IDENTIFICATION OF SOURCES OF DIOXIN-LIKE PCBS IN SEDIMENTS OF JAPAN BY A CHEMICAL MASS BALANCE APPROACH


*Research Center for Chemical Risk Management, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba 305-8569, JAPAN
**Graduate School of Environment and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, JAPAN

Introduction

Dioxin-like PCBs (IUPAC Nos. 77, 81, 105, 114, 123, 126, 156, 157, 167, 169, and 189) are referred to as dioxin-related compounds and are evaluated together with PCDDs/PCDFs in terms of toxicity. In Japan, the contribution of dioxin-like PCBs to the total TEQ of human intake is comparable to that of PCDDs/PCDFs. Understanding the contributions from different PCB sources is important for developing effective countermeasures against dioxin pollution.

The major sources of dioxin-like PCBs in Japan are considered to be those released from use or disposal of industrial PCB products and formed as byproducts during thermal processes. In this study, we estimated the contributions of these sources to the accumulation of dioxin-like PCBs in sediments using a chemical mass balance (CMB) approach and assuming that the dioxin-like PCBs in sediments mainly originated from Kanechlorls (KCs: major Japanese PCB products) and incinerator emissions.

Materials and Methods

Chemical mass balance approach

The chemical mass balance (CMB) approach has often been used to estimate the contributions of sources of target chemicals to an environment medium by comparing the compositions of chemicals in source emissions with that in the environment medium. In this study, we estimate the contributions from different sources to the accumulation of PCB congeners in a sediment. The contributions of individual sources \( j \) (5) are calculated by minimizing \( \chi^2 \), as shown by

\[
\chi^2 = \sum_{i=1}^{k} \left( \frac{1}{C_i} \left( C_i - \sum_{j=1}^{p} a_j S_j \right) \right)^2
\]

where \( C_i \) is the mass concentration of congener \( i \) in the sediment, \( a_j \) is the mass fraction of congener \( i \) for source \( j \), \( k \) is the number of congeners, and \( p \) is the number of sources (\( k>p \)). This approach is applicable under the following hypotheses.

1) Each source possesses a unique property (\( a_j \)) that is not common to other sources.
2) Selected sources and their values of \( a_j \) are adequate.
3) The values of \( a_j \) of the emission from a source hardly change in the environment.

In general, the input values of \( a_j \) have a certain extent of variability and uncertainty. Considering this, we also used the CMB approach with a Monte Carlo method by Crystal Ball Pro for Windows 4.0g (Decisioneering, Inc.).
**Source data**

KC-300, 400, 500, and 600, which are Kanechlor products, and incinerator emission were considered as the sources of dioxin-like PCBs in sediments.

The input values of $a_{ij}$ for KCs were obtained from the concentrations of PCB congeners in KCs reported by Takasuga et al. 6, Boonyathunanondh et al. 7, Kannan et al. 8, and Hirai et al. 9. Figure 1 shows the geometric means and geometric standard deviations of the concentrations of PCB congeners in KCs. The geometric standard deviations were calculated based on the within-congener variability for all congeners assuming that the variances in the different congeners are identical.

The input values of $a_{ij}$ for incinerator emissions were obtained from the concentrations of dioxin-like PCBs in emissions from 230 waste incinerators and from the concentrations of PCB-170 and 180 in emissions from 10 incinerators reported by Tokyo Metropolis 10. These incinerators include municipal solid incinerators, industrial incinerators, and small-scale incinerators. The ratios of the concentration of each congener to the total concentration of dioxin-like PCBs in emissions from various incinerators were almost the same (as shown in Fig. 2).

There are more than four orders of magnitude of differences between PCB congener concentrations in each KC, whereas there are small differences between PCB congener concentrations in emissions from waste incinerators. Thus, the mass fractions of PCB congeners ($a_{ij}$) in KCs were markedly different from those in incinerator emissions, so that it is possible to identify the relative contributions of KCs and incinerator emissions to the accumulation of PCB congeners in sediments. However, it may be difficult to identify the relative contributions of each KC since the isomer compositions are similar between KCs 6-9.

**Sediment data**

The concentrations of PCB congeners in the sediment cores in Tokyo Bay (southeast of Tokyo Metropolitan City) and Lake Shinji (in a rural area), Japan, determined in our previous studies 11, 12 and in surface sediments recently collected from 542 points distributed throughout Japan during the fiscal year 1999 reported by the Environment Agency of Japan 13 were used. Fourteen congeners (dioxin-like PCBs and PCB-170 and 180) were analyzed for the Lake Shinji core and the surface sediments, whereas twelve congeners (dioxin-like PCBs) were analyzed for the Tokyo Bay core.

The ratios of the concentration of each congener to the total concentration of dioxin-like PCBs in the surface sediments collected from 542 points were almost identical (not shown).

**Results and Discussion**

**Trends of contributions of potential sources to the accumulation of PCBs in sediments**

The trends in the contributions from potential sources to the accumulation of PCB congeners in sediments from Tokyo Bay and Lake Shinji were estimated by the CMB approach using the average values of $a_{ij}$ for each source. For Lake Shinji, KC-300 was excluded from the input sources for the CMB since the values of $S_j$ of KC-300 for Lake Shinji were negative.

The results showed that the contribution of the sum of KCs peaked around 1970 and declined thereafter, whereas the contribution of incinerator emissions increased gradually from the 1950s to 1990 (Fig. 3). These trends are consistent with the predicted contribution of emissions based on available information, such as the trend of use of KCs and the increase in the number of incinerators 14.
Contributions of potential sources to the accumulation of PCBs in surface sediments in Japan

The contributions from potential sources to the accumulation of PCB congeners in surface sediments in Japan were estimated by the CMB approach with a Monte Carlo method using geometric means and geometric standard deviations of $a_{ij}$ for each source and the average values of $C_i$ for the 542 sediments. The number of valid results (those with no negative $S_j$ values) was 7,756 in 10,000 iterations. The predicted concentrations of PCB congeners in the sediments, which are given as $\sum_{j=1}^{n} a_{ij} S_j$, were in near-agreement with the measured average concentrations ($C_i$) (Fig. 4). This result supports the assumption that most of the dioxin-like PCBs in the sediments originated from KCs and incinerator emissions.

The estimated contributions of incinerator emissions to the accumulation of PCB congeners in surface sediments are shown in Fig. 5. Results indicate that most of the PCB-126 and 169 in the sediments originated from incinerator emissions, whereas most of the PCB-105, 114, 118, 123, 156, 167, 170, and 180 originate from KCs. The contribution of incinerator emissions to the TEQ of dioxin-like PCBs in the sediments would be comparable to that of KCs.

Thus, this study demonstrates the relative contributions of KCs and incinerator emissions to the accumulation of PCB congeners in sediments. Further investigations, however, are needed to confirm the validity of the hypotheses used in this study.

References

Fig. 3. Trends in relative contributions from the sum of Kanechlor and incinerator emissions to the accumulations of PCB-126 and 169 in sediments from Tokyo Bay and Lake Shinji, estimated by a CMB approach.

Fig. 4. Comparison of the concentrations of PCB congeners in surface sediments in Japan between measured average values and the values predicted by a CMB approach with a Monte Carlo method. The median and 5th, 25th, 75th, and 95th percentiles of the predicted values in 7,756 iterations are given.

Fig. 5. Contributions from incinerator emissions to the accumulation of PCB congeners in the surface sediments in Japan, estimated by a CMB approach with a Monte Carlo method. The median and 5th, 25th, 75th, and 95th percentiles of the predicted values in 7,756 iterations are given.