Formation and contamination of PCDD/Fs, PCBs, PeCBz, HxCBz and polychlorophenols in the production of 2,4-D products

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HIGHLIGHTS

- PCDD/Fs, PCBs, HxCBz, PeCBz and polychlorophenols in 2,4-D were analyzed.
- Relationship between the precursors and UPPOPs was discussed.
- Emissions of PCDD/Fs and dl-PCBs in China were evaluated.
- A suggestion on 2,4-D production was developed to reduce UPPOPs emission.

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ABSTRACT

The concentrations and profiles of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), pentachlorobenzene (PeCBz), hexachlorobenzene (HxCBz) and polychlorophenols in 2,4-D were investigated in this study. Two 2,4-D acid and three 2,4-D butyl ester enterprises were selected as typical 2,4-D producers. The total concentrations of 2,3,7,8-PCDD/Fs in the 2,4-D samples ranged from 355 to 35080 ng kg⁻¹ and the corresponding TEQ values were in the range of 13.4 and 694.6 ng WHO-TEQ kg⁻¹. The concentrations of total PCBs in the 2,4-D were in the range of 16.1 and 8023 ng kg⁻¹, and the WHO-TEQ values of the PCBs were between 0.057 and 108.3 ng WHO-TEQ kg⁻¹, while total PCBs were between 1486 and 47342 ng kg⁻¹. The average emission factors were 414.4 μg WHO-TEQ t⁻¹ for PCDD/Fs and 21.9 μg WHO-TEQ t⁻¹ for PCBs. The polychlorobenzenes and polychlorophenols impurities may play a key role in the PCBs and PCDD/Fs formation. The impurities of PCDD/Fs and PCBs in 2,4-D may increase the risk for the human and environmental health.

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are recognized as toxicologically significant environmental contaminants (Chang et al., 2011; Du et al., 2011) and classed as unintentional persistent organic pollutants (UPPOPs) and subject to the Stockholm Convention on POPs. Exposure to these POPs is a matter of great concern because of their toxicity, which is known to induce hormone-dependent cancers and undesirable reproductive effects in humans and wildlife. POPs are difficult to degrade and can be easily accumulated and magnified in organisms, making POPs considerably harmful to humans and the environment (Nie et al., 2012). PCDD/Fs and PCBs are released as impurities during several chemical production processes, such as polychlorophenols, polychlorobenzenes, and organic chlorinated pesticides, which also

represent the important sources of PCDD/Fs and PCBs in China (Ni et al., 2005; Liu et al., 2012).

2,4-D (including 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenoxyacetic acid butyl ester, etc.) is a series of systemic herbicide widely used in broad-leaved weeds, including rice, wheat and forage grass and one of the world's most common varieties of herbicide because of its general consumption and low cost. Low concentrations of 2,4-D are used as plant growth regulators to induce callus formation. The production and consumption of 2,4-D has grown rapidly in recent years, and in 2010, the production of 2,4-D reached 40000 tons in China.

Accidental or occupational exposure of livestock and man to 2,4-D and its derivatives may occur, although the concentrations exceeding 300 mg kg⁻¹ in the livestock, and 67 mg kg⁻¹ in man are usually required to produce clinical manifestations of toxicity (Lee et al., 2001). Furthermore, the impurities of PCDD/Fs and PCBs in 2,4-D products may exert influence on human health and the environment. There is, however, only limited data regarding PCDD/Fs and PCBs in the production of 2,4-D products, and no data relating to PCBs in Chinese 2,4-D products has been reported. The

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purpose of this study, therefore, is to identify and quantify PCDD/Fs and PCBs in the 2,4-D products and to disclose the formation pathway of these impurities in the 2,4-D production. This study is expected to be helpful in controlling the release of PCDD/Fs and PCBs in the 2,4-D production and reducing the amount of unintentional POPs pollution from the production of 2,4-D and related chlorinated products.

2. Experimental section

2.1. Sample collection

Two production processes are commonly used for the preparation of 2,4-dichlorophenoxy acetic acid (hereafter 2,4-D acid). In the first process the phenol is condensed with acetic acid forming phenoxyacetic acid and subsequently chlorinated to produce 2,4-D acid (Fig. 1), while in the second process phenol is chlorinated to 2,4-dichlorophenol and subsequently condensed with chloroacetic acid to produce 2,4-D acid (Fig. 2). The corresponding 2,4-dichlorophenoxyacetic acid butyl ester (hereafter 2,4-D butyl ester) is produced by the esterification of 2,4-D acid with butanol in the presence of a ferric chloride catalyst and chlorine.

In recent years, 2,4-D was only produced in several enterprises in China. Two 2,4-D acid and three 2,4-D butyl ester enterprises were selected as typical 2,4-D producers in this study. Ten 2,4-D product samples, two from each enterprise, were collected and analyzed for PCDD/Fs, PCBs, pentachlorobenzene (PeCBz), hexachlorobenzene (HxCBz) and polychlorophenols. D1 and D2 were 2,4-D acid samples, in which D1 was produced via phenoxyacetic acid and D2 via 2,4-dichlorophenol. D3, D4 and D5 were 2,4-D butyl ester samples. The samples were stored at -20°C prior to analysis.

2.2. Sample extraction and analysis

PCDD/Fs, PCBs, HxCBz, PeCBz and polychlorophenols were analyzed in the samples. The detail analysis process could be found everywhere (Liu et al., 2012). Briefly, the samples were mixed with $^{13}\text{C}_{12}$ -labeled PCDD/Fs, $^{13}\text{C}_{12}$ -labeled PCBs and $^{13}\text{C}_6$ -HxCBz mixture (Wellington Laboratories, Guelph, Canada). Samples D1 and D2 (2,4-D acid) were solved by solution of sodium hydroxide and then the resulting solutions were extracted by hexane, while samples D3, D4 and D5 (2,4-D butyl ester) were solved by hexane. All samples were then purified by passing them through multilayer silica gel and alumina columns. PCDD/Fs and PCBs analyses were performed using an Agilent 6890 high resolution gas chromatograph/Waters Autospec Ultima high-resolution mass spectrometer (HRGC/HRMS) coupled a DB-5 ms fused-silica column ($60\text{ m} \times 0.25\text{ mm i.d.} \times 0.25\text{ }\mu\text{m}$). Prior to HRGC/HRMS analysis, the samples were spiked with a mixture of $^{13}\text{C}_{12}$ -labeled PCDD/Fs and $^{13}\text{C}_{12}$ -labeled PCBs recovery standards. The analysis of HxCBz and PeCBz was carried out using an Agilent 6890/5973N GC/MS equipped with a HP-5 ms capillary column

Fig. 1. Production process of 2,4-D acid via phenoxyacetic acid.

Fig. 2. Production process of 2,4-D acid via 2,4-dichlorophenol.

($30\text{ m} \times 0.32\text{ mm i.d.} \times 0.25\text{ }\mu\text{m}$). Polychlorophenols were derivatized with acetic anhydride and analyzed by Agilent 7890 GC/ECD (Liu et al., 2012). The recoveries of $^{13}\text{C}_{12}$ -labeled PCDD/Fs standards ranged from 50% to 125%, while the recoveries of $^{13}\text{C}_{12}$ -labeled PCBs standards ranged from 60% to 120%. Blank experiments were carried out for the samples at the same time.

3. Results and discussion

3.1. Polychlorophenols in 2,4-D products

According to several reports in the literature (Weber and Hagenmaier, 1999a; Liu et al., 2004; Horii et al., 2008; Altarawneh et al., 2009; Kishi et al., 2010), polychlorophenols serve as the important precursors in the formation of PCDD/Fs. The concentrations of the polychlorophenols in the 2,4-D product samples are shown in Fig. 3.

The total concentrations of polychlorophenols in the 2,4-D acid and 2,4-D butyl ester samples (D1–D5) ranged from 67.6 to 2788.3 mg kg^{-1} . Generally, 2,4-dichlorophenol (2,4-DCP), the important intermediate of 2,4-D production, had the highest concentration among all samples, varying from 46.7 to 2442.6 mg kg^{-1} and the percentages were between 69.1% and 92.7%, with an average of 86.0%. It was followed by *o*-monochlorophenol (*o*-MCP) and 2,6-dichlorophenol (2,6-DCP), which were also major contributors to total polychlorophenols. In addition, some typical precursors of PCDD/Fs, like 2,3,4-trichlorophenol (2,3,4-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TCP) and pentachlorophenol (PCP), were detected in the samples. The formation pathway of polychlorophenols was as follow: first, *o*-MCP formed 2,4-DCP and 2,6-DCP; then 2,4-DCP became 2,3,4-TCP, and 2,4-DCP and 2,6-DCP formed 2,3,6-trichlorophenol (2,3,6-TCP) through further chlorination; later, 2,3,6-TCP and 2,3,4-TCP could be continuously chlorinated to 2,3,4,6-TCP; finally PCP was generated from 2,3,4,6-TCP. With the abundant chlorine, high concentrations of polychlorophenols and high chlorinated phenols were formed.

Fig. 3. Concentrations of the polychlorophenols in 2,4-D samples.

3.2. PCDD/Fs in 2,4-D products

The concentrations of the 2,3,7,8-PCDD/Fs and the WHO-TEQ of PCDD/Fs in the 2,4-D product samples are shown in Table 1. The WHO-TEQ was calculated using World Health Organization factors (WHO-TEFs) (Van den Berg et al., 2006).

According to the research reported by Weber and Hagenmaier (1999b) and Masunaga et al. (2001), 2,4-D acid contained 2.1 ng kg^{-1} and 6800 ng kg^{-1} of the significantly toxic 2,3,7,8-TCDD, respectively. It is clear from Table 1 that the concentrations of 2,3,7,8-TCDD were between 0.15 and 30.1 ng kg^{-1} in the samples. These values were similar to those reported by Masunaga et al. (2001) and much lower than the results of Weber and Hagenmaier (1999b).

The total concentrations of 2,3,7,8-PCDD/Fs in the 2,4-D acid samples, D1 and D2, were 355 and 8034 ng kg^{-1} and the corresponding TEQ values were 13.4 and $267.9 \text{ ng WHO-TEQ kg}^{-1}$, respectively, which were similar to the results reported by Holt et al. (2010). The significant difference found in the concentrations of PCDD/Fs in these two 2,4-D acid samples may be a consequence of the different production processes used in their production and the corresponding difference in raw materials. In the production process of 2,4-D acid via 2,4-dichlorophenol used in D2 production, phenol was chlorinated to 2,4-dichlorophenol firstly, and thus high concentrations of 2,4-dichlorophenol and other polychlorophenols were formed during the chlorination process. In comparison, in the production process of 2,4-D acid via phenoxyacetic acid used in D1 production, relatively low concentrations of 2,4-dichlorophenol and other polychlorophenols were generated during chlorination of phenoxyacetic acid. High concentrations of polychlorophenols were transformed relatively high concentrations of impurities such as PCDD/Fs and PCBs, and the concentrations of PCDD/Fs and PCBs analyzed in the samples, D1 and D2, indicated positive proof.

The total concentrations of 2,3,7,8-PCDD/Fs ranged from 4179 to 35080 ng kg^{-1} and the corresponding TEQ values ranged from 292.8 to $694.6 \text{ ng WHO-TEQ kg}^{-1}$ in 2,4-D butyl ester, D3, D4 and D5, which were obviously higher than those found in the 2,4-D acid samples in this study. The additional PCDD/Fs are formed during the esterification of 2,4-D acid with butanol in the presence of a ferric chloride catalyst and chlorine. 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF make a significant contribution to the toxicity of the

Fig. 4. Homologue profiles of total PCDD/Fs in 2,4-D samples.

PCDD/Fs in all samples. The WHO-TEQ values of 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF in samples D1, D2, D3, D4 and D5 were 58.8%, 73.7%, 74.1%, 77.7% and 45.2% of the total, respectively.

Homologue profiles of the total PCDD/Fs in the 2,4-D samples are shown in Fig. 4. TCDF and PeCDF were found to be the dominant species in all samples, together accounting for over 84.4%, 61.1%, 93.8%, 97.7% and 80.8% of all of the PCDD/Fs detected in the samples D1, D2, D3, D4 and D5, respectively. The high concentrations of tetra- and penta-CDD/Fs might be the result of a relatively high abundance of lower chlorinated chlorophenols, as they could be transformed to PCDD/Fs through ring condensation and rearrangement at the right temperature and appropriate catalysts during the 2,4-D production. The homologue profiles of PCDD/Fs are normally correlated with different pathways of dioxin formation. All samples (2,4-D acid and butyl ester) in this study share similar PCDD/Fs homologue profiles, also indicating a similarity in the formation pathways of PCDD/Fs in 2,4-D production.

3.3. PCBs, PeCBz and HxCBz in 2,4-D products

The concentrations of dioxin-like PCBs (dl-PCBs), PeCBz and HxCBz in the 2,4-D samples are shown in Table 2. The WHO-TEQ values were calculated using WHO-TEFs (Van den Berg et al., 2006).

Table 1
Concentrations of 2,3,7,8-PCDD/Fs in 2,4-D samples (ng kg^{-1}).

PCDD/Fs	2,4-D acid			2,4-D butyl ester		
	D1 (n = 2)	D2 (n = 2) (pg/g)	D6 ^a	D3 (n = 2) (pg/g)	D4 (n = 2)	D5 (n = 2)
2,3,7,8-TCDD	0.15 ± 0.05	12.95 ± 0.55	2.1	24.03 ± 3.5	30.05 ± 0.15	21.1 ± 0.3
1,2,3,7,8-PeCDD	2.85 ± 1.25	100.4 ± 14.5	11	193.1 ± 10.1	405.3 ± 5.3	86.2 ± 0.6
1,2,3,4,7,8-HxCDD	0.10 ± 0.08	33.05 ± 3.55	<5	32.43 ± 3.50	50.8 ± 1.0	10.1 ± 0.1
1,2,3,6,7,8-HxCDD	1.55 ± 0.25	124.9 ± 12.5	<5	154.7 ± 34.4	3164 ± 5.2	130.1 ± 1.9
1,2,3,7,8,9-HxCDD	1.15 ± 0.45	56.65 ± 1.15	<5	64.94 ± 9.24	70.85 ± 6.3	23.4 ± 0.4
1,2,3,4,6,7,8-HpCDD	20.1 ± 3.7	579.1 ± 52.1	<5	404.9 ± 29.5	514.5 ± 4.3	346.4 ± 9.9
OCDD	159.8 ± 8.6	1467 ± 135	<10	888.9 ± 58.4	695.2 ± 5.1	1219 ± 37.9
2,3,7,8-TCDF	9.85 ± 0.05	ND	<2	ND	ND	ND
1,2,3,7,8-PeCDF	1.7 ± 0.1	132.0 ± 16	3.8	52.72 ± 3.89	311 ± 28	526.9 ± 5.2
2,3,4,7,8-PeCDF	23.3 ± 3.7	191.05 ± 15.8	<2	79.95 ± 0.63	219.1 ± 1.9	759.0 ± 14.1
1,2,3,4,7,8-HxCDF	8.0 ± 1.0	138.9 ± 15.5	<5	50.78 ± 5.53	129.2 ± 2.1	840.8 ± 74.6
1,2,3,6,7,8-HxCDF	2.05 ± 0.25	80.45 ± 7.1	<5	33.26 ± 3.20	72.8 ± 2.7	393.5 ± 51.0
2,3,4,6,7,8-HxCDF	4.55 ± 0.55	142.6 ± 8.4	<5	48.51 ± 0.51	91.6 ± 0.3	451.2 ± 10.9
1,2,3,7,8,9-HxCDF	ND	69.9 ± 5.0	<5	ND	58.55 ± 0.1	405.1 ± 3.9
1,2,3,4,6,7,8-HpCDF	29.7 ± 8.1	2068 ± 175	<5	675.7 ± 4.5	954.6 ± 11.5	10216 ± 180
1,2,3,4,7,8,9-HpCDF	2.35 ± 0.05	102.5 ± 14.8	<5	21.10 ± 2.33	158.5 ± 12.5	663.1 ± 30.0
OCDF	88.0 ± 5.9	2735 ± 411	<10	1454 ± 100	1316 ± 27.8	18988 ± 409
$\Sigma 2,3,7,8\text{-PCDD/Fs}$	355 ± 30	8034 ± 893.2	16.9	4179 ± 257	5394 ± 95	35080 ± 817
WHO-TEQ	13.4 ± 2.0	267.9 ± 28.2	27.0	292.8 ± 19.8	606.2 ± 0.2	694.6 ± 19.7

ND: Not detected at the minimum limit of detection.

^a Sample from Masunaga et al. (2001).

Table 2Levels of dl-PCBs, PeCBz and HxCBz in 2,4-D samples (ng kg^{-1}).

dl-PCBs	2,4-D acid			2,4-D butyl ester		
	D1 (n = 2)	D2 (n = 2)	D6 ^a	D3 (n = 2)	D4 (n = 2)	D5 (n = 2)
PCB-77	38.6 ± 1.6	5151 ± 141.5	8.7	2.87 ± 0.12	1.75 ± 0.15	3.1 ± 0.2
PCB-81	1.45 ± 0.35	82.4 ± 1.2	<2	3.14 ± 0.03	0.7 ± 0.1	ND
PCB-105	9.45 ± 1.15	532 ± 16.7	2.1	2.09 ± 0.05	0.75 ± 0.25	2.05 ± 0.05
PCB-114	2.5 ± 0.4	16.85 ± 1.05	<2	0.60 ± 0.06	2.55 ± 0.45	1.25 ± 0.55
PCB-118	17.7 ± 2.2	591 ± 69.7	5	4.45 ± 0.14	4.6 ± 0.9	6.7 ± 0.2
PCB-123	3.65 ± 0.25	140.8 ± 25.8	<2	0.18 ± 0.06	ND	1.8 ± 0.0
PCB-126	4.2 ± 0.1	1065 ± 143.1	<2	0.36 ± 0.06	0.6 ± 0.1	3.45 ± 0.15
PCB-156	3.35 ± 0.45	202.6 ± 8.0	<2	0.66 ± 0.11	1.4 ± 0.1	7.9 ± 0.4
PCB-157	1.2 ± 0.1	114.6 ± 11.0	<2	0.12 ± 0.06	ND	7.75 ± 0.05
PCB-167	0.85 ± 0.05	54.25 ± 2.25	<2	0.27 ± 0.03	0.25 ± 0.05	10.7 ± 0.5
PCB-169	0.85 ± 0.25	56.65 ± 5.55	<2	0.66 ± 0.06	1.6 ± 0.1	3.95 ± 0.25
PCB-189	1.5 ± 0.1	20.85 ± 2.15	<2	0.69 ± 0.03	2.3 ± 0.0	20.25 ± 0.45
Σ dl-PCBs	85.3 ± 7.8	8023 ± 369	15.8	16.1 ± 0.03	16.5 ± 0.2	68.9 ± 1.9
WHO-TEQ	0.451 ± 0.006	108.28 ± 13.9	0.0032	0.0571 ± 0.0040	0.109 ± 0.013	0.466 ± 0.022
PeCBz	2015 ± 311	63 255 ± 981	–	372 ± 82	3084 ± 622	788 ± 152
HxCBz	709 ± 149	2490 ± 490	–	667 ± 128	ND	2907 ± 551

ND: Not detected at the minimum limit of detection.

^a Sample from Masunaga et al. (2001). **Fig. 5.** Homologue profiles of total PCBs in 2,4-D samples.

The concentrations of dl-PCBs in the 2,4-D acid samples, D1 and D2, were 85.3 and 8023 ng kg^{-1} , respectively, which were higher than those reported in 2,4-D acid by Masunaga et al. (2001). The concentration of PCB-77 in samples D1 and D2 corresponded to 45.3% and 64.2% of the dl-PCBs, respectively, representing the most predominant dl-PCBs congener in the samples, with following PCB-118 and PCB-126. The concentrations of dl-PCBs in samples D3, D4 and D5 were 16.1, 16.5 and 68.9 ng kg^{-1} , respectively, and PCB-118 and PCB-189 were the dominant congeners accounting for 31.9%, 41.8%, 39.1% of the dl-PCBs, respectively.

The WHO-TEQ values of the dl-PCBs were in the range between 0.057 and 0.47 $\text{ng WHO-TEQ kg}^{-1}$ in the 2,4-D butyl ester, D3, D4 and D5, which was similar to that found in D1 and significantly lower than that detected in D2. PCB-126 was found to be the predominant congener, contributing over 93.1%, 97.9%, 37.7%, 55.2% and 74.1% of the dl-PCB WHO-TEQs in the samples D1, D2, D3, D4 and D5, respectively, followed by PCB-169.

Homologue profiles of the total PCBs in the 2,4-D samples are presented in Fig. 5. It can be seen that the most abundant congeners were TeCB in samples D1, D2, D3 and D4 while TeCB, NoCB and DeCBs was found to be predominant groups in sample D5. In addition, the relatively high total PCBs were found in all samples. Total PCBs in the samples D1, D2, D3, D4 and D5 were 1486, 47 342, 24 770, 1549 and 13 352 ng kg^{-1} , respectively.

Table 2 shows that the concentrations of PeCBz and HxCBz were higher than those of PCBs in the 2,4-D samples. In addition, the

concentrations of PCBs, PeCBz and HxCBz in all samples share the similar trends, indicating a close relationship between PCBs concentrations and polychlorobenzenes concentrations in 2,4-D production. Polychlorobenzenes, the important precursor of PCBs and PCDD/Fs (Liu et al., 2004), may be condensed and reacted with polychlorophenols to form PCBs and PCDD/Fs during the 2,4-D production process at the right temperature. Thus, the purification process for the dioxin precursors such as polychlorophenols and polychlorobenzenes plays a pivotal role in controlling the formation and release of PCBs and PCDD/Fs during 2,4-D production process, and therefore protecting the human and environmental health.

4. Conclusions

From data presented in this study it can be summarized that the concentrations of PCDD/Fs, PCBs, PeCBz, HxCBz and polychlorophenols shared the similar trends in all samples, which hints polychlorophenols and polychlorobenzenes could possibly serve as the main reaction intermediates in the formation of PCDD/Fs and PCBs in the production process of 2,4-D products (Liu et al., 2012).

The emission factors of the PCDD/Fs and PCBs were calculated from the analyzed data. The average emission factors in 2,4-D products were 414.4 $\mu\text{g WHO-TEQ t}^{-1}$ for PCDD/Fs and 21.9 $\mu\text{g WHO-TEQ t}^{-1}$ for PCBs. The derived emission factor of PCDD/Fs found in this study was relatively low compared with other chemical sources, such as chloranil and pentachlorophenol production. Furthermore, it was lower than the emission factor listed in the Dioxin Toolkit (700 $\mu\text{g TEQ t}^{-1}$). In China, in 2010, the production of 2,4-D was 40 000 tons and the emissions of PCDD/Fs and PCBs were 16.5 g WHO-TEQ and 0.88 g WHO-TEQ, respectively.

In addition, the total incremental intake amounts of PCDD/Fs and PCBs for the workers involved the accidental or occupational exposure of 2,4-D would be 27.8 pg kg^{-1} and 1.47 pg kg^{-1} body weight, respectively, given the absorb of 2,4-D was 67 mg kg^{-1} body weight (Lee et al., 2001). The impurities of PCDD/Fs and PCBs in 2,4-D may increase the health risk for the workers exposed to 2,4-D.

It is our expectation that PCDD/Fs and related unintentional POPs resulting from the production of 2,4-D should attract considerable attention because of the concentrations of POPs and the extensive use of 2,4-D products. These impurities should be

purified before using 2,4-D products to reduce the release of POPs and to protect the environment.

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