Bulletin of Environmental Contamination and Toxicology (2019) 102:287–296
https://doi.org/10.1007/s00128-018-2519-x

# Emission of Unintentionally Produced Persistent Organic Pollutants from Some Industrial Processes in Northern Vietnam

**Hue Nguyen Thi[1,2] · Thuy Nguyen Thi Thu[1,3] · Long Pham Hai[1] · Hai Nguyen Thanh[1] · Hai Chu Viet[1] · Hue Chu Thi[4] · Truong Nghiem Xuan[5] · Nguyen Hoang Tung[1]**

Received: 30 August 2018 / Accepted: 8 December 2018 / Published online: 13 December 2018


## Abstract

Concentrations of PCDD/Fs, dioxin-like PCBs (dl-PCBs), PeCB and HCB were determined in flue gas, fly ash and bottom ash samples collected from brick production, steel production, and zinc production plants, an industrial waste incinerator and a medical waste incinerator in northern Vietnam to understand the contamination levels, accumulation patterns and extent of emission. Total TEQs concentrations of PCDD/Fs and dl-PCBs in flue gas and ash samples from these industrial plants ranged from 0.304 to 50.55 pg/Nm$^3$ and 1.43 to 440 pg/g, respectively. PeCB and HCB residues in flue gas samples ranged from 0.839 to 46.59 ng/Nm$^3$ and 1.16 to 60.5 ng/Nm$^3$, respectively. The emission factors of 4.8–740 ngTEQs/tonne for PCDD/Fs and dl-PCBs, 67.12–240.7 µg/ton for PeCB and 11.64–889.3 µg/ton for HCB were obtained in flue gas samples. This is among the first reports on the emission factor of PCDD/Fs, dl-PCBs, PeCB, HCB in brick production, zinc production and waste incineration in Vietnam.

**Keywords** PCDD/Fs · Pentachlorobenzene · Hexachlorobenzene · Metallurgy · Waste incineration · Vietnam

Contamination of unintentionally produced persistent organic pollutants (U-POPs) listed under the Stockholm Convention are global concerns because of their extremely environmental persistence, long-range transport, high toxicity and bioaccumulation (Broman et al. 1992; Gouin et al. 2004; Van den Berg et al. 1998; Vorkamp and Riget 2014). U-POPs released from industrial activities and thermal processes are difficult to control, especially in developing countries like Vietnam because of being contaminated from raw materials and fuels, low-level production and waste treatment technologies. Emissions of U-POPs such as polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs), hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) from thermal processes were investigated for several industrial sectors like waste incineration, open burning, metallurgy, coking and chemical industry (Liu et al. 2009, 2013; Nie et al. 2011, 2012a; Zhang et al. 2011). In Vietnam, U-POPs monitoring capability is still limited, hence the database of emission levels and profiles of these contaminants are inadequate, especially for HCB and PeCB. Previous study reported concentrations of PCDD/Fs in stack gas and fly ash from some steel production and cement kiln plants in Vietnam to estimate their emission factors. Dioxin emission factor from the steel production plants in Vietnam were markedly higher than those from some developed European countries whereas emission factors of some cement kilns were relatively low (Thuong et al. 2014). Our recent study reported the first time for the levels and emissions of PeCB and HCB in fly ash and bottom ash from some waste incinerators and steel production plants (Hue et al. 2016). However, no investigation has

✉ Hue Nguyen Thi
nthue2003@gmail.com

✉ Nguyen Hoang Tung
nhtung79@gmail.com

1 Vietnam Academy of Science and Technology, Institute of Environmental Technology and Graduate University of Science and Technology, 18 Hoang Quoc Viet, Hanoi, Vietnam

2 University of Science and Technology of Hanoi, 18 Hoang Quoc Viet, Hanoi, Vietnam

3 Faculty of Chemistry, TNU University of Science, Thai Nguyen University, Tan Thinh Ward, Thai Nguyen, Vietnam

4 Faculty of Chemistry, VNU University of Science, 19 Le Thanh Tong Street, Hanoi, Vietnam

5 Vietnam - Russia Tropical Center, Ministry of Defense, Nguyen Van Huyen Street, Hanoi, Vietnam

been conducted to simultaneously measure concentrations of PeCB, HCB, PCDD/Fs and dl-PCBs in industrial samples in Vietnam.

In this study, industrial samples including flue gas, fly ash and bottom ash were collected from a brick production plant, a steel production plant, a zinc production plant, an industrial waste incinerator and a medical waste incinerator in an industrial zone of northern Vietnam, and the concentrations of different groups of U-POPs such as PCDD/Fs, dl-PCBs, HCB and PeCB were determined to understand status of the contamination as well as characteristics and extent of the emission. The study would contribute to update on the national database of U-POPs in Vietnam for the effort of the country to fulfill obligations under the Stockholm Convention.

## Materials and Methods

Relevant information on the industrial plants such as capacity, operating time, and average emission flow is given in Table 1. The industrial plants investigated in this study comprise brick production, steel production, zinc production, industrial waste incinerators and medical waste incinerator located in some industrial zones from northern Vietnam during 2015. Flue gas samples were collected from the incinerators and stack of brick, steel and zinc production plant based on the isokinetic method given in the Method 23 of US EPA (US EPA 2017). The duration time for collection of one stack gas samples was approximately 5–6 h. For each flue gas sample, both particulate and gas phase were collected by a quartz fiber filter and a chamber containing Amberlite XAD-2 adsorbent, respectively. Fly ash samples were collected from the exhaust system or dust filtering bags of the steel and zinc production plants. Bottom ash samples were manually collected from the bottom of the incinerators and exit door of the zinc production furnaces. A total of four flue gas samples, two fly ash and four bottom ash samples were collected. Details about number of industrial samples collected in this study were given in Table 2.

PCDD/Fs and dl-PCBs were analyzed following the EPA methods 1613B and 8290A (EPA 1994a, b, 2017). The $^{13}C_{12}$-labelled EDF-4053 was spiked as an extraction standard, and EDF-4055 was spiked as a recovery standard for PCDD/Fs, respectively. For flue gas samples, the XAD-2 resin and quartz fiber filter were combined for a representative sample. The samples were then Soxhlet extracted for 24 h with 200 mL of toluene. The fly ash samples were air dried and sieved to less than 1 mm; 10 g of each sample was then Soxhlet extracted with 200 mL of toluene for 24 h. The extracts were then treated with concentrated $H_2SO_4$, KOH, and subjected to a multi-layer clean up column consisting of anhydrous $Na_2SO_4$, KOH-silica gel, $H_2SO_4$-silica gel, and $AgNO_3$-silica gel. PCDD/F congeners were separated from PCBs congeners by activated carbon column, and further cleaned up by alumina column. The final extract was spiked with $^{13}C_{12}$-PCDD/Fs labelled internal standards, concentrated to 0.1 mL and injected into high resolution gas chromatography coupled with high resolution mass spectrometric system (HRGC-HRMS) for quantification.

Concentrations of PCDD/Fs and dl-PCBs were quantified by using Micromass Autospec Ultima system (Waters Co. Ltd.) equipped with a 7890A gas chromatograph (Agilent Co. Ltd.) using DB-5MS capillary column (60 m × 0.25 mm I.D, 0.25 µm film thickness, J&W Scientific Inc., Folsom, CA). The mass spectrometer was operated at a resolution of greater than 10,000 in positive electron impact mode (EI). Data was obtained in the selected ion record (SIR) mode. Quantification was based on isotope dilution method using the labeled $^{13}C_{12}$-PCDD/Fs and dl-PCBs standards (EPA 1994a, 2008, 2017). TEQ values were calculated based on the detected congeners and using the toxic equivalent factors (TEFs) issued by WHO in 2005 (Van den Berg et al. 1998). The recoveries of PCDD/Fs and dl-PCBs ranged from 85% to 96%. For flue gas samples, the method detection limit (MDL) was 0.05 pg/m$^3$ for tetra- to heptachlorinated dioxins, furan and dl-PCB congeners, and 0.5 pg/m$^3$ for OCDD/Fs. The MDL for ash sample was 0.05 pg/g for tetra- to heptachlorinated dioxin, furans, and dl-PCBs, and 0.1 pg/g for OCDD/Fs.

Analytical procedure for PeCB and HCB was followed to the method US EPA 8121 (US EPA 1994b). Samples were extracted by Soxhlet system with a mixture solvent of hexane and acetone (1:1, v/v) for 16 h. The clean-up

**Table 1** Information of the industrial plants investigated in this study

| | Capacity (tonne/h) | Average emission flow rate (Nm$^3$/h) | Technology, air pollution control device (APCD) | Average operating time (h/year) |
|---|---|---|---|---|
| Brick production plant | 5.8 | 16,500 | Tunnel kiln, circulating furnace | 6530 |
| Steel production plant | 6.0 | 31,000 | Blast oxygen furnace, bag filter | 8040 |
| Zinc production plant | 1.0 | 14,700 | Reverberatory furnace, electrostatic dust filter | 7000 |
| Industrial waste incinerator | 0.25 | 20,000 | Grate incinerator, semi-dry scrubber | 2640 |
| Medical waste incinerator | 0.2 | 15,000 | Grate incinerator, no APCD | 1536 |

**Table 2** Mass concentrations and TEQs of PCDD/Fs, dioxin-like PCBs, PeCB and HCB in different industrial samples collected from northern Vietnam

| | Flue gas sample (pg/Nm$^3$) | | | | Fly ash sample (pg/g) | | Bottom ash sample (pg/g) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Brick production plant (n = 1) | Steel production plant (n = 1) | Zinc production plant (n = 1) | Industrial waste incinerator (n = 1) | Steel production plant (n = 1) | Zinc production plant (n = 1) | Zinc production plant (n = 2) | | Medical waste incinerator (n = 2) | |
| | | | | | | | Mean | Range | Mean | Range |
| Mass concentrations | | | | | | | | | | |
| PCDD/Fs | | | | | | | | | | |
| 2,3,7,8-TCDD | 0.37 | 3.97 | 4.27 | < MDL | 0.26 | 15.45 | 0.21 | 0.15–0.27 | 8.55 | 2.940–14.16 |
| 1,2,3,7,8-PeCDD | 0.33 | 2.29 | 10.31 | < MDL | 0.18 | 49.21 | 0.265 | 0.17–0.36 | 32.59 | 4.78–60.4 |
| 1,2,3,4,7,8-HxCDD | 0.14 | 0.69 | 3.66 | < MDL | 2.1 | 29.07 | 0.335 | 0.18–0.49 | 20.07 | 1.77–38.37 |
| 1,2,3,6,7,8-HxCDD | 0.24 | 1.41 | 8.31 | 0.056 | 0.27 | 62.67 | 0.44 | 0.25–0.63 | 34.43 | 3.88–64.98 |
| 1,2,3,7,8,9-HxCDD | 0.27 | 1.2 | 5.61 | 0.05 | 0.25 | 46.23 | 0.36 | 0.18–0.54 | 38.84 | 2.88–74.79 |
| 1,2,3,4,6,7,8-HpCDD | 0.7 | 2.49 | 11.91 | 0.31 | 0.4 | 190 | 1.95 | 1.9–2 | 110 | 12.3–209 |
| OCDD | 1.333 | 2.0 | 7.633 | 0.667 | 3.333 | 220 | 8.333 | 6.67–10 | 73.33 | 26.67–120 |
| 2,3,7,8-TCDF | 1.75 | 29.48 | 32.05 | 0.14 | 1.28 | 280 | 1.17 | 0.79–1.55 | 130 | 80.5–190 |
| 1,2,3,7,8-PeCDF | 1.167 | 16.43 | 31.9 | 0.14 | 0.7 | 270 | 1.083 | 0.7–1.467 | 125 | 28.7–220 |
| 2,3,4,7,8-PeCDF | 1.02 | 13.25 | 32.83 | 0.28 | 1.1 | 450 | 1.515 | 1.19–1.84 | 220 | 37.16–405 |
| 1,2,3,4,7,8-HxCDF | 0.97 | 8.38 | 27.08 | 0.23 | 0.46 | 300 | 0.96 | 0.63–1.29 | 145 | 17.03–275 |
| 1,2,3,6,7,8-HxCDF | 0.76 | 7.42 | 24.42 | 0.221 | 0.58 | 290 | 0.745 | 0.64–0.85 | 150 | 15.49–290 |
| 2,3,4,6,7,8-HxCDF | 0.72 | 4.61 | 17.83 | 0.338 | 0.42 | 320 | 0.955 | 0.84–1.07 | 160 | 20.92–290 |
| 1,2,3,7,8,9-HxCDF | 0.41 | 1.75 | 6.49 | 0.088 | 0.19 | 91.52 | 0.345 | 0.28–0.41 | 47.06 | 4.31–89.8 |
| 1,2,3,4,6,7,8-HpCDF | 1.48 | 8.22 | 33.02 | 0.75 | 0.7 | 6440 | 2.93 | 2.66–3.2 | 300 | 33.8–560 |
| 1,2,3,4,7,8,9-HpCDF | 0.32 | 1.17 | 5.7 | 0.091 | 0.2 | 1010 | 0.705 | 0.23–1.18 | 48.6 | 3.6–93.6 |
| OCDF | 0.667 | 1.333 | 8.667 | 0.367 | 0.333 | 270 | 1.833 | 1.667–2 | 75.83 | 8.33–140 |
| Dioxin-like PCBs | | | | | | | | | | |
| 3,4,4′,5-TCB (81) | 4.4 | 29.2 | 23.8 | 0.9 | 1.3 | 260 | 1.05 | 1–1.1 | 85.05 | 44.9–125 |
| 3,3′,4,4′-TCB (77) | 1.8 | 13.47 | 11.33 | 1.033 | 0.967 | 190 | 0.967 | 0.88–1.07 | 34.35 | 27.03–41.67 |
| 2′,3,4,4′,5-PeCB (123) | < MDL | < MDL | < MDL | < MDL | < MDL | < MDL | < MDL | – | < MDL | – |
| 2,3′,4,4′,5-PeCB (118) | < MDL | 0.054 | 0.072 | < MDL | < MDL | 2.240 | 0.018 | 0.01–0.023 | 0.048 | 0.028–0.068 |
| 2,3,4,4′,5-PeCB (114) | 0.667 | 3.333 | 4.667 | 0.433 | 0.667 | 83.330 | 0.833 | 0.667–1.0 | 9.667 | 3.33–16.0 |
| 2,3,3′,4,4′-PeCB (105) | 6.333 | 23.67 | 32.67 | 4.333 | 5.0 | 1180 | 7.833 | 5.33–10.33 | 31.5 | 17.67–45.33 |
| 3,3′,4,4′,5-PeCB (126) | 2630 | 20,330 | 399,700 | 1020 | 2170 | 521,100 | 1750 | 1630–1870 | 1,424,000 | 660,700–2,187,000 |
| 2,3′,4,4′,5,5′-HxCB (167) | 0.667 | 3.0 | 6.0 | 0.267 | 0.333 | 160 | 1.333 | 1.33–1.33 | 12.5 | 4.0–21 |
| 2,3,3′,4,4′,5-HxCB (156) | 2 | 6.0 | 12.0 | 0.667 | 0.667 | 470 | 2.833 | 2–3.667 | 24.67 | 7.667–41.67 |
| 2,3,3′,4,4′,5′-HxCB (157) | 0.333 | 2.0 | 4.667 | 0.2 | 0.133 | 120 | 0.67 | 0.67–0.67 | 11.33 | 3.333–19.33 |
| 3,3′,4,4′,5,5′-HxCB (169) | 380 | 840 | 3580 | 81 | 120 | 31,750 | 230 | 200–260 | 11,095 | 3280–18,910 |
| 2,3,3′,4,4′,5,5′-HpCB (189) | 0.333 | 1 | 79.33 | 0.133 | 0.1 | 55.33 | 0.5 | 0.33–0.67 | 16.18 | 3.2–29.17 |

**Table 2** (continued)

| | Flue gas sample (pg/Nm$^3$) | | | | Fly ash sample (pg/g) | | Bottom ash sample (pg/g) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Brick production plant (n = 1) | Steel production plant (n = 1) | Zinc production plant (n = 1) | Industrial waste incinerator (n = 1) | Steel production plant (n = 1) | Zinc production plant (n = 1) | Zinc production plant (n = 2) | | Medical waste incinerator (n = 2) | |
| | | | | | | | Mean | Range | Mean | Range |
| PCDDs | 3.383 | 14.05 | 51.7 | 1.16 | 6.793 | 620 | 11.89 | | 320 | |
| PCDFs | 9.263 | 92.05 | 220 | 2.645 | 5.963 | 9720 | 12.24 | | 1400 | |
| Dioxin-like PCBs | 3030 | 21,250 | 403,400 | 1100 | 2300 | 555,400 | 1200 | | 1,435,000 | |
| Total PCDD/Fs | 12.65 | 106 | 270 | 3.804 | 12.76 | 10,340 | 24.14 | | 1725 | |
| PeCB | < MDL | 46,588 | < MDL | 839 | 970 | 4780 | 3220 | 340–6100 | 7160 | 2420–11,900 |
| HCB | 4092 | 23,196 | 60,500 | 1162 | 1380 | 160 | 890 | 610–1170 | 22,570 | 2330–42,800 |
| TEQ concentrations | | | | | | | | | | |
| PCDD/Fs | | | | | | | | | | |
| 2,3,7,8-TCDD | 0.37 | 3.97 | 4.27 | – | 0.26 | 15.45 | 0.21 | 0.15–0.27 | 8.55 | 2.94–14.16 |
| 1,2,3,7,8-PeCDD | 0.33 | 2.29 | 10.31 | – | 0.18 | 49.21 | 0.265 | 0.17–0.36 | 33.0 | 4.78–60.4 |
| 1,2,3,4,7,8-HxCDD | 0.014 | 0.069 | 0.366 | – | 0.21 | 2.907 | 0.034 | 0.18–0.49 | 2.007 | 0.177–3.837 |
| 1,2,3,6,7,8-HxCDD | 0.024 | 0.141 | 0.831 | 0.006 | 0.027 | 6.267 | 0.044 | 0.25–0.63 | 3.443 | 0.388–6.498 |
| 1,2,3,7,8,9-HxCDD | 0.027 | 0.12 | 0.561 | 0.005 | 0.025 | 4.623 | 0.036 | 0.18–0.54 | 3.884 | 0.288–7.479 |
| 1,2,3,4,6,7,8-HpCDD | 0.007 | 0.025 | 0.119 | 0.003 | 0.004 | 1.899 | 0.02 | 1.9–2 | 1.107 | 0.123–2.091 |
| OCDD | 0.001 | 0.001 | 0.003 | < MDL | 0.001 | 0.067 | 0.003 | 6.667–10 | 0.022 | 0.008–0.036 |
| 2,3,7,8-TCDF | 0.175 | 2.948 | 3.205 | 0.014 | 0.128 | 27.86 | 0.117 | 0.79–1.55 | 13.37 | 8.049–18.69 |
| 1,2,3,7,8-PeCDF | 0.035 | 0.493 | 0.957 | 0.004 | 0.021 | 8.086 | 0.033 | 0.7–1.467 | 3.772 | 0.861–6.683 |
| 2,3,4,7,8-PeCDF | 0.306 | 3.975 | 9.849 | 0.084 | 0.33 | 130 | 0.455 | 1.19–1.84 | 66.45 | 11.15–121 |
| 1,2,3,4,7,8-HxCDF | 0.097 | 0.838 | 2.708 | 0.023 | 0.046 | 30.44 | 0.096 | 0.63–1.29 | 14.68 | 1.703–27.65 |
| 1,2,3,6,7,8-HxCDF | 0.076 | 0.742 | 2.442 | 0.022 | 0.058 | 28.71 | 0.076 | 0.64–0.85 | 15.18 | 1.549–28.81 |
| 2,3,4,6,7,8-HxCDF | 0.072 | 0.461 | 1.783 | 0.034 | 0.042 | 32.28 | 0.096 | 0.84–1.07 | 15.73 | 2.09–29.37 |
| 1,2,3,7,8,9-HxCDF | 0.041 | 0.175 | 0.649 | 0.009 | 0.019 | 9.152 | 0.035 | 0.28–0.41 | 4.706 | 0.431–8.981 |
| 1,2,3,4,6,7,8-HpCDF | 0.015 | 0.082 | 0.33 | 0.008 | 0.007 | 64.44 | 0.029 | 2.66–3.2 | 2.988 | 0.338–5.637 |
| 1,2,3,4,7,8,9-HpCDF | 0.003 | 0.012 | 0.057 | 0.001 | 0.002 | 10.08 | 0.007 | 0.23–1.18 | 0.486 | 0.036–0.936 |
| OCDF | 0.001 | 0.001 | 0.003 | < MDL | < MDL | 0.081 | 0.001 | 1.667–2.0 | 0.023 | 0.003–0.043 |
| Dioxin-like PCBs | | | | | | | | | | |
| 3,4,4′,5-TCB (81) | 0.001 | 0.003 | 0.002 | < MDL | < MDL | 0.026 | < MDL | < MDL | 0.009 | 0.004–0.013 |
| 3,3′,4,4′-TCB (77) | 0.001 | 0.004 | 0.003 | < MDL | 0.001 | 0.057 | < MDL | < MDL | 0.010 | 0.008–0.013 |
| 2′,3,4,4′,5-PeCB (123) | – | – | – | – | – | – | – | – | – | – |
| 2,3′,4,4′,5-PeCB (118) | – | < MDL | < MDL | – | – | 0.067 | < MDL | < MDL | < MDL | < MDL |
| 2,3,4,4′,5-PeCB (114) | 0.0 | < MDL | < MDL | < MDL | < MDL | 0.003 | < MDL | < MDL | < MDL | < MDL |
| 2,3,3′,4,4′-PeCB (105) | 0.0 | < MDL | < MDL | < MDL | < MDL | 0.035 | < MDL | < MDL | < MDL | < MDL |

**Table 2** (continued)

| | Flue gas sample (pg/Nm$^3$) | | | | Fly ash sample (pg/g) | | Bottom ash sample (pg/g) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Brick production plant (n = 1) | Steel production plant (n = 1) | Zinc production plant (n = 1) | Industrial waste incinerator (n = 1) | Steel production plant (n = 1) | Zinc production plant (n = 1) | Zinc production plant (n = 2) | | Medical waste incinerator (n = 2) | |
| | | | | | | | Mean | Range | Mean | Range |
| 3,3′,4,4′,5-PeCB (126) | 0.079 | 0.61 | 11.99 | 0.031 | 0.065 | 15.63 | 0.05 | 0.05–0.06 | 42.72 | 19.82–65.62 |
| 2,3′,4,4′,5,5′-HxCB (167) | < MDL | < MDL | < MDL | < MDL | < MDL | 0.005 | < MDL | < MDL | < MDL | < MDL |
| 2,3,3′,4,4′,5-HxCB (156) | < MDL | < MDL | < MDL | < MDL | < MDL | 0.014 | < MDL | < MDL | < MDL | < MDL |
| 2,3,3′,4,4′,5′-HxCB (157) | < MDL | < MDL | < MDL | < MDL | < MDL | 0.004 | < MDL | < MDL | < MDL | < MDL |
| 3,3′,4,4′,5,5′-HxCB (169) | 0.011 | 0.025 | 0.107 | 0.002 | 0.0036 | 0.955 | 0.007 | 0.006–0.01 | 0.33 | 0.09–0.57 |
| 2,3,3′,4,4′,5,5′-HpCB (189) | < MDL | < MDL | < MDL | < MDL | < MDL | 0.002 | < MDL | < MDL | < MDL | < MDL |
| PCDDs | 0.773 | 6.616 | 16.46 | 0.072 | 0.707 | 80.42 | 0.612 | | 51.6 | |
| PCDFs | 0.821 | 9.727 | 21.98 | 0.199 | 0.653 | 340 | 0.945 | | 138 | |
| Dioxin-like PCBs | 0.093 | 0.645 | 12.11 | 0.034 | 0.071 | 16.8 | 0.06 | | 43.1 | |
| Total PCDD/Fs | 1.594 | 16.34 | 38.44 | 0.271 | 1.36 | 420 | 1.557 | | 189 | |
| Total TEQs | 1.685 | 16.98 | 50.55 | 0.304 | 1.43 | 440 | 1.613 | | 232 | |

experiments were conducted with silica gel containing 10% (w/w) activated charcoal, and copper powder. PeCB and HCB were quantified by using a gas chromatography coupled with mass spectrometry (GC/MS) system using a SPB-608 ms column (30 m length × 0.25 mm I.D × 0.25 µm film thickness) and also quantified by isotope dilution method using labeled $^{13}C_6$-HCB and PeCB standards. The recovery of HCB and PeCB was in the range of 89%–98%, and the MDL was 0.1 ng/g dry wt.

## Results and Discussion

PeCB and HCB were detected in flue gas samples with concentrations ranged of 0.839–46.59 ng/g and 1.16–60.5 ng/g, respectively (Table 2). The patterns of the contaminants are similar to PCDD/Fs with higher levels found in the steel and zinc production plants. HCB residues in the brick production plant were higher than in the industrial waste incinerator, while higher PeCB concentration were encountered in flue gas from the steel production plant (Table 2). These data are among the first on unintentionally produced PeCB and HCB in flue gas from Vietnam. PeCB levels from the steel plant were higher than those reported in magnesium smelter and coking plants in China; copper and aluminum scrap smelting in Poland (Nie et al. 2011; Liu et al. 2009; Grochowalski et al. 2007). HCB concentrations in flue gas from various plants in Vietnam varied considerably, from 1.1 to 60.5 ng/g (mean: 22.2 ng/g). These levels were similar to a magnesium smelting plant (Nie et al. 2011), but lower than those in scrap metal recycling plants (Nie et al. 2012b).

Concentrations of PCDD/Fs, and dl-PCBs from the flue gas, bag filter dust and bottom ash samples collected from the incinerators and the production plants in an industrial zone from northern Vietnam are presented in Table 2. Concentrations of PCDD/F and dl-PCBs in flue gas samples ranged from 3.804 to 270 pg/Nm$^3$ and 1.1 to 403.4 ng/Nm$^3$, respectively. The total TEQ concentrations of PCDD/Fs and dl-PCBs were in the range of 0.304–50.5 pg/Nm$^3$. In general, PCDD/Fs and dl-PCBs concentrations were the highest in flue gas samples collected from the zinc production plant, followed by the steel production plant, the brick production plant and the industrial waste incinerator. Levels of PCDD/Fs congeners were 2–3 orders of magnitude lower than those of dl-PCBs. The contamination patterns of HCB in the investigated plants were similar to those of PCDD/Fs and dl-PCBs, showing higher levels in the zinc and steel production plants and lower residues in the brick production plant and the waste incineration. Information of PCDD/Fs emission from flue gas in Vietnam is very limited. PCDD/Fs concentrations in flue gas from the zinc production plant in this study were comparable to those found in an electric arc furnace (EAF) steel plant (0.234 ng/Nm$^3$), but lower

than a blast oxygen furnace (BOF) steel plant (0.557 ng/$Nm^3$) investigated in northern Vietnam (Thuong et al. 2014). These levels were few orders of magnitude lower than those in flue gas collected from primary and secondary copper smelters and scrap metal recycling plants in China (0.2–1407 ng/$Nm^3$, Nie et al. 2012a, b) and various ferrous and non-ferrous foundries (copper, lead and zinc) in Korea (0.001–32.401 ng TEQ/$Nm^3$, Yu et al. 2006). However, compared to a magnesium smelting plant in China (176 pg/$Nm^3$ and 218 pg/$Nm^3$, Nie et al. 2011), PCDD/Fs concentrations in the steel production and zinc smelting plants in Vietnam were in a similar range (106 and 270 pg/$Nm^3$, Table 2). This result suggests the potential release of dioxins and dioxin-like compounds from metallurgy plants in northern Vietnam. PCDD/Fs and dl-PCBs in flue gas sample from the industrial waste incinerator and the brick production plant were relatively low (3.84 and 12.65 pg/$Nm^3$, respectively), and these levels were generally less than those reported in flue gases from municipal waste incinerators from Korea, China, Spain and France (Choi et al. 2008; Li et al. 2016, 2017; Ni et al. 2009; Abad et al. 2006; Nzihou et al. 2012). The emission levels of PCDD/Fs and dl-like PCBs in flue gas samples from waste incinerators were still lower than the criteria level of 600 pg/$Nm^3$ in the Vietnamese regulation on emission of industrial waste incinerator (Vietnam technical regulation on emission of industrial waste incinerators 2010).

The concentrations of PCDD/F and dl-PCB congeners in fly ash from the zinc production plant (10.34 ng/g) were much higher than from the steel production plant (12.76 pg/g); and the total TEQ concentrations in these two plants were 440 and 1.43 pg/g, respectively. While in bottom ash, PCDD/Fs concentrations in the zinc production plant were also remarkably lower than those in fly ash collected from the bag filter. Fly ash is known to be potential media for U-POPs releases in non-ferrous metallurgical processes such as in copper smelting and production (Wang et al. 2015). Concentrations of PCDD/Fs and dl-PCBs in bottom ash from the medical waste incinerator were higher than those from the zinc production plant. The lack of air pollution control device in medical waste incinerator may result in higher concentrations of PCDD/Fs and dl-PCBs in ash samples. Compared to various metallurgical processes in Korea, the levels of PCDD/Fs in ash samples from Vietnam were higher than those in fly ash from ferrous foundries and a lead production plant, but lower than those in copper, zinc and aluminum production plants (Yu et al. 2006).

Overall, our result suggests the extent of contamination of PeCB and HCB is similar to some metallurgy processes in China and Poland, while PCDD/Fs levels were in lower range. This preliminary investigation is among the first data on these U-POPs from industry in Vietnam. The concentrations of U-POPs in ash samples in this study are still lower than the Vietnamese hazardous waste threshold levels (3 mg/kg for PeCB, 0.15 mg/kg for HCB, 5 µg/kg for PCDDs and 10 µg/kg for PCDFs) (Vietnam technical regulation on hazardous waste thresholds 2009). The contamination profile of U-POPs in flue gas followed the order of the zinc product plant > steel production plant > brick production plant > industrial waste incinerator and similarly, these compounds in ash samples also decreased in the order of the zinc product plant > steel production plant or industrial waste incinerator. In addition, the extent of contamination in Vietnam were generally lower than those reported previously for other countries, except for flue gas and fly ash samples from the zinc production plants, where PCDD/F and PeCB levels were comparable to those from some non-ferrous metallurgical processes in China (Nie et al. 2011).

Congener profiles of PCDD/Fs and dl-PCBs were evaluated in term of both mass concentrations and TEQs of emissions of these U-POPs (Figs. 1, 2). In flue gas samples, the proportions of PCDFs congeners were generally higher than PCDDs. In particular, some dibenzofuran congeners such as 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, 2,3,4,6,7,8-HxCDF were predominant, accounting for 10.1%–44.7% of the total PCDD/Fs concentrations. The fractions of these congeners were particularly high in flue gas from the steel and zinc production plants (44.7% and 30.6% of the total PCDD/Fs concentration, respectively). OCDD showed relatively high fractions in the industrial waste incinerator and the brick production plant. The patterns of OCDD were similar to those reported from magnesium, copper smelting process and EAF steel production furnace in China, Taiwan and Korea (Nie et al. 2011, 2012a; Wang et al. 2009; Yu et al. 2006). In terms of TEQ congener pattern (Fig. 2), high proportions of 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD were observed due to higher TEF values. Similar to mass concentrations, 2,3,4,7,8-PeCDF also accounted for high TEQ proportions for most of the samples analyzed. Risk assessment should be considered for these congeners due to their high contributions to total TEQs.

Congener profiles in fly ash samples of the zinc production plant were different from those in bottom ash and flue gas. In particular, two congeners of 1,2,3,4,6,7,8- and 1,2,3,4,7,8,9-HpCDF in the fly ash appeared predominant. In contrast, OCDD, OCDF and 1,2,3,4,6,7,8-HpCDF accounted for larger fractions in the bottom ash. Fly ash is an important factor for estimating the formation of PCDD/Fs during the thermal processes, and the predominance of hexa- and hepta-dibenzofuran congeners in fly ash were documented in many previous studies, be consistent with our study. Profiles of bottom ash from the zinc production plant and the medical waste incineration showed some differences with high proportion of OCDD in the zinc plant and the dominance of PCDFs congeners in the incinerator (Fig. 1), suggesting a different mechanism for the formation of PCDD/

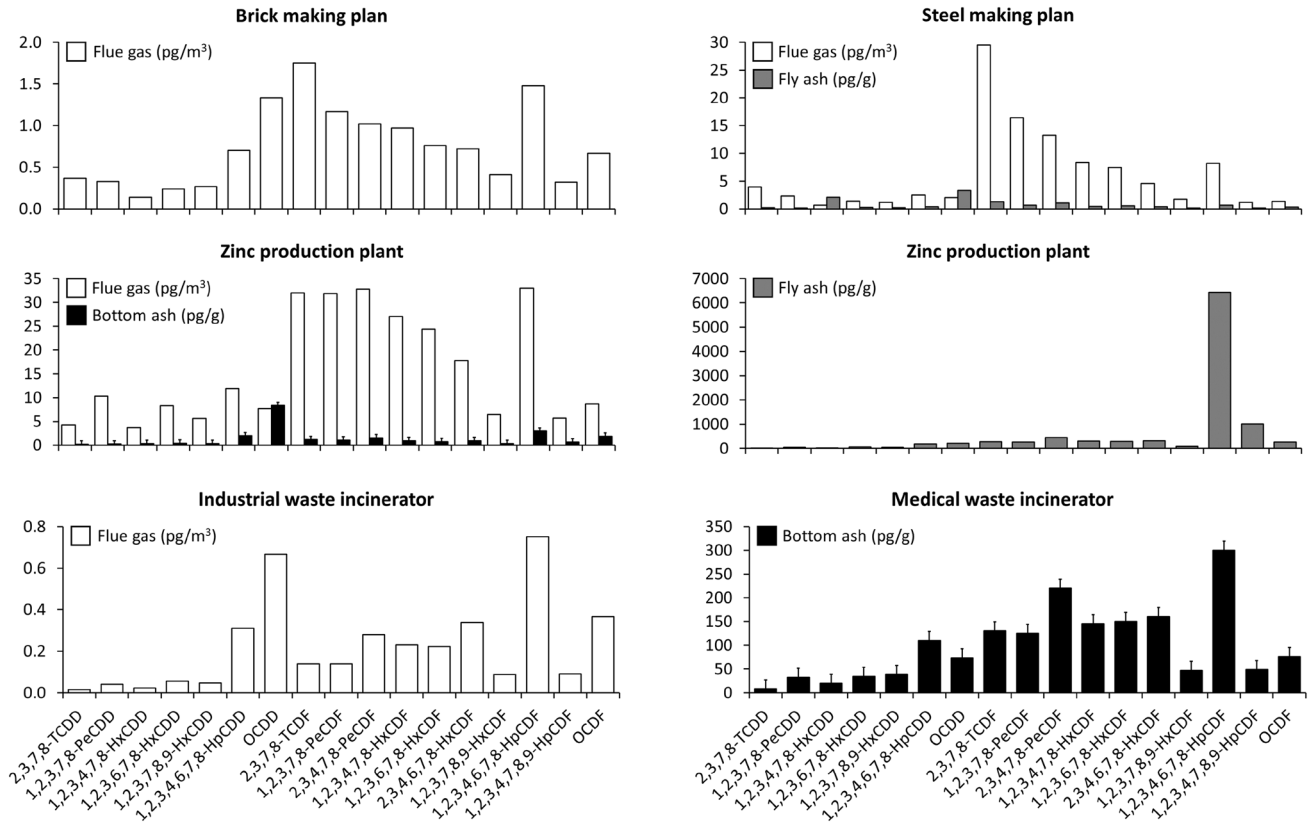


**Fig. 1** Profiles of mass concentrations of PCDD/Fs in the flue gas, fly ash, and bottom ash samples from the investigated industrial sectors. Vertical bars represent the mean PCDD/Fs mass concentrations

Fs congeners. The ratio of PCDFs/PCDDs concentrations is often considered to explore the possible mechanisms of formation of PCDD/F congeners in various industrial processes (Everaert and Baeyens 2002; Anderson and Fisher 2002; Ba et al. 2009a). The ratio of PCDFs/PCDDs in flue gas and ash samples from this study ranged from 2.28 to 6.55 and 0.87 to 15.6, respectively. The ratio of more than one suggests that *de novo* synthesis may be the main mechanism of the formation of PCDD/Fs in metallurgical and waste incineration processes investigated in this study. Ba et al. (2009a) also suggested that the de novo synthesis was major mechanism for PCDD/Fs releases in a secondary zinc smelting plant in China. In addition, temperature and the variations of scrap metal feeds and industrial wastes among plants might account for the differences in congener profiles (Wang et al. 2009). Further studies with larger number of samples are needed to provide a better characterization of emission profile of PCDD/Fs in these industrial facilities.

As for dl-like PCBs, the predominance of non-ortho PCB-126 was observed in most of the samples analyzed in term of both mass concentrations and TEQs (Table 2). This is in agreement with a number of previous studies in some metallurgical process and waste incineration (Nie et al. 2011, 2012a; Yu et al. 2006; Choi et al. 2008). Otherwise, the pattern was different from those reported in a scrap metal processing plant in China, showing the dominance of mono-ortho coplanar congener PCB-105 and PCB-118 (Nie et al. 2012b).

The emission factors and emission amounts in flue gas and fly ash from the investigated industrial plants were estimated based on the TEQs concentrations (for PCDD/Fs and dl-like PCBs), mass concentrations (for PeCB and HCB) and the basic information of the plants, and are given in Table 3. The concept of estimation of emission factor and emission amount was similar to that described in previous studies (Thuong et al. 2014; Hue et al. 2016). The emission factors of PCDD/Fs and dl-PCBs estimated for flue gas samples ranged from 4.8 to 740 ng TEQ/tonne, with the highest value observed for the zinc production plant (Table 3). These values were much lower than those reported in magnesium production, secondary copper and aluminum production in China (Ba et al. 2009b; Nie et al. 2011, 2012a). Emission factor for the zinc production plant in this study was higher than ferrous and zinc foundries, but lower than lead and aluminum plants investigated in Korea (Yu et al. 2006). The emission factors estimated for fly ash and bottom ash were remarkably lower than those in flue gas, ranging from 0.007 to 23.2 ng TEQ/ton. These levels were lower than those

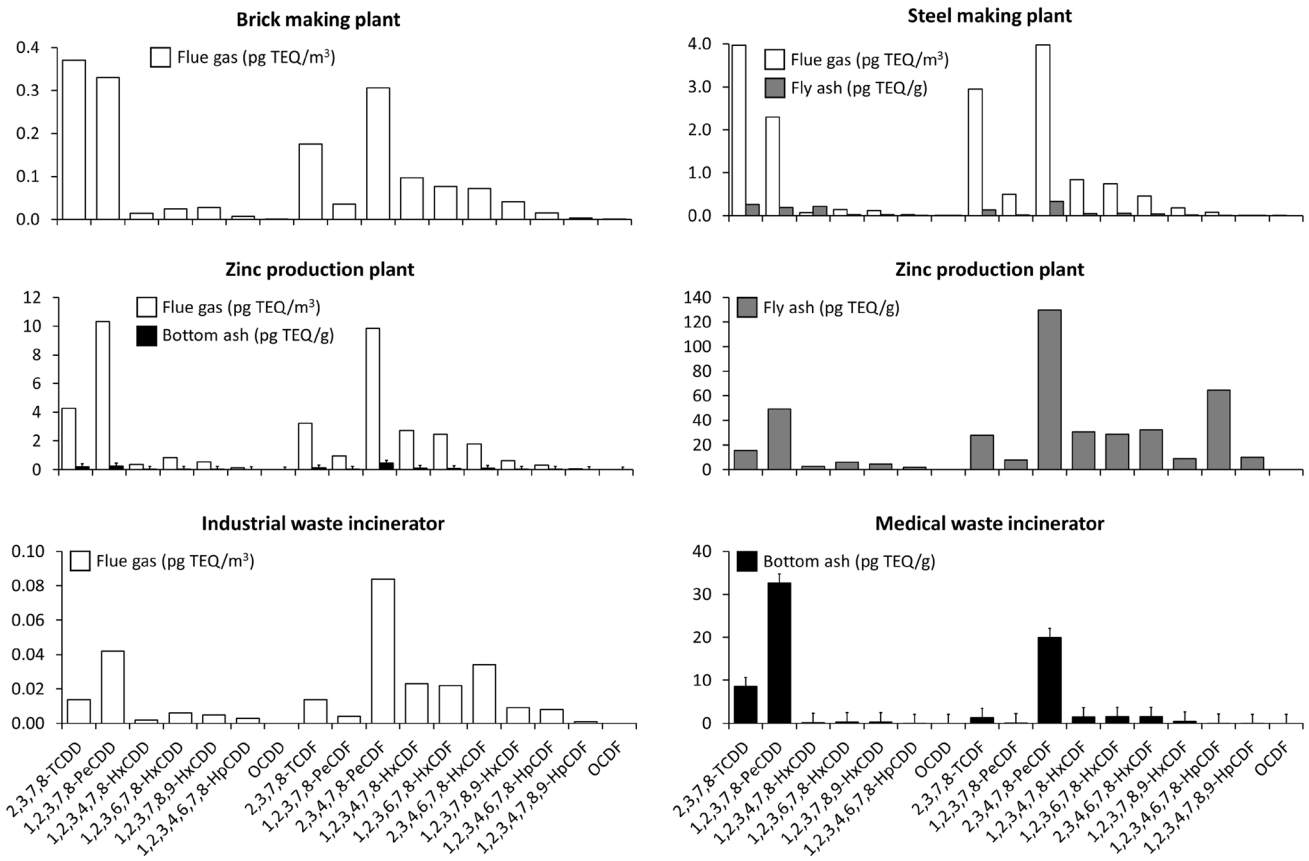


**Fig. 2** Profiles of TEQs concentrations of PCDD/Fs in the flue gas, fly ash, and bottom ash samples from the investigated industrial sectors. Vertical bars represent the mean TEQ concentrations

estimated for fly ash in secondary lead and zinc production in China (Ba et al. 2009a).

Emission factors of PeCB and HCB in the steel production plant were 240.7 and 119.8 µg/ton, respectively (Table 3). These levels were in similar range to the primary copper smelters based on ausmelt smelting furnace and oxygen-enriched side-blown bath smelting furnace, but lower range than the secondary smelters using reverberator in China (Nie et al. 2012a). PeCB and HCB emission factors in this study were also lower than those in magnesium production process in China (Nie et al. 2011). As for ash samples, the emission factors ranged from 0.8 to 2260 ng/tonne for PeCB and HCB, which were substantially lower than those in flue gas. These levels were generally lower than those reported in a coke plant in China, except for bottom ash in the medical waste incinerator. The emission factors for PeCB and HCB in bottom ash from the medical waste incinerator were 716 and 2260 ng/tonne, respectively, which were similar to those reported in the coke plant in China (Liu et al. 2013).

The total emission amounts of U-POPs were also estimated based on the emission factor and yearly activity levels of the investigated industrial plants (Table 3). The emission amounts of PCDD/Fs and dl-PCBs were in the range of 180–5200 µg TEQ/year for flue gas sample; and 1.33–32.22 µg TEQ/year for ash samples. Emissions of PeCB (44.3–11610 mg/year) and HCB (61.35–6225 mg/year) were much higher than those of PCDD/Fs and dl-PCBs. The total TEQs emissions from flue gas of the zinc and steel production plants were in the range to those reported in zinc, lead and primary copper production, but lower than secondary copper and magnesium production plants in China (Ba et al. 2009a, b; Nie et al. 2012a, 2011). The emission of PeCB and HCB from flue gas in this study were still remarkably less than those reported for the magnesium production plant in China (653 and 403 g/year, respectively) (Nie et al. 2011).

In summary, we conducted a preliminary survey to evaluate the levels and patterns and extensions of unintentional emission of PCDD/Fs, dl-PCBs, PeCB and HCB in flue gas and ash samples of some industrial plants in northern Vietnam. Our results are among the first data reported for some industrial processes in Vietnam including zinc production, brick production and medical waste incinerators. The emission potential of these U-POPs was generally in lower or comparable range to those reported for some industrialized

**Table 3** Emission factors and emission amounts of U-POPs from flue gas and ash samples in the investigated industrial sectors from northern Vietnam

| | Emission factor (*) (ng/tonne) | | | | | | | Emission amount (*) (μg/year) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | PCDDs | PCDFs | dl-PCBs | Total PCDD/Fs | Total TEQs | PeCB | HCB | PCDDs | PCDFs | dl-PCBs | Total PCDD/Fs | Total TEQs | PeCB | HCB |
| Flue gas sample | | | | | | | | | | | | | | |
| Brick production plant | 2.2 | 2.336 | 0.265 | 4.535 | 4.8 | – | 11,640 | 83.29 | 88.46 | 10.02 | 170 | 180 | – | 440,900 |
| Steel production plant | 34.18 | 50.26 | 3.332 | 84.44 | 87.77 | 240,700 | 119,800 | 1650 | 2420 | 160 | 4070 | 4234 | 11,610,000 | 5,781,000 |
| Zinc production plant | 240 | 323 | 180 | 565 | 740 | – | 889,300 | 1690 | 2260 | 1250 | 3955 | 5200 | – | 6,225,000 |
| Industrial waste incinerator | 5.76 | 15.92 | 2.72 | 21.68 | 24.4 | 67,120 | 92,960 | 3.802 | 10.51 | 1.795 | 14.310 | 16.1 | 44,300 | 61,350 |
| Fly ash sample | | | | | | | | | | | | | | |
| Steel production plant | 0.004 | 0.003 | 0.0 | 0.007 | 0.007 | 4.85 | 6.9 | 0.658 | 0.607 | 0.066 | 1.265 | 1.33 | 902 | 1280 |
| Zinc production plant | 0.402 | 1.706 | 0.084 | 2.108 | 2.192 | 23.9 | 0.8 | 5.911 | 25.07 | 1.235 | 30.98 | 32.22 | 350 | 11.76 |
| Bottom ash sample | | | | | | | | | | | | | | |
| Zinc production plant | 0.061 | 0.095 | 0.006 | 0.156 | 0.162 | 322 | 89 | 0.9 | 1.389 | 0.088 | 2.289 | 2.377 | 4730 | 1308 |
| Medical waste incinerator | 5.16 | 13.74 | 4.3 | 18.9 | 23.2 | 716 | 2260 | 15.48 | 41.22 | 12.9 | 56.7 | 69.6 | 2150 | 6770 |

*Emission factors and amounts are estimated based on TEQ concentrations for PCDD/Fs and dl-PCBs, and mass concentrations for PeCB and HCB

countries such as China and Korea. However, the contamination of PeCB and HCB were relatively high in some industrial processes such as steel and zinc making. Further comprehensive investigations on various kinds and numbers of industrial plants are needed to provide a basis for national inventory of U-POPs in Vietnam.

**Acknowledgements** The authors wish to acknowledge financial support from the Vietnam National Foundation for Science and Technology Development (NAFOSTED) under the grant number 104.04-2015.45. We also wish to thank the various industrial facilities for their kind cooperation and support for collection of flue gas and ash samples.

## References

Abad E, Martınez K, Caixach J, Rivera J (2006) Polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin-like PCBs in flue gas emissions from municipal waste management plants. Chemosphere 63:570–580

Anderson DR, Fisher R (2002) Sources of dioxins in the United Kingdom: the steel industry and other sources. Chemosphere 46:371–381

Ba T, Zheng M, Zhang B, Liu W, Su G, Xiao K (2009a) Estimation and characterization of PCDD/Fs and dioxin-like PCB emission from secondary zinc and lead metallurgies in China. J Environ Monit 11:867–872

Ba T, Zheng M, Zhang B, Liu W, Xiao K, Zhang L (2009b) Estimation and characterization of PCDD/Fs and dioxin-like PCBs from secondary copper and aluminum metallurgies in China. Chemosphere 75:1173–1178

Broman D, Rolff C, Naf C, Zebuhr Y, Fry B, Hobbie J (1992) Using ratios of stable nitrogen isotopes to estimate bioaccumulation and flux of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in two food chains from the Northern Baltic. Environ Toxicol Chem 11:331–345

Choi KI, Lee SH, Lee DH (2008) Emissions of PCDDs/DFs and dioxin-like PCBs from small waste incinerators in Korea. Atmos Environ 42:940–948

EPA (1994a) Method 1613: tetra-through octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS

EPA (1994b) Method 8121: chlorinated hydrocarbons by gas chromatography-capillary column technique

EPA (2008) Method 1668B: chlorinated biphenyl congeners in water, soil, sediment, biosolids, and tissue by HRGC/HRMS

EPA (2017) Method 23: determination of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofurans from stationary sources

Everaert K, Baeyens J (2002) The formation and emission of dioxins in large scale thermal processes. Chemosphere 46:439–448

Gouin T, Mackay D, Jones KC, Harner T, Meijer SN (2004) Evidence for the ''grasshopper'' effect and fractionation during long-range atmospheric transport of organic contaminants. Environ Pollut 128:139–148

Grochowalski A, Lassen C, Holtzer M, Sadowski M, Hudyma T (2007) Determination of PCDDs, PCDFs, PCBs and HCB emissions from the metallurgical sector in Poland. Environ Sci Pollut R 14:326–332

Hue NT, Thuy NTT, Tung NH (2016) Polychlorobenzenes and polychlorinated biphenyls in ash and soil from several industrial areas in North Vietnam: residue concentrations, profiles and risk assessment. Environ Geochem Health 38:399–411

Li Y, Yang Y, Yu G, Huang J, Wang B, Deng S, Wang Y (2016) Emission of unintentionally produced persistent organic pollutants

(UPOPs) from municipal waste incinerators in China. Chemosphere 158:17–23

Li J, Lv Z, Du L, Li X, Hu X, Wang C, Niu Z, Zhang Y (2017) Emission characteristic of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) from medical waste incinerators (MWIs) in China in 2016: a comparison between higher emission levels of MWIs and lower emission levels of MWIs. Environ Pollut 221:437–444

Liu G, Zheng M, Liu W, Wang C, Zhang B, Gao L, Su G, Xiao K, Lv P (2009) Atmospheric emission of PCDD/Fs, PCBs, hexachlorobenzene, and pentachlorobenzene from the coking industry. Environ Sci Technol 43:9196–9201

Liu G, Liu W, Cai Z, Zheng M (2013) Concentrations, profiles, and emission factors of unintentionally produced persistent organic pollutants in fly ash from coking processes. J Hazard Mater 261:421–426

Ni Y, Zhang H, Fan S, Zhang X, Zhang Q, Chen J (2009) Emissions of PCDD/Fs from municipal solid waste incinerators in China. Chemosphere 75:1153–1158

Nie Z, Zheng M, Liu W, Zhang B, Liu G, Su G et al (2011) Estimation and characterization of PCDD/Fs, dl-PCBs, PCNs, HCB and PeCBz emissions from magnesium metallurgy facilities in China. Chemosphere 85:1707–1712

Nie Z, Liu G, Liu W, Zhang B, Zheng M (2012a) Characterization and quantification of unintentional POP emissions from primary and secondary copper metallurgical processes in China. Atmos Environ 57:109–115

Nie Z, Zheng M, Liu G, Liu W, Lv P, Zhang B et al (2012b) A preliminary investigation of unintentional POP emissions from thermal wire reclamation at industrial scrap metal recycling parks in China. J Hazard Mater 215–216:259–265

Nzihou A, Themelis N, Kemiha M, Benhamou Y (2012) Dioxin emissions from municipal solid waste incinerators (MSWIs) in France. Waste Manag 32:2273–2277

Thuong NV, Nam VD, Hue NTM, Son LK, Thuy NV, Tung HD, Tuan NA, Minh TB, Huy DQ, Minh NH (2014) The emission of polychlorinated dibenzo-p-dioxins and dibenzofurans from steel and cement kiln in Vietnam. Aerosol Air Qual Res 14:1189–1198

Van den Berg M, Birnbaum L, Bosveld AT, Brunstrom B, Cook P, Feeley M et al (1998) Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. Environ Health Perspect 106:775–792

Vietnam technical regulation on emission of industrial waste incinerators (2010) QCVN 30: 2010/BTNMT. Ministry of Natural Resources and Environment Vietnam

Vietnam technical regulation on hazardous waste thresholds (2009) QCVN 07:2009/BTNMT. Ministry of Natural Resources and Environment Vietnam

Vorkamp K, Riget FF (2014) A review of new and current-use contaminants in the Arctic environment: evidence of long-range transport and indications of bioaccumulation. Chemosphere 111:379–395

Wang JB, Hung CH, Hung CH, Chang-Chien GP (2009) Polychlorinated dibenzo-p-dioxin and dibenzofuran emissions from an industrial park clustered with metallurgical industries. J Hazard Mater 161:800–807

Wang M, Liu G, Jiang X, Xiao K, Zheng M (2015) Formation and potential mechanisms of polychlorinated dibenzo-p-dioxins and dibenzofurans on fly ash from a secondary copper smelting process. Environ Sci Pollut Res 22:8747–8755

Yu B-W, Jin G-Z, Moon Y-H, Kim M-K, Kyoung J-D, Chang Y-S (2006) Emission of PCDD/Fs and dioxin-like PCBs from metallurgy industries in S. Korea. Chemosphere 62:494–501

Zhang T, Fiedler H, Yu G, Ochoa GS, Carroll WF Jr, Gullett BK, Marklund S, Touati A (2011) Emissions of unintentional persistent organic pollutants from open burning of municipal solid waste from developing countries. Chemosphere 84:994–1001