Integrating on-line and off-line measurement for assessment of potential human exposure to particle-bound polycyclic aromatic hydrocarbons (pPAHs) in Bangkok, Thailand

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Abstract

A photoelectric aerosol sensor (PAS), which provides continuous signal in relation to the total particle-bound polycyclic aromatic hydrocarbons (pPAHs) concentration, was used to measure the real-time concentrations in the vicinity of road in Bangkok (Thailand). The measurements at roadside and general areas were carried out for approximately seven consecutive days in March and in August 2001. Potency equivalency factors (PEFs) of classified carcinogenic PAHs, which have been developed by the California EPA, was applied to assess the lifetime cancer risk of potential human exposure to these substances from the real-time measurement. A satisfactory linear correlation was obtained between the total amount of pPAHs detected by the PAS and the total PEF-weight concentration of seven carcinogenic PAHs determined by gas chromatography/mass spectrometry (GC/MS). At roadside, no large difference in average pPAHs concentration were observed between both periods studied, whereas larger difference was found at the general area, giving the ratio of the average concentration of the former to that of the latter a value of 2:1. This suggests that pPAHs more dispersed during the second campaign, due to stronger wind flow observed. As a result, the background cancer risk estimated at the general area of the second period was about 1.5 times higher than that of the first period. At roadside areas, including at ground and 4-storey height levels, an additional cancer risk due to road traffic was 1.2 x 10⁻⁶ and 7.1 x 10⁻⁷, respectively. In addition, the additional risk of the motorized road user during workday was estimated as 1.8 x 10⁻⁶. This approach could then give a simpler way to assess the potential risk associated with human exposure to pPAHs.
1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been received increased attention in recent years in air pollution studies with respect to their mutagenic, and carcinogenic properties. In view of this health concern, particle-bound PAHs (pPAHs) are considered to be more hazardous substance to human body through breathing, and they are very likely to cause an increase in the lung cancer risk. Consequently, monitoring the level of pPAHs in urban atmospheric situation has become more important.

For continuous air pollution screening, determination of pPAHs concentration using traditional chemical analysis methods, including gas chromatography/mass spectrometry (GC/MS), high-performance liquid chromatography (HPLC), are likely to be costly and time consuming. To obtain continuous temporal variation of pPAHs concentrations, in particular for fine particle, the use of a device capable of giving real-time detection of pPAHs concentration appears attractive. A Photoelectric Aerosol Sensor (PAS) is a type of the instruments, which is able to fulfil such purposes. This technique provides only the sum of PAHs concentration, without giving information on individual PAH species. There has been demonstrated, the relationship between gas chromatographic chemical analysis of filter extracts, with the PAS signal output: the remarkable result was that over a large range of concentrations with a linear relationship between the total concentration of PAHs adsorbed on the particles and PAS output was found [1,3,6]. It should be noted that overestimation of human exposure risk might be considerable if we directly assess it based on the total PAHs concentration detected by the PAS alone. However, once PAS detection can be converted to carcinogenic PAHs determined by the traditional methods, it would offer rather simple methodology to estimate potential human exposure to pPAHs.

The aim of this work is to integrate the on-line continuous monitoring response with off-line measurement using GC/MS, in order to assess the risk of potential human exposure to pPAHs in urban air environment. Bangkok, which is the capital city of Thailand, was selected as a typical mega city in developing countries, suffering from severe air pollution due to traffic congestion.

2 Methodology

2.1 Site description

All measurements were carried out in a residential/commercial area in the Bangkok metropolitan area. The climate of Bangkok is classified as tropical savanna with three seasons – hot (March – mid-May), wet (mid-May – October), and cool (November – February) [5]. The sites were located in the Chulalongkorn University in order to represent inner-urban environments. The location and configuration of sampling points is illustrated in Figure 1. All sampling sites were categorized as roadside (BRS1 and BRS2 sites) and general area (BGA). In addition, the observation of indoor pPAHs concentration at the BID site, as shown in Figure 1, was also performed.
2.2 On-line measurement

The PAS used for the determination of the total pPAHs concentration is the PAS2000CE, manufactured by EcoChem Messtechnik GmbH, Germany. It works on the basis of photoelectric ionization of the particles, where the diameter limit is at approximately 1 μm, induced by ultraviolet light of a KrBr-excimer lamp on PAH absorbed particles. The lamp is used to offer a high intensity UV radiation with the wavelength of 207 nm, which is chosen for ionizing the PAH absorbed aerosols, especially for three or more ringed PAH, while gas molecules and non-carbon aerosols remain neutral. The PAH absorbed on the surface of particles emit electrons, which are subsequently removed when an electric field is applied. The remaining positively charged particles are then collected on the filter element inside an electrometer, where the charge is measured. The resulting electric current establishes a signal, which is proportional to the concentration of total PAHs. The output of this analyzer is a direct reading of the total concentration of pPAHs in nanogram per cubic meter, having been calibrated by the manufacturer. The measurement data at 2-min intervals were taken in this study.

Two monitoring campaigns were conducted in March and in August 2001 in order to obtain the difference of total pPAHs concentration in dry and wet season, respectively. Each monitoring was performed for seven consecutive days during March 2-9 and August 5-14, respectively.

In addition, hence the PAS2000CE is a small handheld model, the assessing either non- or occupational personal exposure of pedestrians and motorized road users (i.e. motorbike or motor tricycle driver) to pPAHs was also performed during the period of 2:00-4:00 p.m. of August 10 and from 7:30-8:00 a.m. of August 14,
2001. This observation was carried out along Phaya Thai Rd. (see Figure 1) near the sampling sites.

2.3 Off-line measurement

Among the 16 PAHs species identified by US EPA as priority pollutants, the online technique takes into account 11 PAHs species absorbed on particulate matter, including Phenanthrene (Phe), Anthracene (Anth), Pyrene (Pyr), Benzo[a] anthracene (B(a)A), Chrysene (Chry), Benzo[b]fluoranthene (B(b)F), Benzo[k] fluoranthene (B(k)F), Benzo[a]pyrene (B(a)P), Indeno[1,2,3-cd]pyrene (I(1,2,3-cd)P), Dibenzo[a,h]anthracene (D(a,h)A), Benzo[g,h,i]perylene (B(g,h,i)P). A site-specific comparison between the PAS2000CE analyzer output and the total of 11 PAHs selectively determined by an off-line technique was then carried out. Further, the correlation between the values obtained by both techniques was considered and it was applied to estimation of human health risk of selected PAHs from the PAS2000CE output.

A high volume air sampler, HV-500-5S (manufactured by SIBATA Scientific Technology Ltd.), at a flow rate of 400 l/min was operated along with on-line monitoring. Twelve samplings were taken place during both campaigns. After each sampling, each filter was stored at a temperature of 4 °C under dark conditions. Each filter was also referred to a blank one that handled an equivalent treatment. Samples were extracted in 10 ml dichloromethane in an ultrasonic bath for 30 min. and were concentrated first by a rotating evaporator and then by a N2 flow. Instrumental analysis was carried out by GC/MS (Hewlett-Packard Model 6890 Series). A 1-μl of each sample extract was injected using the auto-sampler injector. Quantitative data for the target PAHs were acquired in the selected-ion monitoring (SIM) technique.

2.4 Estimation of lifetime cancer risk

The Office of Environmental Health Hazard Assessment (OEHHA) of the California Environmental Protection Agency (Cal/EPA) has developed a potency equivalency factor (PEF) for assessing the impact of carcinogenic PAHs in ambient air. Due to the limited amount of data currently available for risk assessment of B(a)P, the inhalation unit risk of 1.1 x 10^{-3} (µg/m^3)^{-1} is used as the best value for inhalation exposure [4]. The concentrations of carcinogenic PAHs are weighted by their PEFs, then, the lifetime cancer risk can be estimated as the following expression [2]:

\[
\text{Cancer risk} = PEF \times \text{concentration (ng/m}^3) \times \text{conversion factor (0.001 µg/ng)} \times \text{unit risk (µg/m}^3)^{-1}
\]

Table 1 shows the list of 11 detectable PAHs by the PAS2000CE as mentioned above, and that have been classified as carcinogenic PAH by either the International Agency for Research on Cancer (IARC) or US EPA. Moreover, the
existing PEFs of seven classified carcinogenic PAHs that could be utilized for estimating the cancer risk from the on-line measurement are also given in Table 1.

Table 1. PEF weighting scheme for 11 PAHs detectable by PAS2000CE

<table>
<thead>
<tr>
<th>Eleven PAHs detectable by PAS</th>
<th>IARC 2A</th>
<th>US EPA 2B</th>
<th>PEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phc</td>
<td>/</td>
<td>/</td>
<td>-</td>
</tr>
<tr>
<td>Anth</td>
<td>/</td>
<td>/</td>
<td>-</td>
</tr>
<tr>
<td>Pyr</td>
<td>/</td>
<td>/</td>
<td>-</td>
</tr>
<tr>
<td>B(a)A</td>
<td>/</td>
<td>/</td>
<td>0.1</td>
</tr>
<tr>
<td>Chr</td>
<td>/</td>
<td>/</td>
<td>0.01</td>
</tr>
<tr>
<td>B(b&amp;k)F</td>
<td>/</td>
<td>/</td>
<td>0.1</td>
</tr>
<tr>
<td>B(a)P</td>
<td>/</td>
<td>/</td>
<td>1.0</td>
</tr>
<tr>
<td>I(1,2,3-cd)P</td>
<td>/</td>
<td>/</td>
<td>0.1</td>
</tr>
<tr>
<td>D(a,h)A</td>
<td>/</td>
<td>/</td>
<td>0.1</td>
</tr>
<tr>
<td>B(g,h,i)P</td>
<td>/</td>
<td>/</td>
<td>-</td>
</tr>
</tbody>
</table>

To focus a view of health effect in this study, the cancer risk as expressed in eqn (1) was assigned for assessing potential human exposure to pPAHs. The concentrations of the seven carcinogenic PAHs determined by the chemical analysis were weighted by their PEFs (as reported in Table 1), and were plotted with the PAS2000CE output. The correlation between total PEF-weighted concentration and total pPAHs concentration measured by the on-line monitor was utilized. Consequently, the PEF-weighted concentration in eqn (1) could be obtained by the linear regression equation as below:

\[
\text{Total PEF-weighted concentration (ng/m}^3\text{)} = a + b \times \text{(PAS2000CE output)}
\]

(2)

where \(a\) is the intercept, and \(b\) is the regression coefficient. Since the on-line technique gives time dependent pPAHs concentration, the factor of specific exposure time period was considered. Therefore, the cancer risk can be finally estimated by:

\[
\text{Cancer risk} = \text{Total PEF-weighted concentration (ng/m}^3\text{)} \times \text{conversion factor (0.001 \mu g/ng)} \times \text{exposure time ratio} \times \text{unit risk (\mu g/m}^3\text{)}
\]

(3)

3 Results and discussion

3.1 Daily average profiles of total pPAHs concentration

Original time series data of total pPAHs concentration at 2-min interval were smoothed and irregular variations were eliminated by using a moving average of order 29. The data sets of hourly average during the period of March 3-8 (hot season), and August 7-13 (wet season), 2001 at all sampling sites were selected to
display daily average profile of the total pPAHs concentration as illustrated in Figure 2. The daily changes in pPAHs concentration of both campaigns were generally similar. The pPAHs concentration suddenly elevated in early morning hours, decreased in the midday, and increased again in the evening.

At the BRS1 site, the 24-h average concentrations over the observations period were similar. On the other hand, the pPAHs concentrations at the BRS2 and BGA sites during the wet season were relatively higher than those in the hot season, giving the ratios of the average concentration of the former to that of the latter of 1.3:1, and 2:1, respectively. When considering the sampling sites at the same level, the pPAHs concentration at roadside (BRS2) in the hot and wet seasons was respectively 3.3 and 2.2 times higher than that at general area (BGA). This is probably due to stronger wind speed observed in the wet season, giving more diffusion of pPAHs pollutant.

3.2 Relationship between total PAHs concentration selectively determined and PAS2000CE output

Figure 3(a) shows the correlation between the total concentration of the selected 11 PAHs determined by GC/MS and the average of total pPAHs concentration output from PAS2000CE in each time period during the both samplings. A good linear correlation could be obtained with the R² value of 0.709. The total of PAHs adsorbed on the particulate surface measured with PAS technique was greater, by about one order of magnitude, than the sum of the eleven PAHs selectively determined with the off-line technique. Agnesod et al. [1] have reported the same difference in the order of magnitude between off-line sampling technique and the measurement result with PAS technique. A possible explanation for this event is the different selectivity of the two methods used. The on-line analyzer can measure wider coverage of the PAHs which are sensitive to the source of ionization, for
instance alkyl-PAHs isomers, methyl-PAHs isomers, Coronene, Benzo[e]pyrene, whereas the off-line method regards individual PAHs selectively determined.

A satisfactory correlation between total PEF-weighted concentration and total pPAHs concentration measured by the on-line monitor could be also obtained with the $R^2$ values of 0.627, as illustrated in Figure 3(b). As a result, the total PEF-weighted concentration in eqn (2) can be expressed as:

$$Total\ PEW-weighted\ conc.\ (ng/m^3) = 0.2944 + 0.0091 \times PAS2000CE\ output$$  (4)

### 3.3 Lifetime cancer risk of potential human exposure to pPAHs

To investigate the cancer risk of potential human exposure to pPAHs, the total PEF-weighted concentration as expressed in the eqn (4) was utilized. In addition, the results from the daily average profiles as shown in Figure 2 were also used to estimate the risk. The lifetime cancer risk is, therefore, estimated by:

$$Cancer\ risk = \int_{t_1}^{t_2} \frac{C dt}{(0.0091 \times 0.2944 + 0.001 \times \frac{T_{exp}}{24}) \times 1.1 \times 10^{-3}}$$  (5)

where $C$ is the pPAHs concentration determined by PAS2000CE at time $t$, $T_{exp}$ is the exposure time period.

As the BGA site represented the general area in this study, the cancer risk of the people at this site was then considered as background cancer risk. Consequently, the cancer risk of potential human exposure to pPAHs at the BRS1 and BRS2 sites were considered as additional lifetime cancer risk due to road traffic. The results are summarized in Table 2.
Table 2. Background and additional lifetime cancer risk of potential human exposure in the vicinity of road in Bangkok

<table>
<thead>
<tr>
<th></th>
<th>March 3-8, 2001</th>
<th>August 7-13, 2001</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background risk</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BGA</td>
<td>4.3E-07</td>
<td>6.4E-07</td>
</tr>
<tr>
<td>Additional risk</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BRS1</td>
<td>1.3E-06</td>
<td>1.1E-06</td>
</tr>
<tr>
<td>BRS2</td>
<td>7.4E-07</td>
<td>6.8E-07</td>
</tr>
<tr>
<td>BID</td>
<td>6.0E-07</td>
<td></td>
</tr>
</tbody>
</table>

The background cancer risk was estimated as 6.4 \times 10^{-7} at the general area, the BGA site, in the second period, showing relatively higher than that of 4.3 \times 10^{-7} in the first period. This is probably due to wider dispersion of the pPAHs during the second measurement. This indicates that the exposure of the people at the general area in the wet season was relatively higher than that in the hot season. Average value of the additional cancer risk at roadside due to the road traffic was calculated as 1.2 \times 10^{-6} and 7.1 \times 10^{-7} at ground (BSR1) and 4-storey height levels (BRS2), respectively. The percentage decrease of the additional cancer risk from the ground level to the 4-storey height level was approximately 40%. At the same receptor level, no large difference in the additional risk between indoor and outdoor area was observed, giving the ratio of indoor to outdoor exposure risk of 0.88.

From Figure 2, the daily average profile of total pPAHs concentration clearly showed the peak during the morning period. It is desirable to know the percentage contribution of the additional cancer risk during that period, especially at roadside area. The daily profiles of the total pPAHs concentration at the roadside during the whole sampling periods were then subdivided into three periods, including morning (4:00-12:00), daytime (12:00-20:00), and nighttime (20:00-4:00). The results are illustrated in Figure 4.

Figure 4: Percentage contribution of additional cancer risk during a day at the roadside area during the whole sampling periods in hot (a) and wet (b) seasons. NT: nighttime, MN: morning, DT: daytime.

The additional cancer risk during the morning period contributed 35-43% of the total additional cancer risk in a day. For daytime and nighttime periods, the corresponding values were 28-34%, and 29-32%, respectively. As the results, no
A large difference in the range of percentage contributions of the additional cancer risk was observed. This indicates that the potential personnel exposure to total pPAHs for the people in proximity of road in Bangkok was almost the same throughout a day.

Figure 5 shows the profiles of total pPAHs concentration observed for assessing the exposure risk of pedestrians and motorized road users. The additional cancer risks of the pedestrian and motorized road user were also estimated, as shown in Table 3.

Table 3. Additional lifetime cancer risk of pedestrian and motorized road user

<table>
<thead>
<tr>
<th></th>
<th>Pedestrian (exposure period: 1h)</th>
<th>Motorized road user (exposure period: 8h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Morning</td>
<td>Afternoon</td>
</tr>
<tr>
<td>Additional cancer risk</td>
<td>5.9E-08</td>
<td>5.2E-08</td>
</tr>
</tbody>
</table>

From Table 3, the additional cancer risk of pedestrian either in the morning or in the afternoon was similar. Then, if the people spent the time everyday for walking beside the main street for approximately 1 hour, their additional cancer risk was estimated as $5.5 \times 10^{-8}$. In the case of motorized road user (i.e., motor tricycle drivers), the cancer risk was estimated as occupational group, assuming exposure time of 8 hours workday. Consequently, the additional risk of the motor tricycle driver during workday was estimated as $1.8 \times 10^{-6}$. From Figure 5, if the motorized road user exposure to the highest level of the pPAHs (1359 ng/m$^3$) throughout a work period, their additional risk will be estimated as $4.6 \times 10^{-6}$.

According to the criteria for risk reduction under the California’s Air Toxics Hot Spots Information and Assessment Act of 1987 (Collins et al., 1998), all the estimated lifetime cancer risks in this study are still at a level not requiring public notification (since $< 10^{-5}$). However, we should carefully realize and pay attention...
to the potential personnel exposure to pPAHs of motorized road users, especially motor tricycle and motorbike drivers, which their additional cancer risk was 1.5 and 2.8 times higher than those of the people at the roadside and general area, respectively. Moreover, if we consider their highest potential exposure risk (i.e., $4.6 \times 10^5$), the additional cancer risk becomes 4 and 7 times higher than those of the people at the roadside and general area, respectively.

4 Conclusion

The real-time monitoring could be successfully applied to assess the potential risk associated with human exposure to pPAHs in this study. The estimation of cancer risk could be carried out by applying a satisfactory linear correlation between the total PEF-weighted concentration of seven carcinogenic PAHs and total amount of pPAHs as detected by the on-line monitor. The percentage contributions of additional cancer risk due to road traffic were similar during a day. The background cancer risk at general area in the wet season was relatively higher than that in the hot season due to wider dispersion of the pPAHs. The additional cancer risk at roadside was estimated as $1.2 \times 10^4$ and $7.1 \times 10^{-7}$ at ground and 4-storey height levels, respectively. In the case of motorized road user, especially motorbike and motor tricycle drivers, their additional risk was estimated as $1.8 \times 10^4$.

References


