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Characterization of PCDDs/PCDFs Profiles of Various Emission Sources

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The homologue and congener profiles of PCDDs/PCDFs were characterized for various emission sources in an industrial complex in the west of Seoul, the capital of Korea, in order to identify the own profile and to compare the emission characteristics at each emission source. Waste incinerators and manufacturing industrial plants were identified as the major emission sources. PCDDs/PCDFs were sampled three times from stack emission of each facility and all congeners of PCDD/PCDF were analyzed. The homologue profile was calculated as the ratio of the concentration of each homologue to the total concentration of all homologues. The congener profile was calculated as the ratio of the concentration of each 2,3,7,8-substituted congeners to the total concentration of homologues from Cl_4DDs/DFs to Cl_8DDs/DFs. The congeners from Cl_1DDs/DFs to Cl_3DDs/DFs were emitted more from manufacturing industry sources and the congeners from Cl_4DDs/DFs to Cl_8DDs/DFs were emitted more from waste incineration sources. The homologue profiles and congener profiles by concentration were different according to emission sources, but the congener profiles by toxic equivalents (TEQ) value were similar among the sources. Therefore, PCDDs/PCDFs profiles in various emission sources could be characterized with homologue profiles and congener profiles by concentration, but not by the congener profile with TEQ value.

Key words: congener, emission source, homologue, PCDD/PCDF profile

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs) are persistent organic pollutants that are toxic, bio-accumulative, and can be transported to long distance. They are released into the air as by-products of various industrial processes. Measurement of PCDDs/PCDFs concentration in fly ash, off-gas emission from municipal solid waste incineration[1)], other similar sources and studying their effect in human health, ecosystem and the environment is essentially important. Usually, PCDDs/PCDFs are formed by thermal reactions as by-products of industrial processes that use heat, or by chemical reactions in processes that use chlorine gas in the temperature range 250-450°C[2-8)]. The most significant emission sources of PCDDs/PCDFs are waste incinerators, steel industries, non-ferrous metal manufacturing facilities and cement industries. In Korea, the concentration of PCDDs/PCDFs emitted from waste incinerators has been regulated since 1997, and that from steel industries, non-ferrous metal manufacturing facilities and cement industries has been regulated since 2008. In addition, ambient air and soil quality around an emission source must be sampled to investigate the influence of such sources in the surrounding environment[9)].

In many papers, the main source of PCDDs/PCDFs in an area was determined by comparing the pattern or profile of PCDDs/PCDFs only by the concentrations of individual homologue or toxic congener in environmental samples. However, given the only concentration of each homologue or toxic congener, it is

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difficult to determine the relationship between emission source and environmental samples in an area. Rappe[10] defined the term "pattern" and "profile" that the pattern is expressed as the proportions of all isomers within a group of isomers, and the profile is expressed as the ratio the concentrations of each isomer to the sum of all isomers within a group. Further, Rappe[10] reported that the patterns of PCDDs/PCDFs in most of the incineration or combustion sources seem to be containing almost the similar isomers. The available data indicates a larger variation in the profiles than in patterns from different sources. Cleverly[11] also reported that the dominant compounds in profiles of 2,3,7,8-substituted congeners can differ according to emission sources or the air pollution control devices (APCDs) used. Ogura[12] compared the homologue profiles and congener profiles to identify the combustion sources. The homologue profiles of combustion sources were more varied than their congener profiles; therefore emission sources may be better identified using the former than the latter.

However, Addink[13] and Wehrmeier[14] reported that the homologue ratios in samples from waste incinerators are similar, regardless of incineration conditions or gas cleaning methods. Abad[15] reported that the pattern of ambient air had the same ratios as the stack gas in an area assumed to be influenced by incinerators. From these references it is clear that in order to identify the emission source and environmental samples, the congener profile is more useful than the congener pattern. Similarly, homologues profile is more useful than congener profile.

Therefore, in this study, we characterized the homologue and conger profiles of PCDDs/PCDFs in various emission sources in order to identify their behavior in each source and to compare the emission characteristics between sources.

2. Materials and Methods

2.1 Emission sources and tested facilities

The emission sources were classified largely into waste incineration sources and manufacturing industry sources. The tested facilities were 3 municipal solid waste incinerators (MSWIs), 8 industrial solid waste incinerators (ISWIs), 3 infectious waste incinerators (IWIs), 6 waste-pulp and -paper incinerators (WPPIs), 5 nonferrous metal industry facilities (NMIFs), 7 iron and steel industry facilities (ISIFs) and 9 chemical industry facilities (CHIFs). The number of tested facility was based on the distribution of each emission source in this industrial complex. The waste incinerators had cooling system such as waste hea boiler and APCDs such as cyclone, scrubber, semi-dry absorber, bag filter and selected catalytic reator. NMIFs and ISIFs had electric furnace. CHIFs had chemical reaction in process or boiler. Input material was municipal solid waste in MSWIs; industrial solid waste (excluding hazardous waste) in ISWIs; medical and infectious waste in IWIs; waste paper and waste synthetic resins in WPPIs; copper, zinc and nonmetal waste in NMIFs; scrap iron and ferroalloys in STIFs; and synthetic resins and solvents in CHIFs.

2.2 Sampling and analysis methods

The stack sampler and gas probe were used to sample PCDDs/PCDFs. PCDDs/PCDFs were collected three times in stack emission of each facility in a sampling train. The sampling system consisted of a probe, a cylindrical filter, two impingers (one was filled with 250 ml of distilled water, and the other was empty), a sorbent (XAD-2) trap, and two impingers (one was filled with 150 ml of ethylene glycol, and the other was empty). After sampling, the collected PCDDs/PCDFs samples were extracted and pretreated according to the Korean Standard Testing Method for Dioxins and Furans in stationary sources emissions[16]. To analyze mono-, di- and tri-chlorinated dibenzo-*p*-dioxins (DDs) / dibenzofurans (DFs), the previous papers were referred[17,18,19]. The calibration standards of mono-chlorinated DD (Cl_1DD), di-chlorinated DD (Cl_2DD) and tri-chlorinated DD (Cl_3DD) and three $^{13}C_{12}$-labeled standards of Cl_1DD, Cl_2DD and Cl_3DD were prepared. To analyze tetra-, penta-, hexa-, hepta- and octa-chlorinated DDs / DFs (Cl_4-,Cl_5-,Cl_6-,Cl_7-,Cl_8DDs/DFs), 15 kinds of $^{13}C_{12}$-PCDDs/PCDF was used as internal standard based on Korean Standard Testing Method for Dioxins and Furans in stationary sources emission[16]. Analyzer used was high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS; JEOL 700D) above 10,000 resolution with an SP-2331 column of 60 m × 0.32 mm ID × 0.25 um. Toxic equivalents (TEQ) values were calculated by the international toxicity equivalency factor (I-TEF).

2.3 Profile development methods

In this paper, the profile development methods were referred to the Cleverly's methods[11]. The homologue profile was expressed as the ratio of the concentration of each homologue to the total concentration of PCDDs/PCDFs. The congener profile was expressed as the ratio of the concentration or TEQ value of 2,3,7,8-substituted congeners to the concentration of homologues from Cl_4DDs/DFs to Cl_8DDs/DFs.

- Homologue profile: concentration of each homologue / concentration of all homologues
- Congener profile by concentration: concentration of each 2,3,7,8-substituted congener / concentration of homologues from Cl_4DDs/DFs to Cl_8DDs/DFs
- Congener profile by TEQ value: TEQ-value of each 2,3,7,8-substituted congener / concentration of homologues from Cl_4DDs/DFs to Cl_8DDs/DFs

3. Results and Discussions

3.1 Emission characteristics of PCDDs/PCDFs in various emission sources

In flue gas emission from various emission sources we measured the concentrations of 210 congeners from Cl_1DDs/DFs to Cl_8DDs/DFs; the concentrations of 136 congeners from Cl_4DDs/DFs to Cl_8DDs/DFs; the concentrations and TEQ value of 2,3,7,8-substituted congeners of PCDDs/PCDFs in order to investigate the emission characteristics and to develop the profiles.

The distribution of homologues and congeners is shown in Fig. 1. The homologue distribution results showed that the most dominant homologue was Cl_4DFs in MSWIs, IWIs and WPPIs; Cl_5DFs in ISWIs; Cl_1DFs in NMFIs, ISIFs and CHFIs. The second dominant homologue was Cl_5DFs in MSWIs; Cl_6DFs in ISWIs; Cl_3DFs in IWIs; Cl_3DFs and Cl_5DFs in WPPIs; Cl_2DFs in NMFIS and ISIFs; Cl_1DDs in CHFIs. The next dominant homologue was Cl_3DFs in MSWIs, NMFIs

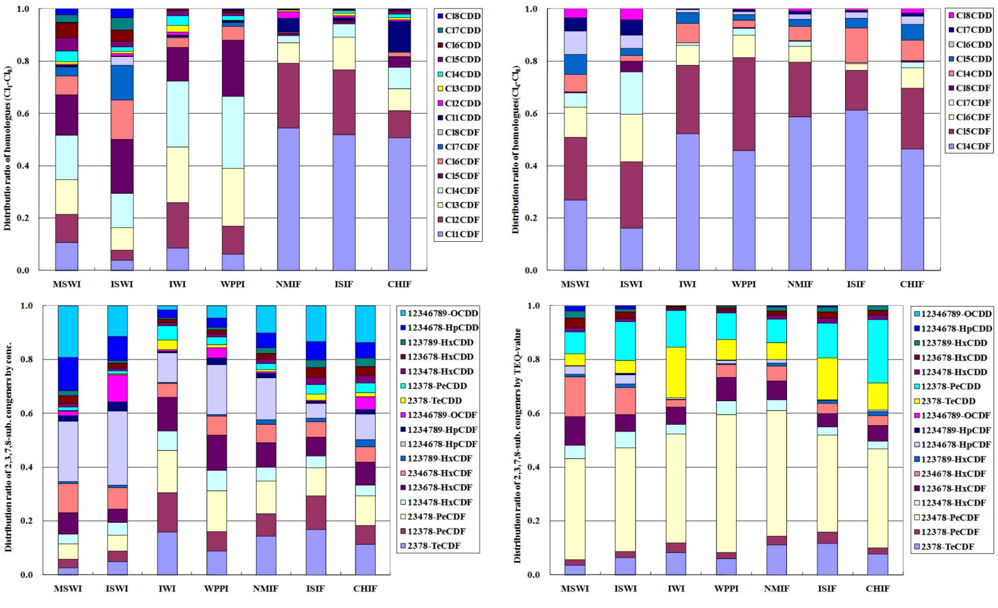

Fig. 1. Distribution ratio of PCDDs/PCDFs in various emission sources.

and ISFIs; Cl_4DFs and Cl_7DFs in ISWIs; Cl_2DFs in IWIs and WPPIs; Cl_3DFs and Cl_4DFs in CHFIs. From industrial facilities, Cl_1DFs were emitted more than 50% and from waste incinerators, Cl_4DFs and Cl_5DFs were emitted above 30-40%. In waste incinerators, the emission characteristics were different according to the type of waste incinerated, even though waste incinerators were having the similar APCDs. On the other hand, in the NMIFs and ISIFs which had similar process (electric furnace) and APCDs, the emission characteristics of PCDFs were similar, although the input materials were different. In CHIFs, the emission characteristics were different than other emission sources.

The proportion of 10 homologues from Cl_4DDs/DFs to Cl_8DDs/DFs to total homologues from Cl_1DDs/DFs to Cl_8DDs/DFs was 63.7% in MSWIs, 81.9% in ISWIs, 48.5% in IWIs, 60.4% in WPPIs, 4.6% in NMIFs, 8.4% in ISIFs and 17.7% in CHIFs. Thus, it is clear that the homologues from Cl_1DDs/DFs to Cl_3DDs/DFs are emitted more from industry facilities than from waste incinerators, and homologues from Cl_4DDs/DFs to Cl_8DDs/DFs are emitted more from waste incinerators than from industry facilities.

The distribution of 2,3,7,8-substituted congeners by concentration shows that the most dominant congener was 1,2,3,4,6,7,8-HpCDF in MSWIs, ISWIs, WPPIs and NMFIs; 2,3,7,8-TeCDF and 2,3,4,7,8-PeCDF in IWIs; 2,3,7,8-TeCDF in ISIFs; 1,2,3,4,6,7,8,9-OCDD in CHFIs. The second dominant congener was OCDD in MSWIs, ISWIs and ISIFs; 1,2,3,7,8-PeCDF in IWIs; 2,3,4,6,7,8-PeCDF in WPPIs; 2,3,7,8-TeCDF in NMFIs and CHFIs. The next dominant congener was 1,2,3,4,6,7,8-HpCDD and 2,3,4,6,7,8-HxCDF in MSWIs; 1,2,3,4,6,7,8,9-OCDF in ISWIs; 1,2,3,6,7,8-HxCDF in IWIs and WPPIs; 2,3,4,7,8-PeCDF in NMFIs and CHFIs; 1,2,3,7,8-PeCDF in ISFIs.

The proportion of 2,3,7,8-substituted congeners to total homologues from Cl_1DDs/DFs to Cl_8DDs/DFs was 11.5% in MSWIs, 34.0% in ISWIs, 1.9% in IWIs, 6.5% in WPPIs, 3.7% in NMIFs, 2.0% in ISIFs and 8.1% in CHIFs. Therefore, it shows that the congeners from Cl_1DDs/DFs to Cl_3DDs/DFs are emitted more from industry facilities than from waste incinerators, and congeners from Cl_4DDs/DFs to Cl_8DDs/DFs are emitted more from waste incinerators than industry facilities.

The distribution of 2,3,7,8-substituted congeners by TEQ value, in the all emission sources, 2,3,4,7,8-PeCDF was most dominant congener. The second dominant congener was 2,3,4,6,7,8-HxCDF in MSWIs; 1,2,3,7,8-PeCDD in ISWIs, WPPIs and CHIFs; 2,3,7,8-TCDD in IWIs and ISIFs; and 2,3,7,8-TeCDF in NMFIs.

The distribution of homologues and 2,3,7,8-substituted congeners based on concentration was different in emission sources, but the distribution of 2,3,7,8-substituted congeners by TEQ value was similar. Therefore, it is difficult that using the distribution of 2,3,7,8-substituted congeners by TEQ value the emission characteristic of each emission source was found.

3.2 Homologue profiles of PCDDs/PCDFs in various emission sources

Fig. 2 shows the homologue profiles of PCDDs/PCDFs in various emission sources. The homologue profile was expressed as the ratio of the concentration of each homologue to the total concentration of PCDDs/PCDFs. The homologue profiles of PCDDs/PCDFs in waste incinerators were distinguishable according to the type of waste incinerated. Cl_4DF were the most dominant homologue in MSWIs, IWIs and WPPIs, but Cl_5DF were the most dominant homologues in ISWIs. The second dominant homologue was Cl_5DF in MSWIs, Cl_6DF in ISWs, and Cl_3DF in IWIs or WPPIs.

Considering all industrial sources, the most dominant homologue was Cl_1DF. In NMIFs and ISIFs, the second dominant homologue was Cl_2DF. In NMIFs and ISIFs the homologue profiles of PCDFs were similar, but those of PCDDs were different. CHFIs had a unique profile of PCDD/PCDF homologues; the dominant homologue was Cl_1DF followed by Cl_1DD. This means that CHFIs emit a large proportion of Cl_1DDs/DFs. Therefore, PCDD/PCDF profiles of various emission sources could be characterized by quantifying the proportions of homologues present.

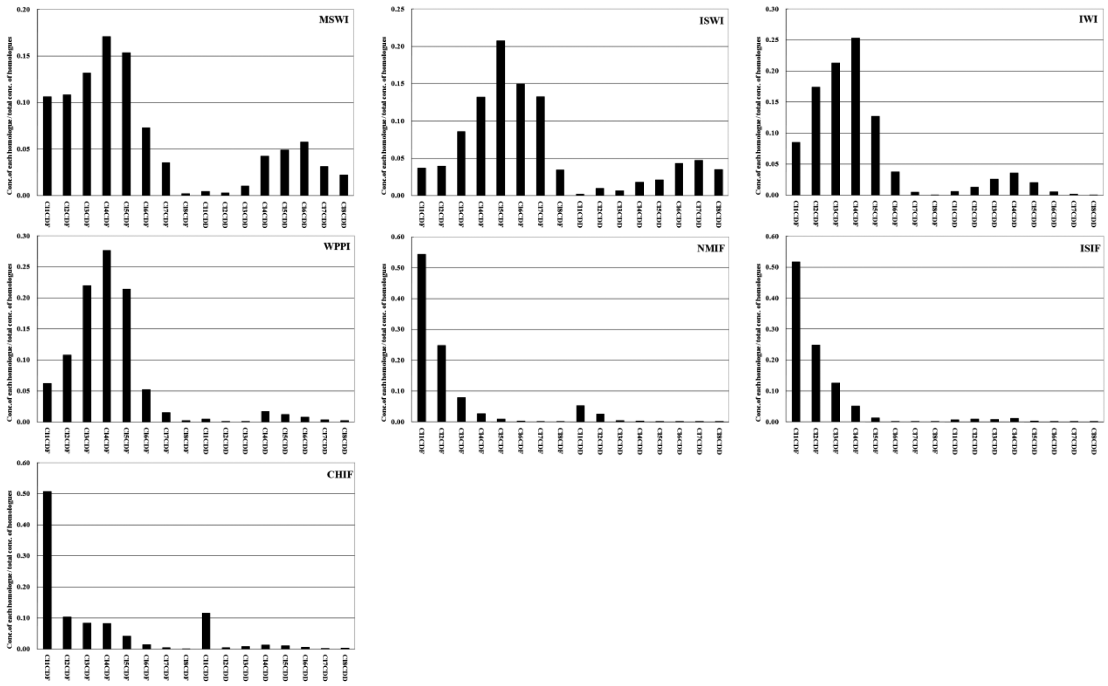

Fig. 2. Homologue profiles of PCDDs/PCDFs in various emission sources.

3.3 Congener profiles of PCDDs/PCDFs in various emission sources

Congener profiles of PCDDs/PCDFs by concentration in various emission sources are shown in Fig. 3. The congener profiles of PCDDs/PCDFs were expressed as ratios of the concentration of 2,3,7,8-substituted congeners to the concentration of homologues from Cl_4DDs/DFs to Cl_8DDs/DFs. In sources except IWIs, OCDD was the most dominant congener and the second dominant congener was 1,2,3,4,6,7,8-HeCDD. In IWIs, 1,2,3,7,8-PeCDD was the most dominant congener and the second dominant congener was 2,3,7,8-TeCDD. The congener profiles of PCDDs/PCDFs in various waste incinerators were distinguishable according to the type of waste, but those in various industry facilities were similar. Therefore, PCDD/PCDF profiles of waste incineration sources could be characterized by quantifying the proportions of 2,3,7,8-substituted congeners with concentration present, but PCDD/PCDF profiles in various industrial sources could not be characterized by quantification of the proportions of 2,3,7,8-substituted congeners with TEQ-value present.

Fig. 4 shows the conger profiles of PCDDs/PCDFs in various emission sources by TEQ value. The congener profiles of 2,3,7,8-substituted PCDDs/PCDFs were expressed as the ratio of TEQ value of 2,3,7,8-substituted congeners to the concentration of homologues from Cl_4DDs/DFs to Cl_8DDs/DFs. The most dominant congeners were 2,3,4,7,8-PeCDF in MSWIs; 1,2,3,7,8-PeCDD in ISWIs, WPPIs, NMIFs and CHIFs; and 2,3,7,8-TeCDD in IWIs and ISIFs. The second dominant congeners were 1,2,3,7,8-PeCDD in MSWIs, IWIs and ISFIs; 2,3,4,7,8-PeCDF in ISWIs and NMFIs; and 2,3,7,8-TeCDD in WPPIs and CHIFs. The congener profiles in various emission sources were similar, except the congener profile in MSWIs. Therefore, PCDD/PCDF profiles of waste incineration sources could be characterized by quantification of the proportions of 2,3,7,8-substituted congeners by TEQ-value present, but PCDD/PCDF profiles of various industry sources could not be characterized by quantification of the proportions of 2,3,7,8-substituted congeners by TEQ-value present.

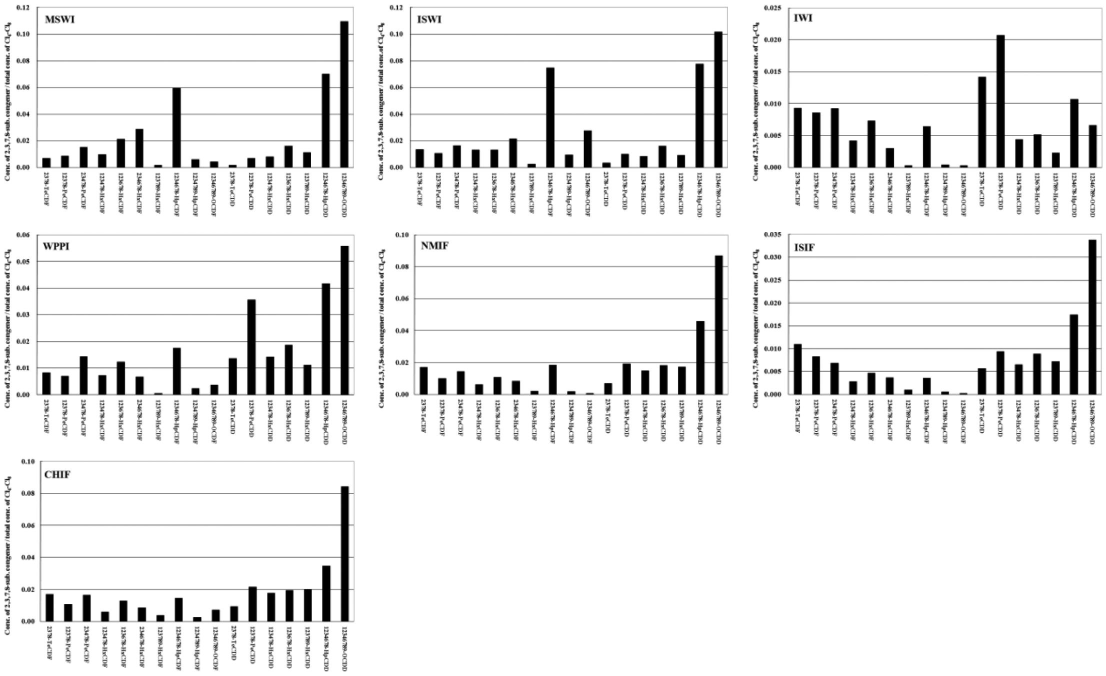

Fig. 3. Congener profiles of PCDDs/PCDFs with concentration in various emission sources.

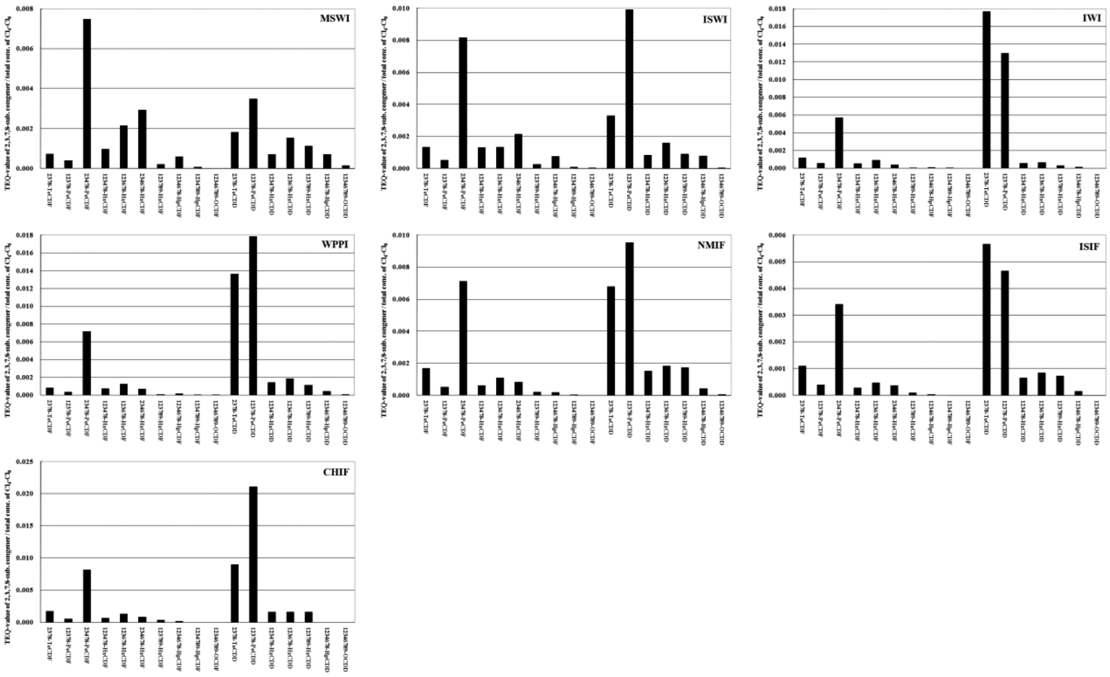

Fig. 4. Congener profiles of PCDDs/PCDFs with TEQ-value in various emission sources.

4. Conclusions

We characterized the homologue and conger profiles of PCDDs/PCDFs in various emission sources in order to identify the profile of each emission source and to compare the emission characteristics among emission sources. The results obtained allowed the following conclusions:

(1) The homologues/congeners from Cl_1DDs/DFs to Cl_3DDs/DFs are emitted more from industrial facilities than from waste incinerators. Homologues from Cl_4DDs/DFs to Cl_8DDs/DFs are emitted more from waste incinerators than from industrial facilities.

(2) The homologue profiles of PCDDs/PCDFs in various emission sources were different, so these differences allowed the various emission sources to be characterized.

(3) The 2,3,7,8-substituted congener profiles of PCDDs /PCDFs with concentration were slightly different among various sources; these differences allowed the various emission sources to be characterized.

(4) The 2,3,7,8-substituted congener profiles of PCDDs /PCDFs with TEQ value were similar in various emission sources, because of which characterization of the various sources was difficult.

(5) The homologue profile of PCDDs/PCDFs and 2,3,7,8-substituted congener profile of PCDDs/ PCDFs with concentration is more useful than that with TEQ value to characterize PCDD/PCDF in various emission sources.

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