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ESTIMATION OF POLYCHLORINATED BIPHENYL SOURCES IN SEDIMENT USING A BAYESIAN SEMI-FACTOR MODEL WITH CONSIDERATION OF UNIDENTIFIED SOURCES

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Introduction

It is known that polychlorinated biphenyls (PCBs) in the environment in Japan are mostly derived from PCB products, including Kanechlor (KC), and that these pollutants are released unintentionally through combustion. However, PCBs unintentionally included in chemical products such as pigments, have recently attracted attention. There have been many reports of considerable concentrations of PCBs detected in the environment, and it is considered that environmental pollution by PCBs derived from sources other than PCB products is spreading. In this context, this study discussed a method for the quantitative estimation of the sources of PCBs in the environment using a Bayesian semi-factor model (CMBK2), which is one of the chemical balance models, and applied it to samples of sediment from Muroran Port in Hokkaido, Japan.

Materials and methods

<Sediment sample>

For details of the survey spots, pretreatment, and measurement results, please refer to the previous report[1]. The authors surveyed 17 spots inside the port and 4 outside (Fig. 1). To sample the sediment, 10 cm of the surface layer was sampled using an Ekman–Birge bottom sampler in June 2008. The samples were air-dried and ground with a porcelain mortar. A small amount (several grams) of this sediment was taken, a surrogate was added, and extraction was performed using a high-speed solvent extraction device (Dionex ASE300) using toluene. The extracted liquid was treated several times with concentrated sulfuric acid and then it underwent a multi-layered silica gel process (Hexane elution, and excluding silver nitrate silica gel), a silver nitrate silica gel process (5% DCM/Hx elution), and HPLC. Subsequently, the liquid was concentrated, a syringe spike added, and then it was measured by high-resolution GC/MS (JEOL MS-700D).

<CMBK2>

The observation equation in CMBK2 is expressed by the following equation. For details, please see the previous reports[2].

$$q_i = \sum_{j=1}^{n} p_{ij} t_j + w_i \left(1 - \sum_{j=1}^{n} t_j \right) + u_i$$

Since unknown variables are estimated with a posterior distribution, the significance of estimation results was evaluated with posterior mean ±2.0 posterior standard deviation (2σ prediction interval). If zero is not included in the 2σ prediction interval, it is considered that the possibility of becoming zero is sufficiently low. Accordingly, let us describe it like “it is not zero significantly.”

Results and discussion

<Principal component analysis>

The explanatory variables used for the analysis with CMBK2 were optimized using principal component analysis (PCA). As PCB sources, the authors assumed four types of PCB product: KC300, KC400, KC500, and KC600; combustion; and two types of pigment: azo and phthalocyanine. The characteristics of the congeners derived from each PCB source were studied with reference to previous reports[3,4,5]. In this study, variables were selected and processed based on the points listed below. PCA was conducted for several model cases and the analysis results discussed.

(1) Major congeners derived from KC were selected so that their amounts were constant among homologues.

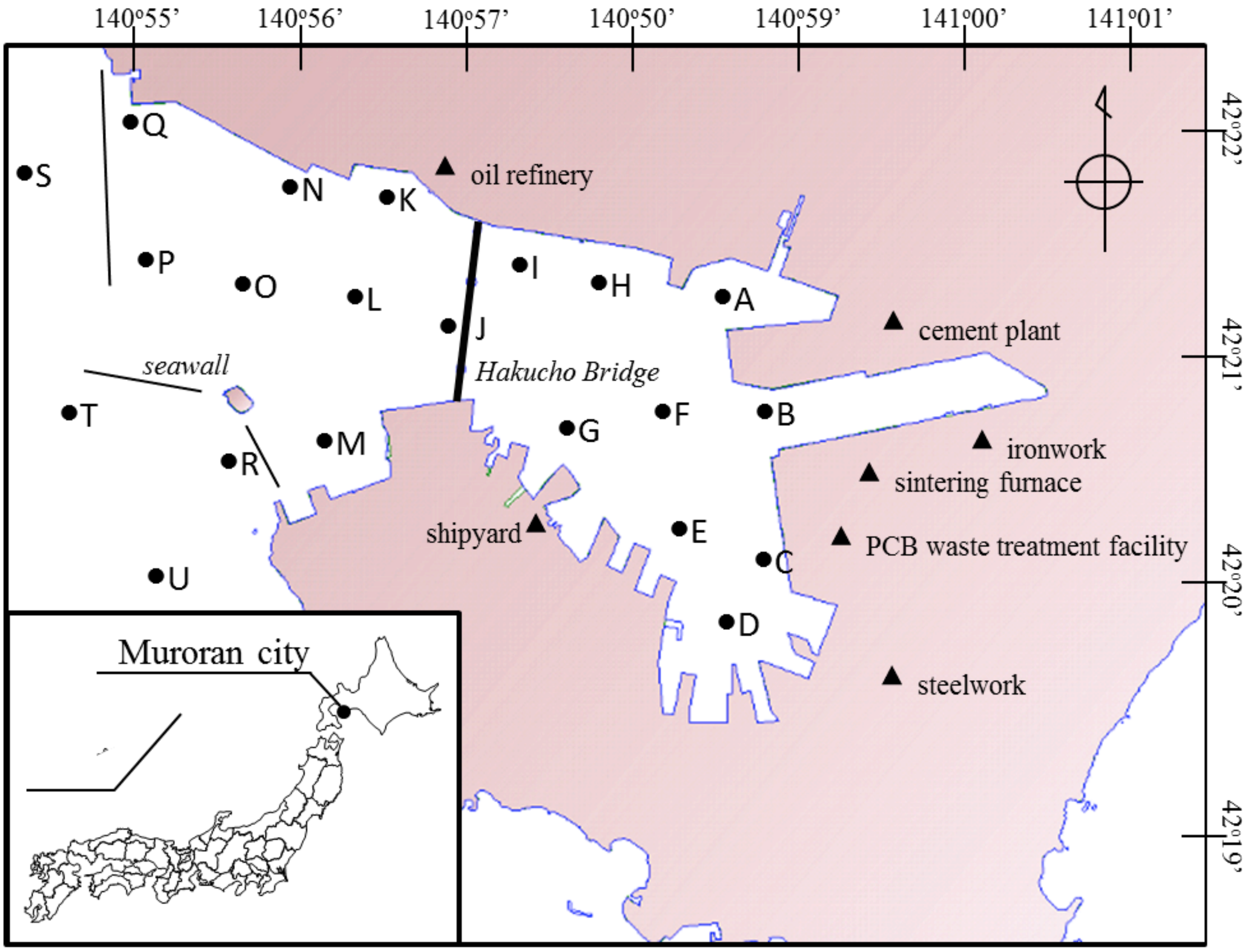

Fig.1 Station locations of surface sediments from Muroran Port.

(2) As for congeners derived from combustion, those congeners rarely included in KC and pigments, and detected specifically in the combustion source, were selected.
(3) The congeners derived from pigments were selected as much as possible.
(4) The homologues and congeners of MoCBs, whose analysis precision was low, were excluded from the analysis.
(5) The number of congeners selected from their respective homologues was made constant as much as possible.
(6) The concentration ratio of each homologue was included in the explanatory variables.
(7) Undetected congeners were set to 0.

In the case where PCA was conducted with the 56 types of explanatory variable, shown in Table 1, the factor loadings of pollution sources that converged for each category could be separated sufficiently, and the variables whose factor loadings were large were included homogeneously within the factors whose eigenvalues were large. In this case, the cumulative contribution rate of the first principal component (PC1) to PC5 is over 90%, the eigenvalue of each PC exceeds 1, and all data can be described by PC1–PC5. Figure 2 shows the PC score diagram for PC1–5. As for PC1, KC300, 400, 500, and 600 are plotted in the order from positive to negative values, and so it was considered as the PC that describes the number of chlorine substituents of PCBs, especially the difference in KC. As for the factor loadings of PC2, the explanatory variables derived from KC of tri- to

Table 1 Components used for calculation

PCB-5/8, 11, 15, 16, 17, 18, 20/33, 22, 28, 31, 32, 35, 44, 49, 52, 56, 64, 66, 70, 74, 77, 87/115, 93/95/98, 97, 99, 101, 105, 110, 118, 126, 132, 136, 138, 139/149, 141, 151, 153, 163/164, 169, 170, 174, 179, 180, 182, 183, 189, 208, 209, DiCBs, TrCBs, TeCBs, PeCBs, HxCBs, HpCBs, OcCBs, NoCBs

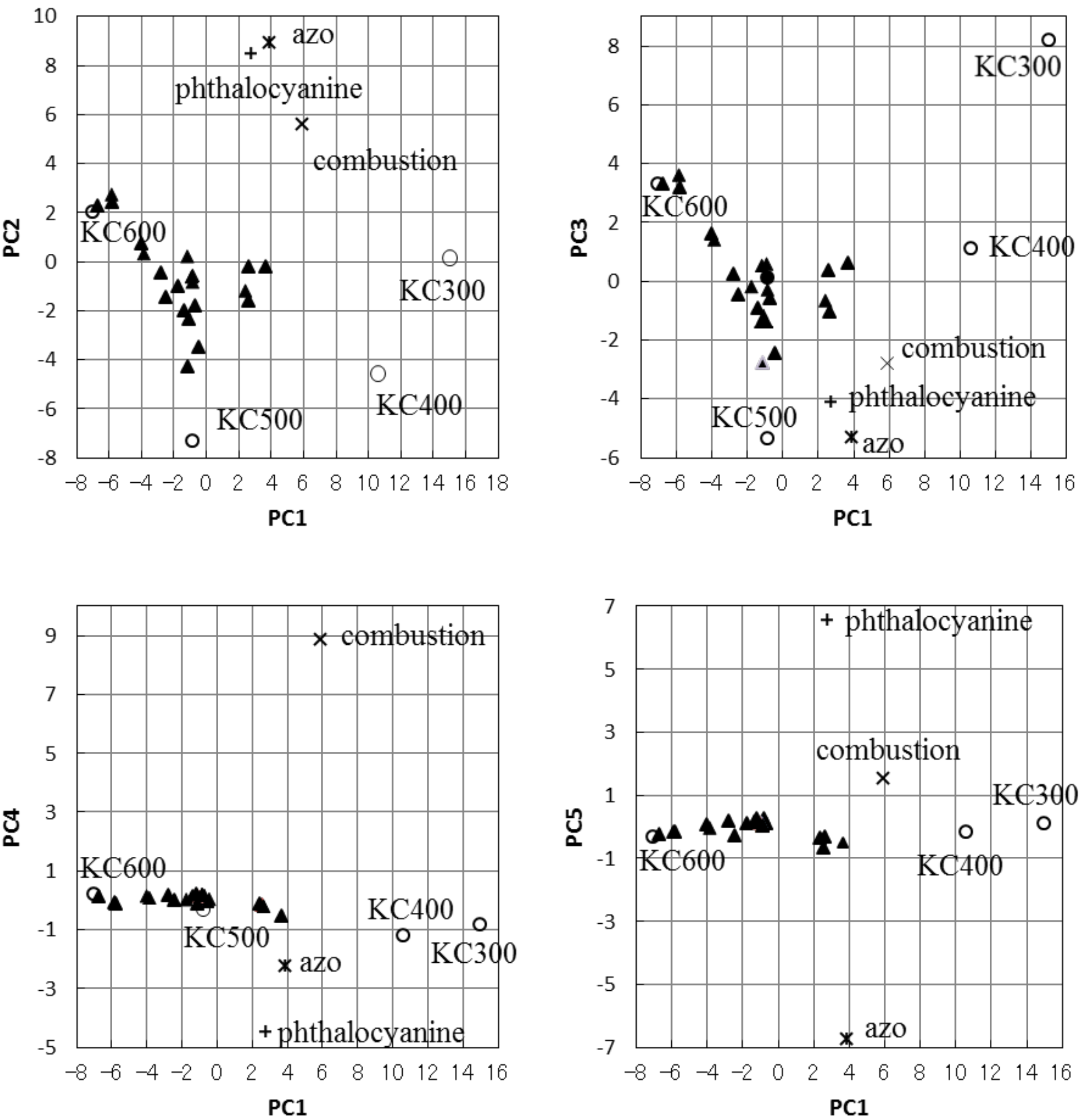

Fig. 2 Principal component score plots in the analysis of 56 kinds of explanatory variables: PC1 vs PC2, 3, 4, 5

hexa-chlorinated substances are negative, while the explanatory variables of the tri- to hexa-chlorinated components not derived from KC, such as PCB-35, 77, 126, and 169, and mono-, di-, and hepta- and more highly chlorinated substances are positive. In the PC score diagram, KC and the other pollution sources are plotted in mutually opposite directions. Therefore, it was considered that PC2 is the PC that describes whether a pollutant is derived from KC. For the factor loadings of PC3, the KC components of tri-chlorinated substances, such as PCB-16 and 28 are positive, while the KC components of penta-chlorinated substances, such as PCB-87 and 110 are negative. Therefore, this was considered as the PC that describes the difference in the number of chlorine substituents between KC300 and KC500. As for the factor loadings of PC4, the explanatory variables derived from combustion, such as PCB-15, 116, 169, and 189 are positive and they were considered as the PCs that describe the contribution of combustion. As for the factor loadings of PC5, the components derived from azo pigments, such as PCB-11, 35, and 77 are negative, while the components derived from phthalocyanine pigments, such as PCB-209 and 208 are positive. Therefore, they were considered as the PCs that describe the contribution from pigments.

<Estimation based on CMBK2>

The level of contribution from each pollution source was estimated by applying CMBK2 to the sediment samples from Muroran Port, with the 56 explanatory variables shown in Table 1. Figure 3 shows the contribution rate of each PCB source at each sampling spot. At every station, all the pollution sources that registered above a certain level of contribution (>2.8%) were not zero significantly. The contribution of unidentified pollution sources was <1% at every spot. However, it cannot be said that it was not zero significantly, i.e., the influence of unidentified pollution sources was insignificant. Therefore, the sources of PCBs in the sediment could be described satisfactorily by the assumed seven source types. Inside the port (St. A–Q), it was found that the contributions of KC500 and KC600 were significant and that these two accounted for over 76% (except St. P). In particular, at St. A, L, and O, KC600 accounted for over 94%. In addition, KC400 accounted for 0.3–16%; KC300, azo pigments, and combustion accounted for several percent, and the contribution rate of phthalocyanine pigments was nearly zero. At St. P and sites outside the port (St. R–U), it was found that the contributions of KC500 and KC600 were significant, as inside the port, although KC300 and the azo pigments accounted for several tens of percent (except St. U), whereas they hardly contributed to the pollution inside the port. KC500 and KC600 can be considered derived from ship-bottom paints, while a certain level of influence of azo pigments other than PCB products can be detected. This indicates that the PCB sources other than KC cannot be ignored.

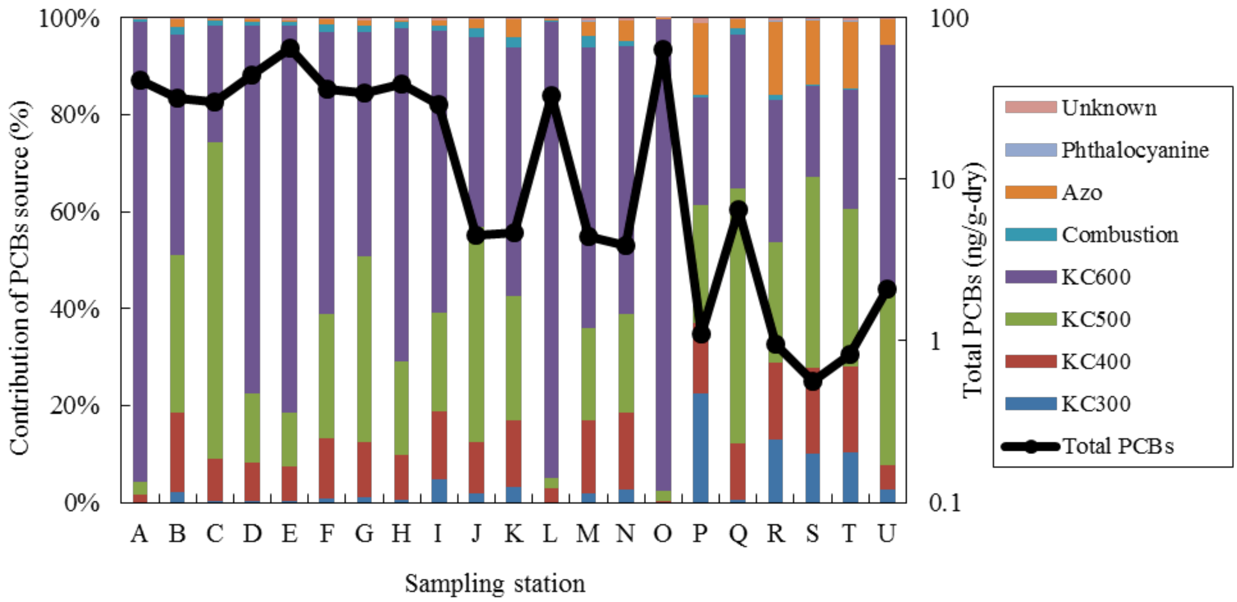

Fig. 3 Results for PCBs sources in the Muroran Port sediments determined by CMBK2 analysis.

Acknowledgements:

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