# TIME TRENDS 2001-2011 IN HUMAN SERUM LEVELS OF PCDD/Fs FROM KOREA

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## Introduction

Ever since dioxins were first declared to be a probable human carcinogen by EPA in 1985[1], they are still ubiquitous contaminants from anthropogenic sources that are almost exclusively produced by thermal and chemical industrial processes[2, 3].

In Korea, there are currently 32 municipal solid waste incinerators (MSWIs) and about 1000 incinerators of various sizes in service, indicating that incineration has become an important method for treating wastes. The emission quantity of PCDD/Fs in waste incinerators was 891.6 g I-TEQ/year in 2001, but this quantity decreased by 92% (75.4 g I-TEQ/year) in 2006[4]. Nevertheless, the potential health risks from stack emissions have encouraged a substantial amount of research on possible effects on the environment and populations living in the vicinity of these facilities[5-9]. Furthermore, dioxin levels were found to be reduced in the blood of non-occupationally exposed subjects living near an incinerator facility[10, 11].

The purpose of this study is to determine the levels of PCDD/Fs in human serum of subjects working in MSWIs, those living near MSWIs, and those living far from MSWIs population to evaluate the potential influence of the incinerators on serum dioxin levels. During the last decade, we collected blood samples yearly to evaluate the levels of serum dioxin with regard to age of individuals and with regard to temporal trends. To avoid confusion, resulting all TEQ concentrations in this study were derived using the WHO-2005 TEFs[12].

## Materials and methods

### -Blood Sampling

A total of 954 blood samples were obtained from volunteers during the period 2001–2011. A total of 35, 53, 45, 73, 72, 177, 202, 204, and 93 blood samples were collected in 2001, 2002, 2003, 2005, 2007, 2008, 2009, 2010, and 2011, respectively. Information regarding the age, occupational history, and medical history was obtained by conducting a survey. All samples were kept frozen at -20ºC until analysis.

### -Chemical analysis

Approximately 40 g of serum was added to a 1000 mL separating funnel and spiked with a set of $^{13}$C-labeled PCDD/Fs (EPA-1613LCS; Wellington Laboratories Inc., Canada) as the surrogate internal standard. Each sample was extracted 3 times using 200 mL of a 2:1 acetone/hexane mixture. In brief, the samples were subjected to further cleanup via multilayer-silica and alumina columns. The cleaned extract was then analyzed by HR/MS using an HP 6890N GC coupled with a JEOL 800D mass spectrometer after addition of a $^{13}$C-labeled recovery standard. The analytical procedures used in this study have been previously described in detail[13-15].

### -Quality assurance/Quality control

Procedural blanks were analyzed for every 9 samples to check for interference and/or contamination from the solvents and glassware. The limit of detection (LOD) for each PCDD/F congener was estimated to be 2.5 times the signal to noise (S/N) value determined for procedural blanks. Quality control standards for PCDD/Fs were analyzed after every 10 samples to monitor for instrument stability. The recoveries of $^{13}C_{12}$-labeled PCDD/Fs spiked into each sample were in the range of 80% to 120% in accordance with EPA method 1613.

## Results and discussion

### -Levels of PCDD/Fs in each group

The mean $TEQ_{PCDD/Fs}$ concentration of all subjects was 9.29 TEQ pg/g lipid. The mean $TEQ_{PCDD/Fs}$ levels in groups W (workers at the MSWIs), Near (residents living <3 km from the MSWIs), and Far (residents living >10 km away from the MSWIs) were 8.52, 9.41, and 9.12 pg TEQ/g lipid, respectively. First we compared the serum levels of PCDD/Fs among three subgroups. However, the levels of PCDD/Fs among the subgroups showed no statistical difference when using ANOVA (p=0.066). The distribution of the congeners in each group shows consistency with the pattern observed for the each subgroup (Fig. 1(a)). These results indicated that emission from the MSWIs should not cause any significant additional exposure to PCDD/Fs for the population living in the vicinity of the facilities. Therefore, all subjects were considered as metropolitan populations. We thus examined the levels of PCDD/F for gender dependence. The mean $TEQ_{PCDD/Fs}$ values in male and female participants were 8.90 and 9.49 pg TEQ/g lipid, respectively, and there were no significant differences for concentrations (p=0.174). Women generally have a larger relative fat mass and therefore a larger distribution volume for fat-soluble substances. Thus, the PCDD/F levels of females might be expected to be higher than those of males. However, no difference was found in our measured serum samples. This result suggested that the amount of PCDD/Fs ingested via foodstuffs had been minimized[16]. Also all subjects were divided into two groups, 18~40 (Young) and 40~70 (Old) respectively by age. Our results showed that high serum PCDD/Fs levels were found in older people than in younger people. In Fig. 2, our results had statistically significant difference (p<0.001) between two groups. Because of PCDD/Fs long half-life, PCDD/Fs accumulate with age and exposure[17]. The overall serum profiles were dominated by 1,2,3,7,8-PeCDD, 2,3,4,7,8-PeCDF, and 1,2,3,6,7,8-HxCDD congeners, which accounted for about 68% of the total PCDD/Fs TEQ in the human serum samples (Fig. 1(b)).

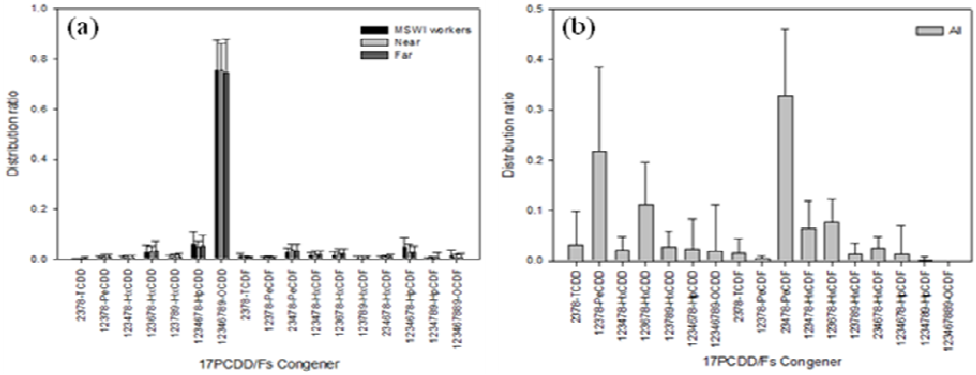


Figure 1. Profiles of average level of 17congeners compared with (a) total PCDD/Fs and (b) total TEQ of PCDD/Fs in human serum.

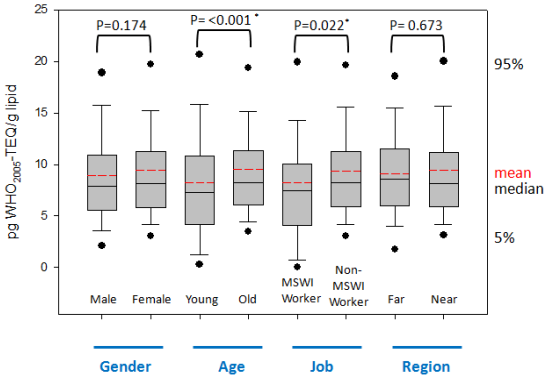


Figure 2. Comparison of the serum TEQ levels of PCDD/Fs according to the gender, age, occupation, and region of residence.

**-Time trends of serum PCDD/Fs**

Fig. 3 illustrates the yearly change of concentrations of PCDD/Fs in human serum samples. The observed non-decreasing of levels in human serum for PCDD/Fs levels within the past ten years is unexpected, considering its half-life and the reduction of emission to the environment [18-20]. Generally, 10 pg TEQ/g lipid for PCDD/Fs was retained in human serum samples during our survey. So we further investigated the homologues for each year of the serum using PCA. Fig. 4 demonstrates the factor score plot for two components. The similarities in the PCDD/Fs patterns sampled at each year are outlined in the PCA sample scores plot (Fig. 4).

In summary, our data indicate that emissions from MSWIs do not cause significant additional exposure to PCDD/Fs for the population living in the vicinity of the facilities, and the level of background exposure was minimized to draw a narrow range of TEQs. Additionally, there were no clear declining trends in PCDD/Fs levels in human serum samples during a 10-year survey. But there were positive associations between age and dioxin levels in human serum. Our data did not clearly indicate reduction of PCDD/F levels in human serum. However, it is clear that the deviations in dioxin levels have declined continuously.

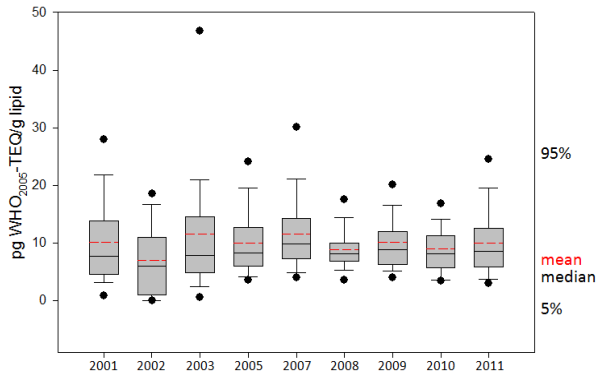

Figure 3. Time trend 2001–2011 of PCDD/F levels.

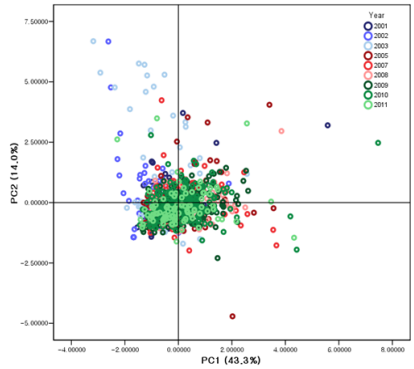

Figure 4. PCA score plot for the relationship among PCDD/F homologue in each year human serum samples.

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