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Addendum

REPORT ON THE PRODUCTION OF CARBON TETRACHLORIDE AND ITS FEEDSTOCK USES IN CHINA (DECISION 75/18 (b) (iii))

Background

1. At its 75th meeting, the Executive Committee decided to invite the Government of China to undertake a study on its country's production of carbon tetrachloride (CTC) and its use for feedstock applications and to make the results of the study available to the Executive Committee by the end of 2018 (decision 75/18(b)(iii)).

2. In line with decision 75/18(b)(iii), on behalf of the Government of China, the World Bank submitted the report on the production of CTC and its feedstock uses on 21 October 2019.

3. As the report contains information considered commercially sensitive, the present document only contains a brief summary of the report and the Secretariat's comments. The full report is available to Executive Committee members upon request.

Objectives of the report

4. The objectives of the report were to understand chloromethane[1] (CM) production, CTC by-products and the operations of CM production, as well as the feedstock uses of CTC in producing non-ODS chemicals; to analyze and evaluate the emission status of CTC in CM production, and all its conversion and feedstock using processes; and to submit a project report summarizing the findings.

Survey coverage and methodology

5. A survey was conducted for all 15 CM producers[2] and 23 CTC feedstock users in China, among

[1] Chloromethane plants produce methyl chloride, methylene chloride, chloroform and carbon tetrachloride.
[2] A new CM producer started operations in the year 2018; this sixteenth producer was not included in the present study.

which site visits were undertaken at five CM producers and eight CTC feedstock users.[3]

6. Technical information related to CTC production, uses and emissions was obtained through:

(a) The questionnaire survey, which included information on production processes and technologies used for CM production, conversion and feedstock uses of CTC and the corresponding CTC emissions, and the enterprises' recognition and suggestions for lowering CTC emissions in all related processes;

(b) Site visits for checking the questionnaire information, verifying the status of the production lines, the advancement of the process technology, the quality of management systems of the enterprises, the estimated amount of CTC emissions and the potential emission points; and for discussing with technicians on possible approaches for lowering CTC emissions;

(c) Management information system (MIS) available at FECO/MEE; and

(d) Information from the literature review.

7. Based on the information collected, a profile of CTC supply and use was developed, including technical information related to CM production, CTC conversion and feedstock uses, as well as the emission status and control level of CTC in all those processes.

8. A model for evaluating CTC emissions was developed taking into account CTC streams based on production flow chart, CTC content of the streams based on the quality index of products that determines CTC content, on direct measurement, or on process conditions and/or engineering experience. Theoretically, the CTC amount among all CTC-streams must meet the material balance, which is the basis for assessing the reliability and consistency of the data. For the CM production process, "mass balance of chlorine" is used to assess the accuracy of the data provided by the enterprises. For the conversion of CTC inside the CM production enterprises and feedstock uses of CTC for the production of non-ODS chemicals, "mass balance of CTC" is used as a preliminary criterion. For a specified production process, the potential or maximum emission amount of CTC may be evaluated with the known flow rate, CTC content, temperature, pressure and other necessary conditions of all CTC streams, along with their final usage or disposal processes before discharging to the environment.

9. Based on the types of the CTC streams, the enterprises were required to have the questionnaire filled out by the technical staff for a specified production process. The data included the process technology, the flow chart of the production, the flow rate and the CTC content of all CTC-streams involved. Actual data were used, if available; if not, the data were estimated via process calculation or best empirical estimate. Finally, a mass balance was made by the enterprise to ensure the internal consistency among all data sets. Then, the authenticity of the data was verified by the project expert in terms of the detailed characteristics of the production process, the professional expertise and engineering experience of the expert. If the data were questionable, the expert would communicate with the technician and make revisions according to the actual conditions in the enterprises, until all data from reliable measurement, correct process calculation or rational empirical estimation were in order.

10. The emission amount of CTC in all production processes was evaluated based on the above assessments; experts from Beijing University of Chemical Technology (BUCT), FECO, and senior

[3] Of the 38 enterprises, 36 provided information; two enterprises stopped production in 2015 and had no CTC purchase and consumption from 2015 to 2017. As per the TOR, at least four CM production enterprises and six feedstock users should undergo site visits; the latter should cover three mainstream CTC conversion technologies i.e., CTC to methyl chloride, CTC to perchloroethylene and CTC to chloroform.

engineers from all related enterprises were involved in the modelling process for this analysis. On this basis, the emission amount of CTC in three subsectors as well as the overall emission in China was obtained.

Survey results

Chloromethane and CTC production

11. There are 44 production lines installed at 15 CM production enterprises with total production capacity of 2,350,000 tonnes per annum. CMs (CH_2Cl_2 and $CHCl_3$) are produced by reacting methyl chloride (MeCl) with Cl_2. The actual production of CM and CTC is given in Table 1.

Table 1: Production of chloromethanes and CTC in China (mt)

Particulars	2015	2016	2017
Chloromethane production	2,055,221	2,264,813	2,586,052
CTC production	97,161	105,675	122,759
Percentage of CTC production	4.73%	4.67%	4.75%

12. The CTC produced is used for conversion to non-ODS chemicals at the CM production facilities, as a process agent use, for laboratory and analytical uses that are given exemptions, and for feedstock uses.[4] CTC use for conversion to other chemicals and feedstock uses accounts for more than 99 per cent of the CTC production; less than 1 per cent of CTC production is used for laboratory and analytical uses and as a process agent.

13. During the period 2015 to 2017, the stock level for CTC grew from 1,435.9 mt at the beginning of 2015 to 7,046.6 mt at the end of 2017. Stock changes are a result of the difference between CTC production and consumption, as a part of regular business operations.

14. Six enterprises that produce CTC, use crude CTC as feedstock to produce CTC and, therefore, do not have any heavy distillate residue. Further, all CM producers are required to incinerate waste residue through qualified hazardous waste management companies for disposal, and the disposal has to be undertaken using sound disposal technologies approved under the Montreal Protocol.

15. In 2017, CTC emissions from CTC production were 391.26 mt (0.32 per cent of CTC production), which includes actual emission of CTC of 25.64 mt and potential emission of 365.62 mt.[5] The CTC emission is very low and in line with advanced process technology and onsite management and controls. The enterprises have installed cryogenic condensers in tank outlets to reduce volatile emission from the tail gas of CTC tanks; CTC incinerators are operational in most of the enterprises; closed systems with advanced cargo-tank and product-tank connections for avoiding any CTC emissions the in loading/unloading process and onsite management; and process controls and advanced equipment used to minimise emissions of CTC during maintenance.

Conversion of CTC to non-ODS chemicals

16. Out of 15 CM production facilities, 234,500 mt per annum is dedicated to the conversion[6] of CTC to six non-ODS chemicals, i.e., MeCl, chloroform, perchloroethylene (PCE), hydrochloric acid,

[4] The feedstock use referred here is by enterprises that buy CTC from CM producers, i.e., conversion applies to CM producers and also encompasses their feedstock use.

[5] Potential emission is derived based on technical assessment of possible emission of CTC from various waste streams and is estimated based on product disposal methods; unlike actual emissions which is based on direct estimate of CTC in emission streams, potential emissions are based on usage of products or disposal methods for the CTC streams that could have different CTC levels, before discharge to the atmosphere.

[6] In China, CTC is converted in CM plants to other chemicals including methyl chloride, methylene chloride and chloroform.

pentafluoropropane (PFP[7]) and pentafluorobutane (PFB[8]).

17. For the years 2015 to 2017, the production of CTC converted to non-ODS chemicals was 62,854 mt, 70,807 mt and 83,450 mt, respectively. Of this, CTC used for conversion to MeCl, chloroform, PCE and HCl accounts for more than 99 per cent; and CTC used for PFP and PFB accounts for less than 1 per cent. The proportion of CTC used for PFP and PFB decreased from 0.91 per cent in 2015 to 0.36 per cent in 2017.

18. The process of production of the four non-ODS chemicals that consume more than 99 per cent of CTC used for conversion to non-ODS chemicals is different. MeCl is produced using four reactants, i.e.: CTC, H_2O, methanol and HCl, and the product ratio of MeCl/HCl can be adjusted by the feeding ratio of methanol/H_2O; chloroform is produced by reacting CTC with hydrogen; PCE production involves two reactions, namely the exothermic chlorination of alkane to CTC and endothermic pyrolysis of CTC to PCE.

19. There are other two PCE production processes in China, namely, the acetylene chlorination process and the C1-C3 alkane chlorination process. No CTC intermediate or by-product is formed in the former process, but CTC by-product is produced in the latter process. The acetylene chlorination process is used as the main production technology of PCE due to the low price and the availability of acetylene in China. In the C1-C3 alkane chlorination method, PCE is generated from chlorine and dichloropropane; the final PCE product is obtained through distillation of the resulting CTC and PCE mixture. In this process, raw CTC intermediate is reclaimed and fed back into to the reactor where CTC is further pyrolysed to PCE. All CTC intermediate is consumed in the PCE production process.

20. The conversion ratio (i.e., quantity of CTC used for producing one unit of output products) for MeCl and PCE varied across producers, and for some producers, it varied on an annual basis; the conversion ratio for chloroform, HCl, PFP and PFB did not show such variance. The conversion ratio can change depending upon variations in the feeding ratio of input chemicals like $H_2O$and methanol in the case of MeCl and CTC, and alkanes in the case of PCE.

21. The maximum emission of CTC from the processes that convert CTC to non-ODS chemicals in 2017 was 102.20 mt; this included 17.93 mt of actual emission and 84.27 mt of potential emission. This translates to 0.14 per cent of CTC converted to other non-ODS chemicals. The emission ratio of CTC is quite low, which is reportedly in line with the advanced CTC conversion technology and process management for the large scale, continuous and highly automatic production process. All the CM producing enterprises converting CTC are designed specifically for converting their CTC by-product; strict measures similar to that used in the CM production process are used to lower CTC emissions greatly.

Feedstock use of CTC

22. CTC is used as a feedstock for the manufacture of other chemicals; there are 21 active feedstock users[9] in China. The quantity of CTC used as a feedstock increased from 29,199 mt in 2015 to 42,158 mt in 2017. The top five feedstock uses of CTC consume 93.6 per cent of the total quantity of CTC used as feedstock in 2017; the bottom three feedstock uses of CTC consumed less than 0.5 per cent of CTC used as feedstock.

23. For all feedstock users, material conversion ratios varied for individual enterprises on a year-on-year basis and across enterprises for the same feedstock use.

[7] PFP is HFC-245fa
[8] PFB is HFC-365mfc
[9] Those 21 active feedstock users excludes the CM producers that have their own internal conversion of CTC, except for the one CM producer that also buys CTC to augment its internal production.

24. The maximum emission of CTC from the feedstock use of CTC for 2017 was 177.92 mt; this included 39.37 mt of actual emission and 138.55 mt of potential emission. This translates to 0.42 per cent of CTC used as a feedstock. The emission amount and emission ratio are low, demonstrating a high utilisation rate of CTC by adjusting the reaction conditions, recycling CTC in the production process and advanced production technology and management of CTC.

Other uses

25. The report identified the use of CTC for laboratory and analytical uses and as process agents; the quantity of CTC used for these applications is less than 1 per cent of total CTC production.

Environment monitoring

26. The report also provided the following suggestions for environmental monitoring:

(a) All enterprises that lack waste-treatment capability should be closed, to avoid pollution arising from process facilities that do not have good quality environmental monitoring and good management of wastes;

(b) All waste water and waste gases must be centralized and treated to the set standards before discharging into the environment; periodic supervision and detection of the contaminated effluents of the enterprises should be conducted and actions should be taken when emission standards are not adhered to;

(c) To control emissions from fugitive gas, environmental monitoring inside and around the enterprise should be conducted by the local environmental bodies; when emission of pollutants exceeds the set standards, the enterprises may be required to stop production immediately for remediation and even close their production facilities, if necessary;

(d) According to the regulations issued in 2016, "illegal discharge, dump and disposal of hazardous wastes over 3 mt" constitutes a crime of serious environmental pollution, and should be transferred to the public security organs for the application of penalties. All chemical enterprises have their own task and annual target for the "energy saving and emission reduction", and thus their total amount of waste discharged is under strict supervision and monitoring;

(e) The CM production enterprises should treat their heavy residue from CTC distillation towers containing 20 to 60 per cent CTC by using their onsite incinerators, rather than sending the residue to a contracted hazardous waste treatment centre to avoid potential emissions of CTC;

(f) Inspection and supervision should be conducted regularly by the environmental protection bodies for all enterprises with production, conversion and feedstock uses of CTC. This will make it possible to properly capture the CTC production, consumption and emission status of those enterprises;

(g) CTC management and policy training should be provided to the enterprises regularly, and CTC management inside the enterprises should be strengthened; and

(h) PCE production enterprises should also be covered under ODS supervision and management in the future.

Secretariat's comments

27. The Secretariat noted that the report not only provided comprehensive information on the country's production of CTC and its use for feedstock applications, including CTC supply and use, in line with decision 75/18(b)(iii), but also provided information on estimated emissions of CTC. The Secretariat also noted the substantial efforts undertaken by the Government of China in providing the report.

28. During the review of the report, and keeping in view decision 75/18(b), the Secretariat requested clarifications relating to: the overall supply of CTC and it use; how its use was monitored and the associated reporting framework; and the level of emissions presented in the report. The responses to the Secretariat's comments are presented below.

CTC supply, monitoring and reporting framework

29. The World Bank explained that the purpose of the CTC report was to provide information in response to the concerns expressed by one member related to the global level of CTC emissions. The terms of reference (TOR) were prepared accordingly by China.

30. In terms of a general overview of CTC supply and the use monitoring and reporting framework, the World Bank explained that:

(a) The Ministry of Ecology and Environment (MEE) has been strictly managing CM producers to meet the requirements of CTC controls under the Montreal Protocol since the complete phase-out of CTC production and consumption for controlled use in China in 2010;

(b) The ODS management system bans the use of CTC; CTC consumption is only allowed for some laboratory analysis and process agent uses, as permitted by Parties to the Montreal Protocol, and is subject to a quota licensing management system;

(c) Feedstock use is subject to an annual registration management system. Seven enterprises with CTC sales qualifications in the country (three are CM producers, three are dealers that buy from the three producers and one is a distillation enterprise buying CTC residue from one of the CTC producers), are subject to annual sales registration management. They are only allowed to sell CTC to enterprises holding CTC consumption quotas or with registration qualification from the MEE for feedstock use. All CTC enterprises must report relevant CTC production, sales and consumption data to the MEE;

(d) In addition to the above-mentioned monitoring system, the MEE has imposed additional control measures on enterprises generating CTC as by-product since 2019 to prevent CFC-11 illegal production. The Government of China has imposed measures requiring all CM production enterprises to install a whole-process, real-time monitoring system. Mass flow meters for CTC by-product have been installed, covering CTC measurement in *inter alia* production, storage, conversion, sales, and residual liquid. The system aims to enable online monitoring of CM enterprises; and

(e) Starting from June 2019, the MEE has dispatched supervisory working groups to all 16 CM production enterprises nationwide to carry out on-site inspections of CTC crude output, purification, residue, storage, conversion and sales and other key processes to ensure legal use. The MEE will continue to improve the system of laws and regulations and intensive supervision and law enforcement.

31. The Secretariat requested additional information *inter alia* relating to the establishment, de-bottlenecking and capacity-expansion of CM production in China; reconciliation of CTC use for conversion

to other chemicals/feedstock uses and the associated material conversion ratios; regulations for monitoring and reporting wastes that could have CTC and the method of disposal of such wastes; and emission monitoring at enterprises that produce CTC or generate CTC as a part of the production process. The World Bank indicated that those questions were beyond the scope of the CTC survey report, and would be addressed separately.

32. On variances in material conversion ratios, the World Bank informed the Secretariat that the consultant was looking into the details. The Secretariat noted that some reported material conversion ratios appeared to vary by year within the same enterprise, which would make comprehensive monitoring of CTC difficult.

33. Regarding the CTC content in chloroform, a raw material used for the production of HCFC-22, which is alternately indicated at 0.005 per cent and 1.00 per cent in the report, the World Bank indicated that the consultant would be looking further into this issue. On a question relating to whether further technology upgrades could further reduce the concentration CTC in chloroform, the World Bank mentioned that this issue needed further research and that more information was not available.

34. The Secretariat requested clarifications on purchase of CTC for conversion to other chemicals by one CM producer. The World Bank clarified that with one exception, all CM production plants exclusively use CTC produced in-house. The CM producer that also purchases CTC to augment its in-house by-production is registered both as a CTC producer and as a CTC feedstock user. Conversely, a CM producer that only converts CTC produced in-house does not need to register as a feedstock user. Irrespective of whether a CM producer is also a feedstock user, all CM producers are required to have internal conversion capacity.

35. The Secretariat noted the recommendation for environmental monitoring by the local environmental bodies inside and around CTC-related enterprises, and that when emissions exceeded the set standards, the enterprises may be required to stop production. The Secretariat considers this recommendation to be particularly useful, though its implementation may take some time. Monitoring inside and around CM production facilities could be prioritized as a means to identify, or rule out, potential significant sources of CTC emissions.

CTC emission calculation

36. On the issues relating to emission of CTC, the Secretariat noted a report published on "Continued emissions of the ozone-depleting substance carbon tetrachloride from eastern Asia", in Geophysical Research Letters in September 2018.[10] In that report, emissions of CTC from China were approximately 16 Gg/year, which is more than a factor of 20 higher than the emissions of 0.67 Gg/year estimated in the report on the production of CTC and its feedstock uses in China. On the question relating to possible explanations for this difference, the World Bank suggested that this question would be better reserved for the Meeting of the Parties, and its Scientific Assessment Panel (SAP) and Technology and Economic Assessment Panel (TEAP).

Monitoring CTC generated from PCE production using C1-C3 alkane chlorination method

37. The Secretariat requested clarification on monitoring of CTC which is produced using the C1-C3 alkane chlorination method during PCE production and fed back into the production process; regulatory controls on CTC use for PCE production through the alkane chlorination method; and monitoring of

[10] Lunt, M. F., Park, S., Li, S., Henne, S., Manning, A. J., Ganesan, A. L., et al. (2018). Continued emissions of the ozone-depleting substance carbon tetrachloride from eastern Asia. *Geophysical Research Letters, 45*. https://doi.org/10.1029/2018GL079500

enterprises that generate CTC through processes like thermal chlorination of C1-C3 alkanes under ODS monitoring and control. The World Bank reported that the consultant was looking into those details.

Observations

38. The Secretariat notes the substantial efforts undertaken by the Government of China in providing the report on the production of CTC and its feedstock uses, and the estimated emissions of CTC contained in the report. The Secretariat notes that the total emissions of CTC estimated in the report constituted only 0.5 per cent of the CTC production in 2017 in line with advanced process technology and onsite management and controls. The report also provides recommendations relating to CTC use, monitoring systems for production, conversion and feedstock uses, and emission monitoring and emission reduction for consideration by the Government of China; these interventions would be useful in improving the system of laws and regulations and intensive supervision and law enforcement.

39. Part I of document UNEP/OzL.Pro/ExCom/84/22/Add.1 describes a set of activities related to CM production and the process agent sector to be undertaken by the Government of China to monitor the sustainability of the phase-out, and presents Secretariat's comments on those activities.[11] The Executive Committee may wish to consider information contained in the present document along with the relevant information presented in the above-mentioned document.

Recommendation

40. The Executive Committee may wish:

(a) To note the report on the production of carbon tetrachloride and its feedstock uses in China (decision 75/18(b)(iii) contained in document UNEP/OzL.Pro/ExCom/84/22/Add.2;

(b) To consider whether to request the Government of China to monitor perchloroethylene plants in the context of its discussions on the report on progress in the implementation of activities listed in decision 83/41 contained in UNEP/OzL.Pro/ExCom/84/22/Add.1; and

(c) To invite the Government of China, through the World Bank, to submit an updated report on the production of carbon tetrachloride and its feedstock uses in China to the last meeting of 2021 taking into consideration the information contained in documents UNEP/OzL.Pro/ExCom/84/22/Add.1 and Add.2.

[11] UNEP/OzL.Pro/ExCom/84/22/Add.1, paragraphs 24 to 31 and 70 to 83.