UNIVERSITI PUTRA MALAYSIA

A REVIEW ON OCCURRENCE OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN PM2.5 SAMPLES IN SOUTH EAST ASIA AND THEIR POTENTIAL CARCINOGENIC RISK

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BY

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ABSTRACT

A REVIEW ON OCCURRENCE OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN $PM_{2.5}$ SAMPLES IN SOUTH EAST ASIA REGION AND THEIR POTENTIAL CARCINOGENIC RISK

MUHAMMAD HAKIM HAMSANI

Introduction: Polycyclic Aromatic Hydrocarbons (PAHs) are one class of chemical products found naturally in crude oil, tar and gasoline. They are also created by the burning of coal, oil, gas, wood, waste and tobacco. These PAHs sources could attach to particles in the air and form airborne particles**.**Particulate matter with aerodynamic diameters of less than 2.5 mm ($PM_{2.5}$ or fine particulate matter) is of particular concern since they can penetrate the respiratory system easily when inhaled and deposit deeply into the lungs' bronchioles and alveoli. **Objectives:** This paper presents a review for literatures obtained from Scopus database from year 2011 to 2021 from countries in SEA region and assess their carcinogenic health risk. **Methodology:** Literatures are search using the Scopus search engine using the main keyword and filtered the results to only researches conducted in SEA countries. The reported concentrations of polycyclic aromatic hydrocarbons (PAHs) from these literatures were used to calculate health risk assessment using incremental lifetime cancer risk (ILCR) equation. **Results and Discussion:** The concentration of PAHs in $PM_{2.5}$ ranged from 0.378 ± 0.348 ng m^{-3} to 224 ng m^{-3}. The lowest concentration of PAHs in $PM_{2.5}$ sample was reported in Prince of Songkhla University (Phuket Campus) in southern Thailand while the highest concentration was reported in rural area of Lampang Province in northern Thailand located in Thoen District. **Conclusion:** The concentration of PAHs in $PM_{2.5}$ in rural area was higher compared to urban area. The carcinogenic health risks due to inhalation of $PM_{2.5}$ in the studies reported in SEA were in the acceptable risk level (ILCR < 10^{-4})

Keywords: polycyclic aromatic hydrocarbon, $PM_{2.5}$, South East Asia, urban, rural

ABSTRAK

TINJAUAN TERHADAP KEBERADAAN HIDROKARBON AROMATIK POLISIKLIK (HAP) DIDALAM SAMPEL $PM_{2.5}$ DI ASIA TENGGARA DAN POTENSI RISIKO KANSER

MUHAMMAD HAKIM HAMSANI

Pengenalan: Hidrokarbon Aromatik Polikiklik (HAP) adalah satu kelas produk kimia yang terdapat secara semula jadi dalam minyak mentah, tar dan petrol. Mereka juga diciptakan oleh pembakaran arang batu, minyak, gas, kayu, sampah dan tembakau. Sumber PAH ini boleh melekat pada zarah-zarah di udara dan membentuk zarah-zarah di udara. Bahan partikulat dengan diameter aerodinamik kurang dari 2.5 mm ($PM_{2.5}$ atau zarah partikulat halus) menjadi perhatian kerana mereka dapat menembusi sistem pernafasan dengan mudah apabila dihirup dan masuk ke dalam bronkiol dan alveoli paru-paru. **Objektif:** Kajian ini menyajikan tinjauan semua literatur yang diperoleh dari pangkalan data Scopus dari tahun 2011 hingga 2021 dari negara-negara di wilayah SEA dan menilai risiko kesihatan karsinogenik bahan berkait..**Metodologi:** Literatur dicari menggunakan mesin carian Scopus menggunakan kata kunci utama dan menyaring hasilnya hanya untuk penyelidikan yang dilakukan di negara-negara SEA. Jumlah HAP dari literatur ini digunakan untuk mengira penilaian risiko kesihatan menggunakan persamaan ILCR.**Keputusan dan Perbincangan:** Julat kepekatan HAP dalam $PM_{2.5}$ adalah 0.378 ± 0.348 ng m^{-3} hingga 224 ng m^{-3}. Sampel kepekatan HAP terendah terletak di Universiti Prince of Songkhla (Kampus Phuket) di selatan Thailand sementara yang tertinggi terletak di kawasan luar bandar Provinsi Lampang di utara Thailand yang terletak di Daerah Thoen **Kesimpulan:** Risiko kesihatan karsinogenik melalui pernafasan $PM_{2.5}$ dalam kajian yang dilaporkan di SEA berada pada tahap risiko yang boleh diterima (ILCR <10-4)

Kata kunci: hidrokarbon aromatik polisiklik, $PM_{2.5}$, Asia Tenggara, bandar, luar bandar

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LIST OF ABBREVATIONS

PAHs	Polycyclic Aromatic Hydrocarbons
US EPA	United State Environmental Protection Agency
SEA	Southeast Asia
ILCR	Incremental Life Cancer Risk
IRIS	Integrated Risk Information System
HMW	High Molecular Weight
MMW	Medium Molecular Weight
LMW	Low Molecular Weight
DOE	Department of Environmental
$PM_{2.5}$	Particulate Matter 2.5
PM_{10}	Particulate Matter 10
RTVM	Road Traffic Volume Malaysia
BaP	Benzo(a)pyrene
ATSDR	Agency for Toxic Substances and Disease Registry
IARC	International Agency for Research on Cancer

TLV	Threshold Limit Value
REL	Recommended Exposure Limit
PEL	Permissible Exposure Limit
MCL	Maximum Concentration Level
ACGIH	American Conference of Governmental Industrial Hygienists
CCME	Canadian Council of Ministers of the Environment
NIOSH	The National Institute for Occupational Safety and Health

CHAPTER 1

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are one class of chemical products found naturally in crude oil, tar and gasoline. They are also created by the burning of coal, oil, gas, wood, waste and tobacco. These PAHs sources could attach to particles in the air and form airborne particles. High-temperature cooking forms PAHs for meat and also other ingredients. Naphthalene is a commercially manufactured PAH for the processing of other chemicals and mothballs in the United States. A number of PAHs are found in cigarette smoke.

PAHs mixtures are commonly exposed to people as a result of air exhaust, wood smoke, tobacco smoke, and asphalt fumes, which are widely used for exposing polluted air motor vehicles. PAHs are eaten by people by consuming fried or burnt meats, or else food with PAHs particulates settled from the air. After PAHs are ingested or breathed through air, it will enter the skin or even passed on the body transforms PAHs into a decomposition substance called urinary metabolites and faeces.

The PAHs are an organic compound group consisting of two or more fused aromatic rings. PAHs are primarily the product of anthropogenic processes, notably incomplete organic fuel combustion. The PAHs are distributed across the atmosphere.

The environmental life of PAHs is also driven by nature processes, such as volcanic eruptions and forest fires. PAHs can exist both in the particulate and gas phases, depending on their volatility. n the gaseous phase, light molecular weight PAHs (LMW PAHs) with two or three aromatic rings are emitted, whereas in particulate phase, high molecular weight PAHs (HMW PAHs) with five or more rings are emitted. In addition, PAHs in the atmosphere can photodegrade and react with other pollutants such as nitrogen oxides, sulphur dioxide and ozone. (Lee, 2010).

The incomplete react with organic matter causes a widespread dispersion and moving of PAHs. Some PAHs and their epoxides are highly toxic to microorganisms and higher systems, including humans, mutagenic and/or carcinogenic. PAHs are pervasive natural toxins essentially created during the incomplete combustion of natural materials (for example wood coal, petroleum and oil). Sources from anthropogenic activities predominate; however, some PAHs in the environment originate from natural sources, such as open burning, regular misfortunes or leakage of oil or coal stores, and volcanic activities. (Abdel-Shafy & Mansour, 2016).

PAHs are distributed by atmospheric reactions and exist almost everywhere due to their widespread sources and persistent properties. In the gaseous or particulate phases of ambient air, humans are exposed to PAHs mixtures. Long-term exposed to a high PAHs concentration has been linked to health problems. When some PAHs are carcinogens, inhaling PAHs in particulate matter poses a potentially serious health risk, including an increased risk of lung cancer. research on PAHs in particulate matter (PM), such as PM_{10} and $PM_{2.5}$ in ambient air, has become more focused in recent years (Lee, 2010).

Anthropogenic sources of PAHs coal gasification include residential heating, and liquefying plants, carbon black, coal-tar pitch, and asphalt mining, coke and aluminium production, catalytic cracking towers, and associated operations in oil refineries, as well as motor vehicle exhaust.

PAHs have two or more single or fused aromatic rings in their molecules, with a carbon molecule shared between rings. PAHs with up to six fused aromatic rings are often classified to as "small" PAHs, while those with more than six aromatic rings are known to as "large" PAHs. Due to the availability of samples of different small PAHs, most research on PAHs has been carried out on small PAHs (Abdel-Shafy & Mansour, 2016). PAHs have high melting and boiling points, low vapour pressure, and extremely low aqueous solubility. The latter two characteristics tend to reduce as molecular weight increases, but oxidation resistance decreases. Aqueous solubility of PAHs decreases with each additional ring. PAHs in organic solvents, meanwhile, are very soluble because they are strongly lipophilic. PAHs are also exhibited with various functions such as light sensitivity, heat resistance, conductivity, emission power, resistance to corrosion and physiological action. (Abdel-Shafy & Mansour, 2016).

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1.2 Problem Statement

Particulate matter with aerodynamic diameters of less than 2.5 mm ($PM_{2.5}$ or fine particulate matter) is of particular concern since they can penetrate the respiratory system easily when inhaled and deposit deeply into the lungs' bronchioles and alveoli. Fine particles correlated with mutagenic and carcinogenic chemicals, such as polycyclic aromatic hydrocarbons (PAHs), can contribute to or potentially lead to extreme health risks (Li et al., 2009).

PAHs are discovered in the ambient air. The atmospheric partitioning of PAH compounds between the particulate and gaseous phases significantly affects their atmospheric fate and transport and how they enter the human body (Abdel-Shafy & Mansour, 2016). There are harmful, mutagenic and/or carcinogenic properties of several PAHs. PAHs are highly lipid- soluble and hence easily absorbed from the gastro- intestinal tract of mammals. They are rapidly distributed in a wide range of body fat tissues with a strong propensity to localise. Metabolism of PAHs occurs with oxidation or hydroxylation as the first step through the cytochrome P450-mediated mixed function oxidase system (Samanta et al., 2002).

In the atmosphere, PAHs are released mainly through the incomplete combustion of organic matter. Either natural or anthropogenic sources of combustion may be used. Volcanoes and forest fires are among the natural causes. The anthropogenic sources, however are exhaust from cars, agricultural fires, power plants, and industrial sources. In addition, PAHs tend to be found in urban environments in greater concentrations than in rural environments, as most sources of PAHs are located in or near urban centres (Z. Wang et al., 2013)

Incomplete combustion of organic materials such as coal, oil and wood are the primary cause of PAHs. For industrial purposes, PAHs are not synthesised chemically. Nevertheless, for many PAHs, there are a few industrial applications. They are mainly used in pharmaceuticals, agricultural products, photographic products, thermosetting plastics, materials for lubrication and other chemical industries as intermediaries (Abdel-Shafy & Mansour, 2016). By different chemical behaviour, PAHs impact humans. Interference with the normal activity of cell membranes as well as with membrane-associated enzyme systems is known to be the mechanism of toxicity. Carcinogenic and mutagenic effects have been shown to be induced and are potent immunosuppressants. Their effects on the growth of the immune system, humoral immunity, and host resistance have been reported (Rengarajan et al., 2015).

1.3 Study Justification

$PM_{2.5}$ particles are so tiny that they can penetrate deep into the lungs and into the bloodstream. The properties of PAHs play a major role affecting human health through inhalation. As countries develops day by day, all these industrial have cause the rise of the particulate matter in the environment. Automobile traffic emissions, mainly related to diesel vehicles, were the major contribution to high PAHs levels in the ambient air, although some other contributions, such as coal and wood were identified.

Thus, this study provides a general overview to understand the current occurrence of PAHs exposure from available $PM_{2.5}$ samples focusing in SEA countries. With the advancement of future technology in industries and transportation, it is critical to assess the current level of potential health risk associated with PAHs exposure due to its ubiquitous properties in the environment, specifically in the atmosphere. Besides that, this health risk assessment will assist further in providing supporting evidence to determine the plan of action in national environmental planning programmes.

1.4 Research Questions

i. What is the estimated carcinogenic health risk of PAHs that reported in $PM_{2.5}$ samples in SEA due to inhalation?

1.5 Research Objectives

i. To review the literatures related to PAHs in $PM_{2.5}$ samples in SEA obtained from Scopus database from the year 2011 to 2021.
ii. To assess the carcinogenic health risk of PAHs that reported in $PM_{2.5}$ samples in SEA due to inhalation

1.6 Conceptual Framework

Figure 1.1 shows the main focus of this review where studies are related to PAHs from environment in the $PM_{2.5}$ samples. The independent variable is the calculated carcinogenic health risk assessment from the maximum concentration of PAHs through inhalation.

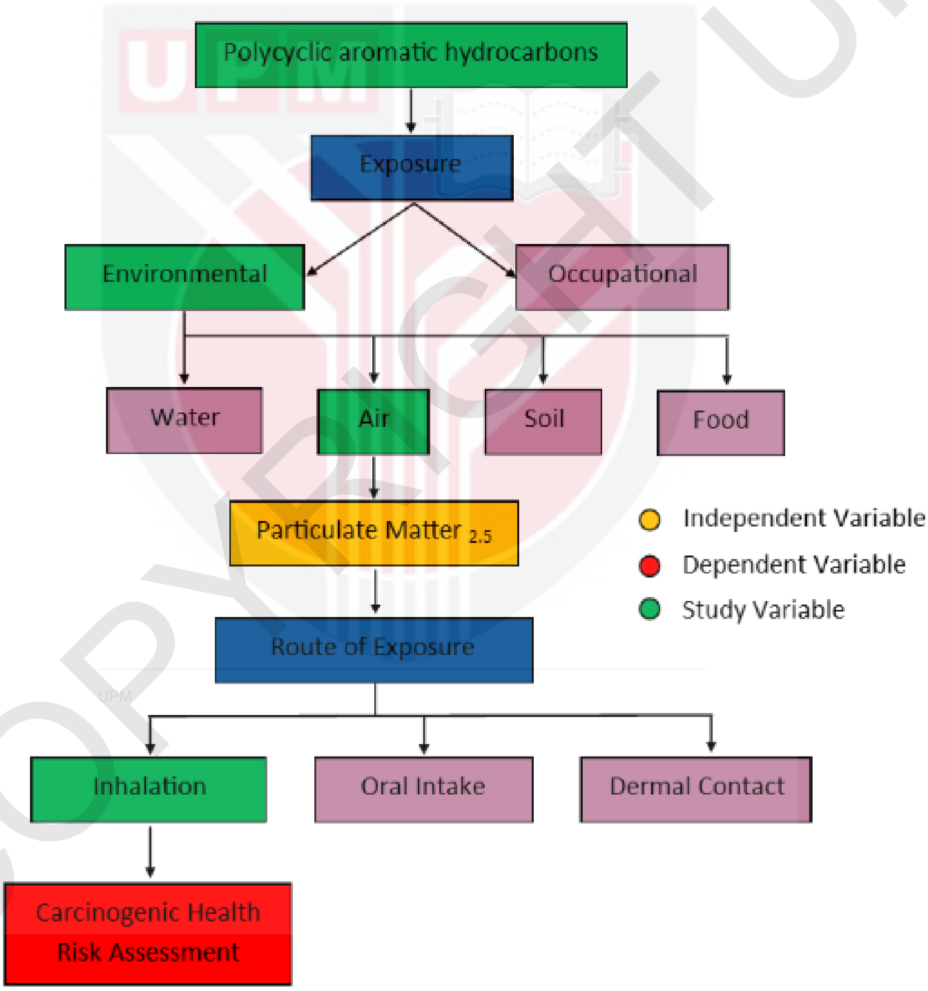


Figure 1.1 Conceptual framework

CHAPTER 2

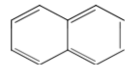
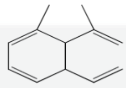
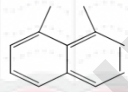
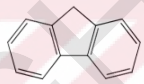
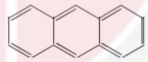
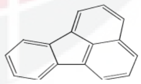
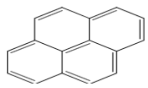
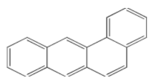
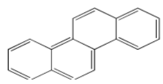
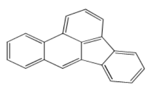
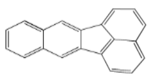
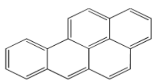
LITERATURE REVIEW

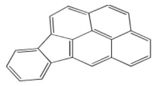
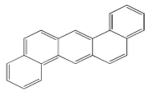
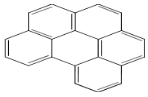
2.1 Origins of PAHs

PAHs caused by the incomplete combustion of organic matter, of which benzo-a-pyrene is the most frequently studied and calculated. In the world, they are widely distributed and human exposure to them is inevitable. A variety of them are carcinogenic and mutagenic, such as benzo-a-pyrene, and they are generally believed to make a large contribution to the overall human cancer burden. Their presence in the ecosystem is reflected by their presence in many kinds of uncooked food at measurable levels (Phillips, 1999).

PAHs are usually generated when a saturated hydrocarbon is burned in an oxygen-deficient environment, which is known as incomplete combustion. PAHs are formed through two basic mechanisms: pyro-synthesis and pyrolysis. The United States Environmental Protection Agency (USEPA) has designated 16 PAHs as priority compounds, as shown in Table 2.1.

Table 2.1: The 16 PAHs according to U.S Environmental Protection Agency

PAH Compound	Chemical Formula	Structural Formula	No. of rings	Vapor Pressure (Pa, 25°C)	TEF
Naphthalene	$C_{10}H_{12}$		2	11.14	0.001
Acenaphthylene	$C_{12}H_{8}$		3	3.87	0.001
Acenaphthene	$C_{12}H_{10}$		3	3.07	0.001
Fluorene	$C_{13}H_{10}$		3	1.66	0.001
Phenanthrene	$C_{14}H_{10}$		3	1.06×10^{-1}	0.001
Anthracene	$C_{14}H_{10}$		3	8.6×10^{-4}	0.01
Fluoranthene	$C_{16}H_{10}$		4	8.61×10^{-4}	0.001
Pyrene	$C_{16}H_{10}$		4	5.0×10^{-5}	0.001
Benzo[a]anthracene	$C_{18}H_{12}$		4	5.43×10^{-4}	0.1
Chrysene	$C_{18}H_{12}$		4	4.0×10^{-6}	0.01
Benzo[b]fluoranthene	$C_{20}H_{12}$		5	5.0×10^{-7}	0.1
Benzo[k]fluoranthene	$C_{20}H_{12}$		5	5.2×10^{-8}	0.1
Benzo[a]pyrene	$C_{20}H_{12}$		5	6.0×10^{-8}	1

Dibenzo[ah]anthracene	$C_{22}H_{12}$		5	1.33×10^{-8}	1
Indeno[l23-cd]pyrene	$C_{22}H_{14}$		6	1.27×10^{-7}	0.01
Benzo[ghi]perylene	$C_{22}H_{12}$		6	1.38×10^{-8}	0.1

The key pollutant in urban environments is the respirable particulate matter (S. J. Cao et al., 2017; Y. M. Kim et al., 2001), especially $PM_{2.5}$ (particulate matter with an equivalent diameter of less than 2.5 μm) that could reside long and transport far in the atmosphere (Bai et al., 2020; S.-J. Cao, 2019). Pulmonary function and blood circulation could reach directly into the alveolus and further intervene, causing a series of inhalation and cardiovascular diseases. Moreover, for many hazardous compounds, $PM_{2.5}$ is also a carrier and catalyst (S. J. Cao et al., 2017; J. Wang et al., 2018). The smaller the particle size, the more toxic substances are enriched, such as polycyclic aromatic hydrocarbons, viruses, bacteria and trace elements, and the quicker the toxic substances react and dissolve (Gschwind et al., 2015; K. H. Kim et al., 2015).

2.2 Sources of PAH

The combustion of fuels such as gas, oil and coal create PAH emissions from factories. During the processing of raw materials including primary aluminium, PAHs can also be emitted. Emissions from manufacturing activities such as the processing of primary aluminium, coke, petrochemicals, and rubber tyres, as well as the manufacture of cement, bitumen, and asphalt are additional sources of PAHs.

Agricultural sources of PAHs include open burning of brushwood, grass, moorland heather, and stubble. Many of these operations require burning organic materials under conditions of suboptimum combustion. Therefore, a large number of PAHs are expected to be generated from open biomass burning (Rengarajan et al., 2015).

A wide range of PAHs are present in the atmosphere as a result of the incomplete combustion of organic matter, pollution sources, vehicle exhausts, stationary matter (e.g. coal-fired, electricity- generating power plants), domestic matter (e.g. cigarette smoke and residential wood or coal combustion), area source matter (e.g. forest fires and agricultural burning) (Samanta et al., 2002)

2.3 Properties of PAH

PAHs, according to their number of rings, may vary from gaseous to solid. In their gaseous phase, low molecular mass compounds tend to concentrate, whereas high molecular mass compounds are also particle-associated. When PAHs enter the atmosphere, depending on steam pressure, physicochemical characteristics of aerosols and environmental conditions, they are redistributed as gaseous particles (Lohmann & Lammel, 2004)

PAHs are chemically inert and hydrophobic in themselves. However, in mammalian cells they undergo metabolic activation of diol-epoxides that bind covalently to cellular macromolecules, including DNA, triggering DNA replication errors and carcinogenic process inducing mutations. This mechanism of activation was found to occur with all carcinogenic PAHs tested, with modifications in some instances (Phillips, 1999).

2.4 Health effects of PAH

Abdel-Shafy & Mansour (2016) studied that due to the broad-based diffusion of these compounds and their toxicological importance, biological monitoring of exposure to PAHs is of primary interest. The health effects of individual PAHs, however are not exactly similar. In fact, some PAHs are listed by the International Agency for Research on Cancer as confirmed, probable or likely to be carcinogenic to humans (Group 1, 2A or 2B). Many PAHs are widely referred to as carcinogens, mutagens, and teratogens and thus pose a significant threat to human health and well-being. An excess risk of lung cancer is the most important health impact anticipated from inhalation exposure to PAHs.

The effect of PAHs on human health depends primarily on the exposure duration and path, the volume or concentration of PAHs to which one is exposed, and the relative toxicity of the PAHs. Health effects, including subjective factors such as pre-existing health status and age, may also influence a number of other factors. The capacity of PAHs in human beings to cause short-term health effects is not clear.

Symptoms such as eye irritation, nausea, vomiting, diarrhoea, and confusion have resulted from occupational exposure to high levels of pollutant mixtures containing PAHs.

Decreased immune function, cataracts, kidney and liver damage, respiratory disorders, asthma-like symptoms, lung function irregularities and prolonged contact with the skin may cause redness and skin inflammation may be health effects from chronic or long-term exposure to PAHs. If inhaled or ingested in large quantities, naphthalene, a particular PAH, can cause red blood cell breakdown. The adverse effects that may occur primarily depend on the manner in which the person is exposed to PAHs (Rengarajan et al., 2015).

2.5 Legislation related to environmental PAHs exposure control

Government agencies should enforce and regulate norms to restrict PAH emissions in the environment since a mixture of PAHs in the air would be damaging to human health. There are no specific criteria for PAH concentrations in the ambient air in Malaysia. Nonetheless, PAH emissions from industrial activity are closely monitored in order to avoid contamination and accumulation of this hazardous compound in the environment.

In Europe, BaP, as one of the PAHs compounds, has become the target of regulation to regulate detrimental parameters in ambient air, and it has also taken on the role of a marker compound proportional to the total PAHs load, due to its highest toxic equivalent factor, which is a function of concentration multiplied by its toxicity

(Kim et. al. 2013). Existing PAH guidelines and regulations established by several international bodies are listed in Table 2.2

Table 2.2 Standards and regulations related to PAHs in the environment.

Agency	Medium	Level	Comments	References
American Conference of Governmental Industrial Hygienists	Air	0.2 mg m^{-3}	Threshold limit value (TLV) for benzene-soluble coal tar pitch fraction.	ACGIH (2005)
National Institute for Occupational Safety and Health (US)	Air	0.1 mg m^{-3}	Recommended exposure limit (REL) for coal tar pitch volatile agents.	NIOSH (2010)
National Institute for Occupational Safety and Health Administration (US)	Air	0.2 mg m^{-3} for benzene-soluble coal tar pitch fraction	Permissible exposure limit (PEL) for benzene soluble fraction of coal tar volatiles.	NIOSH (2010)
Canadian Council of Ministers of the Environment	Soil	0.6 mg m^{-3}	Total potency equivalents for soil contaminated with coal tar volatiles.	CCME (2010)
U.S Environmental Protection Agency	Water	0.0001 mg L^{-3} 0.0002 mg L^{-3} 0.0003 mg L^{-3} 0.0004 mg L^{-3} 0.0002mg L^{-3}	Maximum concentration level (MCL) for benz(a)anthracene, MCL for benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene	USEPA (2000)

		MCL dibenz(a,h)anthracene MCL for indenol(1,2,3-c,d)pyrene MCL for benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene

CHAPTER 3

METHODOLOGY

Scopus database was mostly used to look for key bibliographies. The search technique was restricted to items written in English and published between 2011 and 2021. Several searches using the same terms as used in the source literature were used to summarise the significant findings.

The keyword used for finding the research in the search engine is "$PM_{2.5}$"and "polycyclic aromatic hydrocarbon". The keyword is used to cover all researches related to $PM_{2.5}$ sampling and polycyclic aromatic hydrocarbons (PAHs).

The studies were chosen as it met the criteria below:

- The research conducted sampling and analysing polycyclic aromatic hydrocarbons compound in $PM_{2.5}$ samples
- The research took place in countries in the South East Asia (SEA) region

The initial search using the keyword shows a result of 546 papers from 2011 to 2021. After filtering all the papers according to the criteria, the number of papers that can be included is 11 papers. 6 of those papers conducted their study in Malaysia, 1 in Singapore and the rest of it in Thailand.

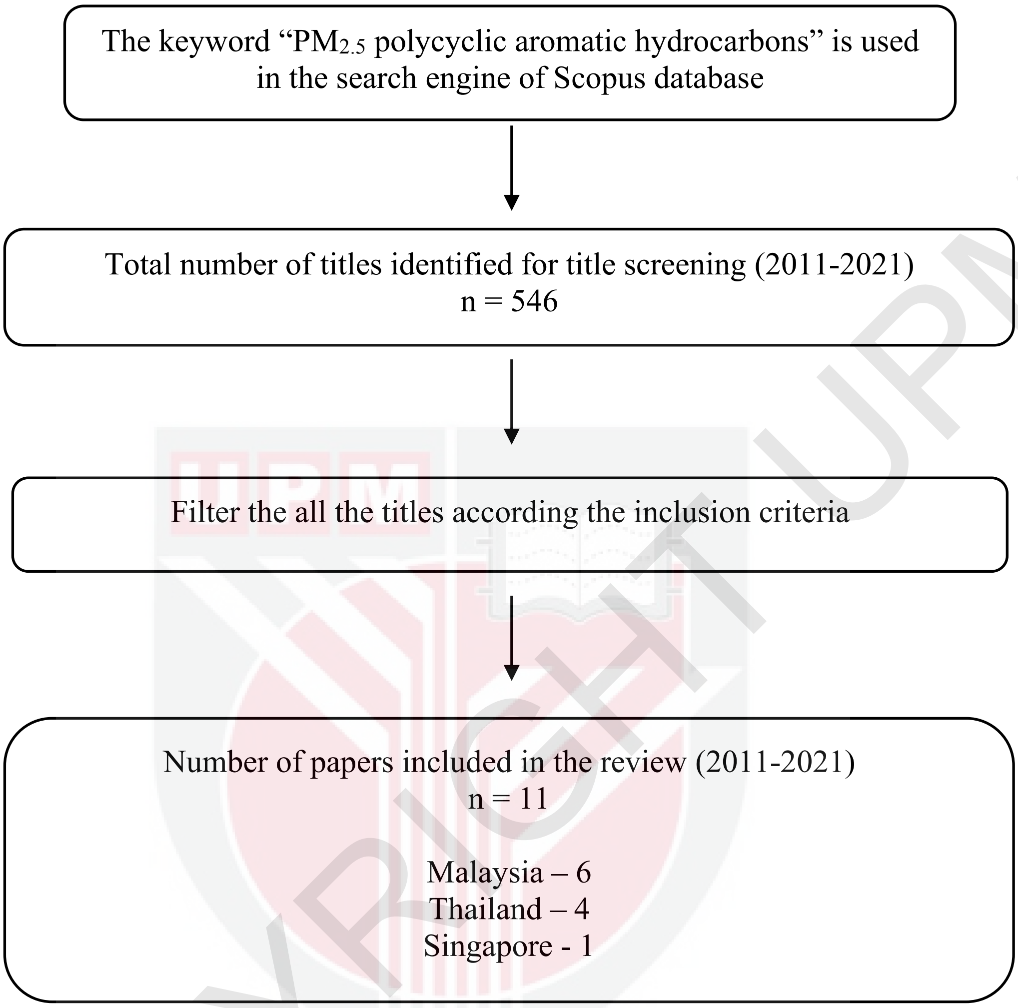


Figure 3.1 Flow Diagram of Study Selection Process

3.2 Health Risk Assessment

Maximum concentrations that reported in the selected papers were used to assess the carcinogenic health risk due to inhalation in the worst-case scenario. Inhalation of air particles contaminated with PAHs was considered for health risk assessment, as $PM_{2.5}$ is aerodynamically very tiny and can penetrate the human respiratory system to the alveolar level. The incremental lifetime cancer risk (ILCR) of the PAHs is calculated by firstly determining the B[a]P equivalent (B[a]Peq), as shown in Eq. (3.1). Afterwards, the ILCR for inhalation routes are calculated as in Eq. (3.2) referring to (Chen & Liao, 2006) and (Peng et al., 2011):

$$\mathrm{B[a]Peq} = \sum(\mathrm{Ci} \times \mathrm{TEF}) \qquad \text{Eq. 3.1}$$

where Ci is the concentration of individual compound in each sample, and TEF indicates toxic equivalency factors, which has a different value for each compound (Table 3.1).

Health risk assessments of PAHs in atmospheric aerosol are based on the inhalation route of exposure. The $\mathrm{ILCR}_{\text{inhalation}}$ was determined by calculating using the equation published by USEPA (1991).

$$\mathrm{ILCR}_{\text{Inhalation}} = \frac{\mathrm{CS} \times \left(\mathrm{CSF\ inhalation} \times \frac{\sqrt[3]{\mathrm{BW}}}{70}\right) \times \mathrm{IR\ inhalation} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT} \times \mathrm{PEF}} \qquad \text{Eq.3.2}$$

where, C is the PAHs concentration, TEF is the toxic equivalency factors, CS is the carcinogenic PAHs based on B[a]Peq, IR is the inhalation rate, EF is the exposure frequency, ED is the lifetime exposure duration, BW is the body weight and ALT is the averaging lifetime for carcinogen. All the parameters used for adult are listed in Table 3.2.

Table 3.1: Toxicity Equivalent Factors (TEF) for individual PAHs

Compound	TEF
Dibenzo[a,h]anthracene	1
Benzo[a]pyrene	1
Benzo[a]anthracene	0.1
Benzo[b]fluoranthene	0.1
Benzo[k]fluoranthene	0.1
Indeno[l23-c,d]pyrene	0.1
Anthracene	0.01
Benzo[g,h,i]peryIene	0.01
Chrysene	0.01
Acenaphthene	0.001
Acenaphthylene	0.001
Fluroranthene	0.001
Fluorene	0.001
2-Methylnaphthalene	0.001
Naphthalene	0.001
Phenanthrene	0.001
Pyrene	0.001

Reference: (Nisbet & LaGoy, 1992)

Table 3.2 Exposure parameters and factors used for health risk assessment

Exposure Factor	Parameters (Adult)	Reference
Exposure frequency, EF (days/year)	365	Ferreira-Baptista and De-Miguel (2005)
Exposure duration, ED (year)	24	USEPA (2011)
Body weight, BW (kg)	60	USEPA (2013)
Averaging time, AT (days) (70years × 365 days/year)	25550	Ferreira-Baptista and De-Miguel (2005)
Inhalation ratio (m^3/day)	20	Wang et al. (2011)
Particulate emission factor(m^3/kg)	1.36E09	USEPA (2011)
CSF inhalation (mg/kg/day)	3.85	USEPA (2012); Peng et al. (2011)

CHAPTER 4

RESULT

For this review, 11 papers that related to PAHs in $PM_{2.5}$ samples are gathered in SEA region, 6 papers from Malaysia, 4 papers from Thailand and one paper from Singapore. Most of the papers already include health risk assessment except 2 papers, one from Malaysia and one from Thailand. Carcinogenic health risks due to inhalation of PAHs in $PM_{2.5}$ were assessed in these two papers using the maximum reported concentration. Information such as maximum concentration sampled, area and result of health risk assessment are tabulated in Table 4.1.

The area of $PM_{2.5}$ sampling in these studies was located at rural, urban and sub-urban area. Each study reported different number of PAHs compound ranged from 14 PAHs to 19 PAHs compound.

4.1 Concentration of PAH

The concentration of PAHs in $PM_{2.5}$ was ranged from 0.378 ± 0.348 ng m^{-3} to 224 ng m^{-3}. The number of PAHs sampled were different between studies that was reviewed but most of the compounds are the listed by USEPA. The lowest concentration of PAHs in SEA was reported at Prince of Songkhla University (Phuket Campus) in southern Thailand (Choochuay et al., 2020). The reported concentration of PAHs in $PM_{2.5}$ samples from this study was 0.3780 ± 0.3480 ng m^{-3}.

The highest concentration reported from all studies from this review was located at rural area of Lampang Province in northern Thailand located in Thoen District which was about 100 km from the central area (Orakij et al., 2017). The concentration of total PAHs in the personal inhalation exposure samples for ranged 4.2 to 224 ng m^{-3}. The values were 1.4-76 times higher than that in urban ambient air.

Table 4.1 Summary of PAHs occurrence in SEA countries

Countries	Area	Compound	Max concentration (ng m^{-3})	Carcinogenic Health Risk Assessment	Reference
Malaysia[a]	Urban	16 PAHs	4.24	Incremental life time cancer risk (ILCR) 3.3562×10^{-5}	Khan et al.,(2017)
Malaysia	Urban Sub-urban Rural	16 PAHs	2.85	Incremental life time cancer risk (ILCR) 1.9×10^{-5}	Othman et al.,(2021)
Malaysia	Urban	13 PAHs	9.94	Lifetime lung cancer risk (LLCR) 3.32×10^{-4}	Suradi et al., (2021)
Malaysia	Urban	16 PAHs	2.87 ± 0.14	Incremental life time cancer risk (ILCR) 1.42×10^{-7}	Sulong et al, (2019b)
Malaysia	Rural	14 PAHs	67.72 ± 49.84	Incremental Life Cancer Risk (ILCR) 1.29×10^{-6}	Sopian et al., (2021)
Malaysia	Sub Urban	16 PAHs	2.79	Lifetime lung cancer risk (LLCR) 5.0×10^{-5}	(Khan et al., (2015)

Thailand	Urban	16 PAHs	45 ± 29	Inhalation Cancer Risk 2.8×10^{-4}	Bootdee et al., (2016)
Thailand	Sub urban Rural	16 PAHs	Sub Urban - 2.572 ± 1.450 (2017) - 2.019 ± 1.503 (2018) Rural - 4.445 ± 3.219 (2017) - 5.214 ± 4.020 (2017)	Inhalation Cancer Risk Sub Urban 4.71×10^{-5} (2017) 3.88×10^{-5} (2018) Rural 1.07×10^{-4} (2017) 1.34×10^{-4} (2018)	Yabueng et al., (2020)
Thailand[a]	Urban	19 PAHs	0.3780 ± 0.3480	Incremental lifetime cancer risk (ILCR) 2.35×10^{-6}	Choochuay et al., (2020)
Thailand	Rural	16 PAHs	4.2- 224	Cancer risk level 6.0×10^{-5}	Orakij et al., (2017)
Singapore	Urban	16 PAHs	4.0	Excess lifetime cancer risk (ELCR) $1.75 \pm 0.38\times10^{-8}$	Zhang et al., (2017)

([a]) No HRA reported

**ILCR was calculated based on the maximum concentration reported

4.2 Health risk assessment

An ILCR sum between 10^{-6} and 10^{-4} has been thought to represents a significant prospective health risk, whilst an ILCR sum larger than 10^{-4} has been assumed to suggest a probable cancer risk. On the other hand, a number of 10^{-6} or less indicates a level of carcinogenic risk that is acceptable (USEPA, 2005). The health risk assessment showed that all the exposure from these studies were not exceeded the safe limit for PAHs exposure. The ILCR for all studies were ranged from $1.75 \pm 0.38 \times 10^{-8}$ to 3.32×10^{-4}. Carcinogenic health risk of exposure to PAHs in $PM_{2.5}$ are summarized in Table 4.1.

Sopian et. al (2021) studied that exposed student who were located 5km from petrochemical industry relatively had a substantially higher cancer risk than the comparative student who were located 20km away from the petrochemical industry. The calculation using ILCR model gives the highest value of 1.29×10^{-6}. Individual differences in body weight, physiology, and PAHs exposure add to the uncertainty in assessing health concerns. The ILCR for the exposed children still in range of acceptable risk limit of the USEPA reference. To manage the limit of non-negligible cancer risks associated with PAHs exposure, effective environmental health management measures are required.

Cancer risk level being used as method of assessment for (Orakij et al., 2017). The estimated excess cancer risk was calculated from the concentrations of nine PAHs. The toxicity equivalency factors (TEFs) used in the estimation of cancer risk assessment. The highest value of cancer risk level calculated is 6.0×10^{-5} which also doesn't exceed the limit. Therefore, the exposure was considered safe for the residents living in that area.

CHAPTER 5

DISCUSSION

The concentration of PAHs measured in countries from SEA region shows that urban area reports a lower PAHs concentration in $PM_{2.5}$ compared to rural area. This shows in research of exposed school students to the nearby petrochemical industry in Dungun, Terengganu which is a rural area (Sopian et al., 2021). The distance is within 5km which is so near causes the concentration of PAHs is quite high in that area.

A greater PAH content was found in several later research on petrochemical air pollution exposure than in this study. (Yuan et al.) discovered a higher PAHs content in a township within 10 km of Taiwan's largest petrochemical complex, with an average PAHs concentration of 15.20 ±15.18 µg g^{-1}. Meanwhile, particle PAHs (PM_{10}) concentrations from petrochemical-related companies in Nigeria's Niger Delta were 9.2 µg m^{-3}. This shows that concentration of PAHs in other research that involves petrochemical company are higher.

5.1. Concentration of PAHs

The lowest concentration of PAHs in $PM_{2.5}$ from this review was 0.3780 ± 0.3480 ng m^{-3} reported at Prince of Songkhla University (Phuket Campus) in southern Thailand (Choochuay et al., 2020). This research sampled 19 PAHs and the concentration of total PAHs in this study are lower than those measured in other areas of Thailand such as Chiang-Mai and Bangkok, which are known as heavily polluted areas (Pongpiachan, 2013). Forest fires, and agricultural waste burning in northern Thailand during the winter release huge amounts of PM into the atmosphere, particularly ultra-fine particles that include $PM_{2.5}$-bound PAHs (Vadrevu et al., 2015). Vehicle emissions are a major source to atmospheric PM in central Thailand. However, the limited availability of PAH data in southern Thailand, particularly Phuket, makes it difficult to pinpoint the sources of pollutants discharged into the atmosphere.

The highest concentration of PAHs in $PM_{2.5}$ samples was reported in Lampang Province in northern Thailand with maximum value of 224 ng m^{-3}. This high concentration probably resulted from cooking with a charcoal open fire. The number of emissions produced by cooking with biomass relies on a variety of factors, including the amount of fuel used, the amount of time spent cooking, the quality of the fuel and cooking stove, as well as the structure and ventilation of the home. The findings suggested that charcoal burning could be a contributing factor to the high lung cancer rate. Because of the high levels of personal exposure induced by microenvironments in the lives of the residents, it was determined that predicting their exposure solely based on the findings of stationary sampling was unreliable. These findings suggest that, in addition to ambient air pollution, rural dwellers are constantly exposed to PM produced from microenvironments through their own activities, such as agricultural residue burning, smoking, and cooking.

5.2. Health Risk Assessment

The ILCR value ranged from ranged from $1.75 \pm 0.38 \times 10^{-8}$ to 3.32×10^{-4}. The highest ILCR value of 3.32×10^{-4} was reported at Kuala Lumpur, Malaysia (Suradi et al., 2021). The lowest ILCR value of $1.75 \pm 0.38 \times 10^{-8}$ was reported at Clementi Road, Singapore. Health risk assessment for most of the papers were already reported except two papers (Choochuay et al., 2020) and (Khan et al., 2017). These value shows that there is no significant health risk in all these researches as there is no value that exceed the limit of 10^{-4}. Although there is no value that exceed the limit, some practice that may contribute to high concentration needs to be reduced or reviewed in order to avoid the effect of prolonged exposure to this carcinogenic compound.

CHAPTER 6

CONCLUSION

6.1 Conclusion

PAHs concentration in $PM_{2.5}$ from countries in SEA region are reviewed in this paper. From the result, rural area records a higher concentration of PAHs compared to the urban area. This is because industry area always located in rural area rather than in the developing urban area. Besides, some practice or habit in rural area such as open burning or cooking using charcoal have an impact to the high concentration of PAHs.

By measuring the concentration of PAH in that area, the health risk can be calculated using the ILCR inhalation equation to measure the exposed risk. As all the values of ILCR does not exceed the limit, the risk is considered as safe but effect of prolonged exposure cannot be understated. Awareness towards the effect of exposure to PAH needs to be enhanced to the residents living under the exposure of PAH. However, lack of research in this SEA region limits the review as more journal would help to see the situation in a bigger picture which will increase the reliability of the results from this review.

6.2 Recommendation

More research on PAHs exposure needs to be conducted especially in this SEA region to obtain a lot more information as it will help to view this issue in a bigger picture. Additional studies will provide a lot more data and which will contribute to decision making of the policy makers. The present data only focus on PAHs in $PM_{2.5}$ and its carcinogenic health risk of inhalation. Future studies on the exposure of PAHs in total suspended particulate (ultra-fine particles, $PM_{2.5}$, PM10 and road dust) via different route of exposures (inhalation, ingestion and dermal contact) is recommended to have an in-depth review.

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