Levels and Distributions of Hexachlorobutadiene and Three Chlorobenzenes in Biosolids from Wastewater Treatment Plants and in Soils within and Surrounding a Chemical Plant in China

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S Supporting Information

ABSTRACT: Although hexachlorobutadiene (HCBD) was recently proposed as a candidate persistent organic pollutant (POP) under the Stockholm Convention, information about its environmental levels and distributions is still very limited. In this work, HCBD was determined in the sewage sludge from 37 wastewater treatment plants (WWTPs) in 23 cities and 17 soils near a chemical plant in China. Three chlorobenzenes (CBs) (1,2,4-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, and hexachlorobenzene) were simultaneously studied to help better understand the environmental behavior of HCBD. Concentrations of HCBD in sludge samples ranged from <0.03 to 74.3 ng/g dry weight (dw) with a median value of 0.30 ng/g dw, which was lower than those of the three CBs. Levels of HCBD were not correlated with capacity of the WWTPs and total organic carbon. For soils, high level of HCBD was found in the sample within the plant, with a rapid decreasing concentration trend with the increase of distance from the plant. It was suspected that releasing as a byproduct during manufacturing of chlorinated chemicals was the primary source of HCBD in the studied location. Further risk assessment indicated that the environmental risk of HCBD to soil organisms and the health risk to employees were very low through soil exposure within the plant.

INTRODUCTION

Hexachlorobutadiene (HCBD), a man-made chlorohydrocarbon, has been listed as a candidate persistent organic pollutant (POP) by the Stockholm Convention in 2011 for its persistence, toxicity, bioaccumulation, and potential long-range transport abilities.¹ It was used as an agricultural fumigant, intermediate in rubber, chlorofluorocarbons and lubricants, hydraulic, heat transfer or transformer liquid, laboratory reagents, as well as wash liquid for removing some hydrocarbons.^{2–4} HCBD has been detected in various samples such as biota,^{5–8} food,^{9–11} water,^{12,13} leachate,¹⁴ sediment,¹⁵ air,¹⁶ and sewage sludge.^{17–19} To our knowledge, HCBD is not intentionally produced in large commercial quantities in China but may be unintentionally produced. Thus, investigations on the local or regional contamination and distributions of HCBD in China are urgently needed.

It had been estimated that approximately 72% of HCBD in influent was prone to accumulate on sludge from wastewater treatment plants (WWTPs).²⁰ Therefore, concentrations of HCBD in sewage sludge can give an important indication on the pollution status at a local/regional basis. Meanwhile, HCBD in sewage sludge can be released to the environment through landfill, incineration and application on land, making WWTPs a possible secondary source of HCBD.² Thus, in order to investigate and control HCBD emission from WWTPs,

quantification of HCBD is an important first step. Soil also plays an important role as a reservoir or sink for HCBD.³ HCBD was also found to be toxic to vine, soil microflora, and earthworms.^{21,22} Soil samples from different industrial plants throughout the United States were found to have detectable levels of HCBD, and the concentrations were found to be associated with the types of production among the plants.²³ However, researches on HCBD contamination from soils are still very limited, and the environmental behavior and exposure risk assessment of HCBD in soils within and surrounding point sources are not well-known.

In this study, HCBD in 37 sludge samples from WWTPs and 17 soil samples within and around a chloro-chemical plant in China were analyzed to investigate the contamination levels and geographic distributions and to estimate the effects of point source and the potential environmental risk. Hexachlorobenzene (HCB), one of the 12 initial POPs under the Stockholm Convention²⁴ and a benchmark substance in the multicompartiment POP transport model (MSCE-POP) to evaluate long-range transport potential and persistence of HCBD,²⁵ and two

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Figure 1. Levels and distributions of HCB, 1,2,4-TCB, 1,2,4,5-TeCB, and HCB in sewage sludge samples from Chinese WWTPs.

other chlorobenzenes (CBs) (1,2,4-trichlorobenzene (1,2,4-TCB), 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB)) were simultaneously studied, which could be helpful to better understand the environmental behavior and fate of HCB.

EXPERIMENTAL SECTION

Sampling Sites and Sample Collection. A total of 37 sewage sludge samples were collected from different WWTPs in China during the period of October 2010 to March 2011. The sampling sites covered 23 cities in 13 Chinese provinces (Figure 1). Basic information of the WWTPs in regard to treatment capacity, serving population, sewage sources (domestic, industrial, or combined), and type of treatment techniques as well as total organic carbon (TOC) of the samples²⁶ are given in the Table S1 in the Supporting Information. All sludge samples were freeze-dried and homogenized, then stored in a fridge at -20°C until analysis.

The selected chemical plant in the Jiangsu province is one of the largest manufacturers of chlor-alkali, chemical intermediates

(such as phenyl isocyanate, hexachlorocyclopentadiene and o-toluidine), flame retardant and pesticides in China. As shown in Figure 2, 17 surface soil samples within and surrounding the plant were collected at September 2011 and March 2012. Distances of the sites to the plant and TOC of the samples are listed in Table S2, Supporting Information. All soil samples were air-dried under room temperature, then store in a fridge at -20°C until analysis.

Chemicals. All reagents (dichloromethane, hexane, petroleum ether ($30-60^{\circ}\text{C}$) were HPLC-grade and supplied by J.T. Baker (Philipsburg, U.S.A.). Silica gel (0.063–0.100 mm) was obtained from Merck KGaA (Darmstadt, Germany), and Florisil (60–100 mesh) was purchased from SUPELCO Company (Sigma, U.S.A.). Analytical grade sulfuric acid, copper powder (100 mesh), and anhydrous sodium sulfate were purchased from Sinopharm Chemical Reagent (Beijing, China). Prior to use, Florisil was activated at 140°C for 7 h and 5% water-deactivated; silica gel and sodium sulfate were heated

Figure 2. Levels and distributions of HCBd, 1,2,4-TCB, 1,2,4,5-TeCB, and HCB in soils within and surrounding the chemical plant in Jiangsu province in China.

at 600 °C for 6 h. Copper was activated with hydrochloric acid (10%, v/v).

The standard solution of chlorinated hydrocarbons mix (concentration: 2000 µg/mL each in hexane, containing 1,2,4-TCB, HCB, HCBd, and 1,2,4,5-TeCB) and phenanthrene- d_{10} (as the injection standard for quantification) were purchased from SUPELCO company.

Sample Pretreatment. A rapid sample pretreatment procedure was developed for the analysis of HCBd, 1,2,4-TCB, 1,2,4,5-TeCB, and HCB in sewage sludge and soil samples. Approximately 0.5 g dry weight (dw) of sewage sludge or 1.0–2.0 g dw of soil sample was mixed with 10 g anhydrous sodium sulfate, then extracted with mixture solvent of dichloromethane/hexane (1:1, v/v) (flush volume 60%) at 100 °C and 1500 psi in two static extraction cycles (10 min) using an accelerated solvent extractor (ASE 350, Dionex, Canada). After extraction, the extract was concentrated to about 2 mL by rotary evaporation and then subjected to cleanup using a multilayer silica-Florisil composite column (column inner diameter 15 mm). For sewage sludge, the column was filled with 6 g of Florisil, 1 g of activated silica gel, 4 g of acid silica gel (30%, w/w), 1 g of activated silica, 5 g of anhydrous sodium sulfate, and 1 g of activated copper powder from bottom to top. For soils, the column was filled with 6 g of Florisil, 4 g of activated silica gel, 5 g of anhydrous sodium sulfate, and 1 g of activated copper powder from bottom to top. The columns were precleaned with 50 mL hexane and then eluted with 150 mL petroleum ether after sample loading. The eluate was concentrated to 50 µL by rotary evaporation and gentle nitrogen gas stream. After spiking with 2 ng of phenanthrene- d_{10} , 2 µL of the final extract was injected into the instrument for quantification analysis.

Instrumental Analysis. Instrumental determination was carried out by a gas chromatograph coupled with a mass spectrometer in electron ionization mode (GC/MS QP2010, Japan) using selected ion monitoring (SIM). Chromatographic separation was achieved using a HP-5MS fused silica capillary column (30 m × 0.25 mm, 0.25 µm film thickness, Agilent,

U.S.A.) with constant flow rate of 1.0 mL/min. The operating conditions for GC were as follows: oven temperature program was initiated at 50 °C (held for 1 min), linearly increased to 100 °C (10 °C/min), and increased to 103 °C at 1 °C/min, then further increased to 230 °C at 10 °C/min (held for 1 min), finally ramped to 280 °C at 20 °C/min and held for 5 min. The analytes were identified by comparing the extracted ion chromatogram with those of standards. The ions of analytes selected for quantification and identification are shown in Table S3, Supporting Information, which were in conformity with those of a former study.¹⁵

RESULTS AND DISCUSSION

Quality Assurance and Quality Control (QA/QC). Strict quality assurance and control measures were executed to ensure accurate identification and quantification. Chromatograms of the analytes in standard solution, sewage sludge and soil samples are shown in Figure S1, Supporting Information. All the target compounds were baseline separated.

Procedural blanks (extraction of anhydrous sodium sulfate following the procedure described above) were performed for every batch of samples. For HCBd, no analyte was found in blanks, and a signal-to-noise ratio of 3:1 was used to calculate the method limit of detection (MDL). The three CBs in the blanks were found in the range 0.07–0.90 ng and the reported results were all blank corrected. MDLs for the three CBs were defined as three times the standard deviations of five procedural blanks. MDLs of the four compounds were 0.01–0.22 ng/g dw for sludge and soil samples. The analytes in samples were nondetectable when the results were less than the MDLs.

The method linear dynamic range (correlation coefficients (R^2) ≥ 0.998) was 0.025–50 ng for HCBd, 1,2,4-TCB, and 1,2,4,5-TeCB and 0.10–150 ng for HCB. The sludge from a WWTP in Hubei (No. A27 in Table S1, Supporting Information) and soil sample around the plant (site B16 in Figure 2) were spiked with standards to determine the method recoveries. Under optimal conditions, the spiking recoveries of the four compounds were acceptable, ranging from 51.3 to

Table 1. Comparison of HCBd and HCB Concentrations with Other Reports (ng/g dw)

location	n	HCBd		HCB		sample type, collected time	ref
		range	mean	range	mean		
China	37	<0.03–74.3	3.12	<0.08–283	22.5	sludge, 2010–2011	this work
China	17	0.04–27.9	2.22	0.10–47.1	7.57	soil, 2010–2011	this work
China	11	<0.14–114	38.8	9–3200	587	sludge, 1998–1999	Cai et al. (2007) ¹⁷
China	31			7.5–318	145	sludge, 2005	Wang et al. (2007) ²⁹
USA		520–8000	4300			sludge	Naylor et al. (1982) ¹⁸
USA		0.1–3740	36			sludge	Jacobs et al. (1987) ¹⁹
USA	4	6.4×10^3 – 9.8×10^5				soil ^a	U.S. EPA (1976) ²³
USA	5	<0.1–9				soil ^b	U.S. EPA (1976) ²³
U.K.	14			6.4–260	42	sludge	Stevens et al. (2003) ²⁷
Korea	6			1.3–21.5	7.7	sludge	Ju et al. (2009) ²⁸
China	5			0.90–11.79	5.44	farm soil	Song et al. (2012) ³⁴
World	191			0.01–5.20	0.68	background soil, 1998	Meijer et al. (2003) ³⁵

^aSoil samples within the plants were collected from the plants mainly producing perchloroethylene and trichloroethylene. ^bSoil samples within the plants were collected from the plants mainly producing chlorine, carbon tetrachloride and triazine herbicides.

117% for sewage sludge and from 55.0 to 119% for soil (Table S4, Supporting Information). The relative standard deviation ($n = 3$) at the spiking levels of 0.5 ng and 5 ng was less than 15% for all analytes. The results indicated that the developed methods were satisfactory for analyzing four target compounds in sewage sludge and soil.

Levels and Distributions in Sewage Sludge. The levels and distributions of HCBd and three CBs in 37 sewage sludge samples are given in Figure 1. The four compounds were detected in most of the sludge samples and their median concentrations were in the following order: HCB (9.64 ng/g dw) > 1,2,4-TCB (1.78 ng/g dw) > 1,2,4,5-TeCB (0.68 ng/g dw) > HCBd (0.30 ng/g dw). The results indicated that HCB was the predominant contaminant and HCBd was found at the lowest level among the targeted compounds.

The detection frequency of HCBd in sludge samples was 76%, and the detectable concentrations ranged from 0.05 to 74.3 ng/g dw with a median value of 0.64 ng/g dw, implying that contamination of HCBd is generally at very low levels in most of studied cities in China. The highest concentration of HCBd was found in the sludge from a WWTP located in Shanghai, which was followed by two samples from Ningbo city in Zhejiang province with concentrations of 7.41 and 10.7 ng/g dw, respectively. A previous study¹⁷ detected HCBd in 11 sludge samples from Chinese WWTPs which were collected during the period from 1998 to 1999. Comparing the concentrations of HCBd in sludge samples from WWTPs located in the same areas such as Xi'an, Lanzhou and Beijing, the values in the previous study (28–112 ng/g dw) were significantly higher than those (<0.03–0.45 ng/g dw) in this work. This could suggest a considerable decrease of HCBd levels in the environment in the past ten years. A similar trend was also found in two early investigations from U.S.A. (Table 1).^{18,19} Spatial distributions of concentrations of HCBd in sewage sludge (Figure 1) showed that samples from WWTPs located in coastal areas with more developed industries such as Shandong, Shanghai, and Zhejiang had higher HCBd concentrations than those from inland areas such as Hubei, Henan, and Shaanxi. This result implied a potential link of levels of HCBd in the environment with the regional economic activities. Correlation analysis between levels of HCBd in sewage sludge and other potential influencing factors such as properties of WWTPs was performed using linear regression analysis. As shown in Table S5, Supporting Information, no

obvious relationships among concentrations of HCBd and the three CBs or with the TOC of sludge were found. The relationships between levels of HCBd and treatment capacity, serving population of WWTPs were also not significant.

Concentrations of 1,2,4-TCB and 1,2,4,5-TeCB were in the range <0.22–26.0 ng/g dw and 0.07–9.25 ng/g dw with detection ratios of 76% and 100%, respectively. Relatively high levels of 1,2,4-TCB were found in sludge samples from Beijing and Shandong while high levels of 1,2,4,5-TeCB were found in the samples from Zhejiang, Shandong, Henan, and Anhui (Figure 1).

HCB was almost detectable in all sludge samples (37/38) which ranged from 3.58 to 283 ng/g dw with a median value of 9.70 ng/g dw. As shown in Table 1, the levels of HCB in the sludge samples were comparable with those in sludge samples from the U.K.²⁷ and slightly higher than those in sludge samples from Korea.²⁸ In the previous work by Cai et al.,¹⁷ concentrations of HCB in the sludge samples collected in 1998–1999 were in the range 9–3200 ng/g dw with a mean value of 587 ng/g dw. The concentrations in sludge samples collected in 2005 decreased to the range 7.5–318 ng/g dw with a mean value of 145 ng/g dw.²⁹ Levels of HCB in the present work were significantly lower than that in those two previous works, suggesting that HCB contamination has continually decreased since the late 1990s. This may due to the fact that usage and production of HCB as pesticides has been banned by the Chinese government as a part of China's National Implementation Plan for Stockholm Convention since 2000.³⁰ However, HCB was still the predominant compound in most of sludge samples and accounted for 70 to 100% of the total of three CBs. This may be attributed to (1) HCB is still produced and used as an intermediate for PCP production in China under the exemption in Stockholm Convention. (2) HCB may be unintentional produced as a byproduct from several processes, such as in the production of chlorinated solvents and wood preservative.³¹ Different from HCBd, no obvious spatial variation was found between coastal cities and inland areas (Figure 1).

Risk Assessment of Sludge for Land Application.

Humans may be exposed to the pollutants in sewage sludge through intake of plants grown on biosolids-amended soil and livestock that are kept on forage grown on biosolids-amended soil.³² According to the risk assessment process from United States Environmental Protection Agency (Part 503 biosolids

rule),³² the limits of HCB and HCB in biosolids causing unacceptable environmental and health effects were 6.0×10^5 and 2.9×10^4 ng/g dw for land application. Levels of HCB (<0.03 – 74.3 ng/g dw) and HCB (<0.08 – 283 ng/g dw) in sludge samples in this work were much lower than those set by Part 503, indicating that the presence of HCB and HCB in the biosolids are relatively safe for animals and human if they were applied to soils.

Levels, Distributions, and Potential Risks in Soils within and Surrounding the Plant. The concentration distributions of HCB, 1,2,4-TCB, 1,2,4,5-TeCB, and HCB in soils within and around the chemical plant are shown in Figure 2. High concentrations of HCB (27.9 ng/g dw), 1,2,4-TCB (18.1 ng/g dw), 1,2,4,5-TeCB (49.6 ng/g dw), and HCB (44.1 ng/g dw) were found in the soil within the plant, which were most likely due to unintentional production as byproducts during the manufacturing of chlorinated hydrocarbons and other chlorinated chemicals. Rapid decreasing concentrations in soils were observed with the increasing distance from the plant, indicating that the manufacturing plant is the primary source of these contaminants in this location.

The highest concentration of HCB found in the sample within the plant was slightly higher than those detected in soils (<0.1 – 9 ng/g) from plants producing chlorine, carbon tetrachloride, and triazine herbicides, while much lower than those in soils (6.4×10^3 to 9.8×10^5 ng/g) from plants producing perchloroethylene and trichloroethylene (Table 1).²³ The concentrations in soil samples around the chemical plant were very low, ranging from 0.04 to 3.33 ng/g dw with a median concentration of 0.23 ng/g dw. During production, HCB might be formed as a byproduct and then released to the soil compartment through atmospheric deposition and disposal of waste containing HCB. A study³³ reported that only about 1% of HCB would likely enter into the soil medium through air–soil interface. Besides, HCB has low mobility in soils due to its high log K_{ow} .¹² These might be the reasons why the concentrations of HCB at the sampling sites 1 km away from the plant were very low and about 100 times lower than that in the soil within the plant. Correlation analysis was also carried out to examine the factors that might affect the HCB concentrations in soils. As shown in Table S6, Supporting Information, correlation coefficients among concentrations of HCB and the three CBs in soils within and surrounding the plant varied from 0.622 to 0.993 ($p < 0.01$). Their significant linear relationships indicated that they may have similar environmental behavior from the point source to the surrounding areas. No obvious relationship was found between levels of HCB and TOC in soils, whereas significant relationship was found between concentrations of HCB and TOC.

HCB could be detected in all soil samples around the plant with a mean value of 5.29 ng/g dw, which were comparable with that (5.44 ng/g dw) in farm soils near another chemical plant producing CBs and pesticide in China³⁴ while much higher than that (0.68 ng/g dw) in global background surface soils.³⁵ The distribution of HCB was somewhat different from those of other three analytes. High concentrations of HCB were not only detected in the soil within the plant but also in samples from site B5 and B13 (22.1 and 47.1 ng/g dw). Therefore, it was suspected that besides the manufacturing plant, there could also be other unknown sources responsible for the high concentrations in soils in these sites.

HCB is toxic, persistent, and has a tendency to be accumulative in soil.^{21,22,36} Therefore, the ecological risk of HCB to the sampling areas was further evaluated numerically using the Hazard Quotient (HQ) approach. HQ can be calculated as dose or EEC divided by screening benchmark, where dose is an estimated amount of contaminant taken by plant, animal or human, EEC is estimated environmental contaminant concentration at the site and screening benchmark is a no-adverse effect level.³⁷ In general, HQ values < 1 indicate that the likelihood of an adverse effect is very low and if the HQ value > 1 , harmful effects cannot be ruled out. The lowest half maximal lethal concentration (LC_{50}) could be used to calculate the predicted no effect concentration (PNEC).^{38,39} However, limited information on the toxicity of HCB to soil organisms was found. We therefore use the LC_{50} data (214 mg/kg for earthworm for 14 days) predicted by EPI Suite Version 4.1 for calculation. HQs of HCB in soil samples within and around the plant were all less than 1 (Table S7, Supporting Information), indicating HCB in these soils are considered to pose no immediate risk. The lack of the toxicity data of HCB in soil increased the uncertainty in this assessment.

Human may also be exposed to the pollutants in soil. The risk of HCB in the soil within the plant to employees was assessed since relatively high concentration was found there. The hazard quotient risk calculation tool⁴⁰ was used to calculate Hq (HQ for one pathway) for accidental soil ingestion, inhalation of contaminated particles or dermal contact with contaminated soil. If the calculated Hq for any pathway is greater than 0.2, health risk to human might exist. The details and results are shown in Table S8, Supporting Information. All HQs were less than 0.2, implying very low adverse effects of HCB in soil to workers in the plant.

■ ASSOCIATED CONTENT

§ Supporting Information

Information of sludge and soil samples, methods, correlation analysis, and hazard quotient for ecological risk assessment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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