Development of the Simple Measurement of Dioxins in Polluted Soils

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Introduction

The environmental quality standards of dioxins such as polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinatedbiphenyls (DL-PCBs) have been established for complex matrices (soil, water, air, etc.) in Japan. Currently, the pollutions of dioxins that exceed the environmental quality standards are reported. The environmental quality standard of soil is 1,000 pg-TEQ/g. At sites of dioxin pollution, many measurements are required to confirm the extent of the dioxin pollution or to confirm the absence of dioxins from restored soil. Conventional methods for measuring dioxins are very expensive and time consuming. Therefore, a quick, inexpensive, and simple method (QMS method) to analyze dioxins is needed[1,2]. We had reported that the Pentachlorodibenzofuran isomers (PeCDFs) are useful indicators for predicting the toxic equivalent quantity (TEQ) of dioxins in flue gas and ambient air[3-5]. In this work, the TEQ indicators of dioxins of polluted soils were investigated from all congeners, including the non-2,3,7,8-substituted compounds. We developed a QMS method for measuring dioxins using TEQ indicators in polluted soils and compared the QMS method with the conventional method as well as the enzyme immunoassay method (EIA method).

Materials and Methods

Samples and sample preparation： The 49 samples of polluted soils were collected from a site of dioxin pollution in Fukuoka Prefecture, Japan. The samples were prepared in accordance with the measurement manual of the Japanese Ministry of the Environment, and the measurement of the samples was carried out on high-resolution gas chromatography / high-resolution mass spectrometry (HRGC/HRMS) (the conventional method). The extent of dioxins at the pollution site was confirmed by that method.

The conventional method： PCDDs, PCDFs, and DL-PCBs were analyzed by HRGC/HRMS (Agilent Technology, 6890 series /Micromass, Autospec-Ultima) above 10,000 resolution with an SP-2331 column (60m×0.25mm i.d. with 0.20µm film thickness) for a Tetra- to Penta- PCDDs/DFs, BPX-DXN (60m×0.25mm i.d.) for Hexa- to Octa- PCDDs/DFs and Non-*ortho*-Co-PCBs, and HT8-PCB (60m×0.25mm i.d.) for Mono-*ortho*-Co-PCBs.

The QMS method： The TEQ indicators of dioxins of the polluted soils were investigated by determining the correlation between the isomer concentration and the TEQ. In the QMS method, 18 samples within 49 samples in the pollution soils were prepared the same as in the conventional method, and the TEQ indicators were analyzed by HRGC/QMS (Agilent Technology, 6980 series/ Agilent Technology, 5973Network) with an DB-17 column (30m×0.25mm i.d. with 0.25µm film thickness). The TEQ of dioxins was predicted from the regression coefficient and the indicator concentration.

The EIA method： The same samples as those used in the QMS method were analyzed by the EIA. In the EIA method, the High Performance Dioxin/Furan Immunoassay Kit (CAPE Technologies LLC, USA) and the High Performance PCB TEQ Kit (CAPE Technologies LLC, USA) were used to predict the TEQ of 18 samples of the polluted soils. The EIA samples of 18 polluted soils were prepared according to the method of Hayashi et al[6].

Results and Discussion

In the conventional method, the TEQ of 49 soil samples at the pollution site were in the concentration range from 0.08 to 49,000 pg-TEQ/g, the TEQ of 16 samples at that site exceeded the environmental quality standard. Figure 1 shows the typical congener pattern of dioxins in those soils. This congener pattern is more specific than that pattern of dioxins in the general environment. We had pointed out previously that a main source of the soil pollution was the waste water from production plants of polycholorobenzen, PCP, CNP, and the like[7]. The grasp of the main source is important to the QMS method and the EIA method, because both of those methods use index isomers.

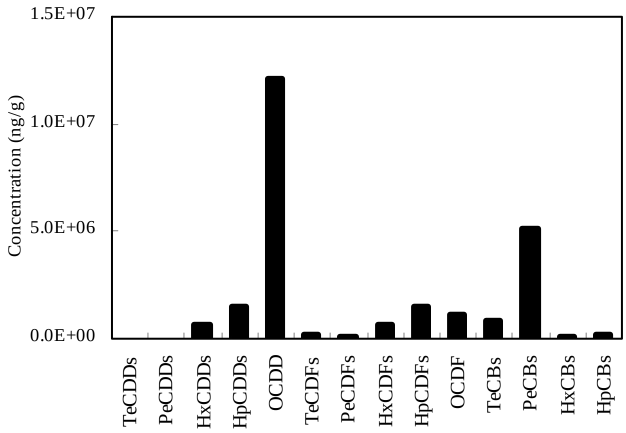

Figure 1. Typical congener pattern of dioxins in the polluted soils

Investigation of the TEQ indicator of soils at the pollution site

Table 1 shows the summary of the correlation between the TEQ of 49 samples and isomer concentrations. The correlation coefficient was high for the isomers of Hepta- to Octa- PCDDs/PCDFs and DL-PCBs. The results of enumerating the isomer with the high correlation coefficient (R) are shown in Table 2. These results suggest that a high correlation coefficient is obtained in TeCDFs, PeCDFs, and HxCDFs. In the TEQ method, the 2,3,4,7,8-PeCDF was adopted as the TEQ indicator, because of being the highest correlation coefficient. Figure 2 shows the correlation between the 2,3,4,7,8-PeCDF concentration and the TEQ. Therefore, the TEQ of the polluted soils are estimated by multiplying the 2,3,4,7,8-PeCDF concentration and the regression coefficient A: ([WHO-TEQ] = 1.2 x [2,3,4,7,8-PeCDF]).

Table 1. Summary of the correlation coefficient of PCDDs/DFs and DL-PCBs

Congener	Correlation Coefficient		
	Minimum	Maximum	Average
TeCDDs	0.0792	0.9314	0.4777
PeCDDs	0.0792	0.5701	0.2924
HxCDDs	0.4656	0.9886	0.7813
HpCDDs	0.8302	0.9895	0.9099
OCDD	—		0.9863
TeCDFs	0.0086	0.9969	0.6257
PeCDFs	0.0781	0.9986	0.6154
HxCDFs	0.0791	0.9983	0.8701
HpCDFs	0.8593	0.9918	0.9551
OCDF	—		0.9847
PCBs	0.3113	0.9876	0.8427

Table 2. Enumeration of isomer with the high correlation coefficient

Rank	Isomer	A	R
1	2,3,4,7,8-PeCDF	1.213	0.9986
2	1,2,3,4,7,8/1,2,3,4,7,9-HxCDF	0.353	0.9983
3	1,2,4,7,8-PeCDF	1.418	0.9970
4	2,3,4,8-TeCDF	2.323	0.9969
5	1,2,3,4,8,9-HxCDF	7.025	0.9962
6	1,2,4,8/1,3,4,6-TeCDF	2.409	0.9957
7	1,2,3,6,7,8-HxCDF	3.679	0.9946
8	1,2,3,9-TeCDF	3.216	0.9941
9	2,3,4,6-TeCDF	10.434	0.9936
10	1,2,3,4,6,9/1,2,3,6,8,9-HxCDF	5.824	0.9913

A：The Regression Coefficient
R：The Correlation Coefficient

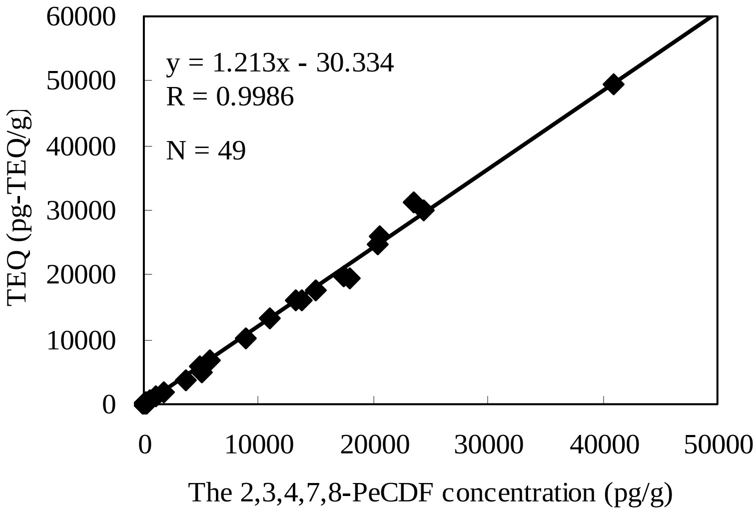

Figure 2. Correlation between the TEQ and the 2,3,4,7,8-PeCDF concentration

Measurement of 2,3,4,7,8-PeCDF with HRGC/QMS (The QMS method)

Figure 3 shows the chromatogram of PeCDFs of a fly ash measured by HRGC/QMS. It was possible to separate 2,3,4,7,8-PeCDF as a single peak by the use of a DB-17 column. In the QMS method, the 2,3,4,7,8-PeCDF concentration of 18 samples of the polluted soils was determined by HRGC/QMS, and the TEQ of samples were estimated by use of the 2,3,4,7,8-PeCDF concentration and regression coefficient. Figure 4 represents the comparison of the TEQ in the conventional method (the HRMS-TEQ) and the predicted TEQ in the QMS method (the QMS-TEQ). The QMS-TEQ was almost equivalent to the HRMS-TEQ, and the QMS-TEQ and the HRMS-TEQ showed a high correlation. Consequently, in the QMS method, it was possible to estimate the TEQ of soils at a pollution site.

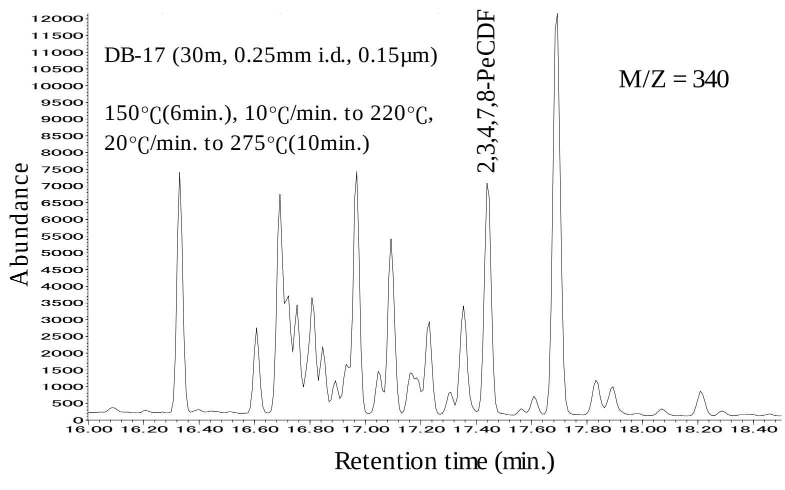

Figure 3. Chromatogram of PeCDF of a fly ash measured by the HRGC/QMS

The EIA method

Figure 5 represents the comparison of the HRMS-TEQ and the predicted TEQ in the EIA method (the EIA-TEQ). The HRMS-TEQ and the EIA-TEQ showed some correlation, but in some cases the EIA-TEQ was very different from the HRMS-TEQ, as a result of the difference between the congener pattern of dioxins in the polluted soils and the cross-reactivity of the EIA method. The congener pattern of this site is the specific pattern as shown in Figure 1, and the HRMS-TEQ of the polluted soils are dependent on the concentration of the isomers shown in Table 2. However, the EIA-TEQ are dependent on the concentration of 2,3,7,8-TeCDD and 1,2,3,7,8-PeCDD. In the EIA method, it is reported that the measurement of TEQ including the preparation is enabled on-site and in a short time[6]. This EIA method is effective for predicting the TEQ of a pollution site.

The QMS method and the EIA method needs the information of congener concentration of dioxins in polluted soils. It is a defect that those methods require in advance measurement of the TEQ of polluted soils in the conventional method. Nevertheless, the predicted TEQ in the QMS method and the TEQ in the conventional method showed a high correlation. Some predicted TEQ in the EIA method was different from TEQ in the conventional method, but the EIA method including extraction and pretreatment enables in very short time. Therefore, it was concluded that the QMS method and the EIA method are available to the screening of dioxins in polluted soils.

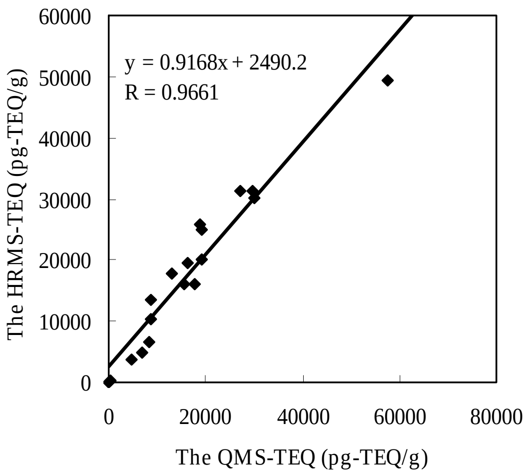

Figure 4. Correlation between the HRMS-TEQ and the QMS-TEQ

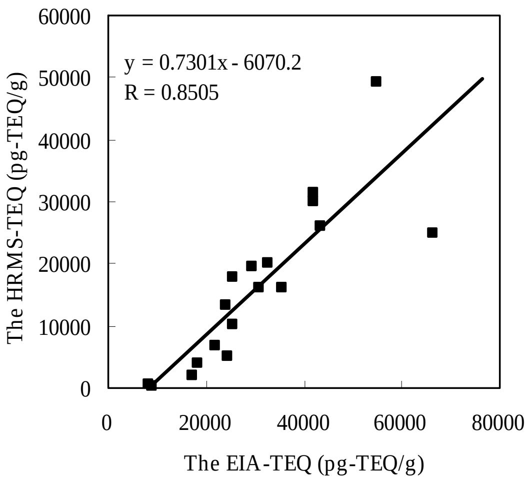

Figure 5. Correlation between the HRMS-TEQ and the EIA-TEQ

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