Simultaneous Monitoring Method of Polycyclic Aromatic Hydrocarbons and Persistent Organic Pollutants in the Atmosphere Using Activated Carbon Fiber Filter Paper

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In order to simultaneously monitor the concentrations of PAHs and POPs in the atmosphere, an activated carbon fiber filter paper (ACFP) was used as the adsorbing material in this study. The pressurized liquid extraction method (PLE method) was used to extract PAHs and POPs collected on the ACFP. Toluene was an effective solvent to extract them from ACFP using the PLE method, but some of PAHs, such as benzo(*a*)pyrene, benzo(*g,h,i*)perylene, dibenzo(*a,h*)anthracene and indeno(1,2,3-*cd*)pyrene, were hardly extracted. These PAHs were adsorbed on the particulate matter in the atmosphere. In general, these forms of particulate matter could be collected using a quartz fiber paper (QFP); these PAHs were efficiently extracted from the QFP using the PLE method with toluene. In this study, the collecting method of the PAHs was modified by using QFP overlapped in front of the ACFP. Atmospheric monitoring of PAHs and POPs in Niigata area was performed using this method, and most of the target compounds were detected. However, some of the POPs, such as aldrin, endrin, mirex, could not be detected. The POPs, such as hexachlorobenzene, α -hexachlorocyclohexane and chlordanes, and most of the PAHs were detected from all of the samples collected throughout the monitoring period. It was confirmed that these methods were effective to simultaneously monitor the concentrations of the PAHs and POPs in the atmosphere.

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Polycyclic aromatic hydrocarbons (PAHs) have not ever been intentionally manufactured or synthesized, as well as dioxins; however, they exist in fossil fuels, such as petroleum and coal. They are organic pollutants produced unintentionally by the combustion of organic compounds, like fossil fuels and waste. Especially, PAHs are formed during incomplete combustion; some PAHs, such as benzo(*a*)pyrene, have high carcinogenicity and mutagenicity for humans and animals. They are contained as a gaseous form and an adsorbed form on suspended particulate matter in the atmosphere; some of them are decomposed immediately upon the irradiation of sunlight. However, by shutting out sunlight they are fairly stable and exist for a long time.¹

PAHs diffuse and move over a wide area with the atmospheric stream and suspended particulate matter. PAHs that fall directly on the ground or are dissolved in rainwater and accumulated in the soil, are subsequently incorporated into the bodies of humans and the animals through their respiration near the ground level.¹⁻³

On the other hand, chemical substances called persistent organic pollutants (POPs), such as PCB and DDT, are easily concentrated in the living body because of their hydrophobicity and fat-solubility.⁴ Also, they can be transported on the earth on a global scale *via* the atmosphere and oceans, and are harmful to human health and the environmental ecosystems.⁵⁻⁹

Since the "Stockholm Treaty Concerning Persistent Organic

Pollutants (the POPs Treaty)" was adopted in May, 2001, every country has taken countermeasures. To verify the effectivity of these measures and actions, the concentrations of POPs in the environment have been mainly monitored in Europe and USA. The monitoring of PAHs has also been carried out in these countries.

During these monitorings, simultaneous sampling and analyzing of PAHs and POPs has been scarcely performed. Generally, quartz fiber filter paper (QFP) or grass fiber filter paper (GFP) has been used as an adsorbing material to collect target compounds of the PAHs and the POPs contained in the atmosphere.^{10,11} In order to collect a gaseous sample, adsorbing cartridges of styrene-divinyl forms have been used;^{12,13} further, polyurethane forms or activated carbon felts have been used as a back-up filter of QFP or GFP.^{6,14-17}

Although it is very important to determine and to evaluate the atmospheric concentrations of the target compounds in the area, it is difficult to exactly determine the concentration of the target compounds in the case of short-term monitoring, like for 24 h, because their atmospheric concentrations vary with an influence of the climate. Therefore, to exactly understand the variational behavior of the target compounds during short-term monitoring, like for one day, it is necessary to collect samples within as short a time interval as possible. For long-term monitoring, like for several months, a sampling method using simple equipment, such as a passive sampler, seems to be useful to continuously collect the target compounds.^{18,19}

The authors have proposed a method using of activated carbon

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Table 1 List of target compounds

PAHs		POPs		Internal standard
Native	Surrogate	Native	Surrogate	
Acenaphthene	$^{-13}\text{C}_6$	Aldrin		9-Bromoanthracene
Acenaphthylene	$^{-13}\text{C}_6$	<i>cis</i> -Chlordane		
Antracene	$^{-13}\text{C}_6$	<i>trans</i> -Chlordane	$^{-13}\text{C}_{10}$	
Benz(<i>a</i>)anthracene	$^{-13}\text{C}_6$	<i>p,p'</i> -DDD		
Benzo(<i>a</i>)pyrene	$^{-13}\text{C}_4$	<i>p,p'</i> -DDE	$^{-13}\text{C}_{14}$	
Benzo(<i>b</i>)fluoranthene	$^{-13}\text{C}_6$	<i>p,p'</i> -DDT	$^{-13}\text{C}_{12}$	
Benzo(<i>g,h,i</i>)perylene	$^{-13}\text{C}_{12}$	Dieldrin		
Benzo(<i>k</i>)fluoranthene	$^{-13}\text{C}_6$	α -Endosulfan		
Chrysene	$^{-13}\text{C}_6$	β -Endosulfan		
Dibenzo(<i>a,h</i>)anthracene	$^{-13}\text{C}_6$	Endosulfan sulfate		
Fluoranthene	$^{-13}\text{C}_6$	Endrin		
Fluorene	$^{-13}\text{C}_6$	Endrin aldehyde		
Indeno(1,2,3- <i>cd</i>)pyrene	$^{-13}\text{C}_6$	HCB	$^{-13}\text{C}_6$	
Naphthalene	$^{-13}\text{C}_6$	α -HCH	$^{-\text{D}_6}$	
Phenanthrene	$^{-13}\text{C}_6$	β -HCH	$^{-13}\text{C}_6$	
Pyrene	$^{-13}\text{C}_3$	γ -HCH	$^{-13}\text{C}_6$	
		δ -HCH		
		Heptachlor		
		Heptachlor epoxide		
		Methoxychlor		
		Mirex

Fig. 1 Sampling apparatus.

fiber filter paper (ACFP) to collect pesticides contained in both the water and the atmosphere.²⁰⁻²⁵ The method has the following three merits: (1) it requires a small quantity solvent to extract target compounds, (2) easy operational procedure and (3) the detected limit of this method is lower than those of other methods.

In this paper, we examine a method used to apply the simultaneous monitoring of PAHs and POPs in the atmosphere.

Experimental

Target compounds

The target compounds were 16 kinds of PAHs and 21 kinds of POPs. These POPs were included in the POPs Treaty, except for three kinds of POPs, such as dioxins, PCB and toxaphene. The metabolites of some of the POPs, hexachlorocyclohexanes (HCHs), endosulfans, heptachlors and methoxychlor, were also included in the group of POPs. These target compounds are listed in Table 1.

Materials

A standard solution of the PAHs, (PAH Solution Mix) was purchased from AccuStandard Inc. A standard solution of PAHs' surrogates, (US 16PAH Cocktail) was purchased from Cambridge Isotope Laboratories, Inc. Standards of hexachlorobenzene (HCB) and mirex were purchased from Wako Pure Chemical Industries, Ltd. Standard solutions of *trans*-chlordane and *cis*-chlordane were purchased from Supelco Co. Ltd. Other standard solutions of POPs (EPA 8080 Pesticides Mix) were purchased from Supelco Co. Ltd. A surrogate solution of α -HCH- d_6 was purchased from Kanto Kagaku Co. Ltd. and surrogate solutions of HCB- $^{-13}\text{C}_6$, β -HCH- $^{-13}\text{C}_6$, γ -HCH- $^{-13}\text{C}_6$, *trans*-chlordane- $^{-13}\text{C}_{10}$, *p,p'*-DDE- $^{-13}\text{C}_{14}$ and *p,p'*-DDT- $^{-13}\text{C}_{12}$ were purchased from Cambridge Isotope Laboratories, Inc. 9-Bromoanthracene (analytical grade, Wako Pure Chemical Industries, Ltd.) was used as an internal standard. Solvents such as acetone, toluene, methylene chloride, ethanol (pesticides grade, Kanto Kagaku Co. Ltd.) were used without any purification to extract and to purify the samples.

An activated-carbon fiber filter paper (ACFP; KF paper p-175, Toyobo Co. Ltd., Japan) was used as an adsorbing material to collect PAHs and POPs contained in the atmosphere. The ACFP was cut into pieces of 47 mm in diameter, put into a Soxhlet extractor and washed sequentially with acetone, toluene and acetone. The washing time was 8 h for each solvent. After removing the solvents under reduced pressure, the ACFP was stocked in a desiccator.

Quartz fiber filter paper (QFP) used a PALLFLEX membrane filter (TISSUQUARTZ 2500QAT-UP, Tokyo Dylec Co. Ltd., Japan), which was also used to collect the target compounds. The QFP was cut into pieces of 47 mm in diameter and heated at 600°C for 4 h. After cooling the QFP to room temperature, it was stocked in a desiccator.

Sampling procedures

A piece of the QFP and two pieces of the ACFP were overlapped and fitted into a stainless-steel filter folder of 47 mm

Table 2 Operational condition of pressurized liquid extraction

Apparatus	ASE-200 (Dionex)
Solvent	Toluene (Acetone)
Temperature	150°C (80°C)
Pressure	2000 psi
Heat time	7 min
Static time	5 min
Flush %	70
Purge time	90 s
Cycles	3
Cell size	11 ml

in diameter to simultaneously collect PAHs and POPs contained in the atmosphere. In front of the entrance of the filter holder, a stainless-steel funnel was connected to prevent the contamination of rain. To collect the target compounds contained in the atmosphere, air was passed through the filter for an arbitrary period at a flow rate of 10 L min⁻¹ by using a connected diafram pump. The flow rate and the total flow volume were monitored by a dry gas-meter. The apparatus used is illustrated in Fig. 1.

Analytical procedures

The stable-labeled internal standards (surrogates) were spiked to filter papers (ACFP and QFP) that contained the collecting the PAHs and POPs. The PAHs and POPs containing their surrogates were extracted from the filter papers with toluene by means of the pressurized liquid extraction method (PLE (toluene) method) using high-speed solvent-extraction equipment (DIONEX, ASE200). The operational conditions of the PLE method using DIONEX ASE200 are given in Table 2.

The extracts were evaporated just to dryness using a rotary evaporator, and the residue was dissolved with 1 ml of methylene chloride (DCM). The solution was cleaned up by means of a Sep-Pak Florisil cartridge (Waters Co.) with 10 ml of DCM. The cartridge was washed before use with 10 ml of DCM. Then, 2 µl of an acetone solution containing 0.5% polyethylene glycol (200 + 300) was added to the eluent, and the mixture was carefully concentrated just to dryness under a nitrogen flow. The residue was then dissolved in 20 µl of an acetone solution containing 0.4 µg of 9-bromoanthracene as an internal standard; the final volume of the solution was adjusted to 100 µl with toluene for a GC/MS analysis. The solution was analyzed with GC/HRMS (HP5890 gas chromatograph coupled to a JEOL SX-102A) at 5000 resolving power in the SIM mode. The concentrations of the PAHs and POPs in the solution were determined using their surrogates as an internal standard. However, the concentrations of POPs that had no corresponding surrogates were determined using the other surrogates, as follows: *trans*-chlordan-¹³C₁₀ was used to determine heptachlor, heptachlor epoxide, aldrin, *cis*-chlordan and α -endosulfan; DDE-¹³C₁₄ was used to determine dieldrin, endrin and β -endosulfan; and DDT-¹³C₁₂ was used to determine DDD, endrin aldehyde, endosulfan sulfate, methoxychlor and mirex.

The operational conditions of GC/MS for determining the PAHs and POPs are given in Table 3. It was difficult to simultaneously determine the concentrations of the PAHs and POPs, because the concentrations of the PAHs, such as fluorene and phenanthrene, exceed 10000-times those of the POPs. Thus, the concentrations of the PAHs and POPs were determined under different operational conditions of GC/MS. Typical SIM chromatograms of the PAHs and POPs are shown in Fig. 2 and Fig. 3, respectively. These figures show SIM

Fig. 2 Typical SIM chromatogram of PAHs. (a) The SIM chromatogram of standard mixture, (b) the SIM chromatogram of sample extracted from the QFP. Peak of target compounds showed as follows: 1, naphthalene; 2, acenaphthylene; 3, acenaphthene; 4, fluorene; 5, phenanthrene; 6, anthracene; 7, fluoranthene; 8, pyrene; 9, benz(a)anthracene; 10, chrysene; 11, benzo(b+j)fluoranthene; 12, benzo(k)fluoranthene; 13, benzo(a)pyrene; 14, indeno(1,2,3-cd)pyrene; 15, benzo(g,h,i)perylene; 16, dibenzo(a,h)anthracene.

Fig. 3 Typical SIM chromatogram of POPs. (a) The SIM chromatogram of standard mixture, (b) the SIM chromatogram of sample extracted from the QFP. Peak of target compounds showed as follows: 1, α -HCH; 2, β -HCH; 3, γ -HCH; 4, δ -HCH; 5, HCB; 6, heptachlor; 7, aldrin; 8, dieldrin; 9, endrin; 10, heptachlor epoxide; 11, *trans*-chlordan; 12, *cis*-chlordan; 13, α -endosulfan; 14, β -endosulfan; 15, *p,p'*-DDE; 16, *p,p'*-DDD; 17, *p,p'*-DDT; 18, endrin aldehyde; 19, endosulfan sulfate; 20, methoxychlor; 21, mirex.

chromatograms of their standard mixtures (a) and monitoring samples extracted from the QFP (b).

Results and Discussion

Blank in the ACFP

The concentrations of the PAHs and POPs containing in the unused ACFP were determined as blank tests by means of the extraction method, as follows: the PAHs and POPs involved in

the ACFP, which was cut into 47 mm ϕ pieces from the sheet, were extracted using the PLE (toluene) method. The PAHs were hardly detected, except for a trace amount of naphthalene, and the POPs were not detected. Therefore, there was no problem to use the ACFP as an adsorbing material of the target compounds, but the ACFP was carefully washed with toluene and acetone before use.

Extraction test of the standard sample

In order to establish a method to extract PAHs from ACFP, extraction tests were performed using the standard reference material (National Institute of Standards and Technology (NIST) SRM1649a, Urban Dust). Extractions were carried out by means of four methods, as follows: (1) the ultrasonic extraction method (US method) using toluene/ethanol (4:1, v/v) as an extraction solvent (US (tol-EtOH) method),²⁶ (2) the US

method using DCM (US (DCM) method),²⁷ (3) the PLE (toluene) method and (4) the PLE method using acetone (PLE (acetone) method). The results obtained from these methods are compared in Table 4.

It was noteworthy that the data, except for dibenz(*a,h*)anthracene, obtained by the PLE (toluene) method showed higher values than those of the other methods. Also, the data obtained by the PLE (toluene) method showed higher values than the certified concentration values of the standard reference material, except for phenanthrene, benz(*a*)anthracene and indeno(1,2,3-*cd*)pyrene. These results showed that the PLE (toluene) method as an extraction solvent was effective.

Recovery test of PAHs

Recovery tests of PAHs from ACFP were carried out as follows. After spiking the PAHs and their surrogates to ACFP, the PAHs were extracted using the PLE (toluene) method. The results of these tests are given in Table 5. Using 9-bromoanthracene as an internal standard, PAHs having two or three rings were recovered at more than 70%, and their coefficients of variation were within 20%. PAHs having more than four rings were recovered in less than 60% and their coefficients of variation were larger than 30%.

On the other hand, using the PAHs' surrogate as an internal standard, most of the PAHs were recovered in more than 60% and their coefficients of variation were within 10%. Although PAHs having more than five rings were recovered in more than 70%, their coefficients of variation had large values. These results showed that the direct extraction of these PAHs from ACFP was difficult, because they seemed to be strongly adsorbed to carbon fiber. These PAHs adsorbed on the particulate matter in the atmosphere could be easily collected using QFP and extracted using the PLE (toluene) method.²⁸ In order to collect the PAHs adsorbed on particulate matter,²⁰ the collecting method only using ACFP was modified by using a QFP overlapping in front of ACFP.

Recovery test of POPs

Recovery tests of POPs were performed from ACFP using the

Table 3 Operational condition for the determination of PAHs and POPs by GC/MS

GC condition	
Apparatus	HP5890 (Agilent)
Carrier gas	Helium 1 ml/min
Injection temp.	300°C for PAHs, 200°C for POPs
Column temp.	100°C (1 min) $\rightarrow$ 20°C/min $\rightarrow$ 150°C (0 min) $\rightarrow$ 6°C/min $\rightarrow$ 318°C (5 min)
Column	DB-5 ms, 60 m $\times$ 0.25 mm i.d.; film thickness, 0.1 μ m
Injection mode	Splitless
Injection volume	1 μ l
Interface temp.	250°C
MS condition	
Apparatus	SX-102A (JEOL)
Ionization voltage	70 eV
Ionization current	300 μ A
Acceleration voltage	10 kV
Ion source temp.	240°C
Resolution	5000
Measuring mode	Lock mass SIM (<i>R</i> = 5000)

Table 4 Analytical results for the standard reference material (NIST SRM1649a, Urban Dust)

PAH	Ring-	Concentration/ μ g g ⁻¹				
		US (tol-EtOH)	US (DCM)	PLE (toluene)	PLE (acetone)	Certified conc.
Naphthalene	2	0.25	0.31	1.55	0.26	—
Acenaphthylene	3	0.08	0.10	0.28	0.04	—
Acenaphthene	3	0.12	0.14	0.14	0.11	—
Fluorene	3	0.11	0.14	0.22	0.16	—
Phenanthrene	3	2.98	2.60	4.00	3.59	4.14
Anthracene	3	0.37	0.40	0.68	0.31	0.43
Fluoranthene	4	5.33	5.63	8.14	6.29	6.45
Pyrene	4	4.44	4.84	6.94	4.92	5.29
Benz(<i>a</i>)anthracene	4	1.54	1.52	2.13	1.39	2.21
Chrysene	4	1.92	1.78	3.91	3.08	3.05
Benzo(<i>b</i>)fluoranthene	5	4.95	4.06	7.18	3.24	6.45
Benzo(<i>k</i>)fluoranthene	5	1.43	1.20	1.93	0.53	1.91
Benzo(<i>a</i>)pyrene	5	1.88	2.38	3.07	1.89	2.51
Benzo(<i>g,h,i</i>)perylene	5	2.52	2.87	4.49	2.31	4.01
Dibenz(<i>a,h</i>)anthracene	5	0.64	0.38	0.44	0.31	0.29
Indeno(1,2,3- <i>cd</i>)pyrene	6	1.93	2.28	3.05	2.40	3.18

NIST SRM1649a: National Institute of Standards and Technology, standard reference material 1649a. US (tol-EtOH), the ultrasonic extraction method with toluene/ethanol (4:1, v/v); US (DCM), the ultrasonic extraction method with methylene chloride; PLE (toluene), the pressurized liquid extraction method with toluene; PLE (acetone), the pressurized liquid extraction method with acetone; certified conc., certified concentration values by NIST.

Table 5 Recovery (%) of PAHs from ACFP using PLE (toluene) ($n = 5$)

PAH	Determination using I.S.		Determination using surrogate	
	Mean	CV	Mean	CV
Naphthalene	72.9	18.5	101.5	12.4
Acenaphthylene	73.5	12.0	97.0	5.4
Acenaphthene	85.6	8.0	100.7	5.0
Fluorene	77.6	11.3	101.5	7.5
Phenanthrene	86.1	6.2	97.3	2.1
Anthracene	78.0	8.4	91.7	3.4
Fluoranthene	57.6	29.9	99.7	1.0
Pyrene	51.4	35.5	100.4	1.8
Benzo(<i>a</i>)anthracene	30.0	61.8	99.0	2.4
Chrysene	30.8	60.3	100.8	2.2
Benzo(<i>b</i>)fluoranthene	6.8	98.1	91.4	8.2
Benzo(<i>k</i>)fluoranthene	9.1	89.5	89.5	17.1
Benzo(<i>a</i>)pyrene	4.4	97.6	88.4	8.3
Benzo(<i>g,h,i</i>)perylene	1.1	90.4	64.3	17.1
Dibenzo(<i>a,h</i>)anthracene	3.0	106.4	87.9	21.2
Indeno(1,2,3- <i>cd</i>)pyrene	1.5	95.2	64.3	17.1

Added amount: each 100 ng.

PLE (toluene), the pressurized liquid extraction method with toluene; I.S., internal standard (9-bromoanthracene); CV, coefficient of variation.

PLE (toluene) method. Most of the POPs were recovered in more than 90% using 9-bromoanthracene as an internal standard; their coefficients of variation were within 10%. Also, using the POPs' surrogates as internal standards, their recoveries were more than 90% and their coefficients of variation were within 10%. These results are given in Table 6.

Comparison of the adsorbing materials

To prevent a breakthrough of the target compounds, a piece of QFP and two pieces of ACFP as an adsorbing material were used as adsorbing materials. The PAHs and POPs were extracted from QFP and ACFP using the PLE (toluene) method.

The collecting abilities of QFP and ACFP for the target compounds were compared with those of the other two adsorbing materials. Air samples were collected in a field using three kinds of adsorbing materials, as follows: (1) a piece of QFP and two pieces of ACFP (QFP + 2ACFP), (2) only an AERO cartridge (SDB400HF, GL Sciences Corporation, Japan) and (3) a piece of the QFP and a piece of Empore disk (SDB-XC, 3 M, USA), and were analyzed. Each adsorbing material was set up in an identical shelter and an air sample was continuously passed through it at a rate of 10 L min⁻¹ for one week. The PAHs and POPs collected on these adsorbing materials were extracted using the PLE (toluene) method or the PLE (acetone) method, and the results were compared.

The concentrations of the POPs obtained using these three adsorbing materials had similar low values, and their fluctuations of the concentration were large. The results of the PAHs are given in Table 7. The values of naphthalene in Table 7 were treated as a reference, because the method blank of naphthalene had a high value, and each recovery of the surrogate was lower than those of the other PAHs.

The concentrations of PAHs having two and three rings, except for phenanthrene, using the adsorbing material (1) were higher than those of adsorbing materials (2) and (3). This finding indicated that these PAHs were breakthroughs from adsorbing materials (2) and (3). To clarify the breakthrough of

Table 6 Recovery (%) of POPs from ACFP using PLE (toluene) ($n = 5$)

POP	Determination using I.S.		Determination using surrogate	
	Mean	CV	Mean	CV
HCB	91.3	4.3	94.3	4.6
α -HCH	90.3	5.8	97.5	2.6
β -HCH	96.8	4.0	98.7	1.5
γ -HCH	86.6	6.8	98.4	2.6
δ -HCH	66.6	18.9	75.2	13.0
Aldrin	94.7	3.7	95.5	2.0
Dieldrin	99.8	2.2	99.3	3.7
Endrin	94.0	9.0	93.3	10.2
Endrin aldehyde	61.8	13.3	61.4	10.6
Heptachlor	99.0	5.5	99.8	3.4
Heptachlor epoxide	96.9	3.6	97.7	2.1
<i>trans</i> -Chlordane	97.0	3.8	97.8	1.6
<i>cis</i> -Chlordane	100.0	2.5	100.9	0.4
<i>p,p'</i> -DDE	101.9	2.2	101.0	3.5
<i>p,p'</i> -DDD	103.2	2.9	102.7	1.2
<i>p,p'</i> -DDT	101.5	3.2	101.0	0.7
α -Endosulfan	100.1	6.0	102.9	3.8
β -Endosulfan	95.7	5.5	95.3	6.3
Endosulfan sulfate	61.4	19.5	61.0	17.2
Methoxychlor	106.9	3.4	106.6	5.9
Mirex	87.3	3.0	87.0	2.2

Added amount: each 10 ng.

PLE (toluene), the pressurized liquid extraction method with toluene; I.S., internal standard (9-bromoanthracene); CV, coefficient of variation.

the PAHs from the adsorbing material, a piece of ACFP was added as back-up filter behind them, and air samples were then passed through. It was difficult to set the ACFP behind adsorbing material (2), because the sampling folder for it was a special form. Thus, the breakthrough tests were carried out only for adsorbing material (3). The results are shown in the right column of Table 7. Some of the PAHs were detected from the back-up filter, which showed remarkable breakthroughs of naphthalene, acenaphthylene, acenaphthene, fluorene and phenanthrene. This finding indicated that some PAHs may also be breakthroughs from the adsorbing material (2).

The concentrations of fluoranthene and pyrene using adsorbing materials (2) and (3) were higher than those of adsorbing material (1). The blank values of fluoranthene and pyrene contained in these adsorbing materials were higher and they had larger fluctuations than those of adsorbing material (1), because adsorbing materials (2) and (3) were not washed with toluene and acetone before use. The values of PAHs having more than five rings were low and their fluctuations were large.

These results showed that adsorbing material (1) was effective for monitoring target compounds contained in the atmosphere. Also, the merits of this sampling method using adsorbing material (1) were low cost and simple manipulation.

Application to the atmospheric monitoring of the PAHs and POPs

The simultaneous monitoring of the PAHs and POPs contained in the atmosphere was performed using adsorbing material (1) for one year from December 2003 to December 2004. Sampling of the atmosphere was carried out every two weeks at two sites (an urban area and a mountainous area) in Niigata prefecture.

Table 7 Comparison of three adsorbing materials with atmospheric concentrations of PAHs

PAH	Ring-	Concentration/ng m ⁻³						
		(1) <i>n</i> = 3 (QFP + ACFP)		(2) <i>n</i> = 3 (AERO cartridge)		(3) <i>n</i> = 3 (QFP + Empore disk)		(3)' <i>n</i> = 1 (only ACFP)
		Mean	Range	Mean	Range	Mean	Range	Value
Naphthalene	2	81.6	69.1 – 99.9	18.6	14.6 – 24.4	7.69	< 0.05 – 12.2	11.5
Acenaphthylene	3	1.70	1.25 – 1.95	0.12	0.07 – 0.14	0.11	0.06 – 0.22	0.59
Acenaphthene	3	7.03	6.00 – 8.48	1.47	1.23 – 1.74	0.40	< 0.05 – 0.94	4.64
Fluorene	3	12.0	7.92 – 15.4	8.51	6.15 – 11.0	6.20	5.36 – 7.22	5.56
Phenanthrene	3	7.89	6.16 – 9.28	8.83	6.07 – 11.0	4.84	3.79 – 6.36	1.43
Anthracene	3	0.56	0.37 – 0.81	0.12	< 0.05 – 0.35	0.05	< 0.05 – 0.14	0.07
Fluoranthene	4	0.89	0.58 – 1.13	2.29	1.82 – 2.71	1.40	0.86 – 1.87	0.15
Pyrene	4	0.49	0.31 – 0.75	1.26	0.82 – 1.60	0.90	0.46 – 1.56	0.05
Benz(<i>a</i>)anthracene	4	< 0.05	< 0.05 – 0.06	0.07	< 0.05 – 0.09	0.07	0.05 – 0.09	< 0.05
Chrysene	4	0.10	< 0.05 – 0.14	0.30	0.17 – 0.38	0.21	0.08 – 0.28	< 0.05
Benzo(<i>b</i>)fluoranthene	5	0.19	0.08 – 0.29	0.43	0.22 – 0.58	0.26	0.11 – 0.39	< 0.05
Benzo(<i>k</i>)fluoranthene	5	0.07	0.05 – 0.09	0.22	0.07 – 0.44	0.11	< 0.05 – 0.15	< 0.05
Benzo(<i>a</i>)pyrene	5	0.45	< 0.05 – 1.12	0.14	< 0.05 – 0.26	0.50	< 0.05 – 1.51	< 0.05
Benzo(<i>g,h,i</i>)perylene	5	0.13	0.10 – 0.17	0.36	0.25 – 0.46	0.12	< 0.05 – 0.29	< 0.05
Dibenz(<i>a,h</i>)anthracene	5	0.05	< 0.05 – 0.11	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Indeno(1,2,3- <i>cd</i>)pyrene	6	0.15	0.12 – 0.22	0.36	0.26 – 0.48	0.20	0.07 – 0.39	< 0.05

(1) A piece of QFP and two pieces of ACFP. (2) Only AERO cartridge (SDB400HF). (3) A piece of QFP and a piece of Empore disk (SDB-XC). (3)' A piece of QFP, a piece of Empore disk (SDB-XC) and a piece of ACFP as back-up filter.

Table 8 Atmospheric concentrations of PAHs

Compound	A Site			B Site			Detection limit
	Min.	Max.	Mean	Min.	Max.	Mean	
Naphthalene ^a	5300	86000	24000	230	37000	12000	10
Acenaphthylene	550	7600	2300	87	2100	310	1
Acenaphthene	990	8700	3500	56	820	390	8
Fluorene	3300	16000	6300	500	3100	1800	100
Phenanthrene	3100	16000	6000	780	4300	1700	10
Anthracene	200	960	430	40	410	92	20
Fluoranthene	530	6400	1500	150	1600	410	10
Pyrene	260	2000	720	80	750	250	20
Benz(<i>a</i>)anthracene	12	540	120	9	150	40	4
Chrysene	36	1300	320	24	610	130	4
Benzo(<i>b</i>)fluoranthene	52	990	420	16	470	160	7
Benzo(<i>k</i>)fluoranthene	15	300	110	N.D.	130	41	7
Benzo(<i>a</i>)pyrene	—	—	—	—	—	—	—
Benzo(<i>g,h,i</i>)perylene	30	510	190	10	220	83	10
Dibenz(<i>a,h</i>)anthracene	40	430	170	N.D.	200	59	9
Indeno(1,2,3- <i>cd</i>)pyrene	N.D.	46	17	N.D.	26	5	40

Unit: pg m⁻³. Min., minimum; Max., maximum; N.D., not detected. a. concentrations of naphthalene were reference values.

The monitoring results are given in Tables 8 and 9. The values of naphthalene were treated as the reference in Table 8, because some kinds of recoveries of naphthalene's surrogate had low values, and naphthalene seemed to breakthrough from the adsorbing material. The values of benzo(*a*)pyrene are not presented in Table 8, because some of the benzo(*a*)pyrene's surrogates were hardly recovered and benzo(*a*)pyrene and its surrogate seemed to resolve in the analytical processes.

The detection limits of the target compounds were determined from the sensitivity for GC/MS and their blank in all analytical procedures. The sensitivity of the target compound was defined under the condition of *S/N* = 10 for its target peak in the standard chromatogram measured by GC/MS. The data are given in Tables 8 and 9. The detection limits of the PAHs ranged from 1 to 100 pg m⁻³. Because the method blank of

fluorene was higher than that of the other PAHs, the detection limit of fluorene was highest (100 pg m⁻³) in all of the PAHs. In the POPs, α - and β -endosulfan had relatively high detection limits of 5.0 and 10 pg m⁻³, respectively, and the detection limits of the other POPs were from 0.25 to 1.0 pg m⁻³.

The PAHs were detected for about one year. The concentrations of the PAHs of the A site in an urban area were usually higher than those of the B site in a mountainous area. The concentrations of fluorene and phenanthrene were especially higher than those of the other PAHs. The concentrations of PAHs having more than five rings increased in the winter at both sites A and B. On the other hand, the concentrations of acenaphthene and fluorene having three rings increased in the summer at site A, but their concentrations were nearly constant at site B.

Table 9 Atmospheric concentrations of POPs

Compound	A Site			B Site			Detection limit
	Min.	Max.	Mean	Min.	Max.	Mean	
Aldrin	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5
cis-Chlordane	4.0	170	47	1.2	32	10	0.25
trans-Chlordane	4.2	170	50	0.8	29	9.3	0.25
p,p'-DDD	N.D.	0.5	N.D.	N.D.	N.D.	N.D.	0.5
p,p'-DDE	1.0	12	5.0	0.5	3.2	1.4	0.25
p,p'-DDT	N.D.	9.2	3.5	N.D.	3.1	0.9	0.5
Dieldrin	0.7	28	10	N.D.	7.4	3.0	0.5
α -Endosulfan	N.D.	150	39	6.6	140	43	5.0
β -Endosulfan	N.D.	13	0.9	N.D.	14	1.3	10
Endosulfan sulfate	N.D.	1.5	0.2	N.D.	1.7	0.4	0.5
Endrin	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5
Endrin aldehyde	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5
HCB	52	170	97	48	120	77	0.5
α -HCH	12	140	63	13	75	34	0.5
β -HCH	0.6	17	6.4	N.D.	3.9	1.6	0.5
γ -HCH	3.1	42	19	3.4	22	10	0.5
δ -HCH	N.D.	29	3.1	N.D.	1.3	0.4	0.5
Heptachlor	1.8	45	16	N.D.	5.9	1.9	0.5
Heptachlor epoxide	0.5	11	3.8	N.D.	2.6	1.3	0.5
Methoxychlor	N.D.	1.5	0.1	N.D.	1.0	1.0	1.0
Mirex	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.25

Unit: pg m^{-3} . Min., minimum; Max., maximum; N.D., not detected.

POPs such as aldrin, endrin, endrin aldehyde and mirex were not detected at all, but chlordanes, HCB and HCHs were continuously detected for about one year. The concentrations of the POPs at site A maintained higher values than those of site B. The concentrations of endsulfans were equal at both sites. It was noteworthy that the concentrations of POPs remarkably increased from spring to summer. Although the concentrations and the fluctuation modes of the POPs were different from those of the PAHs, their characteristics were similar to those described in previous papers.

Conclusions

In this study, we examined a method for the simultaneous monitoring of PAHs and POPs contained in the atmosphere using activated carbon fiber filter paper (ACFP) as the adsorbing material.

The following methods were efficient to simultaneously monitor the concentrations of the PAHs and POPs contained in the atmosphere:

1) The adsorbing material, which consisted of a piece of quartz fiber filter paper (QFP) overlapped in front of the two pieces of ACFP, was effective to collect PAHs and POPs contained in the atmosphere.

2) A pressurized liquid extraction method with toluene as an extraction solvent using high-speed solvent-extraction equipment (PLE (toluene) method) was used to extract PAHs and POPs from the adsorbing material, and the extracted solutions were analyzed with GC/HRMS.

3) The concentrations of PAHs and POPs were determined using their corresponding surrogates as an internal standard.

The simultaneous monitoring of PAHs and POPs contained in the atmosphere using this method was performed every two weeks for one year in Niigata prefecture. The atmospheric concentrations of PAHs having more than five rings increased in the winter and the concentrations of most of the POPs

increased from spring to summer; these characteristics were similar to those given in previous papers.

We plan to study efficient collection methods of naphthalene and effective analytical methods of benzo(a)pyrene.

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