Estimation of TEQ of dioxins in environmental samples and evaluation of their pollution sources on the basis of five indicative congeners

（5 つの指標異性体による環境試料中ダイオキシン類の TEQ の推計と汚染原因の評価）

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理工学専攻（主指導教員 河村清史）

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September 2011

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Doctoral Thesis
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5つの指標異性体による環境試料中のダイオキシン類のTEQの推計と汚染原因の評価
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Abstract

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs), referred to as dioxins, are high toxicity persistent chemicals and widespread environmental pollutants. Japan was one of the most dioxin emitting countries in the world and public concern about dioxin emission from incinerators became particularly heightened in the 1990s. Due to nationwide efforts to tackle the dioxin issues, national dioxin emission has been reduced. However, there remains stock pollution problem. Pollution source identification is important to select effective countermeasures against their environmental contamination. Multivariate statistical analyses by using congener profile have been applied to identify pollution sources of dioxins. However, these analyses are difficult to employ, because they need a number of data sets, complicated calculation and specialized skills. From these backgrounds, a simple and manageable technique for dioxin source identification was proposed in this thesis.

The major sources of dioxins in the environment in Japan have been recognized to be combustion by-products, pentachlorophenol (PCP) formulations, chloronitrofen (CNP) formulations, and PCB products. Data on PCDDs, PCDFs and DL-PCBs from the four sources were analyzed, and indicative congeners whose concentrations were highly correlated with toxic equivalents (TEQs) based on the toxic equivalency factors (TEFs) established by the World Health Organization (WHO) in 2006 (WHO-2006 TEQs) were identified for samples of each source (N 96, 10, 16 and 28 for combustion by-product, PCP, CNP and PCB samples, respectively). The indicative congeners for combustion by-products, PCP formulations and CNP formulations were 2,3,4,7,8-pentachlorodibenzofuran, 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin and 1,2,3,7,8-pentachlorodibenzo-p-dioxin, respectively and those for PCB products were IUPAC Nos. #126- and #105-pentachlorobiphenyls. Moreover, a method for estimating the apportionment of WHO-2006 TEQs from the four sources by using only the concentrations of the above-mentioned five indicative congeners was developed. The method was named "indicative congener method (ICM)". The ICM was applied to the analyzed results of different types of environmental samples collected in Japan to determine the TEQ contributions of the four sources. The obtained results seemed to be reasonable. Unlike multivariate statistical analyses that require complicated computation using large amounts of data, the ICM can be used to estimate the TEQ contributions of the four sources by a simple calculation using only one set of concentrations of the five indicative congeners.

The ICM was applied to examine environmental behavior of dioxins. The paddy-field soil in Japan is polluted by dioxins originated from herbicides, PCP and CNP, which were applied abundantly, and there is a concern that the dioxins contained in paddy-field soil may be transferred to the atmosphere during field burning of rice straw. Therefore, smoke samples were
collected from rice straw burning sites at post harvest paddy fields, and dioxins present in the smoke samples were analyzed. The ICM indicated that the dioxins present in the rice-straw smoke were greatly influenced by those present as impurities in PCP and CNP formulations. Further, in order to evaluate the effects of paddy field soil on the dioxins present in rice-straw smoke, PCDD/PCDF/DL-PCB homologue profiles of rice straw, rice straw smoke and paddy-field soil were compared. The results suggested that the herbicides-originated dioxins and the atmospheric dioxins contributed predominantly to the presence of dioxins in the rice straw smoke, while the contribution of dioxins formed during rice straw burning was relatively minimal. The major sources of the dioxins found in the rice straw smoke were attributed primarily to the paddy field soil adhered to the rice straw surface and secondarily to the air taken by the rice straw. It is concluded that rice straw burning at paddy fields acts as a driving force in the transfer of dioxins from paddy field soil to the atmosphere.

The ICM was also applied to water environment. Ayase River is one of the most polluted rivers by dioxins in Japan. The water samples of the river were collected once per month for a year, and dioxins were analyzed to examine the dioxin sources and their contributions to toxic equivalent (TEQ). The WHO-2006 TEQs ranged from 0.26 to 7.0 pg-TEQ L$^{-1}$ and the average was 2.7 pg-TEQ L$^{-1}$—eight of twelve samples exceeded the environmental quality standard in Japan (1.0 pg-TEQ L$^{-1}$). The TEQ value was high during the irrigation period from May to August. The most part of the dioxins in the river water existed in suspended solids (SS), and it seemed that the river received water with highly-dioxin-contaminated SS in the irrigation period. According to the ICM, the TEQ was mainly contributed by PCP. Moreover, it was also shown that the TEQ contributions of PCP and CNP formulations increased along with the increase of the total TEQ, and the TEQ contribution was dominated by these herbicides during the irrigation period. Therefore, it was concluded that the herbicides-originated dioxins run off from the paddy fields into the river during the irrigation period and increased the dioxins level in the river water.

In order to obtain TEQ, the concentrations of the 29 TEF congeners in total are needed to determine by a gas chromatography/mass spectrometry (GC/MS). The official methods for dioxin analysis require three or more GC/MS measurements with several types of capillary columns, and a long measurement time. Quantifying as many as 29 congeners also requires time and efforts. Therefore, a simplified determination method for dioxin WHO-2006 TEQ in environmental samples collected in Japan was developed based on the ICM. In the simplified method, the five indicative congeners are detected, and TEQ is estimated by the ICM. A GC condition which separates the five indicative congeners from the other congeners by a single GC/MS measurement was searched. As a result, a combination of columns of 10-meter-long DB-5ms (injector side) and 20-meter-long DB-17ms (detector side) was selected. Applying this simplified determination method to various environmental samples (ambient air, river water, river sediment and soil) showed that the estimated TEQ was in good agreement with TEQ obtained by the corresponding official methods.
ダイオキシン類（ポリクロロベンゾパラジオキシン（PCDDs）、ポリクロロベンゾフラム（PCDFs）およびダイオキシン様ポリクロロビフェニル（DL PCBs））は、強毒性の難分解性化学物質で、世界中を汚染している。日本は世界で最もダイオキシン類を排出していた国の一つで、1990年代には廃棄物焼却炉から排出されるダイオキシン類が社会問題となった。国を挙げた対策が効果を奏し、排出量は大幅に削減されたものの、ストック汚染の問題は未だ解決されていない。環境の汚染源を推定する技術は、効果的な対策を講じるためにも重要である。ダイオキシン類の汚染源推定は、これまで、異性体プロファイルを基にした多変量統計解析が用いられてきた。しかしながら、多変量解析は多数の測定データ、複雑な計算、特別な技術が必要で、取り扱いが難しいといった問題があった。そこで、本学位論文では、ダイオキシン類の汚染源を簡便に推算する技術を提案した。

日本国内におけるダイオキシン類の汚染源は、燃焼工程の副生成物、ベンタクロロフェノール（PCP）製剤、クロルエトフェン（CNP）製剤およびPCB製品であると言われている。そこで、これら汚染源データ（燃焼、PCP、CNPおよびPCBについて、それぞれ試料数 N=96、10、16および28）を解析し、各汚染源について毒性等量（TEQ、WHOが2006年に提案した毒性等価係数（TEF）を基に算出したもので、WHO2006TEQと称する）と関連の高い異性体「指標異性体」を探索した。その結果、5つの指標異性体、2,3,4,7,8ベンタクロロジベンゾフラム、1,2,3,4,6,7,8ヘプタクロロジベンゾパラジオキシン、1,2,3,7,8ベンタクロロジベンゾパラジオキシンおよびIUPAC番号#126と#105番のベンタクロロビフェニルが見出された。さらに、これら5つの指標異性体の濃度から、各汚染源に由来するTEQを推算する方法を開発した。この方法を「指標異性体法」と名付けた。指標異性体法を国内で採用された様々な環境実験の測定結果に適用したところ、妥当な推算結果が得られた。大量の測定データと複雑な計算を必要とする多変量統計解析と異なり、指標異性体法が必要なのは5つの指標異性体濃度のみであり、1検体でも推算を行うことができる。

指標異性体法をダイオキシン類の環境動態解析に適用した。国内の水田は、かつて広範に使用されていた除草剤であるPCPとCNPに由来するダイオキシン類で汚染されている。そのため、収穫後の水田で行われている稲穂の焼却により、土壌中のダイオキシン類が大気中へ移行することが懸念される。そこで、水田で行われている稲穂焼却で生じる煙を採取し、その中に含まれているダイオキシン類を分析した。指標異性体法による解析から、稲穂中のダイオキシン類は、製剤の影響を強く受けていることが示された。さらに、水田土壌中のダイオキシン類の煙への影響を明らかにするため、稲穂、稲穂の煙および水田土壌中のPCDDs/PCDFs/DLPCBsの同族体プロファイルを比較した。その結果、稲穂焼却の過程で生成されるダイオキシン類の量は比較的少なく、稲穂中のダイオキシン類は、主に、稲穂表面に付着した水田土壌に由来するものと稲穂中に取り込まれた大気に由来するものによることが示された。以上から、稲穂の焼却は、水田土壌中のダイオキシン類を大気へと移行させる1つの駆動力となっていることが明らかになった。
指標異性体法を水環境にも適用した。埼玉県を流れる緒瀬川は、国内で最もダイオキシン類によって汚染されている河川の一つである。そこで、緒瀬川の河川水試料を毎月1回1年間連続して採取し、ダイオキシン類を分析した。河川水試料の TEQ は、0.26～7.0 pg TEQ L⁻¹の範囲（平均は2.7 pg TEQ L⁻¹）で、12検体中8検体が水質の環境基準（1.0 pg TEQ L⁻¹）を超過した。また、灌溉期である5月から8月に高い値を示した。水試料中のダイオキシン類はほとんどが懸濁物質（SS）中に存在し、灌溉期にはダイオキシン類濃度の高いSSが流入していた。指標異性体法による解析から、PCP 製剤が緒瀬川河川水の TEQ に対して大きく寄与していた。TEQ の上昇とともに、PCP および CNP 製剤の TEQ 寄与割合は増加し、灌溉期には両製剤による寄与がほとんどを占めた。以上から、とくに灌溉期において顕著であるが、両除草剤に由来するダイオキシン類の影響を受けた灌溉水が流入し、緒瀬川河川水中的ダイオキシン類濃度を高めていることが示された。

TEQ を得るためには、TEF の定められた29の異性体濃度をガスクロマトグラフィ/質量分析計（GC/MS）で測定しなくてはならない。そのため、公定法によるダイオキシン測定では異なる分離カラムを用いた GC/MS 測定を複数回行う必要があり、測定には時間がかかった。また、29 もの異性体の定量作業も時間と労力を必要とする。そこで、指標異性体を用いたWHO 2006 TEQ の簡易測定法を開発した。この簡易測定法では、5 つの指標異性体のみを測定し、指標異性体から TEQ を推算する。1回の GC/MS 測定で、5 つの指標異性体を他の異性体から分離できる GC 条件を探索したところ、注入口側に10m のDB 5ms を、検出器側に20m の DB 17ms を連結したカラムが見出された。この条件を用いて各種環境試料（大気、河川水、河川底泥、土壌）を測定し、TEQ を推算したところ、公定法による結果を良好に再現した。
List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

Paper I

Paper II

Paper III

Paper IV

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### Abbreviations

<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CMB</td>
<td>chemical mass balance</td>
</tr>
<tr>
<td>CNP</td>
<td>chlornitrofen (4-nitrophenyl-2,4,6-trichlorophenyl ether)</td>
</tr>
<tr>
<td>DL-PCB</td>
<td>dioxin-like polychlorinated biphenyl</td>
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<tr>
<td>GC</td>
<td>gas chromatograph</td>
</tr>
<tr>
<td>HpCB</td>
<td>heptachlorobiphenyl</td>
</tr>
<tr>
<td>HpCDD</td>
<td>heptachlorodibenzo-p-dioxin</td>
</tr>
<tr>
<td>HpCDF</td>
<td>heptachlorodibenzofuran</td>
</tr>
<tr>
<td>HxCB</td>
<td>hexachlorobiphenyl</td>
</tr>
<tr>
<td>HxCDD</td>
<td>hexachlorodibenzo-p-dioxin</td>
</tr>
<tr>
<td>HxCDF</td>
<td>hexachlorodibenzofuran</td>
</tr>
<tr>
<td>ICM</td>
<td>indicative congener method</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>MS</td>
<td>mass spectrometer</td>
</tr>
<tr>
<td>OCDD</td>
<td>octachlorodibenzo-p-dioxin</td>
</tr>
<tr>
<td>OCDF</td>
<td>octachlorodibenzofuran</td>
</tr>
<tr>
<td>PCA</td>
<td>principal component analysis</td>
</tr>
<tr>
<td>PCB</td>
<td>polychlorinated biphenyl</td>
</tr>
<tr>
<td>PCDD</td>
<td>polychlorinated dibenzo-p-dioxin</td>
</tr>
<tr>
<td>PCDF</td>
<td>polychlorinated dibenzofuran</td>
</tr>
<tr>
<td>PCP</td>
<td>pentachlorophenol</td>
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<td>PeCB</td>
<td>pentachlorobiphenyl</td>
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<td>PeCDD</td>
<td>pentachlorodibenzo-p-dioxin</td>
</tr>
<tr>
<td>PeCDF</td>
<td>pentachlorodibenzofuran</td>
</tr>
<tr>
<td>PMF</td>
<td>positive matrix factorization</td>
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<tr>
<td>PVA</td>
<td>polytopic vector analysis</td>
</tr>
<tr>
<td>RSD</td>
<td>relative standard deviation</td>
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<tr>
<td>SD</td>
<td>standard deviation</td>
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<tr>
<td>SS</td>
<td>suspended solids</td>
</tr>
<tr>
<td>TeCB</td>
<td>tetrachlorobiphenyl</td>
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<tr>
<td>TeCDD</td>
<td>tetrachlorodibenzo-p-dioxin</td>
</tr>
<tr>
<td>TeCDF</td>
<td>tetrachlorodibenzofuran</td>
</tr>
<tr>
<td>TEF</td>
<td>toxic equivalency factor</td>
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<tr>
<td>TEQ</td>
<td>toxic equivalent</td>
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<tr>
<td>WHO</td>
<td>World Health Organization</td>
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Chapter 1

Introduction

1.1. Study background

Polychlorinated dibenzo-\(p\)-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs), referred to as dioxins in this thesis, are known as high toxicity chemicals. Studies with animals have revealed their toxicity. Although there are differences in toxicity among species, in the most sensitive case, the 50% lethal dose of 2,3,7,8-tetrachlorodibenzo-\(p\)-dioxin (TeCDD), the most toxic compound of dioxins, for guinea pigs is 0.6 \(\mu g\) kg \(^{-1}\) body weight (Schwetz et al., 1973). Therefore, 2,3,7,8-TeCDD is called "the most toxic man-made chemical". The clinical manifestations by dioxins to human are as follows: cancer, immune deficiency, reproductive abnormalities, developmental abnormalities, liver damage and chloracne (Schecter et al., 2006).

In addition to the high toxicity, dioxins are persistent chemicals and remain in environment for a long time. The estimated half-life time of PCDDs/PCDFs in paddy-field soil in Japan is 11–45 years (Kato et al., 2009) and that of PCDDs/PCDFs and some DL-PCBs in soil and sediment in the Baltic Proper environment is 6.8–270 years (Sinkkonen and Paasivirta, 2000). In these circumstances, dioxins are included in the list of persistent organic pollutants (POPs) that should be banned and/or limited in their use and geographic spread at a meeting of the Stockholm Convention (UNEP, 2001).

Dioxins are unintentionally formed as by-products during industrial and combustion processes and have widely polluted the environment in the world (UNEP, 1999, 2003; Weber et al., 2008). The most famous environmental contaminations by dioxins are the explosion of a chemical plant at Seveso, northern Italy in 1976 and spraying defoliant "Agent Orange" by the U.S. military in the Vietnam War. The both cases posed health hazards to humans (Hay, 1976 and Stone,
Chapter 1. Introduction

Olie et al. (1977) revealed that waste incineration was one of the dioxin sources in addition to several industrial processes. This means that dioxin pollution had been in our immediate surroundings, not special cases like Seveso and Vietnam. Moreover, in Japan, dioxins were detected in ash and emission gas samples from waste incinerators (Eiceman et al., 1979; Asahi Shimbun, 1983; Asada et al., 1987; Hiraoka et al., 1987; Sakai et al., 1993). Especially in Japan, the environmental pollution by dioxins from waste incinerators was serious because the country’s small land area leaves little room for landfill of wastes, and more than 70% of total wastes in Japan are incinerated (Hiraoka and Okajima, 1994). Japan was one of the most dioxin-emitting countries in the world (UNEP, 1999). In the 1990s, dioxin pollution had often been covered by television stations and newspapers, and the public concern was rapidly increased (Sugisaki et al., 2004).

Against such a background, the Law Concerning Special Measures against Dioxins (the Dioxins Law; Environmental Agency of Japan, 1999) was enacted to reduce dioxin emission in 1999 and went into effect in 2000. This law includes such articles as follows: establishing environmental quality standards for dioxins in ambient air, water (including bottom sediment) and soil; setting emission standards for dioxins in emission gas and effluent of specified facilities; and measures against soil contamination by dioxins. Due to nationwide efforts to tackle the dioxin issues, national dioxin emissions in 2008 has been reduced by approximately 97% from the 1997 level (MOE, 2009b).

As described above, dioxin emission in Japan has decreased. However, dioxin problems have not yet been solved because dioxins are persistent chemicals. In air and water pollution, the concentration level of pollutants is expected to be reduced by diffusion. On the contrary, in soil and sediment, pollutants are poorly diluted and maintained a high level for a long time; as it is called "stock pollution". There still have been some pollution cases that exceed environmental quality standards, especially in sediment (MOE, 2001b, 2002–2008, 2009a). Some new pollution sites might be discovered in the future. The stock pollution remains as the dioxin pollution problems to be challenged to solve.
1.2. Study objectives
As for the stock pollution problems, if a pollution site with the dioxins exceeding environmental quality standard is appeared, the source should be identified to take measures against the pollution. The source identification is an important technique.

Dioxins show characteristic congener profiles depending on its sources. Multivariate statistical analyses on the basis of the profiles have been accepted as ways to identify pollution sources of dioxins. However, these analyses are difficult to employ because they need a large quantity of data, complicated computation and skills for data interpretation as described in the following chapter.

In order to respond quickly to incidents that lead to dioxins pollution, it is necessary to develop a simple method for the rapid identification of the dioxins sources, and such a method would be useful even if it has certain drawbacks. Therefore, a new simple method for estimating the causes of dioxin pollution was developed in this thesis. In the method, unlike the above-mentioned statistical analyses, the estimation can be performed for a single sample without complex calculation and data interpretation skills. Furthermore, the method was applied to examine the environmental behavior of dioxins and to develop a simplified measurement method for dioxin TEQ.

1.3. Contents of this thesis
This thesis is composed of seven chapters shown as follows:

Chapter 1. Introduction
Study background and objectives were stated. Japan was one of the most dioxin emitting countries in the world. Though national dioxin emission has been reduced due to nationwide efforts to tackle the dioxin issue, there still remain stock pollution problems. The source identification is an important technique to take measures against dioxin pollution. Under these circumstances, the objectives were set to develop a new simple method for dioxin source identification and to apply the method for evaluation of the behavior of environmental dioxins and for development of a simplified measurement technique of dioxin TEQ.
Chapter 1. Introduction

Chapter 2. Pollution sources of dioxins and techniques for source identification
The term "dioxins" was defined and the concept of toxic equivalent (TEQ) was explained. Moreover, major dioxin sources and their congener profiles were shown. Further, existing dioxin source identification techniques, multivariate statistical analyses using congener profiles, were overviewed, and the drawbacks of the techniques were pointed out. Multivariate analyses are difficult to employ because they need a number of data, complex calculation and skills for data interpretation. Under these situations, the necessity of a simple and manageable technique for dioxin source identification is explained.

Chapter 3. A novel method for dioxin source identification (corresponding to Paper I)
The subject of this chapter is the main of this thesis. A novel method for dioxin source identification, which apportions TEQ to the four major sources in Japan, was proposed. The author named this method, "indicative congener method (ICM)". Unlike the multivariate analyses, the indicative congener method is so user-friendly that it needs only concentrations of five congeners and easy calculation, and can be applied to single sample.

Chapter 4. Dioxins in rice straw smoke and their origins in Japan (corresponding to Paper II)
The ICM was utilized to evaluate environmental behavior of dioxins in this and the next chapters. Rice is a major agricultural product in Japan, and post-harvest straw is often burned in paddy fields which have been polluted by herbicide-originated dioxins. There is a concern that the dioxins existing in paddy-field soil are transferred to the atmosphere during field burning of rice straw. In chapter 4, therefore, the origins of dioxins in the smoke generated from rice-straw burning in paddy fields in Japan were examined.

Chapter 5. Seasonal change of dioxins in the water of Ayase River (corresponding to Paper III)
In this chapter, the ICM was applied to water environment. Ayase River is one of the most polluted rivers by dioxins in Japan: the concentration of dioxins in the water of the river has continuously exceeded the environmental quality standard. In order to examine the pollution causes of dioxins in the water of Ayase River, water samples were collected every month for a year to analyze dioxins, and source identification was performed by using the ICM.
Chapter 6. A simplified TEQ determination by applying indicative congener method (corresponding to Paper IV)

Dioxin measurement by the official method requires time and effort because 29 congeners established toxic equivalency factor (TEF) values are needed to be quantified to determine TEQ. A simplified measuring method is required to reduce time and effort for measurement. In this chapter, a simplified measuring method to determine dioxin TEQ by applying the ICM was developed.

Chapter 7. Conclusions and perspectives

The discussions in the former chapters were summarized. Moreover, future ideas of this study were mentioned.
Chapter 2

Pollution sources of dioxins and techniques for source identification

2.1. Chemical structure of dioxins and toxic equivalent (TEQ)

PCDDs, PCDFs and PCBs are well known environmental pollutants. Figure 2.1 shows the generic structures of PCDDs, PCDFs and PCBs. Substitution of different number of chlorine atoms for hydrogen atoms gives 75, 135 and 209 possible chemical structures for PCDDs, PCDFs and PCBs, respectively. PCDDs and PCDFs are often collectively called dioxins. Some PCBs (four non-ortho PCBs and eight mono-ortho PCBs) possess toxicity similar to some PCDDs and PCDFs, and they are called dioxin-like PCBs (DL-PCBs; sometimes referred to as coplanar-PCBs). In the Dioxins Law (Environmental Agency of Japan, 1999), dioxins are defined to include PCDDs, PCDFs and DL-PCBs. Accordingly, throughout this thesis, the term "dioxins" will be used to refer to PCDDs, PCDFs and DL-PCBs. Moreover, the term "congener" means each compound of dioxins, and the term "homologue" means a group of congeners with the same carbon frame and the same number of chlorine atoms.

The toxicity of PCDD/PCDF/DL-PCB congeners depends on the number and position of chlorine atoms. In order to assess the overall toxicity of the mixture of dioxins, the concept of toxic equivalent (TEQ) is commonly used. The TEQ value expresses the toxicity as if the mixture was...
Chapter 2. Pollution sources of dioxins and techniques for source identification

composed of pure 2,3,7,8-TeCDD which is the most toxic congener. Each congener has been
assigned dioxin toxic equivalency factor (TEF) based on its relative toxicity compared to
2,3,7,8-TeCDD of TEF 1. TEQ is the sum of the products of each concentration of toxic conge-
ners and its corresponding TEF value.

Table 2.1
TEF systems established by the World Health Organization (WHO).

<table>
<thead>
<tr>
<th>Congener</th>
<th>WHO-1998 TEF</th>
<th>WHO-2006 TEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCDDs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3,7,8-TeCDD</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1,2,3,7,8-PeCDD</td>
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<td>1</td>
</tr>
<tr>
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</tr>
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<td>0.1</td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDD</td>
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</tr>
<tr>
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<td>0.01</td>
</tr>
<tr>
<td>OCDD</td>
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</tr>
<tr>
<td>PCDFs</td>
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</tr>
<tr>
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<td>1,2,3,7,8,9-HpCDF</td>
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<td>OCDF</td>
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<tr>
<td>Non-ortho PCBs</td>
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</tr>
<tr>
<td>3,4,4',5'-TeCB (#81)</td>
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<td>0.0003</td>
</tr>
<tr>
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<td>3,3',4,4',5,5'-HxCB (#169)</td>
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<tr>
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</tr>
<tr>
<td>2,3',4,4',5,5',5'-HxCB (#189)</td>
<td>0.0001</td>
<td>0.00003</td>
</tr>
</tbody>
</table>

* Te: tetra; Pe: penta; Hx: hexa; Hp: hepta; O: octa; CDD: chlorodibenzo-p-dioxin; CDF: chlorodibenzo-
  furan; CB: chlorobiphenyl. Numbers with the symbol "#" indicate the No. of PCB designated by the Inter-
  national Union of Pure and Applied Chemistry (IUPAC).

b Van den Berg et al., 1998.
c Van den Berg et al., 2006.

Varieties of TEF systems had been proposed: Eadon et al. (1986), U.S. EPA (1987), International-TEF (I-TEF; NATO/CCMS, 1988) and Van Zorge (1989) for PCDDs/PCDFs; and Ahlborg et al.
2.2. Pollution sources of dioxins

Unlike PCBs, PCDDs and PCDFs have never been produced intentionally as commercial products. They were produced as unwanted by-products of industrial and combustion processes. Various sources of dioxins are shown in this section.

Impurities of organochlorine agrochemicals. Dioxins can be formed as by-products during the manufacturing processes of chlorine compounds. At first, impurities of organochlorine agrochemicals were noticed as substances responsible to environmental pollution of dioxins. Chlorinated phenols substituted at the ortho position dimerize and form dioxins under alkaline conditions (Ballschmiter and Bacher, 1996), indicating that dioxins are formed at the manufacturing processes of chlorinated phenols and the related agrochemicals.

The most typical dioxin-contained agrochemicals, which were introduced from chlorinated phenols, are 2,4,5-trichlorophenoxycetic acid (2,4,5-T) and 2,4-dichlorophenoxycetic acid (2,4-D). It is well known that the U.S. military used defoliants during the Vietnam War. The most-used defoliant was Agent Orange which was a mixture of equal amounts of the n-butyl esters of 2,4-D and 2,4,5-T (Stellman et al., 2003); these active ingredients contained dioxins as impurities (Rappe et al., 1978; Cochrane et al., 1981; Masunaga et al., 2001a).

Pentachlorophenol (PCP) formulations, which had been widely used as herbicide, pesticide and wood preservative, also contained dioxins (Buser and Bosshardt, 1976; Hagenmaier and...
Chapter 2. Pollution sources of dioxins and techniques for source identification

Brunner, 1987; Masunaga et al., 2001a; Seike et al., 2003). In Japan, PCP was registered as herbicide in 1956 and widely applied in paddy fields mainly in the 1960s (Kobayashi et al., 2004). However, soon after this, PCP was designated as a water pollution-prone pesticide because of its toxicity to fish and shellfish (Yamada, 1992) and unregistered from herbicide in 1990 (Kobayashi et al., 2004).

Aside from chlorinated phenol agrochemicals, diphenylether ones such as nitrophen (NIP, 2,4-dichlorophenyl-4'-nitrophenyl ether), chlomethoxynil (X-52, 2,4-dichloro-1-(3-methoxy-4-nitrophenoxy) benzene) and chlornitrofen (CNP, 4-nitrophenyl-2,4,6-trichlorophenyl ether) also contained dioxins as impurities (Yamagishi et al., 1981). Among them, CNP formulations contained dioxins in relatively high levels (Yamagishi et al., 1981; Masunaga et al., 2001a; Seike et al., 2003). CNP was widely applied as paddy field herbicide next to PCP all over Japan. CNP was registered as herbicide during the period 1965–1996 and mainly used in the 1970s (Kobayashi et al., 2004).

A large amount of PCP and CNP formulations had been applied in the paddy fields all over Japan. The amount of dioxins spread together with the both formulations was estimated at 460 kg-TEQ (Weber and Masunaga, 2005); this value was larger than that sprayed together with the defoliants during the Vietnam War (366 kg-TEQ; Stellman et al., 2003).

Impurities of PCB products. Another dioxin source related to chlorine compounds is PCB products. PCBs are chemically stable and have properties such as non-flammability, high electrical insulation and non-volatility. Because of these excellent properties for industrial materials, PCB products were widely used as electrical insulation oil, heat carrier, flame retardant, lubricating oil and surface coatings for carbonless carbon paper (Miyata, 1992). The manufacturing of PCBs was started in 1954, and approximately 57000 t were manufactured in Japan until 1972 from when they have been slapped a ban on the production and import (Chemical Society of Japan, 1980). Dioxins were present in PCB products (Wakimoto et al., 1988; Noma et al., 2004; Falandysz et al., 2005; Takasuga et al., 2005); moreover, the dioxin content in PCB products was increased by the application of heat (Buser and Rappe, 1979; Rappe et al., 1984).

Combustion by-products. Dioxins are formed during waste incineration process and pre-
sent in the combustion by-products such as flue gas, fly ash and bottom ash (Olie et al., 1977; Hiraoka et al., 1987; Sakai et al., 1993). Other than waste incineration, dioxins are emitted from the facilities with heating and combustion processes as follows: electrical steel making, sintering of iron ore, zinc recovery and aluminum-base alloy manufacturing. These facilities have been designated as specified facilities of emission gas in Japan by the Dioxins Law (Environmental Agency of Japan, 1999). Although other combustion processes such as cremation, run of motor vehicles and smoking also form dioxins, dioxin inventory from these combustion processes is very little; waste incineration is the main generator of dioxins in Japan (MOE, 2009b).

**Other sources.** Aside from organochlorine agrochemicals, PCB products and combustion by-products, chlorine bleaching of kraft pulp in paper industries is also one of the dioxin sources (Swanson et al., 1988; Clement et al., 1989; Rappe et al., 1990). In recent years, the conventional bleaching with chlorine gas has been converted to elementary chlorine free (ECF) bleaching with chlorine dioxide, and the ECF bleaching reduces dioxin formation through kraft pulp bleaching process (Ohi, 2004). In addition to the kraft bleaching process, dioxins are accidentally formed in manufacturing processes of the following materials: caprolactam, chlorinated benzenes, acetylene and violet dioxazine pigments. Facilities with these processes have been designated as specified facilities of waste water in Japan by the Dioxins Law (Environmental Agency of Japan, 1999).

### 2.3. Congener profiles of dioxin sources

Dioxins show characteristic congener profiles depending on their sources (Rappe, 1994). The dioxin sources in the environment in Japan have been estimated (Sakurai et al., 1996, 1998, 2002; Masunaga et al., 2001b, 2003; Ogura et al., 2001a, 2001b, 2005; Yao et al., 2002; Sakurai, 2003; Kobayashi et al., 2004; Iwamoto et al., 2006; Kiguchi et al., 2007; Seike et al., 2007 and Ohba et al., 2009), and the main sources of dioxin pollution are recognized to be PCP formulations, CNP formulations, PCB products and combustion by-products. The homologue and 29 TEF-congener profiles of dioxins in the samples related to these sources are shown in Figures 2.2–2.4.

**PCP formulations.** Figure 2.2 (a) shows the homologue and 29-TEF congener profiles of dioxins in PCP formulations. OCDD is the dominant congener followed by HpCDDs and OCDF,
and DL-PCBs are contained little.

**CNP formulations.** Homologue and 29-TEF congener profiles of dioxins in CNP formulations are shown in Figure 2.2 (b). The percentage of TeCDDs is the highest, and its standard deviation (SD) is relatively low. In TeCDDs, 1,3,6,8-TeCDD and 1,3,7,8-TeCDD are the major congeners (63–82% and 18–27% of TeCDDs, respectively). CNP formulations contain a small amount of PCDFs and little amount of DL-PCBs.

![Figure 2.2](image)

**Figure 2.2.** Homologue and TEF-congener profiles of PCDDs/PCDFs/DL-PCBs in PCP (a, \(N = 10\)) and CNP (b, \(N = 16\)) formulations. D: PCDD, F: PCDF, Numbers with the symbol "#" indicate the IUPAC No. of PCB. Bars indicate the standard deviation (SD) values. Data are cited from Seike et al. (2003).

**PCB products.** As shown in Figure 2.3, DL-PCBs dominate in PCB products. A small amount of PCDFs are contained, and the amount of PCDDs is little. Among DL-PCBs, #118-PeCB and #105-PeCB are the main congeners in all PCB products. Each SD value of detected congeners in all PCB products is relatively low, meaning each PCB product has its own distinguished profiles of homologues and 29-TEF congeners.
Combustion by-products. In construct to dioxin profiles of the above-mentioned chemical products, every congener is present in combustion related samples (Figure 2.4). Moreover, the SDs of every homologue and congener are relatively high. This means that there is no charac-
Chapter 2. Pollution sources of dioxins and techniques for source identification

teristic profile of dioxins in combustion related samples. Czuczwa and Hites (1986) also found a great variation among congener profiles of PCDDs/PCDFs in flue gases from various waste incinerators.

![Homologue and TEF-congener profiles of PCDDs/PCDFs/DL-PCBs in combustion by-products](image)

**Figure 2.4.** Homologue and TEF-congener profiles of PCDDs/PCDFs/DL-PCBs in combustion by-products (a: flue gas, N = 48; b: bottom ash, N = 27; and c: fly ash, N = 21). D: PCDD, F: PCDF, Numbers with the symbol "#" indicate the IUPAC No. of PCB. Bars indicate the SD values. Combustion by-product samples were collected and analyzed by the author and co-workers.

2.4. Existing techniques for source identification of dioxin pollution

Source identification of dioxins pollution is important to select effective countermeasures against the pollution of the environment. Dioxins, persistent chemicals, are considered to re-
main their chemical composition in the environment for a long time; therefore, it is recognized that the congener profile of an environmental sample preserves the information of its sources and can be used as a fingerprint. The origins of dioxins in the environment have been estimated by searching the discriminative source profiles in the fingerprint. This section shows existing techniques for source identification based on the fingerprint.

2.4.1. Pattern classification by using multivariate analysis

In order to recognize the characteristics of complex fingerprints of dioxins, a mixture of a number of congeners, multivariate statistical analyses such as the principal component analysis (PCA; Czuczwa and Hites, 1986; Smith et al., 1990; Marklund et al., 1991; Koester and Hites, 1992; Eitzer, 1993; Wenning et al., 1993; O’keefe et al., 1994; Kjeller and Rappe, 1995; Jiménez et al., 1998; and the list goes on), the cluster analysis (Wenning et al., 1993; Hagenmaier et al., 1994; Götz et al., 1998) and the factor analysis (Götz et al., 1998; Ogura et al., 2005; Ohba et al., 2009) have been utilized. Though these analyses are different in calculation algorithms, they are applied to reach the common purpose that various complex data set are classified into some smaller number of groups based on the similarity. Among them, the PCA is presumably the most frequently performed multivariate analysis for distinguishing dioxin sources.

The PCA transforms a complex data set into a smaller number of variables based on the similarities among each data. Objects (observations, i.e. environmental samples) with $p$ variables ($p$ dimensions, i.e. $p$ chemical components) are compressed into $m$ meaningful variables ($m$ dimensions; $m < p$) without much loss of information (Tanaka and Wakimoto, 1983). According to the reduction of dimension, some key aspects can be found in the complex data set. In the PCA, a large number of environmental samples are required.

Figure 2.5 illustrates the image of the PCA technique. The reduction of dimension is performed by projection of each $p$-dimensional object onto an $m$-dimensional plane which gives the minimum sum of squares in length of the perpendicular lines on the plane from each object (Okuno et al., 1971). The new variables, $z_1, z_2, ..., z_m$, which orthogonalize each other at the median point of the objects and determine the $m$-dimensional plane, are called principal components (PCs); and $z_1, z_2, ..., z_m$ are called the first PC (PC1), the second PC (PC2), ..., the $m$th PC (PC$m$), respectively. The PC of a smaller order provides better account for the features of the
Chapter 2. Pollution sources of dioxins and techniques for source identification

objects. The result of the projection is presented as PC score plots which are illustrated generally in 2-dimensional space such as PC1 vs. PC2. The score plots represent the similarities and differences among objects. Objects which are spatially close are closely related, on the contrary, objects which are spatially far apart are different from each other. In order to identify pollution sources, however, the analyst should relate each PC to the possible sources from characteristic parameters with high factor loading values. Specialized knowledge and skills are required in this work.

Various chemical factors, such as homologues (Smith et al., 1990; Koester and Hites, 1992), 2,3,7,8-chlorine-substituted PCDDs/PCDFs (Marklund et al., 1991; Jiménez et al., 1998), and 29 TEF congeners (Sakurai et al., 2002; Shen et al., 2009), have been used as variables. Czuczwa and Hites (1986) applied the PCA to PCDDs/PCDFs in urban air particulate samples and sediment samples of the Great Lakes. The concentrations of the homologues of tetra- to octa-chlorinated PCDDs/PCDFs were normalized to that of OCDD, and the relative concentrations of the homologues except OCDD were used as variables. The PCA result represented that the PCDDs/PCDFs in the sediment samples from all lakes except Lake Ontario were attributed to air particulates, i.e. combustion by-product; for Lake Ontario, PCP was likely to be a dioxin source other than combustion. Eitzer (1993) performed the PCA on PCDDs/PCDFs in sediment samples collected from Housatonic River, Massachusetts/Connecticut. Eighty-six chromato-
graphic peaks and ten homologues were separately applied as variables. Both results showed that the sediment samples were affected by a point source which attributed to PCB products and non-point one which attributed to atmosphere.

Masunaga et al. (2003) compared the results of the PCDD/PCDF source identification using the PCA with different combinations of variables: specific congeners (82 individual and groups of congeners); 2,3,7,8-chlorine-substituted congeners; 2,3,7,8-chlorine-substituted congeners and homologues; and 2,3,7,8-chlorine-substituted congeners, some other congeners and homologues. They concluded that use of profile of specific congeners was far more effective for source identification. Hashimoto (2004) also showed that results of the PCA depended on the chemicals which would be selected as variables, and that the more variables, the better result was obtained. However, only seventeen 2,3,7,8-chlorine-substituted PCDDs/PCDFs, twelve DL-PCBs, ten PCDD/PCDF homologues, and a few non-2,3,7,8-PCDDs/PCDFs have been reported during conventional dioxin monitoring (NIES, web site).

2.4.2. Source apportionment by using the receptor models

In addition to qualitative comparison of congener profiles, quantitative source apportionments have been performed by using the receptor models. In the receptor models, a pollution load is apportioned to the original sources on the basis of chemical profiles of environmental polluted samples, i.e. receptors. Figure 2.6 illustrates the image of the receptor models. Contribution ratios of the possible sources (and their profiles in chemical composition) are determined by iterative calculation to fit the sum of the products of the contribution ratios and corresponding chemical profiles into the observed chemical composition. The receptor models are categorized roughly into two groups. One is a group of techniques in which the number of sources and their chemical profiles are used as inputs, and includes the chemical mass balance (CMB) models and similar models (Su and Christensen, 1997; Masunaga et al., 2001b; Yao et al., 2002; Sakurai et al., 2003; Iwamoto et al., 2006; Seike et al., 2007). The other is a group to apply multivariate techniques in which both source profiles and their contribution ratios are calculated from environmental samples, and includes the polytopic vector analysis (PVA; Ehrlich et al., 1994; Grundy et al., 1997; Barabás et al., 2004) and the positive matrix factorization (PMF; Iwamoto et al., 2006; Uchimiya et al., 2009; Sundqvist et al., 2010).
Chapter 2. Pollution sources of dioxins and techniques for source identification

CMB models. The CMB models estimate source apportionment by performing the multiple regression analysis, which also requires complicated computation, on the basis of known source profiles. Su and Christensen (1997) apportioned sources to PCDDs/PCDFs in sediment samples from Housatonic River, Lake Huron and Baltic Sea by applying a CMB model. PCDD/PCDF homologues were used as variables, and the possible sources and their PCDD/PCDF homologue profiles were cited from the literatures. As a result, the major PCDD/PCDF source was coal burning before 1955 in the U.S. and 1970 in Europe, and thereafter waste combustion in municipal incinerators. Seike et al. (2007) analyzed PCDDs/PCDFs in preserved paddy soils periodically collected in Japan since 1960 to elucidate their sources and to estimate their mass balance in Japanese paddy fields. Three dioxin sources, two herbicides (PCP and CNP) and combustion by-products, were identified by applying the PCA. Then, a CMB model was performed to estimate contributions by these three sources. As a result, more than 95% of PCDDs/PCDFs in all paddy soils were derived from the herbicides.

The CMB models can estimate source contributions only from a single sample, provided all significant sources are known and their profiles are available. However, it is difficult to identify all sources of dioxins and to cover their congener profiles because there are a variety of prod-
ucts and processes as dioxin sources and congener profiles of the sources vary according to the conditions of formation (Kashiwagi et al., 2006). Combustion-related dioxins especially show non-uniform congener profiles as illustrated in Figure 2.4.

**Multivariate receptor models.** The multivariate receptor models, such as the PVA and the PMF, estimate source profiles and source contributions from observations. These models are special cases of the factor analysis. Ehrlich et al. (1994) applied the PVA to PCDDs/PCDFs in surface sediment samples collected from Newark Bay, New Jersey. Profile of 2,3,7,8-chlorine-substituted PCDDs/PCDFs was used as variables. Five end-members (possible sources) were found, and their contributions in the sediment samples were estimated on the basis of the profiles of the end-members. Uchimiya et al. (2007) performed source apportionment of PCDDs/PCDFs in surface sediment collected from Ichihara Anchorage in northeastern Tokyo Bay by applying the PMF. Eighty three chromatographic peaks of tetra- to octa-chlorinated PCDDs/PCDFs were used as variables. Three possible sources, PCP, CNP and combustion, were found, and PCP contributed more than 90% of the total PCDD/PCDF concentrations in the surface sediment samples from the anchorage.

The multivariate receptor models can estimate sources and their contributions from observations without information of significant sources and their chemical profiles. Instead, these methods require a number of samples that are influenced by the same sources. In addition, quite complicated computation is also needed. Moreover, as well as the PCA, the result depends on the chemical profile which would be used as an input. Specialized knowledge and skills are required to determine the number of sources and to relate the given profiles to the possible sources.

### 2.4.3. Features of techniques for source identification

Source identification techniques which have been utilized for dioxin contamination were presented. These techniques have achieved positive results. However, they also contain some drawbacks. Advantages (+) and drawbacks (−) of these techniques are summarized as follows:

**PCA**

(+) A number of complex data sets can be classified into smaller number of groups to identify...
Chapter 2. Pollution sources of dioxins and techniques for source identification

possible sources.
(-) Complicated computation is needed.
(-) A number of samples are required.
(-) The result depends on the chemicals which would be selected as variables. The more variables used in analysis, the better result are obtained. However, the reports of conventional dioxin monitoring show limited congener information.
(-) Specialized knowledge and skills are required to relate the given PCs to the possible sources.

CMB models
(+ ) Source apportionment can be performed only from a single sample.
(-) Complicated computation is needed.
(-) All significant sources must be identified and source chemical profiles also must be known in advance. However, determination of representative source profiles is difficult, because there are many dioxin sources, and their chemical profiles are not uniform.

Multivariate receptor models
(+ ) Source apportionment can be performed without information of significant sources and their chemical profiles.
(-) Quite complicated computation is needed.
(-) A number of samples are required.
(-) The result depends on the chemicals which would be selected as variables.
(-) Specialized knowledge and skills are required to determine the number of sources and to relate the given profiles to the possible sources.

As described above, existing source identification techniques have some drawbacks. A clear and concise method, which can be performed without complex data sets, complicated computation and specialized skills, is needed for dioxin-source identification.
Chapter 3

A novel method for dioxin source identification

3.1. Introduction
The identification of dioxin sources is important for taking effective measures against dioxin pollution. The sources of dioxin pollution have been identified through statistical analyses performed on congener profiles of environmental samples; however, these methods require large amounts of data and involve complicated calculations as described in the Section 2.4. In order to respond quickly to incidents that lead to dioxin pollution, it is necessary to devise a simple method for the rapid identification of the dioxin sources.

Fiedler et al. (2000) reported an intriguing observation: the concentration of 2,3,4,7,8-PeCDF was proportional to the TEQ, based on the I-TEF, of PCDDs/PCDFs in stack emission gas samples; they proposed a conversion factor for conversion between the concentration of 2,3,4,7,8-PeCDF and the TEQ.

As described in the Section 2.3, combustion by-products, PCP formulations, CNP formulations and PCB products are thought to be the main sources of dioxin pollution in Japan. Therefore, using a method similar to that used in Fiedler et al.’s study, we have previously identified indicative congeners whose concentrations have high correlations with TEQs (based on the WHO-1998 TEF) in samples collected from the four major dioxin sources (Ohtsuka et al., 2007). And then, we selected 2,3,4,7,8-PeCDF, 1,2,3,4,6,7,8-HpCDD, 1,2,3,7,8-PeCDD and IUPAC No. #105-PeCB as indicative congeners for combustion by-products, PCP formulations, CNP formulations and PCB products, respectively. Moreover, we proposed a set of equations that can be used for estimating the apportionment of WHO-1998 TEQs from each source by considering environmental samples from Japan; for the apportionment, only the concentrations of the four indicative congeners are necessary.
The values of WHO-1998 TEF used in our previous study were re-evaluated in 2006 (WHO-2006 TEF); this rendered our estimation method unsuitable for the WHO TEF system. We therefore improved our estimation method for the WHO-2006 TEQ. Indicative congeners whose concentrations were strongly correlated with the WHO-2006 TEQ of each dioxin pollution source were identified by analyzing data from the dioxin sources. Furthermore, using the concentrations of the indicative congeners, we developed a set of equations to estimate the apportionment of TEQs from the four sources on the basis of environmental samples. The method proposed in our previous study gives incorrect results in some cases, and therefore, in this study, we attempt to solve this problem as well.

3.2. Materials and methods

3.2.1. Dioxin source data

Data on combustion by-products were obtained by analyzing flue gas (for \( N = 48 \); \( N \): number of samples), bottom ash (\( N = 27 \)) and fly ash (\( N = 21 \)) samples. These samples were collected from waste incinerators in Saitama, Japan, and were analyzed by us during the period 2001–2006 in accordance with JIS K 0311 (Japanese Standards Association, 1999a). The analysis results revealed that the concentrations of 29 congeners with TEF values exceeded their detection limits.

PCP and CNP data were obtained from the study of Seike et al. (2003). There are two methods for PCP synthesis: (1) the phenol method based on the chlorination of phenol and (2) the hexachlorobenzene (HCB) method based on the hydroxylation of HCB. Among the PCP samples analyzed by Seike et al., six were synthesized by the phenol method and four by the HCB method. For obtaining the CNP data, 16 samples were selected, excluding samples with low dioxin concentrations (WHO-2006 TEQ < 2 ng-TEQ g⁻¹). It was assumed that the process of manufacturing CNP was changed in 1982 and that ten and six samples were produced using the old and new processes, respectively. Concentrations below the inspection standard (MAFF, 2002) were considered to be zero.

Data for PCB products were obtained from Kanechlor samples (KC-300, KC-400, KC-500,
KC-600 and KC-1000) and stockpiled PCB wastes (Noma et al., 2004). Noma et al. (2004) found that there was no significant chemical denaturation of the PCB in the wastes, and the type of Kanechlor to which each PCB belonged was easily identified. Therefore, we adopted the data on PCB in the wastes, considering them to be representative of data for PCB products. Among the stockpiled PCB waste samples, those containing PCB products were identified as KC-300, KC-400, KC-500 and KC-1000. The number of samples of KC-300, KC-400, KC-500 and KC-1000 were 10, 4, 5 and 4, respectively, excluding samples with low dioxin concentrations (WHO-2006 TEQ < 0.22 ng-TEQ g⁻¹). Concentrations below the quantification limit were considered to be zero.

3.2.2. Selection of indicative congeners and derivation of equations for apportionment of TEQs

The WHO-2006 TEQ profiles of the 29 congeners with TEF values were determined using the data from the above-mentioned four sources, and subsequently, the relative standard deviation (RSD) was calculated for each congener. On the basis of these RSDs, the congener(s) whose concentration showed a strong correlation to the TEQ of each source was selected as the indicative congener(s) of the source. Moreover, equations for the apportionment of TEQs from each source by using only the indicative congeners were derived from the ratio of the indicative congener concentration to the TEQ.

3.3. Results and discussion

3.3.1. Equations for apportionment of TEQs from each source

Selection of indicative congeners for each source. Figure 3.1 shows the TEQ profiles of the flue gas, bottom ash and fly ash samples. The main contribution to the TEQ was from 2,3,4,7,8-PeCDF, and this congener had the minimum RSD among all the congeners. Therefore, 2,3,4,7,8-PeCDF was selected as the indicative congener for combustion by-products.

Figure 3.2 shows the TEQ profiles for the PCP formulations and CNP formulations. The main contribution to the TEQ was from 1,2,3,4,6,7,8-HpCDD, and this congener had the minimum RSD among the PCP formulations, regardless of the synthesis method. As for the CNP formulations, the main contribution to the TEQ was from 1,2,3,7,8-PeCDD, and this congener had the
Chapter 3. A novel method for dioxin source identification

minimum RSD among the CNP formulations, regardless of the year of manufacture. Therefore, 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8-PeCDD were selected as the indicative congeners for PCP formulations and CNP formulations, respectively.

Figure 3.1. WHO-2006 TEQ profiles of PCDDs/PCDFs/DL-PCBs in combustion by-products: flue gas (a), bottom ash (b) and fly ash (c). Closed circles indicate the RSD values (%). Te: tetra; Pe: penta; Hx: hexa; Hp: hepta; O: octa; CDD: chlorodibenzo-p-dioxin; CDF: chlorodibenzofuran; CB: chlorobiphenyl. Numbers with the "#" sign indicate the IUPAC no. of PCB.

Figure 3.3 shows the TEQ profiles for the PCB products; in every PCB product, #126-PeCB accounted for almost the entire TEQ. This congener had the minimum RSD among KC-300, KC-400, and KC-500. In the case of KC-1000, the RSDs of #105-PeCB (3.9%) and #118-PeCB (4.8%) were the lowest and second lowest, respectively; the RSD of #126-PeCB was also relatively low (6.4%). Therefore, #126-PeCB was selected as the indicative congener for PCB...
products.

**Figure 3.2.** WHO-2006 TEQ profiles of PCDDs/PCDFs/DL-PCBs in PCP and CNP formulations: PCP formulations manufactured by the phenol method (a) and the HCB method (b); CNP formulations manufactured before 1981 (c) and after 1982 (d). Closed circles indicate the RSD values (%). Data cited from Seike et al. (2003).
Figure 3.3. WHO-2006 TEQ profiles of PCDDs/PCDFs/DL-PCBs in PCB products: KC-300 (a), KC-400 (b), KC-500 (c), KC-600 (d) and KC-1000 (e). Closed circles indicate the RSD values (%). Data cited from Noma et al. (2004).
Table 3.1 shows the average of the ratio of the concentration of the indicative congener to the TEQ for various sources. The ratios for 2,3,4,7,8-PeCDF in flue gas, bottom ash and fly ash were almost same—0.671, 0.702 and 0.647, respectively (0.673 for all 96 data). Therefore, the conversion factor for the conversion of the concentration of 2,3,4,7,8-PeCDF to the TEQ for combustion by-products was set as 0.673. The relation between the TEQ and the concentration of the indicative congener for combustion by-products can be expressed as follows:

\[
\text{TEQ[Combustion]} = \frac{1}{0.673} C^{\text{Combustion}}_{23,4,7,8\text{-PeCDF}}
\]

where \( C \) denotes the congener concentration. The subscript and superscript indicate the con-
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gener and the pollution source, respectively. The source of the TEQ is indicated in brackets.

Similarly, the following two equations—Eqs. (2) and (3)—were obtained from the PCP and CNP data, respectively:

\[
TEQ[PCP] = \frac{1}{29.2} C_{1234678}^{PCP} \text{HpCDD}
\]  
(2)

\[
TEQ[CNP] = \frac{1}{0.742} C_{12378}^{CNP} \text{PeCDD}
\]  
(3)

<table>
<thead>
<tr>
<th>Secondary indicative congener for PCB</th>
<th>Coefficient for congener concentration</th>
<th>Ratio of estimated and measured TEQ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Primary isomer (#126)</td>
<td>Average</td>
</tr>
<tr>
<td>None</td>
<td>0.152 ((= 1/6.58)) -</td>
<td>1.000</td>
</tr>
<tr>
<td>#77-TeCB</td>
<td>0.147</td>
<td>0.969</td>
</tr>
<tr>
<td>#81-TeCB</td>
<td>0.147</td>
<td>0.969</td>
</tr>
<tr>
<td>#169-HxCB</td>
<td>0.144</td>
<td>0.975</td>
</tr>
<tr>
<td><strong>#105-PeCB</strong></td>
<td>\textbf{0.116}</td>
<td>\textbf{0.995}</td>
</tr>
<tr>
<td>#114-PeCB</td>
<td>0.112</td>
<td>0.993</td>
</tr>
<tr>
<td>#118-PeCB</td>
<td>0.124</td>
<td>0.995</td>
</tr>
<tr>
<td>#123-PeCB</td>
<td>0.121</td>
<td>0.987</td>
</tr>
<tr>
<td>#156-HxCB</td>
<td>0.131</td>
<td>0.992</td>
</tr>
<tr>
<td>#157-HxCB</td>
<td>0.130</td>
<td>0.995</td>
</tr>
<tr>
<td>#167-HxCB</td>
<td>0.131</td>
<td>0.992</td>
</tr>
<tr>
<td>#189-HpCB</td>
<td>0.145</td>
<td>0.970</td>
</tr>
</tbody>
</table>

\[a_{PCB}\#_{126} \text{PeCB} + b_{PCB}^{i}\]

*a PCB product data are cited from Noma et al. (2004).

The ratio of the \#126-PeCB concentration to the TEQ was 7.04, 8.18, 5.49, 6.73 and 5.26 in KC-300, KC-400, KC-500, KC-600 and KC-1000, respectively, and the average of the 28 values was 6.58. The ratios in KC-500 and KC-1000 were relatively small and that in KC-400 was relatively large. Therefore, a congener other than \#126-PeCB was selected in order to reduce the difference among the above-mentioned ratios in the PCB products. Since the PCDD/PCDF concentration in the PCB products was very low (Noma et al., 2004), DL-PCBs were suggested as secondary indicative congeners for the PCB products. Using the equation \(TEQ[PCB]

\[a_{PCB}\#_{126} \text{PeCB} + b_{PCB}^{i}\]

we calculated the coefficients for \#126-PeCB (the coefficient \(a\)) and for a second indicative congener \(i\) (the coefficient \(b\)) by considering all the data obtained for all the
28 PCB products; the least-squares method was used in the calculation. It was found that in the case of #105-PeCB, the RSD of the ratio of the estimated TEQ to the measured TEQ was the minimum (Table 3.2). Therefore, #105-PeCB was selected as a secondary indicative congener for the PCB products. The relation between the concentrations of #126-PeCB and #105-PeCB, and the TEQ is as follows:

$$\text{TEQ}[\text{PCB}] = 0.116c_{\text{#126 PeCB}} + 1.13 \times 10^{-4}c_{\text{#105 PeCB}}$$

(4)

Concentrations of indicative congeners of each dioxin source. If Eqs. (1)–(4) are applied to the environmental data, the TEQs will be overestimated because all the indicative congeners detected do not originate from the corresponding source, but include congeners originating from the other three sources. In particular, the following congeners were measurably detected: 2,3,4,7,8-PeCDF in PCP formulations, CNP formulations and PCB products; 1,2,3,4,6,7,8-HpCDD, #126-PeCB and #105-PeCB in combustion by-products; and 1,2,3,7,8-PeCDD in combustion by-products and PCP formulations. Thus, the concentrations of the indicative congeners in the environmental samples were approximated by using the following equations:

$$C_{23478 \text{ PeCDF}} = C_{\text{Combustion 23478 PeCDF}} + C_{\text{PCP 23478 PeCDF}} + C_{\text{CNP 23478 PeCDF}} + C_{\text{PCB 23478 PeCDF}}$$

(5)

$$C_{1234678 \text{ HpCDD}} = C_{\text{PCP 1234678 HpCDD}} + C_{\text{Combustion 1234678 HpCDD}}$$

(6)

$$C_{12378 \text{ PeCDD}} = C_{\text{CNP 12378 PeCDD}} + C_{\text{Combustion 12378 PeCDD}} + C_{\text{PCP 12378 PeCDD}}$$

(7)

$$C_{\text{#126 PeCB}} = C_{\text{PCB #126 PeCB}} + C_{\text{Combustion #126 PeCB}}$$

(8)

$$C_{\text{#105 PeCB}} = C_{\text{PCB #105 PeCB}} + C_{\text{Combustion #105 PeCB}}$$

(9)

where $C$ without the superscript represents the congener concentration in an environmental sample.

From the data in Table 3.1, the concentrations of the congeners 1,2,3,4,6,7,8-HpCDD, 1,2,3,7,8-PeCDD, #126-PeCB and #105-PeCB that originate from combustion can be expressed using the concentration of 2,3,4,7,8-PeCDF originating from combustion, as follows:

$$C_{\text{Combustion 1234678 HpCDD}} \frac{2.37}{0.673} C_{\text{Combustion 23478 PeCDF}}$$

(10)

$$C_{\text{Combustion 12378 PeCDD}} \frac{0.220}{0.673} C_{\text{Combustion 23478 PeCDF}}$$

(11)

$$C_{\text{Combustion #126 PeCB}} \frac{0.540}{0.673} C_{\text{Combustion 23478 PeCDF}}$$

(12)
Similarly, the concentrations of 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCD in PCP formulations, and the concentration of 2,3,4,7,8-PeCDF in CNP formulations can be expressed by Eqs. (14)–(16) below.

The concentration of 2,3,4,7,8-PeCDF in the PCB products was calculated from Eq. (17) below by using the concentrations of #105-PeCB and #126-PeCB in the products. The coefficients were calculated by using the least-squares method and the data obtained from all the 28 PCB products.

Solving Eqs. (5)–(17) for $C_{\text{Combustion}}$, $C_{\text{PCP}}$, $C_{\text{CNP}}$, $C_{\#105}$, $C_{\#126}$, and $C_{\text{PeCDF}}$, we obtain the following equations:

\begin{align*}
C_{\text{Combustion}} &= \frac{0.418}{0.673} C_{\text{PeCDF}} \\
C_{\text{PCP}} &= \frac{0.0215}{29.2} C_{\text{HpCDD}} \\
C_{\text{CNP}} &= \frac{0.0490}{0.742} C_{\text{PeCDD}} \\
C_{\text{PCB}} &= 4.58 \times 10^{-3} C_{\text{PeCDF}} + 2.10 \times 10^{-6} C_{\text{PeCB}} \\
C_{\text{PCP}} &= 1.03 C_{\text{PeCDF}} + 6.41 \times 10^{-4} C_{\text{HpCDD}} + 6.79 \times 10^{-2} C_{\text{PeCDD}} + 4.71 \times 10^{-3} C_{\#126} + 2.16 \times 10^{-3} C_{\#105} \\
C_{\text{CNP}} &= 1.00 C_{\text{PeCDF}} + 3.62 C_{\text{PeCDD}} + 0.239 C_{\text{PeCB}} + 1.66 \times 10^{-2} C_{\#126} + 7.60 \times 10^{-6} C_{\#105} \\
C_{\text{PCB}} &= 1.02 C_{\text{PeCDF}} + 0.330 C_{\text{PeCDD}} + 1.51 \times 10^{-3} C_{\text{PeCB}} + 0.852 C_{\text{PeCDF}} + 5.14 \times 10^{-4} C_{\text{PeCDD}} + 5.45 \times 10^{-2} C_{\#126} + 1.73 \times 10^{-6} C_{\#105} \\
C_{\text{PCB}} &= 1.00 C_{\text{PeCDF}} + 0.639 C_{\text{PeCDD}} + 3.98 \times 10^{-4} C_{\text{PeCB}} + 4.22 \times 10^{-2} C_{\#126} + 2.92 \times 10^{-3} C_{\#105} \\
\end{align*}
Equations (18)–(22) are the correction equations used to reduce the overestimation resulting from the contribution from other sources. Hence, for each congener, the values of $C_i^S$ (estimated concentration of congener $i$ originating from a pollution source $S$) obtained from Eqs. (18)–(22) should not exceed the measured concentration ($C_i$). Moreover, the concentration should not be lower than zero. Therefore, the following assumptions are made: if $C_i^S \leq 0$, then $C_i^S = 0$, and if $C_i^S \geq C_i$, then $C_i^S = C_i$.

**Apportionment of TEQs from each source.** The concentrations of the five indicative congeners originating from their respective sources ($C_{\text{Combustion}}^{\text{PCB}}$, $C_{\text{PCP}}^{\text{PCB}}$, $C_{\text{CNP}}^{\text{PCB}}$, $C_{\text{PCB}}^{\text{PCB}}$, and $C_{\text{PCB}}^{\text{PCB}}$) can be estimated only from the measured concentrations of these congeners in environmental samples ($C_{\text{Combustion}}$, $C_{\text{PCP}}$, $C_{\text{CNP}}$, $C_{\text{PCB}}$, and $C_{\text{PCB}}$); Eqs. (18)–(22) are used for this purpose. The TEQs corresponding to each dioxin source can be obtained by substituting the estimated indicative congener concentrations in Eqs. (1)–(4). Equations (1)–(4) and (18)–(22) were derived from the data for major dioxin sources, and therefore, they are generally applicable to environmental samples from any part of Japan. The estimated total TEQ of an environmental sample ($TEQ[\text{Total}]$) is expressed as the sum of the estimated values of the TEQs originating from the four sources (Eq. (23)). The apportionment of TEQs from the four sources can be performed using the values obtained from Eqs. (1)–(4) and (23).

$$TEQ[\text{Total}] = TEQ[\text{Combustion}] + TEQ[\text{PCP}] + TEQ[\text{CNP}] + TEQ[\text{PCB}]$$  \hspace{1cm} (23)

In the method that was applied to the WHO-TEF 1998 version in our previous study (Ohtsuka et al., 2007), TEQ apportionment was performed by considering the concentrations of the indicative congeners; however, the method has given incorrect results in some cases. In this study, the problem is avoided by adopting two steps for the apportionment: first, the concentrations of indicative congeners originating from their respective sources are estimated, and second, the TEQ apportionment is performed by considering the estimated congener concentrations.

To confirm the validity of the proposed estimation method, the source data used for the development of the method were used in Eqs. (1)–(4) and (18)–(23). If the estimation is correct,
the estimated total TEQ of a corresponding source should be equal to the measured total TEQ (TEQ calculated from the concentrations of 29 congeners with TEF values), and the estimated TEQs of the other three sources should be negligible. Table 3.3 shows the average values of the ratio of the estimated total TEQ to the measured total TEQ for all source data, as well as the standard deviation (SD) of the ratio. The average values were approximately 1 (ranged 0.95 to 1.13) in all cases, and the SDs were small (range: 0.01–0.19), except for PCP (range: 0.26–0.44). The estimated total TEQ was in agreement with the measured total TEQ. Moreover, the corresponding source TEQ contributed significantly to the estimated total TEQ (83–100%), and the effects of the other three sources on the total TEQ were negligible. This result suggests that our estimation method could be used to distinguish the TEQ of one of the four sources from the TEQs of the other three sources.

### Table 3.3

<table>
<thead>
<tr>
<th>Source data</th>
<th>Average</th>
<th>Standard deviation</th>
<th>Contribution of the corresponding source (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion by-product data</td>
<td>1.10</td>
<td>0.16</td>
<td>91</td>
</tr>
<tr>
<td>Flue gas</td>
<td>1.10</td>
<td>0.15</td>
<td>90</td>
</tr>
<tr>
<td>Bottom ash</td>
<td>1.11</td>
<td>0.19</td>
<td>94</td>
</tr>
<tr>
<td>Fly ash</td>
<td>1.08</td>
<td>0.12</td>
<td>89</td>
</tr>
<tr>
<td>PCP formulation data a</td>
<td>1.06</td>
<td>0.39</td>
<td>94</td>
</tr>
<tr>
<td>Phenol method</td>
<td>1.13</td>
<td>0.44</td>
<td>100</td>
</tr>
<tr>
<td>HCB method</td>
<td>0.95</td>
<td>0.26</td>
<td>85</td>
</tr>
<tr>
<td>CNP formulation data a</td>
<td>1.01</td>
<td>0.13</td>
<td>99</td>
</tr>
<tr>
<td>Estimated production date:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>before 1981</td>
<td>1.04</td>
<td>0.06</td>
<td>98</td>
</tr>
<tr>
<td>after 1982</td>
<td>0.96</td>
<td>0.19</td>
<td>99</td>
</tr>
<tr>
<td>PCB product data b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Estimated production date:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>before 1982</td>
<td>1.01</td>
<td>0.06</td>
<td>98</td>
</tr>
<tr>
<td>KC-300</td>
<td>0.96</td>
<td>0.04</td>
<td>97</td>
</tr>
<tr>
<td>KC-400</td>
<td>1.10</td>
<td>0.02</td>
<td>100</td>
</tr>
<tr>
<td>KC-500</td>
<td>1.01</td>
<td>0.04</td>
<td>99</td>
</tr>
<tr>
<td>KC-600</td>
<td>1.08</td>
<td>–</td>
<td>83</td>
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<tr>
<td>KC-1000</td>
<td>1.02</td>
<td>0.01</td>
<td>99</td>
</tr>
</tbody>
</table>

a PCP and CNP formulation data are cited from Seike et al. (2003).
b PCB product data are cited from Noma et al. (2004).

### 3.3.2. Application to environmental data

In order to evaluate the effectiveness of the proposed method, Eqs. (1)–(4) and (18)–(23) were used to estimate the TEQ contributions of the four sources for various environmental sample
data sets. Environmental sample data were obtained by the analysis of ambient air, soil and river sediment samples collected from Saitama, Japan. Only data pertaining to samples whose concentrations in all the 29 congeners with TEF values were equal to or higher than the detection limits were considered. The samples used for obtaining the data were as follows: 57 ambient air samples (collected during the period 2004–2007), 72 soil samples (collected during the period 2004–2005), and 42 river sediment samples (collected during the period 2004–2007). The estimation results are shown in Figure 3.4.

The estimated total TEQ for the ambient air samples was in agreement with the measured value (Figure 3.4 (a)), and the average of the ratios of the estimated total TEQ to the measured total TEQ was 1.06 (SD: 0.13). The contribution of TEQ originating from combustion to the estimated total TEQ was approximately 96%. This result was reasonable because PCDDs/PCDFs in atmospheric deposition in the Kanto region (where Saitama is located) are thought to originate mainly from combustion (Ogura et al., 2001b).

In the case of the soil samples (Figure 3.4 (b)) and river sediment samples (Figure 3.4 (c)), the TEQ contribution of each source to the estimated total TEQ varied significantly, and the total TEQ itself varied considerably (1.0–150 ng-TEQ kg⁻¹ and 3.0–78 ng-TEQ kg⁻¹ in the case of the soil and river sediment samples, respectively). However, the estimated total TEQ was in agreement with the measured total TEQ; the average of the ratios of the estimated total TEQ to the measured total TEQ was 0.96 and 1.06 for the soil and river sediment samples, respectively; the SD was 0.07 and 0.09, respectively.

The TEQ originating from herbicides (PCP and CNP formulations) contributed significantly to the estimated total TEQ (56% of the estimated total TEQ) obtained from the river sediment data (Figure 3.4 (c)). Dioxins from PCP and CNP formulations, which are widely used as herbicides, have previously been detected in soil samples obtained from paddy fields (Seike et al., 2003; Kobayashi et al., 2004; Kiguchi et al., 2007; Seike et al., 2007). The river sediment samples examined in this study are thought to contain dioxins originating from the aforementioned herbicides. The result obtained for river sediment samples seemed to be reasonable.
Figure 3.4. Ratio of estimated and measured total TEQ for environmental samples: ambient air (a), soil (b), and river sediment (c). Samples listed in the descending order of the total TEQ: ambient air (0.032–0.37 pg·TEQ·m⁻³), soil (1.0–150 ng·TEQ·kg⁻¹), and river sediments (3.0–78 ng·TEQ·kg⁻¹).

Soil data analysis revealed that all the four dioxin sources contribute to the total TEQ (Figure 3.4 (b)); some results were similar to those obtained for the ambient air samples, while some others were similar to those obtained for the river sediment samples. The soil samples were collected mainly from agricultural roads and public places such as parks and school grounds. It is thought that the dioxins of the soil samples were mainly influenced by herbicides and atmospheric deposition from flue gas. The result obtained for the soil samples also seemed to be
reasonable. The apportionment of TEQs from the four dioxin sources by the proposed method was found to be accurate for various environmental samples from Japan.

### 3.4. Conclusions

PCDDs, PCDFs and DL-PCBs from the four major sources in Japan—combustion by-products, PCP formulations, CNP formulations, and PCB products—were analyzed to determine the indicative congeners whose concentrations are strongly dependent on the TEQ of each source. The indicative congeners selected for combustion by-products, PCP formulations and CNP formulations were 2,3,4,7,8-PeCDF, 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8-PeCDD, respectively; for PCB products, the indicative congeners were IUPAC nos. #126- and #105-PeCBs. Moreover, a set of equations for estimating the apportionment of TEQs from the four sources was developed by using the concentrations of the five indicative congeners. Application of this estimation method to source data and environmental data showed that it was effective. The estimation method (Eqs. (1)–(4) and (18)–(23)) was developed by considering data on the major dioxin sources in Japan, and therefore, it is generally adaptable to environmental samples from any part of Japan.
Chapter 3. A novel method for dioxin source identification
Chapter 4

Dioxins in rice straw smoke and their origins in Japan

4.1. Introduction

Rice is a major agricultural product in Japan, and post-harvest rice straw is often burned in paddy fields. The smoke generated from rice straw burning (rice-straw smoke) has been investigated as an air pollution source. Rice-straw smoke contains polycyclic aromatic hydrocarbons (Mast et al., 1984; Jenkins et al., 1996) and phenols (Mast et al., 1984). Dioxins are also present in rice-straw smoke (Muto et al., 1993; Gullett and Touati, 2003).

Laboratory-scale rice straw burning experiments performed by Muto et al. (1993) showed that the PCDD/PCDF concentration in the rice-straw smoke generated from the rice straw reaped in Akita, Japan, was 22.5 pg-TEQ g−1 (based on the I-TEF) of raw biomass. Gullett and Touati (2003) tested the rice-straw smoke of the rice straw grown in California, under the conditions of simulated field burning and estimated that the PCDD/PCDF emission factor of rice straw burning was approximately 0.5 ng-TEQ kg−1 (based on the WHO-1998 TEF) of the burned. Further, Shih et al. (2008) reported that the TEQs (based on the I-TEF) of the PCDDs/PCDFs present in the ambient air during the rice straw burning season were 4–17 times those in other seasons in southern Taiwan, and rice straw burning exhibited a significant impact on the PCDD/PCDF concentration level in the ambient air.

A large amount of PCP and CNP formulations were widely used as herbicides for paddy fields in Japan. These herbicides contain dioxins as impurities (Masunaga et al., 2001a; Seike et al., 2003). Though most of these herbicides have been disappeared from the soil of the paddy fields (Kobayashi et al., 2004), the herbicides-originated dioxins are still present (Seike et al.,
Chapter 4. Dioxins in rice straw smoke and their origins in Japan

2003; Kobayashi et al., 2004; Kiguchi et al., 2007; Seike et al., 2007). Moreover, these dioxins run off from paddy fields (Seike et al., 2007) and pollute sediments of rivers (Sakurai, 1996; Kiguchi et al., 2007), lakes (Sakurai et al., 1996; Masunaga et al., 2001b), and bays (Yao et al., 2002; Masunaga et al., 2003). Thus, the paddy fields in Japan work not only as reservoirs of dioxins but also as significant suppliers of dioxins to the environment.

Under these circumstances, there is a concern that the dioxins existing in paddy-field soil are transferred to the atmosphere during field burning of rice straw. However, to the best of our knowledge, the presence of dioxins in the rice-straw smoke directly collected from rice straw burning at paddy fields in Japan has not been investigated as yet.

In this research, rice-straw smoke samples were collected from the rice straw burning sites at post-harvest paddy fields, and dioxins present in these smoke samples were analyzed to determine their congener profiles. Moreover, rice straw and paddy-field soil samples were collected from the same paddy fields and tested to investigate the effect of paddy-field soil on rice-straw smoke: the rice straw samples were burned to obtain rice-straw smoke samples and rice-straw ash samples. The dioxins present in these rice straw, rice-straw smoke, rice-straw ash and paddy-field soil samples were analyzed to determine their relationships. And the origins of the dioxins found in the rice-straw smoke samples were discussed qualitatively by using congener profiles.

4.2. Materials and methods

4.2.1. Sample collection

Rice-straw smoke sampling apparatus. The apparatus for rice-straw smoke sampling is illustrated in Figure 4.1. It comprises smoke-introducing tubes ((1) and (2)), dioxin-collecting devices ((3), (4), and (5)), smoke-suctioning devices ((6) and (7)), and a gas meter for smoke volume measurement (8). Kato and Urano (2000) reported that two ice-water-cooled absorption bottles, one containing 200 mL of water and the other containing 300 mL of diethylene glycol, could be used to recover PCDDs/PCDFs from waste combustion gas. In this study, the same dioxin-recovering devices were applied, but ice-water cooling for absorption bottles was omitted for simplicity due to on-site sampling.
Since the total weight of the rice-straw smoke apparatus is only approximately 7 kg, including a backpack frame, and the necessary power is supplied by a DC 12 V car battery, on-site sampling of smoke can be done. The apparatus aspirates smoke at the rate of approximately 5 L min⁻¹.

Figure 4.1. Smoke-sampling apparatus. (1) Quartz glass tube (length: ca. 1 m; id: 9 mm), (2) Teflon tube (length: ca. 1 m; id: 9 mm), (3) Absorption bottle #1 (200 mL of water), (4) Absorption bottle #2 (300 mL of diethylene glycol), (5) Quartz fiber wool, (6) Air pump, (7) DC battery, and (8) Gas meter.

Field sampling. By using the apparatus illustrated in Figure 4.1, rice-straw smoke samples (sample codes: RSS-A, -B, -C, -D and -E) were collected from five different post-harvest paddy fields (site codes: A, B, C, D and E) in Saitama, Japan during the autumn season in 2002. A part of rice-straw smoke (50–100 L) was aspirated.

Laboratory experiment. Rice straw samples (sample codes: RS-F, -G, -H and -I) left at paddy fields for burning, and paddy-field soil samples (sample codes: PFS-F, -G, -H and -I) were collected from four other paddy fields (site codes: F, G, H and I) to investigate the effect of paddy-field soil on rice-straw smoke. In order to obtain smoke samples from naturally-burned rice straw, each rice straw sample was burned on a stainless-steel tray (590-mm length × 425-mm
width × 110-mm depth). The entire smoke should be collected to discuss mass balance. However, if we do so, a large device which aspirates forcibly the entire smoke sample is required. Unfortunately, such device may prevent rice straw from being naturally burned. Therefore, just as we used for field sampling, a part of the generated rice-straw smoke (sample codes: RSS-F, -G, -H and -I) was collected using the sampling apparatus illustrated in Figure 4.1. Rice straw burning was carried out by adding rice straw to the fire until the collected smoke volume was approximately 100 L.

Prior to sampling, a sampling spike ($^{13}$C$_{12}$-1,2,3,4-TeCDD; Wellington Laboratories, Ontario, Canada) was added to the water contained in the first absorption bottle ((3) in Figure 4.1). The apparatus efficiently recovered the dioxins in the rice-straw smoke samples because the recovery of the sampling spike was good (80–111%).

In order to obtain rice-straw ash samples, naturally dried rice straw of approximately 50 g was burned on the stainless-steel tray. The ratios of the weight of rice-straw ash to burned rice straw ranged from 18% to 23%.

### 4.2.2. Dioxin analysis

**Extraction.** The rice-straw smoke samples were extracted in accordance with JIS K 0311 (Japanese Standards Association, 1999a). Two types of absorption liquids, water and diethylene glycol (Wako Pure Chemical Industries), were filtrated using a filter (GA-55; ADVANTEC, Tokyo, Japan). The sampling apparatus was rinsed with 2 M hydrochloric acid, acetone (Kanto Chemical) and dichloromethane (Kanto Chemical), in sequence. The liquids used to rinse the apparatus were also filtrated with the same filter, and then, the filtrate was combined with the filtrate of absorption liquids. This combined aqueous solution was extracted through liquid-liquid extraction using dichloromethane (3 times). The dichloromethane extract was dehydrated by passing it through a funnel with sodium sulfate anhydrous. The filtrate residue and the quartz fiber wool were Soxhlet extracted together with toluene (Kanto Chemical) for 24 h. The dichloromethane extract and the toluene extract were combined and subjected to the cleanup procedure.

Paddy-field soil samples were dried at room temperature and then sieved through a
2-mm-mesh stainless-steel screen. Rice straw samples were cut into small pieces (approximately 2 cm in length) from the tip to the end. Paddy-field soil, rice-straw ash and rice straw samples were Soxhlet extracted for 24 h: the extracting solvent was toluene for paddy-field soil and rice-straw ash samples, and acetone for rice straw samples.

**Cleanup.** The cleanup procedure was based on JIS K 0311. An outline of the procedure is as follows: $^{13}$C$_{12}$-labeled dioxin cleanup spikes (seventeen 2,3,7,8-chlorine-substituted PCDDs/PCDFs and twelve DL-PCBs; Wellington Laboratories) were added to the above-mentioned extract before cleanup. The extract was treated first with concentrated sulfuric acid and then with 44% sulfuric-acid-impregnated silica gel (Wako Pure Chemical Industries) and column chromatography was performed with 10% silver-nitrate-impregnated silica gel (Wako Pure Chemical Industries). Thereafter, the solution was loaded into an active-carbon-dispersed silica-gel column (Kanto Chemical), washed with hexane, and then eluted with toluene. The toluene solution was concentrated and $^{13}$C$_{12}$-labeled syringe spikes (eight compounds selected from tetra- to heptachlorinated dibenzofurans and biphenyls; Wellington Laboratories) were added to the concentrated solution.

**Measurement.** PCDDs, PCDFs and DL-PCBs were detected using a high-resolution gas chromatograph/mass spectrometer (GC/MS; HP-6890 (Agilent Technologies, Wilmington, DE, USA) + JMS-700 (JEOL, Tokyo, Japan)). The MS was operated under positive EI conditions (resolution: > 10000), and data were acquired in the selected-ion-monitoring (SIM) mode. A chromatographic column "CP-Sil 88 for dioxins" (length: 60 m; id: 0.25 mm; film thickness: 0.10 μm; Varian, Lake Forest, CA, USA) was used for the separation of tetra- to hexachlorinated PCDDs/PCDFs carried out using the following temperature program: 100 °C (2 min)—200 °C (20 °C/min)—250 °C (2 °C/min, 25 min). A chromatographic column DB-5ms (length: 60 m; id: 0.25 mm; film thickness: 0.25 μm; Agilent Technologies) was used for the separation of hepta- to octachlorinated PCDDs/PCDFs and DL-PCBs carried out using the following temperature program: 120 °C (2 min)—180 °C (20°C/min)—260 °C (2°C/min)—320 °C (50 °C/min, 12 min). The ion channels ($m/z$) monitored are listed in Table 4.1. The detection limits for each congener were obtained in accordance with JIS K 0311.

The operation blank samples were prepared for rice-straw smoke, rice straw, paddy-field soil
and rice-straw ash samples in the manner similar to JIS K 0311. The concentrations of PCDDs/PCDFs/DL-PCBs in these operation blank samples were below the detection limits. The recovery of the cleanup spikes was in the range of which JIS K 0311 requires (50–120%). The concentrations less than the detection limits were considered to be zero.

### Table 4.1
Monitored ion channels (m/z) of the target dioxins and corresponding surrogates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Native</th>
<th>13C12-labeled surrogate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Channel 1</td>
<td>Channel 2</td>
</tr>
<tr>
<td>TeCDDs</td>
<td>321.8936</td>
<td>319.8965</td>
</tr>
<tr>
<td>PeCDDs</td>
<td>355.8546</td>
<td>353.8576</td>
</tr>
<tr>
<td>HxCDDs</td>
<td>389.8156</td>
<td>387.8186</td>
</tr>
<tr>
<td>HpCDDs</td>
<td>423.7767</td>
<td>425.7737</td>
</tr>
<tr>
<td>OCDD</td>
<td>459.7348</td>
<td>457.7373</td>
</tr>
<tr>
<td>TeCDFs</td>
<td>305.8987</td>
<td>303.9016</td>
</tr>
<tr>
<td>PeCDFs</td>
<td>339.8597</td>
<td>341.8568</td>
</tr>
<tr>
<td>HxCDFs</td>
<td>373.8207</td>
<td>375.8178</td>
</tr>
<tr>
<td>HpCDFs</td>
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<td>409.7788</td>
</tr>
<tr>
<td>OCDF</td>
<td>443.7398</td>
<td>441.7428</td>
</tr>
<tr>
<td>TeCBs</td>
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</tr>
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<td>PeCBs</td>
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<td>327.8775</td>
</tr>
<tr>
<td>HxCBss</td>
<td>359.8415</td>
<td>361.8385</td>
</tr>
<tr>
<td>HpCBs</td>
<td>393.8025</td>
<td>395.7995</td>
</tr>
</tbody>
</table>

*a Used for quantification.

#### 4.2.3. Data analysis

**Principal component analysis.** In order to examine the origins of dioxins in rice-straw smoke, PCA was carried out in addition to the indicative congener method. The concentrations of the seventeen 2,3,7,8-chlorine-substituted PCDDs/PCDFs, the twelve DL-PCBs, and the eight residual PCDD/PCDF homologues were used as variables. Prior to the PCA, the data set was normalized toward the total PCDD/PCDF/DL-PCB concentration. PCA was performed using KyPlot 5.0 (KyensLab, Tokyo, Japan).

#### 4.3. Results and discussion

##### 4.3.1. Dioxins in rice-straw smoke samples collected at paddy fields

The homologue profiles of the PCDDs/PCDFs/DL-PCBs found in the rice-straw smoke samples (RSS-A, -B, -C, -D and -E) are shown in Figure 4.2 as the percentage of each homologue concen-
PCDDs constituted a significant fraction (70%–92%) of the total concentration, and TeCDDs and/or OCDD were the main homologues in PCDDs. Moreover, 1,3,6,8-TeCDD and 1,3,7,9-TeCDD were the dominant congeners in TeCDDs. According to Masunaga et al. (2001a) and Seike et al. (2003), PCDDs were predominant in PCP- and CNP-originated PCDDs/PCDFs/DL-PCBs, the major homologue in PCDDs was OCDD for PCP formulations and TeCDDs for CNP formulations, and 1,3,6,8-TeCDD and 1,3,7,9-TeCDD were the dominant congeners in CNP formulations. In the light of these findings, the homologue profiles suggested that the dioxins contained in the rice-straw smoke samples were influenced by the PCP- and CNP-originated dioxins. In particular, RSS-B and RSS-E, in which the proportions of PCDFs and DL-PCBs were small (approximately 8% for both samples), were considered to be significantly influenced by PCP and/or CNP. RSS-E was especially affected by PCP because of its high OCDD proportion.

**Figure 4.2.** PCDD/PCDF/DL-PCB homologue profiles of the samples of rice straw smoke collected from actual field burnings.

The indicative congener method (Eqs. (1)–(4) and (18)–(23)) was applied to the rice-straw smoke samples. The result of the apportionment was reasonable because the estimated total TEQs were almost equal to the measured total TEQs—the average ratio of the estimated total TEQ to the measured total TEQ was 1.12 ± 0.18. Figure 4.3 shows the estimated contribution of the TEQs originating from the four major dioxin sources. The contributions of PCP- and CNP-originated TEQs were large (55%–96%). This result was different from that obtained for waste combustion gas because the estimation applying to the waste combustion gas data showed that the combustion-originated TEQ accounted for nearly 100% of the total TEQ (Paper 1). In particular, the results for RSS-B and RSS-E showed that the contribution of the TEQs
originating from PCP and CNP exceeded 90%. To be specific, RSS-E was remarkably affected by PCP because its proportion of PCP-originated TEQ exceeded 70%. These results support the above-mentioned finding that the dioxins in the rice-straw smoke samples were affected by PCP- and CNP-originated dioxins.

Figure 4.3. TEQ contribution of the four major dioxin sources estimated by using indicative congener method for rice straw smoke samples collected from actual field burnings.

4.3.2. Effect of paddy-field soil on dioxins of rice-straw smoke

In this section, the effect of paddy-field soil on dioxins of rice-straw smoke was discussed qualitatively by using congener profiles. Figure 4.4 shows the homologue profiles of the PCDDs/PCDFs/DL-PCBs contained in the rice-straw smoke samples collected by burning rice straw on a stainless-steel tray (RSS-F, -G, -H and -I), the rice straw samples (RS-F, -G, -H and -I; the TEQs ranged from 1.3 to 8.0 ng-TEQ kg\(^{-1}\)) and paddy-field soil samples (PFS-F, -G, -H and -I; the TEQs ranged from 120 to 290 ng-TEQ kg\(^{-1}\)); the profiles show the percentage of each homologue concentration relative to the total PCDD/PCDF/DL-PCB concentration. With regard to the rice-straw smoke samples, PCDDs also constituted a significant fraction (61%-83%) of the total concentration, and TeCDDs and/or OCDD were the main homologues in PCDDs. Moreover, 1,3,6,8-TeCDD and 1,3,7,9-TeCDD were the dominant congeners in TeCDDs. These results corresponded to those obtained for the smoke samples collected from the field burning of rice straw.
Comparing the dioxins of the rice-straw smoke samples with those of their corresponding rice straw samples, the homologue profiles before and after burning the rice straw were found to be similar. Furthermore, the concentrations of the dioxins in the rice-straw ash samples were very low (0.1%–0.6% of those in the burned rice straw). These results suggest that the amount of dioxins formed during the rice straw burning process was smaller than that of the dioxins present in the rice straw, and the dioxins contained in the rice-straw smoke mainly originated from those in the rice straw.
PCDD/PCDF/DL-PCB homologue profiles of the paddy-field soil samples were very similar to those of paddy-field soil contaminated with PCP and CNP formulations reported by Kobayashi et al. (2004), Uegaki et al. (2006) and Kiguchi et al. (2007). PCDDs constituted a significant fraction of the total PCDD/PCDF/DL-PCB content in the paddy-field soil samples, and the proportions of PCDFs and DL-PCBs were very small. TeCDDs and/or OCDD were the main homologues in PCDDs, implying that PCP- and CNP-originated dioxins significantly influenced the dioxins in the paddy-field soil samples. On comparing the dioxins obtained from the rice straw samples with those obtained from the corresponding paddy-field soil samples, the homologue profiles of PCDDs were found to be similar, though the proportions of PCDFs and DL-PCBs were somewhat larger in the rice straw samples. This indicates that the dioxins of the rice straw samples were affected by those originating from the paddy-field soil. Uegaki et al. (2006) reported that the sources of dioxin pollution for rice straw were adhesion of paddy-field soil and intake of the atmospheric gas phase, but the contributions of other sources such as the atmospheric particle phase were small. Considering this result, it can be concluded that PCDFs and DL-PCBs in rice straw are mainly originated from the atmospheric gas phase. Consequently, it is believed that the dioxins in rice-straw smoke are transferred during field burning from the dioxins present in the paddy-field soil adhered to the rice straw surface and from the atmosphere-originated dioxins in the rice straw. It indicates that the emission factor of dioxins from rice-straw burning in Japan can be roughly estimated as the dioxin concentration in the biomass; this is even more so for highly-contaminated rice straw. The dioxins in the rice straw samples ranged in concentration (1.3–8.0 ng-TEQ kg\(^{-1}\)), and it seems that the contamination level of rice straw depends on the amount of adherent paddy-field soil and its dioxin concentration.

### 4.3.3. Result of PCA

In order to identify the relationships among the rice-straw smoke, rice straw and paddy-field soil, PCA was applied to the rice-straw smoke (RSS-A, -B, -C, -D, -E, -F, -G, -H and -I), rice straw (RS-F, -G, -H and -I) and paddy-field soil (PFS-F, -G, -H and -I) samples. The proportions of PC1 and PC2 were 81% and 16%, respectively. Because the cumulative proportion of these two PCs was 97%, it was considered that the most of the dioxins in the rice-straw smoke, rice straw and paddy-field soil samples were related to the sources that contributed significantly to PC1 and PC2. PC1 was particularly the main component that suggested the dioxin sources because
of its high proportion.

The positive values of PC1 were characterized by residual TeCDDs (factor loading 0.94), followed by residual PeCDDs (factor loading 0.56); the negative values of PC1 were characterized by OCDD (factor loading −0.93), followed by 1,2,3,4,6,7,8-HpCDD and residual HpCDD (factor loading < −0.7). On the other hand, the positive values of PC2 were characterized by OCDF (factor loading 0.51), followed by OCDD and residual TeCDDs (factor loading > 0.35); the negative values of PC2 were characterized by 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, residual TeCDFs, residual PeCDFs, and DL-PCBs (factor loading < −0.8).

Figure 4.5 shows the plots of PC1 and PC2 scores. The scores for the dioxin data of the four major dioxin sources (combustion by-products, PCP formulations, CNP formulations and PCB products) and those of the ambient air were calculated using the given scoring coefficients and are also plotted in Figure 4.5. Herbicide (PCP and CNP formulations) data and commercial PCB (Kanechlor: KC-300, KC-400, KC-500, and KC-600) data were the published ones reported by Masunaga et al. (2001a) and Noma et al. (2004), respectively. The waste combustion gas data were obtained through the analysis of the emission gases at six waste incinerators (two municipal solid-waste incinerators, two waste-wood incinerators, and two hospital waste incinerators) in Saitama, Japan. These gases were collected and analyzed by us during the period 2005–2007. The ambient air data were the results of periodical monitoring (four times in a year at 15 sites in Saitama) conducted by Saitama prefecture during the period April 2002–March 2003. The plots for the four major sources were clearly separated, and the ambient air data were clustered together with waste combustion gas data and PCB data.

From the characteristic parameters with high factor-loading values for each principal component and from the score plots of the source data, PC1 is interpreted as PCP in the negative direction and as CNP in the positive direction. PC2 is interpreted as herbicides (PCP and CNP) in the positive direction and as waste combustion and PCB—considered as the pollution sources of the ambient air—in the negative direction.

The proportion of PC1 was high (81%), and PC1 represented a large influence of PCP and CNP formulations. Therefore, the results obtained for congener profiles by the PCA also indicate
that the dioxins contained in the rice-straw smoke samples collected at field burning of rice straw were greatly influenced by PCP- and CNP-ori ginated dioxins. Because the plots of the rice-straw smoke were far from those of waste combustion gas, the congener profiles were different between rice-straw smoke and waste combustion gas. That is, the cause for the presence of dioxins in the rice-straw smoke is not attributed to the combustion of rice straw itself. RSS-B and RSS-E, plotted in the positive area of PC2, are greatly influenced by herbicides. In particular, RSS-E is strongly affected by PCP, as indicated by the fact that its plot is in the area covered by the PCP formulation data. This supports the results concluded from the TEQ apportionment by using indicative congeners and the comparison of homologue profiles, as described above.

_Figure 4.5_. Plots of PCA scores of the first and second principal components for rice straw smoke, rice straw and paddy field soil samples. Scores for PCP, CNP, PCB, waste combustion gas, and ambient air data were calculated from the obtained scoring coefficients. Alphabets (A–I) are site codes.
In the plots of PC1 and PC2 scores, the data points of the rice-straw smoke samples obtained from the laboratory experiment (RSS-F, -G, -H and -I) were located close to those of the corresponding rice-straw samples (RS-F, -G, -H and -I, respectively), indicating that there are similarities in the congener profiles of the rice-straw smoke and the corresponding rice straw. This fact also implies that most of the dioxins contained in the rice-straw smoke were originated from the dioxins present in the rice straw, and the effect of the dioxins formed during the rice straw burning process was relatively small.

The rice straw samples (RS-F, -G, -H and -I) were generally clustered together with the corresponding paddy-field soil samples (PFS-F, -G, -H and -I, respectively), though the rice straw samples were situated somewhat closer to the ambient air. This indicated that the dioxins present in the rice straw were influenced by those in the paddy-field soil. It is considered that the influence of the dioxins originating from the atmospheric gas phase makes the data points of the rice straw samples closer to those of the ambient air. This supports the results obtained from the comparison of homologue profiles.

The PCA also indicates that most of the dioxins in the rice-straw smoke are transferred during rice straw burning primarily from the paddy-field soil adhered to the rice straw surface and secondly from the dioxins present in the rice straw. Therefore, it can be said that rice straw burning acts as a driving force of transition of dioxins from paddy-field soil to the atmosphere. Dioxins vaporized from the heated surface of soil at paddy fields may be included in the smoke generated in practical field burning of rice straw.

4.4. Conclusions

In Japan, rice is a major agricultural product, and the post-harvest rice straw is often burned at paddy fields where a large amount of PCP and CNP formulations had been applied as herbicides. Under these circumstances, the origins of dioxins (PCDDs/PCDFs/DL-PCBs) in rice-straw smoke were examined qualitatively by using congener profiles.

Rice-straw smoke samples were collected from the rice straw burning sites at post-harvest paddy fields, and the dioxins present in the rice-straw smoke were analyzed in order to determine their congener profiles. Moreover, rice straw and paddy-field soil samples were collected,
and the rice straw samples were burned in a laboratory so as to obtain rice-straw smoke samples and rice-straw ash samples. The dioxins in these rice straw, rice-straw smoke, rice-straw ash and paddy-field soil samples were also analyzed in order to determine their relationships and the origins of the dioxins in the rice-straw smoke.

From the comparison of the homologue profiles of PCDDS/PCDFs/DL-PCBs, the apportionment of TEQs performed using indicative congener method, and the PCA, the following conclusions were drawn:

(1) The dioxins found in the rice-straw smoke were greatly influenced by the PCP- and CNP-originated dioxins.

(2) The major sources of the dioxins in the rice-straw smoke were primarily attributed to the paddy-field soil adhered to the rice straw surface and secondly to the air taken into the rice straw. The dioxins formed during rice straw burning contributed only minimally.

(3) Our results suggest that rice straw burning at paddy fields may act as a driving force in the transfer of dioxins from paddy-field soil to the atmosphere.
Chapter 5

Seasonal change of dioxins in the water of Ayase River

5.1. Introduction

In Japan, Ayase River is one of the most polluted rivers by dioxins. According to the survey reports on dioxins in the environment (MOE, 2001b, 2002–2008, 2009b), the concentration of dioxins in the river has continuously exceeded the environmental quality standard of 1.0 pg-TEQ L⁻¹ for river water. In the river basin, there is no facility for discharging waste water that can influence the dioxin concentration of the river water.

As described in the Section 4.1, a large amount of PCP and CNP formulations was widely used as herbicides for the paddy fields in Japan, and these herbicides contained dioxins as impurities (Masunaga et al., 2001a; Seike et al., 2003); the herbicides-originated dioxins still remain in the soil of paddy fields (Seike et al., 2003; Kiguchi et al., 2007). Wet-rice farming needs to induce water from water bodies to paddy fields, and the water is drained back to water bodies. Due to this reason, the herbicides-originated dioxins flow into water bodies from paddy fields (Seike et al., 2007) and pollute the sediment of river and its drainage basin (Sakurai, 1996; Masunaga et al., 2001b; Yao et al., 2002; Masunaga et al., 2003; Kiguchi et al., 2007). Thus, the paddy fields in Japan work as significant suppliers of dioxins to the environment.

Considering the above-mentioned information, there was a possibility that the water of Ayase River was polluted by the herbicides-originated dioxins because a large area of paddy fields existed in the upper part of the river basin. Thus, in this study, the river water samples were collected once per month for a year, and dioxins present in the water were examined to estimate the dioxin sources and their TEQ contributions.
5.2. Materials and methods

5.2.1. Sample collection
Ayase River starts its flow from the northeastern part of Saitama prefecture and flows to south through Saitama prefecture and reaches to Tokyo metropolitan. The river joins Naka River in Tokyo metropolitan and flows into Tokyo Bay. The length of the river is 47.6 km (39 km in Saitama and 8.6 km in Tokyo), and the river basin area is 176 km².

Irrigation to the paddy fields in the river basin starts in late April or early May. The soil in paddy fields is mechanically mixed with pooled water, and then rice seedlings are planted. Rice harvesting is carried out after drying up the paddy fields in September. Therefore, the water through the paddy fields is drained to the river from May to August.

The river water samples were collected at Ayase-shin Bridge (latitude: 35.8739° north, longitude: 139.7588° east) in the middle part of the river every mid-month from April 2004 to March 2005. The number of the water samples was 12 (one sample per month for 12 months). The sample collection was performed at the center of the flow from the bridge using a stainless-steel bucket. The water amount of approximately 40 L was poured with a stainless-steel funnel and a stainless-steel ladle into glass bottles. Also, the water sample for suspended solids (SS) analysis was collected and poured into a polyethylene bottle.

Surface sediment samples were collected in June (irrigation period) and December (non-irrigation period) with an Ekman-Birge sampler from the bridge. Each sediment sample was a mixture of the samples collected from different three points. The mixed sediment was packed into a glass bottle.

5.2.2. Dioxin analysis
The analysis of dioxins in the water and sediment samples was performed in accordance with the official methods designated by Japanese Standards Association (1999b) and Environmental Agency of Japan (2000a), respectively, with some modifications. Prior to the extraction of water sample, acetone solution of three $^{13}$C$_{12}$-labeled dioxins (Wellington Laboratories) was
added to the sample for the validation of extraction performance. Then, the water sample was filtrated by quartz fiber filters (GC-50H, 142 mm; ADVANTEC). The filtrate was passed through extraction disks (C18FF (Octadecyl), 90 mm; 3M, Minnesota, USA). The emptied bottles were rinsed with acetone (Kanto Chemical) and dichloromethane (Kanto Chemical) in sequence. The quartz fiber filters and the extraction disks were separately Soxhlet extracted with toluene (Kanto Chemical) for 24 hours. The bottle rinsed solution and the disk extract were combined, and this combined solution was treated as aqueous phase. The filter extract was treated as particle phase. These liquids were separately subjected to the cleanup procedure. For only the sample collected in April, the aqueous and particle phases were combined together and subjected to the cleanup procedure. The sediment samples were dried at room temperature on a stainless-steel tray and then sieved through a 2 mm-mesh stainless-steel screen. The sieved sediment samples were Soxhlet extracted for 24 hours with toluene and subjected to the cleanup procedure.

Cleanup and GC/MS measurement were performed according to the way described in the Section 4.2.2. Dioxins in the operational blank samples were negligible levels. The recovery of the cleanup spikes was satisfactory and the average recovery rates for PCDDs, PCDFs and DL-PCBs were 91 ± 10%, 88 ± 10% and 89 ± 8%, respectively. The four $^{13}\text{C}_{12}$-labeled dioxins added prior to extraction of the water samples were also well recovered and the average recovery rate was 94 ± 5%. The concentrations less than the detection limits were considered to be zero.

5.2.3. SS measurement

SS in the water samples was measured in accordance with JIS K 0102 (Japanese Standards Association, 1998). The water sample was filtrated through a glass fiber filter (GF/B, 47 mm; Whatman, Kent, UK). The solids remained on the filter was dried at 110 °C for 2 hours and then measured the weight together with the filter.

5.2.4. Data analysis

Principal component analysis. In order to examine the origins of dioxins in the river water, PCA was carried out in addition to the indicative congener method. The TEQs of the seventeen 2,3,7,8-chlorine-substituted PCDDs/PCDFs and the twelve DL-PCBs were used as variables. Prior to the PCA, the congener data set was normalized toward the total TEQ. PCA was per-
formed using KyPlot 5.0 (KyensLab).

5.3. Results and discussion

5.3.1. Seasonal change of dioxin concentration in river water

The total concentration of dioxins in the river water samples (sum of aqueous phase and particle phase) was in the range from 190 to 4700 pg L\(^{-1}\) (average: 1700 pg L\(^{-1}\)) and the total TEQ was in the range from 0.26 to 7.0 pg-TEQ L\(^{-1}\) (average: 2.7 pg-TEQ L\(^{-1}\)). Figure 5.1 shows the seasonal change in the total TEQ of the water samples. The TEQ was 2.0 pg-TEQ L\(^{-1}\) in April, and then drastically rose to 7.0 pg-TEQ L\(^{-1}\)—a maximum value during the sampling period—in May when the irrigation period started. During the irrigation period, from May to August, the TEQ remained to have high concentrations (4.5–7.0 pg-TEQ L\(^{-1}\)). In September, when the non-irrigation period started, the TEQ showed a steep decline and then decreased slowly. Only four samples collected from December to March met the environmental quality standard in Japan (1.0 pg-TEQ L\(^{-1}\)).

![Figure 5.1. Seasonal change in TEQ of the water samples collected from Ayase River.](image)

Result from the dioxin analysis of the water samples, whose aqueous phase and particle phase
were separately measured, showed that the most dioxins existed in the particle phase throughout the year (95 ± 3%). This result is consistent with the physical-chemical property of dioxins that the aqueous solubility of PCDDs/PCDFs is very low (Govers and Krop, 1998). Thus, it was suggested that the dioxins in the water samples stably existed in SS.

5.3.2. Relationship between dioxins and SS

The SS concentrations of the river water samples ranged from 8 to 59 mg L⁻¹ and corresponded to the TEQ (sum of the aqueous and particle phases): the SS concentration was high at the irrigation period and low at the non-irrigation period. However, the ratio of TEQ to SS (TEQ/SS) was not constant as illustrated in Figure 5.2. The value of TEQ/SS tended to be high at the irrigation period and low at the non-irrigation period.

As one of the reasonable sources of SS in river water is sediment, so its contribution to the above-mentioned result was evaluated. The TEQ values of the sediment samples collected in June during the irrigation period and December during the non-irrigation period were 3.3 ng-TEQ kg⁻¹ and 3.7 ng-TEQ kg⁻¹, respectively, showing no significant seasonal changes. Moreover, the TEQ/SS values of the water samples in the irrigation period (100–150 ng-TEQ...
kg 1) were much higher than the TEQ values of the sediment samples. Therefore, in this case, it seemed that the river sediment was not a significant supplier of SS in the irrigation period, and the river received water with dioxin-contaminated SS in the irrigation period. Further discussion will be described later.

Figure 5.3. Seasonal change in TEQ of the water samples collected from Ayase River.

5.3.3. Homologue profile
PCDDs constituted a significant fraction (53–91%) of the total concentration of PCDDs, PCDFs and DL-PCBs. Especially, the fraction of PCDDs exceeded 90% during the irrigation period. OCDD was the main homologue in PCDDs (53–70%) and followed by TeCDDs (20–35%). TeCDDs was dominated by 1,3,6,8-TeCDD and 1,3,7,9-TeCDD (87–99%). According to Masunaga et al. (2001a) and Seike et al. (2003), PCDDs were predominant for PCP- and CNP-originated dioxins; the major homologue in PCDDs was OCDD for PCP formulations and
TeCDDs for CNP formulations, and 1,3,6,8-TeCDD and 1,3,7,9-TeCDD were major congeners in CNP formulations. Figure 5.3 illustrates the homologue profiles of the water samples. These profiles, particularly ones collected in irrigation period, are very similar to that of the soil collected from a paddy field where PCP and CNP had been used in previous years, reported by Uegaki et al. (2006). Therefore, it is suggested that the dioxins in the river water were influenced by the herbicides-originated dioxins, especially by PCP-originated ones. In particular, the influence of the herbicides was high during the irrigation period.

5.3.4. TEQ apportionment

The indicative congener method (Eqs. (1)–(4) and (18)–(23)) was applied to the river water and sediment samples. Figure 5.4 shows the TEQ apportionment. The result was satisfactory because the estimated total TEQs were almost equal to the measured total TEQs and the average in the ratio of the estimated total TEQ to the measured total TEQ was 1.02 ± 0.06. The averages in TEQ contribution of each source for river water samples were 51% (range: 36–64%), 14% (2–20%), 4% (1–9%) and 31% (18–55%) for PCP formulations, CNP formulations, PCB products and combustion by-products, respectively. The TEQ of the river water was largely accounted for by PCP-originated dioxins, and followed by combustion-originated ones. This result is reasonable because the total TEQ (based on the WHO-1998 TEF) of PCDDs/PCDFs in the surface sediment in Tokyo Bay was mainly attributed to PCP formulations and combustion by-products (Yao et al, 2002; Masunaga et al, 2003). The TEQs originated from PCP formulations and CNP formulations highly contributed to the total TEQ (78–81%) during the irrigation period in which dioxins were detected at high concentration.

The results of the TEQ apportionment for the two sediment samples were almost the same for each other but different from the water samples collected during the irrigation period; the herbicides-originated TEQs of the water samples during the irrigation period were much higher than those of the sediment samples. From this point of view, it is also suggested that the river sediment was not a significant supplier of the SS containing highly-concentrated dioxins in the irrigation period.

Figure 5.5 shows the measured total TEQ versus TEQ contributions from the four sources of the water samples. The ratios of PCP and CNP increased along with the increase of the meas-
ured total TEQ. On the contrary, the ratios of combustion and PCB decreased along with the increase of the measured total TEQ. This suggests that the dioxin sources of the river water could be divided into two groups: [PCP + CNP] and [Combustion + PCB]. PCDDs/PCDFs in atmospheric deposition in the Kanto region where Ayase River located are thought to be originating mainly from the combustion by-products (Ogura et al., 2001b). Moreover, the atmospheric deposition samples in the Kanto region contained DL-PCBs, and DL-PCBs collected from some sites were considered to be affected by PCB products (Ogura et al., 2001a). Thus, the TEQ contribution of [Combustion + PCB] in the river water samples was thought to be derived from atmospheric deposition.

From these facts, the following results are concluded. The herbicides-originated dioxins flowed into the river with drain water from the paddy fields during the irrigation period, and the level of dioxins in the river water was increased. In the non-irrigation period, the influence of at-
mospheric deposition appeared relatively largely with the decrease of the inflow of herbicides-originated dioxins.

5.3.5. Principal component analysis

In order to identify the pollution sources of dioxins, the PCA was also applied to the river water samples. The proportions of PC1 and PC2 were 79% and 9% (< 10%), respectively. Because of a large amount of the proportion of PC1, it was considered that the most of the dioxins in the river water samples were influenced by the sources that contributed significantly to PC1.

The positive values of PC1 were characterized by OCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8-PeCDD and OCDF (factor loading > 0.7); the negative values of PC1 were characterized by 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,7,8-HxCDF, 2,3,7,8-TeCDD and DL-PCBs (factor loading < −0.7). On the other hand, no parameter showed high factor loading value (> 0.7 or < −0.7) in PC2: the highest factor loading value was 0.58 for 1,2,3,7,8-PeCDD.

Figure 5.6 shows the plots of PC1 and PC2 scores. The scores for the dioxin data of the four
major dioxin sources (PCP formulations, CNP formulations, PCB products and combustion by-products) were calculated using the obtained scoring coefficients. Herbicides (10 PCP and 16 CNP formulations) data were the published ones reported by Seike et al. (2003). PCB data were the analyzed results of 5 commercial PCBs and 23 stockpiled PCB wastes reported by Noma et al. (2004). The data for combustion were obtained through our analysis of the flue gases (N = 48) collected from waste incinerators in Saitama during the period from 2001 to 2006.

Figure 5.6. Score plots of PC1 and PC2 for the river water samples. The scores of source data (PCP formulations, CNP formulations, PCB products, and flue gas) were calculated from the obtained scoring coefficients.

The plots for the four major sources were clearly separated. From the characteristic parameters with high factor-loading values for each principal component and the score plots of the source data, PC1 is interpreted as [PCP + CNP] in the positive direction and as [Combustion + PCB] in the negative direction. PC2 is interpreted as CNP in the positive direction.
The proportion of PC1 was significant (79%), and PC1 represented a large influence of [PCP + CNP] and [Combustion + PCB]. Therefore, the results obtained for TEQ profiles by the PCA also indicate that the TEQ of dioxins in the river water were influenced by the two combinations of the sources—[PCP + CNP] and [Combustion + PCB]. Especially, PCP and combustion were the major TEQ sources, because the river water sample data were plotted between PCP data and flue gas data.

The PC1 scores for the river samples collected in the irrigation period (May, Jun, July and August) showed higher values in the positive direction which represents [PCP + CNP]. From September, the plots shifted to the negative direction which represents [Combustion + PCB]. The samples collected in December, January, February and March, which met the environmental quality standard, showed higher values in the negative direction. These facts lead that the dioxins in the river water were influenced by the herbicides (PCP and CNP formulations) during the irrigation period, and their influence decreased in the non-irrigation period. On the other hand, the influence of atmospheric deposition (combustion by-products and PCB products) appeared relatively largely in non-irrigation period. The result from the PCA was consistent with the conclusions from the TEQ apportionment by using indicative congener method.

5.4. Conclusions
The water samples of Ayase River were collected once per month for a year, April 2004 to March 2005, and dioxins (PCDDs, PCDFs and DL-PCBs) in the samples were analyzed. The TEQs were ranged from 0.26 to 7.0 pg-TEQ L\(^{-1}\), and the average was 2.7 pg-TEQ L\(^{-1}\). The TEQ value was high in the irrigation period, May, Jun, July and August. The most of the dioxins in the river water existed in particle phase—SS—and it seemed that the river receives water with dioxin-contaminated SS in the irrigation period. The homologue profiles suggested that the dioxins in the water were influenced by the dioxins originated from herbicides, PCP and CNP formulations. The TEQ apportionment by using indicative congener method indicated that the major TEQ contributor in the river water was PCP. Moreover, the TEQ apportionment and the PCA showed that the TEQ contribution of [PCP + CNP] was dominated in the irrigation period and that of [Combustion + PCB] increased in the non-irrigation period. Therefore, it is suggested that the herbicides-originated dioxins run off from the paddy fields into the river during the irrigation period, and in the non-irrigation period, the influence of atmospheric deposition
Chapter 5.  Seasonal change of dioxins in the water of Ayase River

appeared relatively largely with the decrease of the inflow of the herbicides-originated dioxins.
Chapter 6

A simplified TEQ determination by applying indicative congener method

6.1. Introduction
The toxicity of each dioxin congener depends on the number and position of chlorines. For this reason, 2,3,7,8-TeCDD TEQ is generally used for assessment of pollution level. The TEF values are given for 29 dioxin congeners (seventeen 2,3,7,8-chlorine-substituted PCDDs/PCDFs and twelve DL-PCBs) in the WHO TEF systems (Van den Berg et al., 1998, 2006), and TEQ is evaluated by the sum of the products of each concentration of the 29 TEF congeners and their corresponding TEF values. In order to obtain TEQ, the concentrations of the 29 TEF congeners in total are needed to determine by a GC/MS. However, a capillary column, which is used to separate the 29 TEF congeners from the other congeners, has not yet been reported. Consequently, the official methods for dioxin analysis (Japanese Standards Association, 1999b; Environmental Agency of Japan, 2000a, 2000b; MOE, 2001a) require three or more-times GC/MS measurements with several types of capillary columns, and take a long measurement time. For example, the measurement conditions described in the JIS K 0312 (Japanese Standards Association, 1999b) require three or four-times GC/MS measurements with three different capillary columns (total measurement time of 113–182 min); the condition proposed by Matsumura et al. (2002) needs three-times GC/MS measurements with two different capillary columns (total measurement time, 144 min). Quantifying as many as 29 congeners also requires time and efforts. If the number of target congeners can be reduced, it will save a lot of time and efforts for measurement and quantification.

In order to overcome these difficult backgrounds, several methods of simplified determination for dioxins have been investigated. One of them is TEQ estimation using indicative congener(s),
Chapter 6. A simplified TEQ determination by applying indicative congener method

whose concentration has a high correlation with TEQ. Fiedler et al. (2000) reported an intriguing observation that the concentration of 2,3,4,7,8-PeCDF was proportional to the TEQ, based on the I-TEF, of PCDDs/PCDFs in stack emission gas samples, and proposed a conversion factor from the concentration of 2,3,4,7,8-PeCDF to the TEQ. There were some parallel studies for combustion by-products. It was found that the concentration of 2,3,4,7,8-PeCDF was also proportional to the WHO-1998 TEQ of PCDDs/PCDFs/DL-PCBs in stack emission gas (Urano and Kato, 2001; Shibayama et al., 2003) and ash (Shibayama et al., 2003) samples. Regarding environmental media, to the best of our knowledge, only Shibayama et al. (2003) studied this matter in Japan, and showed that 2,3,4,7,8-PeCDF is suitable as an indicative congener for the determination of the WHO-1998 TEQ of ambient air and soil samples, but another congener in addition to 2,3,4,7,8-PeCDF was needed for water and sediment samples. By using their method, the TEQ of environmental samples may be obtained only from the concentration(s) of indicative congener(s), thus reducing the time and efforts for measurement and quantification. However, they also suggested (Shibayama et al., 2003) that estimated TEQ was in disagreement with TEQ obtained by the official method for soil, sediment and water samples in some cases. This may be attributed to the fact that dioxins in the environment in Japan have been brought by multiple sources, as described in the Section 3.1.

It is assumed that the indicative congener method (ICM) could be applied to simplified TEQ determinations, which measure only five indicative congeners. In this case, it would be possible to detect the concentrations of the five indicative congeners by a single GC/MS measurement. Moreover, its application is expected to be useful not only for TEQ determination, but also for source tracing of dioxins because of the ICM’s ability of the source apportionment.

In this study, the development of a simplified TEQ determination method based on the ICM was performed, which estimated TEQ from the concentrations of five indicative congeners obtained by a single GC/MS measurement. Firstly, the effectiveness of the ICM was evaluated by applying to environmental samples collected from all over Japan. Secondly, a suitable combination of two GC capillary columns that separated the indicative congeners from the other congeners by single GC/MS measurement was searched.
6.2 Materials and methods

6.2.1. Dioxin data of geographic information system (GIS)

In order to evaluate the applicability of the ICM as a simplified determination method, it was applied to geographic information system (GIS) data for an environmental survey of dioxins in Japan, published on the website of National Institute for Environmental Studies (NIES; NIES website). Samples whose concentrations of all 29 congeners with their TEF values exceeding their detection limits were selected from those collected in fiscal 2007 (from April, 2007 to March, 2008). The number of selected samples was 354 for ambient air, 96 for water (river, lake, marine and ground water), 361 for sediment (river, lake and marine sediment), and 354 for soil. The total TEQ for the selected samples was calculated from the 29 congener concentrations based on the WHO-2006 TEF; its range was 0.16–17 pg-TEQ m⁻³ for ambient air, 0.23–4.7 pg-TEQ L⁻¹ for water, 0.84–240 ng-TEQ kg⁻¹ for sediment, and 0.52–2600 ng-TEQ kg⁻¹ for soil.

6.2.2. Environmental samples for evaluating the simplified determination method

Various environmental samples, ambient air (N = 26), river water (N = 15), river sediment (N = 38) and soil (N = 29), collected in Saitama prefecture from 2004 to 2008 were used to validate the objective simplified method. These samples were pretreated according to the corresponding official methods for dioxin analysis (Japanese Standards Association, 1999b; Environmental Agency of Japan, 2000a, 2000b; MOE, 2001a), in which the isotope dilution method by using ¹³C₁₂-labeled dioxin surrogates was performed. The dioxin TEQs (based on the WHO-2006 TEF) obtained by the corresponding official methods ranged from 0.038 to 0.51 pg-TEQ m⁻³ for ambient air samples, 0.34 to 8.6 pg-TEQ L⁻¹ for river water samples, 3.0 to 78 ng-TEQ kg⁻¹ for river sediment samples, and 2.9 to 1500 ng-TEQ kg⁻¹ for soil samples.

6.2.3. GC/MS measurement

A high-resolution GC/MS (HP-6890 (Agilent Technologies) + JMS-700 (JEOL)) was used to detect dioxins. The injector temperature and GC/MS interface temperature were set at 290 and 280°C, respectively, and helium was used as a carrier gas (1 mL min⁻¹). The target congeners were separated by using the combination of GC capillary columns, a 10-meter-long DB-5ms
(0.25 mm i.d., 0.25 μm film thickness; Agilent Technologies) and a 20-meter-long DB-17ms (0.25 mm i.d., 0.25 μm film thickness; Agilent Technologies). The GC program was carried out as follows: 130°C (2 min) to 210°C (0 min) at 20°C min⁻¹ and subsequently to 300°C at 3°C min⁻¹, then maintained at 300°C for 4 min (total: 40 min). The MS was operated in the selected ion-monitoring (SIM) mode with a mass resolution of >10000 (Lock mass, PFK), and the electron impact ionization energy was 38 eV with an ion-source temperature of 280°C. The monitored ion channels of the indicative congeners and corresponding ¹³C₁₂-labeled surrogates were the same ones shown in Table 4.1.

6.3. Results and discussion

6.3.1. Validation of the ICM by GIS data

In our previous study (Paper I), the effectiveness of the ICM was evaluated by applying envi-
ronmental samples collected only from Saitama prefecture. In order to enhance the applicability of the ICM to the objective simplified measurement, Eqs. (1)–(4) and (18)–(23) were applied to GIS data containing analytical results from all over Japan. The estimated results were compared with the results obtained by the official method, as shown in Figure 6.1. The average in the ratio of the ICM TEQ to the official-method TEQ was 1.11 (SD: 0.11) for ambient air, 1.00 (SD: 0.11) for sediment, 1.04 (SD: 0.11) for soil, and 0.98 (SD: 0.17) for water. As for water, the value was 0.99 (SD: 0.14), excluding three peculiar samples collected from Mawatashi River in Fukui prefecture, where the water was significantly polluted by dioxins originating from a dye (Kumagai, 2005). Thus, we could prove that ICM is efficient for estimating the TEQ of various environmental samples with a high accuracy for a wide range of TEQ values. This result indicates that the major dioxin sources in the environment in Japan are the above-mentioned four sources (combustion by-products, PCP formulations, CNP formulations and PCB products), and that ICM is applicable to environmental samples collected from any parts of Japan.

6.3.2. Selection of GC column combination

A GC capillary column combination, which effectively separates the five indicative congeners from the other congeners, was searched from commercially available columns. Among the five indicative congeners, the chromatographic isolation of 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD by a same column was of interest in the present study. Table 6.1 gives the separation capacity of various capillary columns for the two congeners. Only these columns with a stationary phase of high polarity, such as SP-2331 and CP-Sil88, can isolate the two congeners from the other congeners. Therefore, it may be possible to separate the indicative congeners from the other congeners by a single GC/MS measurement with these high-polarity columns. However, when a simplified determination method is applied for a screening survey that deals with a large number of samples, a column having a stable stationary phase of lower polarity is more manageable than a sensitive one with a high-polar stationary phase. Thus, a low-polarity column, DB-5ms (0.25 mm i.d., 0.25 μm film thickness), which separates 1,2,3,7,8-PeCDD from the other congeners, a middle polarity column, DB-17ms (0.25 mm i.d., 0.25 μm film thickness), which separates 2,3,4,7,8-PeCDF from the other congeners, and their combinations were examined.

The column combinations examined were as follows: (i) 30-meter-long DB-5ms, (ii) 20-meter-long DB-5ms + 10-meter-long DB-17ms, (iii) 10-meter-long DB-5ms + 20-meter-long DB-17ms,
Chapter 6. A simplified TEQ determination by applying indicative congener method

and (iv) 30-meter-long DB-17ms. The DB-5ms column was set at the injector side because the column bleed from the low-polarity stationary phase of DB-5ms is expected to be smaller than that from the higher polarity one of DB-17ms. Another reason for the order of the columns is that all seventeen 2,3,7,8-chlorine-substituted PCDDs/PCDFs were successfully isolated by only one injection with GC×GC, in which the 5-like GC column (InterCap 5MS/Sil; GL Science, Tokyo, Japan) as the first column and 17-like GC column (InterCap 17MS/Sil; GL Science) as the second column were installed (Hashimoto et al., 2008). Conditioning of the columns was carried out separately before connection. Non-polar fused-silica tubes (SUPELCO, Bellefonte, PA, USA) were set at the both ends of the columns; 2 m × 0.32 mm i.d. for injector side, and 2 m × 0.25 mm i.d. for detector side.

Table 6.1
Surveyed results in specific separation of 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD on various capillary columns.

<table>
<thead>
<tr>
<th>Capillary column</th>
<th>Polarity</th>
<th>2,3,4,7,8-PeCDF</th>
<th>1,2,3,7,8-PeCDD</th>
<th>Ref.</th>
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</thead>
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<td>SP-2331</td>
<td>High</td>
<td>++ **</td>
<td>++</td>
<td>Ryan et al., 1991</td>
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</tr>
<tr>
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<td>+ b</td>
<td>++</td>
<td>Ryan et al., 1991</td>
</tr>
<tr>
<td>DB-225</td>
<td>Middle</td>
<td>++</td>
<td>– c</td>
<td>Ryan et al., 1991</td>
</tr>
<tr>
<td>DB-210</td>
<td>Middle</td>
<td>++</td>
<td>–</td>
<td>Ryan et al., 1991</td>
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<td>++</td>
<td>+</td>
<td>Ryan et al., 1991</td>
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<tr>
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<td>Middle</td>
<td>(++ d</td>
<td>(–)</td>
<td>Current study</td>
</tr>
<tr>
<td>RH-12ms</td>
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<td>++</td>
<td>+</td>
<td>Matsumura et al., 2002</td>
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<td>++</td>
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<td>++</td>
<td>Abad et al., 1997</td>
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<td>None</td>
<td>–</td>
<td>+</td>
<td>Ryan et al., 1991</td>
</tr>
</tbody>
</table>

**++**: Baseline separated.

**+ b**: Partially separated. Distinguishable from neighboring peaks with valley but unsuitable for precise quantification.

**– c**: Co-eluted with other congeners.

( d ): Classification by the authors.

Among the various environmental media, sediment is thought to be one of the meaningful sinks of dioxins, because dioxins are transported to sediment through air deposition (Ogura et al., 2001b), rainfall (Eitzer and Hites, 1989), water inflow (Seike et al., 2007) etc. In fact, the dioxins in the sediment samples in Japan are considered to be attributed to various sources, PCP and CNP formulations (Sakurai et al., 1996, 1998; Masunaga et al., 2001b; Yao et al., 2002; Masunaga et al., 2003; Sakurai, 2003; Kobayashi et al., 2004; Kiguchi et al., 2007), combustion by-products (Masunga et al., 2001b, 2003; Yao et al., 2002; Sakurai, 2003; Ogura et al., 2005;
Ohba et al., 2009), and commercial PCB products (Sakurai et al., 2002; Yao et al., 2002; Ogura et al., 2005; Ohba et al., 2009). For this reason, sediment samples were applied to the four column combinations to search for a suitable combination for an objective simplified determination method.

Table 6.2 gives the average in the ratio of the indicative congener concentration measured with the tested column combinations to that measured by the official method (Environmental Agency of Japan, 2000a). The value for 2,3,4,7,8-PeCDF was almost 1 (range: 1.02–1.03) with the column combinations iii and iv, while it was larger with the column combinations i and ii. On the other hand, the value for 1,2,3,7,8-PeCDD was almost 1 (range: 1.00–1.13) with the column combinations i, ii and iii, while it was larger with the column combination iv. As for the other three indicative congeners (1,2,3,4,6,7,8-HpCDD, #126-PeCB and #105-PeCB), the value was almost 1 (range: 0.93–1.03) with all the column combinations. Figure 6.2 illustrates an example of GC/MS chromatograms of the five indicative congeners in a tested sediment sample measured with the column combination iii. The peaks of #105-/#126-PeCBs and 1,2,3,4,6,7,8-HpCDD were perfectly isolated. Though the peaks of 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD were observed very closely to each neighboring peak, they were separated enough for precise quantification; the degree of separation between the 2,3,4,7,8-PeCDF peak and its nearest one, and that between 1,2,3,7,8-PeCDD and its nearest one were 1.21 (range: 1.15–1.34) and 1.27 (range: 1.09–1.50), respectively. As results, the column combination iii showed a good separation capacity of the five indicative congeners from the other congeners.

<table>
<thead>
<tr>
<th>Indicative congener</th>
<th>Column combination a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>i (DB-5ms: 30 m)</td>
</tr>
<tr>
<td>2,3,4,7,8-PeCDF</td>
<td>1.28 (0.20) b</td>
</tr>
<tr>
<td>1,2,3,7,8-PeCDD</td>
<td>1.13 (0.16)</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDD</td>
<td>1.06 (0.08)</td>
</tr>
<tr>
<td>#126-PeCB</td>
<td>0.93 (0.08)</td>
</tr>
<tr>
<td>#105-PeCB</td>
<td>0.95 (0.06)</td>
</tr>
</tbody>
</table>

a DB-5ms: injector side; DB-17ms: detector side.
b Standard deviation values are given in parentheses.
Chapter 6. A simplified TEQ determination by applying indicative congener method

Figure 6.2. Example of GC/MS chromatograms of the five indicative congeners in a sediment sample measured with the column combination iii (10-meter-long DB-5ms + 20-meter-long DB-17ms).

Figure 6.3. Summarized results in the ratio of TEQ by the proposed method to TEQ by the official method for river sediment samples.
Figure 6.3 shows the result of TEQ for the all of sediment samples, measured using the proposed method with the column combination iii. The TEQ obtained with the proposed method was in good agreement with the official-method TEQ, showing that the average in the ratio of the former to the latter was 1.09 and the SD of the ratio was 0.11. It was shown that the column combination iii was suitable for the objective measuring method.

6.3.3. Application to samples obtained from various environmental media

The five indicative congeners in the ambient air, river water and soil samples were also measured with the column combination iii. As shown in Table 6.3, the average in the ratio of the indicative congener concentration in various environmental media measured with the column combination iii to that measured by the corresponding official methods (Japanese Standards Association, 1999b; Environmental Agency of Japan, 2000b; MOE, 2001a) was almost 1 for all congeners. The results of TEQ are shown in Figure 6.4. The estimated TEQ was in good agreement with the official-method TEQ for samples collected from all environmental media, and the average in the ratio of the former to the latter was 1.08 (SD: 0.08) for ambient air samples, 1.14 (SD: 0.12) for river water samples and 1.00 (SD: 0.08) for soil samples. Therefore, the proposed simplified TEQ determination method was proved to be adoptable for various environmental media in Japan. Compared with the JIS K 0312, this method largely reduced the time to only 22–35% in the measurement. Considering the column exchange and quantification, the reduction of time and efforts are more significant.

Table 6.3
Average in the ratio of the indicative congener concentration in various environmental media measured with column combination iii to that measured by the corresponding official methods.

<table>
<thead>
<tr>
<th>Indicative congener</th>
<th>Ambient air ($N = 26$)</th>
<th>River water ($N = 15$)</th>
<th>Soil ($N = 29$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3,4,7,8-PeCDF</td>
<td>0.99 (0.12) *</td>
<td>1.01 (0.18)</td>
<td>0.95 (0.07)</td>
</tr>
<tr>
<td>1,2,3,7,8-PeCDD</td>
<td>0.95 (0.14)</td>
<td>0.97 (0.17)</td>
<td>1.03 (0.10)</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDD</td>
<td>1.06 (0.05)</td>
<td>1.14 (0.09)</td>
<td>0.99 (0.07)</td>
</tr>
<tr>
<td>#126-PeCB</td>
<td>1.04 (0.07)</td>
<td>0.99 (0.07)</td>
<td>1.03 (0.07)</td>
</tr>
<tr>
<td>#105-PeCB</td>
<td>1.04 (0.04)</td>
<td>1.04 (0.04)</td>
<td>1.01 (0.06)</td>
</tr>
</tbody>
</table>

* Standard deviation values are given in parentheses.

In addition to total TEQ, the proposed method can estimate the TEQ contributions of each source (Figures 6.3 and 6.4). This aspect will be useful for tracing dioxin pollution sources. No
such simplified TEQ determination method has yet been reported to the best of our knowledge.

### 6.4. Conclusions

A simplified determination method of dioxin TEQ was established based on the concentrations of only five indicative congeners (2,3,4,7,8-PeCDF, 1,2,3,4,6,7,8-HpCDD, 1,2,3,7,8-PeCDD, and PCBs of IUPAC Nos. #126 and #105) obtained by single GC/MS measurement. The five indicative congeners were separated from the other congeners with a GC column combination of 10-meter-long DB-5ms (injector side) and 20-meter-long DB-17ms (detector side). Applying the method to various environmental samples collected from ambient air, river water, river sediment and soil showed that the estimated TEQ was in good agreement with the official-method TEQ.

![Figure 6.4. Summarized results in the ratio of TEQ by the proposed method to TEQ by the official method for ambient air, river water and soil samples.](image-url)
Chapter 7

Conclusions and perspectives

7.1. Conclusions
In this thesis, a simple method for dioxin source identification, named "indicative congener method (ICM)", was proposed, and the ICM was applied to elucidate the environmental behaviors of dioxins. Furthermore, a simplified determination method of dioxin TEQ was developed by applying the ICM. In this section, the contents of each chapter were summarized.

Chapter 1. Introduction
Dioxins, persistent chemicals with high toxicity, are widespread environmental pollutants. Japan was one of the most emitted countries of dioxins in the world, and public concern about dioxin emission from incinerators was particularly heightened in the 1990s. Due to nationwide efforts to tackle the dioxin issues, national dioxin emission has been drastically reduced. However, there still remain stock pollution problems. Some new pollution sites might be discovered in the future. In these cases, source identification will be important to select effective countermeasures. Multivariate statistical analyses by using congener profile have been utilized to identify pollution sources of dioxins. However, they have difficulties to apply, because they need a large quantity of data, complicated computation and specialized skills to interpret the results. In these circumstances, a simple and manageable method for dioxin source identification is needed. The objective of this thesis is to develop a new simple method for dioxin-source identification.

Chapter 2. Pollution sources of dioxins and techniques for source identification
Dioxins include PCDDs, PCDFs and DL-PCBs, which consist of two aromatic rings and some chlorine atoms. The toxicity of dioxin congeners depends on the number and position of chlorine atoms, and the concept of toxic equivalent (TEQ) is usually used to assess the overall tox-
Chapter 7. Conclusions and perspectives

Toxicity of the mixture of dioxins. The TEQ value expresses the toxicity of the mixture as if the mixture is pure 2,3,7,8-TeCDD, the most toxic dioxin congener. Each congener has been assigned dioxin toxic equivalency factor (TEF) based upon its relative potency compared to 2,3,7,8-TeCDD which is assigned a TEF of 1. The TEQ value is the sum of the products of each congener concentration and its corresponding TEF value.

Dioxins show characteristic congener profiles depending upon their sources. The origin of dioxins in the environment has been estimated by using multivariate statistical analyses on the basis of the profiles. The principal component analysis classifies a number of complex data sets into smaller number of groups to identify possible sources. However, this requires complicated computation and specialized skills to relate the given principal components to the possible sources. Moreover, the result is dependent on the chemicals which are selected as variables.

The chemical mass balance models perform source apportionment from only a single sample under the condition that all significant sources are identified and chemical profiles of the sources are known in advance. However, determination of representative source profiles is difficult, because there are many dioxin sources and their chemical profiles are not uniform.

The multivariate receptor models, such as the polytopic vector analysis and the positive matrix factorization, perform source apportionment without information of significant sources and their chemical profiles. However, they require quite complicated computation, a number of samples, and specialized skills to determine the number of sources and to relate the given profiles to the possible sources. Under these situations, a clear and concise method, which can be performed without complex data sets, complicated computation and specialized skills, is needed for dioxin-source identification.

Chapter 3. A novel method for dioxin source identification

The major sources of dioxins in the environment in Japan have been recognized to be combustion by-products, PCP formulations, CNP formulations, and PCB products. Data on PCDDs, PCDFs and DL-PCBs from the four sources were analyzed, and indicative congeners whose concentrations were highly correlated with WHO-2006 TEQs were identified for each source. The indicative congeners for combustion by-products, PCP formulations, and CNP formulations were 2,3,4,7,8-PeCDF, 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8-PeCDD, respectively, and those for PCB products were IUPAC Nos. #126- and #105-PeCBs. Moreover, a method for estimating
the apportionment of WHO-2006 TEQs to the four sources by using only the concentrations of
the above-mentioned five indicative congeners was developed. The method was named "indicative congener method (ICM)". The ICM was applied to the different types of environmental
samples such as ambient air, soil and river sediment samples collected in Japan to determine
the contributions of the four sources to TEQ. The obtained values of the contributions seemed
to be reasonable from the viewpoint of features in the environmental samples. Unlike the mul-
tivariate statistical analyses that require complicated computation using large amounts of data,
the ICM can be used to estimate the contributions of the four sources to TEQ by simple calcula-
tion using only one set of concentration data of the five indicative congeners.

Chapter 4.  Dioxins in rice straw smoke and their origins in Japan
The ICM was applied to examine an environmental behavior of dioxins. The paddy-field soil in
Japan is polluted by the dioxins originated from herbicides used in the past, PCP and CNP.
Therefore, there is a concern that the dioxins existing in paddy-field soil are transferred to the
atmosphere during field burning of rice straw. Smoke samples were collected from the rice
straw burning sites at post-harvest paddy fields, and the dioxins present in the samples were
analyzed. The ICM showed that the dioxins present in the rice-straw smoke were greatly in-
fluenced by those contained as impurities in PCP and CNP formulations. Further, in order to
investigate the effects of paddy-field soil on the dioxins detected in rice-straw smoke,
PCDD/PCDF/DL-PCB homologue profiles of rice straw, rice-straw smoke and paddy-field soil
were compared. The results suggested that the herbicides-originated dioxins and the atmos-
pheric dioxins contributed predominantly to the dioxins in the rice-straw smoke, while the
contribution of dioxins formed during rice-straw burning was relatively minimal. The major
sources of the dioxins found in the rice-straw smoke were attributed primarily to the pad-
dy-field soil adhered to the rice straw surface and secondarily to the air taken by the rice straw.
It is concluded that rice-straw burning at paddy fields plays as a driving force in the transfer of
dioxins from paddy-field soil to the atmosphere.

Chapter 5.  Seasonal change of dioxins in the water of Ayase River
The ICM was also applied to dioxins pollution in water environment. Ayase River is one of the
most polluted rivers by dioxins in Japan. The water samples of the river were collected once
per month for a year, and dioxins were analyzed to examine the dioxin sources and their con-
tributions to TEQ. The WHO-2006 TEQs ranged from 0.26 to 7.0 pg-TEQ L\(^{-1}\), and the average was 2.7 pg-TEQ L\(^{-1}\)—eight of twelve samples exceeded the environmental quality standard in Japan (1.0 pg-TEQ L\(^{-1}\)). The TEQ value was high during the irrigation period from May to August. The most part of the dioxins in the river water existed in SS and it seemed that the river received water with highly-dioxin-contaminated SS in the irrigation period. According to the ICM, the TEQ was mainly contributed by PCP formulation. Moreover, it was also shown that the contributions of PCP and CNP formulations to TEQ increased along with the increase of the total TEQ and the contributions were dominated by these herbicides during the irrigation period. Therefore, it was concluded that the herbicides-originated dioxins run off from the paddy fields into the river during the irrigation period and increased the dioxins level in the river water.

Chapter 6. A simplified TEQ determination by applying indicative congener method

In order to obtain TEQ by the official measurement method, the concentrations of the 29 TEF congeners in total are needed to determine by a GC/MS. The official methods for dioxin analysis require three or more times’ GC/MS measurements with several types of capillary columns, and need a long measurement time. Quantifying as many as 29 congeners also requires time and efforts. Therefore, a simplified determination method for dioxin WHO-2006 TEQ in environmental samples collected in Japan was developed based on the ICM. In the simplified measuring method, the five indicative congeners are detected by a single GC/MS measurement and TEQ is estimated by the ICM. The selected GC condition which separated the five indicative congeners from the other congeners was a combination of columns of 10-meter-long DB-5ms (injector side) and 20-meter-long DB-17ms (detector side). Applying this simplified determination method to various environmental samples (ambient air, river water, river sediment and soil) showed that the estimated TEQ was in good agreement with TEQ obtained by the corresponding official methods.

7.2. Perspectives

The ICM was developed by using the data of major dioxin sources in Japan, and therefore, it must be generally adaptable to the environmental samples collected from any parts of Japan. Because of this, the ICM can be useful for checking the quality of the analytical values. If a TEQ calculated from 29 TEF congeners is quite different from the estimated TEQ by the ICM, it can't
be denied that there are some mistakes in the quantification of TEQ from 29 TEF congeners, such as assignment error of the chromatographic peak (Ohtsuka et al., 2011).

The ICM is specially applied to the dioxins in the environmental samples of Japan which are mainly polluted by the dioxins related to combustion by-products, PCP formulations, CNP formulations and PCB products. However, the underlying concept will be applicable to the other geographic regions with different types of dioxins sources. In these cases, the estimation equations should be modified appropriately.

The ICM was applied to simplify dioxins TEQ measurement. The time required for the measurement except pretreatment was approximately 40 minutes, and corresponds to only 22–35% of the time needed by the JIS K 0312. The measurement time will be even shorter with the improvement of a column dimension, GC temperature program and so on. In this method, only five congeners are required to be monitored and, therefore, the sensitivity of the detector may be improved. Thus, the sample size is expected to be reduced. Moreover, a general-purpose detector such as a lower resolution MS, may be adoptable instead of a high-resolution one, even though a lower resolution MS detector may require careful use because the retention times of 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD are almost the same (Figure 6.2) and the monitoring ion channel of 1,2,3,7,8-PeCDD (m/z 355.8546) may be interfered by the mass channel of 355.8941 (13C12-2,3,4,7,8-PeCDF) at a lower mass resolution.

Compared with the existing techniques for dioxin source identification, the ICM is a simpler and more manageable. The author hopes that the ICM will be contributory to take measures against dioxins pollution.
Chapter 7. Conclusions and perspectives
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