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RESEARCH ARTICLE

PCDD/Fs accumulation in pine needles: variation with species and pine needle age

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Abstract Pine needles have been used for many decades as a cheap and convenient biosampler to monitor atmospheric levels of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), collectively known as PCDD/Fs. However, it is unknown whether accumulation of PCDD/Fs varies according to pine tree species or pine needle age, which hampers the precise application of this biosampler. We collected 0.3–2.3-year-old pine needles from four different species of pine at three sites in Hangzhou City, Zhejiang Province, China. The PCDD/Fs were quantitatively analyzed by gas chromatography high-resolution mass spectrometry. The results show that *Pinus massoniana* and *Cedrus deodara* absorbed more PCDD/Fs than *Pinus thunbergii* and *Pinus parviflora* at the same site. More cuticular wax and cuticular cell secretions in the pine needles from *P. massoniana* and *C. deodara*, as observed by scanning electron microscopy (SEM), might explain this discrepancy. The PCDD/Fs concentrations in 0.3-, 1.3-, and 2.3-year-old pine needles, indicated that concentrations increase with ascending age. This may be ascribed to the enhancement of lipids and cuticular waxes with age in pine needles as indicated by the lipid contents and morphologies observed by SEM. Our results may be useful for selecting the species and age of pine needles used for biosampling, especially for monitoring PCDD/Fs in large areas where the pine species growing in one place may differ from those in another place.

Keywords Pine needles · Species · Age · PCDD/Fs

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), collectively known as PCDD/Fs, are the most important persistent organic pollutants, and they have been listed in the Stockholm Convention on Persistent Organic Pollutants due to their high toxicity, global distribution, and bioaccumulation in animal and human bodies. Most PCDD/Fs are initially formed during the combustion of fossil fuels and are then emitted into the air (Weber et al. 2011). Therefore, monitoring PCDD/Fs in the air is a key issue for controlling the dispersal of these compounds into other environmental compartments, such as water and soil, etc. Generally, PCDD/Fs in the air are collected by using an active sampler, and then, they are isolated and measured using chemical treatments and gas chromatography high-resolution mass spectrometry (GC-HRMS). An active sampler can acquire an airborne sample in a short time, and the subsequent analyses yield a direct quantitative concentration of PCDD/Fs. Compared to active samplers, passive samplers are easier to use and are suitable for sampling over large areas. Although the data collected by passive samplers differs from those by active samplers, they are indicative of the air concentrations of PCDD/Fs and are comparable between samples (Kylin et al. 1994). During the past three decades, many plants and vegetables such as pine needles, mosses, tree barks, and lichens have been used as passive samplers to identify pollution sources and to measure global and regional contamination levels of persistent organic pollutants (Tremolada et al. 1996; Holoubek et al. 2000; Thomas et al. 2002; Augusto et al. 2013). For example, Thomas et al. (2002) monitored PCDD/Fs using a native pasture sward, and Safe et al. (1992) monitored PCDD/Fs of wood-preserving chemicals using pine needles. Accumulation of organic pollutants in plants is due to their uptake of pollutants from the atmosphere (Calamari et al. 1991). The cuticular wax in the plant, especially leaf wax, considered to play a very important role in the absorption process (Simonich and Hites 1995).

Pine needles are the most commonly used biosamplers because of their high lipid content and their wide geographical distribution. They had been used for monitoring PCDD/Fs, polychlorinated biphenyls, and other chlorinated organic compounds in the environment (Safe et al. 1992; Kylin et al. 1994; Strachan et al. 1994; Ok et al. 2002; Hanari et al. 2004; Bochentin et al. 2007; Wyrzykowska et al. 2009; Falandysz et al. 2012). To monitor PCDD/Fs in the atmosphere, Ok et al. (2002) studied pine needle samples collected from 30 points in five cities in South Korea between 1998 and 1999, and Bochentin et al. (2007) studied 25 Scotch pine needle samples collected at various sites across Poland between October 21 and 27, 2002. Chen et al. (2012) reported PCDD/Fs concentrations in pine needles in 38 cities in China. The results showed that the concentrations related to industrialization and meteorology of the cities. These studies contributed to the prospective use of pine needles as biosamplers. However, whether PCDD/Fs accumulation differs with pine's species, needle age remains unclear, and it hampers the precise application of this biosampler.

The aim of this study was to investigate the amount of PCDD/Fs in pine needles of different ages from four species. We collected pine needles from *Pinus thunbergii*, *Pinus massoniana*, *Cedrus deodara*, and *Pinus parviflora* in Hangzhou City. The concentrations of PCDD/Fs were measured using GC-HRMS. We also analyzed the lipid and heavy metal contents and observed the physical structure of the pine needles to explain their accumulation of PCDD/Fs. We determined whether accumulation of PCDD/Fs in pine needles differs with leaf age or pine species and defined a reference criteria for selecting which pine species and which pine needle age to employ as a biosampler.

Experimental

Chemicals and standards

Solvents, including dichloromethane, hexane, methanol, acetone, and toluene, were American Chemical Society (ACS) certified grade and obtained from Honeywell Burdick & Jackson (Morristown, NJ, USA). Silica gel (70–230 mesh) and the basic alumina used in the cleanup procedure purchased from Merck (Darmstadt, Germany). Standards of $^{13}C_{12}$-labeled PCDD/Fs purchased from Cambridge Isotope Laboratories Inc. (MA, USA).

Sampling

Four different species of pine needles, *P. thunbergii*, *P. massoniana*, *C. deodara*, and *P. parviflora* were collected from July 19 to 25, 2014 at three sampling sites in Hangzhou City. The three sites were the suburb of Hangzhou Botanical Garden, the suburb of Yuquan Campus at Zhejiang University, and a site around a municipal waste incinerator plant (MWIP) of Qiaosi, in the urban area of Hangzhou (Fig. S1). The age of the pine needles defined by using the method described in our previous work (Chen et al. 2012). Generally, pine bud shoots appear in March and April in these areas; therefore, they are a quarter of 1-year-old when they are collected in July. Accordingly, 2- and 3-year-old pine needles were exactly 1.3 and 2.3 years old. Twenty samples from the upper canopy were collected at approximately 1.5–4.0 m above the ground and from different sides of the tree. The pine needles were cut off with scissors, and those of the same age were mixed to form a representative sample. The samples were wrapped in aluminum foil that had been baked at 450 °C for 5 h before use and stored at −20 °C until further analysis. The detailed sample locations and ages are summarized in Table 1.

Sample preparation and instrumental analysis

Pine needle samples were washed, freeze-dried, and pulverized using the procedure described in our previous work (Chen et al. 2012). We performed the cleanup procedure for PCDD/Fs analysis in accordance with the US Environmental Protection Agency (EPA) Method 1613. The sample preparation and GC-HRMS conditions for PCDD/Fs analysis detailed in the Supporting Information.

Elemental analyses

The contents of C, H, and N of the dried pine needles were measured with an Elementar Vario EL III elemental analyzer (Hanau, Germany). The concentrations of nutrient elements and heavy metals in the washed and grounded samples were analyzed using an Agilent 7700 series inductively coupled plasma mass spectrometer (ICP-MS). Sample preparation for ICP-MS analysis described in detailed in the Supporting Information.

Lipid content in pine needles

Approximately 5 g of pine needles were Soxhlet extracted with toluene to determine the lipid content. The extract condensed to

Table 1 Sampling locations and characterization of the pine needles

Sample site[a]	Age (year)	N[b]	C (dw%)	H (dw%)	N (dw%)	H/C	N/C	Extract (dw%)
Cedrus deodara								
MSW plant	0.3	4	46.90	6.11	1.42	1.55	0.03	3.45
MSW plant	1.3	4	48.19	5.81	1.60	1.44	0.03	5.02
Yuquan	0.3	4	47.24	5.72	1.44	1.44	0.03	3.62
Yuquan	1.3	4	48.38	5.64	1.31	1.39	0.02	4.88
Garden	0.3	5	47.05	6.21	1.34	1.57	0.02	3.26
Garden	1.3	5	48.22	5.58	1.41	1.38	0.03	4.92
Garden	2.3	3	48.31	5.67	1.42	1.40	0.03	5.31
Pinus thunbergii								
Yuquan	0.3	5	44.88	5.44	1.15	1.44	0.02	3.92
Yuquan	1.3	4	49.74	5.33	0.92	1.28	0.02	5.62
Garden	0.3	4	45.36	5.21	1.21	1.37	0.02	3.63
Garden	1.3	4	51.28	5.47	1.40	1.27	0.02	5.49
Garden	2.3	5	50.96	5.82	1.17	1.36	0.02	5.73
Pinus parviflora								
Yuquan	0.3	4	48.62	5.44	1.63	1.33	0.03	3.72
Yuquan	1.3	5	51.25	5.94	1.49	1.38	0.02	5.67
Garden	0.3	5	49.54	5.32	1.54	1.28	0.03	3.33
Garden	1.3	5	50.20	5.67	1.50	1.35	0.03	4.75
Pinus massoniana.								
Yuquan	0.3	5	48.62	5.90	1.10	1.45	0/02	2.87
Yuquan	1.3	4	49.19	6.09	1.12	1.48	0.02	4.58
Garden	0.3	4	49.16	5.68	1.21	1.38	0.02	2.43
Garden	1.3	4	49.76	5.66	1.03	1.35	0.02	4.67

[a] Yuquan (Yuquan Campus of Zhejiang University): latitude N 30° 21′, longitude E 120° 16′; garden (Hangzhou Botanical Garden): latitude N 30° 15′, longitude E 120° 06′; municipal waste incinerator plant (MWIP) of Qiaosi): latitude N 30° 15′, longitude E 120° 07′

[b] The number of samples collected and then mixed to yield the representative samples

1 mL by rotary evaporation and then dried to a constant weight under nitrogen gas. The lipid content was calculated as the percentage of dry sample weight (dw, Table 1).

Scanning electron microscopy of pine needles

A JSM-6360LV scanning electron microscope (SEM; JOEL, Tokyo, Japan) was used to observe the stomata and epidermic cells. We calculated the density of the stomata and the area of each stoma pore using the grid on the SEM photograph of the needles (Table S3 in the Supporting Information). The pretreatment method described in detail in the Supporting Information.

Results and discussion

Bulk characterization of pine needles

The ability of PCDD/Fs to absorb to pine needles, either via a gas-to-solid or a solid-to-solid process, is dependent on the environmental conditions (e.g., temperature and wind) and pine needle characteristics (e.g., age, wax content, surface area, lipid content, composition, and architecture) (Paterson et al. 1990). Although the microclimate may vary at each sampling site, we assumed that the air temperature and wind were similar at Hangzhou Botanical Garden and the nearby site at Yuquan Campus at Zhejiang University (Fig. S1). Therefore, pine needle characteristics might be a more important influence on the absorption behavior of PCDD/Fs.

The bulk organic chemical compositions of the pine needles listed in Table 1. The C, H, and N contents of the pine needles as dw percentages were 44.88–51.28, 5.21–6.21, and 1.27–1.57 %, respectively. There were no pronounced differences in the C, H, and N contents between the four species of pine needles. The H/C atomic ratios of all samples were 1.27–1.57. These results demonstrate that the chemical compositions of the four species of pine needles collected from three sites were more or less similar, with only a narrow range of variation. Notably, for each species, there were no significant differences in atomic ratios of H/C for 0.3-, 1.3-, and 2.3-year-old pine needles.

Slight differences in organic chemical composition between the four species of pine needles were observed between one pair of *C. deodara* and *P. massoniana* and another pair of *P. thunbergii* and *P. parviflora*. The former pair had a higher H/C ratio than the latter pair, indicating that *C. deodara* and *P. massoniana* contain different lipids or wax-like substances than *P. thunbergii* and *P. parviflora.*

The concentrations of nutrient elements and heavy metals (Mg, K, P, Cu, Ni, Cd, and Zn) changed little between species and ages (Table S1). The concentrations of K and P decreased with age, which is consistent with the results from Lamppu and Huttunen (2003). However, the Mn concentrations varied between the sampling sites, whereby the Mn concentrations in samples from the university campus and the MWIPs were less than those from the botanical garden. This might be due to the increased Mn leaching from the soil caused by an increased SO_4 deposition at the more polluted campus and MWIP (Devisser 1992). Overall, the concentrations of nutrient elements and heavy metals (except Mn) in the pine needle samples occurred within a narrow range, suggesting that they may not significantly affect concentrations of PCDD/Fs.

The lipid contents of the pine needles differed from the trend for the atomic ratios of H/C. The lipid contents were similar between the four species but differed with age. The lipid contents increased from 3 to 4 % in 0.3-year-old needles and from 4 to 5 % in 1.3-year-old needles. This discrepancy might significantly affect the absorption of hydrophobic compounds into the pine needles. The various lipids in pine needle include phospholipids, terpenoids, flavonoids, lignans, and shikimic acid (Ketchie et al. 1987). Tricyclic diterpenes are specific lipids in conifer needles. Detailed chemical compositions of lipids in our samples will be examined in a future study.

Morphology of pine needles

The morphological characteristics of the pine needles, including stomata location, stomata density, epidermic cells in the epidermis, and extracellular secretions from the epidermis are presented in the Supporting Information. In summary, wax and extracellular secretions adhered to both the upper and lower epidermis of *C. deodara* and *P. massoniana*. All stoma of these species were full of wax and extracellular secretions, with some even overflowing from the stoma outlets (Figs. S19, S21, S27, and S29). However, we observed less wax and cellular secretions on the lower epidermis of *P. thunbergii* and on the upper epidermis of *P. parviflora*. The more wax and extracellular secretions in needles of *C. deodara* and *P. massoniana* than in needles of *P. thunbergii* and *P. parviflora* coincides with the results given by the atomic ratio of H/C. The wax and extracellular secretions adhering to the epidermis increased with ascending age for all four species, which is consistent with the lipid contents of the pine needles.

PCDD/Fs concentrations in pine needles with varying age and species

The total concentrations of PCDD/Fs and 17 2,3,7,8-chlorine-substituted congeners are listed in Table S2. PCDD concentrations for all ages and all pine species were 3.92–95.19, 6.53–69.46, and 59.96–115.91 pg/g (dw) for the three sites of Hangzhou Botanical Garden, Yuquan Campus of Zhejiang University, and MWIP, respectively; whereas the PCDF concentrations in those pine needles were 3.51–42.74, 11.57–60.60, and 119.98–230.02 pg/g (dw), respectively. The above concentrations corresponded to 0.35–7.54, 1.88–8.39, and 17.59–28.47 TEQ pg/g dw (World Health Organization toxic equivalents). The PCDD/Fs concentrations increased in the order Hangzhou Botanical Garden < Yuquan Campus of Zhejiang University < MWIP, which is reasonable because the anthropogenic activities and PCDD/Fs emissions also decreased in this order. This result supports the conclusion made by Chen et al. (2012) that pine needles are good biosamplers. They studied the PCDD/Fs concentrations in the pine needles from 38 cities in China and found that the PCDD/Fs varied over three orders of magnitude and related well to the air pollution in the cities (Chen et al. 2012).

The total concentrations of 17 2,3,7,8-chlorine-substituted congeners in four species of pine needles from Hangzhou Botanical Garden are listed in Fig. 1 For 0.3-year-old pine needles, the concentration order is *P. thunbergii* < *P. parviflora* < *P. massoniana* < *C. deodara.* The PCDD/Fs concentrations in pine needles from Yuquan Campus of Zhejiang University also followed this order (Fig. 2).

Regarding 1.3-year-old pine needles from Hangzhou Botanical Garden, the concentrations of Σ2,3,7,8-PCDD/Fs in the pair of *P. massoniana* and *C. deodara* were significantly different to that of *P. thunbergii* and *P. parviflora*, which in each pair were not different. However, *P. massoniana* and *C. deodara* contained almost twice the PCDD/Fs than *P. thunbergii* and *P. parviflora.* We also found the same trend for the four species of pine needles taken from Yuquan Campus of Zhejiang University (Fig. 2). Similar concentrations of PCDD/Fs in *P. massoniana* and *C. deodara* pine needles are significant because these species distributed widely in China can act as biosampler.

Most pine needles wither after 2 or 3 years of growth. We therefore only collected 2.3-year-old pine needles of *P. thunbergii* and *C. deodara* from Hangzhou Botanical Garden (Fig. 1). The concentrations of Σ2,3,7,8-PCDD/Fs were 70.7 and 129.5 ng/g, respectively. Similar to the 1.3-year-old needles, the concentration of Σ2,3,7,8-PCDD/Fs in *C. deodara* was almost double that of *P. thunbergii.* We found that with increasing age of pine needles from a given species, the concentrations of PCDD/Fs increased almost linearly (Figs. 1 and 2). The older pine needles accumulated more PCDD/Fs than the younger pine needles. This phenomenon also observed by Di Guardo et al.

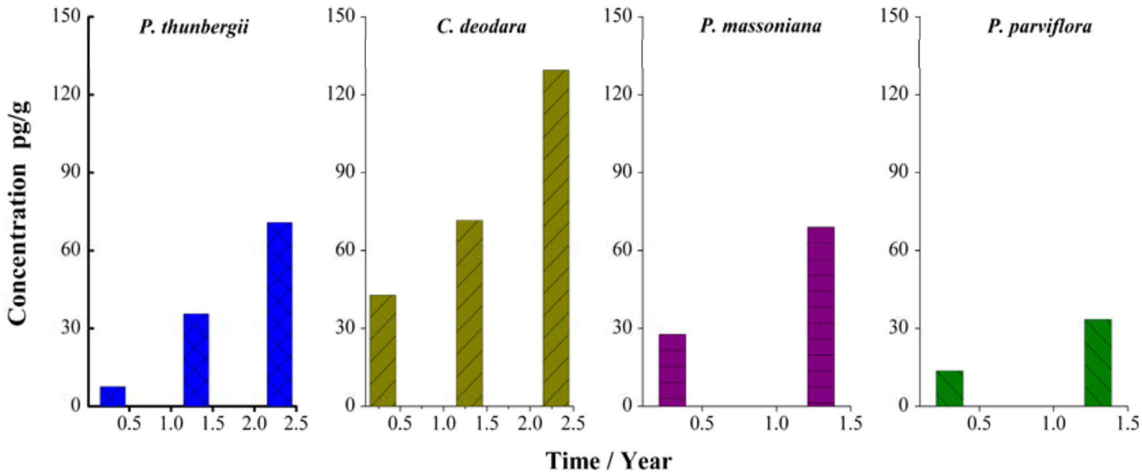

Fig. 1 The PCDD/Fs contents of pine needles from Hangzhou Botanical Garden (pg/g dry weight)

(2003) for dichlorodiphenyltrichloroethane (DDT) concentrations in pine needles of different ages.

To examine the variation in PCDD/Fs in pine needles from the Botanical Garden and the university campus with species and age, we excluded the differences in meteorological conditions between the samples because these two sites are close to each other (Fig. S1). The physical characteristics and chemical composition of the pine needles should be taken into account. The stomatal density and the area of stomatal pores in the epidermis are key controllers for CO_2 to enter pine needles for photosynthesis, and therefore, they closely relate to the partial pressure of CO_2. The stomatal parameters for our samples listed in Table S3. The area of stomatal pores increased in the order *P. thunbergii* < *P. massoniana* < *C. deodara* < *P. parviflora*, which differs from the order of the PCDD/Fs concentrations. The stomatal density and the area of the stomatal pores did not seem to affect the absorption of PCDD/Fs into pine needles.

SEM micrographs show that the stomata of *C. deodara* and *P. massoniana* were almost full of wax and lipids (Figs. S21, S27, and S29). These materials also accumulated on the edges of stomata of *C. deodara.* In comparison, the stomata of *P. thunbergii* and most stomata of *P. parviflora* were empty of these materials. There were more secretions and waxes on the upper and lower epidermis of *C. deodara* and *P. massoniana* needles than that on *P. thunbergii* and *P. parviflora* (Figs. S6, S8, S12, and S14). This explains why *C. deodara* and *P. massoniana* contained higher concentrations of PCDD/Fs than *P. thunbergii* and *P. parviflora*. Epicuticular wax consists of long-chain polyesters and monoterpenes that may act as a reservoir for PCDD/Fs (Hiatt 1998; Reischl et al. 1989; Keymeulen et al. 1995).

The varied number of resin channels in pine and spruce needles used to explain the variation in DDT concentrations (Di Guardo et al. 2003). Based on the SEM micrographs, the number of resin channels did not explain the PCDD/Fs concentrations in needles from the different species (Figs. S33, S31, S32 and S33).

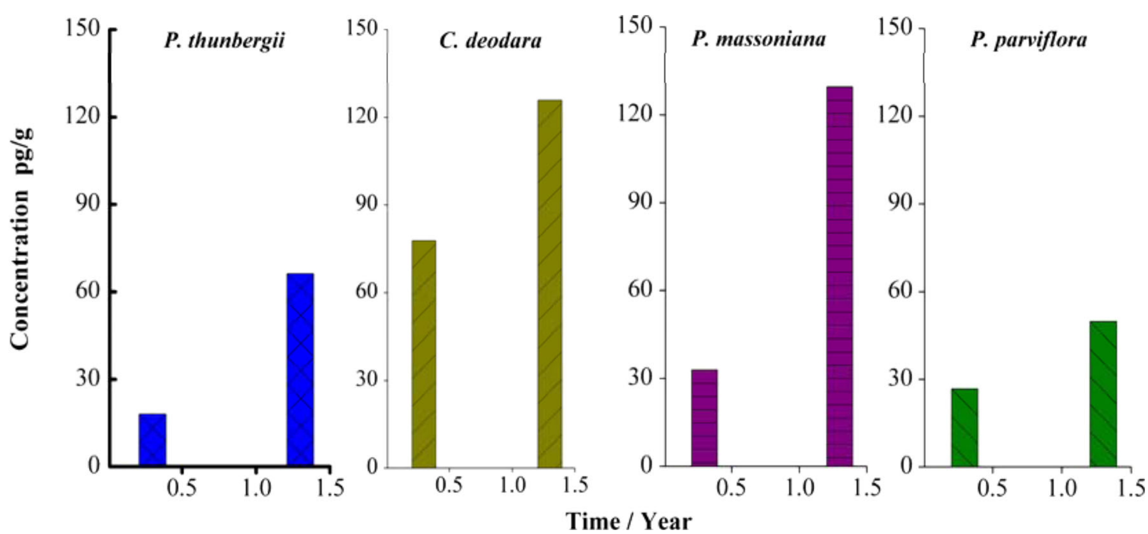

Fig. 2 The PCDD/Fs contents of pine needles from Yuquan Campus (pg/g dry weight)

The C, H, and N contents represent the bulk chemical compositions of pine needles; therefore, they may not be as sensitive to variation as the wax measurements. However, the small difference in atomic ratio H/C between one pair, *C. deodara* and *P. massoniana*, and the other pair, *P. thunbergii* and *P. parviflora*, can explain the variation in PCDD/Fs between the species.

The mobile nutrients and heavy metals may significantly affect the longevity of pine needles but not the concentrations of PCDD/Fs in pine needles. The reasons are as follows: (1) Pine needle longevity may largely influence needle mass but does not affect the wax and lipid content, whereas the wax and lipid content did affect the PCDD/Fs concentrations in the needles. (2) Needle longevity may not be very pronouncedly different from the samples because the concentrations of mobile nutrients and heavy metals occurred within a narrow range in our samples (Table S1).

The increasing PCDD/Fs concentration in pine needles with age would be related to the accumulation of cuticular wax and extracellular secretion, which increased the lipid contents and the time for absorption. The cuticular wax and lipid contents were higher for the 1.3-year-old pine needles than 0.3-year-old needles based on the SEM images (Figs. S2 and S3).

The lipid and cuticular wax represent different components of pine needles. Only some waxes were extracted with toluene. It seems that cuticular waxes are a more suitable proxy than lipids to indicate the absorption capacity of pine needles. Böhme et al. (1999) also reported that PCDD/Fs may accumulate in non-extractable lipids, such as in cutins. Nevertheless, the cuticular wax in pine needles cannot be quantified as readily as the lipids.

Integrating all of the aspects mentioned above, we reach the following conclusions. (1) PCDD/Fs absorption occurs on the surface of pine needles. Interior processes, as evidenced by stomatal density and area, may not be involved in this process. (2) Based on their absorption capacity of PCDD/Fs, pine needles are useful biosamplers for PCDD/Fs. (3) The PCDD/Fs concentrations varied with pine needle species, but they all increased with pine needle age.

The concentration and relative percentage profiles of 17 2,3,7,8-chlorine-substituted congeners in pine needles are shown in Figs. 3 and S35. The concentration of congener profiles are more or less similar (Fig. 3), except for the 1.3-year-old samples from the MWIP site due to the PCDD/Fs emissions. The relative percentage profiles of each species, as shown in Fig. S35, resemble each other. High octachlorodibenzodioxin (OCDD) and low values of other congeners coincide with congener profiles of soil samples near MWIP in Hangzhou, indicating the origin of combustion and photodegradation in the air (Yan et al. 2008).

The slight changes in congener percentage profiles between pine needle species can be found in Fig. S35A and B. The phenomena may be ascribed to the differences in PCDD/Fs distributing equilibrium between air and pine needle or to the degradation of PCDD/Fs in the pine needles. The low-chlorinated PCDD/Fs with high octanol-air partition coefficients (K_{oa}) will readily reach equilibrium, whereas high-chlorinated PCDD/Fs with low K_{oa} need time to reach equilibrium (Bakker et al. 2001). The K_{oa} may change with species and age; therefore, we may anticipate slight variations in the congener profile. Variation in the degree of degradation and loss of low-chlorinated PCDD/Fs by photochemical reactions can result in slight changes of congener percentage profiles between samples.

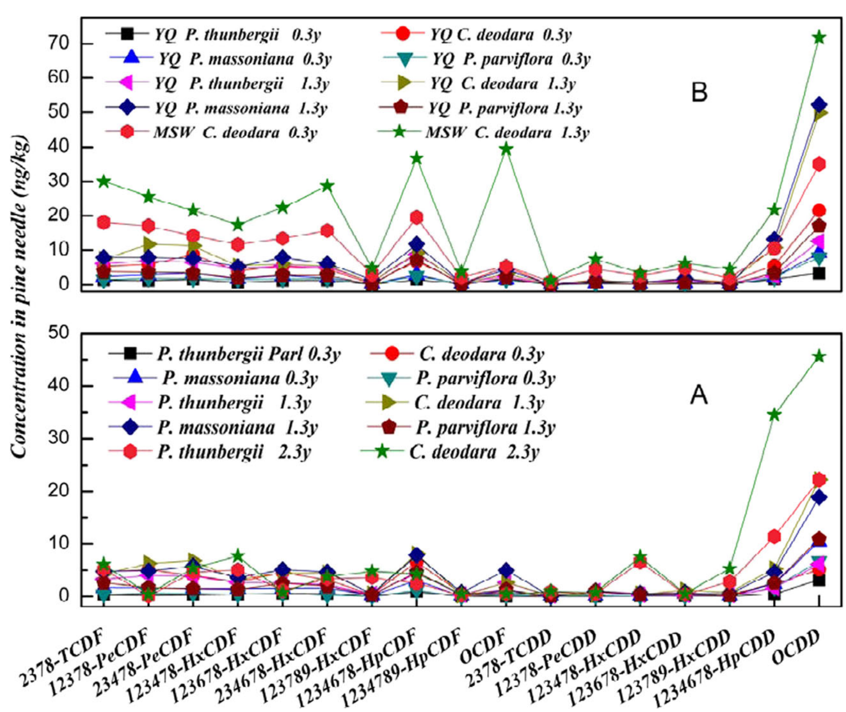

Fig. 3 Congener profiles of PCDD/Fs in pine needles from Hangzhou Botanical Garden (**a**) and Yuquan Campus/municipal waste incinerator plant (MWIP, **b**)

In fact, the concentrations of PCDD/Fs of pine needles increased with age, implying that degradation is limited and that absorption of PCDD/Fs had not reached a maximum. We may infer that the absorption capacity of PCDD/Fs in pine needle is large and that pine needles may be an appropriate biosampler for PCDD/Fs. The 2- or 3-year-old pine needles may be preferred according to the balance between withering age of pine needles and PCDD/Fs concentration.

Conclusion

We found that accumulation of PCDD/Fs varied with pine tree species or pine needle age. In terms of the same species, concentrations of PCDD/Fs of different year-old pine needles increased with ascending age. This indicates that absorption of PCDD/Fs into pine needle may take a long time to reach equilibrium.

At the same age, the *P. massoniana* and *C. deodara* absorbed similar amounts of PCDD/Fs and more than *P. thunbergii* and *P. parviflora* at the same site. The difference in cuticular wax and cuticular cell secretions in the pine needles observed by SEM might explain the discrepancy (Figs. S2–S33). Relative congener distributions of PCDD/Fs in the four species of pine needles were more or less similar, indicating no selective absorption occurring in the different pine needles. The above results may be useful for selecting the species and age of pine needles that are useful for biosampling, especially for monitoring PCDD/Fs in large areas where the species of pine growing in one place may differ from those in another place.

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