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PCDD/F LEVELS IN PINE NEEDLES SAMPLED FROM DALIAN, CHINA

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are typical persistent organic pollutants (POPs) covered by the "Stockholm Convention on Persistent Organic Pollutants", which was signed by the China government in May of 2001. For non-polar semivolatile compounds, intake from the air is the most important process for the uptake of organics in plant leaves[1,2]. Pine needles can be used as passive samplers to investigate the air pollution of POPs[2-8].

Dalian is a seaside city situated in north latitude 38°43'N-40°10'N and east longitude 120°58'-123°31'. The main industries at Dalian include shipbuilding, chemical engineering, locomotive building, tourism, exhibition and software. It is the purpose of this study to evaluate the atmospheric levels of PCDD/Fs at Dalian using pine needles as passive samplers.

Materials and Methods

Sampling. In the urban area of Dalian, 16 sampling points were selected. In addition, a sampling point at an island that is about 100 km away from Dalian and was considered as a less-polluted area, was also included. The sampling time was May 2001. One-year-old pine (*Cedrus deodara*) needles were sampled and stored at -20°C until further analysis.

Analysis: Using commercial heat insulant plastic bags, the pine needles were transferred to laboratory by airlines, where the standard PCDD/Fs analysis method[9] was followed for PCDD/F analysis. Briefly, $^{13}C_{12}$-labeled internal standards were spiked before extraction that was carried out using chloroform/toluene by a shaker. The extract was passed over anhydrous sodium sulfate to remove water. Purification of the extract was performed using a sandwich-column, an alumina-column, and a florisil-column in turn. The eluent was concentrated to about 1 ml and then the recovery standard was added. The final extract was concentrated to ca. 10 µl. Quantification was performed on a HRGC/HRMS by tracing the two most abundant signals of the isotope cluster of the molecular ions.

Results and Discussion

The sampling points were selected to characterize four typical regions in the urban area of Dalian, which are scenic areas (S10, S16), residential areas (R1, R3, R4, R11, R14, R15), areas with heavy traffic (T2, T5-T9, T12, T13) and a less-polluted remote area (L17). The analytical results show that

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there are no large variations for the levels of the 2,3,7,8-substituted PCDD/Fs among the 17 sampling points.

Table 1. The pine needle levels of 2,3,7,8-substituted PCDD/Fs at three typical locations (Toxic Equivalents (TEQ) is based on the toxic equivalency factors developed by the World Health Organization[14])*

Compounds	R1	R14	S16
2,3,7,8-T_4CDD	0.19	0.55	n.d.
1,2,3,7,8-P_5CDD	0.40	0.68	n.d.
1,2,3,4,7,8-H6CDD	0.13	0.36	n.d.
1,2,3,6,7,8-H6CDD	0.17	0.55	n.d.
1,2,3,7,8,9-H6CDD	0.15	0.36	n.d.
1,2,3,4,6,7,8-H7CDD	0.98	2.50	0.60
O_8CDD	3.33	12.50	4.44
2,3,7,8-T4CDF	1.56	2.95	0.58
1,2,3,7,8/1,2,3,4,8-P5CDF	1.31	2.50	0.38
2,3,4,7,8-P5CDF	1.27	2.73	0.36
1,2,3,4,7,8/1,2,3,4,7,9-H6CDF	0.92	2.73	0.31
1,2,3,6,7,8-H6CDF	0.96	2.73	0.38
1,2,3,7,8,9-H6CDF	n.d.	0.11	n.d.
2,3,4,6,7,8-H6CDF	0.92	2.27	0.49
1,2,3,4,6,7,8-H7CDF	2.08	5.68	1.02
1,2,3,4,7,8,9-H7CDF	0.17	0.43	0.13
O_8CDF	0.83	2.73	1.27
TEQ (WHO 1998, Humans)	1.79	4.09	0.40

* n.d. not detectable.

The PCDD/F levels at the two sampling points, S16 and L17, are relatively low, which is consistent with the fact that S16 stands for a scenic area and L17 is located at a remote island. Although the other scenic site S10 locates in the Dalian Forest Zoo, it is not far from the main entrance of the Zoo where there are heavy traffic and many residential buildings. Thus the PCDD/F levels for S10 are not as low as for locations S16 and L17. The pollution levels for the locations R1, R4, T5, T7, S10, and T12 are comparable and relatively low. The regions characterized by the sampling points T8, T13 and R14 may be relatively heavily impacted by pollution. Around the sampling point T8, there are a thermoelectricity plant, a diesel engine plant, and a wastewater treatment plant. Thus it is reasonable that the PCDD/F levels are high in this location. The sampling points T13 and R14 locate in the downtown characterized by extremely heavy traffic. The levels of 2,3,7,8-substituted PCDD/Fs at three typical locations, R1, R14 and S16, are shown in Table 1.

Both $\sum T_4$-O_8CDDs and $\sum T_4$-O_8CDFs for the samples collected at Dalian are significantly lower than corresponding levels for pine needles sampled from pentachlorophenol wood-preserving sites in the USA[10]. The $\sum T_4$-O_8CDD/Fs levels in the pine needles sampled from Dalian are all less than 205 ng/kg (dry weight), and lower than the corresponding levels in spruce needles collected from industrial, urban, rural, waste landfill and highway areas in Germany[11]. In addition, the levels of PCDD/F congeners in the spruce needles of Germany[11] were typical of a combustion pattern in which $\sum T_4$-O_8CDFs is generally equal or greater than the $\sum T_4$-O_8CDDs; the dominant PCDDs are H_6-O_8CDDs, whereas the dominant PCDF congeners are the T_4-P_5CDFs. Generally, the patterns of 2,3,7,8-substituted PCDD/Fs for the pine needle samples collected at Dalian are similar to the pattern for the spruce needles in Germany[11]. The only discrepancy is that for the Dalian pine needles samples, $\sum T_4$-P_5CDD congeners are dominant. The PCDD/Fs in Dalian should mainly come from coal or fuel burning for thermoelectricity, domestic heating, and various vehicles.

The ratios of plant to air concentrations lead to a pseudo-plant/air partition coefficient (K_{PA}) with the unit of pg/g. For polychlorinated biphenyls (PCBs), linear relationships between logK_{PA} and logarithms of octanol/air partition coefficient (logK_{OA}) for *Pinus sylvestris* were established[6]. Supposing that the relationships are true for *Cedrus deodara* and can be extrapolated to PCDD/Fs, the K_{PA} values for PCDD/Fs between *Cedrus deodara* and air can be calculated using the K_{OA} values estimated previously[12] at the typical temperature of 10°C in Dalian. The estimated K_{PA} values for selected 2,3,7,8-substituted PCDD/Fs are listed in Table 2. As K_{PA} increases with the degree of chlorination, higher chlorinated PCDD/F congeners tend to partition into the pine needle phase strongly.

Table 2. The estimated K_{PA} values for selected 2,3,7,8-substituted PCDD/Fs

PCDD/F congeners	K_{PA} (m^3/g)
2,3,7,8-T_4CDD	70-145
1,2,3,7,8-P_5CDD	113-295
1,2,3,4,7,8-H_6CDD	176-563
1,2,3,6,7,8-H_6CDD	184-598
1,2,3,7,8,9-H_6CDD	172-541
1,2,3,4,6,7,8-H_7CDD	257-983
O_8CDD	425-2058
2,3,7,8-T_4CDF	76-163
1,2,3,7,8/1,2,3,4,8-P_5CDF	124-335
2,3,4,7,8-P_5CDF	129-356
1,2,3,4,7,8/1,2,3,4,7,9-H_6CDF	207-716
1,2,3,6,7,8-H_6CDF	212-741
1,2,3,7,8,9-H_6CDF	206-708
2,3,4,6,7,8-H_6CDF	216-759
1,2,3,4,6,7,8-H_7CDF	256-977
1,2,3,4,7,8,9-H_7CDF	340-1479
O_8CDF	535-2884

Based on the K_{PA} values, the air levels of 2,3,7,8-substituted PCDD/Fs were estimated. Recently, Park and Kim[13] reported on PCDD/F concentrations in Korean atmosphere. In comparison, the maximal estimated air levels in Dalian of the 2,3,7,8-substituted PCDD/Fs are lower than in the residential areas of Korean cities, except for 2,3,7,8-T_4CDD/Fs, for which the maximal estimated air levels in Dalian are comparable with the corresponding values in the residential areas of Korean cities.

Conclusions

It is the first time in China to investigate the atmospheric PCDD/Fs levels using pine needles as passive samplers. Compared with other regions in the world, the PCDD/F levels in the pine needles and air from the urban area of Dalian are low. The PCDD/Fs in Dalian atmosphere are mainly emitted from various coal or fuel combustion processes.

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References

1. Keymeulen, K., Görgényi, M., Héberger, K., Priksane, A., Langenhove, H. V., 2001. Atmos. Environ., 35: 6327-6335.
2. Hiatt, M. H., 1998. Anal. Chem., 70: 851-856.
3. Holoubek, I., Křínek, P., Šeda, Z., Schneiderová, E., Holoubková, I., Pacl, A., Tříska, J., Cudlín, P., Čáslavský, J., 2000. Environ. Pollut. 109: 283-292.
4. Simonich, S. L., Hites, R. A., 1995. Environ. Sci. Technol., 29: 2905-2914.
5. Tremolada, P., Burnett, Y., Calamari, D., Jones, K. C., 1996. Environ. Sci. Technol., 30: 3570-3577.
6. Ockenden, W. A., Steinnes, E., Parker, C., Jones, K. C., 1998. Environ. Sci. Technol., 32: 2721-2726.
7. Hiatt, M. H., 1999. Environ. Sci. Technol., 33: 4126-4133.
8. Thompson, T. S., Treble, R. G., 1995. Chemosphere, 31: 4387-4392.
9. Schramm, K.-W., Henkelmann, B., Kettrup, A., 1995. Water Res. 29, 2160–2166.
10. Safe, S., Brown, K. W., Donnelly, K. C., Anderson, C. S., Markiewicz, K. V., McLachlan, M. S., Reischl, A., Hutzinger, O., 1992. Environ. Sci. Technol., 26: 394-396.
11. Reischl, A., Reissinger, M., Thoma, H., Hutzinger, O., 1989. Chemosphere, 18: 561-568.
12. Chen, J. W., Harner, T., Schramm, K. -W., Quan, X., Xue, X. Y., Wu, W. Z., Kettrup, A., 2002. Sci. Total Environ., 300:155-166.
13. Park, J. S., Kim, J. G., 2002. Chemosphere, 49: 755-764.
14. Van den Berg, M., Birnbaum, L., Bosveld, B.T.C., Brunstrom, B., Cook, P., Feeley, M., Giesy, J. P., Hanberg, A., Hasegawa, R., Kennedy, S. W., Kubiak, T., Larsen, J. C., van Leeuwen, F. X. R., Liem, A. K. D., Nolt, C., Peterson, R. E., Poellinger, L., Safe, S., Schrenck, D., Tillitt, D., Tysklind, M., Younes, M., Waern, F., Zacharewski, T. 1998. Environ. Health Perspect., 106, 775–792.