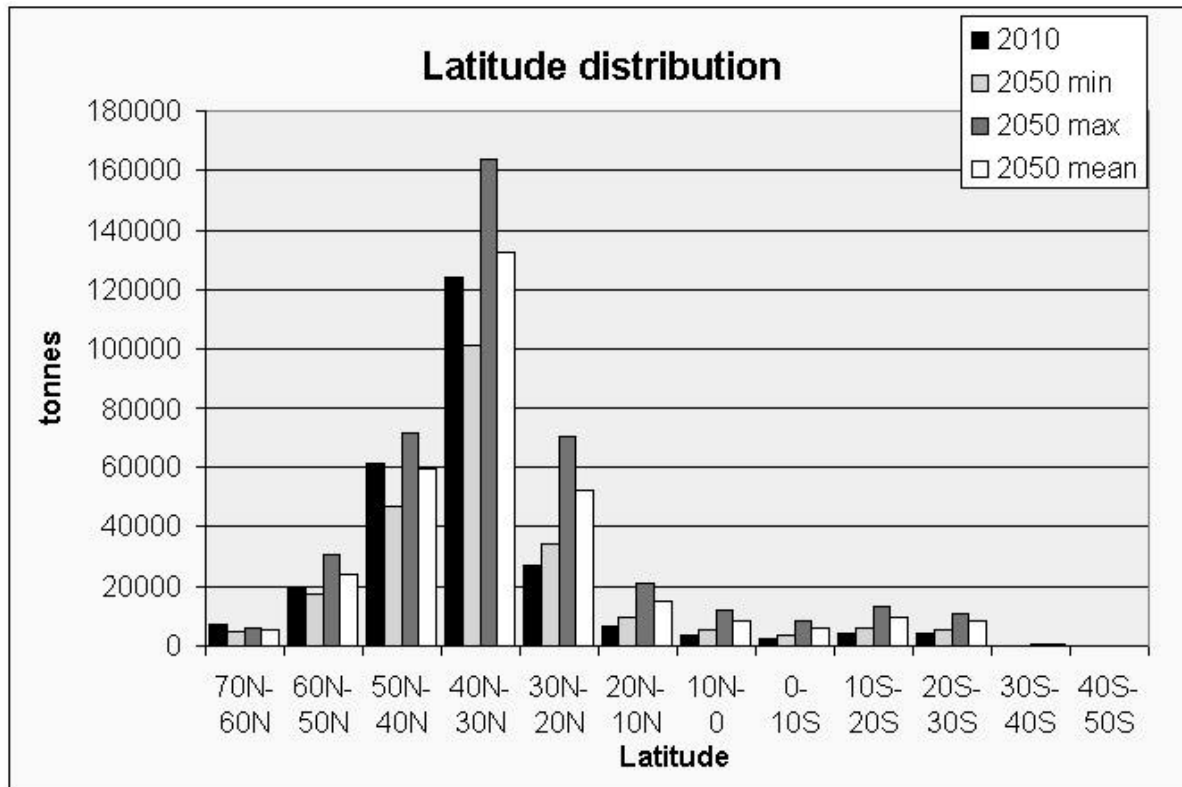
Appendix 2 Table 13 Data for regions which are non-signatory to the Montreal Protocol

<b>Percentage technically-possible substitution by region and by solvent - MTS</b>								Likely % substitution rate (LAR)	CC % substitution
	CTC	CFC-113	1,1,1-TCA	TCE	PCE	MC	HCFC		
W. Europe	Phased out	Phased out	Phased out	75.0	35.0	30.0	50.0	30	100
Japan	Phased out	Phased out	Phased out	85.0	30.0	30.0	50.0	60	70
USA	Phased out	Phased out	Phased out	40.0	50.0	85	100		
Can-Aus	Phased out	Phased out	Phased out	85.0	30.0	30.0	0.0	60	70
Other A2	Phased out	Phased out	Phased out	85.0	30.0	30.0	0.0	60	70
Russia	80.0	50.0	90.0	90.0	45.0	40.0	0.0	40	115
Other CEIT	80.0	50.0	90.0	90.0	45.0	40.0	0.0	40	115
China	100.0	45.0	64.0	85.0	30.0	30.0	0.0	50	100
India	40.0	50.0	80.0	70.0	40.0	35.0	0.0	35	115
Other A5(1)	80.0	50.0	90.0	90.0	45.0	40.0	0.0	40	115
Non-signatory	80.0	50.0	90.0	90.0	45.0	40.0	0.0	40	115

Appendix 2, Table 14 Intermediate percentages used for calculations

<b>Percentage overall potential substitution by region and by solvent</b>							
	CTC	CFC-113	1,1,1-TCA	TCE	PCE	MC	HCFC
W. Europe	0.0	0.0	0.0	22.5	10.5	9.0	15.0
Japan	0.0	0.0	0.0	35.7	12.6	12.6	30.0
USA	0.0	0.0	0.0	34.0	42.5		
Can-Aus	0.0	0.0	0.0	35.7	12.6	12.6	0.0
Other A2	0.0	0.0	0.0	35.7	12.6	12.6	0.0
Russia	32.0	20.0	36.0	36.0	18.0	16.0	0.0
Other CEIT	32.0	20.0	36.0	41.4	20.7	18.4	0.0
China	50.0	22.5	32.0	42.5	15.0	15.0	0.0
India	14.0	17.5	28.0	28.2	16.1	14.1	0.0
Other A5(1)	32.0	20.0	36.0	41.4	20.7	18.4	0.0
Non-signatory	32.0	20.0	36.0	41.4	20.7	18.4	0.0

Appendix 2 Table 15 Potential overall substitution of each solvent type and in each region, in percent. This takes into account the technical feasibility and the probability in each cell. Where there are no input data, the percentage is set at zero. The rationale is explained in each worksheet and in Table 14.



Appendix 2 Chart 1 Latitude distribution of estimated "upper bound" nPB emissions (black bars) and possible 2050 emissions (min. light grey; max. dark grey, mean white) based on potential economic growth patterns. It can be seen that mid-latitude Northern Hemisphere emissions are likely to remain substantially constant whereas subtropical, tropical and Southern Hemisphere emissions will increase. Note that the 2050 predictions cannot be more than guesswork, because of numerous uncontrollable factors. These predictions assume that no country with an estimated zero emission in 2010 will develop industrially before 2050. The growth assumptions used for this are:

Article 5(1) nations: average annual (2010-2050) industrial growth rate: 1 – 3%  
 CEIT nations: average annual (2010-2050) industrial growth rate: 1 – 3%  
 Other nations: average annual (2010-2050) industrial growth rate: -0.3% – -1%

Latitude range	Upper Bound	2050 min	2050 max	2050 mean
70N-60N	7068	4730	6272	5501
60N-50N	19289	17548	30560	24054
50N-40N	61430	46920	71351	59136
40N-30N	124191	101534	163590	132562
30N-20N	26659	33867	70087	51977
20N-10N	6438	9586	21002	15294
10N-0	3654	5440	11918	8679
0-10S	2553	3802	8329	6065
10S-20S	4046	6025	13199	9612
20S-30S	4270	5324	10936	8130
30S-40S	127	190	416	303
40S-50S	121	81	107	94
	<b>260155</b>	<b>235253</b>	<b>495408</b>	<b>321647</b>

Appendix 2 Table 15 Data used to plot Appendix 2 Chart1.

### Appendix 3: Potential manufacturing quantities

The quantity of nPB that can be manufactured depends on the quantity of bromine that can be produced. The Task Force has confirmed that there is no physical resource limit on the quantity of nPB that can be manufactured. There are four major sources of bromine that may be commercially exploited:

- underground bromide-rich salt deposits and brines, such as are found and exploited in many countries including China, India, Turkmenistan, the United Kingdom and the United States.<sup>21</sup>
- surface waters rich in bromides, such as the Dead Sea and some thermal springs
- bitterns<sup>22</sup> from edible salt production
- sea water – either as is or concentrated from desalination plants – such as bromine production by chlorine-blowing into sea water (Samejima 2000).

According to one reference (Encyclopaedia Britannica: 1998), “the chief commercial source of bromine is ocean water,” presumably including bitterns. This means that there is no limit to the quantity of bromine that may be produced, if demanded. Probably all the bromine production in Japan is from sea water (Samejima 2000). It is considerably less costly to produce bromine from bitterns (containing essentially magnesium salts, including bromide, with a specific gravity of 1.24 –1.25) than from seawater (SG 1.025). Solar evaporation of sea water to produce salt is widely practised in latitudes from about 50°N to 50°S, particularly in the Bahamas, France, India and the USA. The quantity of bitterns available is limited only by the demand for salt.

Underground sources are also limited by the pumping capacity either of natural brines, such as in India and Poland or where water is injected into rock salt deposits to form a brine, such as in China, United Kingdom and USA.

#### *Current production of bromine supply*

The Task Force reviewed production estimates from various sources. The Dead Sea Bromine Group (DSBG) reports that their production (200,000 metric tonnes of bromine compounds per year) is about 35% of global elemental bromine production with 50% of global production estimated to be in the USA. (DSBG

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<sup>21</sup> Weifang (2000) reports that Shouguang China has a 4000 million m<sup>3</sup> of bittern, 320 million metric tonne workable reserve of salt and 1.26 million tons of bromine. This is the Laizhou Bay region of China, which is mined by a number of companies, including one of the largest producers of bromine products in the world – Ocean Chemicals (Ocean 2000).

<sup>22</sup> Bitterns are the residual brine left over from the solar crystallisation of salt. Because bromides have a higher solubility than chlorides, the bitterns are rich in them, mainly the magnesium and calcium salts.

1998 and 2000). The global annual production would therefore be about 570,000 metric tonnes, of which 200,000 metric tonnes are produced by the DSBG and 290,000 metric tonnes by the two largest producers in the USA and 80,000 metric tonnes produced elsewhere.<sup>23</sup>

Roskill (1997) estimates a 1996 annual production of 468 thousand metric tonnes, with growth at 8% per annum.

Another source (ChemExp 1999) estimates that the US production is 325,000 metric tonnes with 93% or 302,000 metric tonnes produced by the two largest US manufacturers.

The latest United States Geophysical Survey (USGS) (USGS 2000) reports the production presented below (adapted).

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<sup>23</sup> Fourteen major producers were invited to provide data for this report, but only one responded

World Mine Production, Reserves and Reserve Base:			
	Mine production (metric tonnes)		Reserves <sup>6/</sup> (metric tonnes)
	1998 (reported)	1999 (estimated)	
United States <sup>1/</sup>	230,000	231,000	11,000,000
Azerbaijan	2000	2000	300,000
China	40000	40000	NA
France	2000	2000	1,600,000
India	1005	1005	( <sup>7/</sup> )
Israel	180000	180000	( <sup>8/</sup> )
Italy	300	300	( <sup>7/</sup> )
Japan	20000	20000	( <sup>9/</sup> )
Spain	100	100	1,400,000
Turkmenistan	200	200	700,000
Ukraine	3000	3000	400,000
United Kingdom	30000	30000	( <sup>7/</sup> )
<b>World total (rounded)</b>	<b>510,000</b>	<b>510,000</b>	<b>NA</b>

World Resources: Resources of bromine are virtually unlimited. The Dead Sea in the Middle East is estimated to contain 1 billion tons of bromine. Seawater contains about 65 to 85 parts per million of bromine or an estimated 100 trillion tons. The bromine content of underground water in Poland has been estimated at 36 million tons.

- 1/ Sold or used by U.S. producers.
- 2/ Imports calculated from items shown in tariff section.
- 3/ Includes recycled product beginning in 1993.
- 4/ Defined as imports - exports + adjustments for Government and industry stock changes.
- 5/ See Reference Appendix B.
- 6/ See Reference Appendix C for definitions.
- 7/ From waste bitters associated with solar salt.
- 8/ From the Dead Sea.
- 9/ From seawater.

Because there is currently no audited reporting of bromine production, estimates of total global production differ. For example, the USGS reported considerably lower increases in production from 410,000 metric tonnes in 1994 to 510,000 metric tonnes in 1998 and Dibble (2000a) estimated 1997 global production of 644,000 metric tonnes for 1997 with 1996 US production estimated at 247,000 metric tonnes. However, all data sources confirm that bromine is extracted in many countries, from varied sources, and that there are virtually infinite reserves.

Taking into account all these estimates, the Task Force's best estimate for 2000 is 600,000 to 700,000 metric tonnes.

### ***Bromine market expansion***

The global market for bromine is expanding at 6 – 8% annually (USGS 1994 and 1998), (Roskill 1997), with 3% expansion in the USA (ChemExp 1999) and major expansion taking place elsewhere. New capacity can be implemented in only 2-3 years.

In Jordan, a new bromine-producing plant is scheduled to come on line in 2002 with a capacity of 50,000 metric tonnes/year of elemental bromine and 45,000 metric tonnes/year for flame retardants and calcium bromide (used in the petroleum industry) (ChemExpo 1999).

In Russia commercial concentrations of iodine, bromine and other elements are available from underground waters (Sirius 2000).

In Turkmenistan there are significant undeveloped mineral resources with 10 chemical enterprises involved in the production of bromine and other minerals (US State Dept. 1999), (SOET 1996).

Ukraine, already a small producer, has further reserves. Poland also has very large reserves of bromine but there are no reported plans for exploiting this in the near future.

China has 15 identified manufacturers of elemental bromine (Jimzheng 2000, Chemnet 2000). The biggest manufacture, Shandong Weifang Chemical Ocean Group, produced 20,000 metric tonnes of bromine in 1999 (Chinaweifang 2000).

Based on the above information, a conservative global estimate of annual elemental bromine production is 1,000,000 metric tonnes by 2010, at the current rate of expansion.

### ***Apportioning of bromine production to nPB and other uses***

Because bromine has many applications, it is necessary to determine the quantities available to manufacture nPB. Bromine is currently used for:

- ethylene dibromide, used in leaded motor fuel. Quantities used are declining as countries shift to lead-free fuel formulations.
- tetrabromobisphenol A (TBBPA), used as a flame retardant for a number of widely manufactured plastics – use is expected to diminish within the next decade (WEEE 2000, IVF 2000) as non-halogenated alternatives are implemented (Nelco 2000, Isola 2000, NEC 2000, Plastics 2000).
- other flame retardants – expected to decrease in response to health and safety concerns with Europe already prohibiting applications of one brominated product for fabrics coming into contact with the skin.
- methyl bromide (MB) – scheduled for phaseout under the Montreal Protocol.
- calcium bromide and organic bromides used in the petroleum industry, such as for improving the performance of drilling – expected to increase over time.



- miscellaneous uses in water treatment, pharmaceutical, photographic and other industries currently representing about 10-15% of the total production – expected to increase.

In the USA, 40 percent is used for flame retardants, 24 percent for drilling fluids, 12 percent for brominated pesticides (mostly methyl bromide), 7 percent for water treatment and 17 percent for miscellaneous uses including drugs and fine chemical intermediates, photographic chemicals and rubber additives (ChemExpo 1999). This is not representative of global uses because leaded fuels are prohibited in the United States and the use of bromine for water treatment is higher in the USA than most other countries.

Because major applications of bromine in leaded motor fuel, flame retardants and methyl bromide will decrease sharply over the next decade and because production is expected to increase, it is estimated that 200,000– 250,000 metric tonnes of bromine could be available to produce 308,000 – 385,000 metric tonnes of nPB<sup>24</sup> by 2010. In reality, the demand is not very likely to reach these figures.

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<sup>24</sup> The weight of bromine in nPB is proportional to the atomic weight of bromine divided by the molecular weight of nPB =  $79.9/123 = 0.65$  (to two significant figures).

## Appendix 4: Environmental, toxicological and safety concerns of nPB

### *Environmental effects*

nPB has a number of environmental effects:

- ozone-depletion
- volatile organic compound
- climate change (it has a very low GWP)
- acid rain precursor
- possible ground water contamination

Under European and United States regulations (VOC, 1999), all nPB solvents are classified as Volatile Organic Compounds (VOCs). The effect of nPB on climate change is very small.

### *Toxicology*

OSHA (2000) summarises 28 studies of the toxicity of nPB.

#### *Acute Toxicity*

Pure nPB has a relatively low acute toxicity in rats: inhalation LC<sub>50</sub> (4 hour) = 7000 ppm; oral LD<sub>50</sub> = 2 g/Kg body weight.

#### *Sub-chronic Toxicity*

Two recent papers (Ichihara 2000a, Ichihara 2000b) report that nPB is reproductively and neurologically toxic to a single strain of male laboratory rats at exposure levels of 200 ppm and above over a continuous 12 week period.

- “...this agent should be very cautiously used in the workplace, from the viewpoint of its male reproductive toxicity” (Ichihara 2000a).
- “1-Bromopropane may be seriously neurotoxic to humans and should thus be used carefully in the workplace” (Ichihara 2000b).

The isomer, *iso*-propyl bromide, has also been shown to have similar toxic effects (Ichihara 1997), substantiated by an epidemiological study (Ichihara 1999) that showed severe occupational health effects on workers exposed to *iso*-PB. No epidemiological study on humans exposed to nPB has been identified by the TEAP. According to Ichihara (1997, 2000b), the neurological effects on rats may be worse with nPB than with *iso*-PB, but the opposite is true for reproductive toxicity.

Some experts have criticised the Ichihara studies, maintaining that an 8 hour/7 day per week exposure regime over 12 weeks does not reproduce the typical 8 – 10 hour per day, 5 – 6 day per week workplace exposure. EPA is reviewing the Ichihara studies because of concerns regarding not only exposure protocol, but also the limited number of animals used, lack of mating or offspring produced and nPB formulations used. A 2-generation study funded by the Brominated Solvents

Consortium was initiated to overcome some of the limitations of the Ichihara studies so that the reproductive and developmental risks associated with nPB could be more fully evaluated. The BSOC studies used parent animals exposed over a significant portion of their lives prior to mating, during the mating process, and during the developmental phase in utero. Parents and offspring are being evaluated for all target organs (e.g., liver and brain) toxicity, as well as for reproductive endpoints and developmental milestones. The in-life portion of the test was completed in late 2000 and pathological examinations of tissues are near completion.

In late 2000, some, but not all, manufacturers of nPB solvent blends reduced their recommended exposure levels from 100 ppm. One manufacturer reduced the recommended exposure limit to 10 ppm (Great Lakes), three to 25 ppm (Albemarle, Dead Sea Bromine Group, and Petroferm) and one to 50 ppm (M.G. Chemicals). At least one major manufacturer of molecular nPB has not offered nPB solvent blends (Elf Atochem 1997) and one manufacturer has halted sales of nPB solvents blends (Great Lakes, 2000). The International Labour Organisation website states: "Insufficient data are available on the effect of this substance on human health, therefore utmost care must be taken." In the past twenty years the exposure limits for methyl bromide have gone from 20 to 15 to 5 to 1 ppm as experience with human exposure accumulated and additional toxicity studies were conducted. Health documentation of human exposure to nPB is very limited and toxicity testing is not yet complete.

#### *Chronic toxicology*

No chronic toxicology tests have been completed. The US Occupational Safety and Health Administration (OSHA) requested the US National Toxicology Program (NTP) to study nPB (OSHA 1999). The NTP Center for the Evaluation of Risks to Human Reproduction has also requested further studies (FR 2000a) and the Interagency Committee for Chemical Evaluation and Coordination (ICCEC) have made recommendations (FR 2000b) for a study of nPB, regarding:

- carcinogenicity
- reproductive and developmental toxicity
- toxicokinetics
- mechanistic studies
- neurotoxicity
- genotoxicity
- exposure studies in workers

The NTP has selected nPB for planned carcinogenicity/toxicity and organ systems studies, as of 13 November 2000 (NTP 2000).

"OSHA believes a very high priority should be placed on conducting tests that would shed light on whether such large exposures pose a potential for human reproductive toxicity and in addition may pose a cancer risk, before the number of persons exposed grows from the hundreds to the tens of thousands or more." (OSHA 1999).

## Recommended Exposure Level and Websites for Companies Marketing nPB

Company	Trade Name	Recommended exposure level ppm	Country
Great Lakes Chemicals.	Hypersolve	10	USA
Albemarle	Abzol	25	USA
France			
Dead Sea Bromine Group		25	Israel
Petroferm	Lenium	25	USA
M.G. Chemicals	Contact Cleaner - NPB Heavy Duty	50	Canada
Adhesive Technologies	Not manufacturing	100	USA
Albatross USA	VDS-3000	100	USA
Alpha Metals	VaporEDGE 1000	100	USA
Amity UK	Leksol	100	UK
Enviro Tech International	Ensolv	100	USA
Poly Systems USA	Solvon	100	USA
Tech Spray	1640 Bulk	100	USA
Baker.	1-bromopropane		USA
Micro Care			USA

### URLs:

[http://www.greatlakeschem.com/environmental/MSDS\\_PDF/00354.pdf](http://www.greatlakeschem.com/environmental/MSDS_PDF/00354.pdf)

<http://www.albemarle.com/acrofiles/bc0068f.pdf>

[http://www.deadseabromine.com/Brome/brome.nsf/0a03dde88bb2d9c7422567760036799d/51c3e639b1ababb642256a09003141f7/\\$FILE/8613\\_ennpropylbromide.pdf](http://www.deadseabromine.com/Brome/brome.nsf/0a03dde88bb2d9c7422567760036799d/51c3e639b1ababb642256a09003141f7/$FILE/8613_ennpropylbromide.pdf)

<http://www.petroferm.com/PTF-053/pdf/msds/petroferm/LENIUM-ES-01MSDS.pdf>

<http://www.mgchemicals.com/msds/4091-aerosol.html>

<http://www.adhesivetech.com/tbcompare.html>

<http://www.albatross-usa.com/elsolvent.htm#VDS1000>

<http://www.alphametals.com/products/msds/1999100012.pdf>

[http://www.amityinternational.com/2MSDS/Leksol\\_MSDS.htm](http://www.amityinternational.com/2MSDS/Leksol_MSDS.htm)

[http://www.ensolv.com/Regulatory\\_Info.htm](http://www.ensolv.com/Regulatory_Info.htm)

[http://www.solvon.com/Products/Solvon\\_AER/solvon\\_aer.html](http://www.solvon.com/Products/Solvon_AER/solvon_aer.html)

<http://www.techspray.com/ms1273.htm>

<http://hazard.com/msds/mf/baker/baker/files/b5152.htm>

<http://microcare.com/ssg/q-m4.html>

### *Safety issues*

There is disagreement concerning the closed-cup flash point of nPB but there is agreement that nPB does not have an open-cup flash point. At least one manufacturer advertises there is no closed-cup flash point (Albemarle 2000), while the US OSHA gives a closed cup flash point of 21 °C (OSHA 1999). Another authority quotes a closed-cup flash point of -14 °C with lower and upper explosive limits of 4% and 8% respectively (ChemTec 2000).