

Development of a Screening Method for Dioxins in Polluted Soils

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Introduction

The environmental quality standards for dioxins such as polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (DL-PCBs) have been established for complex matrices (soil, water, air, etc.) in Japan. Currently, dioxin pollution that exceeds the environmental quality standards is being reported. The environmental quality standard of soil is 1,000 pg-toxic equivalent quantity (TEQ)/g. At sites of dioxin pollution, many measurements are required to grasp the extent of dioxin pollution or to confirm the absence of dioxins from restored soil. At present, dioxins in the soil are analyzed using the measurement manual provided by the Ministry of the Environment, Japan. The official method for measuring dioxins is very expensive and time consuming, however, so a quick, inexpensive, and simple method to analyze dioxins is needed^{1,2}. The introduction of simplified measurement methods for dioxins in soil is forthcoming from the Ministry of the Environment of Japan.

In a simplified measurement method, the measurement accuracy, sensitivity, quality control, and the like may have to be sacrificed a little. From the viewpoint of environmental administration, in suspected regions of dioxins pollution, the confirmation of exceeding the environmental quality standard is the most important feature of such a method.

We previously reported that the pentachlorodibenzofuran isomers are useful indicators for predicting the TEQ of dioxins in flue gas and ambient air³⁻⁵.

Consequently, we developed a screening method for dioxins in polluted soil. In that screening method, we focused on the accurate discrimination of an environmental quality standard excess of dioxins in soil. This screening method was composed of a combination of three techniques: (i) the ultrasonic extraction of moistened soil⁶, (ii) the refining by the suction manifold for solid phase extraction (the suction manifold) using multilayer silica gel column and activated carbon column⁶, and (iii) the measurement of TEQ indicators with high resolution gas chromatography / high resolution mass spectrometry (HRGC/HRMS). In this work, we describe the development of a measurement method of TEQ indicators in the screening method and compare the screening method and the official method.

Materials and Methods

Ultrasonic extraction of moistened soil

One gram of soil was collected in a centrifuge glass tube, to which a clean-up spike was added. Water to 30% (0.3 mL) was added to the soil prior to the extraction of dioxins. The conditions for the ultrasonic extraction are shown in Table 1. In the solvent of the order of Table 1, dioxins in soil were extracted by ultrasonic waves and were centrifuged. The supernatant solvents in each extraction were mixed. That mixed solvent was washed with n-Hexane washing water. The extract solution (the n-Hexane layer) was dehydrated with sodium sulfate.

Table 1. The condition for the ultrasonic extraction

Sample	1 g (dry weight)
Solvent	1 2N HCl aq. 5 mL
	2 Acetone 5 mL
	3 Acetone : n-Hexane = 1 : 1
	4 5 mL
Extraction Time	10 min.
Centrifugation Time	5 min.

Refining by the suction manifold using a multilayer silica gel column and an activated carbon column

In the refining, we used a connection column with a multilayer silica gel column and an activated carbon column. The refining conditions are shown in Figure 1. Quartz glass filters were put into the bottom and top of the multilayer silica gel column (inside diameter 20 mm), and then 0.5 g of silica gel, 4 g of silica gel impregnated with sulfuric acid [44% (mass fraction)], 2.5 g of silica gel impregnated with silver nitrate [10% (mass fraction)], 0.5 g of silica gel and 2 g of sodium sulfate were packed in sequence into that tube. Quartz glass filters were also put into the bottom and top of the activated carbon column (inside diameter 10 mm). Sodium sulfate, 5 mm thick, silica gel impregnated with porous graphitized carbon, 10 mm thick, and sodium sulfate, 5 mm thick, were layered one by one. Solutions were made to flow at a rate of approximately 5 ml/min. by a suction manifold. The extract solution and 60 mL of n-Hexane were run into the connection column. Dioxins were eluted by 10 mL of toluene from the reversed activated carbon column. The toluene fractionation was concentrated at 50 μ L by nitrogen gas flow and a heating block. After elution and concentration, a syringe spike was added to the concentrated solution so we could measure the TEQ indicators.

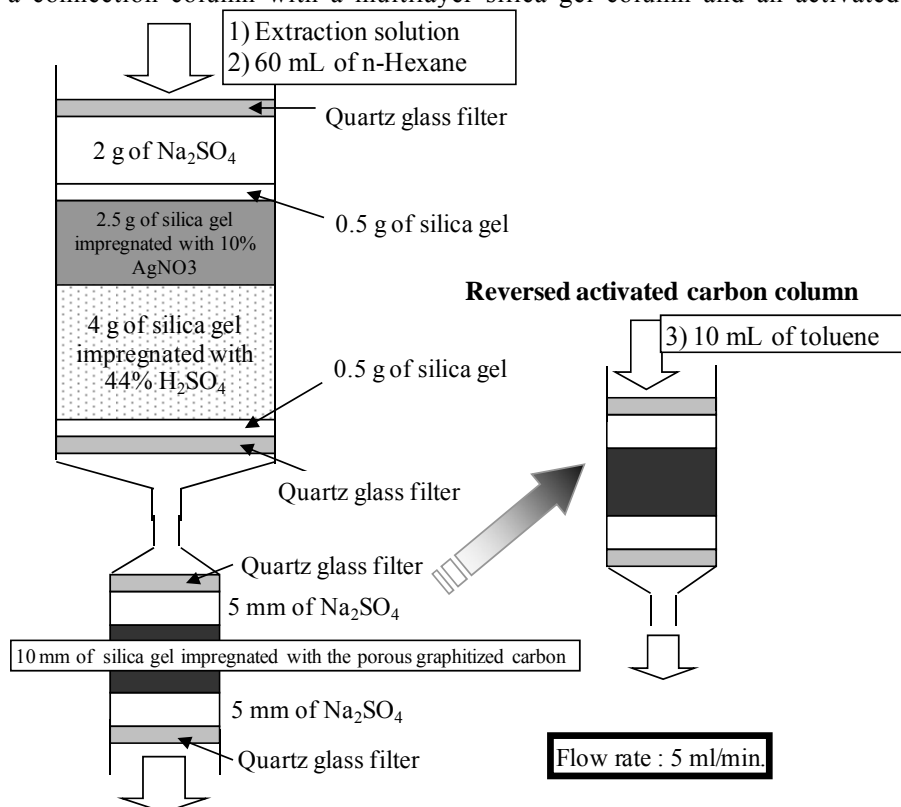


Figure 1. The refining condition of the screening method

Sodium sulfate, 5 mm thick, silica gel impregnated with porous graphitized carbon, 10 mm thick, and sodium sulfate, 5 mm thick, were layered one by one. Solutions were made to flow at a rate of approximately 5 ml/min. by a suction manifold. The extract solution and 60 mL of n-Hexane were run into the connection column. Dioxins were eluted by 10 mL of toluene from the reversed activated carbon column. The toluene fractionation was concentrated at 50 μ L by nitrogen gas flow and a heating block. After elution and concentration, a syringe spike was added to the concentrated solution so we could measure the TEQ indicators.

Measurement of TEQ indicators by HRGC/HRMS

Environmental soil samples (400 samples) were collected in Fukuoka prefecture, Japan, from 2000 to 2006. Dioxins in the soil samples had been measured using the official method. PCDDs, PCDFs, and DL-PCBs were analyzed by HRGC/HRMS with capillary columns such as the SP-2331, BPX-DXN, and HT8-PCB. The analyzed data consisted of isomer specific data (116 parameters), and those data have been stored in the dioxins database, which is composed of soils of 0.0063 - 43000 pg-TEQ/g. From the dioxins database, soil data of 10 - 1000 pg-TEQ/g were extracted, and the isomers that satisfied the following four conditions were determined: (i) high TEQ correlation, (ii) could be isolated by GC, (iii) could be detected in the comparatively high concentration, (iv) could be isolated independent of pollution sources. The estimated formula of TEQ was obtained by combining two kinds of TEQ indicators. The TEQ indicators were analyzed by HRGC/HRMS (Agilent Technology, 6890 series /Waters, Autospec Premier) with a SP-2331 capillary column (Supelco 30 m \times 0.25 mm \times 0.20 μ m).

Results and Discussions

Verification of the ultrasonic extraction and refining

The ultrasonic extraction and refining were verified in the soil standard sample (The Japan Society for Analytical Chemistry, Certified Reference Material JSAC 0421). The standard soil was pretreated by the methods of Table 1 and Figure 1, and that treated solution was measured by HRGC/HRMS according to the official method. Table 2 shows that the measured data were compared with the certified reference data, and the recovery of the clean-up spike in the pretreatment of the screening method. All isomer concentrations were in the range of 74-120% (average 99%) for the certified data, and the TEQ was 96% for the certified data. In the pretreatment of the screening method, the recoveries of the clean-up spike were in the range of 43-108% (average 77%). Therefore, the recovery was slightly lower, but we adopted this extraction and refining as a pretreatment in the screening method.

Measurement of TEQ indicators by HRGC/HRMS

From the dioxins database, we selected 52 sample soils of 10-1000 pg-TEQ/g. The TEQ indicators, which satisfied the four conditions shown above, were chosen by isomer specific data (116 parameters) of the 52 samples (Table 3). The isomers in Table 3 can estimate TEQ alone. Two TEQ indicators were chosen from Table 3 for more accurate estimation of TEQ, and the combination of two TEQ indicators with the highest correlation for TEQ were selected. We found that the combination of the parameters of [1,2,3,4,7-/1,4,6,7,8-PeCDF] and [1,2,3,4,6,7,8-HpCDF] was most suitable, and we obtained the following formula:

$$\text{TEQ estimated formula} = 0.91 \times [1,2,3,4,7-/1,4,6,7,8\text{-PeCDF}] + 0.11 \times [1,2,3,4,6,7,8\text{-HpCDF}]$$

Next, the TEQ indicators in soils pretreated in the official method were analyzed quantitatively by HRGC/HRMS, and TEQ were estimated. The estimated TEQ showed a high correlation for TEQ. 1,3,6,8-TeCDD and OCDD were also analyzed at the same time to determine the pollution source.

Using the parameters of [1,2,3,4,7-/1,4,6,7,8-PeCDF] and [1,2,3,4,6,7,8-HpCDF] in the dioxins database, we calculated the TEQ of 400 soil samples using the formula. Figure 2 shows the comparison of TEQ measured by the official method and TEQ estimated by the formula. As Figure 2 indicates, TEQ near 1000 pg-TEQ/g, which is the environmental quality standard of dioxins in soil, was accurately distinguished. In addition, the estimation of TEQ was possible even in the wide range from 0.0063 to 43000 pg-TEQ/g.

Table 2. The comparison of the measured data and the certified data, and the recovery of the clean-up spike in the pretreatment of the screening method.

	The measured data	The certified data	Recovery
	pg/g	pg/g	
2,3,7,8-TeCDD	1.1	1.5	57%
1,2,3,7,8-PeCDD	8.0	9.0	68%
1,2,3,4,7,8-HxCDD	8.2	8.4	108%
1,2,3,6,7,8-HxCDD	18	19	106%
1,2,3,7,8,9-HxCDD	25	22	94%
1,2,3,4,6,7,8-HpCDD	120	140	92%
OCDD	790	680	66%
2,3,7,8-TeCDF	12	11	46%
1,2,3,7,8-PeCDF	20	17	64%
2,3,4,7,8-PeCDF	18	19	60%
1,2,3,4,7,8-HxCDF	21	23	85%
1,2,3,6,7,8-HxCDF	22	23	87%
1,2,3,7,8,9-HxCDF	2.4	2.1	93%
2,3,4,6,7,8-HxCDF	31	32	93%
1,2,3,4,6,7,8-HpCDF	94	96	91%
1,2,3,4,7,8,9-HpCDF	12	13	83%
OCDF	75	75	61%
3,4,4',5'-TeCB(#81)	6.7	9.5	43%
3,3',4,4'-TeCB(#77)	80	100	48%
3,3',4,4',5'-PeCB(#126)	41	38	60%
3,3',4,4',5,5'-HxCB(#169)	13	12	72%
2',3,4,4',5'-PeCB(#123)	22	20	73%
2,3',4,4',5'-PeCB(#118)	540	540	67%
2,3,3',4,4'-PeCB(#105)	200	210	74%
2,3,4,4',5'-PeCB(#114)	9.0	9.4	78%
2,3',4,4',5,5'-HxCB(#167)	60	57	101%
2,3,3',4,4',5'-HxCB(#156)	110	100	84%
2,3,3',4,4',5'-HxCB(#157)	42	39	85%
2,3,3',4,4',5,5'-HpCB(#189)	23	22	101%

We found that the combination of the parameters of [1,2,3,4,7-/1,4,6,7,8-PeCDF] and [1,2,3,4,6,7,8-HpCDF] was most suitable, and we obtained the following formula:

Table 3. The regression coefficient and the correlation coefficient between the TEQ and the TEQ indicator

	The regression coefficient	The correlation coefficient
1,2,3,6,7,8-HxCDD	2.33	0.896
1,2,4,8-/1,3,6,7-TeCDF	1.00	0.833
2,3,7,8-TeCDF	2.99	0.827
1,2,3,4,7-/1,4,6,7,8-PeCDF	1.40	0.855
1,2,3,4,8-/1,2,3,7,8-PeCDF	1.37	0.870
1,2,4,6,9-/1,2,6,7,8-PeCDF	1.68	0.868
1,2,3,4,6,8-HxCDF	1.04	0.860
1,2,3,4,7,8-/1,2,3,4,7,9-HxCDF	0.589	0.850
1,2,3,6,7,8-HxCDF	1.36	0.838
1,2,3,4,6,7,8-HpCDF	0.163	0.849

$$\text{TEQ} = A \times \text{Isomer concentration}$$

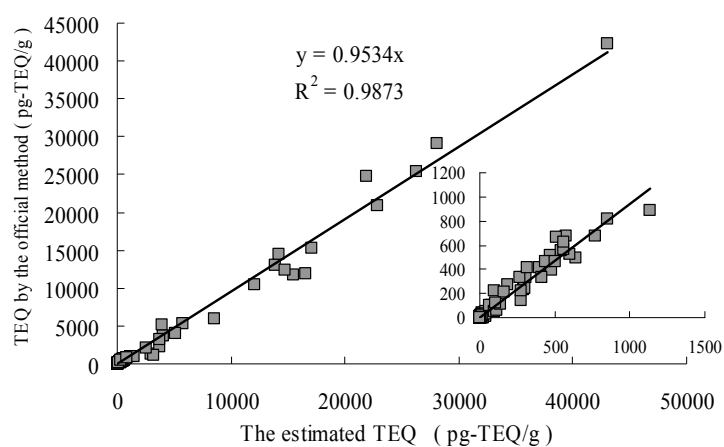


Figure 2. The comparison of TEQ measured by the official method and TEQ estimated by the formula.

Comparison of the screening method and the official method

The screening method was validated with the official method using soil samples. The soils of a few dioxins pollution sites and the soils of a general environment were used as a sample. Table 4 shows the comparison of TEQ by the official method and TEQ by the screening method. The Ministry of the Environment of Japan is seeking a simplified method for measuring the dioxins in soil. In the simplified measurement method, "the ratio of TEQ by simplified method against TEQ by the official method is in the range of 0.5 – 2.0" is one of the evaluation conditions. As indicated in Table 4, TEQ by this screening method in all samples was in the range of 0.5~2.0 of the ratio for TEQ by the official method. In addition, in comparison with the official method in our laboratory, our testing clarified that 85% reduction of the measuring time, 60% reduction of the measurement cost (not including the initial cost or labor costs) and 85% reduction of the solvent use were possible. Therefore, we concluded that the screening method could be sufficiently utilized to determine the environmental quality standard excess of dioxins in soil.

Table 4. The comparison of TEQ by the official method and TEQ by the screening method

Samples	TEQ		TEQ(Screening) / TEQ(Official)
	The official method	The screening method	
A	12,000	8,100	0.68
B	12,000	11,000	0.92
C	3,900	4,200	1.08
D	41,000	39,000	0.95
E	14,000	11,000	0.79
F	41,000	42,000	1.02
G	48,000	40,000	0.83
H	2,000	2,710	1.36
I	76	61	0.80
J	230	310	1.35
K	52	32	0.62
L	28	30	1.07
M	650	1,300	2.00
N	1,700	1,900	1.12
O	530	480	0.91
P	370	340	0.92
Q	68	87	1.28
R	250	310	1.24

pg-TEQ/g

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