Investigation of Target Isomers as an Indicator for Toxic Equivalents Quantity of Dioxins

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Introduction

In the official Japanese method, the toxic equivalent quantities (TEQs) of dioxins such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (Co-PCBs) are evaluated by determining isomer concentrations with toxic equivalency factors (TEFs). The analysis of dioxins using high-resolution gas chromatography / high-resolution mass spectrometry (HRGC/HRMS) is expensive, time-consuming, and requires highly trained instrument operators. For this reason, a quick, inexpensive, and simple method to analyze dioxins is in demand. Recently, statistical analyses have indicated that PCDD/DF congeners and some precursors show promising correlations with TEQ values, suggesting that these compounds can act as TEQ indicators. [1 - 4] TEQ indicators are useful for estimating TEQ values. In these studies, only the congener total values and/or concentrations of 2,3,7,8-substituted compounds were used. We have been investigating TEQ indicators of dioxins in ambient air and exhaust gas using all congeners, including non-2,3,7,8-substituted compounds seldom evaluated until now.[5] In this work, common TEQ indicators of dioxins were investigated from all congeners, including the non-2,3,7,8-substituted compounds, in environmental mediums such as exhaust gas, ambient air, soil, sediment, and river water, in order to assess the applicability of these indicators to a simplified method of dioxin analysis.

Materials and Methods

Environmental medium samples, including exhaust gas, ambient air, soil, sediment and river water were collected in Fukuoka prefecture, Japan from 2000 to 2003. Dioxins in each medium sample were measured with the Japanese Industrial Standards (JIS)[6 - 7] and the measurement manual of the Ministry of the Environment. PCDDs, PCDFs and Co-PCBs were analyzed by HRGC/HRMS (Agilent Technology, USA, 6890 series /Micromass, UK, Autospec-Ultima) above 10,000 resolution with a SP-2331 capillary column (Supelco, USA, 60m×0.25mm i.d. with 0.20µm film thickness) for a Tetra- to Penta- PCDDs/DFs, BPX-DXN capillary column (SGE, Australia, 60m×0.25mm i.d.) for Hexa- to Octa- PCDDs/DFs and Non-*ortho*-Co-PCBs, and HT8-PCB (Kanto Chemical, Japan, 60m×0.25mm i.d.) for Mono-*ortho*-Co-PCBs. The correlation for the TEQ value was analyzed on isomers of the Tetra- to Octa- PCDDs/DFs that were separated by these columns and Non-/Mono-*ortho*-Co-PCBs. The data consisted of a total of 128 parameters, including isomer specific data (118 parameters) and congeners concentration (10 parameters). The samples of 38 exhaust gases, 144 ambient airs, 187 soils, 105 sediments and 114 river waters were used. The TEQ value of dioxins of each medium sample used in this study are shown in Table 1.

Table 1. The TEQ value of dioxins of each medium sample

Medium	Number of data	TEQ				Unit
		Min.	Max.	Mean	Median	
Exhaust gas	38	0.001	10.917	1.373	0.183	ng-TEQ/Nm^3 [O_2 = 12%]
Ambient air	144	0.006	0.455	0.103	0.077	pg-TEQ/m^3
Soil	187	0.019	889.936	11.997	0.651	pg-TEQ/g-dry
Sediment	105	0.079	114.057	10.127	1.972	pg-TEQ/g-dry
River water	114	0.015	0.980	0.282	0.204	pg-TEQ/L

Results and Discussion

Table 2 summarizes the results of the correlation analysis between the isomer concentration and the TEQ value for each medium. The results of the enumeration of the isomer with the highest correlation coefficient are shown in Table 3 for each medium. Using Factor A in Table 3, we estimated the TEQ value by multiplying the isomer concentration (WHO-TEQ = A x Isomer concentration). From Table 2 and Table 3, it was confirmed that some of the isomers correlate highly with TEQ value. In exhaust gas, ambient air, and soil, the correlation coefficient between the TEQ value and the isomer concentration was high for the isomers of HxCDFs and PeCDFs. In sediment, the correlation coefficient was high for almost all of the isomers of PCDFs. In river water, the correlation coefficient was lower than in the other mediums, but it was high for almost all of the isomers of Hepta- to Octa-PCDDs/DFs. In various mediiums, good correlations between the TEQ value and the isomer concentration were observed in 1,2,4,6,9- / 1,2,6,7,8-PeCDF, 1,2,3,4,6,8-HxCDF, 1,2,4,6,7,8-HxCDF, and 1,2,3,4,6,7-HxCDF in spite of the non-2,3,7,8-substituted compounds. Table 3 shows that 1,2,3,6,7,8-HxCDF, 1,2,4,6,9- / 1,2,6,7,8-PeCDF, 1,2,3,4,6,8-HxCDF, 1,2,3,4,7,8- / 1,2,3,4,7,9-HxCDF, and 2,3,4,7,8-PeCDF are common TEQ indicators of a simple dioxin analysis in most of the environmental medium samples.

In all mediums, even the non-2,3,7,8-substituted compounds were demonstrated to indicate TEQ values. Generally, in our simple method for analyzing dioxins in environmental medium samples, 2,3,4,7,8-PeCDF is used as a predictor of TEQ values. It is concluded that the non-2,3,7,8-substituted compounds evaluated in this study were effective in calculating TEQ values more accurately. In our method, the non-2,3,7,8-substituted compounds are useful as internal standards because of their nontoxicity and safety.

Table 2. The summary of the correlation coefficient of PCDDs/DFs, Co-PCBs with WHO-TEQ

	Exhaust gas (n = 38)			Ambient air (n = 144)			Soil (n = 187)		
	MIN.[a]	MAX.[a]	Total[b]	MIN.[a]	MAX.[a]	Total[b]	MIN.[a]	MAX.[a]	Total[b]
TeCDDs	0.6605	0.9297	0.7832	0.2391	0.8674	0.3786	0.0111	0.8916	0.7782
PeCDDs	0.7984	0.9918	0.8785	0.4903	0.9345	0.8591	0.3206	0.9214	0.8216
HxCDDs	0.8082	0.9026	0.8501	0.6930	0.8833	0.7636	0.7567	0.9627	0.8928
HpCDDs	0.7257	0.7648	0.7473	0.6006	0.6332	0.6187	0.9080	0.9337	0.9214
OCDD	-	-	0.6031	-	-	0.0356	-	-	0.8778
TeCDFs	0.5996	0.9403	0.8634	0.0542	0.8977	0.8443	0.0160	0.9781	0.8868
PeCDFs	0.5686	0.9977	0.9162	0.3202	0.9843	0.9546	0.3350	0.9951	0.9832
HxCDFs	0.8335	0.9719	0.9361	0.6060	0.9713	0.9599	0.0117	0.9841	0.9618
HpCDFs	0.6810	0.8198	0.7792	0.5068	0.8707	0.7991	0.8138	0.9626	0.9164
OCDF	-	-	0.4061	-	-	0.4604	-	-	0.8559
Non-*ortho*-Co-PCBs	0.6620	0.8720	0.7478	0.3335	0.9109	0.4656	0.7753	0.9890	0.8433
Mono-*ortho*-Co-PCBs	0.2669	0.7645	0.4780	0.1862	0.7639	0.3015	0.7186	0.7767	0.7691

	Sediment (n = 105)			River water (n = 114)		
	MIN.[a]	MAX.[a]	Total[b]	MIN.[a]	MAX.[a]	Total[b]
TeCDDs	0.1561	0.8642	0.5028	0.1158	0.8170	0.6709
PeCDDs	0.2543	0.6990	0.4507	0.4454	0.8082	0.6511
HxCDDs	0.5126	0.8957	0.7126	0.5075	0.9128	0.8638
HpCDDs	0.8249	0.9288	0.8857	0.8108	0.8475	0.8313
OCDD	-	-	0.9232	-	-	0.8587
TeCDFs	0.2136	0.9678	0.7791	0.0862	0.6901	0.7641
PeCDFs	0.0515	0.9797	0.9587	0.0774	0.8169	0.6866
HxCDFs	0.3294	0.9602	0.9546	0.2643	0.8938	0.8169
HpCDFs	0.8611	0.9476	0.9306	0.4634	0.8763	0.8161
OCDF	-	-	0.9202	-	-	0.8116
Non-*ortho*-Co-PCBs	0.8390	0.8825	0.8706	0.2078	0.6462	0.2271
Mono-*ortho*-Co-PCBs	0.4237	0.7092	0.5930	0.2898	0.5661	0.4210

[a] MIN. and MAX. shows minimum and maximum of the correlation coefficient between the isomer concentration and the TEQ value in every congener, respectively.

[b] Total shows the correlation coefficient between the congeners concentration and the TEQ value.

Table 3. The enumeration of the isomers with the high correlation coefficient

Rank	Exhaust gas (n = 38)			Ambient air (n = 144)			Soil (n = 187)		
	Isomer	Factor : A	correlation coefficient : R	Isomer	Factor : A	correlation coefficient : R	Isomer	Factor : A	correlation coefficient : R
1	**2,3,4,7,8-PeCDF**	**1.5164**	**0.9977**	**2,3,4,7,8-PeCDF**	**1.5674**	**0.9843**	1,2,4,6,9 / 1,2,4,7,8-PeCDF	5.0336	0.9951
2	1,2,3,8,9-PeCDF	15.6924	0.9939	1,2,3,4,7,8 / 1,2,3,4,7,9-HxCDF	1.0668	0.9718	1,2,4,7,8-PeCDF	3.1878	0.9947
3	**1,2,3,7,8-PeCDD**	**4.4446**	**0.9918**	**1,2,3,6,7,8-HxCDF**	**1.2289**	**0.9704**	1,2,3,4,7 / 1,4,6,7,8-PeCDF	3.6898	0.9905
4	1,2,4,8,9-PeCDF	9.7675	0.9913	1,2,3,6,7-PeCDF	2.3603	0.9616	**3,3',4,4',5,5'-HxCB(#169)**	**22.7452**	**0.9890**
5	2,3,4,6,7-PeCDF	1.0647	0.9886	1,2,3,4,6,7-HxCDF	0.9696	0.9561	**1,2,3,6,7,8-HxCDF**	**4.8496**	**0.9841**
6	1,2,3,6,7-PeCDD	6.8737	0.9811	1,2,4,6,9 / 1,2,4,7,8-PeCDF	1.4904	0.9527	1,2,3,4,6,8-HxCDF	1.5553	0.9785
7	1,2,3,8,9-PeCDD	6.9135	0.9790	1,2,3,4,8 / 1,2,3,7,8-PeCDF	1.1764	0.9465	[illegible]	11.4131	0.9781
8	1,2,4,6,7 / 1,2,4,8,9-PeCDD	3.2757	0.9751	1,3,4,7,8 / 1,2,3,6,8-PeCDF	0.9525	0.9455	1,2,3,4,6-PeCDF	17.7367	0.9687
9	1,2,3,4,7,8 / 1,2,3,4,7,9-HxCDF	1.6598	0.9719	1,2,4,6,7-PeCDF	1.7468	0.9454	1,2,3,4,6,7-HxCDF	6.9664	0.9724
10	1,2,3,4,9-PeCDF	11.5148	0.9683	1,2,4,7,9 / 1,3,4,6,7-PeCDF	1.4966	0.9446	1,2,6,7,9-PeCDF	44.4224	0.9682
11	1,2,3,4,6,7-HxCDF	1.6213	0.9671	1,3,4,6,7,8 / 1,3,4,6,7,9-HxCDF	0.6550	0.9441	1,2,4,7 / 1,3,6,7-TeCDF	6.0107	0.9674
12	**1,2,3,6,7,8-HxCDF**	**1.7569**	**0.9664**	1,2,3,4,6,8-HxCDF	0.9797	0.9424	1,2,4,8,9-PeCDF	17.4490	0.9665
13	1,2,3,6,9-PeCDD	5.5991	0.9643	1,2,3,4,7 / 1,4,6,7,8-PeCDF	1.2027	0.9418	1,3,4,7,8 / 1,2,3,6,8-PeCDF	11.4674	0.9661
14	1,2,4,6,9 / 1,2,4,7,8-PeCDF	1.3179	0.9596	1,3,4,6,8-PeCDF	1.6175	0.9402	**2,3,4,7,8-PeCDF**	**4.8914**	**0.9637**
15	2,3,4,6,8-PeCDF	1.1084	0.9454	1,2,4,6,8-PeCDF	1.5050	0.9365	1,2,4,6,7,8-HxCDF	0.6521	0.9634

Rank	Sediment (n = 105)			River water (n = 114)		
	Isomer	Factor : A	correlation coefficient : R	Isomer	Factor : A	correlation coefficient : R
1	1,2,3,4,7 / 1,4,6,7,8-PeCDF	4.4755	0.9797	**1,2,3,6,7,8-HxCDD**	**1.2754**	**0.9128**
2	1,2,3,4,8 / 1,2,3,7,8-PeCDF	3.5214	0.9757	**2,3,4,6,7,8-HxCDF**	**2.1511**	**0.8938**
3	1,2,4,6 / 1,2,6,8-TeCDF	2.8015	0.9678	**1,2,3,6,7,8-HxCDF**	**1.9139**	**0.8919**
4	1,2,4,6,7,8-HxCDF	0.3345	0.9602	**1,2,3,4,6,7,8-HpCDF**	**0.1077**	**0.8763**
5	1,2,4,7,8-PeCDF	1.7013	0.9593	**1,2,3,4,6,7,8,9-OCDD**	**0.0021**	**0.8587**
6	1,2,4,6,9 / 1,2,4,7,8-PeCDF	2.8123	0.9577	1,2,3,6,7,9 / 1,2,3,6,8,9-HxCDD	0.2903	0.8579
7	1,2,3,4,8,9-HxCDF	5.9724	0.9548	1,2,3,4,6,8-HxCDF	0.5959	0.8528
8	1,2,4,6,8-PeCDF	0.9479	0.9529	**1,2,3,4,6,7,8-HpCDD**	**0.0492**	**0.8475**
9	**1,2,3,4,6,7,8-HpCDF**	**0.1312**	**0.9476**	[illegible]	0.1848	0.8423
10	1,2,4,6,7-PeCDF	7.5854	0.9424	1,3,7,8-TeCDD	1.8921	0.8170
11	1,2,3,4,6,8-HxCDF	1.2532	0.9422	1,2,3,4,8 / 1,2,3,7,8-PeCDF	2.1281	0.8169
12	**1,2,3,4,7,8,9-HpCDF**	**0.6207**	**0.9361**	1,2,4,6,7,8-HxCDF	0.1811	0.8135
13	1,2,3,4,7,8 / 1,2,3,4,7,9-HxCDF	0.4451	0.9354	**1,2,3,4,6,7,8,9-OCDF**	**0.0445**	**0.8116**
14	1,2,7,8-TeCDF	5.1575	0.9326	1,2,3,4,6,7,9-HpCDD	0.0387	0.8108
15	**1,2,3,4,6,7,8-HpCDD**	**0.0837**	**0.9288**	1,2,3,4,7 / 1,2,4,6,9-PeCDD	1.6264	0.8082

(Dotted box) Isomer with the high correlation in three mediums

(Grey box) Isomer with the high correlation in four mediums

Bold face: The 2,3,7,8-substituted isomers

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