Controlling polycyclic aromatic hydrocarbons emission of peri urban air Jakarta

Miftahudin¹, S Hudiyono³, R H S Koestoer² and Budiawan³

¹ Student at School of Environmental Science, Universitas Indonesia, Jakarta – Indonesia
² School of Environmental Science, Universitas Indonesia, Jakarta – Indonesia
³ Chemistry Department of Universitas Indonesia, Depok - Indonesia

Abstract. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the atmosphere and well-known to be carcinogenic and mutagenic. They are products of incomplete combustion. In urban, PAHs are almost entirely anthropogenic. Peri-urban Jakarta was selected as the field of this study where traffic air pollution and its health effects have long been a serious problem due to the heavy traffic and the chronic state of traffic congestion. Previous studies on roadside measurements reported ambient air concentration of the sum of 16 PAHs in particulate at roadside ranged from 3 to 330 ng/m³. Trees have demonstrated feasibility to reduce toxic PAHs from peri-urban Jakarta roadside environments by accumulating particle bond PAHs on their surface area of leaves. Resulted characteristics this study provides interesting technique for controlling the PAHs pollution problem in the peri-urban area of Jakarta and this in turn can be utilized by area which similar characteristic.

Keywords: PAHs, roadside, air pollution, peri-urban, congestion

1. Introduction

Infrastructure development of the city and the establishment of industrial centers are mostly accompanied by increased production of vehicles. All of these resulted in an accumulating congestion and traffic density. Jakarta city development also provides opportunities for the surrounding area to contribute in changing environmental carrying capacity which is related to the peri-urbanization process. The peri-urbanization process able to create environmental carrying capacity around the road to the peri-urban area that has character of urban traffic congestion but its territory as rural character. Increased air pollution caused by congestion in the region is expected to occur in the morning and afternoon when activities of people who works in the Jakarta business center but live in the peri urban areas of Jakarta.

A review of socio-economic activities related to the mobilization of urban peri-urban societies has been widely discussed, but very less explains the impact of urban peri-urban air quality due to traffic congestion on urban-peri urban road as a necessity of travel for people living in urban peri urban areas and work in urban areas. This study focus on decreasing of peri urban air quality caused by PAHs emission in road to outside Jakarta. Jalan raya Bekasi, Jalan Daan Mogot and Jalan Raya Bogor represent most of road to peri-urban area around Jakarta which has an accelerated urbanization as a result of its location bordered with capital city Jakarta and rapid economic growth. This paper demonstrated feasibility to reduce toxic PAHs from peri-urban Jakarta roadside environments by accumulating particle bond PAHs on their surface area of plant leaves.
Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the atmosphere and well-known to be carcinogenic and mutagenic matters [1]. They are products of incomplete combustion and pyrolysis of fossil fuels and other organic materials from natural and anthropogenic sources. In urban and industrial atmospheres, PAHs are almost entirely anthropogenic [2]. PAHs exist in the atmosphere in both vapor and particulate-phase [3]. PAHs are initially generated in the gas phase, and they are adsorbed on pre-existing particles undergoing condensation during further cooling of the emission. Low molecular weight PAHs tend to be more concentrated in the vapor-phase while the ones with higher molecular weight are often associated with particulates [4].

PAHs released from many types of pollution source floats in the air for sometimes, but the organic matter will later be removed from the atmosphere both in vapour phase and condensed form, absorbed and deposited on water, soil and plant foliage (Nicola et al., 2008). In general lighter, less hydrophobic particulates are dispersed in the environment at greater distance than heavier, more hydrophobic particulates. As for PAHs, the important property is their lipophilicity they may accumulate in fat tissue of vertebrates and invertebrates, also in lipophilic parts of plants, accumulation can take place [5]. In addition, leaf characteristics such as leaf surface, waxes, hairs and number of stomata play an important role in PAH uptake and accumulation[6].

Plant exposure to PAHs can occur in various ways. The particulate accumulation on the leaf surface depends on particle size, speed of deposition and leaf surface properties. Particulate-bonded PAHs may be taken up directly via the stomata or be deposited on the leaf surface, while gaseous PAHs may be accumulated in leaves by equilibrium partitioning, kinetically limited dry vapour deposition, particle-bound deposition, depending on the physicochemical properties of the investigated compound [7].

Being hydrophobic these organic compounds may be absorbed by the leaf surfaces. Therefore leaves of plants grown by the roadside are expected to contain high levels of organic compounds originating from vehicular exhaust. Due to the various factors, some plants have high tolerance, hence might have the ability to absorb PAHs in the atmosphere. These plants can be an excellent agent. They can also assist in the removal of pollutants from the environment (bioremediation). It is important to understand abundance and distributions of PAHs in the vapor phase and in the particulate phase so that air pollution caused by both PAHs phase can be efficiently controlled.

Peri-urban Jakarta was selected as the field of this study, where traffic air pollution and its health effects have long been a serious problem due to the heavy traffic and the chronic state of traffic congestion. Road traffic is the main transport. Diesel buses have been the primary public transport, and private vehicles using both gasoline and diesel as well as motorcycles have been increasing (Dinas Perhubungan Dalam Angka, 2013). Previous studies on roadside measurements reported ambient air concentration of the sum of 15 PAHs in Jakarta, detected 74 ng/m$^3$, and it referred two times higher than that in Serpong involving 34 ng/m$^3$ with similar distribution pattern of PAHs in both two locations. Ratio calculation of individual PAHs indicated that PAHs pollution in ambient air majority produced from petroleum [8].

This research was test an analytical method for the determination of various PAHs in vapor phase and in the particulate phase samples taken by a low-volume collection system (MiniVol portable air sampler). Our optimized method was applied to determine PAHs concentrations in particulate collected from different areas of peri urban Jakarta and hence look for vehicle congestion and temporal dependence of particulate and PAHs concentration. The result of this study provides interesting information for solving the air pollution problem in the local area of peri urban Jakarta.

2. Methods

2.1. Sampling site

The sampling location was selected to represent the outer Jakarta metropolitan (Figure 1). The selection was representative of the city, including the meteorological conditions of the area, and other considerations, e.g., minimize obstructions between source and sampler, maximize unrestricted flow, and consider the reasonable separation distance between roadway and the sampler probe inlet.
The sampling site was located at B1, T1 and T3 (Fig.1), away from areas subject to point source emissions. Possible traffic pollution is expected since most of the sampling site are around traffic congested and peri urban buffer zone Jakarta entry. The sampling point of receptor was 0.5 km from to the wind direction as point source. The sampler inlet was on the roof top of a building for the ease of access, power supply, and security reasons.

![Sampling location](image_url)

**Figure 1. Sampling location**

2.2. **Sampler**

A high volume air sampler was used to collect particulate matter with 10 μm size cutoff (PM10). The sampler was fitted with quartz microfiber filters (QMA, 20.3×25.4 cm). Prior to installation in the sampler, filters were annealed in an oven at 550 °C for 12 h overnight. A batch of 21 samples was taken with the HVS at flow rate of 1.0 m³/min for typically 24 h on sequential days from January to February, 2016.

2.3. **Sample preparation**

2.3.1 **Extraction**

In brief, filter samples wrapped with aluminum foil were removed from the freezer at the time of sample preparation and allowed to warm to room temperature for approximately 1 hour in sealed polytetrafluoroethylene bags. Once conditioned, a quarter of the filter was cut, weighed (samples and
method blanks (± 0.5 g GF filter) were weighed on an analytical balance, and then folded and placed in a 100-mL stainless steel Accelerated Solvent Extractor (ASE) cell. Prior to use, each ASE cell had been pre-cleaned by rinsing with organic solvents and baking overnight. Each ASE cell was filled with anhydrous sodium sulfate and 15 μl, equivalent to 12.5–150 ng, of isotopically labeled recovery surrogates in 1.25–10 ng/μL solutions (including acenaphthene-d10, fluranthene-d10, benzo(a)pyrene-d12, and triphenylene-d12) was distributed equally among the tops of the cells. Then, cells were capped, put in the extractor, and extracted using dichloromethane (DCM) (100 °C, 1500 psi, 2 cycles of 5 min, 150 % flush volume). The extract was concentrated to 0.5 mL in evaporator with nitrogen, and the solvent was exchanged to hexane. The sample was spiked with isotopically labeled PAHs for use as recovery surrogates.

2.3.2 Cleanup and purification
Interferants were removed from extracts using silica adsorption chromatography utilizing a solid-phase extraction cartridge packed with 20 g silica, eluted in three fractions with 50 ml hexane for the first, 100 ml DCM for the second, and 50 ml ethyl acetate for the third (fraction 2 as analyzed for PAHs). Extract volumes were reduced using an evaporator. The target fractions were concentrated to 0.3 ml (300 μl) with ethyl acetate rinses under a gentle stream of nitrogen and spiked with 15 μl of a 10-ng/μl isotopically labeled internal standard solution prior to analysis. Blank extracts were carried through the entire method together with batches of three to five samples.

2.4. Analysis
Analyte separation, detection, and identification were performed by gas chromatography mass spectrometry (GC-MS) on an Agilent 7890A gas chromatograph equipped with an Agilent DB EUPAH Column (20 m x 0.18 mm x 0.14 μm film thickness) and 5975C mass selective detector. The oven temperature was ramped from 40°C (3 min) to 310 °C (10 min) at a rate of 40°C/min. Persistent organic pollutant (including PAHs) concentrations in filter extracts were determined by GC-MS in the selected ion monitoring (SIM) mode using electron impact (EI). The target analyte list was comprised of 83 compounds including PAHs, pesticides, isotopic surrogates, and pesticide degradation products. Target analyte loss was corrected by surrogate recovery using target analyte-to-surface response ratios in calibration curves. The mean recovery over the entire analytical method for all surrogates in all samples was more than 60%.

2.5. Ability of plants to absorb PAHs
Traffic volume sampling procedure was carried out using a handy camera which automatically records traffic volume observation area. The calculation of the volume of traffic (traffic volume) was done by count the number and type of vehicles recorded in the image sampling. The geographic coordinates that have been obtained from the next road segment converted to UTM coordinates for obtaining long road segment and total length in units of meters along the wind direction. The length of this segment further used as input in the modeling of FLLS. Geographic coordinates of receptors that are around the road determined using GPS. Determined the orientation of the receptor lies against street. Geographic coordinates subsequently converted to UTM coordinates to get a unit of length in meters. The receptor determined distance the segment of road. Distance receptor on the road nearest segment used as input in determination of conditions atmospheric stability.

Distribution and type plant around separation distance between roadside and sampling point was observed. Distribution and type plant index assessed from 0,0-0,35 for poor index, 0,35-0,70 for moderate and >0,7 for good index. The ability of plants to absorb PAHs released to the atmosphere by vehicle emission was observed by measuring the PAHs concentration in air sample of 1 km from the roadside source.
3. Results and discussions

The sampling area plays an important role in the amount of PAHs concentrations in ambient air. PAHs concentrations in the traffic-congested areas were clearly higher than that in the settlement area. The results revealed that PAHs in 3 different locations peri urban outer road of Jakarta are generated from automobile internal combustion, which may confirm from the ratio of PAHs component. Diagnostic ratio can help to identify possible emission sources. The quantity IND/(IND+BPER) can be used to identify traffic sources. The BaP/BPER ratio was also used for characterization of the PAH sources. The low BaP/BPER ratio (< 0.60) is evidence of greater emission of BPER from traffic sources.

Accumulation of PAHs in plants is mostly affected by the physical and chemical factors of the organic compounds themselves. Uptakes of compounds from soil through plant roots are usually a pathway of organic compounds with high water solubility. These hydrophilic compounds move into the inner roots and distributed within the plant. Experiments was conducted using ryegrass, an important agricultural grassland species in Central Europe as samples, have shown that the primary mechanism of atmospheric deposition for many semi-volatile organic compounds to be dry gaseous deposition. Dry gaseous deposition is a diffusive process, which chemicals being deposited to bring the vegetation into equilibrium with the gas phase [9]. Field studies, also with ryegrass, indicated that equilibrium is not approached for very non volatile compounds due to slow uptake kinetics compared to the contaminant storage capacity of the vegetation. However, for persistent chemicals of intermediate volatility such as the higher chlorinated benzenes or the lower chlorinated biphenyls, an approximate equilibrium can be expected for many plant species [7]. Uptake of PAHs also depends on physiological parameters of plants including specific area of leaves, surface hair, stomata density, lipid content and cuticle structure. For instance, PAHs concentrations in hairy leaves are significantly higher than those in smooth leaves [9].

Comparison between hazel leaves, which have the densest covering of hairs on both adaxial (upper) and abaxial (lower) surfaces, oak leaves with relatively shorter and less hair, and ash leaves which are essentially hairless with recessed capitates hairs present on the adaxial surface only [9] shows that there were significant but small differences between PAHs concentrations in the three species and leaf pubescence may provide one explanation for the observed difference. Supporting evidence for the influence of leaf hairs on PAHs concentrations was found in the higher PAHs for concentrations of the majority of the particle bounded 4-, 5- and 6-ring PAHs are found in hazel [9].

The concentrations of all individual PAHs compounds in the cuticles were higher than those in the inner tissues [10]. There were also general decreasing trends in both cuticle and tissue concentrations from the lower molecular weight compound to the higher molecular weight compounds. The inner tissue concentrations seemed to decrease faster than the cuticle concentration did [10]. The low molecular weight PAHs were derived primarily from volatile PAHs in the air while high-molecular weight PAHs come from particulate PAHs deposition. Simonich and Hites collected the samples of the bark, leaves, needles and seeds of sugar maple and white pine and found a positive correlation between PAHs and lipid content. This shows that the different amount of PAHs concentration among the different plant tissues from the same site can vary according to the lipid content of the plants [11].

4. Conclusions

Higher PAHs concentration were mainly caused by local emission source. The lower PAHs concentration were observed were likely due to easier dispersion of air pollutants, wash out effect, and to lesser content and photo degradation. The sampling area plays an important role in the amount PAHs concentrations in ambient air. In the same season, PAHs concentrations in the traffic-congested areas were clearly higher than the community areas which have plant along road boundaries. This study
showed that area with good plant distribution have greater air quality because of ability plants to absorb and becoming agent to remove PAHs emission.

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