Convenient Substitute Indices to Toxic Equivalent Quantity for Controlling and Monitoring Dioxins from Waste Incinerators

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Introduction

Considerable labor, high technical skill and extreme costs are required to measure polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar polychlorinated biphenyl (Co-PCBs) individually for obtaining the toxic equivalent quantity (TEQ) values. In addition, new TEF have been proposed by the World Health Organization (WHO) in 1998. Therefore, it is necessary to convert the conventional international TEQ (I-TEQ) values to the WHO-TEQ values. On one hand, it was found that there were high amounts of chlorobenzenes (CBZs) in the flue gas. Moreover, it had been found that there were many unknown genotoxic compounds in the flue gas, and some of them were expected to be semi- and non-volatile organohalogen compounds (SNVOX). Therefore, the correlations of the WHO-TEQ values with the conventional I-TEQ were examined beforehand by experimental and literature data in a large number of waste incinerators. The relationships between the TEQ values and the concentrations of total, each toxic isomer of PCDDs/PCDFs and each homologue of CBZs were also investigated. In addition, the correlations among the concentrations of SNVOX, which was developed as a new hazardous index, and PCDDs/PCDFs were examined. From these results, more convenient substitute indices to the TEQ values were proposed for controlling and monitoring dioxins from waste incineration facilities.

Experimental

Investigated Facilities

The concentrations of PCDDs/PCDFs/Co-PCBs (dioxins), CBZs and SNVOX were measured under usual operation conditions in incineration facilities of municipal solid waste (MSW) equipped with a stoker type furnace and in incineration facilities of industrial waste (IW) equipped with a rotary kiln or a fluidized bed type furnace. Their flue gas treatment systems were respectively different, but the treatments using an activated carbon or a catalyst were not put to use in these facilities.

Sampling and Analytical Method

Dioxins, CBZs and SNVOX were collected by a sampling train, which was consisted with a filter, 200 mL of water and 300 mL of diethylene glycol in a cooling box [1]. It was made clear that this sampling train could be sufficiently collect $Cl_{4\text{-}6}BZs$ whose boiling points were higher than ca. 240°C [2]. These collection samples were extracted, purified with a multi-layer silica column and fractionated with an alumina column. The sufficient concentrations of each isomer of dioxins were analyzed by a quadruple type of GC/MS (Shimadzu QP5050A) equipped with an injection part of the programmed temperature vaporization (PTV). Analytical method of CBZs or SNVOX was described in another report [2,3].

Results and Discussion

Correlation of WHO-TEQ with I-TEQ

The correlation of the WHO-TEQ values of PCDDs/ PCDFs/Co-PCBs (ng-TEQ/m^3) with the I-TEQ values of PCDDs/PCDFs (ng-TEQ/m^3) was examined for 50 experimental data in the 4 incineration facilities of MSW and 55 literature data from 55 incineration facilities of IW by Japan Environment Agency. Results are shown in Figure 1. It was found that there was positive correlation in a wide concentration range of 10^5 for a large number of different facilities. The correlations could be expressed by equation (1). Therefore, the I-TEQ values can be exactly converted into the WHO-TEQ values. The correlation of the WHO-TEQ values of PCDDs/PCDFs (ng-TEQ/m^3) with the I-TEQ values of PCDDs/PCDFs (ng-TEQ/ m^3) could be also expressed by equation (2). In addition, these correlations show that Co-PCBs are only ca. 3% of PCDDs/PCDFs as the TEQ values, which is within the error range of the measurement.

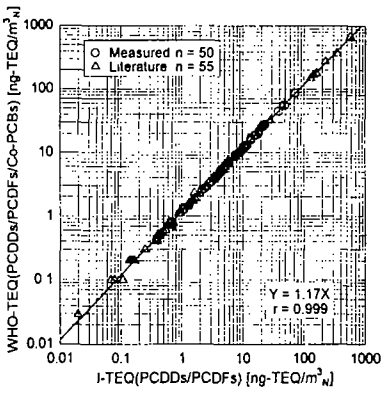

Figure 1 Correlation of WHO-TEQ (PCDDs/PCDFs/Co-PCBs)with I-TEQ (PCDDs/PCDFs)

[WHO-TEQ of PCDDs/PCDFs/Co-PCBs] = 1.17 [I-TEQ of PCDDs/PCDFs], r =0.999 (1)

[WHO-TEQ of PCDDs/PCDFs] = 1.14 [I-TEQ of PCDDs/PCDFs], r =0.999 (2)

Relationship between Total Concentration of PCDDs/PCDFs and TEQ

The relationship between the total concentrations (ng/m^3) of PCDDs/PCDFs and the I-TEQ values (ng-TEQ/m^3) was examined in 10 facilities. The total concentration and the I-TEQ values showed a good correlation in a wide concentration range from ca.10,000, and the correlation could be expressed by equation (3). Furthermore, it was confirmed that considerable amount of the literature data from the 148 incineration facilities of MSW and IW and the 17 crematories under usual operation conditions could also be expressed by the same equation (3) in a wide concentration range of 10^5.

$$[\text{I-TEQ of PCDDs/PCDFs}] = 0.012\,[\text{total PCDDs/PCDFs}]^{1.05}, \quad r = 0.99 \qquad (3)$$

From equation (1), the correlations of the WHO-TEQ values with the total concentrations of PCDDs/PCDFs could also be expressed as equation (4).

$$[\text{WHO-TEQ of PCDDs/PCDFs/Co-PCBs}] = 0.014\,[\text{total PCDDs/PCDFs}]^{1.05} \qquad (4)$$

These equations show that the TEQ values, which required high skill and an enormous amount of effort to analyze isomers, can be estimated from the total concentrations of PCDDs/PCDFs, which can be easily obtained by analyzing the homologue.

Relationship between Concentration of 2,3,4,7,8-P_5CDF and TEQ

The relationships between the concentration of each toxic isomer of PCDDs/PCDFs and the I-TEQ values of PCDDs/PCDFs were examined for 61 experimental data in the 9 incineration facilities and the 55 literature data from the 55 facilities by Japan Environment Agency. It was shown that 1,2,3,7,8-P_5CDD and 2,3,4,7,8- P_5CDF contribute to ca. 49% in the average of I-TEQ values. And though the contribution of 1,2,3,7,8-P_5CDD fluctuated, the contribution of 2,3,4,7,8-P_5CDF was stable. Figure 2 shows the relationship between the concentrations of 2,3,4,7,8-P_5CDFs (ng/m^3) and the I-TEQ values (ng-TEQ/m^3). The positive correlation was obtained and it could be expressed by equation (5) in a wide concentration range of 10^5 for various incineration facilities.

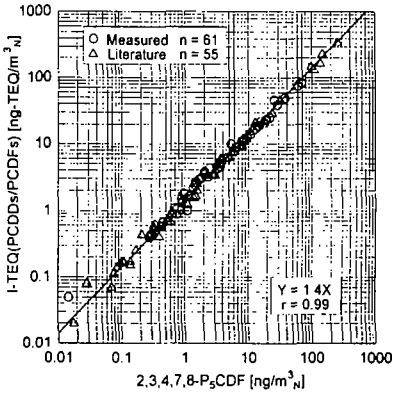

Figure 2 Relationship between 2,3,4,7,8-P_5CDF and I-TEQ in 64 facilities

[I-TEQ of PCDDs/PCDFs] = 1.4 [2,3,4,7,8-P_5CDF], r = 0.99 (5)

The correlation of the WHO-TEQ values (ng-TEQ/m^3) with the concentration of 2,3,4,7,8-P_5CDF (ng/m^3) could be also expressed as equation (6) using equation (1).

[WHO-TEQ of PCDDs/PCDFs/Co-PCBs] = 1.6 [2,3,4,7,8-P_5CDF] (6)

These equations show that 2,3,4,7,8-P_5CDF having TEF of 0.5 contributes to ca. 36% and ca. 31% of the I-TEQ values and the WHO-TEQ values, respectively. The TEQ values can be estimated from the concentrations of 2,3,4,7,8-P_5CDF, which can be easily and rapidly determined by a GC/MS, because the determination for the other toxic isomers of 16 PCDDs/PCDFs and 12 Co-PCBs can be omitted. And, we have only to prepare one standard substance and one analytical column of GC/MS.

Relationship between Concentrations of CBZs and TEQ

The relationships between the concentrations of tetrachlorobenzenes, pentachlorobenzene, or hexachlorobenzene (μg/m^3) and the I-TEQ values of PCDDs/PCDFs (ng-TEQ/m^3) were examined in a wide concentration range in the 5 incineration facilities. It was found that similar correlations with each homologue of $Cl_{4\text{-}6}$BZs were obtained and it showed a slightly better correlation in comparison with the total concentration of $Cl_{4\text{-}6}$BZs.

From the above results, it is shown that the concentrations of each homologue of $Cl_{4\text{-}6}$BZs may be used as convenient substitute indices. However we recommend the concentration of Cl_5BZ as a more convenient substitute index to the TEQ values of dioxin, because Cl_5BZ has no isomers and a lower toxicity in comparison with Cl_6BZ and its recovery in the sampling and concentrating procedure was higher than Cl_4BZs [2].

The correlation of the I-TEQ values (ng-TEQ/m^3) with the concentration of Cl_5BZ (μg/m^3) is shown in Figure 3 and could be expressed by the following equation (7).

[I-TEQ of PCDDS/PCDFs] = 2.1 $[Cl_5BZ]^{1.1}$, r = 0.92 (7)

Using equation (1), the correlation of the WHO-TEQ values of PCDDs/PCDFs/Co-PCBs (ng-TEQ/m^3) with Cl_5BZ (μg/m^3) could be also expressed as equation (8).

[WHO-TEQ of PCDDs/PCDFs/Co-PCBs] = 2.4 $[Cl_5BZ]^{1.1}$ (8)

These equations show that the TEQ values can be estimated from the concentrations of Cl_5BZ,

which can be analyzed very easily [2]. Furthermore, because the concentrations of Cl_5BZ were higher than 0.01μg/m^3 in many waste incineration facilities, the sampling volume can be decreased. This means that the sampling time can be shortened to several minutes and the time variation of the concentrations of Cl_5BZ in stack gas can be automatically monitored and then the time variation of the TEQ values of dioxins can be estimated.

Relationship between Concentrations of SNVOX and PCDDs/PCDFs

The relationships between the SNVOX (μg-Cl/m^3) and the I-TEQ (ng-I-TEQ/m^3) is shown in Figure 4 for various waste incineration facilities whose systems for the incineration and the flue gas treatment were different widely. The SNVOX were in the range from ca. 1.5 to ca. 1200 μg-Cl/m^3. Namely, the concentrations of SNVOX were different a thousand times among the facilities. The relationship could be approximated by the following equation (9) for the five facilities in the wide concentration ranges, though there was a little scatter.

$$[\text{I-TEQ}] = 0.060\ [\text{SNVOX}]^{1.0} \qquad r = 0.91 \qquad (9)$$

From the correlation, the I-TEQ or WHO-TEQ could be estimated approximately from the SNVOX. And it is possible to use the SNVOX for controlling dioxins as well. However, it is more important to use the SNVOX for monitoring and controlling unknown hazardous halogenated compounds not only dioxins. Consequently, the concentration of SNVOX, which could be measured easily by a non-specialist, thought to be one of the useful indices for monitoring and controlling hazardous pollutants in flue gas from the waste incineration facilities.

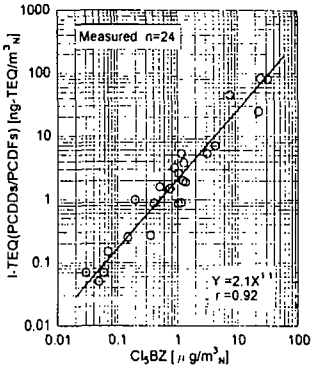

Figure 3 Relationship between pentachlorobenzene(Cl5BZ) and I-TEQ in 5 facilities

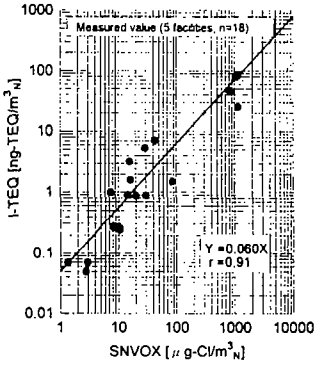

Figure 4 Relationship between semi- and nonvolatile organic halogen(SNVOX) and I-TEO in 5 facilities

References

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