### **DOES FOREST FIRE INCREASE THE PCDD/Fs LEVEL IN SOIL?**

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#### Introduction

PCDD/Fs are ubiquitous pollutants in the contemporary environment. These compounds have been founded in deep sediment core, pre-industrial soil, and even in remote locations. This is the evidence that there are natural sources of PCDD/Fs in the environment (1). With the 'trace chemistry of fire' hypothesis, Bumb et al. first suggested that PCDDs are formed by "common" combustion and have been presented in the environment since the advent of fire (2). After this hypothesis was proposed, many studies have been conducted to test the hypothesis. In studies on the wood combustion products, some researchers have reported that forest and brush fires were the major sources of PCDDs and PCDFs in the environment (3, 4). Sheffield estimated that about 58.7 kg PCDDs were produced in Canadian forest fires, annually (4). According to US and UK inventories, 208 g I-TEQ/yr and 0.4  $\sim$  12 g I-TEQ/yr of PCDD/Fs were released from forest fire by estimation (5, 6). The direct air sampling during forest fire is necessary to confirm the natural PCDD/Fs formation from forest fire, however, this is very difficult due to unexpected fire. The vapor and particle phase (as a chiefly ash form) of PCDD/Fs from forest fire were released to the atmosphere and deposited on soil. Therefore, several studies indirectly measured PCDD/Fs levels in soil, ash and vegetation samples after forest fire, but the results were not enough to confirm the effect of forest fire as a natural source of PCDD/Fs on environment (7, 8).

The objectives of this study are to evaluate the effect of forest fire on the PCDD/Fs levels in soil with time and investigate the PCDD/Fs homologue patterns in Korean soil samples.

### Material and Methods

**Sampling:** The soil samples were collected at five sites after large-scale forest fire on east coast areas in Korea. The soil sampling was performed periodically after forest fire in three sites (Kosung (G), Kangnung (K) and Samchuk (S)). These soils were sampled to a depth of  $0 \sim 5$  cm with including ash fraction. In the other sites (Donghae (D) and Pohang (P)), the soil samples were collected within one week after forest fire and the ash samples were collected separately. Also, as for control, soil samples in each site were taken at unburned areas. All samples were stored at -5°C until extraction.

**PCDD/Fs analysis:** The air-dried soil samples (20g) were extracted using a Dionex ASE-200 Accelerated Solvent Extractor with toluene. The extracted samples were washed with  $H_2SO_4$  until the color disappeared and then neutralized with hexane rinsed water. Sample cleanup was carried out in two stages; silica gel column and activated acidic alumina column capped with anhydrous  $Na_2SO_4$ .

PCDD/Fs were analyzed by high-resolution gas chromatography / high-resolution mass spectrometry (Hewlett-Packard Model 6890 series / JMS 700T) with a DB-5MS column. The MS

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was operated at 10,000 resolutions under positive EI conditions (38 eV electron energy), and data were obtained in the selected ion monitoring (SIM) mode.

*Chemical analysis:* The pH, organic matter, total nitrogen, available P, and exchangeable K, Na, Ca and Mg were analyzed in the soil samples

#### **Results and Discussion**

**Concentrations:** The levels of PCDD/Fs in the burned soils that were analyzed ranged from 37 pg/g to 370 pg/g ( $0.32 \sim 4.82$  pg I-TEQ/g), and in the unburned soils from 40 pg/g to 210 pg/g ( $0.75 \sim 1.63$  pg I-TEQ/g) (Table 1). The concentrations of PCDD/Fs in soils 1 month after fires were higher than in corresponding unburned soils. However, at 5 and 9 months after fire, the concentrations of PCDD/Fs in soils decreased approximately 70% compared to 1 month after fire. These decreases are shown in Figure 1, which also gives the change in soil organic matter content. These trends can be explained by the fact that after forest fires the levels of PCDD/Fs and organic matter in soils increase because of the ash layers produced during the biomass burning, and then decrease with time as these ash layers are lost.

Tab	le I.	PCDD/Fs	concentrations	in	soil	and	ash	samples
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	[Unit : pg/g (pg I-TEQ/								
		Burned	Control						
	1 month	5 month	9 month	Control	ASN				
G	368.40 (4.82)	130.25 (1.26)	119.56 (1.30)	123.67 (0.90)					
К	196.65 (2.60)	97.85 (0.68)	37.36 (0.32)	157.56 (0.91)					
S	311.43 (3.72)	122.49 (1.42)	167.45 (1.35)	163.36 (1.24)					
D	85.58 (0.97)			43.90 (0.75)	160.41 (1.63)				
Р	184.62 (2.66)			205.23 (1.63)	183.14 (2.93)				



Figure 1. Organic matter contents in soil and PCDD/F concentration (TEQ) changes 1, 5 and 9 month after forest fire



*Homologue Profile:* Figure 2 shows soil and ash PCDD/Fs homologue profiles. The unburned soil samples showed OCDD dominated profile. The OCDD dominated profile was considered to be the characteristic profile of background soil samples (9). At 1 month after forest fires, soil showed relatively low contribution of OCDD and increased level of less chlorinated PCDD and PCDF compared to the unburned soil. The increase of the less chlorinated PCDD and PCDF indicated that the soil was affected by the source of PCDD/Fs. The ash produced during the forest fire showed that TCDF and PeCDF were more predominant profile and this profile was similar to the ash and chimney soot profiles from wood burning reported in previous studies (4, 10). This result indicated that PCDD/Fs were introduced to the soil after the forest fire by the ash layers produced during the wood burning. Therefore the forest fire was considered to be the source of PCDD/Fs. At 5 months after fire, soil showed OCDD dominated profile which shown in unburned soil. It is likely that the PCDD/Fs profile of soil was changed with time because of the loss of the ash layers by wind and rain erosion.



Figure 2. Homologue profiles for burned soils 1, 5 and 9 month after forest fire, unburned soil and ash samples

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**Summary:** The results of this study show that the ashes produced during wood burning, indicating that forest fires are the source of PCDD/Fs increase the levels of PCDD/Fs in soils. However, these increases in soils are temporary and then returned to the levels of unburned soils with time as ash layers are lost. Therefore it is likely that some portion of the PCDD/Fs produced during forest fires are introduced into the atmosphere, and some into the hydrosphere; therefore, further air and water samplings are required in order to estimate the total PCDD/Fs formed by forest fires.

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