

Hexachlorobutadiene emissions from typical chemical plants

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HIGHLIGHTS

- Unintentional HCBd production in typical chemical plants was investigated.
- The highest HCBd concentrations were found in the bottom residue.
- Tri/tetrachloroethylene production processes were important HCBd sources.

ARTICLE INFO

Article history:

Received 4 June 2020

Revised 21 July 2020

Accepted 26 August 2020

Available online 11 October 2020

Keywords:

Hexachlorobutadiene

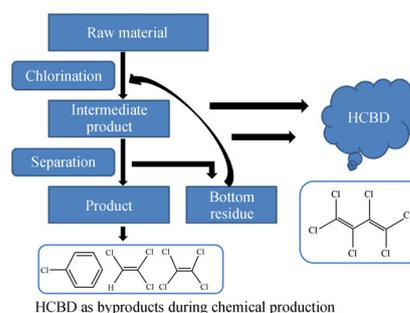
Chemical plant

Chlorobenzene

Trichloroethylene

Tetrachloroethylene

GRAPHIC ABSTRACT



ABSTRACT

Hexachlorobutadiene (HCBd) was classed as a persistent organic pollutant under the Stockholm Convention in 2015. HCBd is mainly an unintentionally produced by-product of chlorinated hydrocarbon (e.g., trichloroethylene and tetrachloroethylene) synthesis. Few studies of HCBd formation during chemical production processes have been performed, so HCBd emissions from these potentially important sources are not understood. In this study, HCBd concentrations in raw materials, intermediate products, products, and bottom residues from chemical plants producing chlorobenzene, trichloroethylene, and tetrachloroethylene were determined. The results indicated that HCBd is unintentionally produced at much higher concentrations in trichloroethylene and tetrachloroethylene plants than chlorobenzene plants. The sum of the HCBd concentrations in the samples from all of the trichloroethylene and tetrachloroethylene production stages in plant PC was 247000 µg/mL, about three orders of magnitude higher than the concentrations in the tetrachloroethylene production samples (plant PB) and about six orders of magnitude higher than the concentrations in the chlorobenzene production samples (plant PA). The HCBd concentrations were highest in bottom residues from all of the plants. The concentrations in the bottom residue samples contributed 24%–99% of the total HCBd formed in the chemical production plants. The bottom residue, being hazardous waste, could be disposed of by incineration. The HCBd concentrations were much higher in intermediate products than raw materials, indicating that HCBd formed during production of the intended chemicals. The results indicate the concentrations of HCBd unintentionally produced in typical chemical plants and will be useful in developing protocols for controlling HCBd emissions to meet the Stockholm Convention requirements.

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1 Introduction

Hexachlorobutadiene (HCBd) is persistent and toxic and can undergo long-range transport in the environment. HCBd has been added to the Stockholm Convention list of

persistent organic pollutants (UNEP, 2015, 2017). HCBd was previously manufactured for use in elastomers, fungicides, heat transfer liquids, herbicides, hydraulic fluids, pesticides, rubber, and transformers and can be unintentionally produced during the production of other chemicals (UNEP, 2013; Wang et al., 2018). HCBd is the most nephrotoxic aliphatic chlorinated hydrocarbon (Duprat and Gradiski, 1978). There are no known natural sources of HCBd in the environment (Lecloux, 2004; Kong et al., 2020). Intentional production of HCBd in

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Europe stopped in the late 1970s (Denier van der Gon et al., 2007; UNEP, 2013), and HCBd has never been sold commercially in Canada or the USA (Lecloux, 2004; Honing, 2007; UNEP, 2013). However, unintentional production as a by-product continues. Unintentional HCBd production during chlorinated chemical production in the USA reached 14000 t in 1982 (UNEP, 2013). Large amounts of HCBd are produced as a by-product of chemical production processes. HCBd is not intentionally produced in China, but there are many sources of unintentionally produced HCBd (e.g., commercial chemical production and waste incinerators) to the environment (Zhang et al., 2018a; Guo et al., 2020).

In previous studies, HCBd has been detected in many matrices, including water (Barrek et al., 2009; Cho et al., 2014; Chen et al., 2015), air (Juang et al., 2010; Logue et al., 2011), soil (Tang et al., 2014; Zhang et al., 2014; Berger and Schwarzbauer, 2016), food (Surma-Zadora and Grochowalski, 2008; Fernandes et al., 2019), leachate (Matejczyk et al., 2011), sediment (Lee et al., 2000; Solé et al., 2013; Pinto et al., 2016), biota (Tang et al., 2014, 2016), and sewage sludge (Zhang et al., 2014). HCBd emitted to the environment is now mainly unintentionally produced during chemical (e.g., chlorinated hydrocarbon, particularly trichloroethylene and tetrachloroethylene) production processes (Lecloux, 2004; USEPA, 2017; Wang et al., 2018). Cement production, magnesium production through electrolysis, organochlorine compound production, waste incineration, and other waste treatment processes are potential sources of HCBd (UNEP, 2013; Zhang et al., 2019). However, little information on unintentional HCBd production is available. Considerable amounts of persistent organic pollutants are emitted by thermal industrial plants such as chemical plants (Liu et al., 2004a, 2004b; Liu et al., 2018), steelmaking plants (Li et al., 2014), and municipal solid waste incinerators (Zhao et al., 2015; Li et al., 2016) in China each year. Such plants may also be important sources of HCBd. China is a signatory of the Stockholm Convention, and identifying primary sources of HCBd is the first step in implementing the convention. The results of the study presented here are expected to be useful reference data for developing protocols for decreasing HCBd emissions from chemical plants to support implementation of the Stockholm Convention.

2 Materials and methods

2.1 Chemical plants and sample collection

Samples from three chemical plants (labeled PA, PB, and PC) that produce chlorobenzene and vinyl chloride were analyzed for HCBd. Chlorine and benzene are the raw materials used to produce monochlorobenzene in plant PA. In the process, HCl is eliminated, then separation and distillation processes are performed to give the monochlorobenzene product. Chlorine, dichloroethane, and carbon tetrachloride are the raw materials used to produce tetrachloroethylene in plant PB. Tetrachloroethylene is isolated by performing distillation, condensation, and other processes. Trichloroethylene and tetrachloroethylene are both produced in plant PC. Acetylene and chlorine are the raw materials. Tetrachloroethane is produced in an acetylene chlorination tower and then further chlorinated to give pentachloroethane. HCl is eliminated, then multi-tower separation processes give trichloroethylene and tetrachloroethylene. Information on the plants is shown in Table 1. A total of 13 samples of raw materials, intermediate products, products, and bottom residues were collected from the plants. Information on the samples is shown in Table 2. Between 200 and 500 mL of a sample were collected in a brown glass bottle, which was wrapped in aluminum foil and stored in a self-sealing bag to avoid contamination and volatilization. The samples were stored at -18°C until analysis.

2.2 Sample analysis

The organic reagents (acetone, dichloromethane, and *n*-hexane) were of pesticide residue analysis grade and were acquired from Avantor Performance Materials (Allentown, PA, USA). Silica gel and anhydrous sodium sulfate were baked at 550°C for 6 h before use. Florisil (60–100 mesh) was baked at 550°C for 12 h before use. $^{13}\text{C}_4$ -labeled HCBd was provided by Cambridge Isotope Laboratories (Andover, MA, USA).

Few analytical methods are available for determining HCBd in chemical products. We therefore modified a standard method for determining HCBd in drinking water to characterize the chemical samples by gas chromatography. First, a sample was rotary evaporated to 100 mL,

Table 1 Raw materials, products and operating conditions of the three chemical plants

| Abbreviation of chemical plant | Main products | Raw material | Production processes | Reaction temperature ($^{\circ}\text{C}$) | Product output (kg/a) |
|--------------------------------|--|--|--|---|--|
| PA | Monochlorobenzene | Chlorine, Benzene | $\text{C}_6\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{HCl}$ | 75–79 | 4×10^7 |
| PB | Tetrachloroethylene | Chlorine, Dichloroethane, Carbon tetrachloride | $\text{C}_2\text{H}_4\text{Cl}_2 + 5\text{Cl}_2 \rightarrow 2\text{CCl}_4 + 4\text{HCl}$ $2\text{CCl}_4 \rightarrow \text{C}_2\text{Cl}_4 + 2\text{Cl}_2$ | 585–625 | 8×10^7 |
| PC | Trichloroethylene, Tetrachloroethylene | Acetylene, Chlorine | $\text{C}_2\text{H}_2 + 2\text{Cl}_2 \rightarrow \text{C}_2\text{H}_2\text{Cl}_4$ $\text{C}_2\text{H}_2\text{Cl}_4 \rightarrow \text{C}_2\text{HCl}_3 + \text{HCl}$ $\text{C}_2\text{HCl}_3 + \text{Cl}_2 \rightarrow \text{C}_2\text{HCl}_5$ $\text{C}_2\text{HCl}_5 \rightarrow \text{C}_2\text{Cl}_4 + \text{HCl}$ | 200–285 | 1.7×10^7 , 1.5×10^7 |

Table 2 Detailed information of the 13 collected samples

| Abbreviation of chemical plant | Samples | Sample name | Sample type |
|--------------------------------|---------|--|----------------|
| PA | PA1 | Mixture of benzene and chlorine liquid after HCl removal process | Raw materials |
| | PA2 | Benzene solution for recycling | Raw materials |
| | PA3 | Final monochlorobenzene product | Product |
| | PA4 | Reaction bottom residue | Bottom residue |
| PB | PB1 | Carbon tetrachloride as raw material | Raw material |
| | PB2 | Dichloroethane as raw material | Raw material |
| | PB3 | Reaction bottom residue | Bottom residue |
| | PB4 | Final tetrachloroethylene products | Product |
| PC | PC1 | Crude tetrachloroethane | Intermediate |
| | PC2 | Refined tetrachloroethane | Intermediate |
| | PC3 | Reaction bottom residue | Bottom residue |
| | PC4 | Final trichloroethylene products | Product |
| | PC5 | Final tetrachloroethylene products | Product |

then the solution was passed through a column containing silica gel and Florisil. The sample was then concentrated to 1 mL by rotary evaporation and under a gentle stream of nitrogen. The HCBd concentration in the sample was then determined using an Agilent 7890A GC/5975 MSD gas chromatograph mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). The chromatographic column was an HP-5ms (30 m long, 250 μm i.d., 0.25 μm film thickness; Agilent Technologies). A high concentration (1 $\mu\text{g}/\text{mL}$) standard solution was analyzed using the gas chromatograph mass spectrometer in full scan mode. The standard spectrum was used to identify appropriate quantitation and confirmation ions.

2.3 Quality assurance and control

A HCBd standard was used to identify and quantify HCBd in the samples. A 1 $\mu\text{g}/\text{mL}$ HCBd standard in *n*-hexane was prepared and treated in the same way and at the same time as the samples. The HCBd recovery was 91.9%, which met the HCBd analysis requirements. A laboratory blank (*n*-hexane) was analyzed with each batch of samples following the same preparation procedure. HCBd was not detected in the blanks. The method detection limit was defined as the concentration giving a signal-to-noise ratio of 3. The HCBd concentrations in all the samples were at least three times higher than the detection limit.

3 Results and discussion

3.1 HCBd concentrations in samples from the different chemical plants

The HCBd concentrations in samples collected from the chemical production plants are shown in Fig. 1. The

highest HCBd concentrations were found in the samples from chemical plant PC (which produced trichloroethylene and tetrachloroethylene from acetylene and chlorine). The HCBd concentrations in the PC crude tetrachloroethane (PC1), refined tetrachloroethane (PC2), bottom residue (PC3), trichloroethylene (PC4), and tetrachloroethylene (PC5) samples were 2200, 2500, 243000, 0.076, and 0.071 $\mu\text{g}/\text{mL}$, respectively. The HCBd concentrations in the plant PA (which produced monochlorobenzene from benzene and chlorine) benzene and chlorine mixture after HCl removal (PA1), benzene solution for recycling (PA2), monochlorobenzene (PA3), and bottom residue (PA4) samples were 0.002, 0.0004, 0.023, and 0.008 $\mu\text{g}/\text{mL}$, respectively. The HCBd concentrations in the plant PB (which produced tetrachloroethylene from dichloroethane, carbon tetrachloride, and chlorine) carbon tetrachloride (PB1), dichloroethane (PB2), bottom residue (PB3), and tetrachloroethylene (PB4) samples were 0.003, 0.006, 506, and 0.396 $\mu\text{g}/\text{mL}$, respectively. Much more HCBd was produced during trichloroethylene and tetrachloroethylene production than during chlorobenzene production. Processes involved in the production of chemicals such as carbon tetrachloride, chloromethane, hexachlorocyclopentadiene, tetrachloroethylene, and trichloroethylene have previously been found to be important sources of HCBd (Zhang et al., 2019).

3.2 HCBd concentrations during different processes

The HCBd concentrations in the samples from the different stages of the chemical plants are shown in Fig. 1. The HCBd concentrations in the benzene and chlorine mixture after HCl removal (PA1) and the reaction bottom residue after rectification (PA4) collected from plant PA were comparable, but the concentration in the final monochlorobenzene product (PA3) was highest.

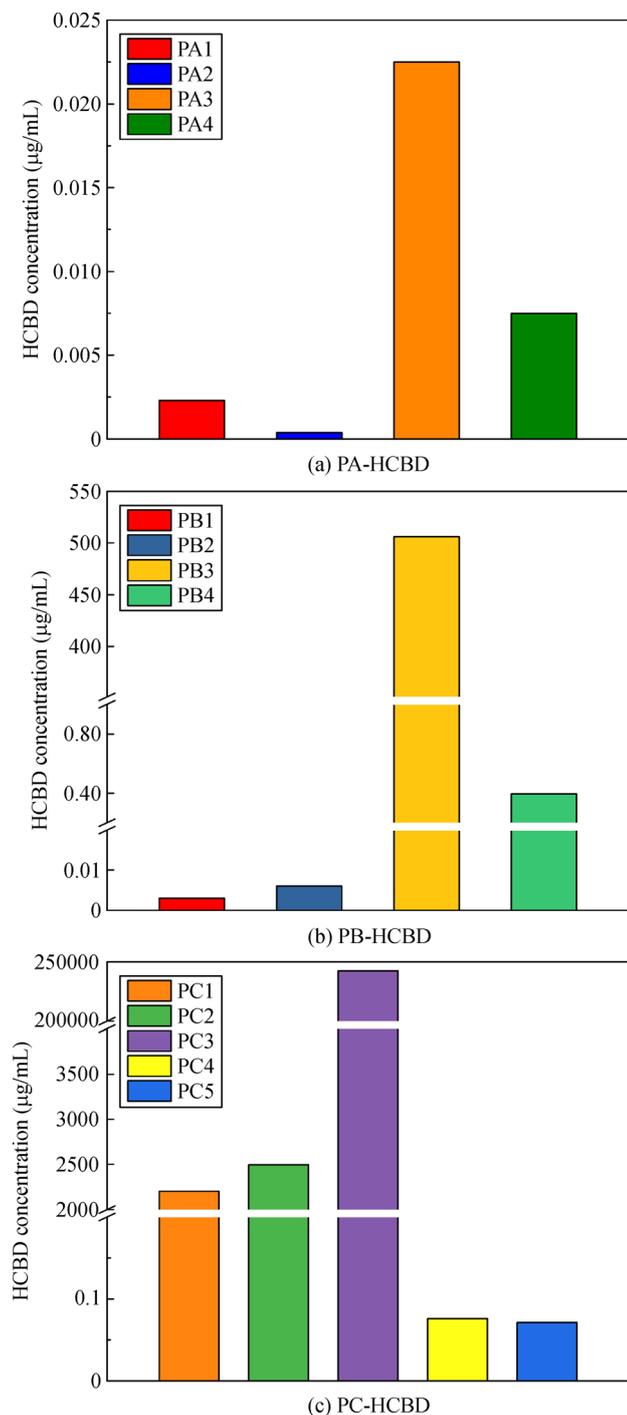


Fig. 1 Hexachlorobutadiene (HCBd) concentrations in the (a) plant PA samples, (b) plant PB samples, and (c) plant PC samples.

Monochlorobenzene is used as a raw material for producing some pesticides (Hu et al., 2020). About 40000 t of monochlorobenzene are produced by plant PA each year, so 0.8 t of HCBd could be transferred to pesticides produced from monochlorobenzene. The emission factor could also be used to assess HCBd concentra-

tions in other monochlorobenzene production plants.

The HCBd concentrations in the samples from different stages of plant PB, which produced tetrachloroethylene from carbon tetrachloride, were different, as shown in Fig. 1(b). The HCBd concentration in the bottom residue was markedly higher than the concentrations in the other samples and three orders of magnitude higher than the concentration in the tetrachloroethylene product. As shown in Fig. 1(c), the highest HCBd concentrations were found in the chlorination process samples (PC1 and PC2) and the bottom residue.

The highest HCBd concentrations for all three plants were found in the bottom residue samples (see Fig. 2). The next highest concentrations were found in the intermediate products (PC1 and PC2) and products (PA3, PB4, PC4, and PC5). The lowest concentrations were found in the raw materials (PA1, PA2, PB1, and PB2). These results indicated that HCBd was produced during the chemical production processes.

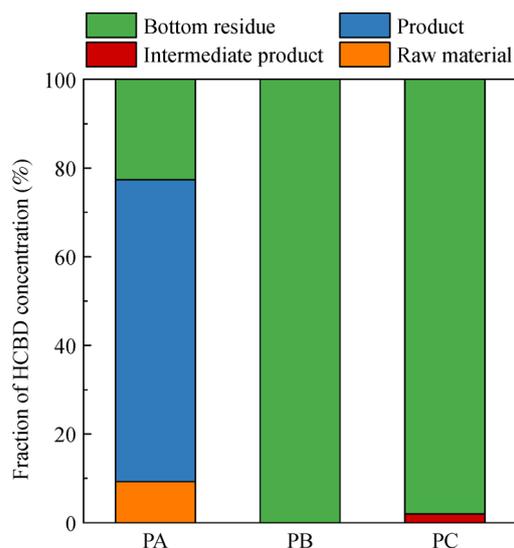


Fig. 2 Concentration fraction of HCBd found in the samples from the different stages of each chemical plant.

3.3 Factors affecting HCBd occurrence during the chemical production processes

The mechanisms involved in the formation of HCBd and polychlorinated dibenzo-*p*-dioxins and dibenzofurans during chemical production processes are similar. Cyclopentadienyl and phenyl formed through C–H bond rupture in benzene can be oxidized and chlorinated to give 1,3-butadienyl radicals and chlorophenoxy species, which can form HCBd and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (Zhang et al., 2018b; Zhang et al., 2019). This pathway could have led to HCBd formation from benzene in plant PA.

Bottom residue is a heavy residue remaining after distillation of the final product. The dominant components of the bottom residue samples were the target products. HCBd was an important by-product that was also found in the bottom residue samples. The bottom residue samples contained higher HCBd concentrations than the samples from the other processes, so the HCBd concentrations in the bottom residue samples from plants PB and PC were compared. The HCBd concentration in the bottom residue from plant PC (which produced tetrachloroethylene and trichloroethylene) was about three orders of magnitude higher than the HCBd concentration in the bottom residue from plant PB (which produced tetrachloroethylene). There are three possible reasons for this.

1) When carbon tetrachloride is used to produce tetrachloroethylene in plant PB, a C–Cl bond in tetrachloroethylene could break to give a trichlorovinyl radical that could react with another tetrachloroethylene molecule to give HCBd (Tirey et al., 1990). When acetylene is used to produce trichloroethylene and tetrachloroethylene in plant PC, acetylene could be converted into dichloroacetylene via chlorination or elimination of HCl. Dimerization of dichloroacetylene in the presence of a metal catalyst could give a metallacyclic intermediate. Chlorinated metallacyclopentadiene could be converted into HCBd via oxidative chlorination with CuCl_2 at 150–400°C (Wehrmeier et al., 1998). Acetylene is used as a raw material to produce tetrachloroethylene and trichloroethylene in plant PC, and HCBd could easily be produced in that plant. This would explain the high HCBd concentrations in the plant PB and PC bottom residues.

2) The formation of HCBd may require large amounts of Cl_2 . Plant PC (which uses a chlorine: acetylene ratio of 2:1) uses twice as much Cl_2 as plant PB (which uses a chlorine: dichloroethane: carbon tetrachloride ratio of 1:1:0.7), which could explain the HCBd concentrations being higher in the plant PC samples than the plant PB samples.

3) The optimum temperature range for polychlorinated dibenzo-*p*-dioxin and dibenzofuran formation is 250°C–400°C (Addink and Olie, 1995; Chang and Huang, 2000; Huang and Buekens, 2001). The temperature ranges in which HCBd can form from CCl_4 and acetylene are 750°C–900°C and 150°C–400°C, respectively (Tirey et al., 1990; Wehrmeier et al., 1998; Sherry et al., 2018; Zhang et al., 2018b). The plant PB processes using CCl_4 as a raw material are performed at 585°C–625°C, i.e., lower than the temperature at which HCBd would form. The plant PC processes are performed at 200°C–285°C, i.e., within the temperature range at which HCBd will form from acetylene. Therefore, the temperatures used to produce tetrachloroethylene caused larger amounts of HCBd to form during the plant PC processes than during the plant PB processes.

4 Conclusions

The HCBd concentrations in 13 samples from chlorinated hydrocarbon production plants were determined. The HCBd concentrations for each plant decreased in the order bottom residue > intermediate product > product > raw material. For the plants producing trichloroethylene and/or tetrachloroethylene, the HCBd concentrations were highest in the bottom residue samples. The HCBd concentrations in the PC and PB bottom residue samples were 243000 and 506 $\mu\text{g/mL}$, respectively. The results indicated that larger amounts of HCBd may be formed in trichloroethylene and tetrachloroethylene plants than chlorobenzene plants. HCBd is more likely to be produced during chlorination processes than separation processes. These results will help identify the sources of HCBd in chemical production plants and will be useful in developing protocols for effectively controlling and decreasing HCBd emissions from chemical plants.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant Nos. 21936007 and 21906165), the CAS Interdisciplinary Innovation Team (Grant No. JCTD-2019-03), and the Youth Innovation Promotion Association of the Chinese Academy of Sciences (Grant No. 2016038).

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