# LEVELS AND CHARACTERISTICS OF PCDD/FS IN CAMPHOR (CINNAMOMUM CAMPHORA) TREE BARK FROM SOUTH JIANGSU, CHINA

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## 1. Introduction

Polychlorinated dibenzo-*p*-dioxin and dibenzofurans (PCDD/Fs) are primarily formed as unintentional by-products of incomplete combustion and chemical processes that involve chloride-containing substances. PCDD/Fs are highly toxic to humans, bioaccumulative in ecosystems and persistent in various environmental compartments.

Atmospheric transport is a primary pathway for the transfer of semi-volatile organic carbons (SVOCs) to terrestrial and aquatic ecosystems via deposition. Therefore, ambient air is often sampled to characterize the PCDD/Fs pollution. Both active and passive samplers have been used to collect ambient air. Active sampler methods have weakness of high-cost, short sampling period and electricity requirement. Passive sampler methods have been widely applied to conduct atmospheric environment study on a regional scale. However, passive sampling lasts weeks to months and is unable to capture the chemicals in the particulate phase. In contrast, particulate POPs can bioaccumulate in the vegetation by wet and dry deposition. Tree bark is easy and inexpensive to sample. As a result of high lipid content and large surface area, tree bark allows them being used as a good passive sampler for lipophilic POPs with high $K_{OW}$ values, even when present at low atmospheric concentrations. Furthermore, life-time of tree barks usually ranges from 3 to 5 years; thus, bark acts as an integrating sampler during this period. Therefore, tree bark has been widely used to monitor different inorganic and organic pollutants, such as heavy metal, salts, PAHs, OCPs, PCBs, PBDEs and PCDD/Fs.

Jiangsu is one of most rapidly developing provinces in China, the south of which is distributed with high and new technology industry parks including IT, new material and pharmaceutical industries. With high-speed economic development and urban expansion, the environment undergoes severe pollution especially for the atmosphere. Therefore camphor tree bark was used in this study as a biomonitor to investigate the levels and profiles of PCDD/Fs at South Jiangsu Province.

## 2. Materials and methods

### 2.1 Sampling

Ten sampling sites located as illustrated in Fig.1 were chosen to represent different cities across the studied region. Camphor tree barks of ~10 $cm^2$ were chiseled from each tree at a height of 1.5 m above the ground level. The camphor trees were chosen without moss and lichens surrounded. The bark samples were then wrapped in aluminum foils and carried to the lab. All of the samples were stored at −20ºC until chemical analysis.

### 2.2 Analytical procedures

Before the pretreatment, the tree bark was freeze-dried and grinded. And then approximately 18 g of tree bark

was extracted in ASE with 50% *n*-hexane in acetone. In the meantime, 3 g diatomite and 5μL EPA 1613 LCS (Wellington Laboratories Inc.) were added in the extraction cell. The extract was then filtered with 10 g $Na_2SO_4$ and concentrated and exchanged into 15 ml hexane. 3 g $MgSiO_3$ was then added and frozen for half an hour. Afterwards, the extract was subject to re-filtration with 3g $Na_2SO_4$, concentration, multilayer silica column and activated carbon impregnated silica column purification sequentially. 0.5 ml final elution by rotary evaporation was concentrated under gentle nitrogen flow followed by addition of $^{13}C$-labelled isotope standards (EPA 1613 ISS, Wellington Laboratories Inc.), and then the concentrated extracts were diluted to 50 ml with *n*-decane and transferred to a PTFE sealed vial for instrument analysis.

Fig. 1 Map of sampling sites in South Jiangsu

PCDD/Fs was determined using HRGC-HRMS (Agilent 6890N/Waters Autospec Ultimate NT) equipped with a DB-5MS capillary column (60 m long, i.d. 0.25 mm, film thickness 0.25μm) in EI mode at 650 MA ionization current and 8 kV ionization accelerate voltage with a mass resolution of >10000. Recovery of the labeled standards ranged from 20% to 97% for tetra- to octa- CDD/Fs which all fall within the acceptable ranges set by HJ 77.2-2008 method.

## 3. Results and discussion

### 3.1 Atmospheric PCDD/Fs concentrations

The toxic equivalent (TEQ) concentrations (pg I-TEQ/(g•dw)) of PCDD/Fs of the ten samples covering six cities across South Jiangsu are displayed in Fig. 2. The results indicated that all the 2,3,7,8-substituted congeners were detected in these samples with a total TEQ concentration ranging from 5.55 to 12.2 (average: 7.20). The air samples from site #5 had the highest level of all sampling sites, which may be attributed to flue gas emissions from Shagang Group nearby. The mass loadings (pg /(g•dw)) of all samples ranged from 418 to 938 with an average concentration of 635. The levels of PCDD/Fs in South Jiangsu air did not exhibit obvious spatial variation between suburb, residential and industrial areas. The reason is possibly due to that the air on this regional scale mixed completely and thus the airborne PCDD/Fs characteristics in urban area differed slightly from that of suburban site. The PCDD/Fs concentrations in Nantong are lower than Wuxi in general which may result from differences in level of economic and industrialized development. Air samples from other cities are limited so as not to do such comparisons. The levels of PCDD/Fs in tree bark have been reported in previous studies and shown in Table1. The PCDD/Fs concentrations found in this study were 2 times lower than that of e-waste dismantling area in China, but much higher than the background level and of the same magnitude as the concentrations in industrial areas reported overseas. The comparisons indicated that the tree bark as a biomonitor have accumulated amount of PCDD/Fs.

### 3.2 Homologues and congeners profiles of PCDD/Fs

Relative abundance of homologues of PCDD/Fs in tree bark samples (*n*=10) were calculated and displayed in Fig. 3. The data were all normalized to the summation mass of total homologues. Generally, the concentrations

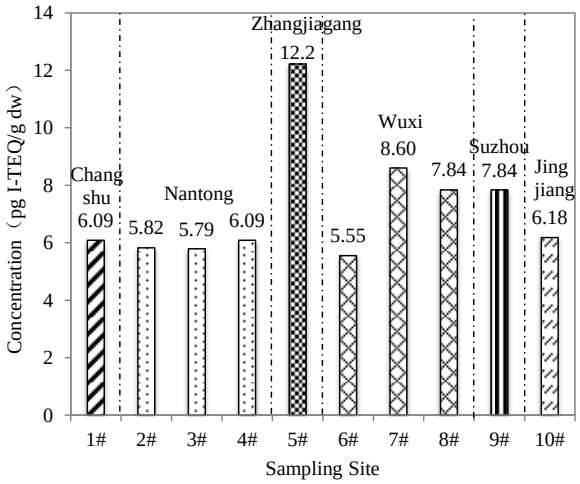



Fig. 2 TEQ concentration of PCDD/Fs at each sampling site

of PCDF homologues in tree bark samples were higher than those of PCDD homologues with the same degree of chlorination, except for OCDD and OCDF. Similar profiles were observed for all sites which were characterized by the decreased concentration with increased degree of chlorination, except for OCDD. Among seventeen 2,3,7,8-substituted PCDD/Fs congeners, the main contribution to total PCDD/Fs mass followed this trend: OCDD (26.7%)>1,2,3,4,6,7,8-HpCDF(14.6%)>2,3,7,8-TCDF(8.9%)>OCDF(7.8%)>2,3,4,7,8-PeCDF(7.4%). As for the PCDD/Fs TEQs in tree bark, 2,3,4,7,8-PeCDF contributes to 43.0% of the total I-TEQ followed by 2,3,7,8-TCDF(10.4%),2,3,7,8-TCDD(9.9%),1,2,3,6,7,8-HxCDF(7.3%) and 1,2,3,4,7,8-HxCDF(7.3%).

Table 1 Comparison with worldwide levels of PCDD/Fs in tree bark samples (dry weight, pg/g)

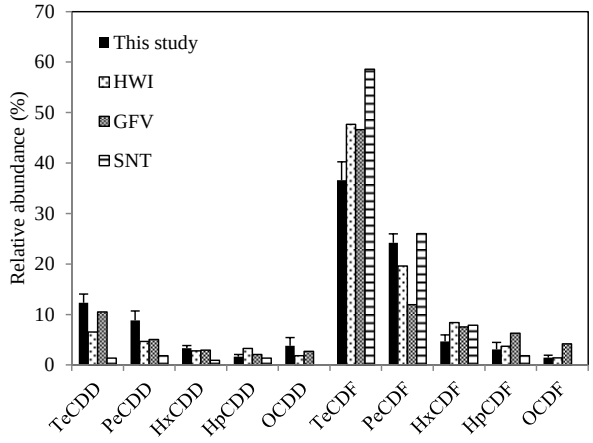
| Site, Country | ΣPCDD/Fs[a] | I-TEQ | References |
|---|---|---|---|
| South Jiangsu, China | 418-938 (635)[b] | 5.55-12.2 (7.20) | This study |
| Luqiao District, China | $1.8\times10^3$ | 22.8 | [1] |
| Park Ridge, Illinois, USA | $232.0\times10^{3c}$ | | [2] |
| Rhine Valley, Germany | 392-1420 | 3.9-17.8 | [3] |
| Kabul, Afghanistan | <2 | | [4] |

Note:[a] sum of total PCDD/Fs (tetra- to octa-CDD/Fs); [b]average value; [c] pg/g lipid weight.

### 3.3 Potential emission sources of PCDD/Fs

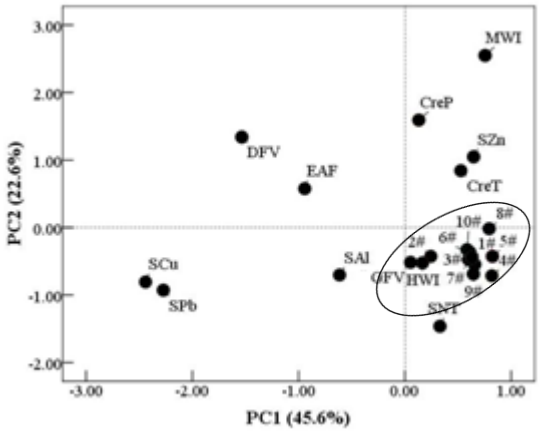
Incineration processes has been approved to be the main sources of atmospheric PCDD/Fs in urban areas, which can be further classified into stationary and mobile incinerations, respectively. Stationary industrial sources consisting of waste incineration, iron and steel and secondary nonferrous metal production are the major contributors of PCDD/Fs in China. Mobile emission sources include fuel combustion from vehicles. The profiles of all samples are found to have no significant difference (T test, $p>0.05$) and the $\sum C_{PCDDs}/\sum C_{PCDFs}$ ratios were universally lower than 1.0, which indicated that the homologue profiles enriched in PCDFs and can be grouped as “source ” dominant type. Compared to the typical source profiles of PCDD/Fs (shown in Fig. 3), we found that the homologue profiles in tree bark are similar to those of hazardous waste incineration (HWI), gas-fueled vehicles (GFV) and sintering machine (SNT). To identify the possible pollution sources for all selected tree barks as indicatives of ambient environment, their PCDD/Fs homologue profiles together with that obtained from facilities of the four investigated types of stationary and mobile emissions sources were analyzed by PCA by using the mass fractions of tetra- to octa- homologues as variables. Figure 4 presents the score plot from PCA, which factor 1 explains 45.6% of the total variance, while factor 2 explains 22.6% of the total variance. The data

points with similar homologue profiles were closely located, while those which had divergent patterns were located further apart. The score plot reveals that the data points of the ten samples and those of HWI, GFV and SNT were closely located that suggests the homologue profiles were similar to each other and were different from those of other facilities. Since the homologue profiles of all samples exhibit typical characteristics as those associated with heat processes such as fossil fuel combustion, combined with the field investigations we extrapolate that HWI and GFV may be two of main emission sources for atmospheric PCDD/Fs in South Jiangsu.




Note: error bar is standard deviation of total ten samples.

Fig. 3 Relative abundance of PCDD/Fs homologues in tree bark samples




HWI-hazardous waste incineration, MWI-municipal waste incineration CreP-panel cremator, CreT-trolley cremator, SNT-sinterer, EAF- electric arc furnace, SPb-Secondary Pb, SAl-Secondary Al, SCu-Secondary Cu SZn-Secondary Zn, DFV-diesel fuel vehicle, GFV-gas fuel vehicle

Fig. 4 Score plot from PCA

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