

POLYCHLORINATED DIBENZO-*P*-DIOXINS AND DIBENZOFURANS IN THE AMBIENT AIR OF SHANGHAI

Yongmei Yu ^{1,2}, Xiaolei He ¹, Xianwei Li ¹

¹Environment & Resources Division, Baosteel Research Institute, Shanghai 201900, China

²Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Introduction

In most European countries, the sintering process is recognized as a significant source of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) emission ⁽¹⁾. In China, there is a limited data concerning dioxins level in the atmosphere, however the recent studies revealed that the primary ferrous ore sintering, secondary lead smelting, and secondary aluminum smelting are the major sources of dioxin emission ⁽²⁾.

The aim of this study is to evaluate the effect of primary ferrous ore sintering on dioxin level in the ambient air of Shanghai. The air samples are collected in three different sites in Shanghai. The obtained PCDD/F congener profiles are presented and compared with the literature data. Additionally, we present the PCDD/F congener profile determined in a local stack flue gas of sinter plant.

Materials and Methods

The ambient air samplings were performed in three different parts of Shanghai (Figure 1). Site A (north-east part of Shanghai) is located in neighbourhood of the sintering plants. Site B (south-west part of Shanghai) is a business center surrounded by high buildings and dominated by heavy traffic. Site C (north-east part of Shanghai) is located near to the East China Sea.

All of the air samplings were performed in March of 2008 and almost at the same meteorological conditions. Southeasterly wind from the East China Sea was predominant during the sampling. The effect of an air mass on PCDD/Fs level measured in the sites A, B and C can be omitted because the site A is located at leeward and in the distance from sites B and C.

Sampling: Air samples were collected by the high-volume TE-1000 sampler (Tisch Environmental, Village of Cleves, OH) according to procedures given in EPA Method TO9A. The sampler was equipped with a Whatman quartz-fiber filter (102 mm diameter,) for collection the particle phase, and a polyurethane foam (PUF, 60 mm x 76 mm) for collection the PCDD/Fs in gas phase. The sampling was performed at the flow rate of 0.225 m³ min⁻¹, approximately. The flow rate was calibrated before and after sampling. Each sample was collected for six to seven consecutive days until the sampling volume reached 2300m³.

The stack flue gas samples, including replicate emission sample and a sampling method blank, were collected isokinetically from the main sinter plant stacks through a heated glass-lined sampling probe according to EPA Method 0023A. The gas-phase was trapped on XAD-2 resin (Supelpak[®]-2, USA) while the particulate was collected by Whatman quartz fiber filter (82.6 mm diameter). Some particulate adsorbed by sampling probe was

also collected by rinsing it with acetone, dichloromethane and toluene. Each stack flue gas sampling was performed for approximately 3 hours. The PUF cartridge and XAD-2 resin were spiked with a known amount of PCDD/F surrogate standards (EPA23 SS, Wellington, Canada) before sampling.

Analytical procedure: The air and stack flue gas samples were analyzed according to EPA Method T09A and EPA 23A. Generally, all the samples were extracted in the Soxhlet apparatus (Universal Extraction System, B-811, BÜCHI, Switzerland) with toluene for 24 hours. The $^{13}\text{C}_{12}$ -labeled PCDD/F internal standards (EPA 23 IS, Wellington, Canada) were spiked to the samples prior to extraction and then were used for measurement of the concentration of the unlabeled native analytes. The toluene extract was concentrated by rotary evaporator up to 0.1 mL and the toluene was replaced to 15 mL hexane. Then the extract was treated with concentrated sulphuric acid. Finally the sample was cleaned-up by multi-layered silica chromatography columns, and basic alumina chromatography column.

The final sample was spiked with known amount of standard spiking solution (EPA23 RS, Wellington, Canada), and analysed by high-resolution gas chromatography combined with high-resolution mass spectrometry (HRGC–HRMS) (Waters AutoSpec Premier, UK) equipped with DB5 ms column (60 m x 0.25 mm x 0.25 μm). The type of injection was splitless, the injection volume was 1 μl , injection port temperature was 280°C, temperature was programmed as follows: 140°C, held for 4 min, increased by 8°C min^{-1} to 220°C, increased by 1.4°C min^{-1} to 260°C, increased by 4°C min^{-1} to 310°C, held for 5min. Helium was used as the carrier gas and the flow rate was 1.0 ml/min. The analyzer mode of the selected ion monitoring with a resolving power at 10000 was used. The electron energy was set to 35 eV, and the source temperature was set to 280°C. All data were analyzed using the software Mass Lynx version 4.0 (Micromass, Manchester, UK).

Results and Discussion

Figure 2 presents the total level of 17 2,3,7,8-chlorine substituted PCDD/Fs determined in the air samples, collected in three different sites of Shanghai. The values on y-axis are normalized and symbolize the level of PCDD/Fs. From Figure 1 it can be seen that the PCDD/Fs are present in all air samples, however the level of PCDD/Fs measured in the site C is much lower in comparison with their level determined in sites A and B. The site B and site A show similar total level of PCDD/Fs, however the site B represent the atmosphere of the business center, while the site A is primary ferrous ore sintering working place.

In order to find what is the main source of dioxins emission into the atmosphere of Shanghai the congeners profiles determined in these three sites were prepared and are shown on Figure 3. Each selected congener was normalized by reference to the total weight of all 2,3,7,8-substituted congeners. From the Figure 3 it can be seen, that the PCDD/F congeners profile determined in the air of site A is similar to those sampled in site B with the OCDF, 1,2,3,4,6,7,8-HpCDF and OCDD (in order of quantity) as the most dominated congeners. Among the PCDD/Fs determined in air of site C dominate the OCDD, 1,2,3,4,6,7,8-HpCDF and OCDF (in order of quantity). From the comparison of the obtained results with the literature data ⁽³⁾ it was found, that the profiles congeners of sites A and B reflect the profile of PCDD/Fs typical for medical waste incineration while the profile

congeners of site C is typical for municipal solid waste incineration(MSWI) and crematoria.

The congeners profiles of 17 PCDD/Fs determined in stack flue gas from sintering plant located in site A is shown in Figure 4. As can be seen the congeners are dominated by the low chlorinated PCDFs, mainly tetra- and penta-such as: 2,3,4,7,8-PeCDF, 1,2,3,4,6,7,8-HpCDF, 2,3,7,8-TeCDF and 1,2,3,7,8-PeCDF (in order of quantity). The profile obtained in this study is very similar to those obtained in stack gas samples taken from sintering plants in Taiwan⁽⁴⁾. It indicates that the obtained congener profiles of the 2,3,7,8-substituted PCDD/Fs can be treated as the signatures of the sinter plants and can be helpful to understand the main source of PCDD/Fs emission in the air of Shanghai. However, the profiles of the PCDD/F congeners determined in the air (Fig 3, site A) and in flue gas of the sintering plant (Fig 4, Site A) are very different. It indicates that, up to now, the primary ferrous ore sintering is probably not the main source of dioxin emission to the atmosphere of Shanghai, although as it was indicated in the literature⁽²⁾ it is the major source of dioxins emission into the environment. However, municipal solid waste incineration and crematoria are important potential sources of dioxin emission. Moreover, diesel-fueled and gas-fueled vehicles should not be neglected owing to the heavy traffic in Shanghai.

Acknowledgements

The authors wish to thank the Director of the Environmental Monitoring Station of Nanhui and the Environmental Engineering Department of East China University of Science and Technology for their support of this piece of work.

References

1. Aries E., Anderson D.R., Fisher R., Fray T. A.T., Hemfrey D. *Chemosphere* 2006,5 ;1470
2. Zhu J., Hirai Y., Yu G., Sakai S., *Chemosphere*, 2008, 70; 703
3. EPA/600/R-01/012, March 2001, Final www.epa.gov/ncea
4. Wang L. C., Lee W. J., Tsai P. J., Lee W. S., Chang-Chien G. P., *Chemospher*, 2003, 50;1123

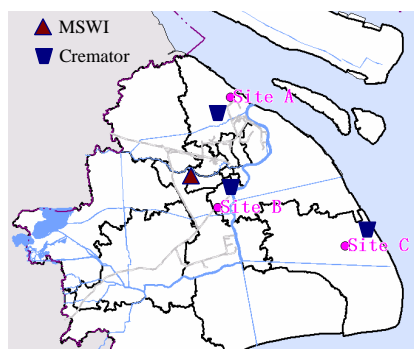


Figure 1 Sampling sites and relevant landmarks in Shanghai.

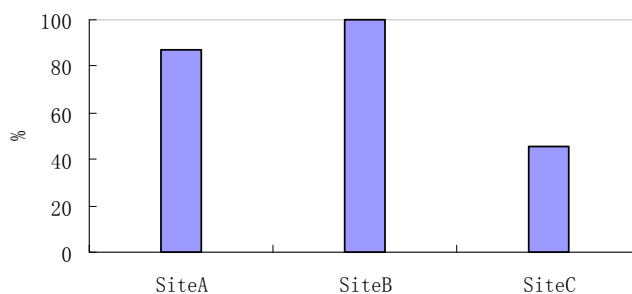


Figure 2 Total level of 17 PCDD/Fs in ambient air of Shanghai

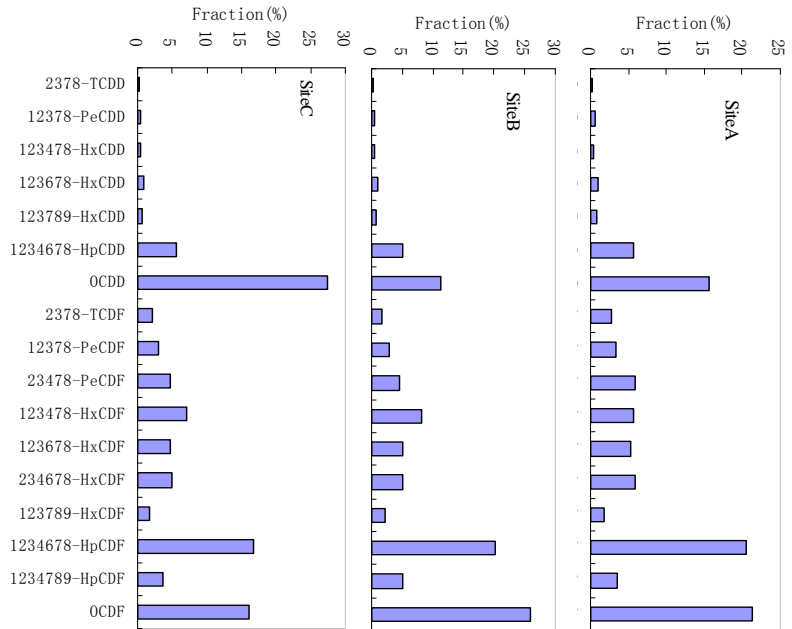


Figure 3 PCDD/F congeners profiles in the ambient air of Shanghai in the sites A, B and C

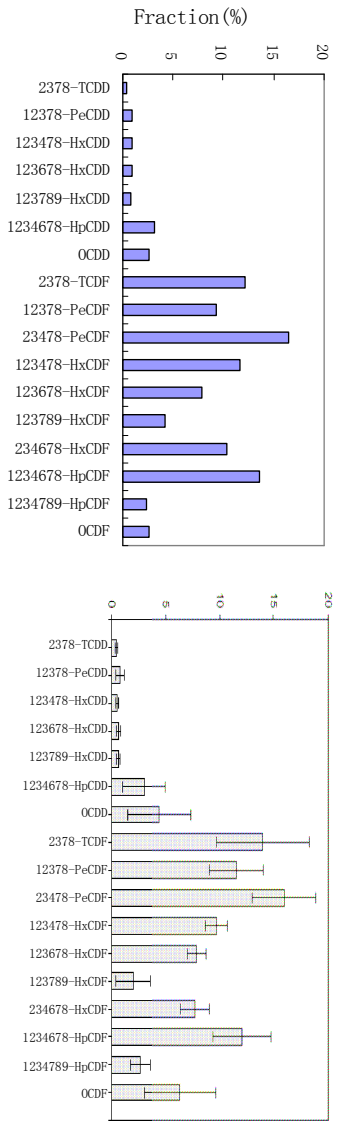


Figure 4 PCDD/F congeners profiles in the stack flue gas of a sinter plant from Site A (this study) and Taiwan⁽⁴⁾