Calibration and Field survey of Passive Air Samplers for Persistent Organic Pollutants

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Abstract

Commonly, the high volume air sampler or low volume air sampler is the most widely used for sampling POPs in ambient air. These methods need pump which requires costly sampling equipment and a source of electricity, so it is not feasible for conducting sampling everywhere. Therefore more feasible approach that was employed here was to use passive air samplers (PAS). PAS consists of polyurethane foam (PUF) covered with a stainless steel chamber to investigate gas-phase concentration of polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs). PAS and low-volume air sampler were deployed for about two months simultaneously from July to August 2009 and from December 2009 to January 2010 in Kobe. Data obtained using passive air sampler (PAS) was compared to active low volume air sampling data in order to estimate the sampling rate, verify the effectiveness from the point of view of isomer patterns.

Introduction

Passive air sampler (PAS) is very superior for monitoring long-term trends, which can enable the cost-effective collection of monthly or seasonally integrated air samples. PAS are chemical accumulators that rely on air currents to deliver chemical to the adsorbent materials. POPs diffuse into the sampling media during exposure and integrate the air concentrations over the sampling period. The PUF-based PAS is probably the most widely used because they are easy to prepare, extract and handle, and inexpensive. In this study, the uptake of POPs by PUF-based PAS we developed was characterized which allows air concentrations to be determined and all isomers of PCBs were analyzed. Here target compounds are PCB, HCH, HCB, chlordane, nonachlor, mirex. PCB had been widely used until 1972 in Japan as mainly electric appliances, heat exchange fluids, carbonless paper, capacitors of the fluorescent lights and the amount of PCBs produced during 1954 and 1971 is 58000 tons in Japan. PCBs consist of 209 differently chlorinated congeners. PCBs product produced by Kaneka Chemical, KC-300, KC-400, KC-500,KC-600 were of different congeneric proportions and purposes. Principal isomers differ among PCB products. For this reason, we have been tried to analyze all isomers of PCBs using HRGC/HRMS. The final target of this study is to investigate air concentrations and patterns of PCBs by PAS. Hexachlorocychlohexane (HCH) is a manufactured chemical that exists in eight chemical forms called isomers. Technical HCH is pesticide consisting if a mixture of five stable isomers which have been shown to have serious short- and long-term health effects; the isomers are • : 60-70%, • : 10-12%, • : 6-10%,• : 3-4% and • : 3-4%. HCB is a fungicide formerly used as a seed treatment,especially on wheat to control the fungal•• disease bunt. It is also a by-product of the manufacture of industrial chemicals including

carbon tetrachloride, perchlorethylene, trichloroethylene and pentachlorobenzene. It is also a known impurity in several pesticide formulations, as well as can be present in those processes that generates dioxins and furans. Technical chlordane was the mixture of more than 140 compounds, and was mainly used for termite control in Japan from 1950. In 1968 it was banned for agriculture, however used for termite control, until the Chemical Substances Control Law restricted it in 1986. This mixture is complex including 40% of octachlorinated isomers, 20% of nonachlorinated isomers, 4.8% of heptachlorinated isomers, and 7.3% of hexachlorinated isomers.

Materials and Method

Passive Air Sampler (PAS) and Active Air Sampler (AAS)

PAS consist of an accumulating/adsorbing medium that has a high retention capacity for the target analytes. We followed the theory of uptake of POPs by PUF disks described in the paper.[1] A PUF disk is supported on a metal rod in a central position between the upper and lower bowls which is made of two stainless steel to buffer the air flow to the disk and to shield it from precipitation and light. There were two objects to the investigation. Objective 1 was to calibrate the samplers against the conventional AAS, to derive the information on field based uptake rate by collecting samplers after different exposure times. Eight PAS were deployed simultaneously to derive the uptake rate from July to August 2009. These samplers were collected in series one-by-one every week. Weekly low volume air samplers were also taken at the same site. Polyurethane foams (PUF ; 9cm diameter ; 5cm thick ; surface area 268cm^2 ; mass5.5g ; volume 318cm^3 ; density 0.017g/cm^3) were pre-cleaned by acetone solvent using soxlet extraction. The low volume air sampler mounts quartz micro fiber (QMF, 150mm in diameter) and three same polyurethane foams with sample amount being approximately 1000m^3 and the flow rate 100L/min. Objective 2 was to compare the results derived from the different shape of PUF, thick and thin type. Thick type is the noted above PUF. Thin type PUF is 9cm diameter ; 1cm thick ; surface area 155cm^2 ; mass 1.5g ; volume 64cm^3 ; density 0.024g/cm^3 . These PAS were deployed simultaneously for 8 weeks from December 2009 to January 2010. The samples were analyzed by high resolution gas chromatography device(HP 6890)/ a high resolution mass spectrometer(JEOL Ltd.JMS-800D).

Results and discussions

Uptake rate study

Theoretically, an uptake profile for POPs to PUF can be divided into 3 sections; a linear uptake phase, a curvilinear uptake phase and equilibrium partitioning. During the linear state, sampling (or uptake) rates (m^3/day) can be calculated from the concentration of analytes in the PUF (pg), normalized to the exposure time (day), divided by the average concentration of analytes in the air over the sampling

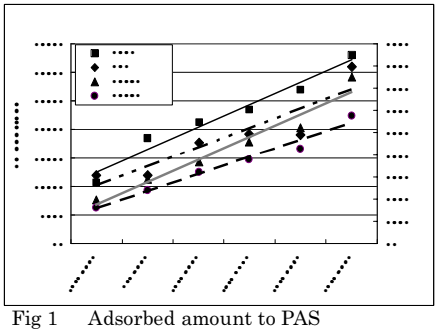

Fig 1 Adsorbed amount to PAS

••(#28: primary axis, #3,#118,#153: secondary axis)

period (pg/m^3) obtained by the low volume air sampler. The accumulated PCB amount generally increased linearly in the PAS over time during the sampling period as examples.(Fig.1) The adsorbed amount to PAS of other isomers also increases up to two months in this experiment. In this study period, target compounds don't reach equilibrium, suggesting that PAS have a capacity to continue linear uptake beyond 2 months tested here. So this time period is considered to be in the linear stage and sampling rate (SR) can be calculated according to the aforementioned theory. SR for each PCBs homologue (mono to octa), total PCB and POPs are shown in Table1.

Table 1 SR (sampling rate) for PCBs and selected POPs

During the first to sixth week of our study, the sampling rate was higher than in following weeks.
This phenomenon is reported in other study.[2] According to this article, SR was 2-3 times higher than in following weeks. No target compounds were detected from blank samples, nevertheless, our all results also show the similar phenomenon. (Fig 2) As pointed out by this article, there is a possibility that there is a two phase uptake mechanism, with a rapid sorption to the surface followed by a slower diffusion into the interior of the PUF disk. Concerning this mechanism, more detailed study which clarify the initial exposure period are needed.
SR were found to be increased with increasing chlorination in general.
SR of dominant isomer was shown in Table 2.

PCB Homologue and isomer pattern comparison

PAS and AAS samples are collected at urban area simultaneously for 8 weeks in summer. Di to tetra is dominant and Homologue pattern has a similarity. This result indicates PAS is a practical method at the point of view of not only sampling rate but also Homologue profile. Same patterns were seen at other monitoring point by PAS. KC-300 was widely used in carbonless paper, KC-400 and 500 in electric appliances and these Homologue pattern reflect the usage of PCB products. In the same way, abundant PCB congeners were shown in Fig 3.
PCB-#18,#31,#28,#52/#69,#43/#49,#70 were dominant isomers of these by both PAS and AAS.

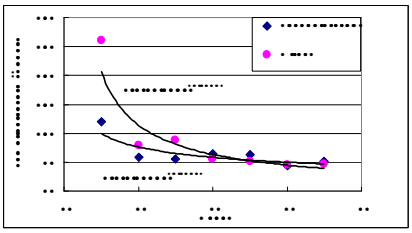

Fig 2 temporal change of SR

Table 2 SR of selected PCB congener (average of 6 to 8 weeks)

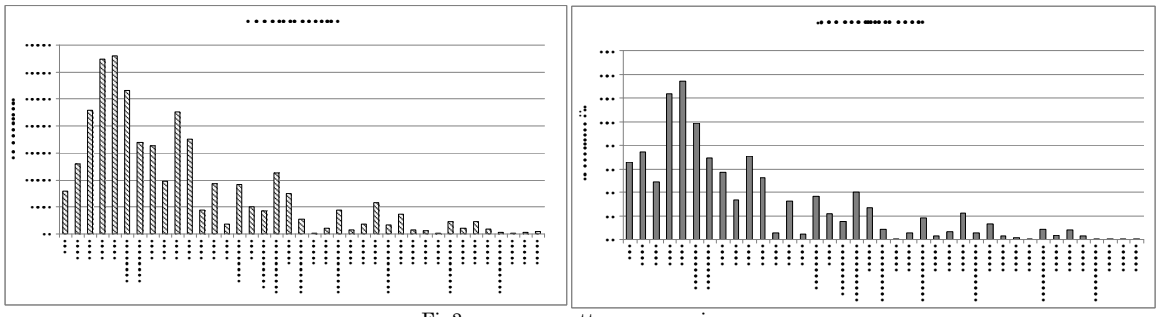

Fig3 congener pattern comparison

PUF shape comparison study

Thick and thin type PUF were compared by deploying simultaneously at urban site in winter. Thick type had more adsorption capacity (in aspect of adsorbed amount) than thin type in proportion to surface area. And when normalized to surface area, SR was the almost same value. And that is for example SR for #118 is 5.7m^3/day , 3.8 m^3/day and normalized values are 0.021 m^3/day/cm^2, 0.024 m^3/day/cm^2 respectively. This result shows that thick type PUF has more ability to detect low-level concentrations than thin type.

Location study

In a separate study PAS were deployed for about 2 months at 2 points (urban, rural area). Sequestered concentrations and the aforementioned sampling rates were used to calculate atmospheric concentrations. Table 3 shows the concentration level of POPs in urban and rural area seasonally. The results seem to show a good agreement with the concentration level of the other survey by ASS. The ratio α/γ-HCH with concentrations of each isomer are useful source indicators. Also this ratio is an indicator of the current use of technical HCH. In this study α/γ ratio was 1.5• • 3.6. This is the reason that these results reflect the usage in Japan where the most part of HCH is • •isomer (on the contrary Linden,• •isomer ratio of HCH is over 99% , had been used in China.) Much more data by PAS should be accumulated seasonally at many points to illustrate a phenomenon of these.

Table 3 Concentration level by PAS at urban and rural site (pg/m^3)

Acknowledgement

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Reference

1 Karla Pozo,Seasonally Resolved Concentrations of Persistent Organic Pollutants in the Global Atmosphere from the First Year of the GAPS Study,Environ.Sci.Technol.2009,43,796-803 2 Chakra Chaemfa, Field calibration of polyurethane foam (PUF) disk passive air samplers for PCBs and OC pesticides, Environmental pollution 156,2008,1290-1297