The levels of Dioxins and PCBs in ambient air and the attempt of predicting the concentration by numerical simulation technique

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Abstract

Estimating the risk of hazardous substances, it is important to comprehend the process of exposure to human or ecosystem , how those substances are emitted to environment and transferred through multimedia environment.

For this purpose, we primarily developed the sampling method by Low-volume air sampler which was verified compared with the method of Hi-volume air sampler used all the while. This method is very valid for the long term monitoring and useful for evaluating the concentration level in the local area.

Using this method, the declining trend of Dioxins and PCBs in ambient air was confirmed.

Next we conduct a comprehensive investigation on passive air samplers which exceed in mobility and the cost of maintaining system. Furthermore we have attempted to predict the concentration of Dioxin using numeric simulation technique.

Introduction

Commonly the concentration of dioxins in the atmospheric environment had generally been measured through the use of a high volume air sampler (Hi-vol.) by continuous collection of 1,000 m^3 of the sample over a 24-hour period. However, sampling for only 1 day may be affected by the weather conditions and so on . Hence, sampling with a low volume air sampler (Low-vol.) was studied as a practical collection method for measuring long-term, average concentrations. The results of average concentrations, etc. of dioxins using Low-vol. are reported in comparison with the measurement results using Hi-vol. PCB concentration level in ambient air using Low-vol. was investigated. Regarding the sampling location and period, monitoring was carried out in urban, industrial, rural area and collected continuously for about one month. PCB concentration declines year by year especially in industrial area . As for seasonal variation, the concentration is higher in summer than in winter because of volatility characteristics. We also attempted to monitor the ambient air by passive air sampler (henceforth, PAS) and Low-vol over the same period. PAS is often used for chemical accumulators that can be used to assess ambient concentrations. In some case, PAS may be the only option. Because active sampling using conventional Hi-vol. requires pumps and a source of electricity and it is very costly, not always feasible. That's why we consider this PAS option.

In the result, PCBs homologue distribution corresponds to each other reflecting the characteristics of the region. In order to use PAS quantitatively to assess ambient air concentration, it is necessary to know the sampling rate etc. This is the challenge facing our laboratory now. So further study is needed to presume the concentration level.

Another approach to grasp the behavior of persistent organic compounds in multimedia environment to estimate the risk, is the computer simulation technique.

The most representative multimedia model used for this object is fugacity model Ⅲ developed by Mackay,D.[1] This model is one box model which can predict the chemical residue resulting from dispensation, reagency, ,degradation etc in each media (air, soil, water, sediment) and suitable for estimating long-term, average concentration.

we applied oneboxtype-multimedia model to the Hyogo prefecture area and are able to recreate the present state. What model should be selected depends on what the target is, i.e. local area distribution or distribution of each media.

Materials and Method

Method for Long-term Monitoring of Dioxins in the Atmospheric Environment

The Low-vol. can mount quartz micro fiber (QMF, 150mm in diameter) and three polyurethane foam (PUF, 85mm in diameter×50mm). Samples of environmental air were collected continuously using this equipment over two period, from August 1 to 15 and from August 15 to September 1, with each sample consisting of approx. 500m^3 in volume and a flow rate of approx. 23 L/min. For the Hi-vol., samples were collected continuously using quartz micro fiber(QMF, 203mm×254mm) and two polyurethane foam (PUF, 85mm×50mm) for the same period as the Low-vol. case, with the sample amount being approx. 1,000m^3 and the flow rate approx. 700L/min. The samples were pretreated, concentrated to 100 uL and subjected to the analyses of polychlorinated dibenzo-para-dioxins(PCDDs), plychlorinated benzofuran(PCDFs) and coplanar PCB(Co-PCB) via a high resolution gas chromatography device(HP 5890)/ a high resolution mass spectrometer(JEOL Ltd.JMS-700)

Long term monitoring for PCB in ambient air using Low-vol.

Monitoring was carried out from 2000 to 2008 in Hyogo prefecture, and conducted at three points at Nishiwaki (rural area), Takasago (industrial are), Kobe (urban area). Analysis method is as already reported.[2]

Monitoring the ambient air by PAS

Low-vol. and PAS are deployed at the same point over the same period. PAS is consist of one polyurethane foam (PUF) covered with two stainless steel bowls to eliminate the wind effect or prevent from the rain.

Isotopically-labeled compounds that do not exist in air, i.e., surrogate, are added to the sampling medium (PUF) prior to exposure. Based on their loss (which will vary according the influence of meteorological parameters etc.), a more accurate, quantitative air concentration can be determined. Isotopically -labeled compounds of

IUPAC No.#3,#15,#31,#52,#118, #153,#180,#194,#206,#209 (these are obtained from Wellington Laboratory Inc.,Canada) are used as surrogate.

Oneboxtype-Multimedia model simulation

The structure of Multimedia model is shown in Fig.1-1.

This model is composed of seven environmental media boxes, i.e., Atmoshpere (gas,particle),water (liquid, particle), biota, soil, sediment.

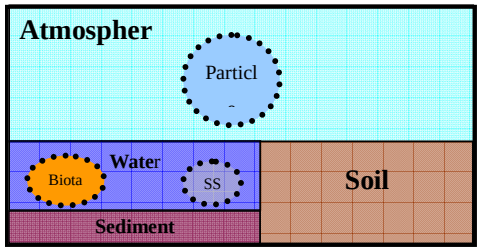

Fig.1-1 Structure of Multimedia

Fig.1-2 illustrates the circulation of dioxin considered in this model..

It is assumed that pesticide containing Dioxin as impurity is discharged to soil, and hazardous substances containing Dioxin from incinerator is discharged to air and water.

Parameters used this model, transfer constant, equilibrium constant , degradation consant is mainly subjected by estimation.

Simulation condition is as follows.

［Simulation period］ 1960-2010 year

［target compound］ Dioxin (toxic isomer of PCDDs,PCDFs)

［target area］ Hyogo prefectural (except Kobe city)

［programming language］ Compaq Visual Fortran ver.6.5

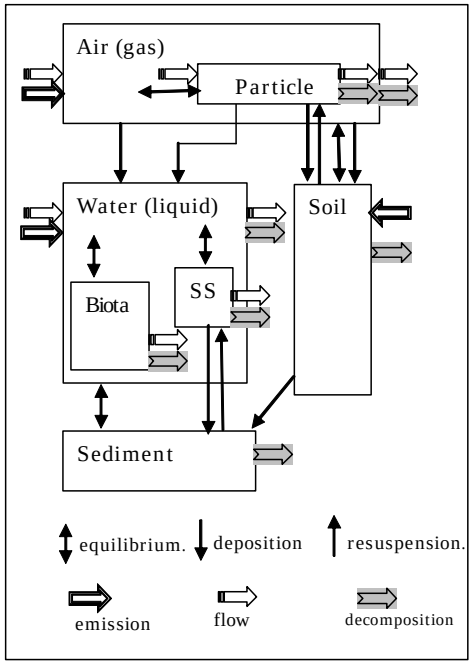

Fig.1-2 Circulation of dioxins in environment

Basis Equation is as follows.

$$\frac{dMi}{dt} = \sum_{j=1}^{MN} f_{eq}ij + f_{emi}i + f_{fl}i + f_{\deg}i + \sum_{j=1}^{MN} f_{dprs}ij$$

i,j : identification character of media

MN : total number of media

M_i :amount of Dioxin in media i (mol)

f_{eq} : mass transfer flux resulted from equilibrium (mol/s)

f_{emit} : emission flux (mol/s) f_{fl} : advection flux (mol/s)

f_{deg} :degradation flux (mol/s) f_{dprs} :deposition, export, resuspension flux (mol/s)

Results and discussions

Comparison of the two monitoring method (Hi-vol. vs. Low-vol.)

Fig.2 shows daily variations of dioxin concentrations (before toxicity equivalentce conversion) concentrations measured by the Hi-vol. and Low-vol. During the measurement, there were almost no changes in weather conditions: no rain and temperatures of about 30℃. Differences between the maximum and minimum values were 36 times in actual concentrations and 39 times in TEQ concentrations (after toxicity equivalence

conversion) for dioxin. On the other hand, as for Co-PCB , it was 5 times in actual and 35 times in TEQ.

The measurement results are shown in Table 1 (The values for the Hi-vol. method represent average values during the measurement.) Despite the almost unchanging weather conditions, the results showed variances in the measurements using the Hi-vol. method. However, the average values for the actual and TEQ concentrations were almost the same for the Hi-vol. and Low-vol. method.

Fig.3 illustrates the homologue distribution of the total values of the actual concentrations for PCDDs and PCDFs (the total values of the concentrations of PCDDs and PCDFs before toxicity equivalence conversion) measured by Hi-vol. and Low-vol. The values by Hi-vol. method represent the average values by homologue distribution during the part of the measurement (from August 1 to 15). Overall they show almost the same homologue distribution.

	Dioxin(pg/m^3)		Co-PCB(pg/m^3)	
	Hi-vol.	Low-vol.	Hi-vol.	Low-vol.
8/1～15	7.4	6.9	10	11
8/15～9/1	9.5	10	10	14

Table.1 Concentration of Dioxin and Co-PCB(Hi-vol. vs. Low-vol)

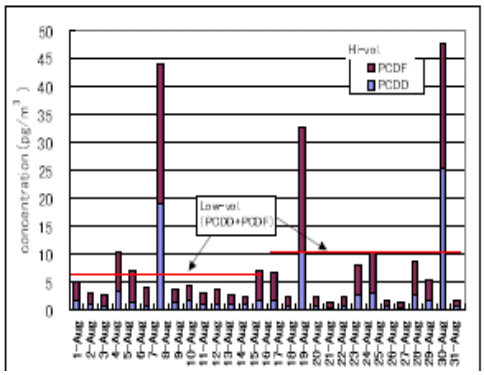

Fig.2 Daily variations of Dioxin

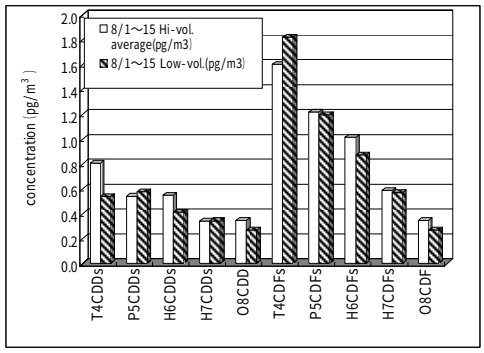

Fig.3 Homologue distribution of the total values measured by the Hi-vol. and Low-vol.

The trend of PCB concentration level in ambient air by the Low-vol.

In Japan, trend of PCB use is at the peak in 1970 and the total use of those from 1954 to 1972 is about 58,000t. PCB have been detected about 100ng/m^3 in early 1970's, but recently level off at about 1ng/m^3.

Fig.4 shows the trend of PCB concentration at Takasago (industrial area) from 2000 to 2008. At industrial area, concentration declines year by year, about 0.9ng/m^3 in 2001 to 0.2ng/m^3 in 2008.

At another two places, concentration fluctuate approximately around 0.2ng/m^3 and after 2004 generally continue to be flat.

As for seasonal variation, concentration of PCB is higher in summer than in winter due to volatile characteristics. This phenomenon is shown prominently at Takasago (industrial area).

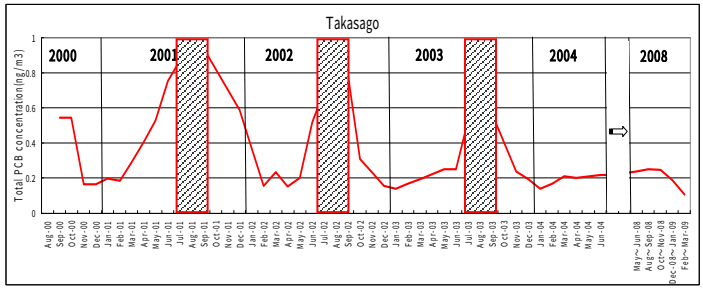

Fig.4 The trend of PCB concentration (from 2000 to 2008) Shaded regions represent summer season.

Attempt of monitoring by PAS

Adsorbed amount to PAS (ng) and concentration measured by Low-vol. (ng/m^3) are shown in Fig.5. The relationship between the two correlate roughly. But further research is needed to estimate effective sample volume concerning each isomer. So we are now studying this theme based on Passive sampler theory by M.E.Bartkow.[3]

It is said that PCB homologue distribution reflects product use.

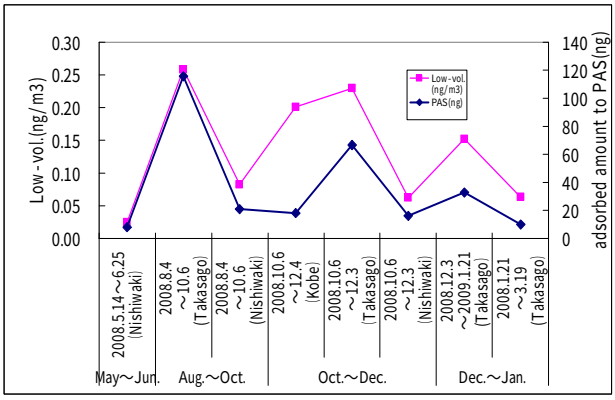

Fig.5 Adsorbed amount to PAS and Concentration by Low-vol.

Fig.6 shows homologue distribution measured by Low-vol. and PAS. Homologue distribution characterizes the sampling site, and is in good agreement with each other, i.e., Low-vol. and PAS method.

Data for isomer distributions of various generation sources is needed to be accumulated in order to estimate the origin from the homologue distributions and isomer distributions observed.

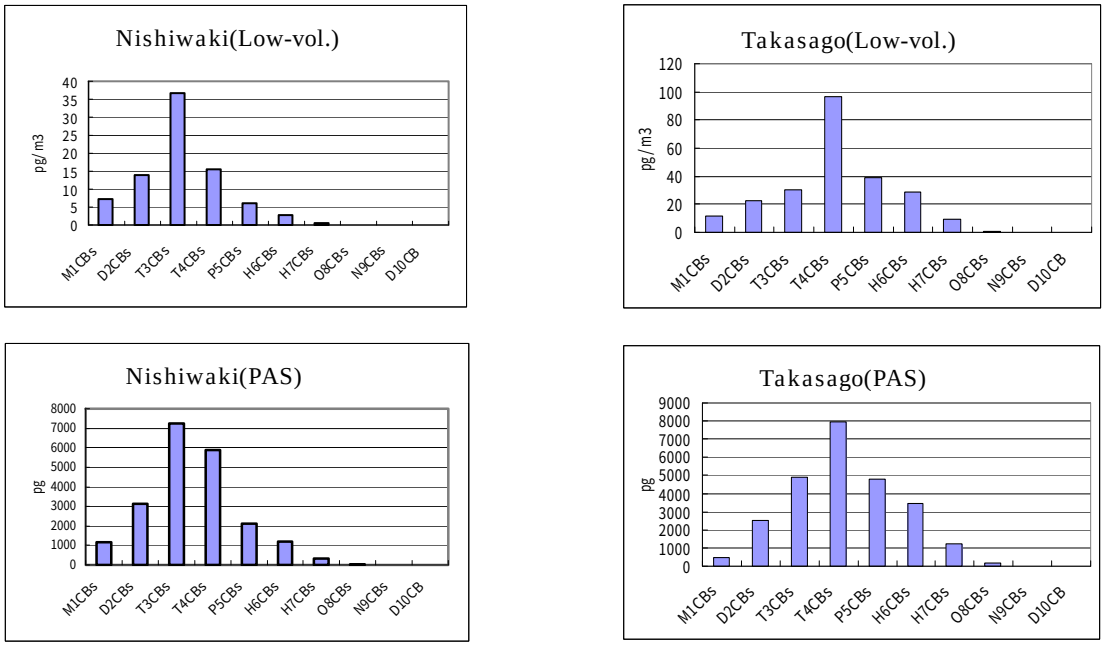

Fig.6 Homologue Pattern comparison (Low-vol. vs. PAS)

Numerical simulation result by oneboxtpye-multimedia model

Calculated value and observed value of Dioxin (classified by the chlorine number of 17 toxic isomer) in each media in 2000 are shown in Fig.7. Concerning air and water, there is a similarity between calculated and

observed value. But concerning soil and sediment, the peak homologue varies from chlorine number to another.

In soil and sediment, it is difficult to simulate by onebox-model not being complete mixing in real environment.

Using this model, prediction of environmental fate was perfomed.

This result shows that the concentration of air and water change in almost the same proportion in accordance with the emission of dioxin.

It's for this reason that Dioxin is not so persistent in these media. The concentration in soil is soaring in 1960's due to use of pesticides from 1960's to 1980's.

Compared to another environmental media, sediment is declining slowly after declining of another media's.

This phenomenon recreates the accumulation of Dioxin to the sediment as reported in other papers.

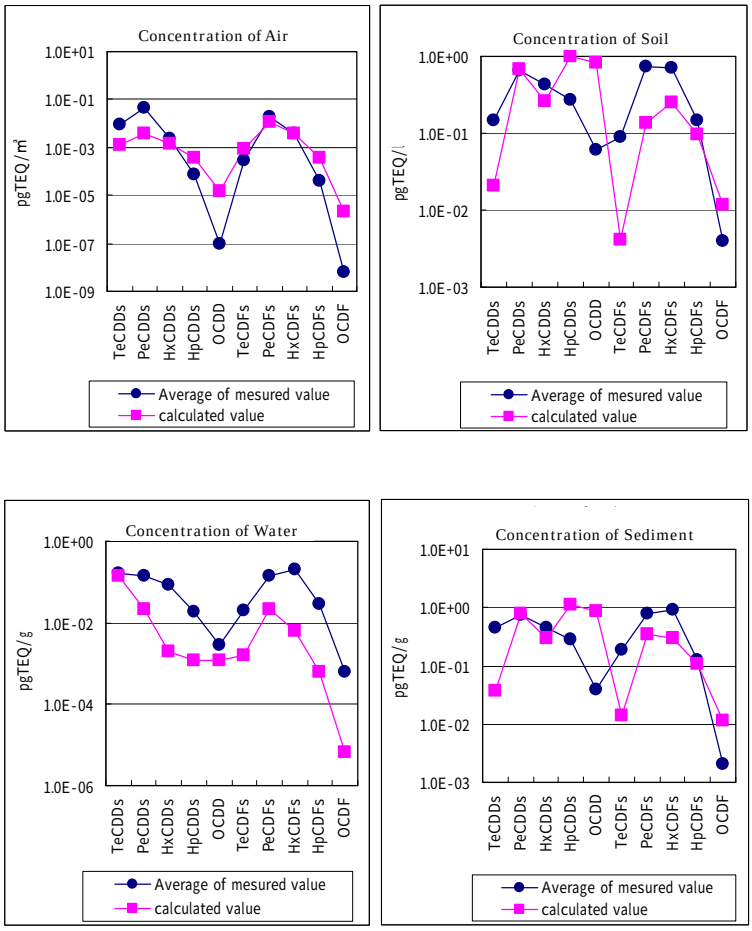

Fig.7 Comparison of calculated with observed value

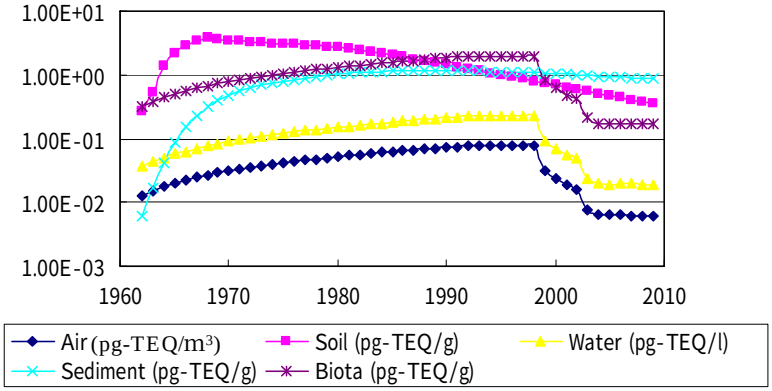

Fig.8 Concentration of Dioxins in fate simulation

Reference

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2 C.Matsumura, M.Tsurukawa, T.Nakano,2002, Elution orders of all 209PCBs congers on capillary column "HT8-PCB", Journal of Environmental Chemistry,12,855-865

3 Batkow,M.E.,Booij,K., Kennedy,K.E.,Muller, J.F.,Hawker,D.W.,2005, Passive air sampling theory for semivolatile organic compounds. Chemosphere 60, 170-176