

## PASSIVE AIR SAMPLING OF POPs ACROSS ASIA: POLYCYCLIC AROMATIC HYDROCARBONS

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### Introduction

Polycyclic aromatic hydrocarbons (PAHs) are mainly released into air as by products from incomplete combustion of fossil fuels or organic matter. PAHs have been recognized as carcinogens, mutagens and considered as one of persistent organic pollutants. Ideally, simultaneous measurements of air concentration in different locations are required to evaluate the relative importance of sources, atmospheric processes, and the long-range atmospheric transport potential of PAHs<sup>1,2</sup>. Such global spatial and temporal mapping studies could be on a range of scales, from around potential point sources, across cities, or even globally<sup>3,4</sup>. Concentrations of organic pollutants in air are traditionally obtained from samples collected by active samplings such as high-volume air sampler, which are expensive and require power source. Various studies have been used to evaluate passive air sampler (PAS) to overcome and complement the weakness of active sampler. PAS accumulate chemicals via diffusion and therefore do not require electricity. Semi-permeable membrane device, polyurethane foam (PUF) and XAD resin based sampler have been most widely tested and used PAS, among which PUF based PAS has been used for global monitoring of organic pollutants<sup>5,6,7</sup>.

Air pollution is one of major environmental concerns that many of the Asian nations paying for the rapid development seen in the past few decades. AMETEC is an APEC Marine Environmental Training and Education Center in KIOST, South Korea with the aim to transfer the current knowledge on the environmental sustenance to developing nations in Asia Pacific region. AMETEC has organized the three training workshops on the title "Passive Air Sampling: Long range transport of pollutants" from 2010 to 2012. Ten participants from 8 Asian countries including China, India, Indonesia, Malaysia, Micronesia, Philippines, Sri Lanka, Thailand and Vietnam participated this program. In order to understand air pollution in Asia, PUF-type passive air samplers used under the GAPS (Global Atmospheric Passive Sampling) Network were deployed and maintained by AMETEC trainees. Participants exposed the PAS for one to three months at the rural and urban surrounding in their countries (Fig. 1), then brought the PUF disks to KIOST to attend the workshop, and analyzed themselves with the assistance of KIOST staffs. The samples were used to measure PAHs and organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). In this paper, the contamination status and characteristics of PAHs in the Asian atmosphere were discussed.

### Materials and methods

#### Sample Collection

The PUF disk (14 cm diameter; 1.35 cm thick; surface area, 365 cm<sup>2</sup>; mass, 4.40 g; volume, 207 cm<sup>3</sup>; density, 0.0213 g cm<sup>-3</sup>) passive air sampler is housed in a stainless steel chamber consisting of two stainless steel domes ("flying saucer" design) that protect the foam disks from direct precipitation (rain), sunlight, and coarse particle deposition. Air is allowed to flow over the disk surface, entering the chamber through a ~2.5 cm gap between the two domes<sup>8</sup>.

Prior to exposure, PUF disks were precleaned by sequential Soxhlet extraction using mixed acetone and methanol (16 hrs) and then for another 16 hrs using petroleum ether. After cleaning, the PUF disks were desiccated under vacuum for removing of excess solvent. Prior to and after sample collection and during shipping, PUF disks were stored in solvent-rinsed, stainless steel (round) box having Teflon-lined lids. A total of 64 samplers were deployed successfully for 28-95 days (every year from June to October, 2010-2012) at 22

locations from 9 countries. Participants installed PASs in both urban and rural areas at each location. At the end of the deployment period, the disks were retrieved by the participants and stored at  $-20^{\circ}\text{C}$  until extraction. Previous studies have shown that the uptake of most non-polar hydrophobic chemicals by PUF disk samplers are air-side controlled with an initial linear sampling rate ranged between 3 to  $6\text{ m}^3\text{ day}^{-1}$ <sup>9,10,11,12</sup>. In this study we used a sampling rate for  $5\text{ m}^3\text{ day}^{-1}$ , recognizing that variability in this sampling rate will arise from site to site differences and analytical error.

#### *Chemical Analysis*

The PUF disks were spiked with surrogate PAHs standards (acenaphthene- $d_{10}$ , phenanthrene- $d_{10}$ , chrysene- $d_{12}$  and perylene- $d_{12}$ ) before extraction to assess recovery. The retrieved field-exposed PUF disks over 8 countries were simultaneously extracted using a soxhlet apparatus for 16 hrs with 240 ml of 1:1 DCM/hexane. The sample extracts were concentrated to 1 ml using rotary evaporator. To remove interfering species prior to the GC analysis, extracts were cleaned via column chromatography using a column packed with 20 g of silica gel (5% water) and 10 g of alumina (1% water); the samples were eluted with 100 ml of DCM. The samples were subsequently subjected to HPLC on an instrument equipped with a size-exclusion column. The eluted samples were concentrated and exchanged to 1 ml of hexane. The final volume was adjusted to 0.5 ml under a gentle stream of nitrogen. Terphenyl- $d_{14}$  was used as a GC internal standard. GC-MS analysis was performed on a Agilent 5890 gas chromatograph coupled with a Agilent 5972 mass-selective detector operated in the selective ion monitoring mode.

Laboratory and field blanks were extracted and analyzed in the same way as field samples, most of which satisfied the quality control guidelines (less than three times signal to noise ratio). Detection limits for target PAHs ranged from 0.05 to  $20\text{ ng m}^{-3}$ . The procedural recoveries of surrogate standards range from 62% (acenaphthene- $d_{10}$ ) to 93% (chrysene- $d_{12}$ ). The linearity of calibration standards were calculated by regression analysis with values ranging from 0.99 to 1.00 ( $r^2$ ) for PAHs.

#### **Results and discussion**

The spatial and temporal distribution of atmospheric 15 PAHs and alkylated PAHs using PAS were shown at Fig. 1. Concentrations of 15 PAHs in urban air were in the ranges of  $20.1 - 93.7\text{ ng m}^{-3}$  (average value:  $51.3\text{ ng m}^{-3}$ ) in 2010,  $13.3 - 80.9\text{ ng m}^{-3}$  ( $44.4\text{ ng m}^{-3}$ ) in 2011,  $6.42 - 42.0\text{ ng m}^{-3}$  ( $28.4\text{ ng m}^{-3}$ ) in 2012 (Fig. 1a). Concentrations of 15 PAHs in rural air were in the ranges of  $1.77 - 102\text{ ng m}^{-3}$  (average value:  $32.1\text{ ng m}^{-3}$ ) in 2010,  $8.63 - 80.7$  ( $28.5\text{ ng m}^{-3}$ ) in 2011,  $5.34 - 42.1\text{ ng m}^{-3}$  ( $20.4\text{ ng m}^{-3}$ ) in 2012 (Fig. 1b). Air concentrations of PAHs showed a high gradient from urban to rural, up to  $\sim 7$  times higher in urban sites than in the rural sites. Levels of 15 PAHs in air were similar to those measured for other urban and rural areas in Europe and Africa and lower than other industrialized areas<sup>13,14,15,16</sup>. North China and two Indian sites showed relatively higher concentration than other regions. The relatively high PAHs levels detected at north China are likely associated with dominant emission sources from indoor biomass and coal burning for cooking and heating which occur primarily in towns and villages. The gradient reflects PAH emission sources which are well-known to be proportional to the population density<sup>17</sup>. The temporal fluctuation in concentrations was also evident (Fig. 1a and 1b). Years 2010 and 2011 showed similar concentrations, while lower PAHs concentration was found during period 2012 reflecting the sampling season effects.

Concentrations of alkylated PAHs in urban air were in the ranges of  $19.8 - 75.7\text{ ng m}^{-3}$  (average value:  $44.5\text{ ng m}^{-3}$ ) in 2010,  $10.3 - 64.1\text{ ng m}^{-3}$  ( $37.2\text{ ng m}^{-3}$ ) in 2011,  $1.29 - 12.3\text{ ng m}^{-3}$  ( $6.37\text{ ng m}^{-3}$ ) in 2012 (Fig. 1c). Concentrations of alkylated PAHs in rural air were in the ranges of  $1.63 - 46.1\text{ ng m}^{-3}$  (average value:  $19.5\text{ ng m}^{-3}$ ) in 2010,  $5.15 - 31.1\text{ ng m}^{-3}$  ( $14.4\text{ ng m}^{-3}$ ) in 2011,  $8.44 - 14.5\text{ ng m}^{-3}$  ( $6.76\text{ ng m}^{-3}$ ) in 2012 (Fig. 1d). Vietnam and Thailand showed relatively higher alkylated PAHs than in other regions. The spatial distributions of alkylated PAHs showed different patterns with 15 PAHs, reflecting their different emission sources. This is the first report of alkylated PAHs in air using PAS.

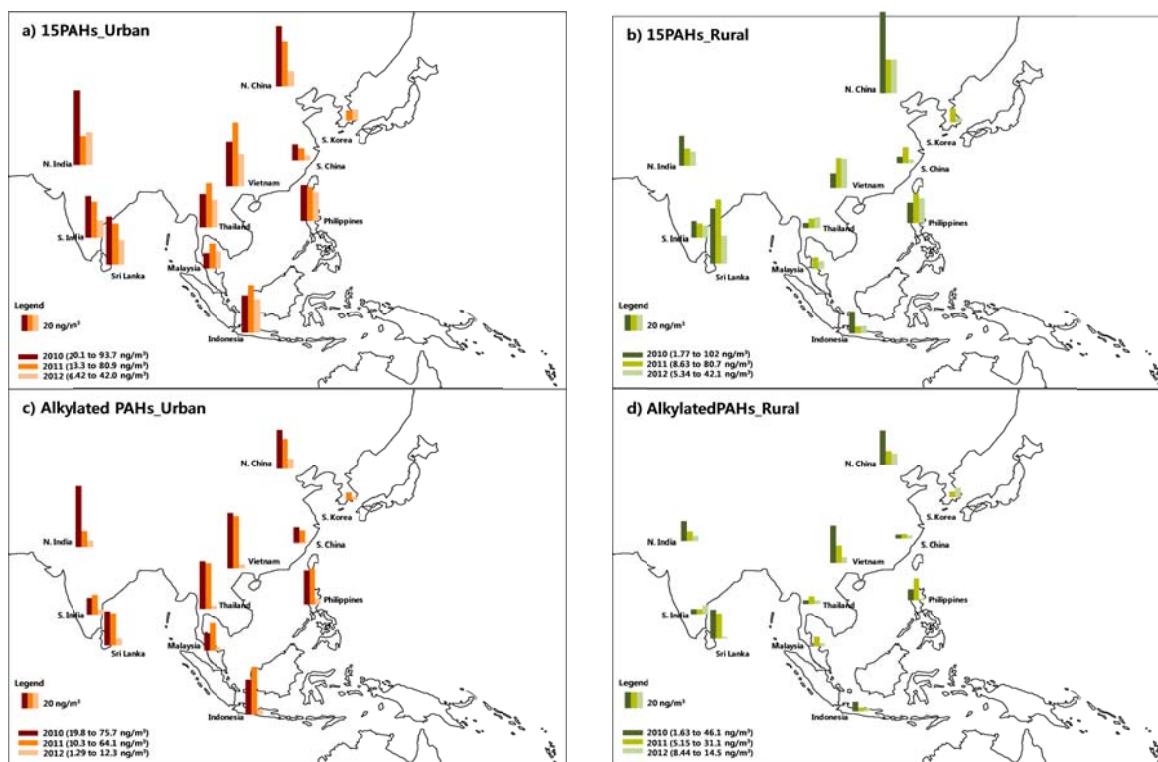


Figure 1. Concentrations of 15PAHs and alkylated PAHs in the Asian air ( $\text{ng m}^{-3}$ )

Relative compositions of PAHs showed similar distribution pattern regardless of urban and rural regions (Fig. 2). Three and four-ring PAHs accounted for more than 90% of the 15 PAHs at most of studied sites. The most dominant PAHs were phenanthrene (~40%), followed by fluoranthene (16%) and pyrene (15%), which are primarily in the gas phase. These PAHs profiles are consistent with other studies. Urban area of Manila, Philippines showed contribution of 68% for 3-ring and 30% for 4-ring PAHs<sup>18</sup>, respectively. Jaward et al.<sup>11</sup> also reported dominant contributions of low molecular weight PAHs across Europe.

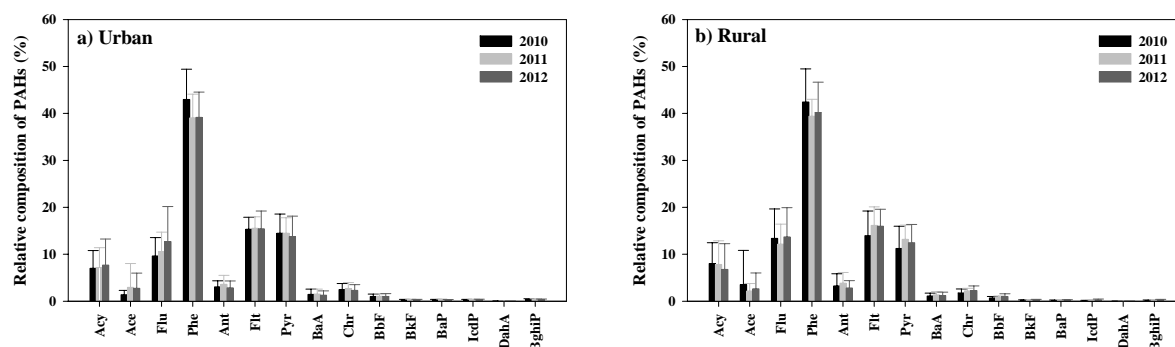


Figure 2. Average compounds profiles of 15 PAHs at urban and rural in Asian air

The concentrations of some source recognition marker compounds and their ratios can provide an indication for possible emission sources. Fig. 3a illustrates a plot of isomer ratios phenanthrene/(phenanthrene+anthracene) (Phe/(Phe+Ant)) against fluoranthene/(fluoranthene+pyrene) (Flt/(Flt+Pyr)) in PAS for source identification. Overall, both Phe/(Phe+Ant) and Flt/(Flt+Pyr) diagnostic ratios demonstrated that combustion processes, rather than unburned fossil fuels, were major sources of atmospheric PAHs. Urban areas in Thailand and Vietnam

showed prevalent contribution of the petroleum combustion. Vehicle exhausts from motorcycles and used cars in these countries have been considered one of the main atmospheric pollution source<sup>19</sup>. Ratios of some alkylated PAHs could indicate relative contribution of petroleum related sources<sup>19</sup>. During three years, urban regions in this study consistently showed higher ratios of 9-methylphenanthrene(9-methylphenanthrene+1-methylphenanthrene) (9/(9+1)-MP) than rural regions, indicating the relative higher contribution of petroleum related pollution sources (Fig. 3b).

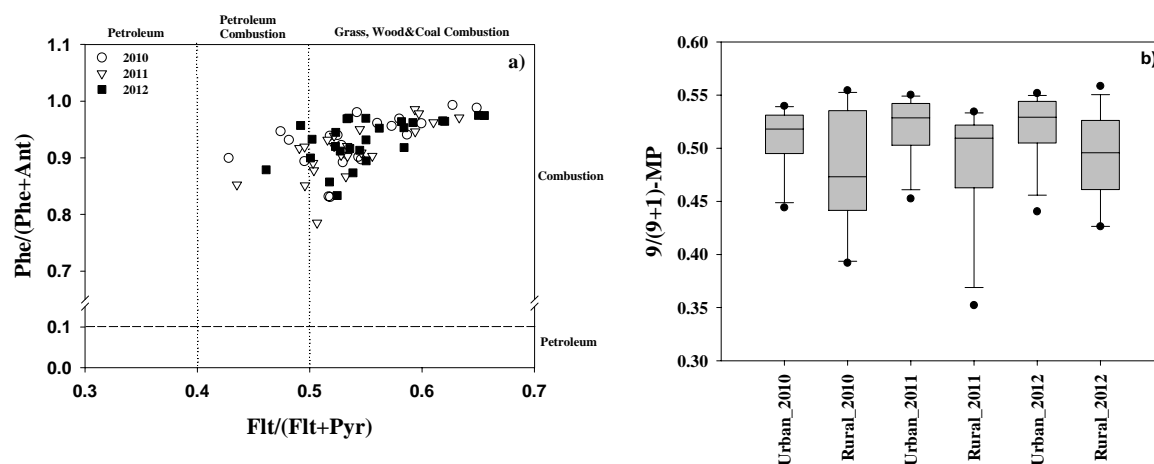


Figure 3. Source identification of PAHs by diagnostic ratios

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