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

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Introduction

Dioxin-like PCBs (IUPAC No. 77, 81, 105, 114, 118, 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 [1]. In Japan, the contribution of dioxin-like PCBs to the total TEQ of human intake is comparable to that of PCDDs/PCDFs [2]. Understanding the contributions of 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 [3, 4]. In this study, we estimated the contributions of these sources to the accumulation of dioxin-like PCBs in sediments by a chemical mass balance (CMB) approach, assuming that most of the dioxin-like PCBs in sediments originate from Kanechlors (KCs: major Japanese PCB products) and incinerator emission.

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 [5]. In this study, we estimate the contributions of different sources to the accumulation of PCB congeners in a sediment. The contributions of individual sources j (S_j) are calculated by minimizing χ^2, as shown by

$$\chi^2 = \sum_{i=1}^{k}\left(\frac{1}{C_i}\left(C_i - \sum_{j=1}^{p} a_{ij} S_j\right)\right)^2$$

where C_i is the mass concentration of congener i in the sediment, a_{ij} 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_{ij}) that is not common to other sources.
2) Selected sources and their values of a_{ij} are adequate.
3) The values of a_{ij} of the emission from a source hardly change in the environment.

In general, the input values of a_{ij} 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 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 all over 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 of the contributions of 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 show 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 of potential sources to the accumulation of PCB congeners in surface sediments in Japan are 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 [13]. 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 $\sum_{j=1}^{p} a_{ij} S_j$, were almost in accordance with the measured average concentrations (C_i) (Fig. 4). This result supports the assumption that most of the dioxin-like PCBs in the sediments originate 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 originate 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 TEQ of dioxin-like PCBs in the sediments is 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

1. Van den Berg et al. (1998) Environmental Health Perspectives 106, 775-792.
2. Ministry of Health and Welfare of Japan (1999) Total diet study 1998.
3. Sakai, S., Hirakawa, K., Takatsuki, H. and Kawakami, I. (2001) Environ. Sci. Technol. 35, 3601-3607.
4. Masunaga, S. (2000) in: Proc. of the 3rd International Workshop on Risk Evaluation and Management of Chemicals, Yokohama, 80-93.
5. Henry, R.C., Lewis, C.W., Hopke, P.K. and Williamson, H.J. (1984) Atmos. Environ. 18, 1507-1515.
6. Takasuga, T., Inoue, T. and Ohi, E. (1995) J. Environ. Chem. 5, 647-675.
7. Boonyathunanondh, R., Watanebe, S., Laovakul, W. and Tabucanon, M. (1995) Fresenius J. Anal. Chem. 352, 261-267.
8. Kannan, N., Tanabe, S. and Tatsukawa, R. (1988) Bull. Environ. Contam. Toxicol. 41, 267-276.
9. Hirai, Y., Masunaga, S. and Nakanishi, J. (unpublished data) PCB concentrations in Kanechlors.
10. Tokyo Metropolis (2001) Results of the investigation of dioxins from waste incinerators 2000.
11. Yao, Y., Takada, H., Masunaga, S. and Nakanishi, J. (2000) Organohalogen Compounds 46, 491-494.
12. Masunaga, S., Yao, Y., Ogura, I., Nakai, S., Kanai, Y., Yamamuro, M. and Nakanishi, J. (2001) Environ. Sci. Technol. 35, 1967-1973.
13. Environment Agency of Japan (2000) Results of the investigation of dioxins in public water 1999.
14. Masunaga, S. (1999) in: Proc. of the 2nd International Workshop on Risk Evaluation and Management of Chemicals 1999, Yokohama, 1-10.

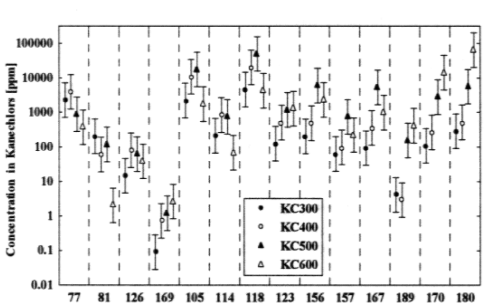

Fig. 1. Concentrations of PCB congeners in Kanechlors, KC-300, 400, 500, and 600, based on the previous reports [6-9]. Plots represent geometric means and error bars represent geometric standard deviations, which were obtained from the within-congener variability for all congeners assuming that the variances in the different congeners are identical.

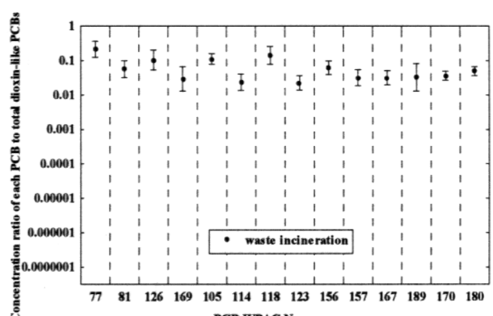

Fig. 2. Ratios of the concentration of each congener to total concentration of dioxin-like PCBs in emissions from 230 waste incinerators [10]. Plots and error bars represent geometric means and geometric standard deviations, respectively.

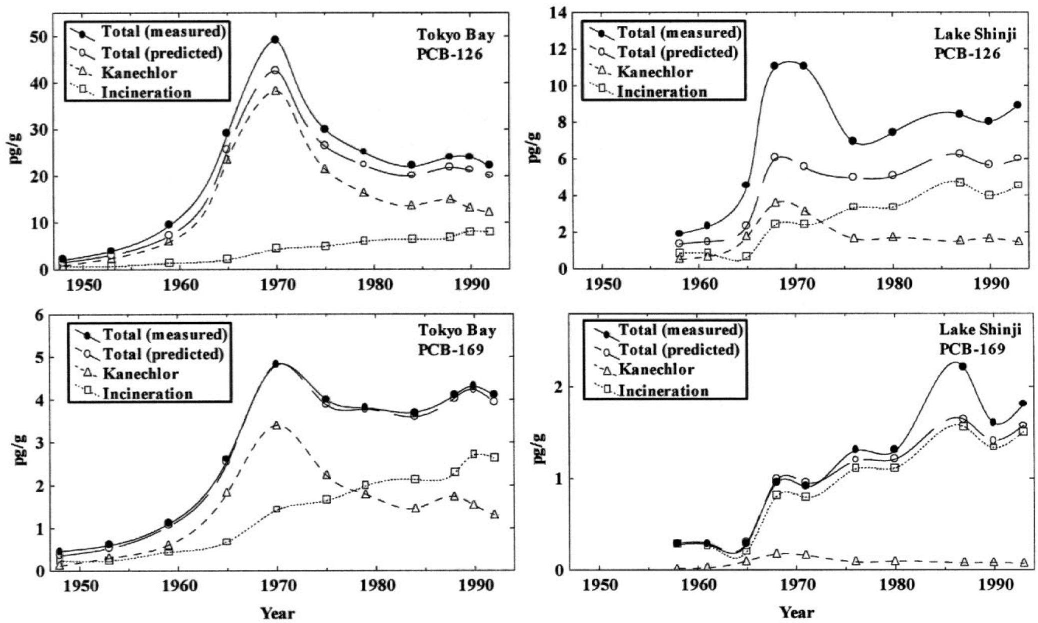

Fig. 3. Trends of relative contributions of the sum of Kanechlors and incinerator emissions to the accumulations of PCB-126 and 169 in sediments from Tokyo Bay [11] and Lake Shinji [12] estimated by a CMB approach.

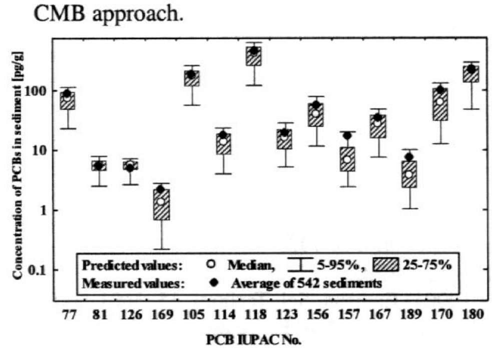

Fig. 4. Comparison of the concentrations of PCB congeners in surface sediments in Japan between measured average values [13] and the values predicted by a CMB approach with a Monte Carlo method. The median and 5th, 25th, 75th, and 95th percentiles of the predicted values in 7,756 iterations are given.

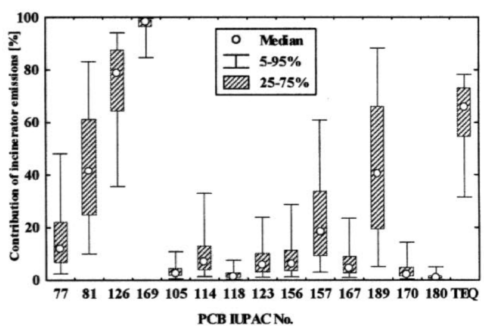

Fig. 5. Contributions of incinerator emissions to the accumulation of PCB congeners in the surface sediments in Japan [13] estimated by a CMB approach with a Monte Carlo method. The median and 5th, 25th, 75th, and 95th percentiles of the predicted values in 7,756 iterations are given.