APPLICATION OF THE CONSTELLATION GRAPHICAL METHOD TO DIOXIN DATA

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs), hereafter referred to as dioxins, are high toxicity persistent chemicals and widespread environmental pollutants.Pollution source identification is important to select effective countermeasures preventing their environmental contamination. Many multivariate statisticalanalyses, such as principal component analysis (PCA),[1] cluster analysis,[2] chemical mass balance (CMB),[3]and positive matrix factorization,[4]have been successfully applied to identify pollution sources of dioxins. However, they also contain some drawbacks. For example, PCA needs a number of samples andcomplicated computation; moreover,it is difficult to interpret the analysis result.CMB requires the chemical profiles of all significant sources of dioxins in advance in addition to complicated computation.We have proposed a toxic equivalent (TEQ) apportionment technique by using indicative congeners with simple calculation (indicative congener method, ICM).[5]Though ICM has accomplished some positive results,[6,7]this method is designated only for four major dioxin sources in Japan (combustion by-product, pentachlorophenol (PCP) formulations, chlornitrofen (CNP) formulations and PCB products). There is no versatile method for dioxin-source identification.Under the circumstance, combined use of some methods is the preferred approach for dioxin-source analysis.In this report, we focused on the Constellation Graphical Method[8] as a new tool of dioxin-source analysis. We discussed the utility of the method by applying selecteddioxin source and environmental data.

Materials and methods

Constellation Graphical Method

Constellation Graphical Method is a method to easily represent multi-dimensional data on a two-dimensional plane, proposed by Wakimoto and Taguri.[8] In the method, the *i*th variable in an object with *n* variables is represented as two-dimensional vector with the length of r_i and the argument of θ_i, and the sum of *n* vectorscorresponds to the object. Where $\Sigma(r_i) = 1$ and $0 < \theta_i < \pi$;because of this limitation, the objects are plotted within the upper half of the unit circle (Fig. 1). The plots look like the stars on the sky, and then the method was namedas “Constellation Graph”.

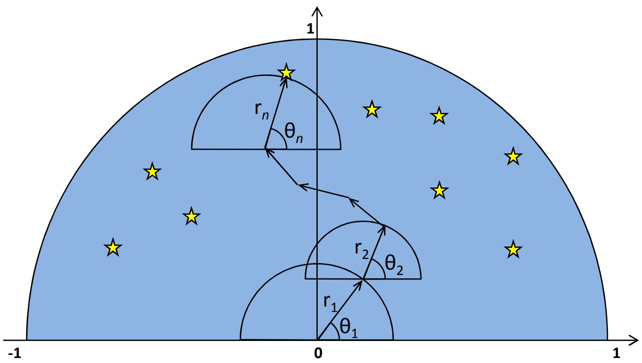

Fig. 1 An illustration of the plot of *n*-variable object by the constellation graphical method. The illustration was derived from the Ref.8.

Dioxin data

Dioxins were unintentionally produced as unwanted by-products during manufacturing and combustion processes;[9]moreover, they were also naturally formed in some minerals.[10]We used data of well-known seven dioxin-sources: three agrochemicals (PCP formulations, CNP formulations, and Agent Orangedefoliant), combustion by-products, PCB products, chlorination by-products, and ball clay.Table 1shows the information of source data used. Concentrations below the detection limits or inspection standards were considered to be zero. DL-PCB data of Agent Orange were not available and we assumed those as zero, because most of DL-PCBs in other agrochemicals,PCP and CNP, were under the inspection limits.[11]

Table 1 Information regarding dioxin-source data used

Source	Note	Ref.
PCP (*N* = 10)		11
CNP (*N* = 16)	Samples of >2 ng-TEQ g^{-1} were selected.	11
Agent Orange (*N* = 33)	Soil (*N* = 19) and Sediment (*N* = 14) from Vietnam, which were likely to be contaminated by Agent-Orange-originated dioxins. Samples of >90% TEQ contribution by 2,3,7,8-tetrachlorodibenzo-*p*-dioxin were selected. DL-PCB data were not available.	12
Combustion (*N* = 96)	Emission gas(*N* = 48), fly ash(*N* = 21) and bottom ash(*N* = 27)collected from waste incinerators in Saitama, Japan.	5
PCB products (*N* = 28)	Kanechlor including KC-300 (*N* = 11), KC-400 (*N* = 5), KC-500 (*N* = 6), KC-600 (*N* = 1) and KC-1000 (*N* = 5).	13
Chlorination (*N* = 15)	River sediment treated withNaClO (*N* = 9) and brine electrolysiswith graphite electrode (*N* = 6).	14, 15
Ball clay (*N* = 5)	American ball clays containing ca. 1500 pg-TEQ g^{-1} of dioxins.	16

In addition to the source data, seasonal data of water of Ayase River, Japan[6] were analyzed.The waters were appeared to be contaminated mainly with PCP-originated dioxins, especially in irrigation period of May, June July and August, followed by combustion-originated ones.[6]

Parameter for Constellation Graphical Method

The Constellation Graphical Methodwas carried out to the source data in various conditions. Table 2shows the parameters (vector length r_i and argumentθ_i) applied.Concentrations of 29 congeners with toxic equivalency factor (TEF) values (TEF congeners)were used for the analysis. TEQ was calculated by using the TEF values established by the World Health Organization in 2006.[17]

Table 2 Parameter condition examined

Condition code	Vector length r_i(normalized as $\Sigma(r_i) = 1$)	Vector argumentθ_i(radian, $0 < \theta_i < \pi$)
I	1/29	Concentration ratio × π
II	1/29	TEQ ratio × π
III	Concentration ratio	TEF × π
IV	TEF ratio	Concentration ratio × π
V	Concentration ratio	TEQ ratio × π
VI	TEQ ratio	Concentration ratio × π
VII	Concentration ratio	$\log TEF_i/\log TEF_{minimumn} \times \pi$ [a]
VIII	$\log TEF_i/\log TEF_{minimumn}$ ratio	Concentration ratio × π
IX	Concentration ratio	$(x-4)/4 \times \pi$ [b]
X	TEQ ratio	$(x-4)/4 \times \pi$

[a]$TEF_{minimumn}$: TEF value of *mono-ortho* PCBs = 0.00003.
[b]*x*: Number of chlorine atoms substituted.

Results and discussion

Figure 2illustrates the examples of the plots of seven dioxin-source data applied by the Constellation Graphical Method. In the condition I (Fig. 2a), all the plots were located on the bottom-right corner and no source data was isolated. However, some sources were separatedin the selected conditions. Inthe condition VII (Fig. 2b), the constellation "CNP", "PCB" and "chlorination" were separated. Combustion-related data were isolated in the condition VIII (Fig. 2c). PCP and ball clay have resemble profileswhich were dominated by octachlorodibenzo-

p-dioxin.[16]The condition X (Fig. 2d) could separate both PCP and ball clay from other sources. There was no condition which perfectly separates all the seven source data; however, the seven were able to be distinguished by combining some conditions (Table 3).

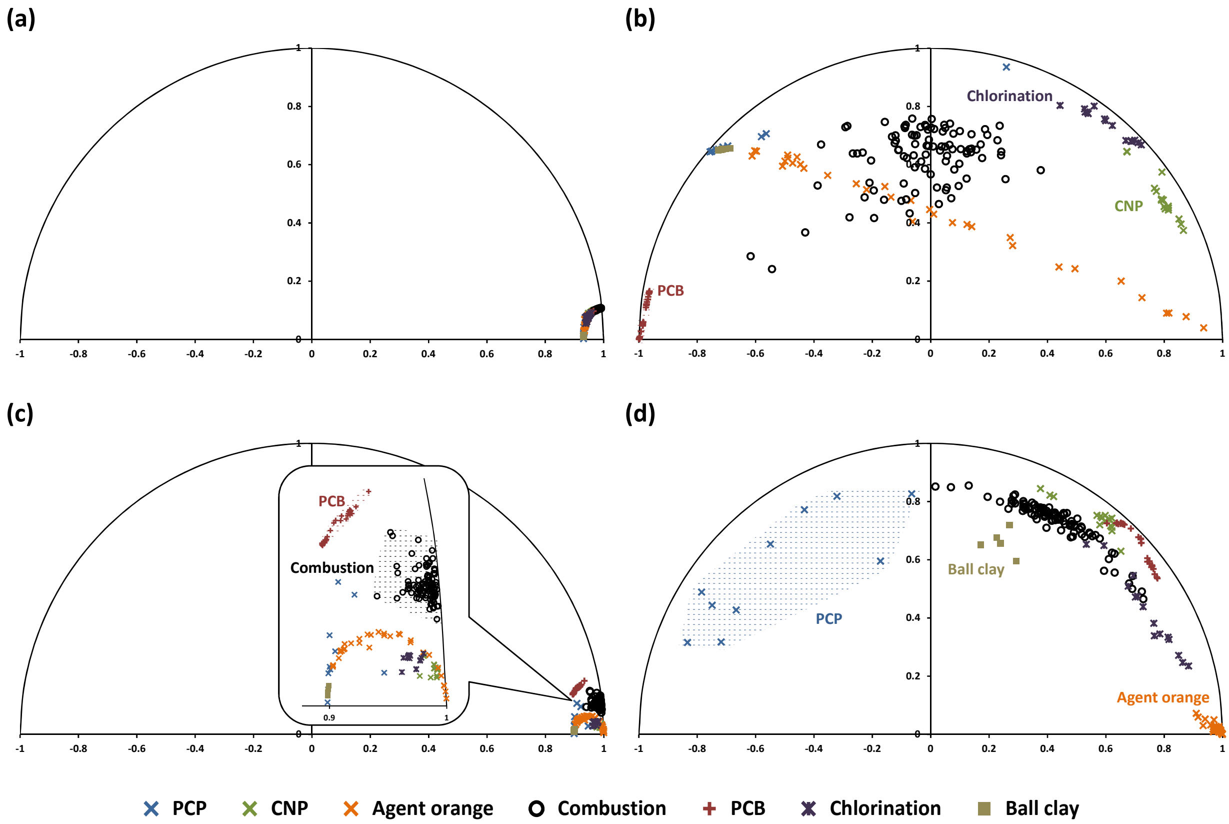

Fig. 2 Examples of the plots of dioxin-source data applied by the Constellation Graphical Method. (a): condition I, (b): condition VII; (c): condition VIII; (d): condition X.

Table 3 Results in separation of source-data plots

Source	Parameter condition									
	I	II	III	IV	V	VI	VII	VIII	IX	X
PCP										+
CNP			+				+		+	
Agent Orange		+[a]	+		+				+	+
Combustion								+		
PCB							+	+		
Chlorination			+	+			+			
Ball clay						+				+

[a]+: Separately plotted from other source data.

The result in condition IX for the water fromAyase River was illustrated in Fig. 3. They were plotted on a straight line between PCP and combustion. Moreover, as is the case in the analysisby using PCA,[6]samples collected in May, June, July and August–the irrigation period–were plotted together and closer to PCP.

The Constellation Graphical Method succeeded in distinguishing the seven source data and categorizing river-water data. Unlike multivariate statistical analyses, thismethod requires simple calculations; moreover, the coordinate of a sample is independent of the other samples. The method will help to qualitativelyidentify source of dioxins in the environment, though not quantitatively.

In this paper, we tested ten parameter conditions and targeted 29-TEF congener profiles. More useful constellations may be obtained by using other parameter conditions and/or other profiles such as 17-TEF PCDD/Fs,PCDD/F homologues, and isomer distribution in a homologue.

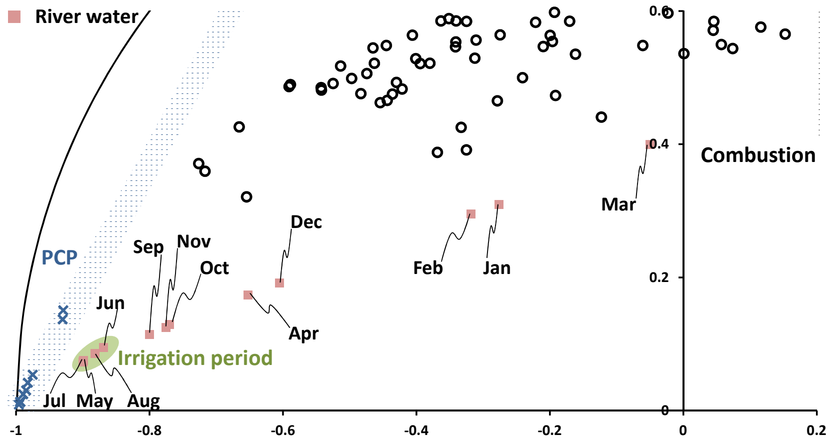

Fig. 3 Plots of river water data applied tothe Constellation Graphical Method in the condition IX. Source data except for PCP and combustion are not illustrated.

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