

Studies on simple sampling of flue gas and congener specific analysis of dioxins for the source estimation

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Introduction

Processes for simplifying and speeding up the measurement of dioxins have been investigated by many researchers, since current methods are painstaking and complex. Most investigations have focused on obtaining the TCDD toxicity equivalent (TEQ)⁽¹⁻³⁾. However, the usefulness of this strategy is limited to identifying the source of dioxins in environmental or biological samples. For pollution source analysis, similarity between the composition of compounds in the environmental sample and the source sample is estimated using a statistical method such as multiple linear regression analysis, principal component analysis, or cluster analysis⁽⁴⁻⁷⁾. For precise determination of the source, as many compounds as possible should be tested as variables. However, except for 2,3,7,8-position chlorine-substituted homologues, it is difficult to collect source data containing numerous congeners of dioxins, due to lack of information on many of these compounds.

In this study, simple sampling methodologies were examined for flue gas emitted by several municipal waste incinerators (MWIs) and all congeners of PCDD/Fs and PCBs were measured. The validity of the method was evaluated by comparison of congener composition with that carried out by the standard method. We then discuss the characteristics of congener composition of dioxins in flue gas from MWIs.

Materials and methods

Incinerators: 4 different types of facilities were chosen for this study. Each had a different scale, operating history, type of furnace and treatment system for flue gas. These details are shown in Table 1. All the facilities are located in urban or suburban areas and regarded as typical municipal waste incinerators in Japan.

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Table 1 Information about the Facilities' flue gas samples collected in this study.

Facility	A	B	C	D
Location	urban area, Tokyo	rural area, Tokyo	sub-urban area,	urban area, Chiba
Operation start year	1982	1985	1989	2003
Combusting matter	municipal waste	municipal waste	municipal waste	municipal waste
Type of furnace	fluidized-bed	full continuous, stoker	fluidized-bed	full continuous, stoker
Ability of combustion	150t/day x 2	70t/day x 2	40t/16hours x 2	135t/day x 3
Treatment of flue gas	bug filter	bug filter, blowing citrate, blowing active carbon	bug filter	bug filter, scrubber, rinse, etc.

Sampling: Flue gas samples were collected from all the facilities using the standard method (*a*), JIS K03118). Samples were also collected at the same time using two simple methods (*b1*, *b2*) using a DIOANA® adsorbent filter (Miura, Japan), at Facilities C and D. A diagram of sampling apparatuses and the relevant conditions is shown in Table 2. The DIOANA® filter is a cylindrical filter, $\phi 18.8$ mm x 110 mm in size, made of fibrous alumina. In the simple method, the adsorbent filter was substituted for an XAD-2® adsorbent plug and impinger bottles. The samples were collected for 24 hours. Volumes ranged from 10.5 to 17.0 kl. Isotope-labelled compounds were spiked into an adsorbent plug or filter to check that sampling had been carried out correctly (sampling spikes, SS). After extraction, labelled compounds, which were different from SS, were added to the extracts (cleanup spikes, CS).

Table 2 Outline of the sampling methods which were investigated in this study.

Method	a	b1	b2
Type	JIS K0311, promulgated	simple	simple
Facility applied	A, B, C, D	C, D	C, D
Sampling time	24 hours	24 hours	24 hours
Components of sampling train	<p>sampling hole</p> <p>↓</p> <p>thimble quarts filter</p> <p>↓</p> <p>impingers</p> <p>↓</p> <p>pump, gas meter</p>	<p>sampling hole</p> <p>↓</p> <p>thimble quarts filter double</p> <p>↓</p> <p>DIOANA</p> <p>↓</p> <p>pump, gas meter</p>	<p>sampling hole</p> <p>↓</p> <p>thimble quarts filter double</p> <p>↓</p> <p>DIOANA, #1</p> <p>↓</p> <p>impinger</p> <p>↓</p> <p>DIOANA, #2</p> <p>↓</p> <p>pump, gas meter</p> <p style="text-align: right;">I II</p>
notes			DIOANA filter, #1 was changed every 6 hours set I and II were individually analyzed

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Table 3 Concentrations (ng/m³N) and TEQs (ng-TEQ/m³N) of PCDD/Fs and PCBs in the flue gas collected using

Facility	A		B		C			D			
Method	a		a		a	b1	b2	a	b1	b2	
Set of collector							I	II		I	II
Oxygen (%)	11.9	13	13.8	13.8	13.8	13.8	13.8	9.6	9.6	9.6	9.6
MoCDDs	0.039	<0.005	0.022	0.0088	0.01	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
DiCDDs	0.03	0.041	0.14	0.2	0.2	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TrCDDs	0.012	0.042	0.16	0.24	0.25	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TeCDDs	0.42	0.27	1.2	2.0	2.3	0.012	0.0091	0.014	0.013	0.00020	0.00020
PeCDDs	0.84	0.47	1.1	1.7	2.0	0.020	0.0066	0.012	0.012	0.00020	0.00020
HxCDDs	1.5	0.83	1.6	3.6	4.5	0.057	0.0068	0.014	0.015	0.00034	0.00034
HpCDDs	1.4	0.38	0.85	2.1	2.5	0.065	0.0018	0.0049	0.0047	<0.005	<0.005
OcCDD	1.5	0.19	0.49	1.00	1.4	0.067	0.0011	0.0041	0.0036	0.00017	0.00017
Total PCDDs	5.6	2.2	5.6	11	13	0.22	0.025	0.050	0.049	0.00092	0.00092
MoCDFs	3.4	0.051	1.4	1.2	1.3	<0.005	0.0063	0.0077	0.0084	<0.005	<0.005
DiCDFs	1.0	<0.005	0.49	0.58	0.60	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TrCDFs	0.97	0.016	0.59	0.70	0.82	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
TeCDFs	1.2	0.12	0.97	1.3	1.6	0.029	0.0031	0.0056	0.0052	0.00054	0.00054
PeCDFs	1.2	0.10	1.2	1.6	2.1	0.039	0.0023	0.0050	0.0051	<0.005	<0.005
HxCDFs	1.2	0.070	1.1	1.7	2.2	0.054	0.0012	0.0028	0.0030	0.00011	0.00011
HpCDFs	0.87	0.032	0.63	1.3	1.6	0.063	0.00075	0.0020	0.0017	0.00013	0.00013
OcCDF	0.35	0.0058	0.23	0.49	0.66	0.044	0.00015	0.00063	0.00056	0.00012	0.00012
Total PCDFs	10	0.40	6.6	8.8	11	0.23	0.014	0.024	0.024	0.00089	0.00089
MoCBs	8.4	0.18	3.2	2.9	5.0	0.023	0.031	0.022	0.030	<0.01	<0.01
DiCBs	1.9	0.28	1.3	1.4	2.1	0.068	0.091	0.031	0.086	0.050	0.050
TrCBs	1.3	0.29	1.4	1.2	2.1	0.068	0.084	0.021	0.062	0.065	0.065
TeCBs	2.9	0.35	0.70	0.58	1.0	<0.01	0.16	0.032	0.030	0.011	0.011
PeCBs	1.1	0.27	0.37	0.23	0.37	0.027	0.22	<0.01	0.012	<0.01	<0.01
HxCBs	1.0	0.023	0.38	0.29	0.37	<0.01	0.11	<0.01	<0.01	<0.01	<0.01
HpCBs	0.65	<0.01	0.25	0.23	0.35	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
OcCBs	0.40	<0.01	0.17	0.18	0.27	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
NoCBs	0.29	<0.01	0.11	0.12	0.17	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
DeCB	0.10	<0.01	0.044	0.045	0.068	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Total PCBs	18	1.4	8.0	7.2	12	0.19	0.70	0.11	0.22	0.13	0.13
Σ PCDD/Fs & PCBs	34	4.0	20	27	36	0.64	0.74	0.18	0.29	0.13	0.13
TEQ	0.14	0.023	0.13	0.20	0.26	0.0056	0.00026	0.00062	0.00069	0.000055	0.000055

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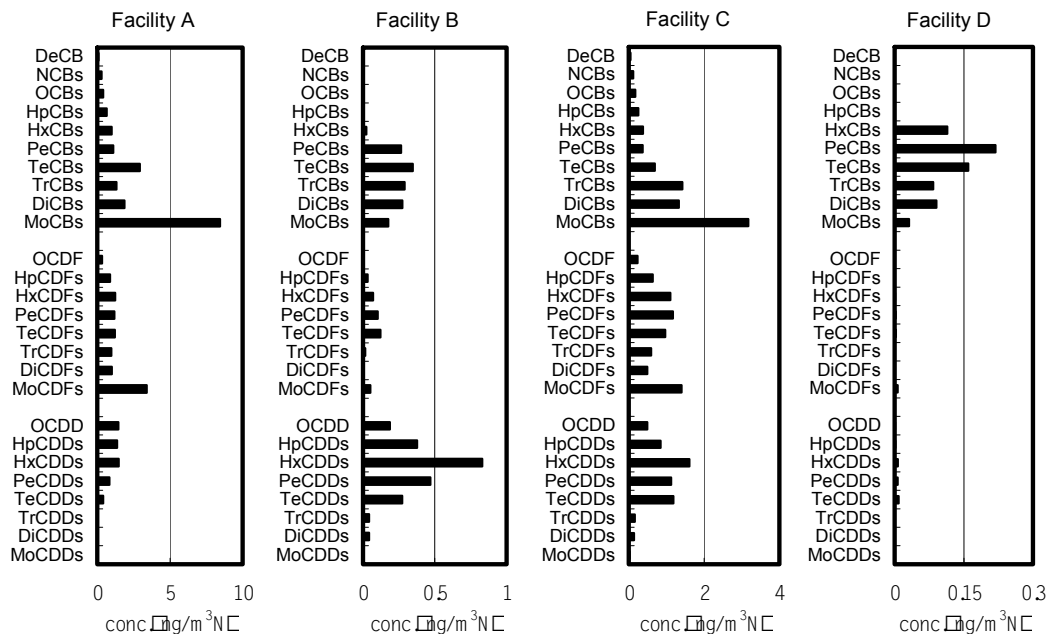


Figure 1 Concentrations (ng/m³N) of congeners of PCDD/F and PCB in flue gas from MWI investigated.

Analysis: All PCDD/F 1-8 chlorine(s)-substituted and PCB 1-10 chlorine(s)-substituted congeners were analyzed and their respective peaks on chromatograms individually assigned and measured. The GC capillary columns used for measurement of PCDD/Fs and PCBs were, respectively, a CP-sil 88 for dioxins (60 m, 0.25 mm i.d., 0.25 µm film thickness, Varian, USA) and an HT-8 (60 m, 0.25 mm i.d., SGE, Australia).

Results and discussion

Sampling spikes were recovered at the rate of 67.4-127.2% (average: 95.5%). There was no significant difference between the recovery rates between the standard and simple methods, so the results did not require compensation by the SS recovery rates.

Characteristics of congener composition of dioxins in flue gas from MWI: A summary of results from the conventional method is shown in Table 3. The range of concentrations and TEQ summed PCDD/Fs and PCBs in the flue gas were 0.74-34 ng/m³N and 0.00026-0.14 ng TEQ/m³N, respectively. Although the concentrations and TEQs varied markedly among the samples, the samples from Facilities A and C appeared to be similar with respect to the composition of the congeners of PCDD/F and PCB as shown in Figure 1; more specifically, it is the composition that the concentration of lower chlorinated PCBs is higher and mono-CDFs and from penta- to hepta-CDD/Fs are high concentrations. The reason is likely to be that both facilities have the same type of furnace and treatment system for flue gas. The quality of waste was also similar.

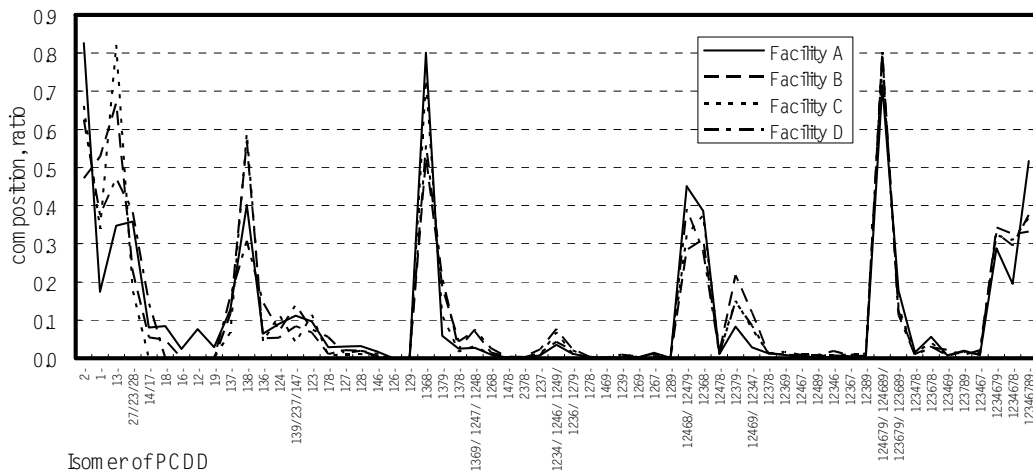


Figure 2 Isomer composition* of PCDDs in the flue gas from the MWIs investigated.

* It was calculated by dividing each isomer concentration by the sum of them in every congener, however, hepta- and octa-chlorinated congeners were treated as one group.

Isomer composition of PCDD/Fs and PCBs in the samples was then investigated. Isomer compositions were calculated by dividing each isomer concentration with the sum of them in every congener while hepta- and octa-CDDs or CDFs were treated as one congener group, respectively. As an example, the isomer compositions of PCDDs of all Facilities are shown as lines in Figure 2. The isomer compositions of PCDD/Fs (PCDFs are not shown in the Figure), were very similar from mono- through octa-chlorinated congeners for all samples. On the other hand, the isomer composition of PCBs was not coincident for all samples, but was similar for Facilities A and C.

The reason for the isomer compositions of dioxins being similar in the flue gas samples from all the facilities is not clear, except that all facilities were municipal waste incinerators. It may be that the isomer composition, which was investigated in this study, is common to most MWIs.

Investigation of simple sampling of flue gas for the source estimation: The concentrations of dioxins collected using the simple sampling methods (methods *b1*, *b2*) were generally higher than those using the conventional methods (method *a*), with a maximum differential of 1.83 times observed between methods *a* and *b1* for Facility C. For Facility D, the concentrations of PCDD/Fs were higher, but PCBs were lower than in the conventional method. However, the levels of these compounds on Facility D may be too low to allow meaningful discussion of the accuracy of the data. Also, the difference expanded with increasing chlorine number on the congener, as shown in Figure 3. This suggests that low-volatility compounds would be trapped more effectively by the simple methods and that high-volatility compounds might be lost when using the conventional method. The result did not entirely support the report by Kajikawa *et al.*⁹⁾, which indicated good agreement between the DIOANA® filter and impinger sampling. It is, needless to say, important not to draw conclusions before a sufficient number of experiments have been carried out.

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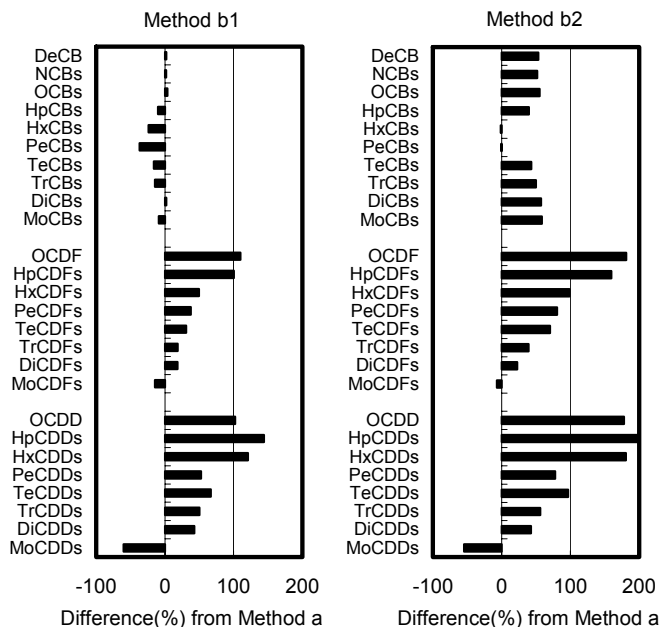


Figure 3 Differences (%) between the simple method and the conventional methods with respect to the congener concentrations of PCDD/Fs and PCBs in flue gas from

All methods agreed on the isomer composition, unlike the concentration and the balance of the congeners with different numbers of chlorine atoms. This is illustrated in Figure 4 as relationships between the component ratios of each isomer. The decision factors (R^2) of regressions were very high (0.945-0.998) for all compounds. It was confirmed that the simple sampling method using a DIOANA® filter can be applied in source-estimating studies that focus on isomer composition.

Although leaking of the sample gas was observed with method *b2*, the amounts of dioxins detected from the sampling plug set II were very small. Indeed, the leaking of dioxins during method *b1* might be greater than with method *b1* because of the longer sampling time per sampling plug. Nevertheless, isomer compositions of dioxins were reasonably coincident for all methods, indicating that the methods investigated in this study should be able to be used for extended periods of up to at least 24 hours.

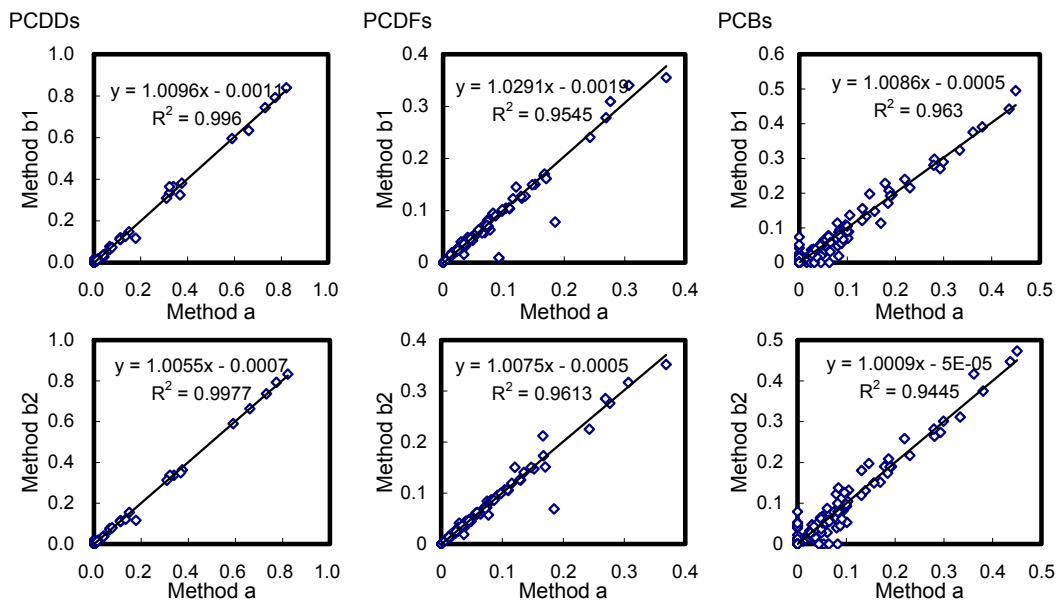


Figure 4 Relationship of the isomer composition* of PCDD/Fs and PCBs between the simple method (b1 or b2) and the conventional method (a) in flue gas from Facility C.

* It was calculated by dividing each isomer concentration by the sum of them in every congener, however, hepta- and octa-chlorinated congeners were treated as one group.

The upper and lower graphs show the relationships between method a and b1, and b2, respectively. The formula shows the approximate mathematical expression for the line in each graph. R^2 indicates the decision factor of the regression.

Acknowledgements

We thank all the parties who assisted us with the sampling of MWI flue gas. This study was promoted as part of an environmental research program (2002) sponsored by the Ministry of the Environment, Japan.

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