# Correlation with total concentration and TEQ concentration of PCDDs/Fs in ambient air in an industrial complex

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**Abstract**

For investigating the correlation with total concentration and TEQ concentration of PCDDs/Fs in ambient air in an industrial complex located in the west from capital. PCDDs/Fs were sampled 10 times at 9 points in the industrial complex in summer and winter. Sampling sites were selected based on the previous data investigated during last 4 years and all congeners of PCDDs/Fs were analyzed. The concentration of PCDDs/Fs in winter showed 1-4 times higher than that in summer and the concentration of particle-phase were higher than that of gaseous-phase. The portion of gaseous-phase increased with decrease in the substituted chlor and the portion of each isomer in a homology became similar with the increased substituted chlor. The correlation with total concentration and TEQ concentration was higher in summer than in winter, and the correlation with concentration of 136 congeners (TeCDDs/Fs-OCDD/F) and TEQ concentration was higher in summer than in winter. And also, the correlation with total concentration of PCDFs and TEQ concentration was higher than that of concentration of PCDDs and TEQ concentration. For the 2,3,7,8-substituted each congeners(as TEQ concentration), the correlation of 2,3,4,7,8-PeCDF and concentration showed the highest.

**Introduction**

Recently, hazardous pollutants in environment and its impact on human and ecosystem are disputed very frequently. Especially, the impacts of the hazardous air pollutants cover a very wide area due to its movement in air and finally absorbed or settled in water and soil. In the past $SO_2$, $NO_2$, CO, $PM_{10}$ and $O_3$ were main monitored pollutants in air, but in the recent years, the interest has risen about toxic organic pollutants in air and the monitoring has intensified. But on line monitoring of toxic micro organic pollutants in air is not easy and the sampling and analysis methods are very complex. Therefore,

the correlation with those pollutants and surrogate of those pollutants are investigated. PCDDs/Fs can be called as main toxic micro organic pollutants having no on line monitoring system. PCDDs/Fs are emitted as by-products from incineration and industrial facilities to ambient air. The concern about PCDDs/Fs in ambient air increased after leakage of PCDDs/Fs from Seveso in Italy, 1976. In Korea concentration of PCDDs/Fs are investigated at 30 points every year since 1999 and in the recent years more investigations are going on in west from capital and the concern over PCDDs/Fs in ambient air is rising. A large industrial complex having various emission sources of PCDDs/Fs are located in the west from capital. The concentrations of PCDDs/Fs in this area were high in the past four years and seasonal variations in concentration were also recorded. We sampled, analyzed and investigated the PCDDs/Fs in ambient air in the industrial complex during winter and summer and correlate it with total concentration and TEQ concentration to find major toxic congeners affecting the ambient air, which will be used for further study to estimate its contribution for air quality in this area.

**Materials and Methods**

PCDDs/Fs were sampled 10 times at 9 points in the industrial complex located in the west from capital. Sampling sites were selected based on the previous data investigated during last 4 years in summer and winter. For sampling, the HVAS (high volume air sampler) with Q/F for particle phase and XAD-2 /PUF for gaseous phase was used. During the sampling, the flow rate was maintained less than 300 L $min^{-1}$ and sampled for 24hrs. All congeners of PCDDs/PCDFs (75 congeners of PCDF and 135 congeners of PCDD) were analyzed according to Korean Standard Testing Method (KSTM) to analyze TeCDDs/Fs-OCDD/F and in addition reference are taken from previous papers to analyze MoCDDs/Fs-TrCDDs/Fs. To analyze MoCDDs/Fs-TrCDDs/Fs, we used labeled standards of $^{13}C_{12}$- MoCDD, DiCDD and TrCDD to clean up and prepared calibration standard with native standards of MoCDD, DiCDD and TrCDD and labeled standards of $^{13}C_{12}$- MoCDD, DiCDD and TrCDD. The concentrated elute of each phase of the PCDDs/Fs samples was also separately analyzed by high resolution gas chromatograph / high resolution mass spectrometer (HRGC/HRMS). The HRGC/HRMS setup consisted of a Hewlett Packard 6890 GC coupled with Jeol 700D. Selected ion monitoring with electron impact of 38 eV was performed above a resolution of 10,000 with an SP-2331 column of 60m × 0.32mm ID × 0.20um. Samples were introduced in splitless mode with a flow rate of 1 ml·$min^{-1}$ helium and the temperatures of injector and ion source were 265 °C. The oven temperature to analyze MoCDDs/Fs- TrCDDs/Fs was 120°C(1min) → 30°C $min^{-1}$ → 200°C → 20°C $min^{-1}$ → 260°C(1min), and to analyze TeCDDs/Fs-OCDDs/Fs was 100°C(1min) → 20C $min^{-1}$ → 200°C → 20°C $min^{-1}$ → 265°C(19.5min). Toxic equivalents were calculated by using the international toxicity equivalency factor (I-TEF).

**Results and Discussion**

The concentration of PCDDs/Fs in 9 sampling points was 7.101-81.477 pg $Sm^{-3}$ (0.060-0.691 pg-I-TEQ $Sm^{-3}$) in summer and 27.564-89.671 pg $Sm^{-3}$ (0.243-0.576 pg-I-TEQ $Sm^{-3}$) in winter. Usually, the concentration in winter was higher than that in summer and the difference is related to the variation of weather. During the sampling period in winter, mainly north wind prevailed and wind velocity was about 1-2 m $sec^{-1}$. Due to low wind speed, mixing and dilution of pollutants were less and the pollutants at sampling point were accumulated for a long time. But in summer there was south wind from high atmospheric pressure at the South Pacific and the wind velocity was about 2-3 m $sec^{-1}$ during the sampling period. And during the daytime the wind velocity was low but at night was high and the wind direction was from land to sea. It means that the movement of air in summer was smoother than in winter and the pollutants at sampling points in summer were not more accumulative than that in winter. The variation of MoCDDs/Fs-TrCDDs/Fs was much more than that of TeCDDs/Fs-OCDDs/CDFs according to the season. It was estimated that the MoCDDs/Fs-TrCDDs/Fs was more volatile than TeCDDs/Fs-OCDDs/CDFs. The portion of particle-phase was above 95% and the portion of particle-phase was higher in winter than in summer. The portion of gaseous-phase increased with decrease in the substituted chlor in general. Furthermore, the portion of gaseous-phase of MoCDDs/Fs were 92.4%, 78.1% for DiCDDs/Fs, 48.1% for TrCDDs/Fs, 42.6% for TeCDDs/Fs, 16.91% for PeCDDs/Fs and 0% for HeCDDs/Fs-OCDD/F. It was known that mainly the PCDDs/Fs in ambient air existed as the particle-phase of PCDDs/Fs and the gaseous-phase of PCDDs/Fs was mostly MoCDDs/Fs-TrCDDs/Fs. The distribution of each isomer in MoCDDs/Fs-TrCDDs/Fs was not similar and its ratio changed with sampling time and point. However, TrCDDs/Fs-HpCDDs/Fs were similar and its ratio did not change much with sampling time and point. Iino et al. suggested the distribution of isomers in homologies became similar with increased number of substituted chlor in ambient air. Therefore, it could be known that the distribution of isomers in homologies except MoCDDs/Fs-DiCDDs/Fs were similar in ambient air and its ratio did not changed much according to the sampling time and point, although the concentration of each homology varied individually with sampling time and point. The correlation coefficients of total concentration and TEQ concentration was 0.6711 in winter and 0.7845 in summer and that of concentration of TeCDDs/Fs-OCDD/F and TEQ concentration was 0.5862 in winter and 0.9619 in summer. On the average, the correlation coefficients of total concentration and TEQ concentration was 0.7387 and that of concentration of TeCDDs/Fs-OCDD/F and TEQ concentration was 0.8603. And also, the correlation coefficients of total concentration of PCDFs and TEQ concentration was 0.6866 and that of concentration of TeCDFs-OCDF and TEQ concentration was 0.8797 and 0.6808, 0.6743 for PCDDs, respectively. Therefore, we known that the correlation with total concentration and TEQ concentration was higher in summer than in winter and higher for PCDFs than for PCDDs. Furthermore, for the 2,3,7,8-substituted each congeners, the correlation coefficients of 2,3,4,7,8-PeCDF and total concentration showed the highest as 0.6333 and as 0.9062 for the concentration of TeCDDs/Fs-OCDD/F. It was known that

2,3,4,7,8-PeCDF is the most suitable congener to find the correlation with concentration and toxicity in this area.

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