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Highly chlorinated unintentionally produced persistent organic pollutants generated during the methanol-based production of chlorinated methanes: A case study in China

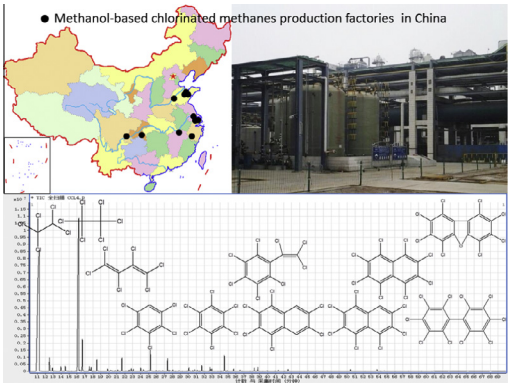
Lifei Zhang [a,*], Wenlong Yang [a], Linli Zhang [a,b], Xiaoxiu Li [b]

[a] State Environmental Protection Key Laboratory of Dioxin Pollution Control, National Research Center for Environmental Analysis and Measurement, 100029 Beijing, China
[b] College of Resource Environment and Tourism, Capital Normal University, 100048 Beijing, China

HIGHLIGHTS

- Numerous unintentionally produced POPs observed in the CCl_4 byproduct.
- Emission profiles of these hazardous substances were distinctive.
- Top three emissions were perchlorinated cyclopentadiene, butadiene, and benzenes.
- TEQ for PCNs was considerably higher than PCDDs/DFs.
- Emission factor of PCDDs/DFs was 364 μg TEQ t^{-1} product for residues.

GRAPHICAL ABSTRACT



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ABSTRACT

The formation of unintentionally produced persistent organic pollutants (POPs) may occur during various chlorination processes. In this study, emissions of unintentionally produced POPs during the methanol-based production of chlorinated methanes were investigated. High concentrations of highly chlorinated compounds such as decachlorobiphenyl, octachloronaphthalene, octachlorostyrene, hexachlorobutadiene, hexachlorocyclopentadiene, hexachlorobenzene, and pentachlorobenzene were found in the carbon tetrachloride byproduct of the methanol-based production of chlorinated methanes. The total emission amounts of hexachlorocyclopentadiene, hexachlorobutadiene, polychlorinated benzenes, polychlorinated naphthalenes, octachlorostyrene, and polychlorinated biphenyls released during the production of chlorinated methanes in China in 2010 were estimated to be 10080, 7350, 5210, 427, 212, and 167 kg, respectively. Moreover, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) were formed unintentionally during chlorinated methanes production, the emission factor for PCDDs/DFs was 364 μg toxic equivalency quotient (TEQ) t^{-1} product for residues, which should be added into the UNEP toolkit for updating. It was worth noting that a high overall toxic equivalency quotient from polychlorinated naphthalenes and PCDDs/DFs was generated from the chlorinated methanes production in China in 2010. The values reached 563 and 32.8 g TEQ, respectively. The results of the study indicate that more research and improved management systems are needed to ensure that the methanol-based production of chlorinated methanes can be achieved safely.

* Corresponding author at: No. 1 Yuhui Nanlu, Chaoyang District, Beijing 100029, China. Tel.: +86 10 84665755; fax: +86 10 84634275.
E-mail address: lfzhang@cneac.com (L. Zhang).

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1. Introduction

The unintentional production of persistent organic pollutants (POPs) occurs during many anthropogenic activities. Measures to decrease or eliminate unintentionally produced POPs are the subjects of Article 5 of the Stockholm Convention (SC). The unintentionally produced POPs of concern are the polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), hexachlorobenzene (HCB), pentachlorobenzene (PeCB), and polychlorinated biphenyls (PCBs) currently. Moreover, polychlorinated naphthalenes (PCNs) and hexachlorobutadiene (HCBD) will be listed in the SC in this year. Industrial chlorination processes are considered to be sources of unintentionally produced POPs, especially for HCB, and have generated large stockpiles and contaminated sites in Australia, Ukraine, and Czech Republic (Weber et al., 2008; Weber et al., 2011). However up to now these were always referred to HCB and HCBD (UNEP, 2012, 2013a). Emissions of unintentionally produced POPs during the production of chlorinated methanes have been investigated in few studies (Markovec and Magee, 1984).

Chlorinated methanes are important industrial chemicals and significant environmental pollutants. There are four chlorinated methanes, methyl chloride, methylene chloride, chloroform, and carbon tetrachloride, and they are used as intermediates in chemical syntheses and as industrial solvents (Leisinger and Braus-Stromeyer, 1995). Chlorinated methanes are manufactured using two different synthetic routes, shown in reactions 1 and 2a–d.

$$CH_4 + Cl_2 \rightarrow HCl + CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 \quad (1)$$

$$CH_3OH + HCl \rightarrow H_2O + CH_3Cl \quad (2a)$$

$$CH_3Cl + Cl_2 \rightarrow HCl + CH_2Cl_2 \quad (2b)$$

$$CH_2Cl_2 + Cl_2 \rightarrow HCl + CHCl_3 \quad (2c)$$

$$CHCl_3 + Cl_2 \rightarrow HCl + CCl_4 \quad (2d)$$

The second reaction (reaction 2a) is performed in one of two ways. One way is in the liquid phase at 100–150 °C under slightly increased pressure, either without a catalyst or in the presence of $ZnCl_2$ or $FeCl_3$. The other, preferred, way is in the gas phase at 300–380 °C and 3–6 bar using a catalyst (such as $ZnCl_2$, $CuCl_2$, or H_3PO_4) on a support (such as SiO_2) or using Al_2O_3 in a fixed or fluidized bed (Weissermel and Arpe, 2003). The low cost of methanol and a growing surplus of HCl produced in a number of chlorination processes have led to the second synthetic route becoming more popular than the first in China. Chlorinated methanes produced in industrial processes are separated by their different boiling points, and carbon tetrachloride and other substances with relatively high boiling points are treated as byproducts.

Recently, Nie et al. (2014) reported that the unintentional release of PCDDs and PCDFs from chemical production industry in China has been underestimated in the first National Implementation Plan (NIP) of China. They also appealed that more assessment is needed in future updates of the Chinese NIP. In the study presented here, the carbon tetrachloride byproduct was collected from a chlorinated methane production factory in China. Highly chlorinated unintentionally produced POPs (PCDDs and PCDFs, together with PCBs, HCB, PeCB, polychlorinated naphthalenes (PCNs), and other perchlorinated compounds) were determined in the carbon tetrachloride so that the emissions of these POPs from the plant could be estimated. The results of the study will be important for assessing the environmental occurrence and behavior of these unintentionally produced POPs and improving their management, since the UNEP toolkit (UNEP, 2013b) does not contain an emission factor for chlorinated methane.

2. Material and methods

The carbon tetrachloride byproduct was collected from a factory in which chlorinated methanes are produced using a methanol-based synthetic route. The factory is a representative company of chlorinated methanes industry in Shandong Province, China. Samples were collected from the high boiling component fractionator and subjected to instrumental analysis immediately without any purification or other preparation procedure. PCDDs/DFs, PCBs, polychlorinated benzenes (PCBz), PCNs, octachlorostyrene (OCS), HCBD, hexachlorocyclopentadiene, perchlorinated *p,p′*-DDE, and tetradecachloro-*o*-terphenyl were purchased from Cambridge Isotope Laboratories (Andover, MA, USA) and from AccuStandard (New Haven, CT, USA).

The samples were analyzed using a gas chromatograph (GC; Agilent 7890A; Agilent Technologies, Santa Clara, CA, USA) coupled with a triple quadrupole mass spectrometer (MS/MS; Agilent 7000B; Agilent Technologies). The GC–MS/MS was used in full scan mode with an inlet temperature of 270 °C, a split ratio of 10:1, helium carrier gas at a flow rate of 1.0 mL/min, and a DB-5MS capillary column (30 m long, 0.25 mm i.d., 0.25 μm film thickness, J&W Company, USA). The oven temperature started at 60 °C, which was held for 10 min, then increased at 5 °C/min to 300 °C, which was held for 10 min. The MS source temperature was 230 °C, electron impact ionization mode was used, the quadrupole temperature was 150 °C, and the scan range was *m*/*z* 45–550. The target compounds were determined using the GC–MS/MS equipped with a 30 m or 60 m DB-5MS capillary column and using electron impact ionization in single ion monitoring mode or multiple reaction monitoring mode. Detailed information on the target compound analysis is provided in the Supplementary data.

3. Results and discussion

3.1. Full scan analysis of the byproduct

Carbon tetrachloride, tetrachloroethylene, and other substances with relatively low boiling points may have been lost during the mass spectrometry solvent delay at the beginning of the analysis, when the mass spectrometry was set not to operate. The main peaks found in the full scan chromatograms (Fig. S1) were identified using NIST MS Search 2.0 software and a MassHunter Workstation (Agilent Technologies). The compounds found in the carbon tetrachloride byproduct (Table 1) were all chlorinated alkanes, chlorinated alkenes, and chlorinated aromatic compounds. The mass spectra of five peaks in the full scan chromatograms could not be identified using the NIST software, but it was possible to determine that these compounds were a chlorinated alkane (No. 11 in Table 1), a chlorinated alkene (No. 13 in Table 1), and three chlorinated aromatics (Nos. 15, 17, and 18 in Table 1) from their *m*/*z* patterns (Fig. S2). It is interesting to note that some polychlorinated compounds were found that were not perchlorinated, suggesting that many different chlorinated compounds are synthesized during the methanol-based production of chlorinated methanes.

As is shown in Table 1, after carbon tetrachloride, the byproduct was dominated by pentachloroethane and hexachloroethane. Certain amounts of pentachlorocyclopropane and tetrachloropropene were also detected. It is worth noting that unintentionally produced POPs, such as HCB, PeCB, and PCBs were also found in the byproduct. These findings are similar to those of Markovec and Magee (1984), who studied waste products generated during the production of carbon tetrachloride and tetrachloroethylene. Detailed quantitative results for the unintentionally produced POPs in the byproduct are given below.