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Estimates of unintentional production and emission of hexachlorobutadiene from 1992 to 2016 in China☆

Lei Wang, Pengju Bie, Jianbo Zhang*

College of Environmental Sciences and Engineering, Peking University, Beijing, 100871, China

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ABSTRACT

Although hexachlorobutadiene (HCBD) has been listed as a persistent organic pollutant (POP) under Annexes A and C of the Stockholm Convention, information about its unintentional production and emission is still very limited. We estimated the historical unintentional production and emission of HCBD during 1992–2016 in China based on aggregated activity data and emission functions. The unintentional production of HCBD increased from 60.8 (95% confidence interval, 38.2–88.5) MT/yr to 2871.5 (2234.2–3530.0) MT/yr during 1992–2016, representing an average annual growth rate of 17.4%. The main unintentional source of HCBD changed from carbon tetrachloride to trichloroethylene production during this period. We estimated that China's cumulative emissions of HCBD were 8211.3 (6131.5–10,579.5) MT during the same period. HCBD consumption and the chlorinated hydrocarbon production sector were the major contributors to total HCBD emissions. Owing to the long-range transport capability of HCBD (8784 km), such high emissions in China may cause adverse effects in other regions.

1. Introduction

Hexachlorobutadiene (HCBD or HCBu) is a halogenated aliphatic compound that is a potent toxin to biological organisms (Cristofori et al., 2013). Animal experiments have demonstrated its nephrotoxicity (Swain et al., 2011; Sadeghnia et al., 2013), hepatotoxicity (Cristofori et al., 2015), genotoxicity (Brüschweiler et al., 2010), and potential carcinogenicity (Kociba et al., 1997). In May 2015, HCBD was listed in Annex A of the Stockholm Convention without specific exemptions owing to its persistence, toxicity, bioaccumulation, and ability for long-range transport. Furthermore, HCBD is unintentionally formed and released from industrial processes and other sources, particularly the production of specific chlorinated hydrocarbons. According to US Environmental Protection Agency (EPA) figures, in 1980, annual HCBD production was estimated at 3300–6600 MT/yr (MT, Metric Tons). However, the unintentional HCBD waste by-product, generated during the production of chlorinated chemicals, was higher than the intentional production by 14,000 MT in 1982 in the US alone (UNEP, 2013). Therefore, to reduce its unintentional production and emission, in May 2017, HCBD was listed in Annex C of the Stockholm Convention as an unintentionally produced persistent organic pollutant (uPOP).

Historically, HCBD was used in industry in the production of elastomers, rubbers, heat-transfer liquids, transformers, hydraulic fluids, insecticides, herbicides, and fungicides. Worldwide production of HCBD was estimated at 10,000 MT in 1982 (UNEP, 2013). Currently, HCBD is no longer intentionally produced in the UN-ECE region (United Nations Economic Commission for Europe), including the USA and Canada. HCBD has been detected in numerous media, including air (Juang et al., 2010; Logue et al., 2011), water (Cho et al., 2014; Chen et al., 2015), soil (Tang et al., 2014; Berger and Schwarzbauer, 2016), sediment (Solé et al., 2013; Pinto et al., 2016), sewage sludge (Zhang et al., 2014), and biota (Tang et al., 2014, 2016), as well as human liver (ATSDR, 2012). In 1990, the US national emission standards that require the use of best control technologies have been developed for sources categories emitting HCBD, including rubber tire production, chlorine production, and miscellaneous organic chemical processes (UNECE, 2007). All by-product HCBD has been disposed of using high-temperature incineration or treated on site. In the US, emissions of HCBD fell from 50,000 to 1064 kg during 1975–2011, and concentrations in the environment also declined (UNEP, 2016; USA, 2016). The situation is similar to that in the UN-ECE regions (UNECE, 2007; EU, 2011).

However, monitoring data from China suggest that high levels of

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* Corresponding author.
E-mail address: jbzhang@pku.edu.cn (J. Zhang).

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emissions have continued until at least recently (Juang et al., 2010; UNEP, 2013). HCBD levels are significantly higher in China compared to other countries, especially in water and air (Table S3–S5 in Supporting Information). For example, the concentration of HCBD in typical drinking water sources from five major river basins ranged from 0.10 to 1.23 μg L^{-1}, with a median of 0.50 μg L^{-1} and a mean of 0.61 μg L^{-1} (Chen et al., 2015). The mean concentration exceeded the WHO recommends a guideline value for drinking water of 0.6 μg L^{-1} (WHO, 2004). It was much higher than concentrations observed in Japan (N.D.–0.000043 μg L^{-1}) (Japan, 2016), Spain (N.D. –0.00005 μg L^{-1}) (Santolaria et al., 2015), Korea (0.029–0.067 μg L^{-1}) (Cho et al., 2014), and Estonia (0.006–0.01 μg L^{-1}) (Estonian, 2012). Atmospheric HCBD concentrations measured in China were also high, e.g., in Zhengzhou (15.5 μg m^{-3}; Nan et al., 2014) and at background stations (0.05–4.88 μg m^{-3}) (Lv et al., 2013). In 2013, the average concentration of HCBD in the urban area of the US was only 0.09 μg m^{-1} (USEPA, 2015). These monitoring data imply that China is a major emitter of HCBD historically. The transport distance for HCBD was calculated as 8784 km using a multicompartment hemispheric transport model (Vulykh et al., 2005). The Committee of the Stockholm Convention recognized that, due to its long-range transport ability, toxicity and bioaccumulation in the environment, HCBD is likely to lead to significant adverse human health and environmental effects (UNEP, 2016). Furthermore, emissions from China could also have detrimental effects on other countries, including remote regions. However, to the best of our knowledge, no studies to date have examined the production and emission of HCBD in China.

In this study, we investigated the unintentional production, use and disposal of HCBD in China. We estimated a historical emission inventory for 1992–2016 using a bottom-up method based on data from industry. Uncertainties in the emission estimates were quantified using the Monte Carlo method.

2. Methodology

2.1. Source categories

There are no natural sources of HCBD in the environment. In addition to intentional production as mentioned earlier, HCBD is unintentionally generated mainly during the manufacture of chlorinated hydrocarbons, particularly trichloroethylene (TCE), perchloroethylene (PCE), and carbon tetrachloride (CTC). Based on information from the Stockholm Convention report on HCBD, "Information on unintentional releases of HCBD," submitted by parties to the Stockholm Convention (http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC11/POPRC11Followup/HCBDInfoRequest/tabid/4813/Default.aspx), as well as other published literature and reports, we classified the anthropogenic sources of HCBD, as shown in Table 1.

Category 1 is the confirmed HCBD sources according to the information in published literature. Category 2 is the possible sources of HCBD, which can't be identified and quantified on the basis of existing information.

For item D, there was only one literature reported HCBD emission from cement manufacturing. According to information submitted to the US Toxics Release Inventory (TRI) program, the estimated atmospheric HCBD emissions for cement manufacturing were 126.06 kg in 2011 (10.73%, a total of 1175 kg HCBD released to atmosphere), but no detailed information is given in the inventory. The mechanism and emission factor are unclear.

For item E, HCBD is a pyrolysis product of PCE at temperatures greater than 700 °C (Tirey et al., 2007). In the real environment, it's unlikely to reach the temperature when using PCE, we assumed pyrolysis of PCE is not a source of HCBD.

For item F, Lenoir et al. (2001) observed the by-product formation of organochlorine compounds including HCBD from laboratory incineration experiment involving acetylene with CuCl2 as a catalyst support, indicating the possible release of HCBD from waste incineration because acetylene is present in all incineration processes. It was also reported that HCBD releases can take place during waste incineration, and those combustion sources of HCBD are similar to those of dioxins, furans and hexachlorobenzene (Environment Canada, 2000). Therefore these substances have similar emission sources and there is a potential for emission reductions for HCBD based on the use of abatement for existing Annex C substances against emissions of HCBD. Many of those control measures already in place for (e.g.) dioxins/PCBs will also be effective at controlling HCBD release. Such measures have been in place for many years now (UNEP, 2016). It is likely that emissions of HCBD from incineration processes is low, in-depth research and enterprise investigation are essential to quantify this. According to information submitted to the US TRI program, the estimated atmospheric HCBD emissions from waste disposal were 400.0 kg, but they didn't clarify this emission is because of HCBD generated in waste disposal, or just because the waste contains HCBD. In this study, we estimated emission from waste incineration contains HCBD in "c-4. High-temperature incineration of HCBD by-product" in Fig. 1.

In this study, we focused on Category 1 sources of HCBD in China. Fig. 1 shows the Category 1 emission sources.

2.2. Activity data and emission factors

2.2.1. HCBD production sector

In China, HCBD has never been produced as the target product, only as a by-product. The by-product proportions of HCBD during different production processes are shown in Table 2.

2.2.1.1. Chlorinated hydrocarbons. We combined literature surveys and field surveys to get the annual production volumes of chlorinated hydrocarbons from 1992 to 2016 in China. The statistical caliber and boundary is the same in different literature, thus the data is comparable. We also conducted a screening and uncertainty analysis of the data; the details are described in Text Section of the Supporting Information.

Trichloroethylene (TCE). Data on the production of TCE during 1992–2000 were obtained from the *2001 China Chemical Industry Statistical Yearbook* (National Bureau of Statistics of China, 2001), and data for 2001–2005, 2008–2010, 2012–2013 were obtained from Xie (2005a), Zhang and Zhao (2010), and Yao (2013). Production levels for 2006, 2007, and 2011 which no data were available were obtained by linear extrapolation based on the above-mentioned data. We assume that the production of TCE would have increased linearly during 2014–2016 based on the trends for 2010–2013 (Yao, 2013). In China, TCE was produced solely by the acetylene method. The annual production of TCE in China is shown in Fig. S1.

Perchloroethylene (PCE). Data on the production of PCE in 1992 and 1995–2000 were obtained from the *2001 China Chemical Industry Statistical Yearbook* (National Bureau of Statistics of China, 2001). Production levels for 1993, 2002, 2004, and 2009–2013 were obtained from Li (1999), Yu et al. (2002), Xie (2005b), and the China Association of the Chlorine–Alkali Industry (2013). Production levels for years for which no data were available were obtained by linear extrapolation based on the above-mentioned data.

In China, two main processes have been used to produce PCE: the acetylene method and the carbon tetrachloride (CTC) method. Prior to 2005, only one factory used the CTC method, which