Development and Assessment of Passive air sampler for Sampling Semi-Volatile Organic Compounds

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Graduate school of UNIST

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Approved by

Major Advisor
Sung-Deuk Choi

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This certifies that the thesis of Eun-Jeong Park is approved.

01. 28. 2013

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Abstract

As increasing about concerns of air quality, demand of air samplers is also increasing. Among the air pollutants, SVOCs are important pollutants because of their toxic properties. There are mainly two sampling method for collecting SVOCs. One is active air sampling and the other is passive air sampling. Most of existing passive air samplers can only collect gaseous phase. However for correct assessment of air quality, passive air samplers which collect both gaseous and particulate phase SVOCs are needed. In this study, we developed new passive air samplers for SVOCs, and we verified the sampler's ability. Among the SVOCs, we selected 16 EPA priority PAHs as target compounds.

We deployed 16 samplers and periodically recovered during 120 days. We also sampled with active air sampler for obtaining the real value of air concentrations. We analyzed the recovered samples with GC/MS.

During sampling period, 8 compounds showed linearity in gaseous phase, and 14 compounds had linearity in particulate phase. There were tendency that heavier compounds were distributed in particulate phase, however lighter compounds were mainly distributed in gaseous phase. Both of samples which were obtained from actively and passively sampling were showed similar patterns.

The cacluated uptake rates are 2 ng/m^3 ~ 21 ng/m^3 in gaseous phase PAHs, and 0.073 ng/m^3 to 18 ng/m^3 in particulate phase PAHs. We identified the ability of developed passive air samplers, and this passive air sampler will be useful for assessing the air quality.

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Chapter 1. Introduction

I. Research background

Industrial expansion could lead human to affluent society. Such as rapid industrialization can allow to human more comfortable life, however due to rapid expansion, in recent years, environmental problems are increased[1]. Many industrial facilities emitted pollutant[2], and other developed devices, such as automobile car[3], were also causing the air pollution. Such phenomenon not limited in one country, it means air pollution have concerned all around world. Especially, Korea were experiencing more rapid industrialization than other country, thus environment problems have been arisen so quickly[4]. Additionally rapid urbanization of China also have affected to Korea[5]. Thus concerns about air pollution are increasing more and more. To control this air pollution, correct assessment of air quality is important.

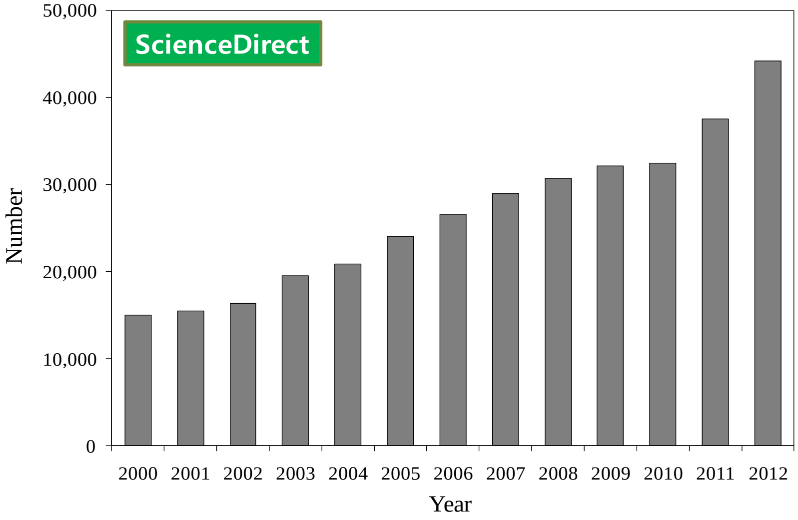
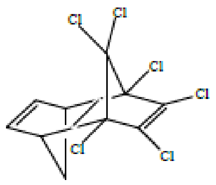


Figure 1. Search results in Sciencedirect which are searched with keyword: Air quality

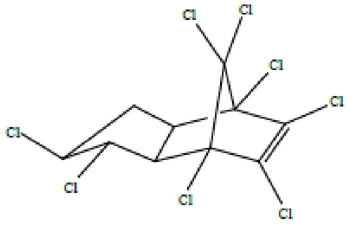
Among the air pollutants, persistent organic pollutants (POPs) are important concerned compounds, because of their characteristics in environment such as toxicity, persistence, bioaccumulation, multimedia fates, and long-range transport[6]. Pollutants are classified three groups according to their steam pressure. Three groups are volatile (>10^{-2} KPa), semi-volatile (10^{-8}~10^{-2} KPa), and nonvolatile (<10^{-8} KPa) compounds[7]. Most of the POPs in air are classified as semi-volatile organic compounds (SVOCs)[8], and these compounds are distributed both gaseous phase and particulate phase[9]. Monitoring of both gaseous and particulate phase SVOCs is important for accurate assessment[10]. Thus efficient device for sampling these SVOCs is important.

II. Persistent Organic Pollutants (POPs) and Semi-Volatile Organic Compounds (SVOCs)

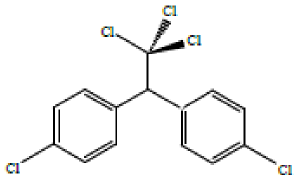
Many priority pollutants are included in SVOCs such as polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polychlorinated biphenyl (PCBs), and polybrominated diphenyl ether (PBDE) etc. These compounds are toxic, persistent, and ubiquitous[11]. Most of SVOCs have same characters with POPs. These SVOCs may influence as menace to terrestrial and aquatic ecosystems[12], and human health once released into the environment. Additionally, their semi-volatile character can allow distributing multimedia fates, thus they have detected in different environmental media such as soil[13], biota[14], water[15], air[16] or even ice-core[17]. These SVOCs are transported by atmospheric pathways and found far from any source, thus not only one nation's effort, but also international efforts are essential to control these compounds. Because of these abovementioned reasons, many countries have studied pollutants including SVOCs, and in 2004, the Stockholm convention appointed 12 POPs. In 2009, additionally 9 pollutants were added to POPs compounds category. Figure 2 shows these 21 pollutants selected by Stockholm convention[18].



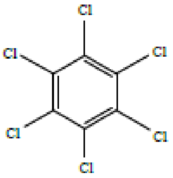
Aldrin



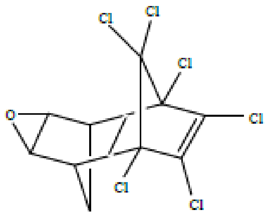
Chlodane



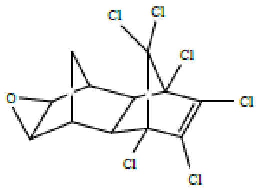
DDT
Dichlorodiphenyl trichloroethane



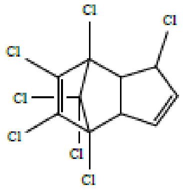
HCB



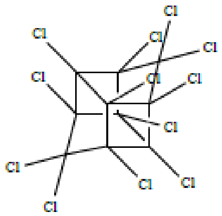
Dieldrin



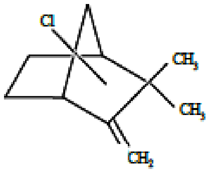
Endrin



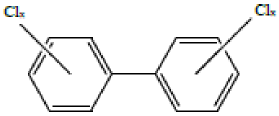
Heptachlor



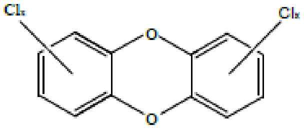
Mirex



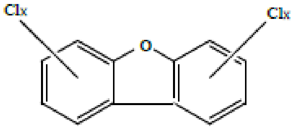
Toxaphene



PCBs

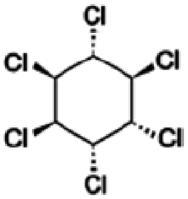


PCDDs

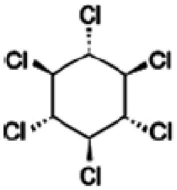


PCDFs

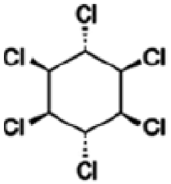
POPs designated in the Stockholm protocol in 2004



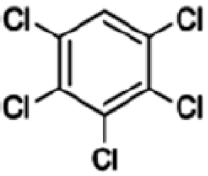
Alpha-HCH



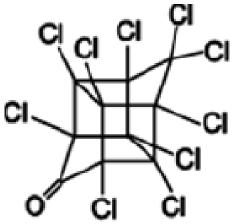
Beta-HCH



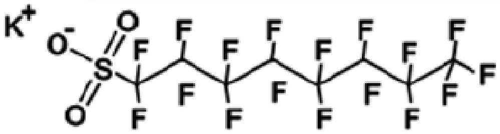
Lindane
Gamma-HCH



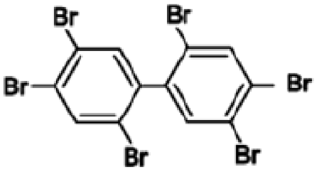
PeCB
Phentachloro-benzene



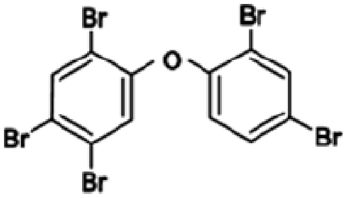
Chlordecone



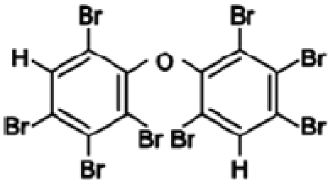
PFOS
Perfluorooctane sulfonic acid



Hexabromo-biphenyl



Tetra/Penta BDE



Hexa/Hepta BDE

9 New POPs additionally pointed in 2009

Figure 2. 21 Persistent Organic Pollutants (POPs) which designated in the Stockholm protocol

III. Air sampling

3.1. Active air sampling

Ministry of environment suggest for air sampling procedure in “Official test method on air pollution”. In there, It is published that air sampling has to separately capture according to particulate and gaseous phase. For sampling, electrical pump is used, thus this method can be sorted by active air sampling[19]. Active air samplers enable SVOCs in both gaseous and particulate phases to be trapped by pumping air through a filter followed by a solid adsorbent[20]. Filter can capture the particulate phase SVOCs, and passed gaseous phase SVOCs are adsorbed in solid adsorbent. Filter is made by glass fiber filter (GFF) or quartz fiber filter (QFF). For adsorbing gaseous phase, XAD and PUF are widely used by adsorbent. Active air sampler exist various device, and among them low-volume air samplers (LVSs) and high-volume air samplers (HVSs) are widely used[21]. Sampling by active air sampler can allow setting the sampling time and flowing rates. In short, it can be possible to regulate the sampling volume.

Although their widely usage, active air samplers have some disadvantage in atmospheric sampling. Generally active air samplers are expensive, thus many researchers have some problem in buying this device. Deployment of active air sampler is also not comfortable and feasible because this device is needed electrical power. That is why they have some constraints of times. Additionally, active air sampling is carried out during short time (some hours or few days), thus they have some errors to exam the average air conditions in specific regions. Therefore, for more convenient and large-scale air quality studies, use of a alternative air sampling method have been demanded. Passive air sampling is an attractive alternative sampling method to substitute active air sampling[22]. Figure 3 shows information about general scheme of active air samplers.

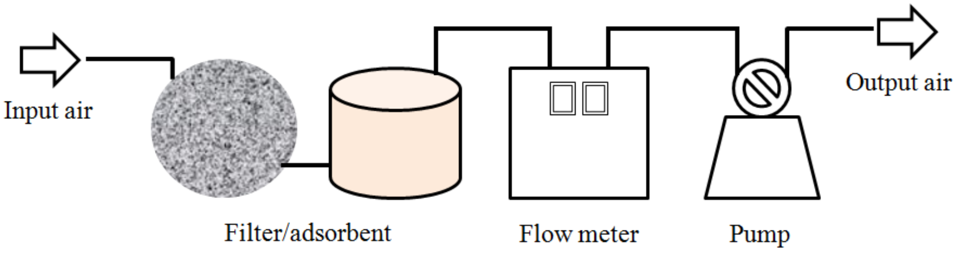


Figure 3. Schematic diagram of a typical active air sampling method

3.2. Passive air sampling

3.2.1. General concept of passive air sampling

A passive air sampler (PAS) collects chemicals from the atmosphere without the aid of a pump. Passive air sampler is consisted with an adsorbent which has a high capability to adsorb target compounds. Because active air samplers have some weakness, after 2000s many researchers have applied and developed passive air sampler for air sampling instead of active air sampler[23].

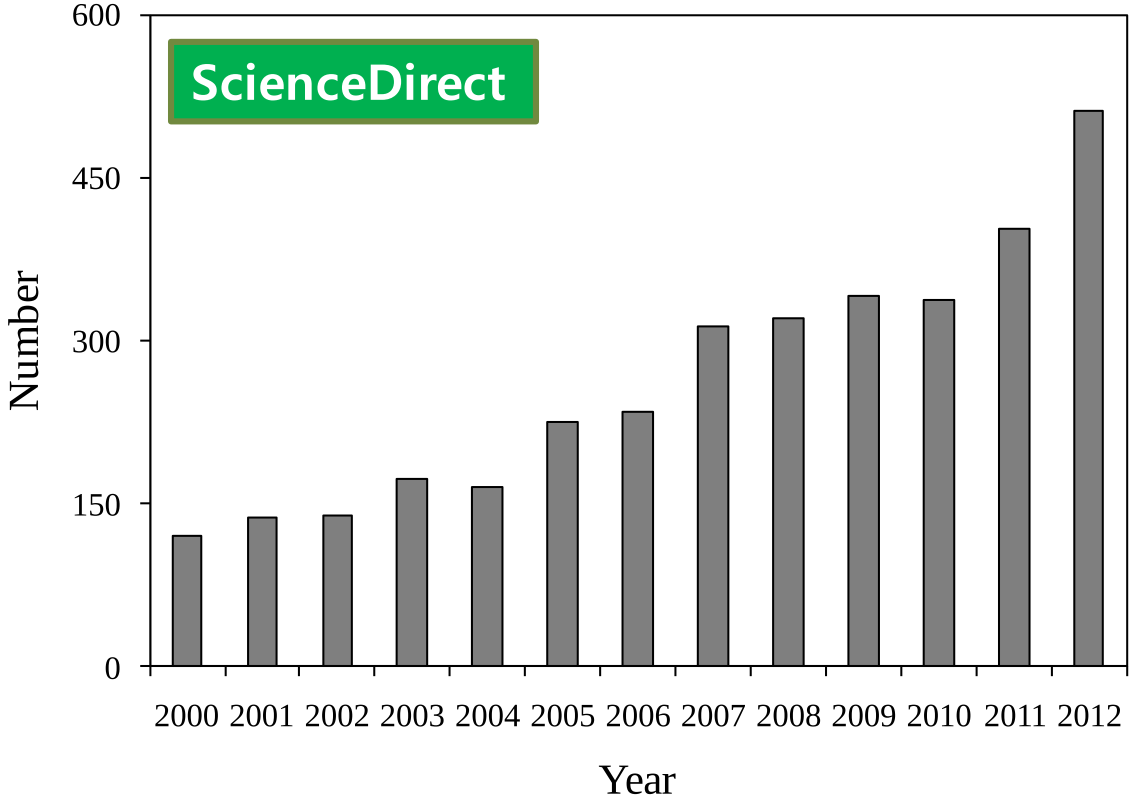


Figure 4. Increasing trends about passive air sampler, search results of Sciencedirect keyword by "passive air sampler" after 2000

Most of passive air samplers are consisted with exterior chamber and adsorption located inside of chamber. Main idea of passive air sampler is very simple. They are sampling chemicals in air by adsorbing their adsorbent during linear uptake period. During sampling period, adsorbent uptakes chemicals with linearity, and after some periods, eventually they leached in equilibrium stage. Therefore adsorbent which is used in passive air sampling has to collect before leaching the equilibrium stage.

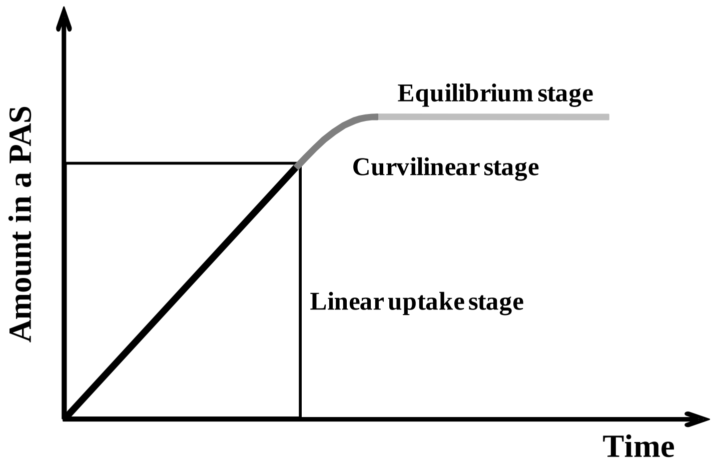


Figure 5. Basic concept of passive air sampler: obtaining method for uptake rate and information about linear uptake stage

The collected adsorbents are analyzed, and divided with uptake rates (m^3/day). With calculating, they can obtain the air concentration in sampling area. At this time, the calculated concentration is average concentration during sampling period. Thus preceding usage of passive air sampler, to know about uptake rate is needed.

$$C_{Air} = C_{PAS} / (R \cdot t)$$

C_{Air} : Concentration of POPs in the atmosphere (pg m^{-3})

C_{PAS} : Amount of POPs in a PAS (ng PAS^{-1})

R : Sampling rate (m^3 day^{-1} PAS^{-1})

t : Deployment period (day)

3.2.2. Previous developed passive air samplers

The semi-permeable membrane device (SPMD) is one of the most popular passive air samplers for monitoring SVOCs in the atmosphere. SPMD was developed by Huckins and firstly it was used in the aquatic environment[24]. SPMD have convenient for usage and it is commercially spread than other passive air sampler[25]. However it has very short linear uptake range, thus sometimes target pollutants, especially having high volatility, and are leached in equilibrium stage before they recovered from sampling sites. Also, after sampling, there are some bothered steps for analysis.

Resin-passive air samplers are using XAD as sampling media. This resin-passive air sampler was developed by Wania et al in Canada[26]. The samplers are consisted with stainless steel mesh cylinder, and inside of cylinder are filled with XAD resin. They receive few influences by weather conditions. Thus they are stable to exterior conditions. Their sampling rates are lower than other samplers, which mean small amount of pollutants are captured in one day. Thus this passive air sampler is appropriate to long term atmospheric monitoring study. However the XAD resin is expensive and needed troublesome steps during pre-cleaning and deployment[27]. Also, their uptake rates are small, thus there are demanded long sampling period for capturing pollutants which are sufficient for detection.

Polyurethane foam disk passive air sampler (PUF-PAS) is most popular sampling device. They are consisted with stainless chamber and polyurethane foam (PUF) disks are used as adsorbing materials[28]. This sampler is cheaper than other samplers and convenience in deployment. The pollutants are leached equilibrium stage after few months. Thus PUF-PAS is appropriate to seasonal monitoring. However this sampler is very sensitive to meteorological conditions, therefore we have to consider the weather conditions of sampling sites. This sampler is also fragile to prevent the particulate phase SVOCs, thus particles in air can positively affect to calculate air concentrations.

SPMD PUF-PAS Resin-PAS

Figure 6. Representative passive air sampler which developed in previous studies

IV. Objective of this study

There are some weakness of both active air sampling and passive air sampling. In aspect of active air sampler, more convenience and inexpensive sampler is needed. And that samplers are too large to conveniently use, thus small sampler is useful for various and coincidental air monitoring in various sampling sites. Previous passive air sampler improved these things, however they also have some disadvantage. Most of developed samplers can monitor only gaseous phase. For assessing air quality, we have to investigate both particulate and gaseous phase. Thus previous passive air samplers have defectiveness for observing accurate air quality.

Therefore, in this study, we developed new passive air sampler which is improved proceeding described weakness. The newly developed passive air sampler is comfortable in usage, and it can separately capture both gaseous phase and particulate phase SVOCs. We also calibrated the developed sampler by deploying the samplers during 120 days to investigate the uptake period. And we also conducted sampling using by active air sampler during that previous for assessing real atmospheric concentrations. From this experiment, we analyzed both gaseous and particulate SVOCs and calculated uptake rates. Among the various compounds of SVOCs, we selected PAHs to representative SVOCs.

Chapter 2. Materials and Methods

I. Design of the sampler

The new design of the passive sampler is shown in Figure 1. The main purpose of the sampler is collecting both gaseous and particulate phase SVOCs. All the part of sampler is made by stainless steel for preventing of corrosion. The upper side chamber is consisted with some supporter and linking device. The linking device has two parts, one is movable and the other is fixed. The bottom of sampler is consisted with two parts of sampling media including a PUF disk (7 cm radius × 1.35 cm thick) and a glass fiber filter (GFF, 9 cm radius) in a sampling chamber that collected for the gaseous and particulate phase SVOCs, respectively.

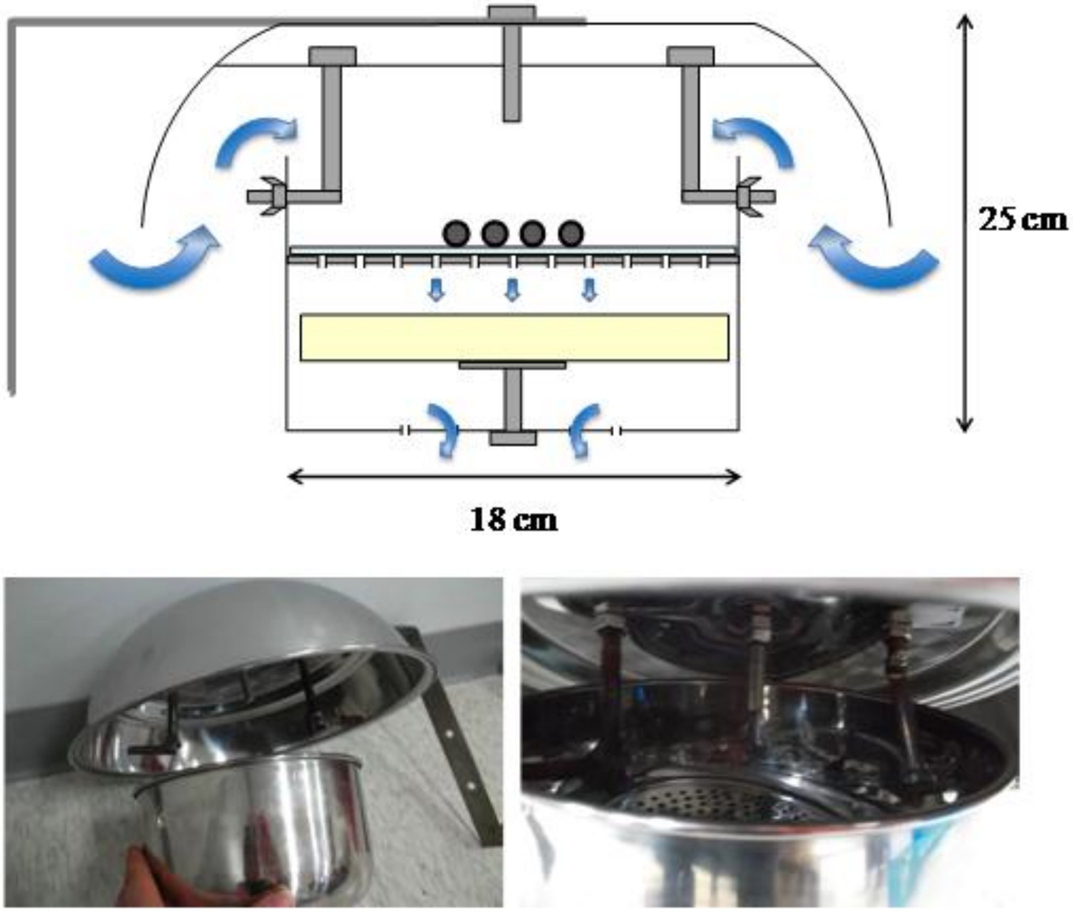


Figure 7. A sectioned drawing of passive air sampler which was developed for this study

Adding the function about separately colleting gaseous and particulate phase SVOCs, the other important function of passive air sampler is movability. Figure 2 shows side view of passive air sampler. By this ability, the sampler can increase their ability of collecting SVOCs. The sampler can be moved by blowing of wind or outside stimulation. By this function, the sampler can increase ability of collection sample. In other words, that can lead increment of uptake rate in passive air sampler.

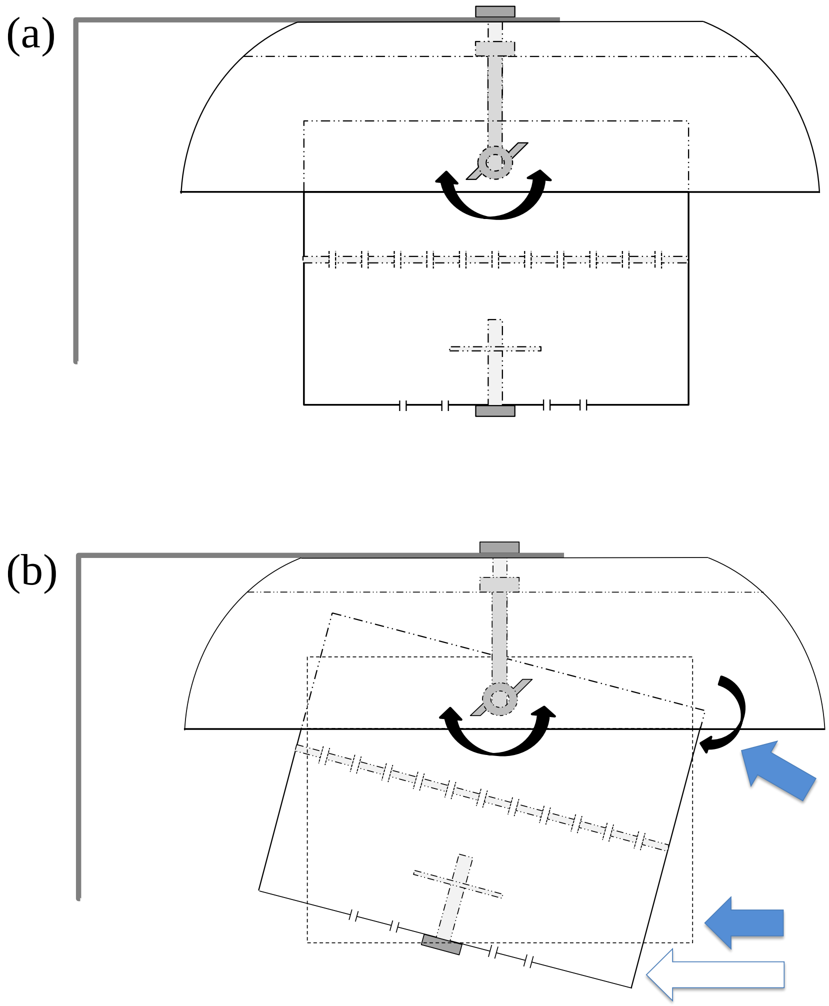


Figure 8. A side view of passive air sampler.

(a) Side view without external stimulation (b) Side view which are affected by wind

II. Target compounds: Polycyclic aromatic hydrocarbons (PAHs)

Among the SVOCs, we select the polycyclic aromatic hydrocarbons (PAHs) for main analyzed compounds. PAHs consist of two or more fused benzene rings in their structures and they contain only carbon and hydrogen[29]. They are found in cigarette smoke, in barbecued and smoked foods, in automobile and diesel engine exhaust, fireplace smoke, and many other common things that people are exposed to[30]. PAHs are chemicals that known or suspected carcinogens linked to human health problems[31]. Analyzing for PAHs in the environment is important in identifying potential sources of cancer exposure and eliminating these as risks. PAHs that founded association with most anthropogenic activities are present as environmental pollution due to their potential impacts on ecosystems and human health. Because PAHs that ubiquitous in the environment are carcinogens and mutagens, they are considered as very hazardous pollutants with toxicity, mutagenicity and carcinogenicity.

PAHs are existed above 200 species, but many researchers select only 16 PAHs which announced priority pollutants in US-EPA. These compounds include naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), Fluranthene (Flt), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IcdP), dibenz(a,h)anthracene (DahA), and benzo(ghi)perylene (BghiP). Structures of 16 PAHs are shown in Figure 9 and chemical and physical properties are shown in Table 1. The 16 PAH compounds various molecular weight and volatility, thus 16-PAHs are appropriated for assessing the ability of passive air sampler which were developed for applying in SVOCs.

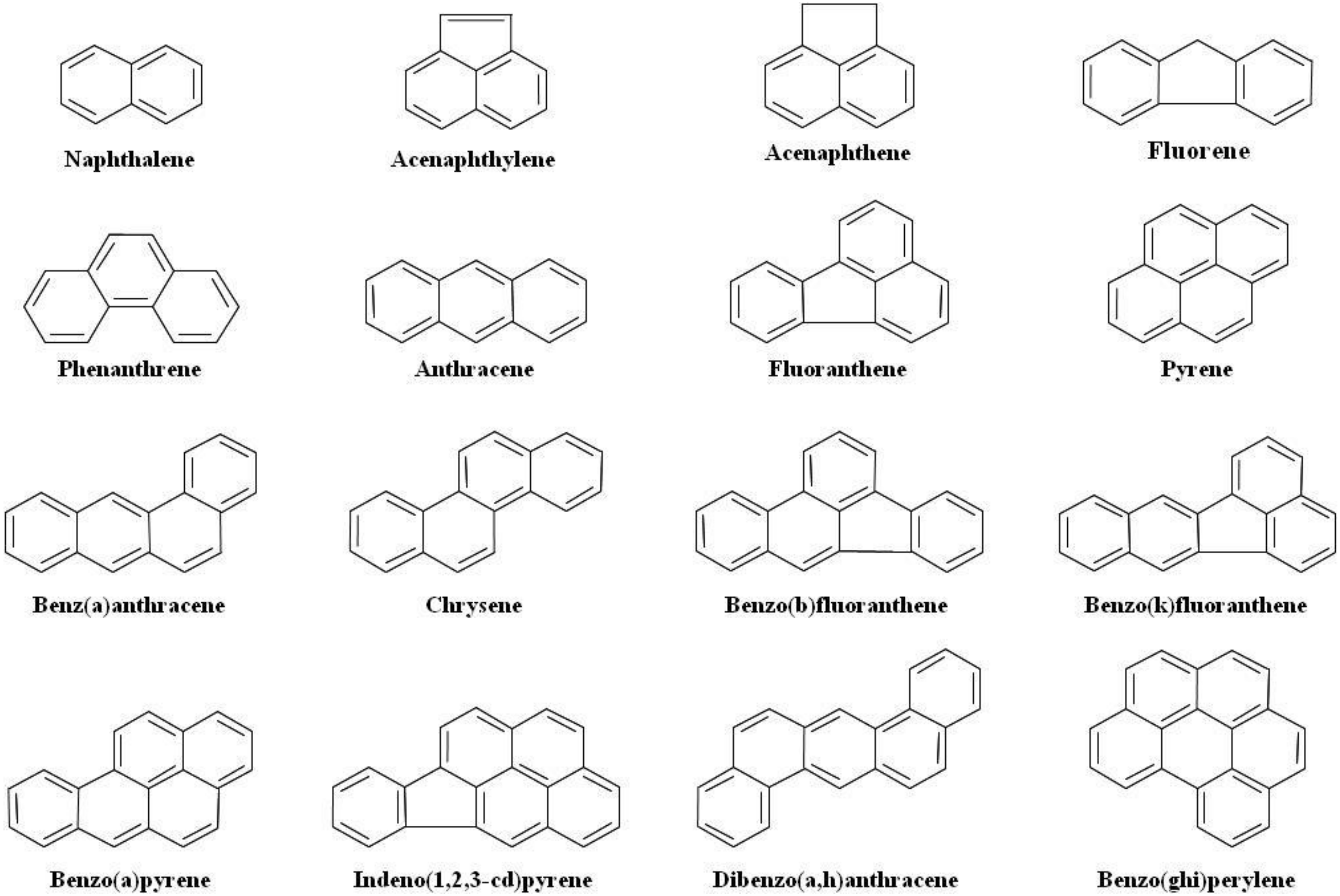


Figure 9. Structures of 16 PAHs on the EPA priority pollutants list

Table 1. Chemical and physical properties of PAHs

Rings	PAH	Composition	MW[a]	Sw[b]	Mp[c]	Bp[d]	$LogK_{ow}$[e]
2	Naphthalene	$C_{10}H_8$	128	31.7	80	218	3.37
3	Acenaphthylene	$C_{12}H_8$	152	3.47	92	265	4.07
	Acenaphthene	$C_{12}H_{10}$	154	3.93	96	279	4.33
	Fluorene	$C_{13}H_{10}$	166	1.98	116	293	4.18
	Anthracene	$C_{14}H_{10}$	178	0.073	216	293	4.45
	Phenanthrene	$C_{14}H_{10}$	178	1.29	101	340	4.46
4	Fluoranthene	$C_{16}H_{10}$	201	0.26	111	340	5.33
	Pyrene	$C_{16}H_{10}$	202	0.135	149	393	5.32
	Benz(a)anthracene	$C_{18}H_{12}$	228	0.014	158	360	5.61
	Chrysene	$C_{18}H_{12}$	228	0.002	255	400	5.61
5	Benzo(b)fluoranthene	$C_{20}H_{12}$	252	0.0012	167	448	6.57
	Benzo(k)fluoranthene	$C_{20}H_{12}$	252	0.00055	217	N.A.[f]	6.84
	Benzo(a)pyrene	$C_{20}H_{12}$	252	0.0038	179	480	6.04
	Dibenz(a,h)anthracene	$C_{22}H_{14}$	278	0.00249	262	496	5.97
6	Benzo(g,h,i)perylene	$C_{22}H_{12}$	276	0.00026	222	N.A.	7.23
	Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276	0.0062	162	N.A.	7.66

[a] Molecular weight

[b] Aqueous solubility in mg/L at 25˚C

[c] Melting point in ˚C

[d] Boiling point in ˚C

[e] Logarithm to the base 10 values of the partitioning coefficient

[f] No relevant data for the report

III. Sample collection

3.1. Sampling sites

The passive air samplers and active air samplers were deployed at outdoor site in UNIST. UNIST are located in Ulsan, where most are industrialized city in Korea. The sampling site, UNIST, is located in rural area in Ulsan. But the university was built only 5 years ago, and some building was being built near by the sampling point during sampling periods. Thus heavy trucks and materials for construction might be influenced the sample. And many people who stay in this university are using car, so the cars also affect the monitoring sample. The detailed location is shown in Figure 10. The sampling point was located between the buildings. The height of the point was about 5 m, and that of surrounding buildings were 30 m. The surrounding building made pathway for passing wind, thus wind of the sampling points were rattling wind than other sites in UNIST.

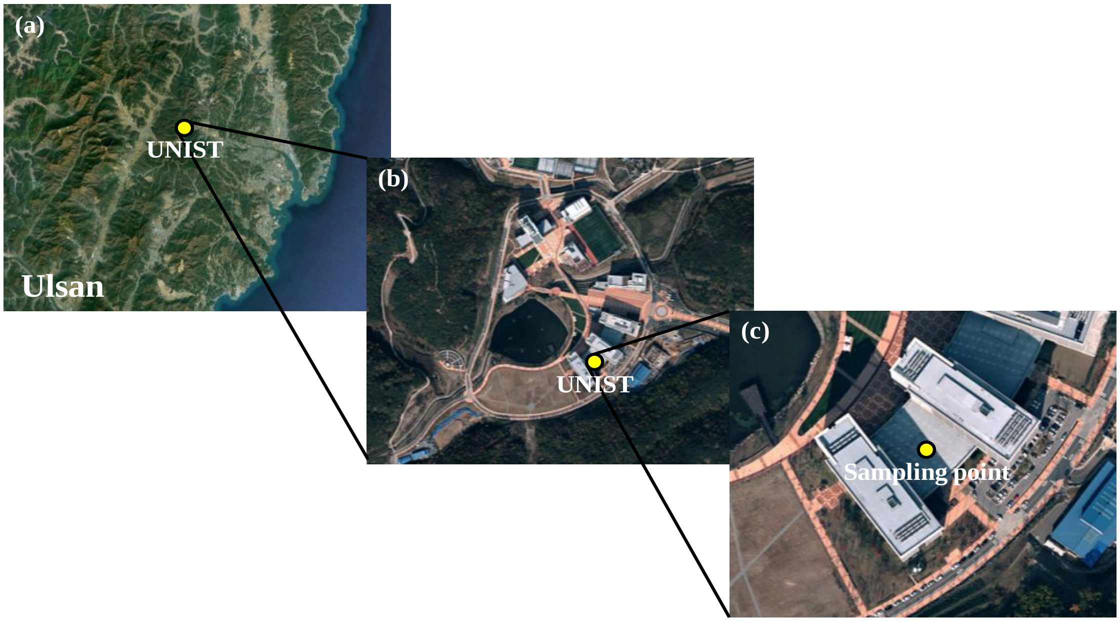


Figure 10. The sampling site, UNIST, in this study (a) Sampling city, (b) Specific sampling site

3.2. Sampling preparation

Prior to sampling, PUF disks were precleaned with acetone and hexan. Firstly we soaked the PUF disks in acetone and irradiated with ultrasonic wave. Following this step, PUF disks were soaked in hexane, and again irradiated with ultrasonic. After that, we dried the PUF disks at the oven which were set at 60 ℃. Before conducting deployment, we preserved the PUF disks by using aluminum foil which was pre-rinsed with acetone and hexane. GFF was baked at oven which was set at 130℃. The passive air samplers which were used in this study, were prewashed with distilled water and wiped with dichloromethane.

3.3. Active air sampling

Duplicated high-volume air samplers were collecting throughout the time course of the experiment. These activeair sampling was conducted for evaluating the actual ambient air concentration of PAHs. High-volume air samplers were deployed alongside the passive samplers. During the passive air sampling period, high-volume air samples were collected ambient air samples during 24 hours per 15 days. Since the gaseous phase and particulate phase PAHs were separately sampled with newly developed samplers, the sampling media were also calibrated and collected individually for each of the two phases by high-volume air samplers. Gaseous phase samples were collected with two pieces of polyurethane foam (4.5 cm radius × 5 cm height) and particulate phase PAHs were sampled by glass microfiber filters (20.3 cm × 25.4 cm, Whatman, United states). For this study we set up the conditions which were loaded in Table 2.

Table 2. Conditions of high-volume air sampler using this study

Items	**Conditions**
High-volume air sampler	HV-700, Sibata, Japan
Speed	700 mL/min
Sampling period	24 hours
Sampling volume	1008 m^3

Figure 11. High volume air sampler for collecting particulate and gaseous phase PAHs

3.4. Passive air sampling

The passive air samplers were deployed at described outdoor location. Samples were collected during 120 days by 16 passive air samplers. Two samplers were withdrawn every 15 days, thus totally eight groups differently had sampling period. Passive air samplers also were separately collecting the gaseous phase and particulate phase PAHs with PUF and GFF. The air sample collected by PUF and GFF were wrapped with pre-cleaned aluminum foil and transported at laboratory. The samples were kept in refrigerator before the other group's sampling was ended. Detailed sampling period is described in Table 3. Figure 12 shows sampling of passive air sampler.

Table 3. Information about sampling period

Passive air sampler		High volume air sampler	
Group 1	2011. 09. 16 ~ 2011. 10. 01	1st collection	2011. 09. 16 ~ 2011. 09. 17
Group 2	2011. 09. 16 ~ 2011. 10. 16	2nd collection	2011. 10. 15 ~ 2011. 10. 16
Group 3	2011. 09. 16 ~ 2011. 10. 31	3rd collection	2011. 10.30 ~ 2011. 10. 31
Group 4	2011. 09. 16 ~ 2011. 11. 15	4th collection	2011. 11. 14 ~ 2011. 11. 15
Group 5	2011. 09. 16 ~ 2011. 11. 30	5th collection	2011. 11. 29 ~ 2011. 11. 30
Group 6	2011. 09. 16 ~ 2011. 12. 15	6th collection	2011. 12. 14 ~ 2011. 12. 15
Group 7	2011. 09. 16 ~ 2011. 12. 30	7th collection	2011. 12. 29 ~ 2011. 12. 30
Group 8	2011. 09. 16 ~ 2012. 01. 14	8th collection	2011. 01. 13 ~ 2012. 01. 14

Figure 12. Passive air sampler for collecting particulate and gaseous phase PAHs

3.5. Meteorological observation during sampling period

Concentrations of SVOCs are highly affected by meteorological conditions during sampling period. Thus we investigated the meteorological conditions in this sampling period. The meteorological information could be obtained from Korea meteorological administration. Actually this information have some deviation, because that measured in other sites of Ulsan. However that is very similar to conditions of this sampling sites, thus in this study we ignored the deviation.

IV. Analysis

4.1. Sample pretreatment

PAHs were highly existed in atmosphere, thus special pre-cleaning was needed for minimizing of pollution. Before starting the pretreatment procedure, we were rinsing all grass apparatus with distilled water, acetone, hexane. After solvent rinsing, we dried residual solvent and enclosed the entrance of glass apparatus for preventing of pollution. Total procedure for analyzing the samples was shown in Figure 5.

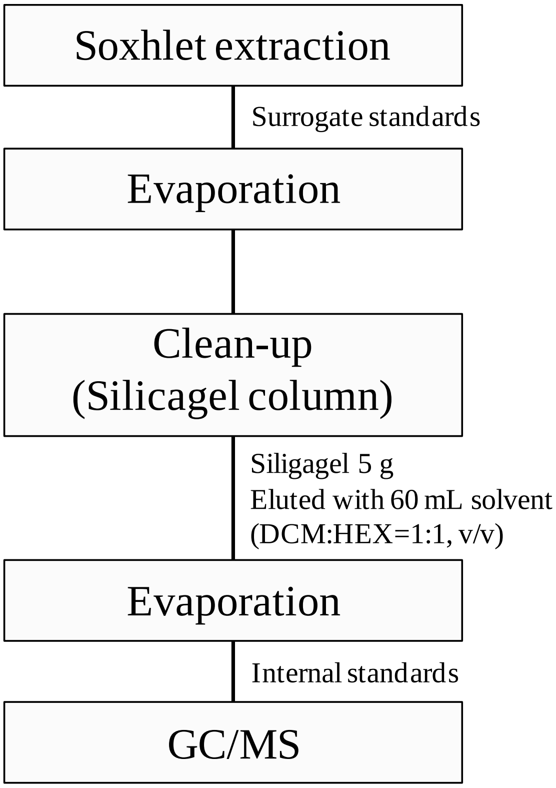


Figure 13. Analytical procedure for the determination of PAHs

4.1.1. Extraction

There are many methods for extraction of solid sample. Among the methods, we choose Soxhlet extraction for extracting PAHs from PUF and GFF samples. Soxhlet extraction is very popular method for analyzing POPs. Apparatus for Soxhlet extraction are composed with three parts, round bottom flask, Soxhlet extractor, and condenser. For extraction, we put the 350 mL mixed solvent (Hexane:Acentone=9:1, v/v) in round bottom flask during 16 hours. In the Soxhlet extractor, we placed PUF or GFF samples. Extration cycles were set about 6 cycles per hours. Extracted solutions were concentrated with rotary evaporator and nitrogen evaporator before reached at 10 mL. The Soxhlet apparatus were shown in Figure 5.

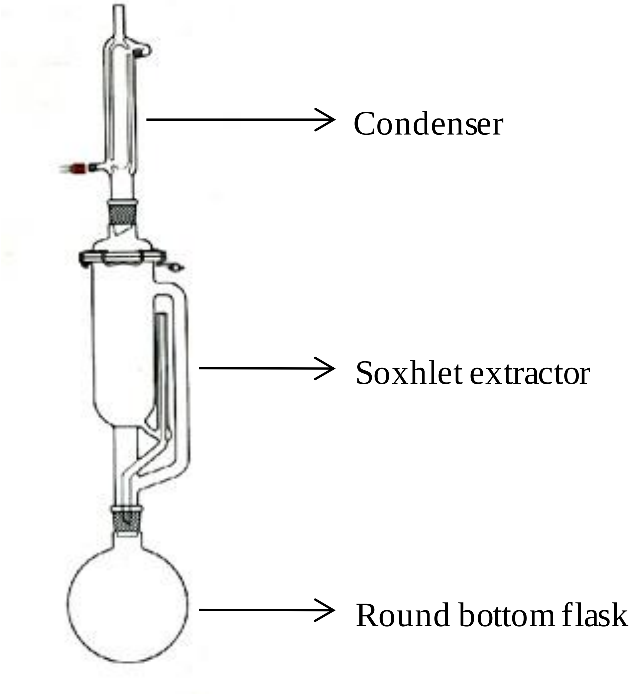


Figure 14. Apparatus for Soxhlet extraction, mainly composed with three parts

4.1.2. Clean-up

There are existed many compounds at extract. If we don't remove the interruptive compounds, we have problem for detection in target compounds. So we conducted clean-up procedure for removing these interruptive compounds. Clean-up procedure is separating method which based the difference of partition coefficient and adsorption coefficient between stationary phase and mobile phase. In this study, we used silicagel powder mixed with anhydrous sodium sulfate as a stationary phase. Silicagel and anhydrous sodium sulfate were activated in 130˚C. The concentrated extracts were passed out 5 g of silicagel column. Many research use column for cleanup. In this study, we filled the silicagel in funnel for increasing the convenience. The silicagel column was presoaked with hexane. Firstly we loaded samples in top of the silicagel column, after that we loaded elution solvent (60 mL of mixed solvent, Hexane:Dichloromethane=1:1, v/v). The eluted solution were evaporated with nitrogen evaporator, and transported in 400 μL insert vial for instrument analysis.

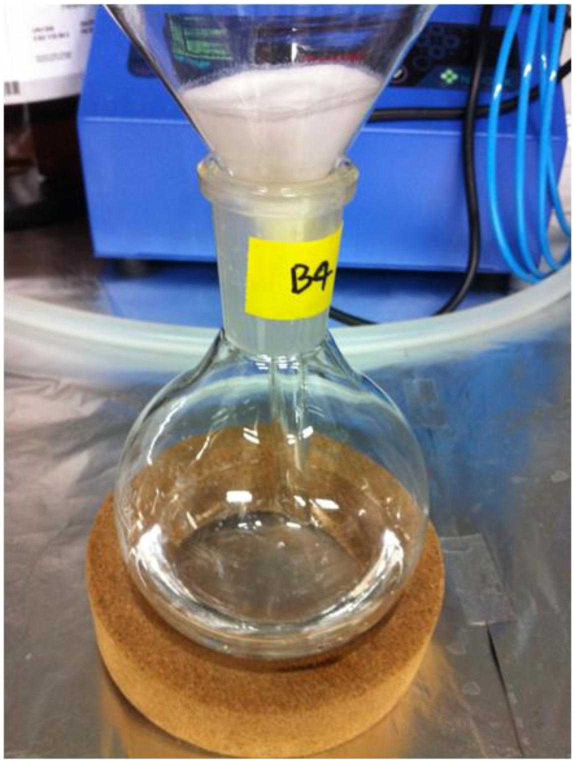


Figure 15. Clean-up procedure for removing interruptive compounds.

4.2. Instrumental analysis

GC/MS were used for analyzing PAHs. One micro liter samples were injected into GC/MS by splitless mode. Gas chromatograph was separating the PAHs and separated PAHs were detected by mass spectrometer with selected ion monitoring (SIM) mode. Limit of quantification of PAHs was selected above three signal to noise ratio (S/N) value. Detailed conditions of instrument were shown in Table 6. Table 7 is showing primary and secondary ion which were selected for selected ion monitoring mode.

Figure 16. GC/MSD using PAHs analysis.

Table 4. GC/MS conditions for analyzing PAHs

Item	**Conditions**
Instrument	Agilent 7890N/5975C MSD
Column	DB-5MS 30 m length, 0.25 mm inner diameter, 0.25 μm thickness
Ion source temp	250˚C
Injector temp	250˚C
Carrier gas	Helium (1.00 mL/min)
Injection mode	Splitless mode, 1 μL
Ionization mode	EI mode
Oven conditions	70˚C (1 min) → 10˚C/min → 240˚C (0 min) → 5˚C/min → 300˚C (5 min)

Table 5. Target ions and qualifier ion used in GC/MSD analysis

Type	PAHs	Target ion	Qualifier ion
Target PAHs	Naphthalene	128	127
	Acenaphthylene	152	151
	Acenaphthene	153	154
	Fluorene	166	165
	Phenanthrene	178	176
	Anthracene	178	179
	Fluornathene	202	203
	Pyrene	202	203
	Benzo[a]anthracene	228	226
	Chrysene	228	226
	Benzo[b]fluoranthene	252	253
	Benzo[k]fluoranthene	252	253
	Benzo[a]pyrene	252	253
	Indeno[1,2,3-cd]pyrene	276	277
	Dibenz[a,h]anthracene	278	279
	Benzo[ghi]perylene	276	277
Surrogate standard	Naphthalene-d_8	136	137
	Acenaphthene-d_{10}	162	164
	Phenanthrene-d_{10}	188	189
	Chrysene-d_{12}	240	236
	Perylene-d_{12}	264	260
Internal standard	p-Terphenyl-d_{14}	244	245

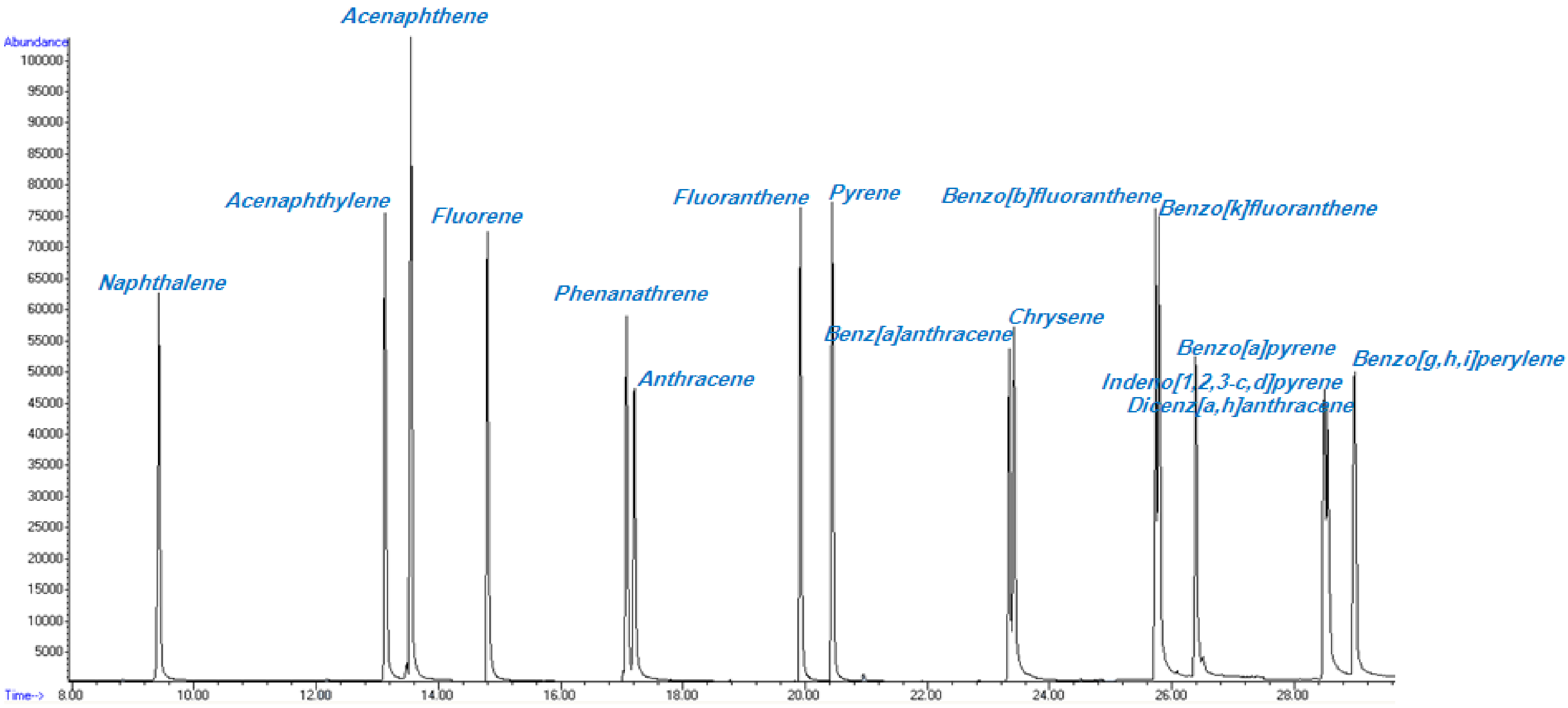


Figure 17. Chromatogram of target compounds in this study

4.3. Quality control

All reagents grade were higher grade than extra pure grade. Before analyzing the sample, we checked the quality of reagents. After we confirmed the purity of reagents, which can interrupt sample analyzing procedure, we started the analysis. We also conducted the experiment with procedure blank. By this, we could check the pollution during the procedure. At blank sample, we detected Naphtalene, Phenanthrene, Benzo(a)anthracene. All sample in this study were conducted by the duplicated samples, and we calculated the concentration by averaging two samples. All the samples were spiked with range of deuterated PAHs (Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, Perylene-d_{12}). Deuterated PAHs can monitor the extraction and cleanup procedure and calculate the concentration of target compounds by internal standard method. The recoveries for the deuterated PAHs were from 65 to 113% for the PUF disk and from 68 to 123% for GFF. S-terphenyl-d_{14} was used for internal standard and that was spiked just before instrumental analysis.

Chapter 3. Results and Discussion

I. Results of meteorological observations

The meteorological conditions showed normal fall and winter conditions in Korea. Average temperature was 10.4˚C, and wind speed was 2.2 m/s. Thus we guess the sampling was conducted under mild weather conditions. During sampling period, there were 25 rainy days and total rainfall was 153.5 mm. The amount of rainfall was not partially large, however they slightly affected sampling for particulate phase PAHs. We showed the meteorological conditions in table 6. The values of temperature and wind speed are averaged value of 15 days, and the amount of rainfalls are total amount during 15 days.

Table 6. Meteorological observation during sampling period

	Sampling period	Temperature(°C)				Wind speed(m/s)				Rainfall (mm)[a]	Wind direction
		Mean	Max	Min	Std	Mean	Max	Min	Std		
G1[b]	2011.09.16.- 2011.10.01.	19.6	24.3	15.2	2.7	2.6	5.5	0.4	1.3	8.4	NNE
G2	2011.10.02.- 2011.10.16.	17.1	23.5	11.9	3.4	1.6	4.7	0.1	1.1	15.5	ESE
G3	2011.10.17.- 2011.10.31.	14.4	19.2	10.2	2.7	2.0	5.0	0.2	1.2	55.5	ENE
G4	2011.11.01.- 2011.11.15.	15.0	19.2	12.1	2.0	1.7	4.3	0.2	1.0	11.2	NNE
G5	2011.11.16.- 2011.11.30.	9.6	15.4	4.6	3.4	1.9	5.0	0.1	1.1	43.7	WNW
G6	2011.12.01.- 2011.12.15.	5.8	10.3	1.9	2.5	2.6	5.7	0.5	1.1	19.0	WNW
G7	2011.12.16.- 2011.12.30.	0.6	5.4	-3.3	2.7	2.7	6.4	0.2	1.6	0.0	NW
G8	2011.12.31.- 2012.01.14.	1.1	6.4	-3.1	2.9	2.6	6.4	0.2	1.4	0.2	NW
Mean		10.4	15.5	6.2	2.8	2.2	5.4	0.2	1.2	153.5	NW

[a] Total amount of rain during selected days

[b] Group of described in Table 3.

II. Active air sampling

For correct assessing the newly developed PAS, we wanted to know the concentration of PAHs at the sampling site. As we checked the concentration of atmosphere, we conducted active air sampling by high-volume air sampler. Table 6 shows concentration of PAHs obtained from active air sampling. This results show distribution and patterns of PAHs in this sampling sites. High-volume air samplers were set speed 700 mL per min and were sampling during 24 hours. We collected 1008 m^3 volume of atmosphere from that sampler. Totally 8 times we collected atmospheric sample and all samples were conducted by duplicate. Thus we could obtain total 16 samples. We separately captured atmosphere by gaseous phase and particulate phase. Pre-treatment and analysis also were conducted separately. The obtained concentrations were conversed by sampling volume. Samples were collected during fall and winter season. During that time, samples normally were showed increasing concentration patterns of total PAHs. Generally, many researchers have shown same results about this study. As time goes on winter, atmospheres are affected from various sources, especially heating system. In PAH case, the pollutants were formed from incomplete combustion, thus this leaded that results. Figure 18 shows total concentration of PAHs according to their sampling times.

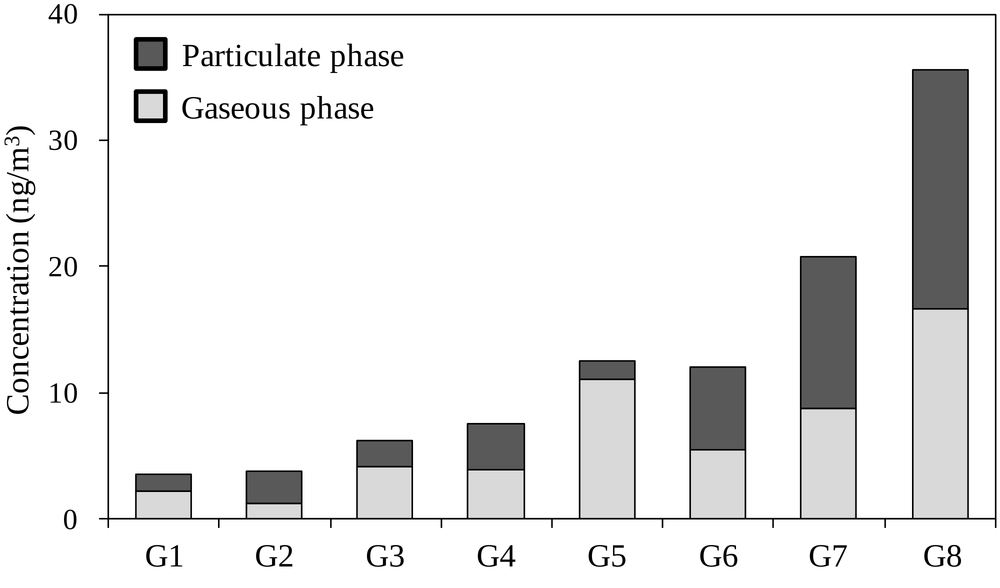


Figure 18. Total concentration of PAHs (gaseous phase + particulate phase) according to sampling period which were sampled by active air sampler.

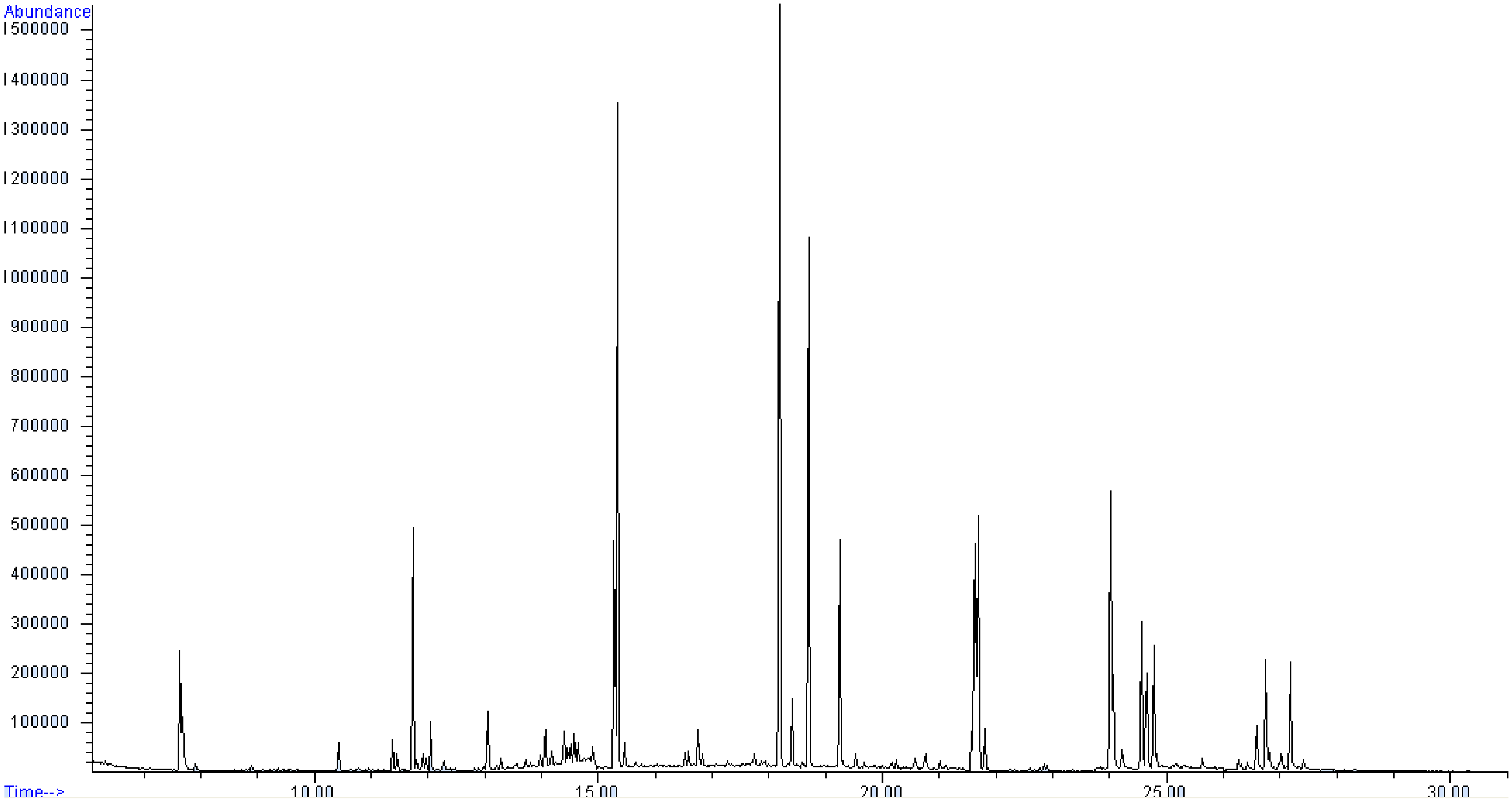


Figure 19. General PAH chromatogram obtained from filter sample (particulate phase PAHs)

Table 7. Concentration of PAHs in gaseous phase sampling from high-volume air sampler (ng/m^3)

Compounds	**G1**	**G2**	**G3**	**G4**	**G5**	**G6**	**G7**	**G8**
Naphtalene	0.36	0.30	0.27	0.68	0.60	1.35	1.68	1.07
Acenaphtalene	0.02	0.02	0.03	0.08	0.11	0.12	0.37	2.08
Acenaphthene	0.05	0.04	0.03	0.08	0.14	0.21	0.26	0.76
Fluorene	0.20	0.14	0.20	0.75	0.78	1.46	2.34	4.29
Phenanthrene	1.04	0.51	2.24	1.45	5.31	1.85	2.90	5.88
Anthracene	0.05	0.02	0.09	0.06	0.05	0.03	0.13	0.49
Fluoranthene	0.24	0.11	0.64	0.42	1.94	0.37	0.63	1.20
Pyrene	0.17	0.08	0.44	0.29	1.61	0.12	0.39	0.86
Benz[a]anthracene	0.02	0.00	0.09	0.02	0.12	0.00	0.01	0.01
Chrysene	0.04	0.00	0.16	0.04	0.27	0.00	0.03	0.01
Benzo[b]fluoranthene	0.00	0.00	0.01	0.00	0.11	0.00	0.00	0.00
Benzo[k]fluoranthene	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
Benzo[a]pyrene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Indeno[1,2,3-cd]pyrene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dibenzo[a,h]anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzo[g,h,i]perylene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total concentration	2.19	1.22	4.20	3.88	11.07	5.53	8.75	16.65

Table 8. Concentration of PAHs in particulate phase sampling from high-volume air sampler (ng/m^3)

Compounds	G1	G2	G3	G4	G5	G6	G7	G8
Naphtalene	0.11	0.11	0.13	0.12	0.17	0.12	0.14	0.19
Acenaphtalene	0.01	0.01	0.01	0.02	0.01	0.05	0.05	0.10
Acenaphthene	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02
Fluorene	0.02	0.03	0.02	0.05	0.04	0.07	0.06	0.11
Phenanthrene	0.14	0.22	0.14	0.45	0.17	1.06	1.33	2.39
Anthracene	0.01	0.01	0.01	0.02	0.02	0.65	0.06	0.13
Fluoranthene	0.22	0.39	0.23	0.51	0.13	1.12	1.77	2.87
Pyrene	0.16	0.29	0.18	0.40	0.11	0.76	1.32	2.12
Benz[a]anthracene	0.06	0.09	0.10	0.16	0.07	0.22	0.61	1.15
Chrysene	0.16	0.28	0.19	0.37	0.09	0.63	1.39	2.29
Benzo[b]fluoranthene	0.13	0.38	0.35	0.55	0.23	0.70	1.96	2.71
Benzo[k]fluoranthene	0.03	0.09	0.09	0.13	0.07	0.16	0.45	0.65
Benzo[a]pyrene	0.08	0.19	0.16	0.31	0.10	0.30	0.97	1.51
Indeno[1,2,3-cd]pyrene	0.08	0.23	0.19	0.32	0.16	0.34	1.04	1.47
Dibenzo[a,h]anthracene	0.01	0.03	0.03	0.04	0.03	0.04	0.13	0.19
Benzo[g,h,i]perylene	0.06	0.17	0.13	0.23	0.11	0.24	0.74	1.01
Total concentration	1.29	2.55	1.97	3.68	1.51	6.49	12.03	18.91

Table 9. Total concentration of PAHs in atmosphere (gaseous phase + particulate pahse) sampling from high-volume air sampler (ng/m^3)

Compounds	**G1**	**G2**	**G3**	**G4**	**G5**	**G6**	**G7**	**G8**
Naphtalene	0.48	0.42	0.40	0.80	0.77	1.47	1.82	1.26
Acenaphtalene	0.03	0.03	0.04	0.10	0.11	0.17	0.42	2.18
Acenaphthene	0.05	0.04	0.04	0.09	0.15	0.23	0.28	0.78
Fluorene	0.22	0.17	0.22	0.80	0.81	1.53	2.40	4.41
Phenanthrene	1.18	0.72	2.38	1.90	5.47	2.92	4.23	8.27
Anthracene	0.06	0.03	0.10	0.09	0.07	0.68	0.19	0.62
Fluoranthene	0.45	0.50	0.88	0.92	2.07	1.49	2.39	4.08
Pyrene	0.33	0.37	0.62	0.69	1.73	0.89	1.71	2.98
Benz[a]anthracene	0.08	0.10	0.19	0.18	0.19	0.22	0.62	1.16
Chrysene	0.20	0.28	0.34	0.42	0.36	0.63	1.43	2.30
Benzo[b]fluoranthene	0.13	0.38	0.36	0.55	0.34	0.70	1.96	2.71
Benzo[k]fluoranthene	0.03	0.09	0.09	0.13	0.09	0.16	0.45	0.65
Benzo[a]pyrene	0.08	0.19	0.16	0.31	0.10	0.30	0.97	1.51
Indeno[1,2,3-cd]pyrene	0.08	0.23	0.19	0.32	0.16	0.34	1.04	1.47
Dibenzo[a,h]anthracene	0.01	0.03	0.03	0.04	0.03	0.04	0.13	0.19
Benzo[g,h,i]perylene	0.06	0.17	0.13	0.23	0.11	0.24	0.74	1.01
Total concentration	3.48	3.77	6.17	7.56	12.58	12.02	20.79	35.56

We also investigated concentration according to PAH compounds. If their molecular weight is lighter, they have pattern which they preferred to distribute in gaseous phase than particulate phase. Previous study, about atmospheric PAHs, reveal that molecular weight is much heavier than 228 (molecular weight of Benzo(a)anthracene and chrysene), the PAH compounds are distributed in particulate phase, however lighter than this, they have higher concentration at gaseous phase. This study also showed got the similar results with other research. These behaviors can explain with physical and chemical properties of sampled PAHs. For example, PAHs have different range of their vapor pressures. Most of lower molecular weight PAHs have higher vapor pressures, thus they prefer to stay in gaseous phase. Whereas higher molecular weight PAHs has lower vapor pressures, thus they were mainly associated to particulates. Therefore, the PAHs distribution profiles in atmosphere were dissimilar to each other. Figure 6 are showing the distribution pattern of PAH according to their compounds.

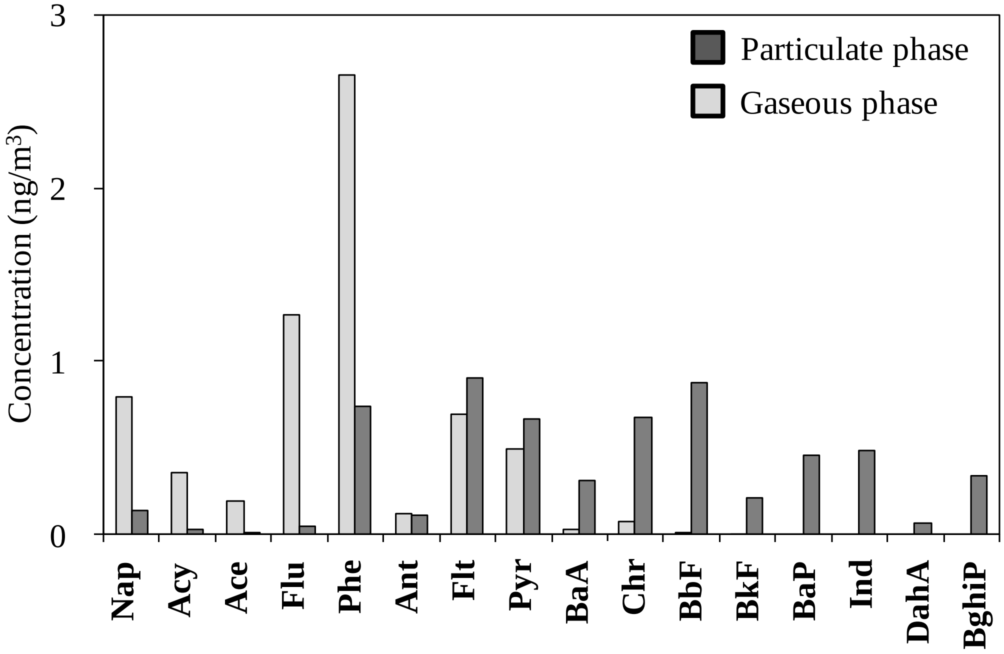


Figure 20. Distribution patterns of PAHs at each compouns obtained from active air sampling.

III. Passive air sampling

Eight groups were passively sampled in this study using a newly developed air sampler. We separately collected the samples by particulate phase and gaseous phase PAHs. In Figure 8, the total concentrations of PAHs are shown. All samples were collected by duplicated samples, and we calculated the concentration by averaging that of samples. For determining uptake rate, we changed sampling period at each groups. First group was collected during 15 days, second group was sampled 30 days. Adding like this, there are eight groups which sampling period is 15 days to 120 days. Results have tendency that as increasing their sampling period, the concentrations were also increased. There are high relationships between total concentrations of PAHs and sampling period. The total concentrations of PAHs were much higher in gaseous phase at every group.

We didn't investigate the difference of concentrations between newly developed samplers and Harner's PUF-PAS, however we found that the newly developed passive air sampler get much lower interference by particulate phase. Harner's PUF-PAS can observe only gaseous phase PAHs, but they can be affected some particulate in the atmosphere. So by developing this sampler, we can increase the reliance of gaseous phase atmospheric concentration of SVOCs.

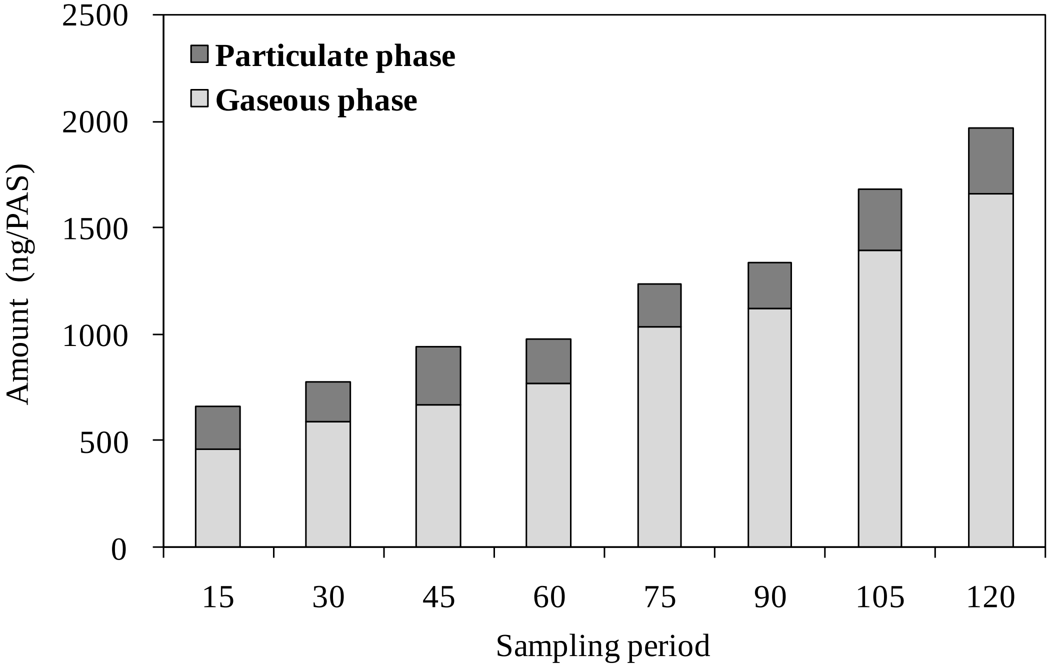


Figure 21. Total concentration of PAHs sampled by passive air sampler

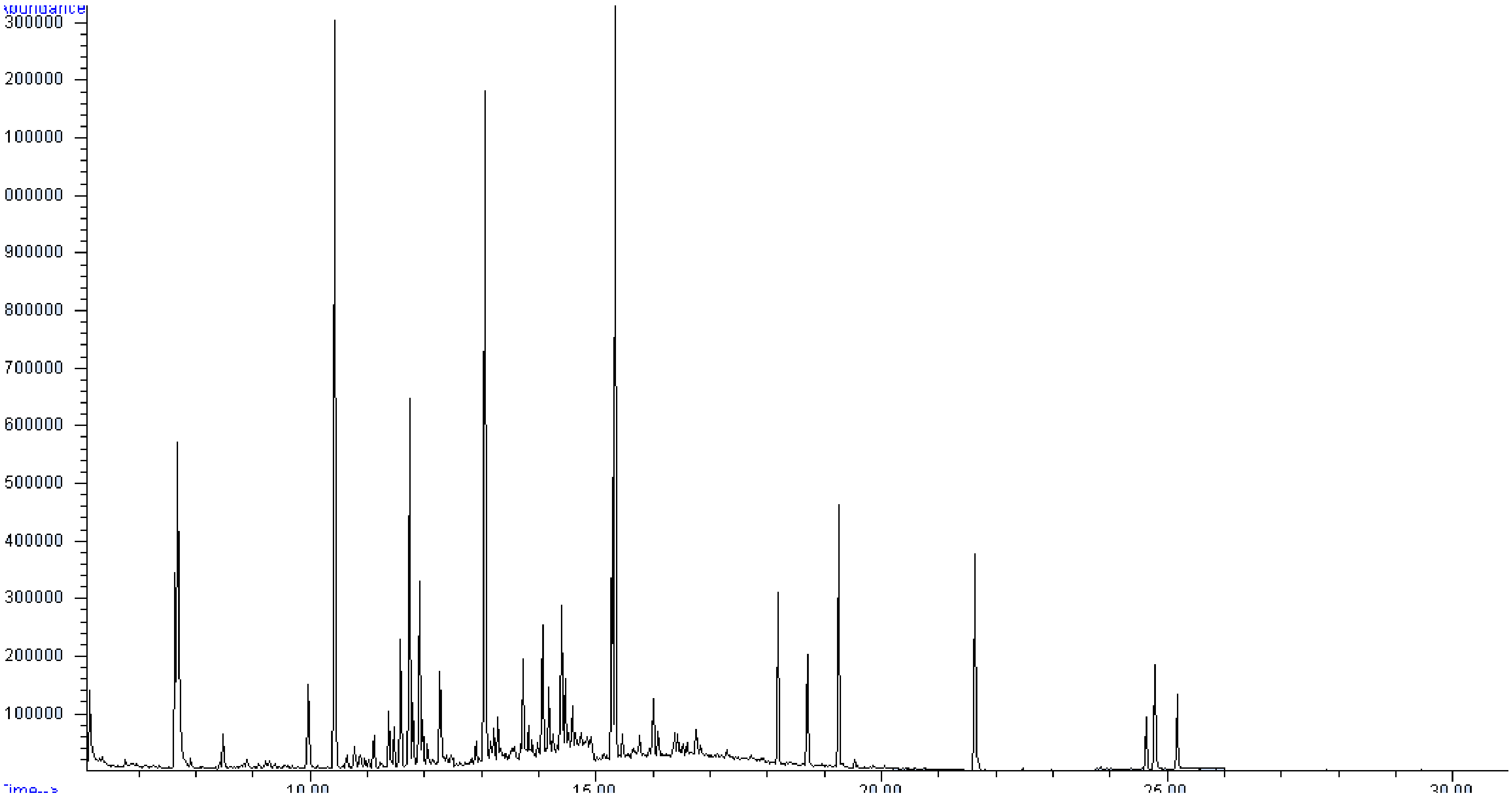


Figure 22. General PAH chromatogram obtained from filter sample (particulate phase PAHs)

Table 10. Concentration of PAHs in gaseous phase sampling by passive air sampler (ng/m^3)

Sampling period (day)	15	30	45	60	75	90	105	120
Naphtalene	274.4	320.7	378.7	366.2	528.5	561.0	705.3	849.4
Acenaphtalene	9.2	10.6	11.0	8.3	16.8	9.9	8.7	7.6
Acenaphthene	17.4	22.5	26.4	34.0	44.4	46.4	47.8	55.0
Fluorene	33.4	50.9	58.5	72.0	103.4	115.7	126.4	170.3
Phenanthrene	93.9	134.7	141.9	201.1	245.4	278.4	358.2	410.6
Anthracene	7.9	9.7	9.2	10.3	11.3	11.5	13.4	12.5
Fluoranthene	15.4	22.7	26.6	46.5	50.0	60.6	78.9	91.9
Pyrene	9.8	15.3	18.0	30.7	31.0	36.6	47.8	48.6
Benz[a]anthracene	2.6	2.7	2.1	2.7	3.0	3.1	3.3	4.2
Chrysene	0.0	0.0	0.0	0.7	1.3	0.2	4.2	6.3
Benzo[b]fluoranthene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Benzo[k]fluoranthene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzo[a]pyrene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Indeno[1,2,3-cd]pyrene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.4
Dibenzo[a,h]anthracene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzo[g,h,i]perylene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total concentration	464.0	589.7	672.5	772.5	1035.0	1123.6	1393.9	1659.9

Table 11. Concentration of PAHs in particulate phase sampling by passive air sampler (ng/m^3)

Sampling period (day)	15	30	45	60	75	90	105	120
Naphthalene	121.6	107.4	157.7	110.9	101.0	93.8	87.5	109.3
Acenaphtylene	4.2	3.7	4.8	3.9	3.8	3.7	5.4	5.8
Acenaphthene	4.6	4.4	5.1	4.5	4.6	4.6	6.5	6.2
Fluorene	15.7	16.3	16.8	14.9	14.0	12.8	12.2	11.3
Phenanthrene	37.0	37.5	46.9	37.5	35.7	38.7	66.6	67.0
Anthracene	6.9	6.9	7.7	6.9	7.1	7.1	8.7	8.4
Fluoranthene	1.2	3.4	8.5	5.1	6.6	10.9	30.0	30.3
Pyrene	0.1	1.6	4.7	2.8	5.0	6.3	18.8	16.2
Benz[a]anthracene	3.1	3.5	4.3	4.2	5.3	6.0	7.7	7.0
Chrysene	0.0	0.0	2.0	1.6	4.4	5.9	11.4	12.1
Benzo[b]fluoranthene	0.0	0.0	0.0	0.0	1.1	3.3	5.5	7.3
Benzo[k]fluoranthene	0.0	0.0	1.3	0.7	2.3	3.1	3.5	1.6
Benzo[a]pyrene	0.0	3.4	7.1	8.2	8.7	10.5	10.7	10.7
Indeno[1,2,3-cd]pyrene	0.2	1.4	2.7	3.4	3.3	5.7	6.8	6.8
Dibenzo[a,h]anthracene	0.0	0.0	0.0	0.0	0.0	0	2.0	1.8
Benzo[g,h,i]perylene	0.0	0.0	0.0	0.0	0.0	2.7	4.2	4.3
Total concentration	194.7	189.3	269.6	204.7	202.8	1698.2	287.6	306.3

Table 12. Total concentration of PAHs in atmosphere (gaseous phase + particulate pahse) sampling by passive air sampler (ng/m^3)

Sampling period (day)	**15**	**30**	**45**	**60**	**75**	**90**	**105**	**120**
Naphtalene	396.0	428.1	536.4	477.2	629.5	654.8	792.8	958.7
Acenaphtylene	13.4	14.3	15.8	12.2	20.7	13.6	14.1	13.4
Acenaphthene	22.0	26.9	31.5	38.5	49.0	51.0	54.3	61.2
Fluorene	49.1	67.2	75.3	86.9	117.3	128.5	138.6	181.6
Phenanthrene	130.9	172.2	188.8	238.6	281.0	317.2	424.7	477.7
Anthracene	14.8	16.6	16.9	17.2	18.3	18.6	22.0	20.9
Fluoranthene	16.6	26.1	35.2	51.6	56.6	71.6	108.9	122.2
Pyrene	10.0	16.8	22.7	33.5	36.0	43.0	66.6	64.8
Benz[a]anthracene	5.7	6.2	6.4	6.9	8.3	9.0	11.0	11.2
Chrysene	0.0	0.0	2.0	2.3	5.8	6.2	15.6	18.4
Benzo[b]fluoranthene	0.0	0.0	0.0	0.0	1.1	3.3	5.5	7.4
Benzo[k]fluoranthene	0.0	0.0	1.3	0.7	2.3	3.1	3.5	1.6
Benzo[a]pyrene	0.0	3.4	7.1	8.2	8.7	10.5	10.7	10.7
Indeno[1,2,3-cd]pyrene	0.2	1.4	2.7	3.4	3.3	5.7	6.8	10.2
Dibenzo[a,h]anthracene	0.0	0.0	0.0	0.0	0.0	0.0	2.0	1.8
Benzo[g,h,i]perylene	0.0	0.0	0.0	0.0	0.0	2.7	4.2	4.3
Total concentration	658.7	779.1	942.0	977.2	1237.8	1338.7	1681.5	1966.2

The overall pattern of PAHs was similar to results obtained from active air sampling. Heavier molecular weight PAHs were distributed in particulate phase than gaseous phase, otherwise lighter PAHs were more distributed in gaseous phase. From the results, we can confirm the separating ability of passive air sampler. In Figure 10, we compared the concentration of gaseous phase PAH with that of particulate phase according to their compounds. The sampling period was different to each other, thus we divided all the concentration of PAH with sampling period. By conducting this step, we can normalize the concentration. However, sample which deployed short time was not sufficient for analyzing especially particulate phase. That means the concentrations of particulate phase PAHs are negatively calculated. Thus the difference of distributional pattern is larger than results which are showing Figure 23.

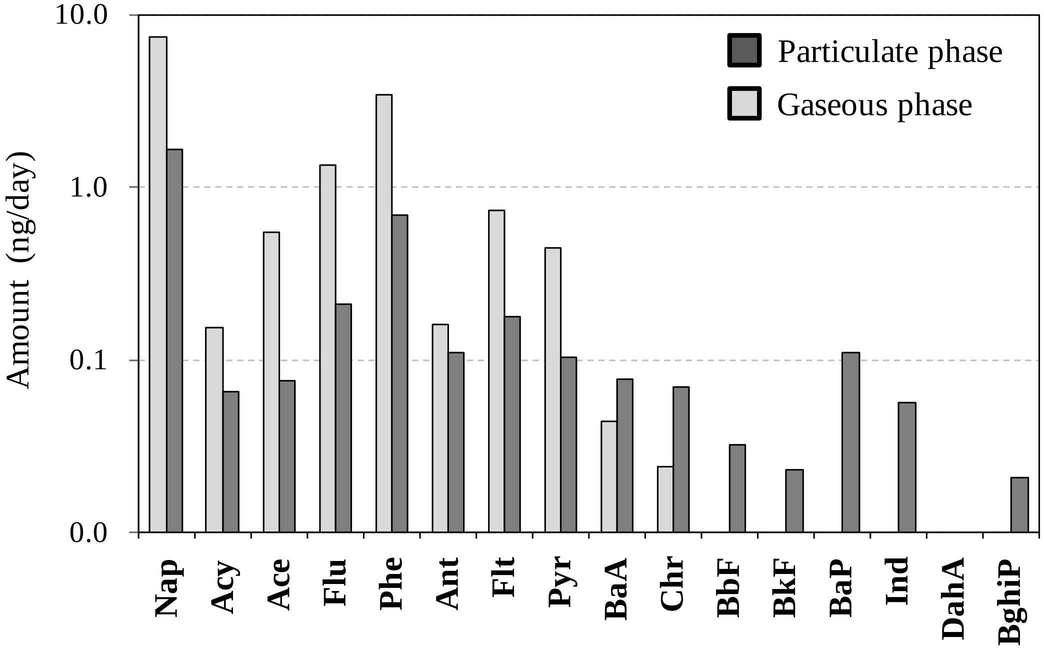


Figure 23. Distribution patterns of PAHs at each compouns obtained from passive air sampling.

IV. Uptake rate study

4.1. Passive air sampler chemical accumulation trends

4.1.1. Gaseous phase PAHs

In passive air sampling study, atmospheric samples have to be collected during linear uptake periods. Thus investigation of linear uptake period is important in this study area. We calculated the linear uptake period, and showed in Figure 24-25. Among the EPA 16 priority PAHs, only eight compounds were shown linearity during 120 days. The other eight PAHs were not detected in the sampled PUF or not shown linearity. The most of detected samples were not leached at equilibrium stage during 120 days. The amounts of PAHs were increased according to increasing sampling period. Among the 16 target PAHs, eight PAHs have linearity with positive correlation value (R^2>0.5). Lighter molecular weight have high linearity, thus this sampler is appropriate for collecting lighter SVOCs which is more distributed in gaseous phase. Most of detected PAHs show linearly increasing properties during four months, from this results we concluded that this newly developed PAHs were appropriate for observing seasonal distribution.

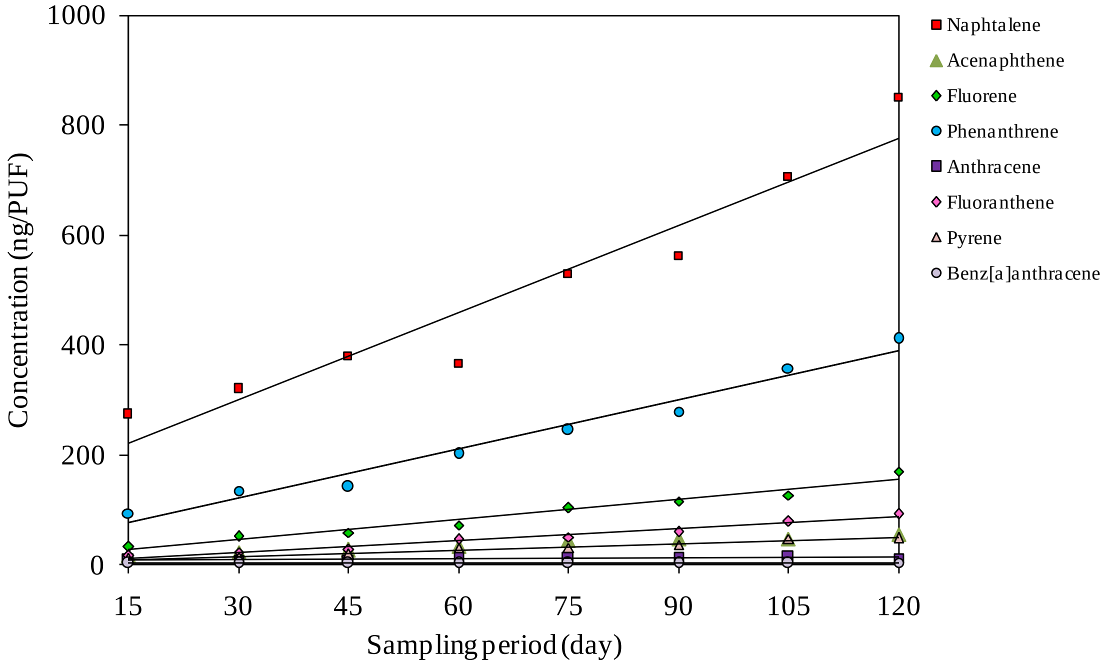


Figure 24. Uptake profiles of PAHs especially eight compounds which were showed linearity.

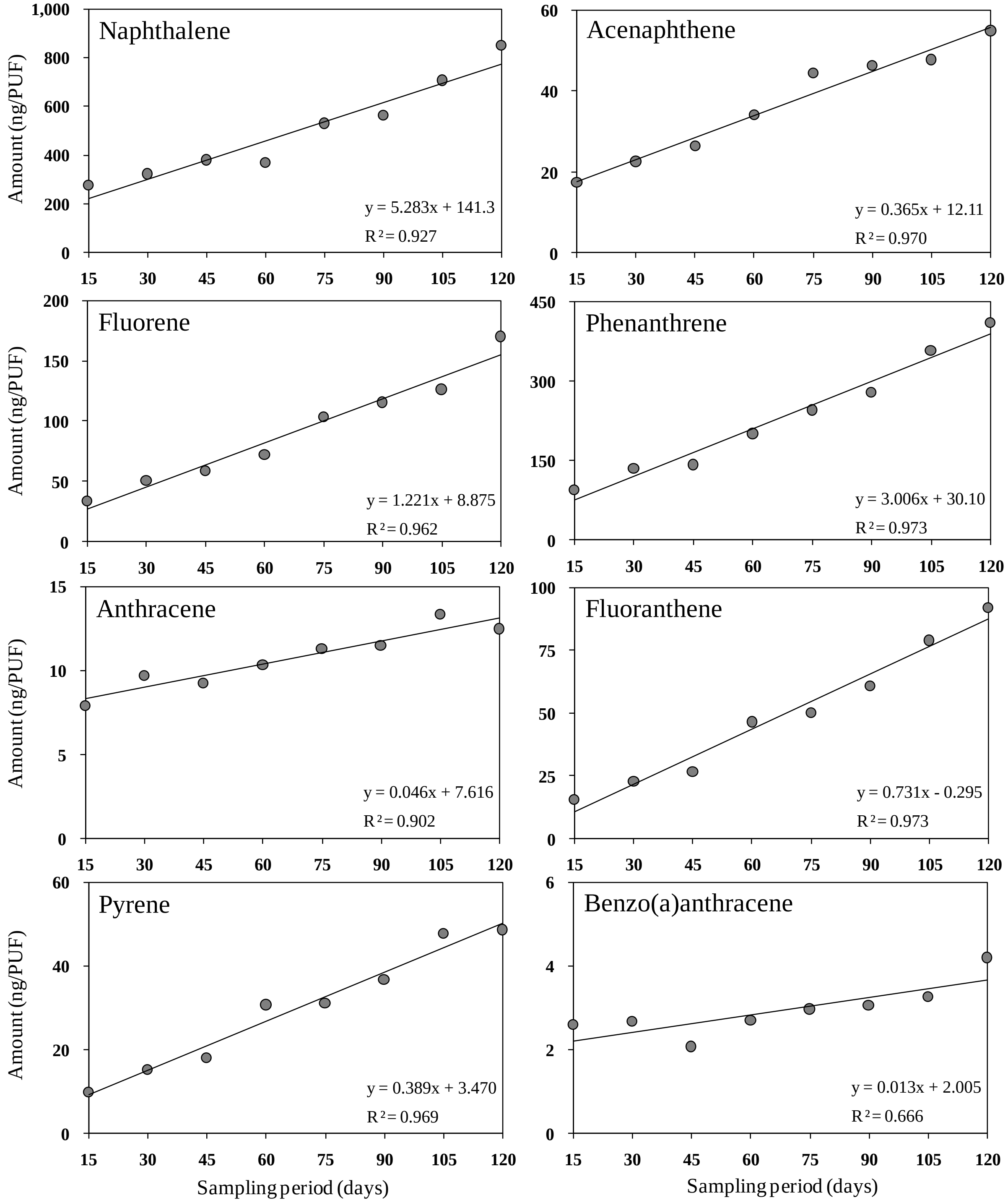


Figure 25. Passive sampler uptake profiles of individual PAHs which shows linearity during sampling period

4.1.2. Particulate phase PAHs

We verified linear uptake properties of newly developed passive air sampler. In previous study, most samplers could capture gaseous phase SVOCs, however in this study, we confirmed the linearity of sampling in particulate phase PAHs. The amounts of PAHs were increased according to increasing sampling period. In particulate phase, there were shown linearity in 13 PAH compounds. Naphthalene, acenaphthylene didn't have linearity in particulate phase. Naphthalene and acenaphthylene have distributed tendency which is more resided in gaseous phase because of its volatility. That of chemical properties leaded these results. Fluorene also didn't show the linearity. That compounds have negative correlation. We could not reveal this reason. Other 13 PAHs showed positive correlation between sampling period and uptake amount (R^2>0.5). However among the 13 PAHs, some compounds have uncertainty. Chrysene was detected when were sampling period above 45 days. Benzo[b]fluoranthene was detected after 75 sampling days. Dibenzo[a,h]anthracene were detected after 105 days. This sampler is suitable for collecting particulate phase SVOCs however more practice for increasing ability of collection will be needed. To sum up, this sampler appropriate for collecting particulate phase SVOCs, as well as gaseous phase SVOCs. Figure 26 are showing all the results of compounds which is having positive correlation. Figure 27 are shown correlation of individual PAH.

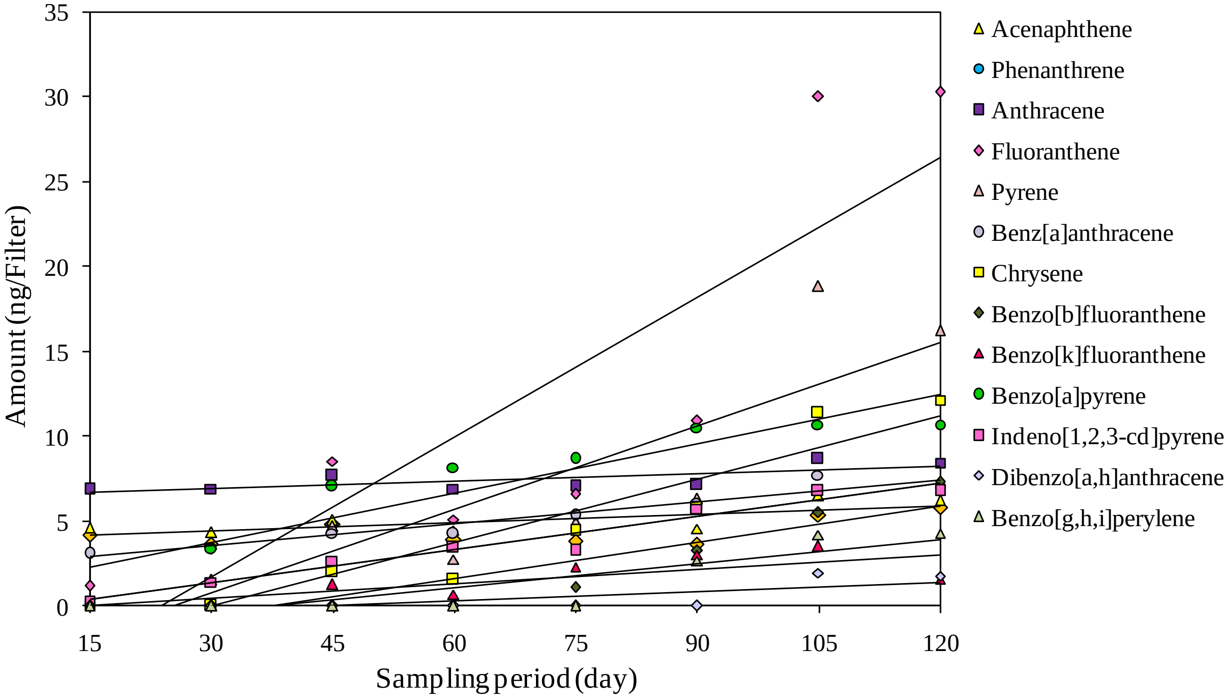
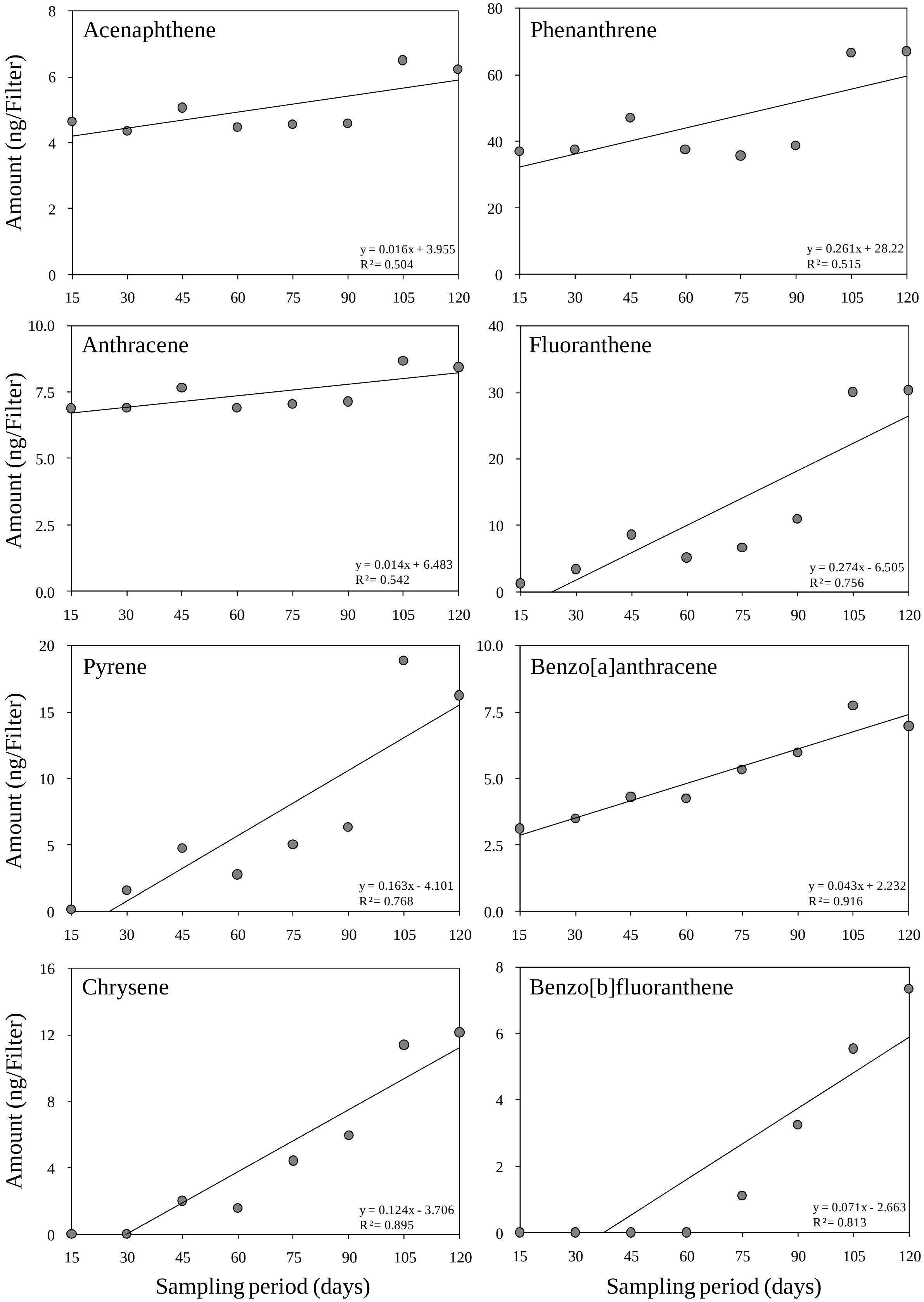


Figure 26. Passive sampler uptake profiles of particulate 14 PAHs


Acenaphthene
y = 0.016x + 3.955
R²= 0.504
Phenanthrene
y = 0.261x + 28.22
R²= 0.515
Anthracene
y = 0.014x + 6.483
R²= 0.542
Fluoranthene
y = 0.274x - 6.505
R²= 0.756
Pyrene
y = 0.163x - 4.101
R²= 0.768
Benzo[a]anthracene
y = 0.043x + 2.232
R²= 0.916
Chrysene
y = 0.124x - 3.706
R²= 0.895
Benzo[b]fluoranthene
y = 0.071x - 2.663
R²= 0.813
Amount (ng/Filter)
Sampling period (days)
15
30
45
60
75
90
105
120
0
2
4
6
8
20
40
60
80
0.0
2.5
5.0
7.5
10.0
10
30
5
15
12
16

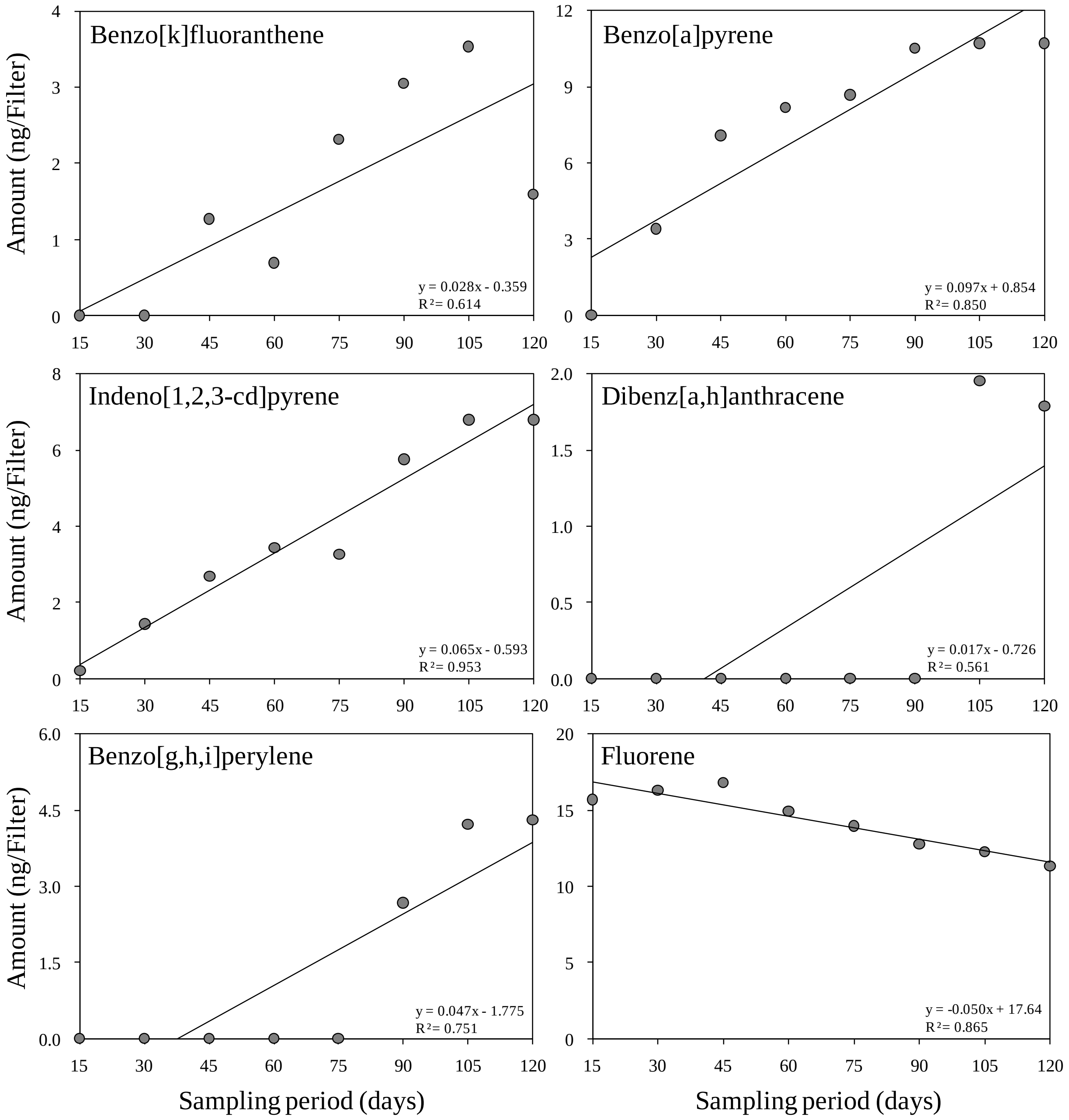


Figure 27. Passive sampler uptake profiles of individual PAHs which shows linearity during sampling period

4.2. Uptake rates

The accumulation of chemical by a passive air sampler can be needed the rate of accumulation during linear uptake period. There are many methods for calculating the uptake rate. Among that we calculated uptake rate by following equation.

$$\mathrm{R} = \frac{\mathrm{C_{PAS}}}{\mathrm{C_{Air}} \times \mathrm{Time}}$$

C_{Air}: Concentration of SVOCs in the atmosphere

C_{PAS}: Amount of SVOCs in an PAS

R: Uptake rate

T: Deployment period

For the calculation, we suppose that actual concentrations of PAHs (C_{Air}) were same with concentrations obtained from active air sampling. In this study, we sampled 8 times, thus we averaged the concentrations obtained from active air samplers during deployed period. For instance, passive air sampler, which deployed during 15 days, were adopted the average of G1 from active air sampling. Otherwise, uptake rate which had sampled during 120 days were calculated with using the average of G1 to G8. The unit of uptake rate is [m^3/day], and this value gives the information how much atmosphere volume can pass in the sampler. Consequently, for calculating concentration in atmosphere, newly developed passive air sampler has to suggest the uptake rate.

4.2.1. Gaseous phase PAHs

Uptake rate can be calculated only in linear sampling period. In this study, there are eight PAHs which show the linearity during sampling period. Thus, we calculate the sampling period for eight compounds in gaseous phase. Table 13 is showing the average PAH concentrations which were used for calculation of uptake rate. The averaging concentrations have increasing tendency according to going to winter. The calculated uptake rates were different to each compound. Also the uptake rates were different to their sampling period. They have a decreasing tendency of uptake rate as the sampling days were larger. The results of uptake rates were shown in Figure 23. We supposed that in first time of sampling period, target compounds were captured in adsorption materials, PUF, and these were leached in first equivalent stage. After that the other compounds are additionally captured at adsorbent (PUF). We concluded and suggested the uptake rate by average of eight uptake rate in this study, however additional study for the first adsorption is needed. However for additional application, we have firstly want to know the uptake rate, thus in this study, we suggested and concluded the uptake rate by averaging the eight value of uptake rate. Uptake rate of each sampler is like that: Naphthalene: 21 m^3/day, Acenaphthene: 11 m^3/day, Fluorene: 5 m^3/day, Phenanthrene: 3 m^3/day, Anthracene: 4 m^3/day, Fluoranthene: 2 m^3/day, Pyrene: 2 m^3/day, Benzo[a]anthracene: 3 m^3/day. More light PAHs have large uptake rate than heavier PAHs.

Table 13. Uptake rate of passive sampler in gaseous phase PAHs. (m^3/day)

Sampling period (day)	**15**	**30**	**45**	**60**	**75**	**90**	**105**	**120**
Naphtalene	0.36	0.33	0.31	0.40	0.44	0.60	0.75	0.79
Acenaphtylene	0.02	0.02	0.03	0.04	0.05	0.06	0.11	0.35
Acenaphthene	0.05	0.04	0.04	0.05	0.07	0.09	0.12	0.20
Fluorene	0.20	0.17	0.18	0.32	0.41	0.59	0.84	1.27
Phenanthrene	1.04	0.77	1.26	1.31	2.11	2.07	2.19	2.65
Anthracene	0.05	0.03	0.05	0.06	0.06	0.05	0.06	0.12
Fluoranthene	0.24	0.17	0.33	0.35	0.67	0.62	0.62	0.69
Pyrene	0.17	0.12	0.23	0.25	0.52	0.45	0.44	0.50
Benz[a]anthracene	0.02	0.01	0.04	0.03	0.05	0.04	0.04	0.03
Chrysene	0.04	0.02	0.07	0.06	0.10	0.09	0.08	0.07
Benzo[b]fluoranthene	-	-	-	-	0.02	0.02	0.02	0.02
Benzo[k]fluoranthene	-	-	-	-	-	-	-	-
Benzo[a]pyrene	-	-	-	-	-	-	-	-
Indeno[1,2,3-cd]pyrene	-	-	-	-	-	-	-	-
Dibenz[a,h]anthracene	-	-	-	-	-	-	-	-
Benzo[g,h,i]perylene	-	-	-	-	-	-	-	-

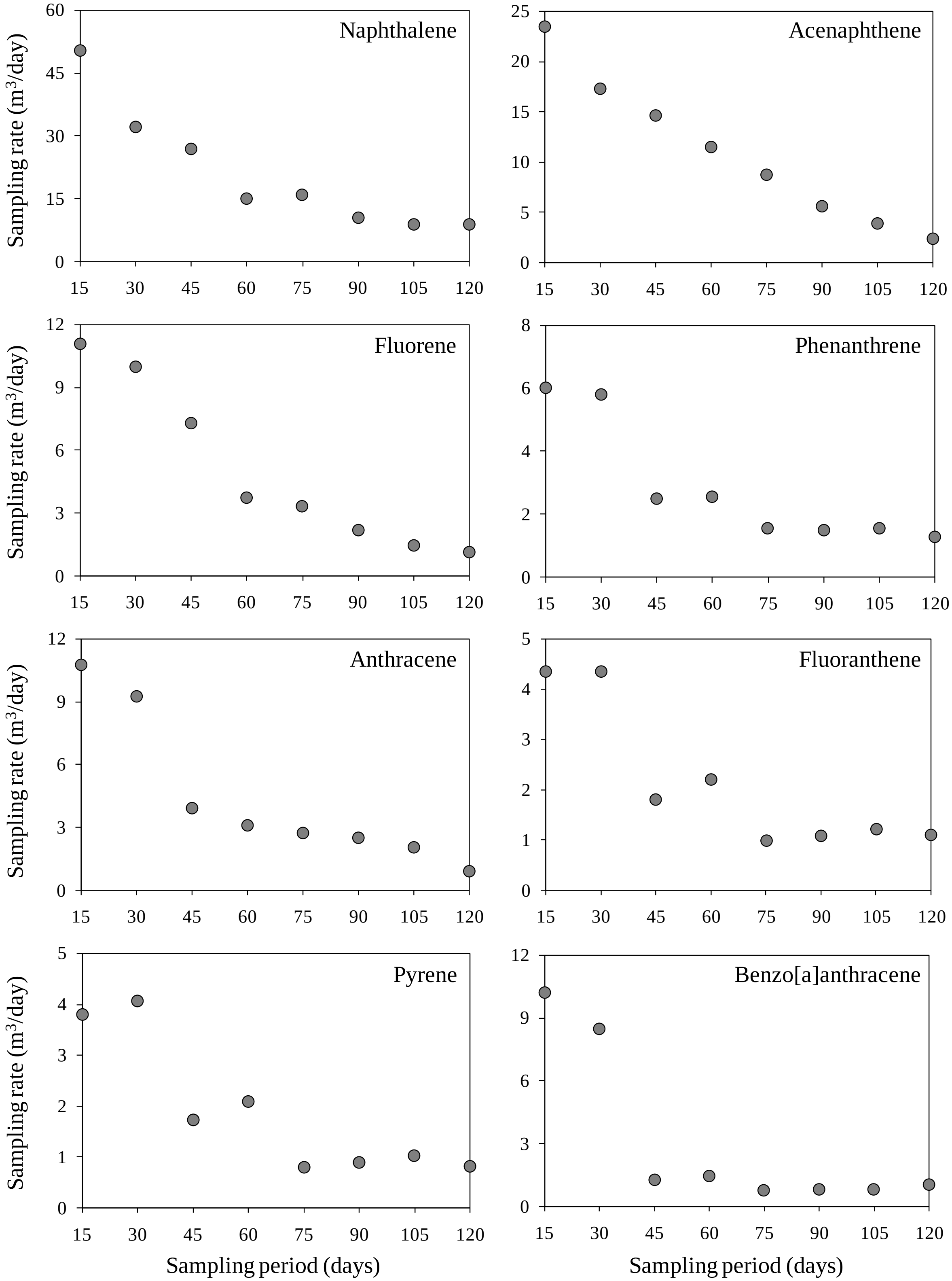


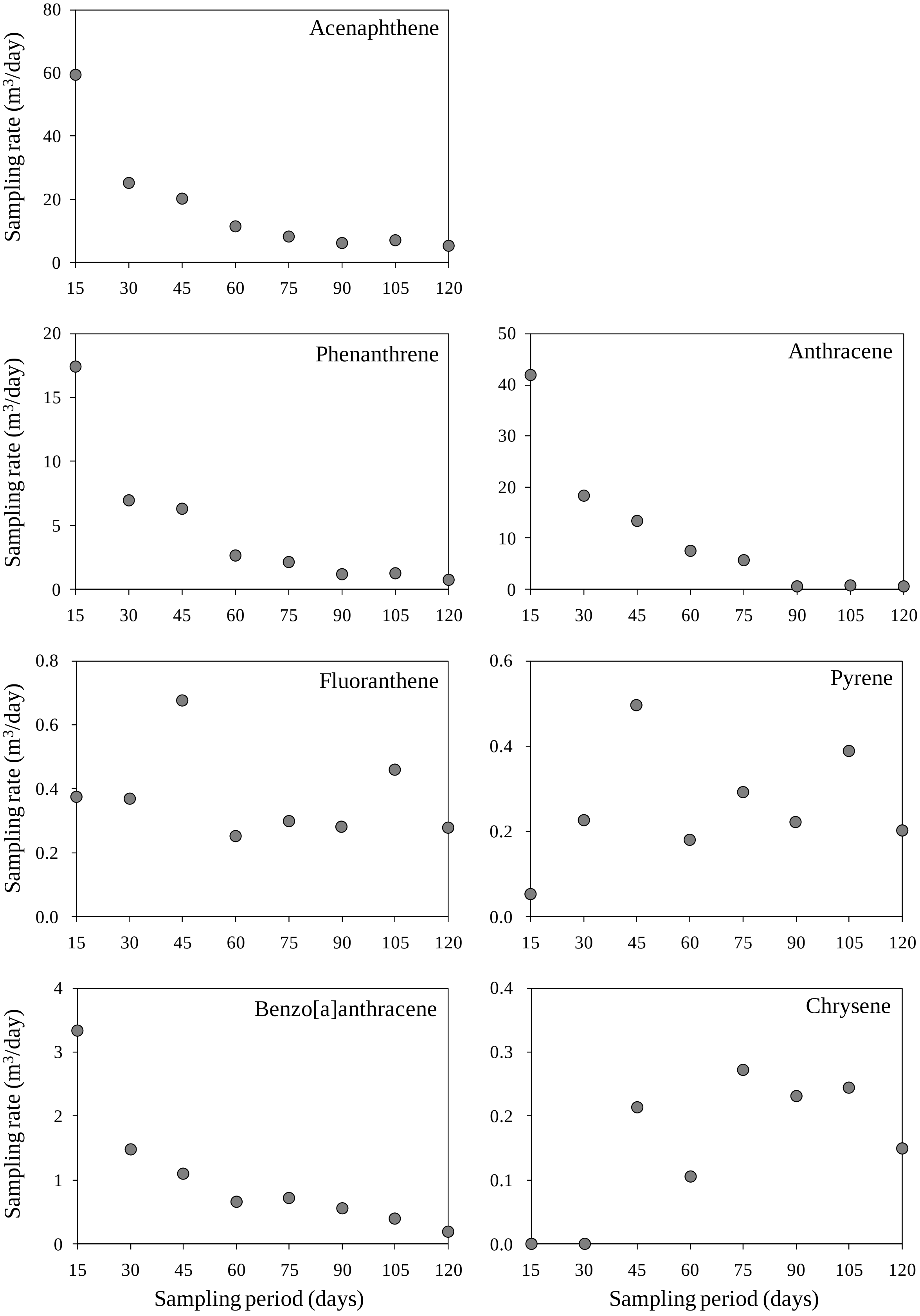
Figure 28. Uptake rate of passive sampler in gaseous phase PAHs which have linearity during sampling period

4.2.2. Particulate phase PAHs

Uptake rate of particulate phase PAHs were calculated from results of samples collected from GFF in passive air sampler. Same as gaseous phase, uptake rate can be calculated only in linear sampling period. In this study, there are 13 PAHs which have the linearity during sampling period. Thus, we calculated the sampling period for 13 PAH compounds in particulate phase. However among the 13 compounds, some compounds (Chrysene, Benzo[a]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenzo[a,h]anthracene, Benzo[g,h,i]perylene) were not detected in some samples, thus we only calculated uptake rate from only detected samples. For instance, uptake rate of dibenz[a,h]anthracene are obtained from averaging two uptake rates which obtained from 105 days of deployment and 120 days of deployment of passive air sampler. Table 14 is shown the average PAH concentrations used for calculation of uptake rate. The average concentrations have increasing tendency according to the season going to winter. The calculated uptake rates were different to each compound. Also the uptake rates were different to their sampling period. They showed a decreasing tendency of uptake rate as the sampling days were increasing. However some compounds didn’t have these tendencies. The results of uptake rates were shown in Figure 29. Uptake rate of particulate phase PAHs are shown slightly lower value than that of gaseous phase PAHs. Thus, effort is needed for increasing the efficiency of sampling. We suggest the uptake rate of particulate phase PAHs. However, after increasing the capturing ability, additional investigation have to be conducted for particulate phase PAHs Averaging calculated uptake rates of each compounds had values, Acenaphthene: 18 m^3/day, Phenanthrene: 4.8 m^3/day, Anthracene: 11 m^3/day, Fluoranthene: 0.37 m^3/day, Pyrene: 0.26 m^3/day, Benzo[a]anthracene: 1.1 m^3/day, Chrysene: 0.20 m^3/day, Benzo[b]fluoranthene: 0.073 m^3/day, Benzo[k]fluoranthene: 0.26 m^3/day, Benzo[a]pyrene: 0.64 m^3/day, Indeno[1,2,3-cd]pyrene: 0.24 m^3/day, Dibenz[a,h]anthracene: 0.33 m^3/day, Benzo[g,h,i]perylene: 0.15 m^3/day.

Table 14. Uptake rates of passive sampler in particulate phase PAHs. (m^3/day)

Sampling period (day)	**15**	**30**	**45**	**60**	**75**	**90**	**105**	**120**
Naphthalene	121.58	107.38	157.72	110.93	100.97	93.84	87.50	109.27
Acenaphtylene	4.22	3.68	4.81	3.95	3.85	3.68	5.36	5.82
Acenaphthene	4.64	4.35	5.07	4.47	4.56	4.58	6.50	6.22
Fluorene	15.67	16.28	16.77	14.90	13.95	12.78	12.23	11.31
Phenanthrene	37.00	37.51	46.93	37.47	35.65	38.73	66.57	67.04
Anthracene	6.89	6.91	7.66	6.91	7.06	7.14	8.66	8.44
Fluoranthene	1.21	3.36	8.54	5.11	6.63	10.94	30.04	30.30
Pyrene	0.13	1.56	4.72	2.77	5.01	6.35	18.84	16.24
Benz[a]anthracene	3.12	3.48	4.30	4.24	5.33	5.98	7.74	6.96
Chrysene	-	-	2.00	1.58	4.42	5.94	11.39	12.15
Benzo[b]fluoranthene	-	-	-	-	1.12	3.25	5.54	7.35
Benzo[k]fluoranthene	-	-	1.27	0.69	2.32	3.05	3.53	1.59
Benzo[a]pyrene	-	3.40	7.07	8.19	8.67	10.52	10.70	10.71
Indeno[1,2,3-cd]pyrene	0.21	1.43	2.69	3.44	3.26	5.75	6.79	6.79
Dibenz[a,h]anthracene	-	-	-	-	-	-	1.95	1.79
Benzo[g,h,i]perylene	-	-	-	-	-	2.67	4.21	4.31


Acenaphthene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo[a]anthracene
Chrysene
Sampling rate (m^3/day)
Sampling period (days)
15
30
45
60
75
90
105
120
0
20
40
60
80
5
10
15
50
0.0
0.2
0.4
0.6
0.8
0.1
0.3
1
2
3
4

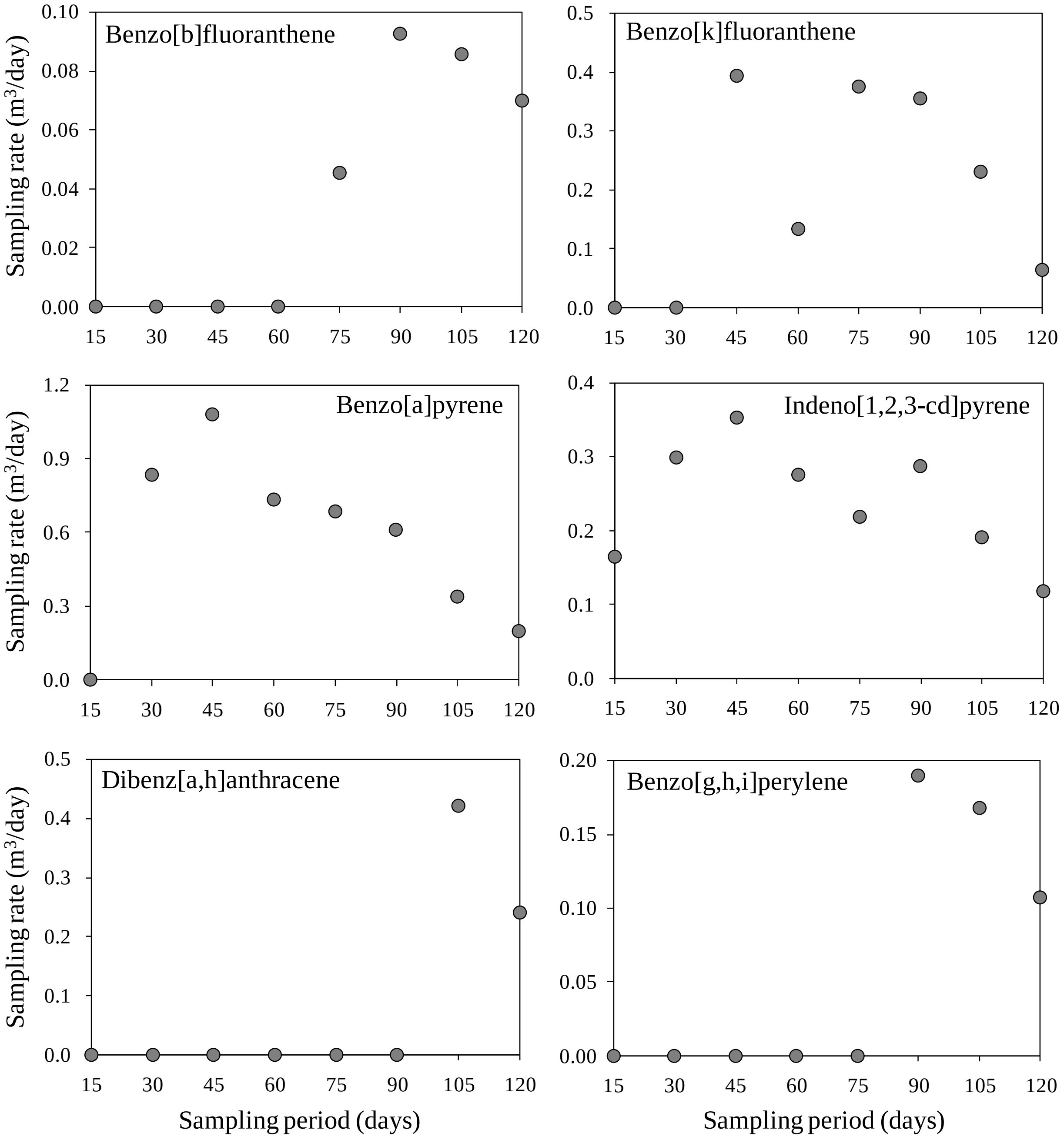


Figure 29. Uptake rates of passive sampler in particulate phase PAHs which have linearity during sampling period

Chapter 4. Conclusions

In this study, we developed new passive air sampler which considered weakness of preceding air sampler. Newly developed sampler can collect both gaseous and particulate phase SVOCs. For increasing efficiency of collection, the bottom part of the sampler is movable. To verify the sampler's ability, we selected PAHs among SVOCs as target compounds. The samplers (n=16) were set up and deployed over a 120 days period at outdoor sites in Ulsan. After deployment 2 samplers were periodically recovered after 15 days. Thus we could get total 8 points of the concentration. For knowing the real states of the sampling sites, we also monitoring the air using the active air samplers. By comprising both passively and actively obtained results, we could get the uptake rates of newly developed passive air samplers. Passively and actively collected results was having very similar patterns of distribution, thus we could convince the ability of the samplers.

In gaseous phase PAHs, among the 16 PAHs, eight PAHs were showed the linearity (R2>0.50). Mainly lighter compounds were having the linearity. In particulate phase total 13 compounds have the linearity (R2>0.50), however some compounds (benzo[b]fluoranthene, dibenz[a,h]anthracene, benzo[g,h,i]perylene) were not sufficient for analysis. In other words, some heavy compounds have a large error in validation results.

The obtained uptake rates of the each compound are 2 ng/m^3 ~ 21 ng/m^3 in gaseous phase PAHs which had a linearity during 120 days. Lighter PAHs had a tendency of smaller uptake rates than heavier PAHs. In this study, we calculated uptake rates of all the 8 groups of samples. We suggest that the uptake rates are averaged value of 8 groups, however the deviation of the each sampler is very large. Thus we also suggest to user that sometimes they use latest value (obtained from 120 days of sampling). The reason is most of compounds are leached the equilibrium after passing some sampling periods.

The uptake rates of particulate phase PAHs are 0.073 ng/m^3 to 18 ng/ m^3. They also showed the equilibrated patterns similar to gaseous phase. There were tendency that heavier compounds have lower value of uptake rates. Generally, the particulate PAHs have lower uptake rates than gaseous phase PAHs.

This study could verify the ability of developed passive air samplers, however we also found some weakness of the samplers. There were large variation among the sampling days, especially results from short time sampling showed large value of uptake rates compared to other results. From that results, we guess that there are second equilibrium steps. Firstly they reached the equilibrium before 15 days of sampling, after that the increased the concentration and leached second equilibrium. However we only investigated the second equilibrium, thus there are large values of intercept in graph (concentration versus sampling periods). Thus we have to further study about these things.

Somehow the newly developed passive air sampler can collect both gaseous phase and particulate phase SVOCs and we confirmed the ability of the sampling. We expect that this sampler will be helpful for assessing the correct air quality.

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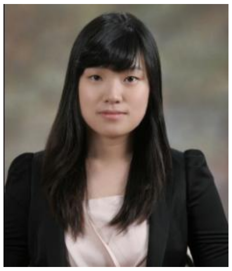
Curriculum Vitae (January 2013)



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Publications in International Journals

[1] Sung-Deuk Choi*, Hye-Ok Kwon, Yoon-Se Lee, **Eun-Jeong Park**, Joo-Yeon Oh, "Improving the spatial resolution of atmospheric polycyclic aromatic hydrocarbons using passive air samplers in a multi-industrial city", Journal of Hazardous Materials, 241–242, 252–258

[2] Eun-Jeong Park, Hye-Ok Kwon, Joo-Yeon Oh, Sung-Deuk Choi*, "Seasonal monitoring of polycyclic aromatic hydrocarbons in the Taehwa river in Ulsan, Korea", In preparation

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[1] 박은정, 권혜옥, 오주연, 최성득*, "태화강 수계의 다환방향족탄화수소 농도수준과 지리적 분포", 한국환경분석학회지 (2012) 15(3), 155-162

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Domestic Patents

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