

ATMOSPHERIC CONCENTRATIONS OF PCDD/Fs AND PCBs IN A TYPICAL E-WASTE PROCESSING AREA IN CHINA

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Abstract

The objective of this study was to measure the ambient concentrations of PCDD/Fs and PCBs in a typical E-waste processing area of Taizhou, China by a short-term sampling scheme in order to evaluate the environmental pollutions and potential health risks caused by E-wastes processing activities. The average ambient concentrations ranged from 2.914-50.55pg m⁻³ for 17 PCDD/Fs with an average of 14.264 pg m⁻³ and 4232-11352pg m⁻³ for 19 PCBs with the mean value of 7219pg m⁻³. The PCDF congeners contributed dominantly to the total concentrations, which corresponds to the profile of PVC combustion. The I-TEQ values ranged from 0.223 to 3.454 pg TEQ m⁻³ with an average of 1.098 pg TEQ m⁻³. The pollution level was higher than the general trend of urban/industrial sites. The atmospheric chemicals in gas phase and particle phase were analyzed separately. About 94% of total PCDD/Fs (gas + particle) resided in the particle phase, while 96% of total PCBs were observed in the gas phase.

Introduction

Atmospheric transport is the primary distribution pathway for moving semi-volatile organic compounds (SVOCs) via deposition to terrestrial and aquatic ecosystems¹. SVOCs can be distributed between the gas phase and particle phase in the atmosphere. The gas-particle partitioning behaviors affect their transport pathways, degradation mechanisms, deposition processes and mode of entry into food chains². In recent years, researches are focusing their interests on the measuring and predicting the environmental partitioning of SVOCs, including PCDD/Fs. However, few works in China were conducted on the atmospheric concentrations, distribution patterns and gas-particle partitioning of PCDD/Fs in the typical electric wastes (E-wastes) processing areas.

Taizhou situates in the southeast coastline of China. It is famous for productions of automobile, plastic moulds, chemicals and electric appliances. In the 1980s, the dismantling operations of E-wastes emerged and boomed in some towns. The scrap transformers containing polychlorinated biphenyls (PCBs) as dielectric fluids were once dismantled in this area. High levels of PCBs in soil and sediment because of accidental spills or illegal releases have been reported³. Until now, most of E-wastes are still simply dismantled or incinerated openly to remove PVC coating to retrieve valuable metals. These activities may be an important source of PCDD/Fs and have seriously polluted the farmland soil of the area⁴.

In this study, PCDD/Fs and PCBs in the ambient air sampled by high-volume air samplers of the typical E-waste dismantling area in Taizhou were measured to evaluate their concentrations, profiles and gas-particle distributions.

Materials and Methods

The climate of Taizhou belongs to typical sub-tropical monsoon, which is characteristic with rich rainfalls (annual volume from 1480 to 1530 mm) and year-round temperatures from 16.9 to 17.3°C. Sampling site B (121°21.675E, 28°32.755N) situates in the commercial center of the town. Site A (121°21.731E, 28°32.724N) and C (121°21.672E, 28°32.772N) are rural areas and in two residential villages of the town. All the sampling sites are above 10m of the ground surface. The sampling dates, sampling volumes, and meteorological data were recorded during the sampling period and are presented in Tab.1.

Air samples were concurrently collected for about 12 hours during sampling periods using high volume air samplers (Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA) according to US EPA Compendium Method TO-9A. The sampler was equipped with a glass fiber filter (GFF) for sampling particle-bound PCDD/Fs and PCBs, following by a glass cartridge for sampling gas phase chemicals. Prior to sampling, the glass fiber filters (GFF, Whatman, 10.16cm diameter) were baked at 450 °C for 6 hours to remove any organic contaminants. The glass cartridge packed with a polyurethane foam (PUF, 6.3cm diameter, 7.6cm length) plug was extracted with acetone for 24 hours in a Soxhlet apparatus. After cleaning, the sampling cartridges were vacuum-dried in desiccators, wrapped with hexane-rinsed aluminum foil and sealed with polyethylene bags.

Table 1 Meteorological data during sampling campaign.

Sample number	Sampling date	Day or Night	Sampling volume (m ³)	Mean temp. ()	Mean relative Humidity (%)
A1	10/28/05	Day	103.4	22.1	63.7
A2	10/29/05	Night	183.7	18.3	70.5
A3	10/30/05	Day	109.0	16.1	70.8
A4	10/31/05	Night	228.2	16.9	61.7
B1	10/28/05	Day	89.9	24.0	58.8
B2	10/29/05	Night	196.5	19.5	67.1
B3	10/30/05	Day	113.8	17.3	66.8
B4	10/31/05	Night	201.4	16.0	71.2
C1	10/28/05	Day	142.0	23.1	61.8
C2	10/29/05	Night	184.0	18.9	67.3
C3	10/30/05	Day	121.2	16.4	71.2
C4	10/31/05	Night	200.6	17.8	64.6

The air flow rate was specified at $\sim 0.25 \text{ m}^3 \text{ min}^{-1}$ at the beginning of sampling. After sampling, the GFF and PUF plug were wrapped with hexane-rinsed aluminum foil for protection from light, and sealed with double layers of polyethylene bags. After transported to the laboratory, air samplers were stored at -20°C until extraction.

The GFF and PUF samples collected from ambient air were analyzed separately in compliance with revised US EPA Method 1613B and USEPA Method 1668A. Briefly, air samples were spiked with a known amount of $^{13}\text{C}_{12}$ -labeled surrogate standards prior to a 24h Soxhlet extraction with toluene. The extract was subsequently refluxed in hexane and subjected to a multilayer silica gel column, followed by clean-up on basic alumina column and florisil chromatography columns. The detailed clean-up procedure was described elsewhere⁵. Prior to HRGC-HRMS analysis, the exact was spiked with a known amount of $^{13}\text{C}_{12}$ -labeled internal standards to determine the recovery efficiencies.

All of the samples were spiked with labeled compounds to monitor the performance of the method. Field blank and laboratory blank were incorporated in the analytical procedure for the purpose of quality control.

Results and discussion

Both gas and particle phase concentrations were included in these data. The average ambient concentrations ranged from $2.914\text{-}50.55 \text{ pg m}^{-3}$ for $_{17}$ PCDD/Fs with an average of 14.264 pg m^{-3} and $4232\text{-}11352 \text{ pg m}^{-3}$ for $_{19}$ PCBs with the mean value of 7219 pg m^{-3} . It was noted that increasing concentrations of PCDD congeners were characterized with increasing degree of chlorination, and HpCD/F and OCDD/F congeners dominated the atmospheric PCDD/F pattern.

The PCDD/PCDF ratio was calculated since variation in the PCDD/PCDF ratio could be due to differences in local emission sources, meteorological conditions, air mass movement, atmospheric residence times and weathering factors⁶. The PCDD/PCDF ratio was mostly < 1 , probably reflecting the dominating pollution source from incineration of E-wastes as would be expected. The ratios for each sampling event ranged from 0.160 to 2.202 with a mean value of 0.587.

The international TEQ (I-TEQ) for the three sites during sampling period ranged from 0.223 to $3.454 \text{ pg TEQ m}^{-3}$, with an average of $1.098 \text{ pg TEQ m}^{-3}$. The congener 2, 3, 4, 7, 8-PeCDF contributed mostly to the total I-TEQ with an average of 46.2%. Other significant contributors to the total I-TEQ were as follows: 2, 3, 4, 6, 7, 8-HxCDF ($\sim 9.7\%$), 1, 2, 3, 6, 7, 8-HxCDF ($\sim 7.5\%$), 1, 2, 3, 4, 7, 8-HxCDF ($\sim 6.5\%$), 1, 2, 3, 7, 8-PeCDD ($\sim 5.0\%$). The PCDF congeners were not only the major contributors to the total concentrations ($\sim 72\%$), but also to the total I-TEQ ($\sim 84\%$). The former contradicted to previous studies², while the latter was in accordance with reported data⁶.

Lohmann and Jones⁷ discussed that TEQs of PCDD/Fs in the atmosphere are typically as follows: remote $< 10 \text{ fg m}^{-3}$; rural $\sim 20\text{-}50 \text{ fg m}^{-3}$; and urban/industrial $\sim 100\text{-}400 \text{ fg m}^{-3}$. Compared to the above data, the pollution level was higher than the general trend of urban/industrial sites.

The mean concentrations of 2, 3, 7, 8-substituted PCDD/Fs during sampling periods were 13.439 pg m^{-3} ($1.765\text{-}51.452 \text{ pg m}^{-3}$) in particle phase and 0.856 pg m^{-3} ($0.190\text{-}2.994 \text{ pg m}^{-3}$) in gas phase. About 94% of total PCDD/Fs (gas + particle) resided in the particle phase. However, about 96% of total PCBs were observed in the gas phase, with average concentrations of 69312 pg m^{-3} ($4210\text{-}10887 \text{ pg m}^{-3}$) in the gas phase and 287 pg m^{-3} ($23\text{-}718 \text{ pg m}^{-3}$) in the particle phase. It was noted that the 2, 3, 7, 8-PCDDs were more in association with particulates in the atmosphere than the 2, 3, 7, 8-PCDFs. This probably reflects the fact that the vapor pressures of PCDDs were slightly lower than that of the furan

groups⁸. The PCDD/Fs tend to be distributed between the gaseous and particulate phases based on molecular weight⁹. The higher chlorinated congeners with higher vapor pressures were more associated in the particle phase. The 2, 3, 7, 8-TCDD/Fs were mainly in the gas phase. The similar trends were also observed in the congener of PCBs. Clearly, the contribution of PCB congeners in the particle phase increased with increasing chlorine substitution. These results were in agreement with previous studies^{6,10}.

Acknowledgments

This work was financially supported by National Natural Science Foundation of China (20607025 and 40590392), Foundation of State Key Laboratory of soil and Sustainable Agriculture and National Basic Research Program of China (2003CB415001)

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