

QUANTIFICATION OF PCB CONCENTRATIONS IN INDOOR AIR BY A STATIC AIR SAMPLER USING YARNS AS TRAPPING MATERIALS

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Abstract

We investigated a method for calculating polychlorinated biphenyl (PCB) concentrations in indoor air from the amounts trapped in static air samplers (SASs) by yarns as trapping materials in order to establish a practical and simple monitoring method. To determine the coefficients required for the calculations, indoor air sampling by yarn SASs and low-volume air samplers was conducted in laboratories over 2 months. The uptake coefficient was determined by dividing the rate of increase in the concentrations of the compounds in the yarn SAS by those atmospheric concentrations measured by a low-volume air sampler. The elimination coefficient was calculated as the ratio of the concentration in the SAS to the atmospheric concentration under equilibrium conditions over 2 weeks. An advantage of this method is that if environmental conditions (air temperature, humidity, wind speed, etc.) do not vary greatly then the atmospheric concentration can be calculated by using a single equation at any place and any time, even when adsorption by the yarn SAS has not reached equilibrium. The calculated atmospheric concentrations of PCBs were within the range of two to three times the concentrations measured by active air samplers (AASs) at 23 to 28 °C.

Introduction

Concentrations of persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) and other organohalogen compounds in the air are usually very low and always changing. Therefore, elaborate monitoring is needed for us to evaluate these air pollutants more accurately. However, it is difficult to provide adequate numbers of active air samplers, which are widely used to measure atmospheric concentrations, because they are usually expensive and large amounts of labor are needed for their transportation and setup. They also require power sources and, in some cases, large areas of space for installation.

In recent years, various types of passive air samplers (PASs) have been developed and demonstrated for the monitoring of pollutants in the atmosphere. Since PASs usually do not need power supplies, are fairly cheap, and do not require large amounts of labor, they can be installed anywhere and can be used for large number of simultaneous monitorings. If atmospheric concentrations could be calculated more rapidly and precisely by PASs, then it would be very beneficial to substitute them for active air samplers (AASs). Many assumptions, however, are needed to estimate atmospheric concentrations by PASs, because the mechanisms of adsorption to PASs are not fully understood¹.

We have been investigating a simple and low-cost method of monitoring of air pollutants that will help to popularize PAS monitoring. The use of yarn in air samplers was one of our ideas in building this concept, because yarn is inexpensive and easy to obtain and handle. In this study, we investigated a simple method of using naked commercial yarns to sample PCBs, which are major contaminants all over the world, in indoor air. When outdoor air is monitored with a PAS, a housing is essential to protect the sampler from rain, solar radiation, and adhesion of particulate substances. A housing is also needed to maintain constant airflow, which has a considerable effect on the sampling rate of substances. However, we regarded the use of a housing as contrary to our aim to develop a supremely simple and low-cost air sampler. Therefore, we called the yarn sampler, which has no housing, a "static air sampler (SAS)", as distinct from other passive samplers. In this study, we measured PCBs in indoor air with yarn SASs and AASs over 2 months and determined the coefficients needed for calculation of the air concentrations. We then compared the estimated concentrations with measured ones.

Materials and Methods

We used a commercial mixed yarn of 60% acrylic fiber and 40% knitting wool. Bunches of yarn 10 cm long were prepared by cutting the yarn into lengths of about 20 cm, tying 30 pieces of yarns into a bunch at the center (Photo 1), and adjusting the weight of the bunch to 4 g. The prepared bunches were subjected to Soxhlet extraction with toluene and then to solvent removal in a vacuum desiccator equipped with an activated carbon filter at the air inlet to avoid contamination.

Sampling was conducted indoors, where the effects of solar irradiation and changes in air temperature, humidity, and wind velocity were minimal, because we needed to reduce the number of parameters that could vary the results. The samplers were hung where they were not exposed to the sun and did not touch the walls or other object. Sampling was performed in two laboratories (A and B) at the National Institute for Environmental Studies. The experiment was performed between 9 July and 19 September 2006. The temperature of the rooms ranged from 23 to 28 °C during the experiments, and wind speed at the sampling points was below 0.1 m s⁻¹ in all laboratories during all experiments.

Sampling was performed by hanging the samplers about 2 m from the floor and about 15 cm apart from each other. Sampling periods were 1 h, 3 h, 6 h, 12 h, 1 day, 3 days, 1 week, 2 weeks, 1 month, and 2 months. At the end of each time, two bunches were collected and then made up as one sample. Active sampling was performed by sucking in ambient air with a low-volume ASS and collecting the contaminants in plugs filled with Amberlite XAD-2 resin; collection was done after 0 days, 1 week, 2 weeks, 1 month, and 2 months from the start of sampling by the yarn SASs. The samplings were conducted as close to each other as possible while minimizing the effects of exhaust air. The XAD-2 plugs were newly replaced each day during the experimental period, and then each plug was analyzed individually. Yarn air samplers were also replaced by new ones each day at the same time as the XAD-2 plugs were changed, and then each yarn was individually analyzed.

After sampling, the yarns were recovered, wrapped in aluminum foil, and sealed in polyethylene bags until extraction of the congeners. An internal standard for clean-up spike and syringe spike (Wellington Laboratories Inc.) was prepared by diluting. The clean-up spike (500 pg) was added to the sample, and Soxhlet extraction was conducted for 8 h with toluene. The extract was concentrated and cleaned up by column chromatography with 5 g of 44 % sulfuric acid – silica gel; the extract was then concentrated and mixed with the syringe spike.

Measurements were conducted by using a high-resolution gas chromatography – high-resolution mass spectrometry system (Agilent 6890 GC and JMS-700, JEOL Ltd., Tokyo, Japan) with splitless injection. The column used was an HT8-PCB (60 m length, 0.25 mm diameter, SGE Analytical Science, Australia).

Results and Discussion

1. Reproducibility of results from yarn air samplers

Five bunches of yarn samplers were hung simultaneously in the same place in laboratory B for 7 days. During the 7-day sampling, the average amounts detected were 1400 pg of TrCB#28; 1600 pg of TeCB#52 / #69; 3300 pg of TeCB#70; 1200 pg of PeCB#110 / #120; and 550 pg of HxCB#153. The ratios of these amounts to the blank values were 230:1, 280:1, 830:1, 340:1, and 280:1, respectively. These results show that the yarn samplers could adsorb sufficient amounts of PCBs. Although the relative standard deviations (RSDs) were large for trace levels of congeners, those of most congeners were less than 20%. Thus, the reproducibility of the results by yarn sampling was acceptable for their use in simple monitoring.

2. Calculation of amounts in the yarns

The theoretical amounts of PCBs in the yarn SASs were calculated by substituting the uptake coefficient (ku') and the elimination coefficient (ke) and the measured concentrations.

$$N_{PAS} = (ku' / ke) C_{Air} (1 - \exp(-ke t)) \quad (1)$$

The uptake coefficient (ku') of PCB congeners in the yarn SASs was calculated by dividing the rate of increase in the concentration of each PCB congener in the yarns per unit time by the average air concentration measured by active sampling in the same period. For calculation of the elimination coefficient (ke), the atmospheric concentrations of PCBs and the concentrations in the yarn sampler had to be in equilibrium. We measured the ratios of the atmospheric concentrations as measured by the low-volume AAS to those in the yarns (C_{Air} / N_{PAS}) over 2 weeks and more of deployment in both laboratories, and their average values. The elimination coefficient was calculated by using the average C_{Air} / N_{PAS} value for each congener and the uptake coefficient.

We compared the theoretical values with the measured amounts in the yarn samplers (Fig. 1). The theoretical values and the measured values stayed within 200% of each other, although they did not completely correspond.



Photo 1 A passive sampler made of yarn

The solid curves in Fig.1 are the ideal uptake curves, calculated by substituting the means of the atmospheric concentrations measured by low-volume air samplers into Equation (1). The times taken to equilibrium can be determined from the ideal uptake curves; they were about 50 h for DiCB#5 / #8 and about 400 h for HpCB#180. The time taken to equilibrium was shorter in the less chlorinated congeners.

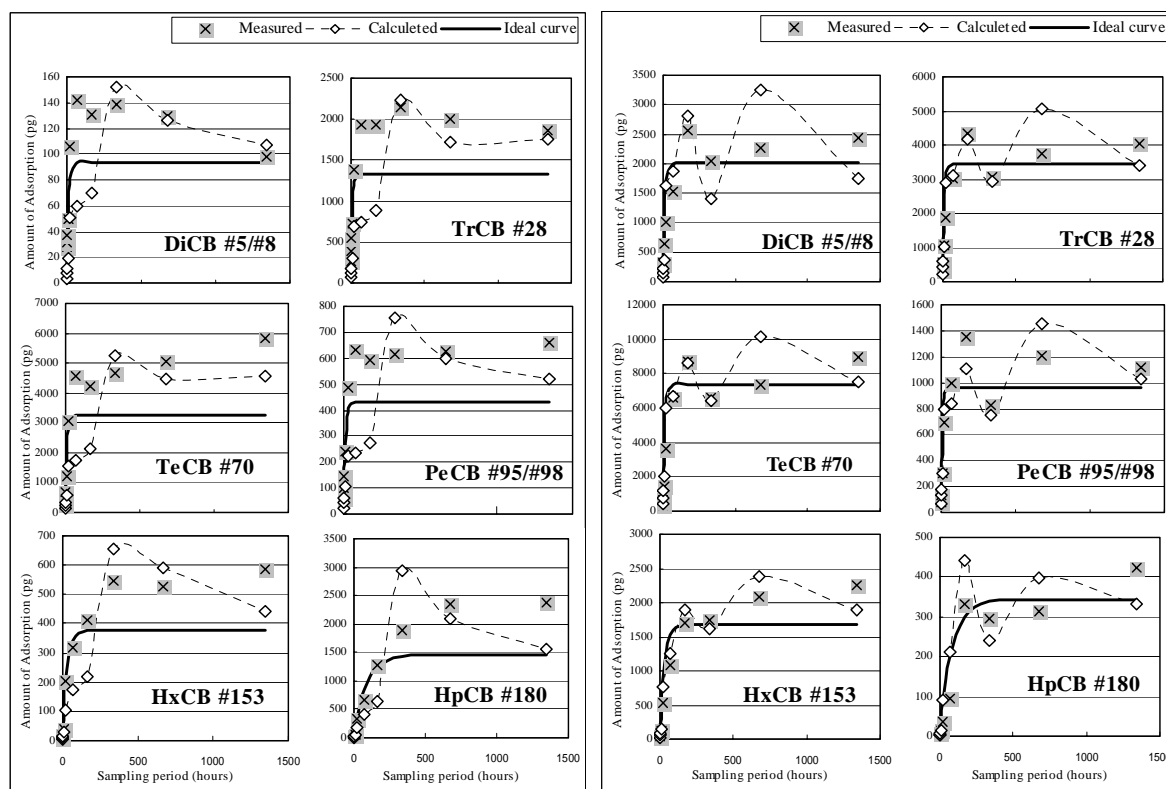


Fig. 1 Changes with time of measured and estimated adsorption of major PCB congeners by yarn PASs in laboratories A and B

3. Estimation of atmospheric concentrations by using yarn SASs

The equation described above can be transformed into an equation for calculating air concentration (C_{Air}) from adsorption by the yarn sampler (N_{PAS}).

$$C_{Air} = (ke / ku') N_{PAS} / (1 - \exp(-ke t)) \quad (2)$$

The PCB concentrations in the indoor air in Laboratories A and B were calculated by substituting the coefficients of uptake and elimination and the PCB concentrations in the yarns, as per Equation (2). We determined the estimated and measured concentrations of PCB congeners 6 h, 2 weeks, and 2 months after the deployment of the yarns (Fig. 2). The estimated concentrations agreed very well with the values measured by active sampling. There were, however, some differences between the estimated and measured values, but only after 6 h in Laboratory A. The differences between their values are probably attributable to instability and measurement errors of both the active and static sampling, because 6 h of sampling might be too short to collect adequate amounts of PCBs for accurate analysis. In other words, at 6 h the effects of small changes in ambient conditions such as temperature and wind speed, and/or fundamental problems such as spatial concentration differences between the locations of the active and static samplers, became obvious and were not averaged. However, the estimation of atmospheric concentrations over 2 weeks almost completely coincided with the measurements in both laboratories.

These results show that this method of estimating PCB concentrations in the air from the amounts in the yarn SASs has advantages. One of them is that once the coefficients of uptake and elimination for the yarn samplers have been determined, the concentrations in air can be calculated by using a single equation [Equation (2)] at any place in any time if the environmental conditions such as air temperature, humidity and wind speed do not

vary greatly; in these experiments, a temperature change of about 5 °C did not markedly affect the results. PCB concentrations in air can be estimated regardless of the stage of the mechanism of substance exchange (adsorption process) between a PAS and the ambient air; it is not necessary for the concentrations of PCBs in the yarns to reach equilibrium. Furthermore, yarn SASs have an advantage over other passive air samplers in that the concentrations of PCBs in SASs usually reach equilibrium within 1 or 2 months— faster than in other passive samplers²; as mentioned above, determination of the elimination coefficients requires the concentrations in the yarns to be equilibrium.

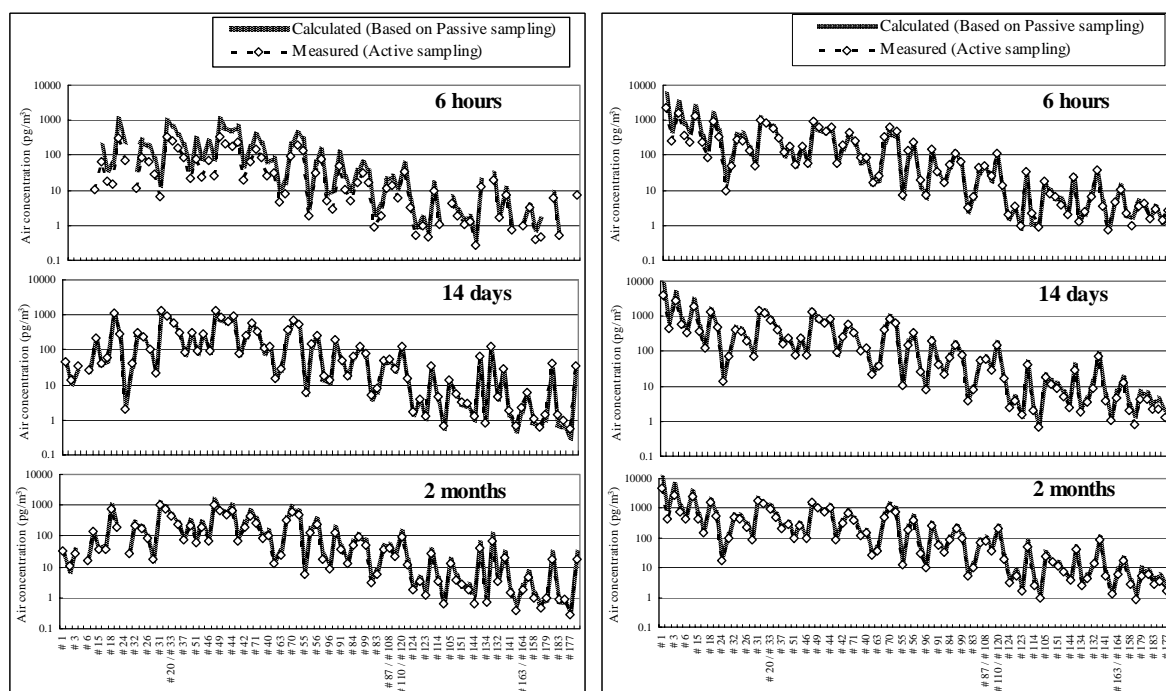


Fig. 2 Comparison of measured PCB concentrations in indoor air with the corresponding values estimated from yarn samplers at each time period in Laboratories A and B

Conclusions

We proposed a method of calculating PCB concentrations in the air from the concentrations in yarn SASs. We investigated the feasibility of this method by comparison with the concentrations measured by low-volume air sampler. Furthermore, we are investigating the use of the yarn SAS under different environmental conditions and comparing it with passive air samplers that use other materials such as PUF and XAD resin; we are also testing its uptake of other POPs and brominated flame retardants. Although the PCBs in the yarn SASs were not isolated into gas and particle-adsorption phases, we achieved this isolation by calculations using Equation (2), which is based on Fick's law of diffusion. We may, however, need more discussions on the mechanism by which yarn SASs trap pollutants if we are to apply this method to a variety of environments.

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References

1. Harner T, Bartkow M, Holoubek I, Klanova J, Wania F, Gioia R, Moeckel C, Sweetman A.J, Jones, K.C. *Environ. Sci. Technol.* 2006; 144: 361.
2. Hashimoto S, Hattori Y, Takasuga T, Ito Y. *Chemosphere* (submitting).