Exposure Assessment of Polycyclic Aromatic Hydrocarbon (PAHs) in Childcare Centers of Muang, Nakhon Ratchasima

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Abstract. This study aims to characterize airborne polycyclic aromatic hydrocarbons (PAHs) as of particulate and vapor phases variation. The samples were collected from the childcare centers where divided into urban and rural areas in Nakhon Ratchasima Province of Thailand. The airborne samples were collected from five childcare centers during the dry season in the year 2017. The PAHs species were determined by the gas chromatography and mass spectroscopy (GS/MS) method. Results show that the total concentrations of PAHs were higher than vapor phase that both similar in urban area and rural area. The dominant PAHs compounds of both urban and rural areas were benzo[α]pyrene, benzo[a]anthracene and indeno[1,2,3-cd]pyrene, respectively. Furthermore, the concentrations of PAHs in municipality (urban) childcare centers were higher than rural childcare centers area of Nakhon Ratchasima province. The risks associated with exposure to PAHs were evaluated using the TEF approach. The estimated value of lifetime lung cancer risks children in urban were significantly (p < 0.05) 2 times of children in rural, thus demonstrating that exposure to PAHs at levels found at urban site may be cause potential health risks.

1. Introduction
The problem of air pollution that affects human health from exposure to various pollutants in the air. Particles of solid particulates are produced by the milling of both organic and inorganic materials which, when released into the atmosphere, can float in the air for a certain period of time and disperse [1]. At the same time, it also acts as a conduit for other substances that adversely affect the health of the particle, such as heavy metals, organic matter volatile or Polycyclic Aromatic Hydrocarbon (PAHs). The United States Environmental Protection Agency (US EPA) has designated 16 PAHs as important carcinogens are Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo (a) anthracene, Chrysene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene, Benzo (a,h) anthracene, Benzo (g,h,i) perylene and Indeno (1,2,3-cd) pyrene PAHs are caused by inadequate combustion of vehicle fuels [2]. People living in urban areas are therefore more likely to experience high levels of PAHs. The condition is stable in both gaseous and particulate state, depending on molecular size and atmospheric conditions. Normally, PAHs with low molecular mass are found in the gas phase due to the change in vapor pressure and high molecular weight PAHs are found in the particle phase [3]. PAHs enter the body through eating. Breathing and skin contact, which PAHs in the air. Dust particles are absorbed into the lungs. Tissue, fat, and fat accumulate in the liver, kidneys and fats. So long accumulated in the body, such as Benzo (a) Pyrene,
Benzo (b) fluoranthene, Benzo (g, h, i) perylene and Indeno (1, 2, 3-cd) Carcinogenicity in Groups 2B refers to a group that is most likely to cause cancer in humans. It can cause lung cancer and respiratory system [4]. When humans are exposed to PAHs. Indoor and outdoor environments can affect both acute and chronic [5]. Based on previous data, the health risk assessment of exposure to PAHs in the Bangkok metropolitan area by Toxic Equivalency Factor (TEF) was 1.35 ng / m³, which is higher than the risk factor for carcinogenicity defined as 1.0 of Benzo (a) Pyrene. Norramit et al. [6] found that PAHs concentrations were equal to 1.86 and 1.54 ng / m³ in urban and non-urban areas. 3.46 and 2.70 ng / m³ in urban and non-urban areas respectively. Slezkova et al. [7] show that urban residents are more likely to experience PAHs than those who live in urban areas. Out of town According to data from the study of the concentration of PAHs inside and outside the school in Rome, Italy, the indoor PAHs amounted to 1.15 ng / m³ and the outdoor area was worth At 0.74 ng / m³ [8], it was shown that those living in the building were more likely to experience PAHs than those living outside the building. In Thailand, there are no studies on the health risk assessment of PAHs in young children classified as “Vulnerable groups” [9]. Have high health risks. This study investigated the levels of both PAHs and gaseous carcinogens. Both indoor and outdoor use, as well as the risk of exposure to PAHs in the child development center between the municipality and the area outside Nakhon Ratchasima municipality. This study evaluated the risk of exposure to PAHs. The data will be used as a basis to reduce the risk of exposure to PAHs.

2. Methods

2.1. Sampling location
The sampling was during the dry season of May 2017 on working days. Daily samples was collected for 6 h (from 8 a.m. to 2 p.m.) that representing the spending time of children in childcare center. The particulate (PM) and vapor phase samples were both collected. The sampling included locations at ten childcare centers were divided into two groups (5 childcare centers in urban area and 5 childcare centers in rural area). The Nakhon Ratchasima province of Thailand. The sampling locations were presented in Figure 1. All childcare centers environment had natural ventilation systems, the classrooms were often ventilated by opening windows. The study locations were generally located at a distance of 500 meters away from main roads. The study area of site1 – site5 was found with high traffic volume and the ventilation through natural window and doors assumed to ventilation rate of more than 20 percent of the area. The average of ambient temperature was 31 degrees celsius (°C) and relative humidity was 58%. For the location of site 6 – site 10. The traffic condition showed with low traffic volume. The average of ambient temperature was 32 °C and relative humidity was 65%. The predominant wind during the study was presented from south and southeast wind.

2.2. Extraction and analysis of PAHs
The analysis of PAHs, air samples were extracted for 6 h with 50 ml n-hexane in soxhlet by TO13A method [4]. The concentration of PAHs were analyzed by gas chromatograph mass spectrophotography (GC/MS) Agilent 6980. The used GC column was a 30 m DP-5 capillary column (0.25 mm id., 0.25 μm film thickness). The column temperature at 80°C hold for 5 min and increased to 290°C at 10 °C/min hold for 35 min. PAHs compounds were identified based on retention times.

2.3. Quality control
Target PAHs standard stock solution of 16 PAHs was used as a recovery standard for the measurement of recovery coefficients from 80% to 120% that recommend by TO13A method. Known volume of standard solutions was spike into the filters of the analysis procedure. This study spiked recoveries ranged from 85% to 107% that indicated acceptable for all 16 PAHs.

2.4 Statistical analysis
For all data sample t-test was applied to determine the statistical significance (p<0.05) of the difference between the mean in both group (childcare center in urban and rural in Nakhon Ratchasima Province).
3. Result and discussion

3.1. Gas-particle distribution of PAHs
The gas-particle phase of 16 PAHs in this study is presented in Figure 2. The phase distribution show in the percentage of the concentration in both phases were naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, benzo (a, h) anthracene, benzo (g, h, i) perylene and indeno (1, 2, 3-cd) pyrene. PAHs found in particles phases larger than vapor phase. Amount of benzo (a) pyrene in particulate phase are 57% of total mass. For the Naphthalene, acenaphthylene, acenaphthene, benzo (a) anthracene and chrysene compound have distribution at all sites are same between vapor and particle phases. High molecule mass of PAHs were found in particle phase than vapor phase. The PAHs phase distributions in both sampling sites of urban and rural areas were similar [3]. This may be explained by the evaporation of PAHs in the room temperature distribution from the outdoor environment to the indoor air. The study of Wang et al. [5] the PAHs in air are divided between vapor and particulate phases depend on the ambient air temperature and humidity.

3.2. Concentration of PAHs in municipality (urban) and outside the municipality (rural) childcare centers of Nakhon Ratchasima province.
The concentration of 16 PAHs are showed in Figure 3. PAHs levels of urban childcare center ranged from 1.00 (minimum) to 2.02 ng m$^{-3}$ (maximum), while rural areas ranged from 0.71 to 1.55 ng m$^{-3}$. The results demonstrated that levels of 16 PAHs were significantly high in urban childcare centers area.
The total concentration of 16 PAHs for urban sites higher 1.3 times than rural sites. These findings concerned to children health impact from PAHs indicated to carcinogenic effects to body in benzo [a] pyrene, benzo [b] fluoranthene, benzo [k] fluoranthene and dibenz [a, h] anthracene compounds [10]. The highest concentration of PAHs is Indeno (1, 2, 3-cd) pyrene at mean of 2.02 ng m⁻³ for 8.6 % of ΣPAHs. The dibenz [a, h] anthracene were second most abundant group of urban childcare centers (8.5 % of ΣPAHs). 16 PAHs such as Benzo (a) pylene, benzo [ghi] perylene are possible human carcinogens. The least compounds of PAHs such as (naphthalene), at the urban childcare centers site less than 4.2 % of ΣPAHs.

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\Sigma[BaP]_{eq} = \Sigma(C_i \times TEF_i) \\
\text{Inhalation cancer risk} = \Sigma[BaP]_{eq} \times UR[BaP]
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### Figure 3
Concentration of PAHs in childcare centers municipality (urban) and outer municipality (rural) of Nakhon Ratchasima province.

3.3. Health risk assessment of PAHs in childcare center of municipality (urban) and outside the municipality (rural) of Nakhon Ratchasima province.

The 16 PAHs are carcinogenic, and their health risks in human can be calculate by BaP-equivalent ([BaP] eq) were calculate from PAHs concentration with toxicity equivalency factors (TEFs) of concentrations shown in equation (1) were multiply by UR [BaP] (unit risk) there are cancer risk shown in equation (2), while unit risk of life time cancer is 1.1 × 10⁻⁶ of 70 years [4].

The results of inhalation cancer risks for 16 PAHs, this study are urban and rural site and health risks of children in childcare center were found PAHs are presented table 1. The estimated of lifetime lung cancer risks based on Benzo[a]pyrene at the urban area were 9.5×10⁻⁶ for PAHs in urban area, and 1.8 times higher rural area is 5.2×10⁻⁶. At the urban area, the values of lifetime lung inhalation cancer risks for childcare center in urban area were higher. The result demonstrates that urban area, higher expose PAHs, and traffic emissions might be the potentially major pollution source of PAHs to childcare center. The childcare center of municipality (urban) of Nakhon Ratchasima province close to major roads this study 500 meter from major road and where emissions from vehicular traffic might be significant effect to human [11]. This study indicated the influence of low temperature during sampling effect to high concentration of PAHs the risks associated with the urban area have
significantly higher than rural area. Therefore a long distance from major road and traffic emissions to protect human health to reduce exposure PAHs in childcare center.

Table 1. Estimated inhalation cancer risk to measured concentrations of PAHs in childcare center.

| PAHs                  | TEF | Cancer Risk  |
|-----------------------|-----|--------------|
|                       |     | Urban        | Rural        |
| Naphthalene           | 0.001 | 6.38E-10 ±0.03 | 2.64E-10 ±0.10 |
| Acenaphthylene         | 0.001 | 6.49E-10 ±0.05 | 3.08E-10 ±0.04 |
| Acenaphthene           | 0.001 | 6.71E-10 ±0.04 | 3.30E-10 ±0.08 |
| Fluorene              | 0.001 | 6.93E-10 ±0.02 | 2.42E-10 ±0.05 |
| Phenanthrene           | 0.001 | 7.15E-10 ±0.03 | 2.53E-10 ±0.03 |
| Anthracene            | 0.010 | 7.04E-09 ±0.01 | 3.41E-09 ±0.07 |
| Fluoranthene          | 0.001 | 7.37E-10 ±0.03 | 3.19E-10 ±0.01 |
| Pyrene                | 0.001 | 7.70E-10 ±0.07 | 3.30E-10 ±0.03 |
| Benz[a]anthracene     | 0.100 | 9.57E-08 ±0.01 | 4.40E-08 ±0.12 |
| Chrysene              | 0.010 | 8.80E-09 ±0.06 | 4.73E-09 ±0.06 |
| Benzo[b]fluoranthene  | 0.050 | 5.39E-08 ±0.03 | 2.81E-08 ±0.02 |
| Benzo[k]fluoranthene  | 0.050 | 5.50E-08 ±0.02 | 3.08E-08 ±0.04 |
| Benzo[a]pyrene        | 1.000 | 9.50E-06 ±0.06 | 5.20E-06 ±0.01 |
| Indeno[1,2,3-cd]pyrene| 0.100 | 1.27E-07 ±0.05 | 7.48E-08 ±0.02 |
| Dibenzo[a,h]anthracene| 0.100 | 1.18E-07 ±0.02 | 6.66E-08 ±0.01 |
| Benzo[ghi]pyrene      | 0.010 | 1.06E-08 ±0.01 | 7.04E-09 ±0.05 |

4. Conclusions
The concentrations of polycyclic aromatic hydrocarbons (PAHs) in childcare centers during dry seasons in Nakhon Ratchasima province of Thailand; the concentration of 16 PAHs in all sampling sites were followed from Benzo (a, h) anthracene, Benzo (g, h, i) perylene, Indeno (1, 2, 3-cd) pyrene, benzo[a]pyrene, Benzo (k) fluoranthene, Benzo (b) fluoranthene, Benzo (a) anthracene, Chrysene, Pyrene, Naphthalene, Acenaphthylene, respectively. The distribution of PAHs between particulate and vapor phases was similar to other studies, with particle phase higher than vapor phase. The major sources of PAHs are the traffic emissions and distance of childcare center from major road. Health risk assessment based on the carcinogenic that the concentrated in urban area were several times higher than rural area indicating a causing PAHs is adverse health effects for children live in childcare center in municipality (urban) Nakhon Ratchasima province.

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