# PROFILE OF PCDD/Fs AND PCBs IN FOREST SOIL

Takakuwa H, Sugiyama N, Matsuda M, Kawano M, Wakimoto T, Morita M
Department of Environment Conservation, Ehime University, Tarumi 3-5-7, Matsuyama, 790-8566, Ehime, Japan

**Abstract**

A study was carried out to determine the concentration profile of PCDD/Fs and PCBs with the depth in forest soil. Forest soil mainly forms three horizons in a descending order, as follows of O including L and H, A and B horizons. The samples of fresh leaves and soil in each horizon were collected in forest and analyzed for PCDD/Fs and PCBs. In almost all fresh leaves and L samples, the order of concentration was PCBs > PCDFs > PCDDs. While, in all H, A and B samples, the order of concentration was PCBs > PCDDs > PCDFs. PCDD/Fs and PCBs were detected at highest concentration in H sample in most cases. The composition of higher chlorinated PCDD/Fs congener seemed to be increased from L to A horizons. Particularly, the composition of PCDDs was critically changed between L and H horizons. PCBs also showed same profile as PCDD/Fs change from L to H horizons. This profile suggests that lower chlorinated PCDD/Fs and PCBs might be disappeared.

**Introduction**

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) have attracted social concern as persistent organic pollutants (POPs) because of their toxicity, bioaccumulation and persistence in the environment. Although, at present in Japan, their emission has been decreased by the strict regulation by the government, relatively large amounts of PCDD/Fs emitted in the past are still remained in the environment. Particularly, it was known that soil is a major reservoir for POPs due to its high storage capacity[1,2,3], and half-lives of PCDD/Fs in soil are the order of ten years or more[4]. And it has been reported that the concentration of PCDD/Fs in suburban forest is in similar concentration in city soil in Matsuyama[5], but forest hasn't been disturbed by human activity. From here onwards, it seemed worthy to know the extent of contamination and distribution of these compounds in forest soil to understand the behavior and fate of PCDD/Fs in soil environment.

PCBs were also analyzed because these compounds are of similar physico-chemical properties and can be a source of PCDFs and DL-PCBs. Samples used for analysis included fresh leaves on the trees because they contribute to absorption/deposition of PCDD/Fs and PCBs from the atmosphere resulting in an accumulation in fallen leaves. Forest soil is formed by three horizons in surface. A top O horizon consists of fallen leaves and partially decomposed organic debris and it is further subdivided into L horizon and H horizon. L horizon consists of fallen leaves and H horizon lying just under L horizon consists of well humified matters. A horizon lying under O horizon consists of accumulation of humified organic matter mixed with the mineral material. B horizon lying under A horizon consists of mineral materials characterized by enrichment in organic matter, sesquioxides, or clay, or development of soil structure. Fig.1 shows soil horizon in forest soil analyzed in this study.

**Materials and Methods**

The target compounds of this study were tetra- to octa- chlorinated PCDD/Fs and tri- to deca- chlorinated PCBs. Samples were collected at six locations in August 1999, six locations in August 2000, three locations in August 2006 in an experimental forest attached to Ehime University, Matsuyama, Japan. In each location, samples were collected and analyzed for fresh leaves on the trees and fallen leaves (L horizon), H horizon (2-5 cm depth), A horizon (5-15 cm depth) and B horizon (more than 30 cm depth).

Clean-up was performed by referring analytical procedure manual for dioxin in soil by Japanese environment agency (2000) as below. Each sample (20-150 g) was treated with HCl (2 N) for 1 h, and then extracted with 500 ml toluene using soxhlet extracter. The extract was cleaned up with multilayer silica gel column chromatography in a descending order, as follows of 10% $AgNO_3$-silica gel (3 g), silica gel (0.5 g), 44% $H_2SO_4$-silica gel (3 g), silica gel (0.5 g), 2% KOH- silica gel (0.5 g), silica gel (0.5 g). After silica gel chromatography, active carbon-dispersed silica gel reversible column chromatography was used for further purification. In addition to these clean-up procedure, clean-up of leaves and L and H horizon samples were achieved using dimethyl sulfoxide partitioning and/or alumina column chromatography. The cleaned-up samples were analyzed using

HRGC/HRMS (Agilent 6890 Series/JEOL JMS 800D) at a resolving power of 10000.

**Results and Discussion**

PCDD/Fs and PCBs were detected in all analyzed samples. Table 1 shows PCDD/Fs concentration determined in samples collected in August 1999 and 2000. Table 2 shows PCDD/Fs and PCBs concentration determined in sample collected in August 2006. In almost all leaves and L horizon samples, the order of concentration was PCBs > PCDFs > PCDDs. And in all H, A, and B horizon samples, the order of concentration was PCBs > PCDDs > PCDFs. Fig.2 show comparison of PCDD/Fs concentrations detected from H and A horizon samples in this study with the reported data of forest soil in foreign countries[6,7,8,9,10]. TEQs were calculated based on I-TEF (1988) in order to compare with the values in literatures. From figure, it is thought that contamination levels of these compounds in Matsuyama forest is similar to these of other foreign countries reported so far.

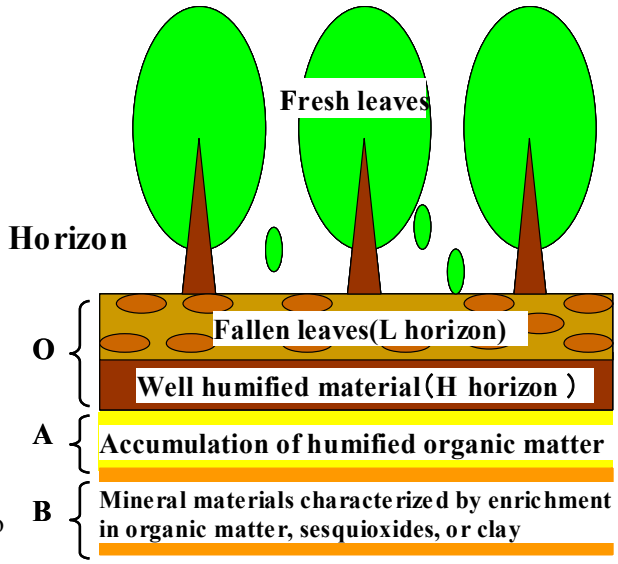


**Fig. 1** Horizon in forest soil

**Table 1** Concentrations of PCDD/Fs in fresh leaves and forest soil collected in August 1999 and August 2000 (pg/g dry-weight)

| | leaves (n=12) | | | L horizon (n=12) | | | H horizon (n=12) | | | A horizon (n=12) | | | B horizon (n=12) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Max. | Min. | mean | Max. | Min. | mean | Max | Min | mean | Max | Min | mean | Max | Min | mean |
| PCDDs | 73.1 | 8.28 | 29.9 | 142 | 68.6 | 120 | 1550 | 74.9 | 735 | 990 | 34.6 | 380 | 204 | 8.26 | 53.2 |
| PCDFs | 108 | 20.4 | 47.8 | 252 | 42 | 142 | 713 | 43 | 356 | 170 | 16.8 | 1000 | 44.2 | 0.674 | 12.5 |
| PCDD/Fs | 164 | 31.8 | 77.6 | 417 | 112 | 262 | 2150 | 118 | 1090 | 51.4 | 1190 | 480 | 231 | 10.9 | 65.7 |
| TEQ* | 2.3 | 0.24 | 0.86 | 4.82 | 0.95 | 2.75 | 15.6 | 1.05 | 8.24 | 5.54 | 0.43 | 2.6 | 1.03 | 0.326 | 0.426 |

*For the calculation of TEQs, WHO TEFs (1997) for PCDD/Fs were used.

**Table 2** Concentrations of PCDD/Fs and PCBs in fresh leaves and forest soil collected in August 2006 (pg/g dry-weight)

| | leaves | | | L horizon | | | H horizon | | | A horizon | | | B horizon | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| PCDDs | 98.6 | 40.2 | 27.6 | 134 | 98.1 | 94.5 | 1350 | 1680 | 1800 | 70.8 | 460 | 44.4 | 13.8 | 20.3 | 2.43 |
| PCDFs | 122 | 58.8 | 23.5 | 201 | 170 | 76.5 | 770 | 981 | 301 | 16 | 102 | 7.24 | 1.52 | 2.94 | 0.818 |
| PCBs | 4600 | 2940 | 2080 | 8740 | 6430 | 2860 | 10100 | 11900 | 4050 | 156 | 872 | 154 | 59 | 61 | 44.7 |
| TEQ* | 2.78 | 0.852 | 0.579 | 3 | 2.76 | 2.15 | 15.2 | 27 | 12.4 | 0.869 | 2.97 | 1.1 | 0.24 | 0.309 | 0.0691 |

*For the calculation of TEQs, WHO TEFs (1997) for PCDD/Fs were used.
Numer1, 2, 3 represent sampling sites.

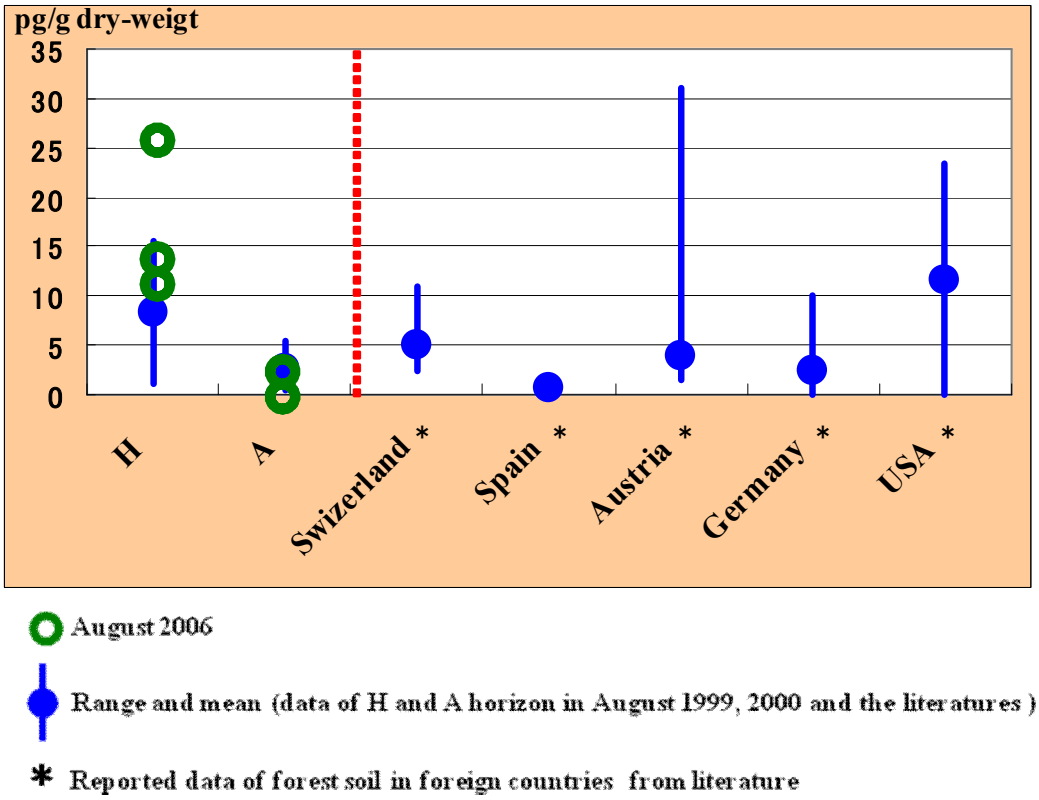


**Fig. 2** PCDD/Fs concentration of soil in Matsuyama and soil in foreign countries

Fig. 3 shows bar graph about PCDDs, PCDFs and PCBs concentrations of each horizon in sampling site number 1,2,3 (Table2). The same trend was confirmed in the other sites. This graph indicates the highest concentration of PCDD/Fs and PCBs were determined in H horizon. And the concentration profile of PCBs was also highly detected in fresh leaves and L horizon.

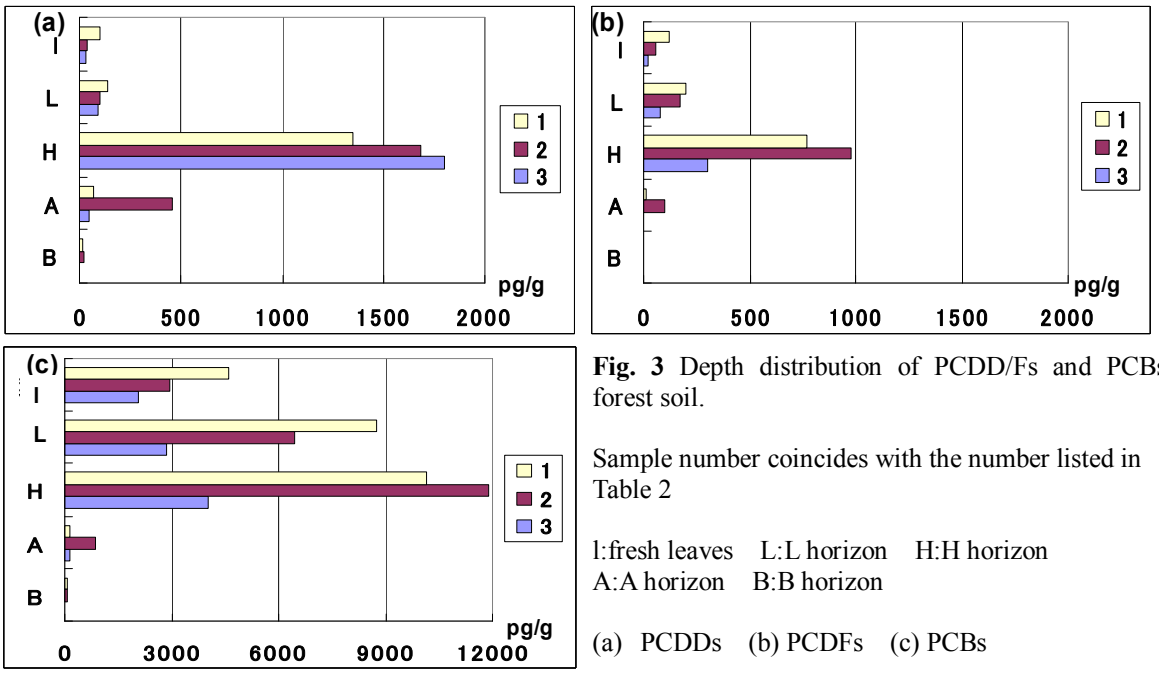


**Fig. 3** Depth distribution of PCDD/Fs and PCBs in forest soil.

Sample number coincides with the number listed in Table 2

l:fresh leaves L:L horizon H:H horizon
A:A horizon B:B horizon

(a) PCDDs (b) PCDFs (c) PCBs

Fig. 4 shows homologue profile of PCDDs, PCDFs and PCBs in sampling site number 1 (Table 2). The similar pattern was confirmed in the other sites. The composition of higher chlorinated PCDD/Fs congener seemed to be increased from L horizon to A horizon. Particularly, the profile of PCDDs is critically changed between L horizon and H horizon. On the other hands, it is clear that lower chlorinated PCBs were increased in deep horizon, but change from L horizon to H horizon was similar with PCDD/Fs. This profile suggests that lower chlorinated PCDD/Fs and PCBs might be disappeared. In addition to it, the PCDD/Fs and PCBs homologue profile might be reflected by the different causing factors such as type of contamination source, leaching, environmental bio-/photo- degradation and vaporization and so on, and detailed analysis is necessary for our full understanding of the pattern.

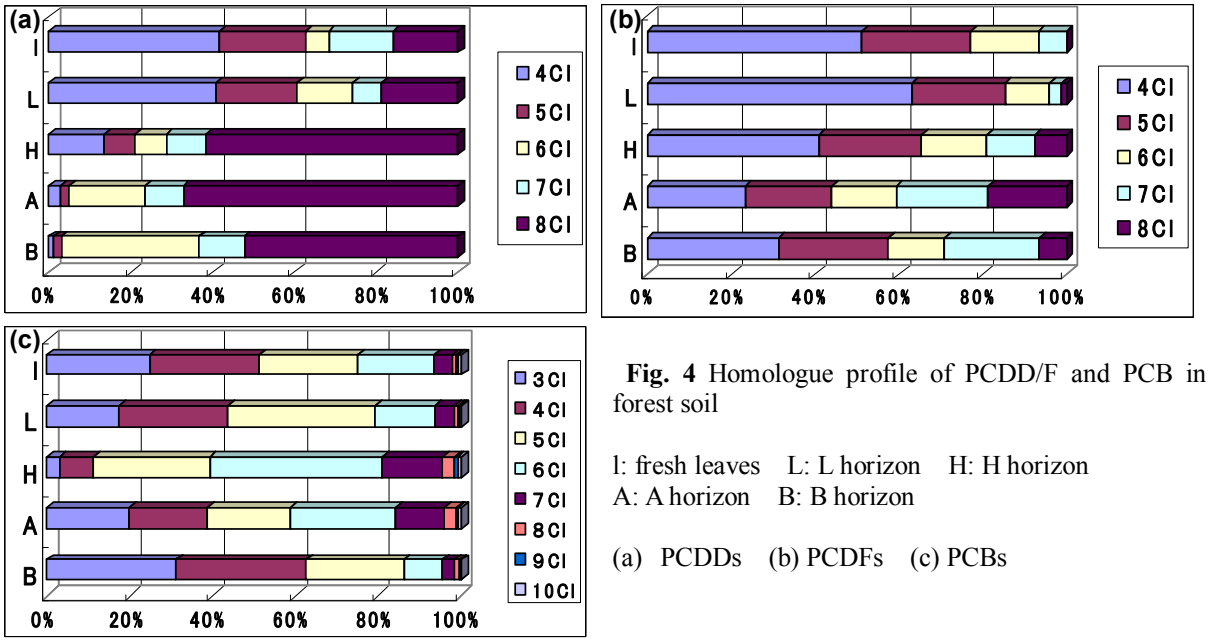


**Fig. 4** Homologue profile of PCDD/F and PCB in forest soil

l: fresh leaves L: L horizon H: H horizon
A: A horizon B: B horizon

(a) PCDDs (b) PCDFs (c) PCBs

**References**

1. Meijer SN, Steinnes E, Ockenden WA; Jones KC. *Environmental Science & Technology* 2002; 36: 2146-2153.
2. Meijer SN, Ockenden WA, Sweetman A, Breivik K, Grimalt JO, Jones KC. *Environmental Science & Technology* 2003; 37: 667-672.
3. Hassanin A, Brivik K, Meijer SN, Steinnes E, Thomas GO, Jones KC. *Environmental Science & Technology* 2003; 38: 738-745.
4. Alcock RE, Jones KC. *Environmental Science & Technology* 1996; 30: 3133-3143.
5. SEIKE N. Environmental behavior of PCDD/Fs in Matsuyama, The United Graduate School of Agricultural Science, Ehime University, Dr. thesis, 1999: 186
6. Peter S, Erika G, Markus Z, Thomas DB, Andre D. *Chemosphere* 2005; 58: 227-234.
7. Karell M, Esteban A, Joseq R. *Chemosphere* 2006; 65: 382-389.
8. Weiss P, Lorbeer G, Scharf S, *Chemosphere* 2000; 40: 1159-1171.
9. Nobel W, Maier-Reiter W, Frinkbeiner M, Sommer B, Kostka-Rick R. *ORGANOHALOGEN COMPOUNDS* 1999; 312: 171-174.
10. Fidler H et al. *ORGANOHALOGEN COMPOUNDS* 1995; 24: 285-292.