Health Risk Assessment of Particulate matter associated with Polychlorinated biphenyls and Polycyclic aromatic hydrocarbons in Bangkok and Chiang mai, Thailand

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Industrial Toxicology and Risk Assessment
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การประเมินความเสี่ยงทางสุขภาพจากพอลิคลอริเนตเทตไบฟีนิลและพอลิไซคลิกแอโรแมติกไฮโดรคาร์บอนของฝุ่นละอองในกรุงเทพมหานครและเชียงใหม่ ประเทศไทย

น.ส.นารีรัตน์ พันธุ์วิทยากูล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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นารีรัตน์ พันธุ์วิทยากูล : การประเมินความเสี่ยงทางสุขภาพจากพอลิคลอริเนตเทตไบฟีนิลและพอลิไซคลิกแอโรแมติกไฮโดรคาร์บอนของฝุ่นละอองในกรุงเทพมหานครและเชียงใหม่ ประเทศไทย. (Health Risk Assessment of Particulate matter associated with Polychlorinated biphenyls and Polycyclic aromatic hydrocarbons in Bangkok and Chiang mai, Thailand) อ.ที่ปรึกษาหลัก : ศ. ดร.วนิดา จีนศาสตร์

ปัจจุบันมลพิษทางอากาศถือเป็นปัญหาหลักที่สำคัญของประเทศไทย เนื่องจากฝุ่นละอองขนาดไม่เกิน 2.5 ไมครอน ($PM_{2.5}$) และฝุ่นละอองขนาดไม่เกิน 10 ไมครอน (PM_{10}) มีปริมาณเพิ่มขึ้นในช่วงฤดูหนาวทำให้มีค่าเกินค่ามาตรฐานกำหนด ซึ่งส่งผลกระทบต่อปัญหาทางสุขภาพ การศึกษาครั้งนี้มีวัตถุประสงค์เพื่อให้ทราบถึงสารประกอบที่ปนเปื้อนอยู่กับอนุภาคฝุ่นละอองในบรรยากาศ ดังนั้นจึงดำเนินการศึกษาหาปริมาณ ความเข้มข้นของสารประกอบพอลิคลอริเนตเทตไบฟีนิล (PCBs) และพอลิไซคลิกแอโรแมติกไฮโดรคาร์บอน (PAHs) ที่ปนเปื้อนในบรรยากาศ ซึ่งได้ทำการสุ่มตัวอย่างจำนวน 8 แห่ง ในช่วงฤดูแล้งระหว่างเดือนธันวาคม พ.ศ. 2561-มิถุนายน พ.ศ. 2562 ได้แก่ จังหวัดเชียงใหม่ จำนวน 3 แห่ง และกรุงเทพมหานครจำนวน 5 แห่ง เก็บตัวอย่างโดยใช้อุปกรณ์พาสซีฟดิสก์โพลียูรีเทน (PAS-PUF) รวมตัวอย่างทั้งหมดจำนวน 24 ตัวอย่าง จากนั้นทำการวิเคราะห์ด้วยเชิงปริมาณโดยวิธีมาตรฐานแก๊สโครมาโตกราฟีแมสสเปคโตรมิเตอร์ (GC-MS) ซึ่งจากผลการศึกษาความเข้มข้นของ PAHs และ PCBs พบว่า มีปริมาณเพิ่มขึ้นในช่วงฤดูแล้ง โดยในจังหวัดเชียงใหม่มีปริมาณ PAH รวมสูงสุด 848 นาโนกรัมต่อลูกบาศก์เมตร ซึ่งมีปริมาณสูงกว่าในกรุงเทพมหานครมีปริมาณ PAH รวมสูงสุด 455 นาโนกรัมต่อลูกบาศก์เมตร เนื่องจากพื้นที่ในจังหวัดเชียงใหม่ในช่วงตั้งแต่เดือนกุมภาพันธ์ถึงเมษายน พ.ศ. 2562 พบว่ามีการเกิดไฟป่า รวมทั้งการปล่อยมลสารทางรถยนต์ และการเผาไหม้แบบชีวมวล ส่วนปริมาณ PCB รวมสูงสุดที่พบในกรุงเทพมหานคร 15 พิโครกรัมต่อลูกบาศก์เมตร ซึ่งปริมาณสูงกว่าในจังหวัดเชียงใหม่มีปริมาณ PCB รวมสูงสุด 2.63 พิโครกรัมต่อลูกบาศก์เมตร นอกจากนี้การรับสัมผัสปริมาณ PAHs และ PCBs โดยทางการหายใจ ในการศึกษานี้พบว่ามีจุดที่ทำการเก็บตัวอย่างมีค่าการประเมินความเสี่ยงอยู่ในระหว่าง 10^{-4}- 10^{-6} ดังนั้นตามคำแนะนำของ US EPA กลุ่มประชาที่ทำกิจกรรมในพื้นที่เก็บตัวอย่างอาจจะมีความเสี่ยงต่อการเป็นโรคมะเร็งได้ อย่างไรก็ตามมลพิษทางอากาศสามารถมีการเปลี่ยนแปลงได้ตลอดเวลาตามฤดูกาล ดังนั้นการจัดการคุณภาพอากาศในจังหวัดเชียงใหม่และกรุงเทพมหานคร จึงเป็นประเด็นสำคัญที่ต้องติดตามและเฝ้าระวัง

สาขาวิชา	พิษวิทยาอุตสาหกรรมและการประเมินความเสี่ยง	ลายมือชื่อนิสิต ....
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Nareerat Punvitayakul : Health Risk Assessment of Particulate matter associated with Polychlorinated biphenyls and Polycyclic aromatic hydrocarbons in Bangkok and Chiang mai, Thailand. Advisor: Prof. WANIDA JINSART, Ph.D.

Atmospheric pollutants have become a severe problem in creating health issues in Thailand. Due to the increase in fine particles in the air environment, the city population is facing acute respiratory problems. For understanding the concentration of polycyclic aromatic hydrocarbon (PAHs) and Polychlorinated biphenyls (PCBs), 24 samplings were done in Chiangmai and Bangkok of Thailand using Polyurethane (PUF) disk passive samplers. There were five sampling sites in Bangkok, and three in Chiang Mai. Data were collected in the dry season from December 2018- June 2019. A total of 24 samples were extracted and further quantitatively analyzed by the standard method using GC-MS. Both PAHs and PCBs concentrations increased during the dry season. In Chiang Mai, the maximum total PAH concentration was found to be 848 ng/m^3, which was higher than that of Bangkok, max. concentration was found to be 455 ng/m^3. On the other hand, the max of the total PCBs found in Bangkok was 15 pg/m^3 were higher than that in Chiang Mai which is max. value 2.63 pg/m^3. However, Bangkok sites had more dominant species PAHs than in Chiang Mai. Particularly, during haze episodes of Bangkok and Chiang Mai from December 2018 to April 2019. The potential sources of PAHs were found as the combined emission of diesel and gasoline vehicles and biomass combustion. The carcinogenic risk associated with inhalation exposure to PAHs and PCBs was estimated to be between 10^{-4}-10^{-6} at some sampling point. It may cause a health effect for people who live in this area for a long term of exposure. The analyzed PAHs and PCBs species indicated their potential sources that related to both biomass burning and traffic in Bangkok and Chiangmai. However, the pollutants' level also had seasonal variations. therefore, air quality management is an essential issue that needs to be monitored in these provinces (cities) of Thailand.

Field of Study: Industrial Toxicology and Risk Assessment   Student's Signature ....
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Nareerat Punvitayakul

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CHAPTER 1

INTRODUCTION

1.1 Background

Thailand now faces many environmental problems, especially, the air pollution problem is currently a serious issue. In big cities such as Bangkok and Chiangmai which is mainly had an air pollution issue from anthropogenic activities such as a traffic road and open burning. These activities emitted verities of pollutants in the air. Air pollution contains a wide of pollutants, ranging from gases to particulate matter which is harmful to humans and the environment. Human certainly exposes air pollutants daily because they are exit around in all types of environments such as indoor and outdoor. These air pollutants may neither be emitted directly into the air from specific sources nor be formed in the atmosphere from chemical reactions. Air pollutants can have both natural and anthropogenic sources; however, anthropogenic sources make the largest contribution such as energy production and transportation. Persistent organic pollutants (POPs) are also a pollutant that considered an adverse health effect and harmful for the environment. POPs are complex mixture which can be found in the atmosphere such as Polycyclic aromatic hydrocarbons (PAHs), Polychlorinated biphenyls (PCBs), Polychlorinated Dibenzofurans (PCDD/PCDF), or polybrominated diphenyl ethers (PBDEs). They wildly distributed and stable in the environment, also can accumulate in human tissue and other organisms. These pollutants have known for the potential health adverse effect. Due to the negative effect of air pollutants to study the distribution of specific substances in different environments and around humans. This requires monitoring of air concentrations which in turn requires a suitable and user-friendly air sampler. Currently, the high-volume sampler is the most widely used approach for sampling pollutions in the air. This approach utilizes a pump that draws air through sampling media that trap pollutants. However, this approach requires costly sampling equipment and a source of electricity, it is not feasible for conducting spatial mapping studies of POPs at remote sites. An alternative and more feasible approach that was employed here was to use passive air samplers (PAS) consisting of polyurethane foam (PUF) disks. PAS is chemical accumulators that rely on air currents to deliver chemicals to the sampler. Thus, they do not require electricity. The uptake of persistent organic pollutants has been characterized which allows air concentrations to be determined. This study was conducted on pollutants by using the PAS approach. Besides, this approach was used for conducted POP around the world. The Global Atmospheric Passive Sampling (GAPS) Network was initiated this approach in 2004 and consists of more than 50 sites on seven continents. The program has demonstrated the plausibility of PAS for spatial mapping POPs. (Harner et al., 2006; Lee et al., 2016; Pozo et al., 2009; Pozo et al., 2004) Ideally, simultaneous measurements of air concentrations in different locations are needed to assess the relative importance of sources, atmospheric processes, and the long-range atmospheric transport potential of POPs.

In the past few years, a serious atmospheric problem occurred in Thailand. A particle trapped and visual in the air. This issue could be causing a health effect on humans and animals without noticeable. The importance of monitoring air pollutants benefits human health. Humans have exposed to air pollution through a basic activity every day such as eating, drinking, breathing, etc., which is, they are exposed to different kinds and amounts of air pollutants when they move from place to place during their daily life. Normally, exposure does not cause any severe effect on human health, however, the sensitive groups, elderly children, or the people who had a disease may be easily associated with a risk of adverse health effects more than healthy people by exposure only a small amount of a pollutant. It might cause a severe effect depending on the concentration in each environment and the time they spend there. The uptake in humans caused by exposure to a pollutant is influenced by many factors. For example, the route of exposure, the magnitude of exposure, the duration of exposure, or the frequency of exposure. Prediction and prevention could be the advantage of decreasing adverse health effects for humans. Exposure assessment is the process involved in estimated and measuring exposure, i.e., identifying and quantifying the exposure that may cause health effects. The exposure assessment is also important in identifying sources emitting harmful pollutants, estimating the number of persons exposed, identifying high-risk groups, and highlighting the control priorities. Therefore, the exposure data is essential in the exposed population identification.

1.2 Research Objectives

1.2.1 To Identify the particulate matter associated with persistent organic pollutants in the air environment in Bangkok and Chiangmai province, Thailand.

1.2.2 To evaluate the risk of PCBs and PAHs on human health.

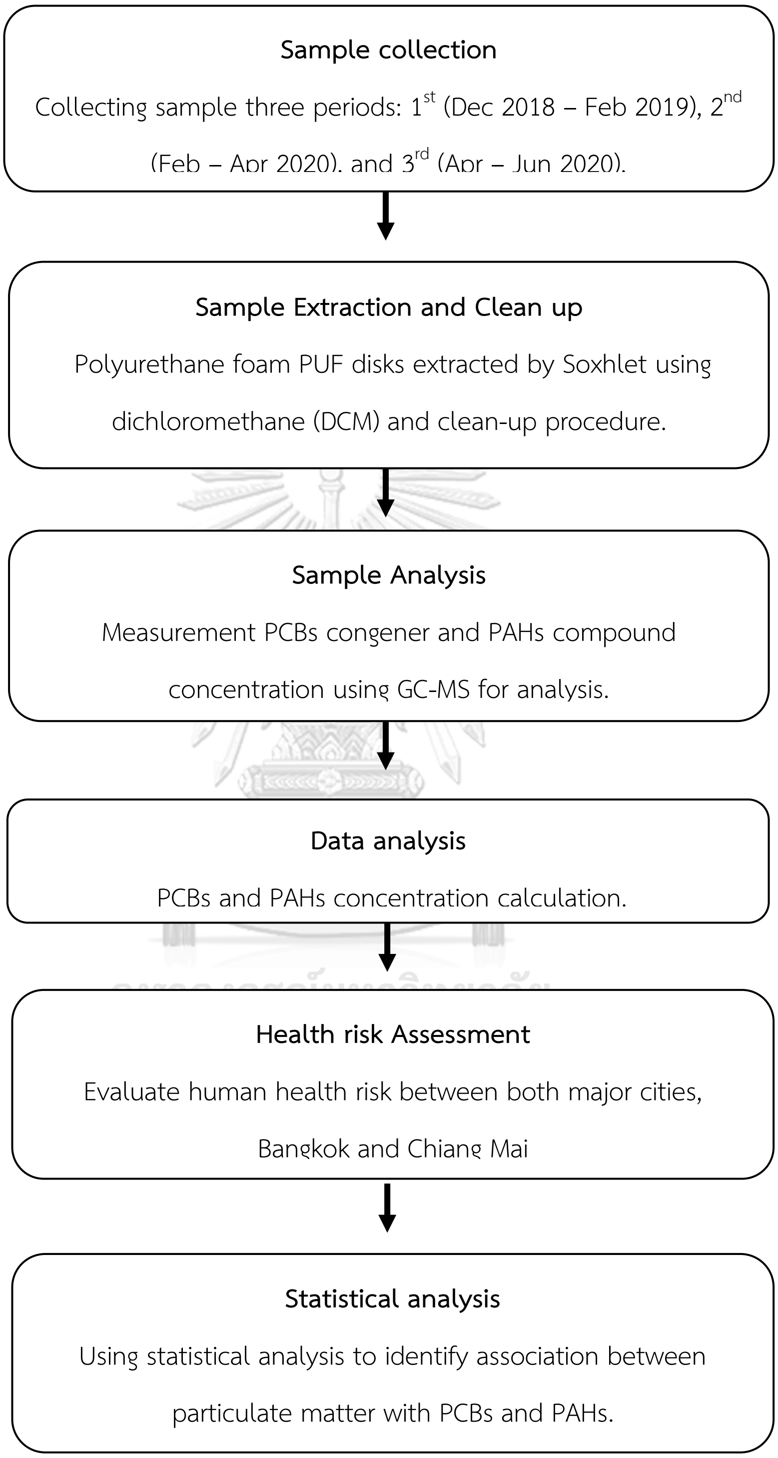
1.2.3 To characterize and quantify the PCBs and PAHs from the passive air sampler in the ambient air of Bangkok and Chiangmai province, Thailand.

1.3 Expect Outcomes

In this research, it is expected as follows:

1. The association of PAHs and PCBs in the ambient air environment in Bangkok and Chiangmai province, Thailand.
2. Quantify the concentration of PCBs and PAHs from the passive air sampler in the ambient air of Bangkok and Chiangmai province, Thailand.
3. Health risk assessment of exposes PCBs and PAHs

1.4 Conceptual Framework



Sample collection

Collecting sample three periods: 1st (Dec 2018 – Feb 2019), 2nd (Feb – Apr 2020), and 3rd (Apr – Jun 2020).

Sample Extraction and Clean up

Polyurethane foam PUF disks extracted by Soxhlet using dichloromethane (DCM) and clean-up procedure.

Sample Analysis

Measurement PCBs congener and PAHs compound concentration using GC-MS for analysis.

Data analysis

PCBs and PAHs concentration calculation.

Health risk Assessment

Evaluate human health risk between both major cities, Bangkok and Chiang Mai

Statistical analysis

Using statistical analysis to identify association between particulate matter with PCBs and PAHs.

Figure 1 : Thesis Conceptual Framework

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Air Sampling techniques

Currently, the high-volume sampler is the most widely used approach for conduction pollutants that adhere to the particle in the air. The air sampling approach can be categorized into two approaches. First, the active air sampler approach needed a pump to draws air through sampling media that trap pollutants. Second, a passive air sampling approach by gaseous diffusion delivers chemical species to a porous uniform material in the passive samplers which take up the compounds by adsorption.

2.1.1 Active Air Sampler

Active air sampling is the most common method to identify PCBs and PAHs in ambient air. These samplers have a sampling module that often consists of two compartments: a filter and a solid adsorbent to collect the particle-associated and the gas phase pollutants, respectively. The filter, often Teflon, glass, or quartz fiber, is placed in the inlet of the sampler. The solid adsorbent normally consists of a polyurethane foam (PUF) plug or a sorbent tube with XAD-2 or Tenax depending on the target pollutants and the capacity required and is located downstream from the filter. Importantly, the adsorbent also retains pollutants that volatilize from the particles on the filter during sampling. A pump is used to draw the air into the sampler, through the filter and the following adsorbent. For example, Mini-volume Air Sampler or MiniVol™ TAS (Figure 2, (a) MiniVol^{TM} Air Sampler (b) MiniVol^{TM} Site Installation) was used for collecting particulate matter which the device manufactured by Air metrics, and used to sample fine particulate matter ($PM_{2.5}$) with a flow rate at 5 L/min. This device gives a result as accurate as data from Federal

Reference Method. With its lightweight and its portability, it makes this device to be an ideal method for remote areas and temporary sites.

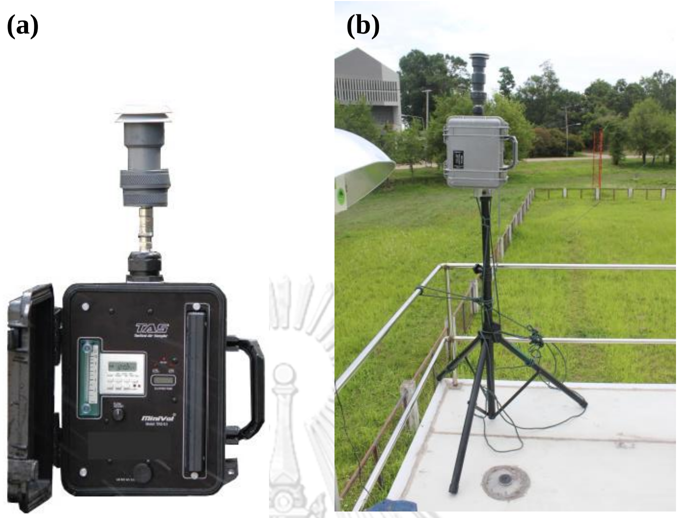


Figure 2 : MiniVol^{TM} Air Sampler

Although the MiniVol™ portable air sampler can be used to collect $PM_{2.5}$, PM_{10}, and TSP samples, it can measure only one type at a time. The pump of MiniVol™ draws air at a flow rate of 5 L/min with a 47 mm filter passing through a particle size separator, which separates 2.5 microns and 10 microns. To collect the TSP sample, the impactor is needed to be removed. The operation of the device starts when the particulate sample is caught on the filter, which must be weighed pre- and post-exposure with a microbalance as accurate as one microgram. The samples are then determined in a unit of microgram/cubic meter ($\mu g/m^3$). This instrument including a battery that can continuously perform for 24 hours and it is also programmable with 7 days timer. Before it is operated, instrument calibration is required to make sure that the sampler has an ambient flow rate of 5 L/min. This calibration method includes differing air temperature and atmospheric pressure from elevation and seasonal changes (Airmetrics, 2008).

2.1.2 Passive Air Samplers (PAS)

Passive air samplers as shown in Figure 3, (a) Schematic representation of the polyurethane form foam (PUF) disk sampling device (b) PUF disk, and (c) Passive air sampler at the sampling site. PAS are low-cost and simple alternatives to traditional active air samplers (pumped) which require a pump, a power source, and a sampling head. In principle, gaseous diffusion delivers chemical species to a porous uniform material in the passive samplers which take up the compounds by sorption processes. On the sampler’s surface, the pollutants permeate through the medium binding to it by Van Der Waal's forces. Uptake of compounds persists until the collection medium and the atmospheric gas phase are in equilibrium or until the sampling process is ceased. Several technologies of passive samplers exist, such as the Ogawa, Lanwatsu, and the passive flux sampler; however, the polyurethane foam (PUF) passive sampler is commonly used for POPs sampling (Bohlin, Jones, & Strandberg, 2010). An alternative and more feasible approach that was employed here was to use passive air samplers consisting of polyurethane foam (PUF) disks. PAS is chemical accumulators that rely on air currents to deliver chemicals to the sampler. The uptake of persistent organic pollutants has been characterized which allows air concentrations to be determined. Moreover, the Global Atmospheric Passive Sampling (GAPS) Network was initiated in 2004 and consists of more than 50 sites on seven continents. The program has demonstrated the plausibility of PAS for spatial mapping POPs. (Harner et al., 2006; Lee et al., 2016; Pozo et al., 2009; Pozo et al., 2004).

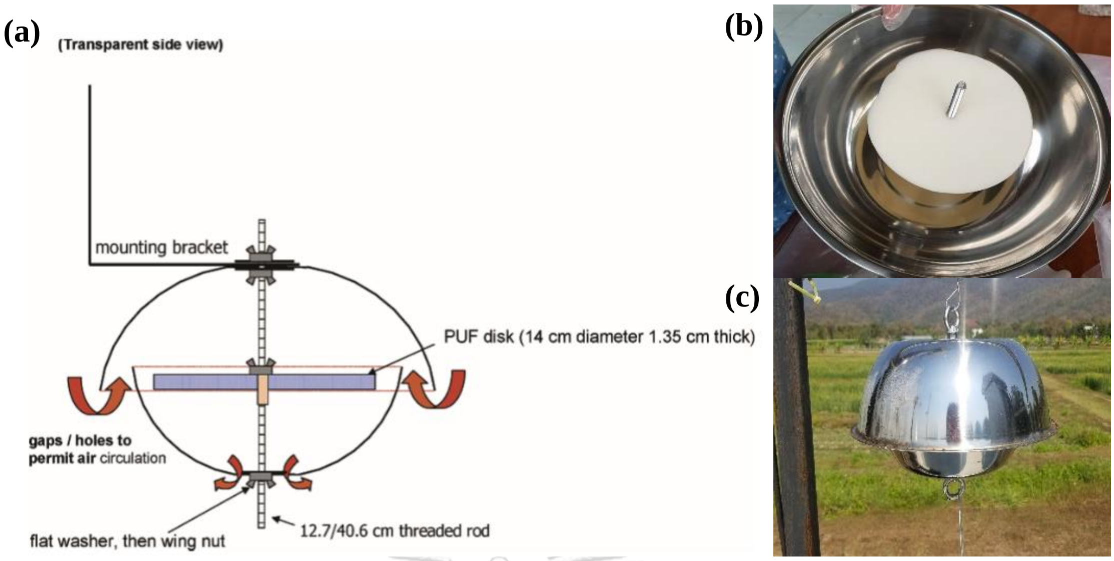


Figure 3 : Schematic representation of the polyurethane form foam (PUF) disk sampling device

The theory of passive air sampler is useful to explain the theory behind the accumulation of pollutants in a passive sampler through mathematical models. The basic theory and mathematical models for passive sampling depend on the type of media the sampling will be performed and the type of sampler used for the sampling. Models and theory for an accumulation of hydrophobic pollutants (e.g. PAH and PCBs) by PAS, especially polyurethane foam (PUF) containing PAS are described by (Pozo et al., 2009; Pozo et al., 2004; Shoeib & Harner, 2002). The PAS medium (PUF) is considered to be a uniform and porous compartment into which pollutants can penetrate and be accumulated. The extent to which the pollutants are enriched relative to air at the partitioning equilibrium is dependent on PUF-air partition coefficient, $K_{PUF\text{-}A}$, which is a property describing the solubility of a pollutant in the PUF compared to air as an Eq.1

$$K_{PUF-A} = \frac{C_{PUF,eq}}{C_{A,eq}}$$

Eq.1

$C_{PUF,eq}$ is the concentration of the pollutant in the PUF-PAS and $C_{A,eq}$ is the concentration of the pollutant in the air when the two phases are in equilibrium and $C_{PUF,eq}$ and $C_{A,eq}$ has the same units (e.g. mol/volume). PAS like PUF with a hydrophobic sampling medium has a high concentration capacity for hydrophobic organic pollutants like PAHs and PCBs. This means that the pollutants are found to a much higher extent in the PAS than the air, at equilibrium. $C_{PUF,eq}$ is, therefore, several orders of magnitude larger than $C_{A,eq}$, and K_{PUF-A} is in orders of 10^{-16}-10^{16} for PAHs and traces organic compounds. The K_{PUF-A} is correlated to the more easily derived and thereby more available octanol-air partition coefficient (K_{OA}). K_{OA} is commonly used as a surrogate when modeling the uptake of PAS. The accumulation of pollutants in a PAS is a balance between uptake and release processes. The exchange of pollutants between the PAS and the air can be described as a first-order kinetic with three consecutive stages: linear, curvilinear, and equilibrium (Figure 3). PAS sampling can be performed either in the linear or equilibrium phases depending on the exposure time, the type of sampling medium, and target pollutants. For example, the time to reach equilibrium for most PAHs and POPs in a PUF-PAS range from weeks to several months/years while the same pollutants reach equilibrium after days in a PAS consisting of polymer-coated glass (POG) The amount of pollutants in the PAS at equilibrium does not change with time provided that the concentration of the pollutant in the air does not fluctuate and the temperature is constant. This consistency does rarely occur and the masses presented by equilibrium samplers may thereby provide a momentary concentration which also is affected by fluctuations in temperature. Sampling in the linear phase, instead, provides time-weighted average concentrations of the pollutants for the exposure time and the results are less influenced by fluctuations in temperature. Typically, the PUF-PAS is used in the linear region when deployed in the field.

The mass transfer of pollutants from the air to the PUF-PAS is described by individual transport processes over several boundary layers depending on the PAS. If the PUF-PAS is deployed without or with protective chambers. Without a protective chamber, the individual transport processes are 1) from ambient air around the PUF-PAS to the interface between the air and the PAS (air-side boundary layer), and 2) from the air-side boundary layer into the PAS.

If a protective chamber is used around the PAS the transport processes are: 1) from ambient air to the air volume inside the chamber; 2) from the air around the PAS (e.g. inside the chamber) to the interface between the air and the PAS (air-side boundary layer), and 3) from the interface (air-side boundary layer) into the PAS. The velocity of the pollutant over each boundary layer is described by a mass transfer coefficient (k, m/day). (Bohlin, Jones, Levin, Lindahl, & Strandberg, 2010)

The air-side mass transfer velocity (k_A) is equivalent to the gas phase deposition velocities of the pollutants in the PUF. The overall mass transfer coefficient (k_O) for all the boundary layers and therefore the overall resistance for transport ($1/k_O$) is given by:

$$\frac{1}{k_0} = \frac{1}{k_A} + \frac{1}{k_{PUF}K_{PUF-A}} + \frac{1}{Q/\,A_{PUF}} \qquad \text{Eq. 2}$$

Where k_A is the mass transfer in the air-side boundary layer, k_{PUF} the mass transfer in the sampler boundary layer, Q (m^3/d) is the flow of air into the chamber and A_{PUF} (m^3) is the surface area of the sampling medium (PUF). 1/kA represents the resistance in the air-side boundary layer, ($1/(k_{PUF}\ K_{PUF-A})$) the resistance in the sampler boundary layer, and (Q/A_{PUF}) the resistance in entering the protective chamber. As described earlier, the K_{PUF-A} or K_{OA} for PAHs and POPs is typically more than 10^7, therefore the resistance of the sampler boundary layer ($1/(k_{PUF}K_{PUF-A})$) is insignificant.

A_{PUF} is small relative to Q and $1/(Q/A_{PUF})$ can also be considered insignificant. Mass transfer of pollutants to the PUF-PAS is therefore controlled by air-side resistance (i.e. $k_O \approx k_A$). The theory described below is based on air-side controlled uptake. A slightly different approach can be used for a PAS where sampler-side resistance is the limiting factor. The accumulation rate of pollutants by the PUF-PAS is equivalent to the rate of uptake minus the rate of loss (Eq. 3).

$$V_{PUF}\left(\frac{dC_{PUF}}{dt}\right) = k_A A_{PUF}\left(C_A - \left(\frac{C_{PUF}}{K_{PUF-A}}\right)\right) \qquad \text{Eq.3}$$

Where V_{PUF} is the volume of the PUF-PAS (cm^3), C_A is the concentration (pg/cm^3) of the pollutant in the sampled air, and C_{PUF} is the concentration of pollutants in the PUF (pg/cm^3). When C_A is constant and the environmental conditions (i.e. wind speed, T) are constant Eq.3 can be integrated and the accumulation can be analytically described as

$$C_{PUF} = K_{PUF-A} C_A (1- \exp - [(A_{PUF}/V_{PUF}) k_A / K_{PUF-A}]t) \qquad \text{Eq.4}$$

Eq.4 describes the accumulation phases in Figure 2.3 in an analytical way. At the beginning of the accumulation when the value of C_{PUF}/K_{PUF-A} is small (due to small C_{PUF}), the only uptake occurs while elimination is negligible and the accumulation trend can be approximated to a linear trend as a function of k_A, $A_{PUF,}$ and C_A (Figure 3a):

$$\frac{V_{PUF}C_{PUF}}{\Delta t} = k_A A_{PUF} C_A \qquad \text{Eq.5}$$

The mass of pollutant sequestered by the PUF-PAS (M_{PUF}, pg) within the linear deployment period (t) is:

$$M_{PUF} = k_A A_{PUF} C_A \Delta t \qquad \text{Eq.6}$$

The term $k_A A_{PUF}$ represents the PUF-PAS's sampling rate (R_S), i.e. the effective volume of air passed through the PUF per time (L/min, or m^3/day). It is equivalent to the flow rate in conventional active air samplers.

$$Rs = \frac{M_{PUF}}{C_A \Delta t} \qquad \text{Eq.7}$$

This is one of the most important terms in PAS since it is used to determine air concentrations (C_A):

$$C_A = \frac{M_{PUF}}{R_S \Delta t} \qquad \text{Eq.8}$$

The PAS can be calibrated to obtain R_S for individual pollutants in specific environments and then used in PAS campaigns to provide air concentrations.

If accumulation continues the concentration of pollutants in PUF (C_{PUF}) increases and consequently, the value of C_{PUF}/K_{PUF-A} also increases tending to equalize the C_A. The uptake is thereby reduced by an increased elimination and the sampling enters the curvilinear phase. A prolonged accumulation results in an equilibrium between C_{PUF} and C_A (Eq. 1) and thereby uptake and elimination rates are the same (Figure 2.3b).

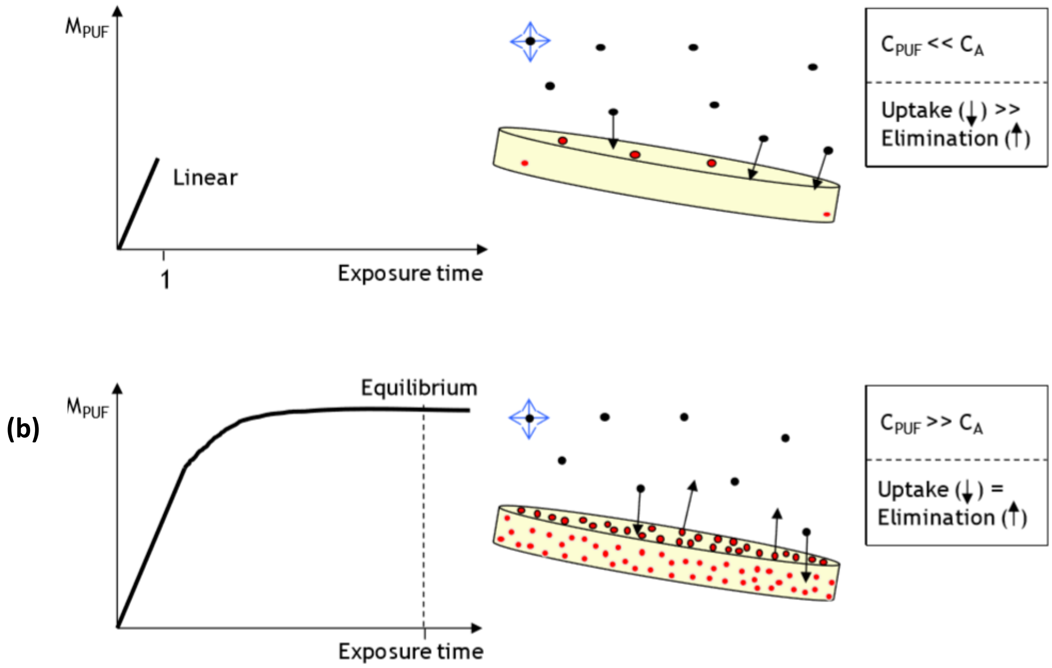


Figure 4: Accumulation stages in PUF-PAS, starting with linear phase and (b) ending with equilibrium phase

The time to reach equilibrium (t_{eq}) is influenced by the sampler design and Physico-chemical properties of the pollutant and can be calculated as follows (Eq.9)

$$t_{eq}=\frac{4.605\,V_{PUF}}{A_{PUF}k_v}K_{PUF\text{-}A} \qquad \text{Eq. 9}$$

Increasing the surface area (A_{PUF}) to volume (V_{PUF}) ratio (i.e. decreasing V_{PUF}/A_{PUF}) of the PUF decreases the time taken to approach equilibrium. A compound with higher $K_{PUF\text{-}A}$ or K_{OA} reaches equilibrium later than one with a smaller $K_{PUF\text{-}A}$ or K_{OA}. It is important to control t_{eq} for the target pollutants in the PUF-PAS of interest to be sure that sampling is held within the linear phase. The most volatile PAHs and PCBs are shown to reach equilibrium in PUF standard configurations after 2-3 weeks while the ones with higher K_{OA} stay in the linear phase for months. (Shoeib & Harner, 2002)

2.1.3 Mass Spectroscopy

Mass spectroscopy is an analytical tool that utilizes energy to convert molecules into gas-phase ionic species whose direction and motion can be manipulated and consequently be detected. A mass spectrometer has four parts: an inlet for transferring samples into the instrument, an ion source that produces the ions, a mass analyzer that uses electric fields controls the direction and motion of ion species, and a detector that measures and amplifies the ion current. Several modes of ionization exist depending on the type of sample and the use of the mass spectrometer (Figure 2.4). For atomic ionization inductively coupled plasma or thermal ionization may be preferred while for molecules electron ionization, chemical ionization, field ionization, and photoionization among others may be used. In electron ionization, a beam of energetic electrons is used to bombard vaporized molecules producing ions. In the context of ICP-MS a sample can either be introduced to the mass spectrometer through solution nebulization (involves acid digestion) or through laser ablation (for solid samples) as in the case of Laser Ablation Inductively Coupled Plasma Mass Spectrometry, LA-ICP-MS (Dass, 2007).

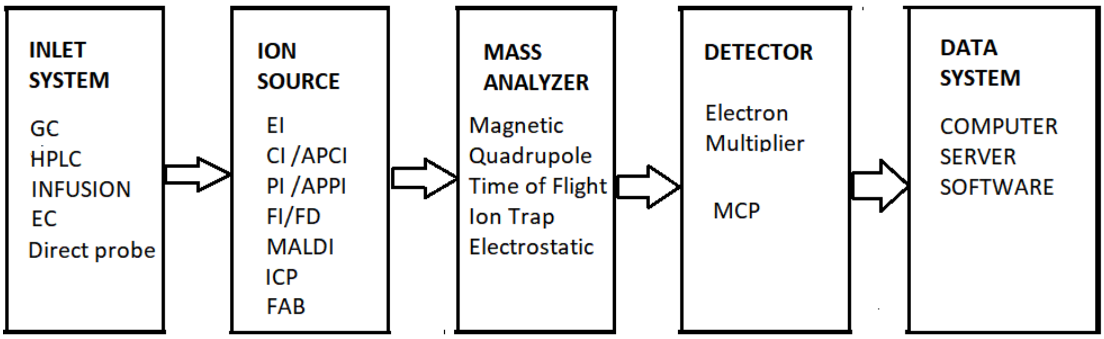


Figure 5 : A schematic showing the layout of a mass spectrometer

In the mass analyzers, several technologies may exist. First, a magnetic sector which uses momentum dispersion and directional focusing to separate ions with different m/e ratios, second and electrostatic analyzer for double focusing (higher resolution) using an electrical field, or a quadrupole mass analyzer that achieves selective mass separation by setting the ions in a vibratory motion in a high-frequency oscillating field over a defined radio frequency (rf) and direct current (dc) potential (Dass, 2007). Usually, two pairs of oppositely charged electrodes are used to ‘mass-filter’ the ions since ions of different m/e and trajectory stabilities will converge and diverge at different rates within the quadrupole as Figure 5 (Douglas A. skoog, Holler., & Stanley R. Crouch, 2017). For example figure 6, when a positive ion enters the quadrupole it will be attracted by the negative electrodes and if the potential is changed (rf) before discharging it changes direction to the positive electrode. Such an ion is said to have a stable trajectory in the x and y-axis and proceeds in the z-direction. The low m/e ions are allowed to pass through by the negative dc electrodes, while the positive electrodes allow the high m/e ions to pass through. If the voltages and rf are chosen within the narrow mass to charge ratio both species reach the detector. In the analysis, the narrow m/e range is scanned from low to high values by manipulating the dc and rf. Whenever the rf-only mode is used as is in the case of the collision cell in a triple quadrupole arrangement, all ions within the transmission range selected are stable in XY directions and proceed in the z-direction. As such polyatomic ion interferences and fragmentation species can be eliminated while specific ions of interest from overlapping signals can be analyzed. Other mass analyzers include the time-of-flight based on velocities and Fourier transform ion cyclotron and orbitrap technologies.

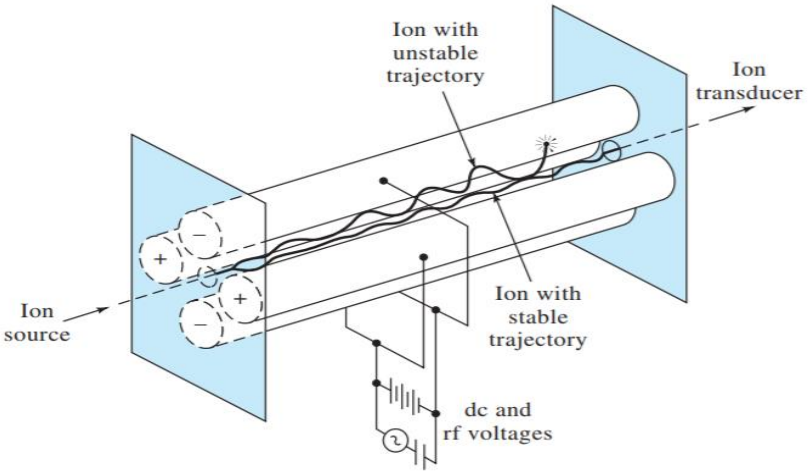


Figure 6 : A quadrupole mass analyzer

2.2 Persistent Organic Pollutants in the Environment

Persistent Organic Pollutants as known as POPs are organic chemical substances which they are carbon-based. They possess a particular combination of physical and chemical properties. The POPs would remain intact exceptionally long periods in the environment, and become widely distributed throughout the environment as a result of natural processes involving soil, water, and air. Moreover, they are accumulated in the fatty tissue of living organisms including humans, and found at a higher concentration at higher levels in the food chain which are toxic to both humans and wildlife. POPs can be classified as intentionally and unintentionally (Figure 2.6). The main source and emission of POPs, initially, twelve POPs have been recognized as causing an adverse effect on humans and the ecosystem and these can be placed in three categories. First, pesticide such as Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene, Mirex, Toxaphene. Second, industrial chemicals such as Hexachlorobenzene, Polychlorinated Biphenyls (PCBs) Third, by-products such as Hexachlorobenzene, Polychlorinated Dibenzo-p-dioxins, and Polychlorinated Dibenzofurans (PCDD/PCDF), and PCBs. However, the Stockholm Convention also classified the initial 12 POPs as shown in Table 1 (UNEP (2008)

Table 1 : Pollutants classified as pops by Stockholm Convention on POPs and their respective action of a treaty

Initial 12 POPs, 2001		Additional POPs,2009-2010	
Name	Action (Annex)	Name	Action (Annex)
Aldrin	Elimination (A)	α-Hexachlorocyclohexane	Elimination (A)
Chlordane	Elimination (A)	β-Hexachlorocyclohexane	Elimination (A)
Dieldrin	Elimination (A)	Chlordecone	Elimination (A)
Endrin	Elimination (A)	Hexabromodiphenyl	Elimination (A)
Heptachlor	Elimination (A)	Hexabromodiphenyl ether	Elimination (A)
Hexachlorobenzene	Elimination (A)	heptabromodiphenyl ether	
(HCB)	Reduction of unintentional	Lindane	Elimination (A)
	releases (C)	Pentachlorobenzene	Elimination (A)
Mirex	Elimination (A)	Tetrabromodiphenyl ether	Elimination (A)
Toxaphene	Elimination (A)	pentabromodiphenyl ether	
Polychlorinated	Elimination (A)	Perfluorooctanesulfonic acid	Restriction (B)
Biphenyls (PCBs)	Reduction of unintentional	(PFOS)	
	releases (C)	perfluorooctanesulfonyl	
DDT	Restriction (B)	fluoride (PFOSF)	
Dioxins	Reduction of unintentional releases (C)		

Currently, over 160 countries around the world have signed to adopt the Stockholm Convention on POPs. Thailand is one of the countries that have signed under the convention. Each country has to take measures to prohibit the production, use, import, and export of the POPs in Annex A; restrict production and use of POPs in Annex B; and reduce the release of unintentionally produced POPs in Annex C

(Table 1). Moreover, the countries must also conduct a monitoring program to identify the sources, measure continuous levels of POPs, and demonstrate the reduction of POPs. However, it is problematic to fully implement the Stockholm Convention in all the signatory countries. The problems are due to difficulties in controlling and eliminating old stocks and in some cases difficulties in finding and introducing substitute products.

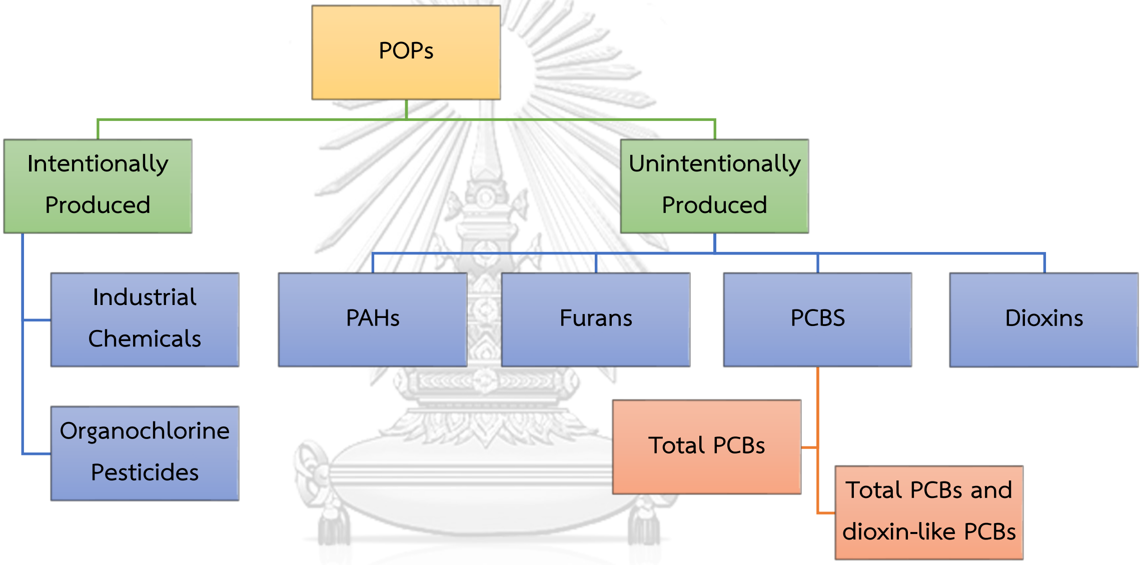


Figure 7 : Group of persistent organic pollutants

2.3 Polychlorinated biphenyls (PCBs)

2.3.1 Properties of Polychlorinated biphenyl

Polychlorinated biphenyls or PCBs are industrially produced organo-halogenated compounds that comprise 209 possible congeners. The properties that made PCBs applicable in the industrial process are their fire resistance. However, their persistence in the environment is the property that has resulted in their perceived toxicological problems. Mixtures of these compounds are contaminated with other agents and have been shown to produce adverse organ and system effects on a variety of animals. Since the mid-1970s, production, and use of PCBs have been eliminated based on chronic animal toxicity data and concern about the environmental persistence of these highly lipophilic compounds which tend to bioaccumulate in living tissues and the food chain. The properties of PCBs have the general formula $C_{12}H_1O_xCl_x$, where the number of chlorines substituted on the biphenyls can range from one to ten resulting in ten forms of polychlorinated biphenyls. Two-hundred nine PCB isomers are theoretically possible in which the number of chlorines in each isomer determines its classification and nomenclature (Figure 8). Pure PCBs are solids at room temperature (25 °C), and their melting points range from 54°C for 2-chlorobiphenyl to 310°C for 2,3,4,5,6,2’,3’,4’,5’,6’ decachlorobiphenyl. Generally, PCBs melting points increase with the complexity of the compound. The chemical mixtures of PCBs used in industry are usually colorless to lightly tinted oils. PCBs are also fat-soluble, water-insoluble, and very stable. They are very resistant to degradation, oxidation, and other chemical agents such as acids and bases. They can withstand extreme temperatures up to 1600°F or 870 °C.

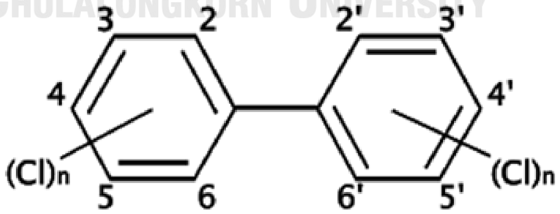


Figure 8 : General molecular structure of Polychlorinated biphenyls (PCBs)

The past usage in Thailand of Polychlorinated Biphenyls, mostly, electric industrial was applied PCBs for electrical products. The main source of PCBs usually came from the transformation and capacity of electrical equipment such as voltage regulators, switches, re-closers, bushings, electromagnets, an oil used in motors and hydraulic systems and, the old electrical devices or appliances containing PCBs capacitors. Nowadays, the usage of Thailand is controlled by the Pollution Control Department (PCD). PCBs have been classified as a hazardous substance, and ban for importation, exportation, production, and possession. Moreover, regulations had issued that PCBs waste must be stored, transported, handled, and disposed of by the procedures of the Notification of the Ministry of Industry of Thailand. Nevertheless, PCBs concentration still has been found in the environment because these compounds have detrimental properties; persistence, and bio-accumulation which is harmful to ecological integrity, wildlife, and humans. Unfortunately, PCBs concentration in the atmosphere field has limited information in Thailand. There were a few studies of PCBs concentration had found in the environment in different areas of the country. Most PCB compound contamination studies in Thailand was in the water, sediment, and marine animals.

The study of contamination of the coral reef on the islands of Samui and Katen located in the western part of the Gulf of Thailand. A total PCBs of 21 PCB from 35 congeners assayed were found in the region. Among the 7 most monitored congeners (PCB-28, 52, 101, 118, 138, 153, 180), PCB -101, 138, and 180 were not found. The sum of these 7 congener concentrations was higher in the reefs than the adjacent terrestrial soil. Aroclor equivalent total PCB concentration was higher in the coral reef in Katen and Samui islands compared to the terrestrial soil of Samui Island as much as a factor of two. The di-, tri-. And tetra-CBS were abundant with lesser amounts of Penta-, Hexa-, Hepta- and Nona- PCB homologs. The research had found that PCB concentration in coral reef trend to decrease from the past compared with the other studies (G. H. Hong et al., 2013).

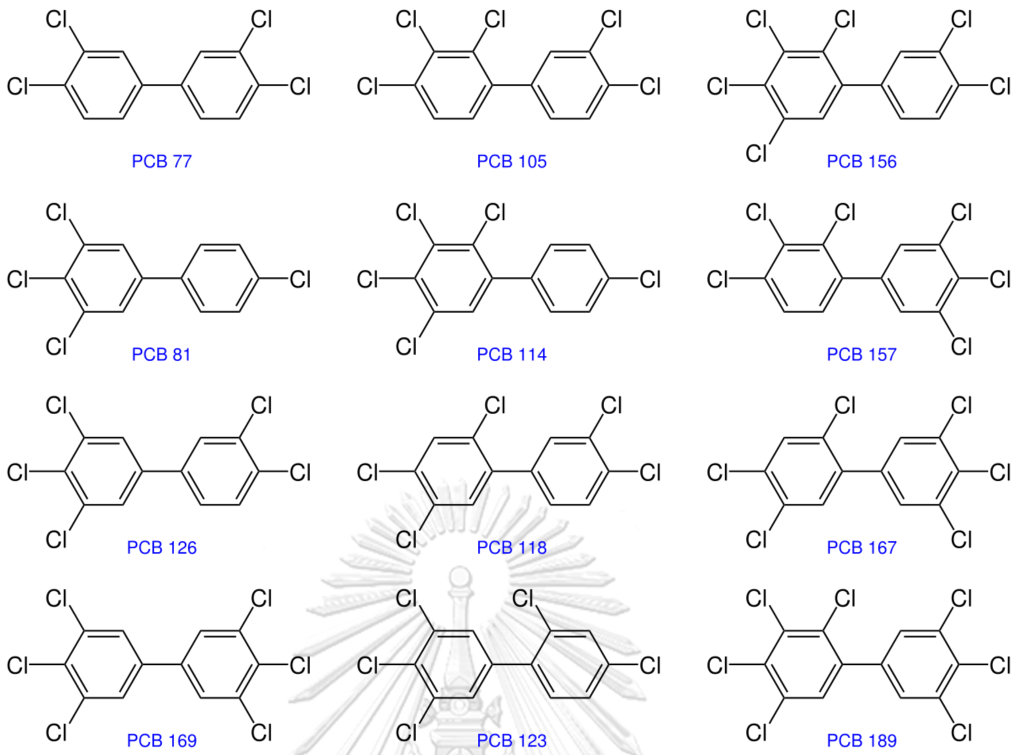


Figure 9 : Dioxin-like PCBs 12 Congeners

Total PCB concentrations, the sum of 22 congeners from 8 sediment samples range from 0.04-3.03 ng/g dry wt. Concentrations of PCBs in sediments from the east coast of Thailand exhibited a smaller variation among locations. Moreover, the authors mentioned the concentration of PCBs on the east coast of Thailand also showed similar results with the range of Sri Lanka which is concentrations of PCBs in this study were very low and much lower than in more industrialized countries such as Japan China, and Korea. The highest PCB concentration in this study was 3.03 ng/g, which could be due to the waste drainage from the industrialized city and the power plant. The possible sources may be from fluids and hydraulic additives. One of the major sources in Thailand is considered to be transformers and capacitors imported by the Electricity Authority of Thailand. (Cheevaporn, 2014)

Philippine has studied the historic PBDEs and PCBs contaminated in Manila Bay and the Gulf of Thailand. The results showed that total PBDEs and PCBs were generally detected at higher concentrations in the upper layers and lower concentrations in the bottom layers. The concentration of total PBDS in Manila bay and the Gulf of Thailand exhibited a trend of increasing from the mid-1980s until the mid-1990s, followed by decrees until the early 2000s, and again an increase in the recent year. This trend has corresponded to the economic condition in the Asian region. The PCBs in this study also increased over time, although earlier than the PBDE, showing a trend of rapid increase, generally followed by a decrease, and again an increase in recent years. The earlier usage of PCBs than PBDEs in the Philippines and Thailand was consistent with the historical usage of PCBs worldwide. Base on the official recorded, the use of PCBs in Thailand started in 1995. Detection of PCBs in layers corresponding to earlier than 1955 would suggest a downward migration of sediment particles through the pore water, or vertical mixing of the sediments possibly through bioturbation. (S.Kwan. et al., 2014)

Moreover, PCBs contamination was also had found in marine ecology. The marine benthic has been studied in Chonburi and Rayong province in Thailand. These marine benthic such as shrimp green mussel and oysters were selected in this study. The researcher was collecting samples from the commercial farm which is located in the open sea and therefore is representative of ecosystem exposure. The average total concentrations varied between species and ranged between 19 and 1100 ng/g lipid adjusted weight (lw). Among the three seafood species studied, the highest concentrations of total PCB were observed in shrimp with average concentrations of 775±230 ng /g lw. For mussels and oysters, the highest concentrations were found at the 454±125 and 304±65 ng/g lw respectively. From these results, it can be concluded that the concentrations of PCBs in this study were rather similar to those observed from other Asiatic areas such as China, Hongkong, Japan, and Malaysia. (Cheevaporn, 2014)

Although, PCB concentration in Thailand may not be a concern in the past, however, the amount of PCB in the environment needs to be monitored continuously due to the increase of new industrial and related pollution activities. Among global concerning, PCBs usage is monitored and used under controlled policies for generated PCBs, notwithstanding, researchers have been continually found the concentration of PCB all around the world.

The study in Turkey has shown a seasonal distribution of PCBs in two regions, one with urban characteristics where traffic is dense (BUTAL) and the other representing the coastal zone Fifty-one air and soil samples were simultaneously collected. Total PCB (Σ82 PCB) levels in the soil samples collected during one year ranged between 105 and 7,060 pg/g dry matter (BUTAL) and 110 and 2,320 pg/g (Mudanya). Total PCB levels in the gaseous phase were measured to be between 100 and 910 pg/m^3 (BUTAL) and 75 and 1,025 pg/m^3 (Mudanya). Variations in the concentrations were observed depending on the season. Though the PCB concentrations measured in the atmospheres of both regions in the summer months were high, they were found to be lower in winter. However, while soil PCB levels were measured to be high at BUTAL during summer months, they were found to be high during the winter months in Mudanya. The 3-CB and 4-CB congeners were found to be dominant in the atmosphere, and 4-, 5-, and 6-CBs were found to dominate in the surface soils. (Yolsal, Salihoglu, & Tasdemir, 2014)

A total of 209 PCBs were conducted for street dust in some of the northern areas of Vietnam (Anh, Watanabe, Tomioka, Minh, & Takahashi, 2019). The PCBs concentration of 2.2-120, 6.6-32, 0.25-0.97 ng/g were measured from an industrial park, an urban area, and a rural community, respectively. Loading of PCBs concentration related to industrialization and urbanization. PCBs pattern of street dust from the industrial park was dominated by lightly chlorinated homologs (Tri-and

Tetra-CBs), while more highly chlorinated homologs (Penta- and Hexa-CBs) were the major contributors to total PCBs in the urban samples, indicating different emission sources. PCB-11, an inadvertently produced congener of pigment manufacturing processes, was detected in all samples with a more elevated proportion in an urban and rural area than an industrial park. The result of this study has revealed complex emission sources of PCBs in study areas.

2.3.2 Human Health effects of Polychlorinated biphenyl

Since PCBs are exceptionally stable and prevail in the environment for a very long time. PCBs induce a wide variety of toxic responses in humans, wildlife, plants, and laboratory animals. They can penetrate the human body through skin contact, by inhalation of PCBs contaminated vapors, and by consuming foods contaminated with PCBs residue. Consumption of foods contaminated by PCBs, especially fish and poultry products appear to the main source of exposure. The national toxicology Program (NTP) and the International Agency for Research on Cancer (IARC) have concluded that PCBs are carcinogenic to humans (IARC, 2006; NTP, 2011). Toxicological studies of PCBs in humans were found to increase the rate of melanoma, gall bladder cancer, brain cancer, liver cancer, biliary tract cancer, gastrointestinal tract cancer, and possibly connected to breast cancer. At the high levels exposed to PCBs through skin contactor by consumption experience skin irritations like severe acne and rashes, nose and lung infections, and eye issues. Moreover, lesser chlorinated PCBs can mimic the body's natural hormones, especially with estrogen. The women exposed to PCBs during their pregnancy may result in serious motor control and neurological issues, and in children, they cause short-term memory loss and lowered IQ. (Reddy, Moniruzzaman, & Aminabhavi, 2019)

2.4 Polycyclic Aromatic Hydrocarbons (PAHs)

2.4.1 Properties of Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons or PAHs are semi volatiles compound compounds that are mostly colorless, white, or pale-yellow solid. They are a ubiquities group of several hundred chemically related compounds, environmentally persistent with various structures, and varied toxicity. It consists of hundreds of individual substances with different physio-chemical properties. The United States Environmental Protection Agency (USEPA) has classified 16 of these as priority PAHs to be targeted for air monitoring (Table 2). The molecular structure of individual PAHs consists of a different number of benzene rings which are fused together in different arrangements (linear, angular, or cluster, Figure 10) Generally, PAHs enter the environment through various routes and usually found as a mixture containing two or more of these compounds. They are commonly detected in air, soil, and water. The general characteristic of PAHs is high melting and boiling points, low vapor pressure, and very low aqueous solubility. The major source of PAHs is the incomplete combustion of organic material such as coal, oil, and wood. PAHs are not synthesized chemically for industrial purposes. Nevertheless, there are a few commercial uses for many PAHs. They are mostly used as intermediaries in pharmaceuticals, agricultural products, photographic products, and thermosetting.

PAHs are semi-volatile compounds which mean that the partition between the gas and particle phases in air. This partitioning is dependent on the number of benzene rings in the molecular structure, which in turn is an important factor for the range of volatility among the individual PAHs.

Table 2 : Basic information of 16 PAHs classified as priority pollutants by USEPA

Full name	**Abbreviation**	**Amount of benzene rings**	**IARC classification on carcinogenicity**
Naphthalene	Nap	2	Group 2B
Acenaphthylene	Acy	3	Not classified
Acenaphthene	Ace	3	Group 3
Fluorene	Flu	3	Group 3
Phenanthrene	Phe	3	Group 3
Anthracene	Ant	3	Group 3
Fluoranthene	Fla	4	Group 3
Pyrene	Pyr	4	Group 3
Benzo[a]anthanthrene	BaA	4	Group 2B
Chrysene	Chr	4	Group 2B
Benzo[b] fluoranthene	BbF	5	Group 2B
Benzo[k] fluoranthene	BkF	5	Group 2B
Benzo[a] pyrene	B(a)P	5	Group 1
Indeno[1,2,3-c,d] pyrene	Ind	6	Group 2B
Dibenz[a,h]anthracene	DaA	6	Group 2A
Benzo[g,h,i]perylene	BgP	6	Group 3

*The IARC classification: Group 1: carcinogenic, Group 2A: probably carcinogenic, Group 2B: possibly carcinogenic, Group 3: noncarcinogenic (IARC, 2006)

Most of the PAHs are present in the gas phase. This partitioning is influenced by temperature relative humidity, and concentrations of the PAHs, total suspended particles, and the chemical composition of particles in the air.

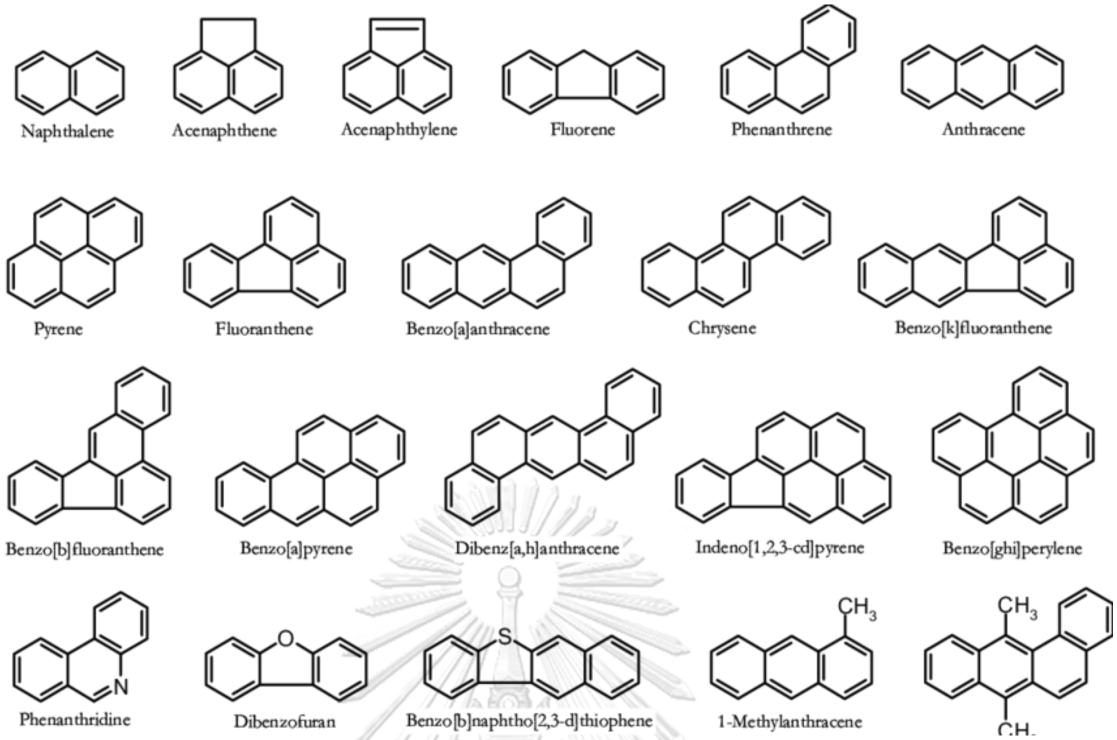


Figure 10 : Molecular structure of 16 PAHs US EPA compounds

Research on air pollution in Thailand usually focus on one aspect of the problem, agricultural emission, metrological conditions, vehicular exhausts. Megacities like Bangkok, mostly vehicular exhausts have been causing an air pollution problem, while in Chiang Mai province, the major problem was an agricultural emission. A major concern pollutant of air pollution is PAHs due to their genotoxic effects and adverse impact on human health. The term polycyclic aromatic hydrocarbon refers to a group of several hundred chemically-related organic compounds having various structures and varied toxicity. Most of them are formed by a process of combustion and subsequent recombination of organic molecules. They are formed during incomplete combustion of organic material emitted from a large variety of industrial processes, motor vehicles, domestic waste burning, and agricultural burning. They occur in the environment as complex mixtures of many components with widely varying toxic potencies.

(Pongpiachan, Hattayanone, & Cao, 2017) has investigated the potential cancer risk resulting from biomass burning in Chiang Mai while the haze period. Sampling was conducted during two periods, during the cold season (December) and spring season (March). The sample was collected by Quartz-fiber filters, using Minivol^{TM} portable air samplers with a flow rate of 5 L/min. Compared to the non-burning period, the magnitude of Σ3,4-ring PAHs in the other world cities was significantly higher. The results of this study indicate that the emission source strength of light molecular weight PAHs in northern Thailand is much lower than the other world cities. The comparison between the other studies had shown Σ5,6-ring PAHs during this period probably resulting from gasoline vehicles passing through the monitoring stations rather than agricultural waste burnings. The results highlight the importance of vehicular exhaust as the major source of $PM_{2.5}$ bound PAHs on a global scale.

In the other study in northern Thailand, high PAH concentrations in airborne were also detected using gas chromatography high-resolution mass spectrometry to determine 16 PAHs and 12 oxy-generated PAHs. The 72 samples were collected in four different locations in Chiang Mai province by using quartz microfiber filters and high-volume air samplers to collect PM_{10}. This study brings forward the first concentration levels of oxy-PAHs in Thailand. The median of the sum of PAHs and oxy-PAHs concentrations was 3.4 ng/m^3 and 1.1 ng/m^3 respectively, which shows the importance of the group of oxy-PAHs as PM_{10} and the results shown that high molecular weight PAHs contributed the most to the ΣPAHs. (Walgraeve et al., 2015)

Moreover, there is a study of assessing risks to adults and preschool children during a biomass burning episode in northern Thailand. The research was emphasized in investigating the potential cancer risk resulting from biomass burning. During the open burning haze episode. PAHs bound to fine particles $PM_{2.5}$ and data methodologies were conducted in nine administrative to estimated and compared with other countries around the world. The average values of Σ3,4-ring PAH and B(a)P $E_{quivalent}$ concentrations were significant in the world urban cities. Besides, the three ways of exposure pathway were investigated. The results were found that the cancer risk related to exposure inhalation appears to be a major exposure and direct ingestion could be a significant potential pathway for preschool children because of hand to mouth behavior of the preschool children in northern. (Pongpiachan, Tipmanee, Khumsup, Kittikoon, & Hirunyatrakul, 2015)

2.4.2 Human health effect of Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbon or PAHs can find in every environment nowadays. The primary emission is anthropogenic activities, during the incomplete combustion of organic materials for example coal, oil, petrol, and wood. Major anthropogenic sources of PAHs include residential heating, coal gasification, coke, and alumina production PAHs are also generated from a natural source such as open burning, natural losses, or volcanic activities. Many PAHs have toxic, mutagenic, and carcinogenic properties. PAHs are highly lipid-soluble and absorbed from the gastrointestinal tract of mammals. 16 PAHs have been identified as being of the greatest concern concerning potential exposure and adverse health effects for humans. Individual PAHs were affecting different adverse health. The International Agency for Research on Cancer classifies some PAHs as known, possibly, or probably carcinogenic to humans (Group1, 2A, or 2B). Some PAHs are well known as carcinogens, mutagens. The most significant health effect to be expected from inhalation exposure to PAHs is an excess risk of lung cancer. The impact of PAHs on human health depends on the length and route of exposure and the amount of concentration. Exposure to PAHs can cause short or long-term health effects. The short-term health effect of PAH exposure can result in symptoms such as eye irritation, nausea, vomiting diarrhea, and confusion. Moreover, the exposure mixture of PAHs also causes skin irritation and inflammation. However, the long-term health effect of exposure to PAHs may decrease immune function, kidney, liver damage, breathing problems, asthma-like symptoms, and lung function abnormalities. The harmful effects that may occur largely depend on the way of exposure. In the laboratory studies, animals exposed to levels of some PAHs over long periods have developed lung cancer from inhalation, stomach cancer from ingesting PAHs in food, and skin cancer from skin contact (Abdel-Shafy & Mansour, 2016).

2.5 Health Risk Assessment

Human health risk assessment consists of four basic steps to estimate the nature and probability of adverse health effects in humans who expose to contaminants in the environmental media for the present and in the future. The four steps of the assessment are shown in Figure 11 (USEPA, 2016).

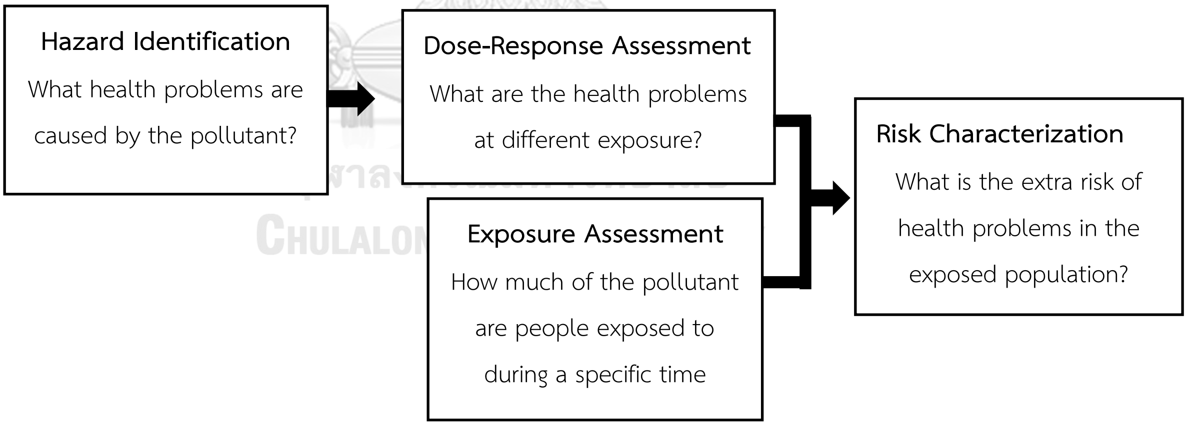


Figure 11 : Four steps of the health risk assessment process

2.5.1 Hazard Identification

Hazard Identification is the process used to determine the exposure to a stressor that can cause an increase in the case of specific adverse health effects (e.g., cancer, birth defects). It is also whether the adverse health effect has occurred in humans, and exposure to a stressor may generate many different adverse effects in a human: diseases, the formation of tumors, reproductive defects, death, or other effects.

2.5.2 Dose-response assessment

Dose-response assessment explains a dose-response relationship describes how the likelihood and severity of adverse health effects are related to the amount and condition of exposure to an agent (the dose provided). Although this refers to the dose-response relationship, the same principles generally apply for studies where the exposure is to a concentration of the agent such as airborne concentrations applied in inhalation exposure studies. The resulting information is referred to as the concentration-response relationship. The term exposure-response relationship may be used to describe either a dose-response or a concentration-response, or other specific exposure conditions (USEPA, 2016).

2.5.3 Exposure assessment

Exposure assessment is the process of measuring or estimating the magnitude, frequency, and duration of human exposure to an agent in the environment or estimating future exposures for an agent that has not yet been released. An exposure assessment includes some discussion of the size, nature, and types of human populations exposed to the agent, as well as discussion of the uncertainties in the above information. Exposure can be measured directly, but more commonly were estimated indirectly through consideration of measured concentrations in the environment, a consideration of models of chemical transport and fate in the environment, and estimates of human intake over time. .USEPA has provided the value of the parameter which was used to calculate in the exposure equation for non-carcinogen in (Eq.10 and carcinogen in Eq.11) (Badmatsybenov, 2018). The parameters were substituted in the equations to find Exposure concentration and Chronic Daily Intake. (see in Appendix)

$$\text{Intake (EC)} = \frac{(\mathrm{C \times IR \times ET \times EF \times ED})}{\mathrm{AT\ or\ ED \times 365\ days}} \qquad \text{Eq. 10}$$

$$\text{Intake (CDI)} = \frac{(\mathrm{C \times IR \times EF \times ED})}{\mathrm{BW \times AT}} \qquad \text{Eq. 11}$$

Where;

Intake (μg/ m^3) = Chronic Daily Intake (CDI) for cancer

= Exposure concentration (EC) for non-cancer

C = Air pollutant concentration (μg/ m^3)

IR = Inhalation rate (m^3/hour)

ET = Exposure time (hour/day)

EF = Exposure frequency (days/year)

ED = Exposure duration (years)

BW = Body weight (kg)

AT = Averaging time (day)

2.5.4 Risk characterization

Risk Characterization conveys the risk assessor's judgments as to the nature and presence or absence of risks, along with information about how the risk was assessed, where assumptions and uncertainties still exist, and where policy choices will need to be made. Risk characterization takes place in both human health risk assessments and ecological risk assessments (USEPA, 2016). HQ value was used to determine the risk of adverse health effects whether it may occur. The HQ equation was shown in Eq.13. HQ can be estimated by dividing the exposure concentration by reference concentrations.

Excess Cancer risk will be estimated by multiplying the chronic daily intake with the cancer slope factor. The cancer slope factor was calculated using unit risk, body weight, time, and inhalation rate according to U.S. EPA. Besides, the cancer slope factor was needed to calculate the cancer risk posed by contaminants. The unit risk was necessary to find to cancer slope factor.

$$HQ = EC / RfC \qquad \text{Eq. 13}$$

Where; HQ = Hazard Quotient

EC = Exposure concentration ($\mu g/ m^3$)

RfC = Reference concentration ($\mu g/m^3$)

The HQ evaluation has the following criteria:

HQ > 1: indicates that adverse effects are likely to occur

HQ ≤ 1: indicates that adverse effects are not likely to occur

Cancer risk use for estimated carcinogenic air pollutants was calculated by this equation

$$\text{Excess Cancer risk} = CDI \times CSF \qquad \text{Eq. 14}$$

Where CSF = Inhalation Cancer slope Factor

Cancer risk > $1x10^{-6}$: indicates that adverse effects are likely to occur

Cancer risk ≤ $1x10^{-6}$: indicates that adverse effects are not likely to occur

2.6 Toxic equivalency factors (TEFs) and Slope Factor (SF)

For PAHs and PCBs studies, scientists developed a toxicity equivalency quotient (TEQ) methodology that evaluates the toxicity and assesses the risks associated with whole mixtures. The toxicity equivalency (TEQ) methodology is a tool to assess the cumulative toxicity of complex mixtures. The TEQ and SF of PAHs compounds and dioxin-like PCBs congener can be used when conducting a risk assessment. The maximum levels for the sum of TEQs a complex mixture of individual PAHs and PCBs were set, since this was determined to be the most appropriate approach based on current toxicological methods used to evaluate the toxicity and carcinogen assessment potential risk of complex chemical mixtures like PAHs and PCBs. The maximum TEF of one is assigned to BaP, and other individual PAHs are relative to BaP as BaP equivalents (BaP_{eq}). PCDDs and PCDFs (dioxins and furans) are typically present in the environment as complex mixtures of each congener that different in the number and location of chlorine atoms. There are 210 of these dioxin and furan congeners present in the environment. The most toxic and best-studied congener is 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD), in which TCDD is the standard for comparison in the methodologies outlined. Because dioxin and furan congeners are typically present in the environment as complex mixtures, With the TEQ method, each congener is assigned a TEF, or toxicity equivalency factor: the ratio of estimated toxicity for a particular congener to the toxicity of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD). The toxicity equivalent and slope factor were used in this study as shown in table 2.3. The potency of PAHs and PCBs to cause carcinogenic health risk was further evaluated using Carcinogenic Toxic Equivalents. This was determined as the sum of the product of the concentrations of individual PAH congeners or ∑PCBs and their toxicity equivalency factor (Table 3). Carcinogenic toxic equivalents calculation of PAHs and PCBs were using as following (Eq.15-16).

$$(BaP)eq = [\sum PAHsi] \times TEFj \quad \text{Eq. 15}$$

$$PCBs\text{-}TEQ = [\sum PCBsi] \times TEFj \quad \text{Eq. 16}$$

2.6 Statistical analysis

Statistical analysis Data analysis was performed using Microsoft Excel programme Individual PAH and PCB concentrations were summarized separately for each sample using descriptive statistics such as means, range, standard deviation. Statistical differences in PAHs and PCBs concentrations between Bangkok ang Chiang Mai.

Table 3 : The toxicity equivalency and Slope Factor of PAHs and PCBs

Compound	TEFs	SF	References
PAHs			
Acenaphthylene	0.001	0.00385	(Nisbet & LaGoy, 1992), (CalEPA, 2015)
Acenaphthene	0.001	0.00385	
Fluorene	0.001	0.00385	
Phenanthrene	0.001	0.00385	
Anthracene	0.01	0.0385	
Fluoranthene	0.001	0.00385	
Pyrene	0.001	0.00385	
Benz[a]anthracene	0.1	0.385	
Chrysene	0.01	0.0385	
Benzo[b]fluoranthene	0.1	0.385	
Benzo[k]fluoranthene	0.1	0.385	
Benzo[a]pyrene	1	3.85	
Indeno[1,2,3-cd]pyrene	0.1	0.385	
Dibenz[a,h]anthracene	1	-	
Benzo[g,h,i]perylene	0.01	0.0385	
PCBs Congener			
Non-ortho PCBs			Slope Factor of Dioxin for calculation excess cancer as follow: Dioxin-like: 150000 Non- dioxin-like: 2 (Note Dioxin like 12 Congeners: PCB-77,81,105,114,118,123,126,156,157,167,169, and PCB 189) (USEPA, 2010)
PCB-77	0.001		
PCB-81	0.00032		
PCB-126	0.1		
PCB-169	0.03		
Mono-ortho PCBs			
PCB-105	0.00003		
PCB-114	0.00003		
PCB-118	0.00003		
PCB-123	0.00003		
PCB-156	0.00003		
PCB-167	0.00003		
PCB-189	0.00003		

CHAPTER 3

RESEARCH MATERIALS AND METHODS

3.1 Sampling Site Information

In this study, five sampling sites were chosen in Bangkok and three sampling sites were chosen in Chiangmai (Figure 12). Bangkok and Chiangmai are the major cities that had an air pollution problem every year, especially during the winter. Bangkok is the capital of Thailand, the city occupies 1,568.7 square kilometers (605.7 sq mi) and has a population of over eight million, or 12.6 percent of the country's population. Currently, air pollutants have been causing a problem in the winter. Due to the overload of population and traffic in the city, the excessive fine particle dust of both PM_{10} and $PM_{2.5}$ become problematic in past five years.

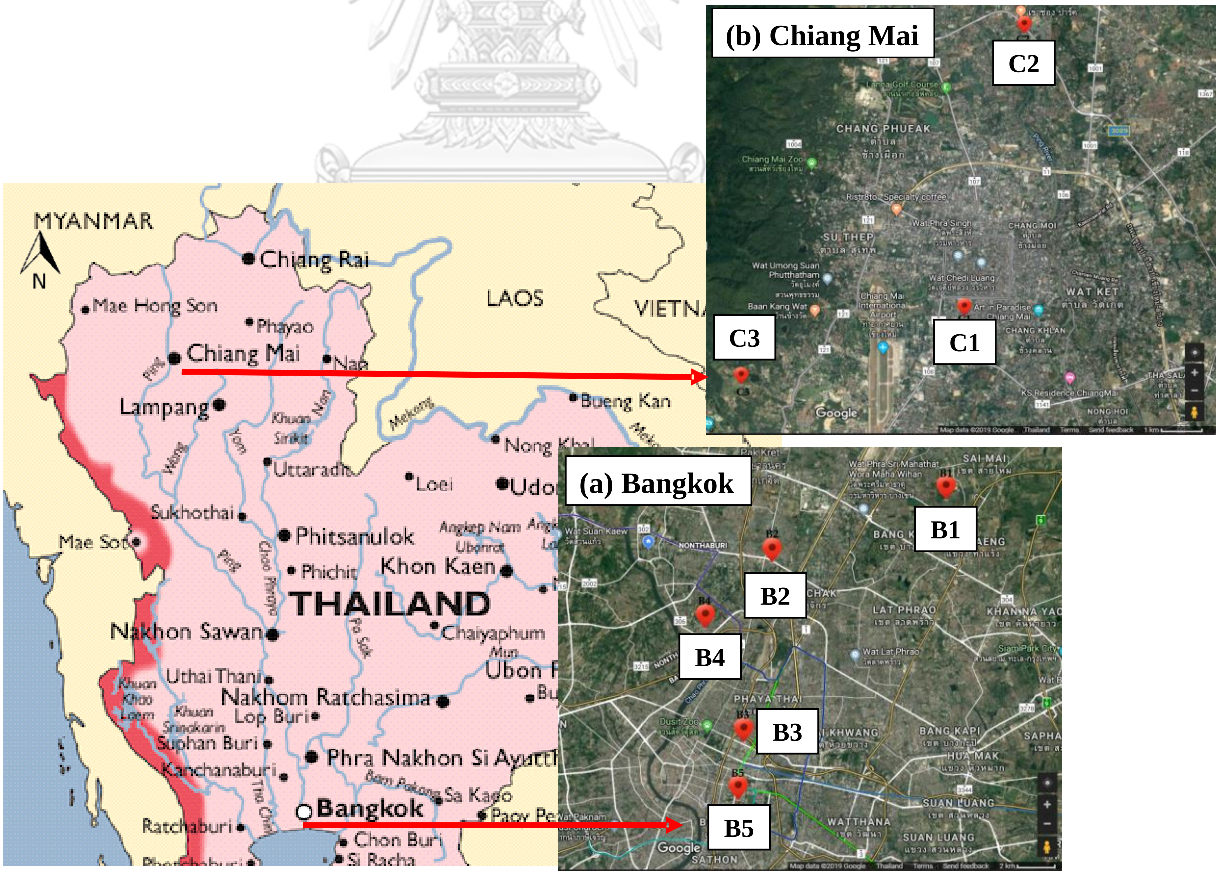


Figure 12 : Location of sampling points in Bangkok and Chiang Mai

All passive air samplers are installed in Bangkok urban areas. The samples were set in an open area about at 10-15 meters height from the ground level without significant obstacles, to allow for the free flow of air around the samples, and all samples were installed far away from the traffic road source as shown in Figure 13 - 15.

Figure 13 : Location of sampling point (B1), Khwaeng Tha Raeng, Bangkok

(b) PAS installation at the sampling site

Figure 14 : Location of sampling points (B2), Khwaeng Thung Song Hong, Bangkok

(b) PAS installation at the sampling site

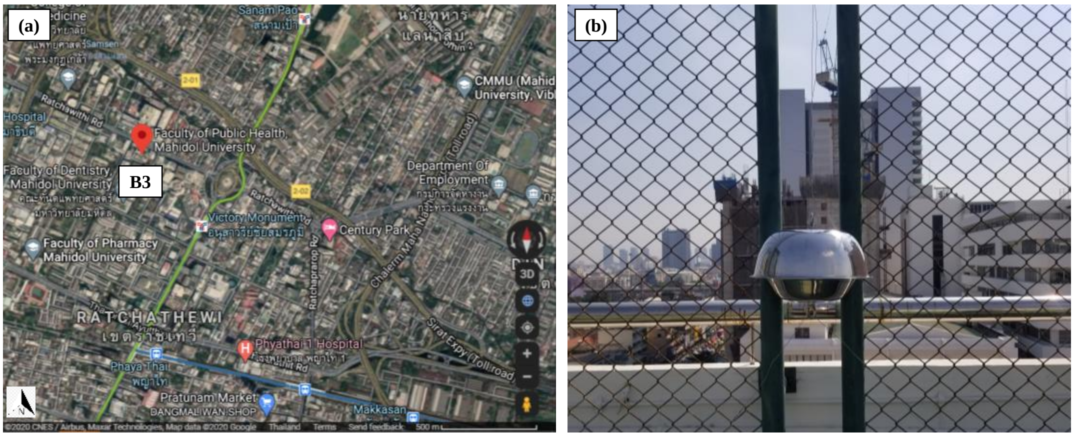


Figure 15 : Location of sampling points (B3), Khwaeng Phaya Thai, Bangkok

(b) PAS installation at the sampling site.

Figure 16 : Location of sampling points (B4), Khwaeng Wong Sawang, Bangkok

(b) PAS installation at the sampling site.

Figure 17 : Location of sampling points (B5), Khwaeng Wang Mai, Bangkok

(b) PAS installation at the sampling site.

Chiang Mai is the biggest city located in northern Thailand. The passive air sampler was installed as same as Bangkok criteria. All samples were installing 10-15 meters height above the ground without any obstacle, and far away from the traffic road as shown in Figure 18 - 20.

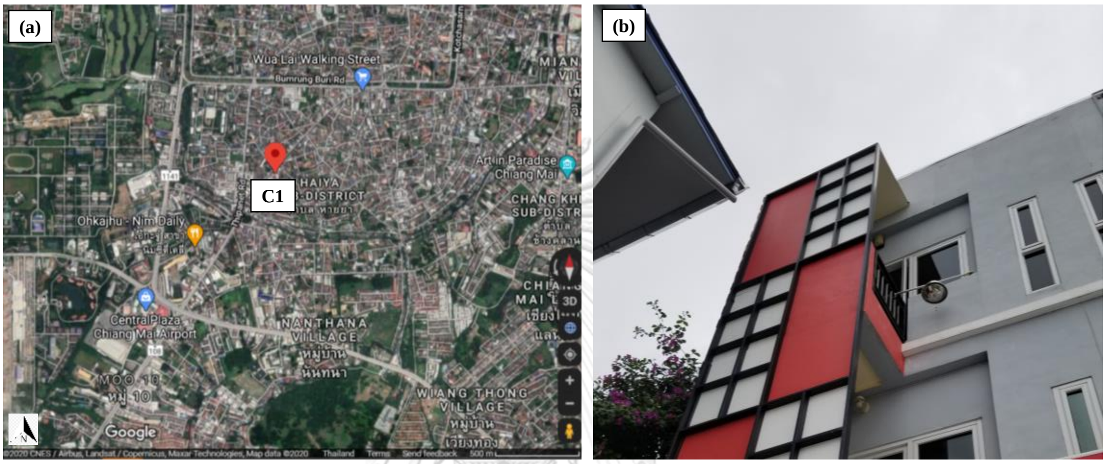


Figure 18 : Location of sampling points (C1), Tambon Hai Ya, Chiang Mai (b) PAS installation at the sampling site.

Figure 19 : Location of sampling points (C2), Tambon Nong Han, Chiang Mai (b) PAS installation at the sampling site.

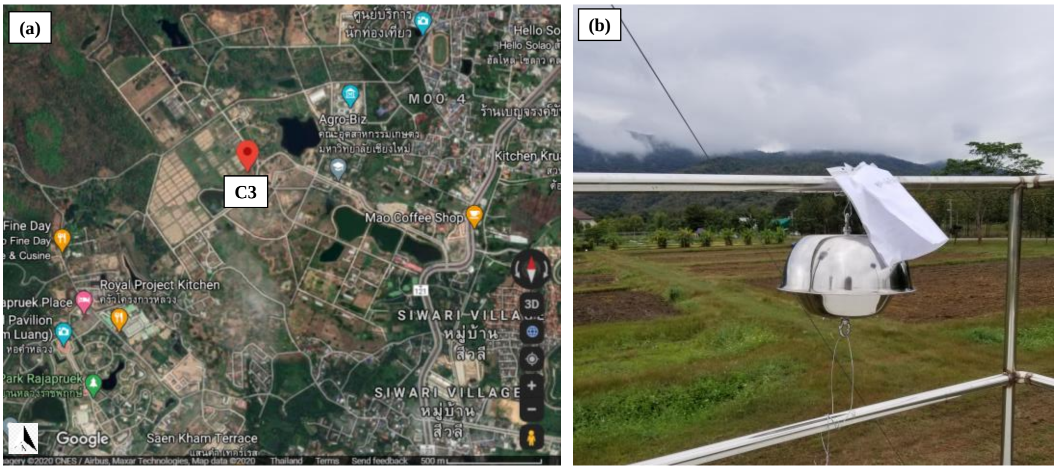


Figure 20 : Location of sampling points (C3), Tambon Su Thep, Chiang Mai (b) PAS installation at the sampling site.

3.2 Sampling Procedures

3.2.1 Sampling of Air

Passive air sampler had used in this study, there were conducted three sites in Chiang Mai, and Five sites in Bangkok. The location of all sampling sites is shown in Table 3. The sampling site selection was chosen in the urban area of both major cities. They were selected by concerning such that the density of population, the land-use map, and ambient are similar. The passive air sampler consists of two stainless steel bowls. The specification of the PAS shelter is shown in table 5. The upper bowl with a diameter of 30 cm, and the bottom bowl of 24 cm. The bowls are fixed on a joint axis, which also supports the polyurethane foam (PUF) disk. All parts of the sampler housing are made of stainless steel.

Table 4 : Urban air samplings sites location

Sampling site	Sampling Code	Sea Elevation	Latitude/Longitude
Bangkok			
Khwaeng Tha Raeng	B1	34	13°53'00.4"N,100°38'07.7"E
Khwaeng Thung Song Hong	B2	38	13°51'10.4"N,100°32'55.4"E
Khwaeng Phaya Thai	B3	66	13°45'57.8"N,100°32'02.5"E
Khwaeng Wong Sawang	B4	71	13°49'17.6"N,100°30'55.2"E
Khwaeng Wang Mai	B5	32	13°44'13.8"N,100°31'47.8"E
Chiang Mai			
Tambon Hai Ya	C1	316	18°46'35.1"N,98°58'58.0"E
Tambon Nong Han	C2	345	18°53'33.9"N,99°00'36.6"E
Tambon Su Thep	C3	351	18°45'40.8"N,98°55'54.6"E

The PAS was deployed in sheltered chambers, as shown in Figure 13-20 (b). The shelter was built to buffers against wind speed effects and prevented sunlight from reaching the disks. A precleaned and weighed PUF disk (14 cm diameter×1.35 cm thick; density 0.0213g/cm^3) was suspended in the center of the two dishes. All samples were transferred to the sampling locations in airtight containers to avoid contamination during transit. Twenty-four samples were successfully deployed over sixty days. At the end of the deployment period, the samples were resealed in their original transport containers. The disks were removed and stored in a sealed bag at -20 °C until extraction.

Table 5 : Specification of Passive air sampler sets used in this study

Sampler specification	**This study**	
Upper dome	Diameter (cm)	30
	Depth (cm)	8.5
Lower dome	Diameter (cm)	24
	Depth (cm)	7
Upper and lower domes	Offset depth (cm)	0.75
	Gap width	2.1
Gap surface area	Area (cm^2)	153.7

The passive air sampling period in this study was focusing on the dry season in Thailand. The average temperature of approximately 29-35 °C (Thai Government Mereologies Data). The dry season included winter and summer in Thailand. There were started from the end of November to the end of May. The winter season is from November to February, and the summer is from March to May. In this study, the samples collected three periods divided by the dry season, and each site was over 60 days duration (Table 6).

Table 6 : Seasonal and duration of air sampling within 60 days

Duration	Period	Days	Season
12 December 2018 – 12 February 2019	1st	61	Strat of the dry season
12 February – 12 April 2019	2nd	60	Dry season
17 April – 17 June 2019	3rd	61	End of the dry season

3.3 Method of Simultaneous Analysis of PAHs and PCBs

3.3.1. Experimental Section

The experiment for detection PAHs and PCBs concentration from air samples were followed as a schematic (Figure 3.10).

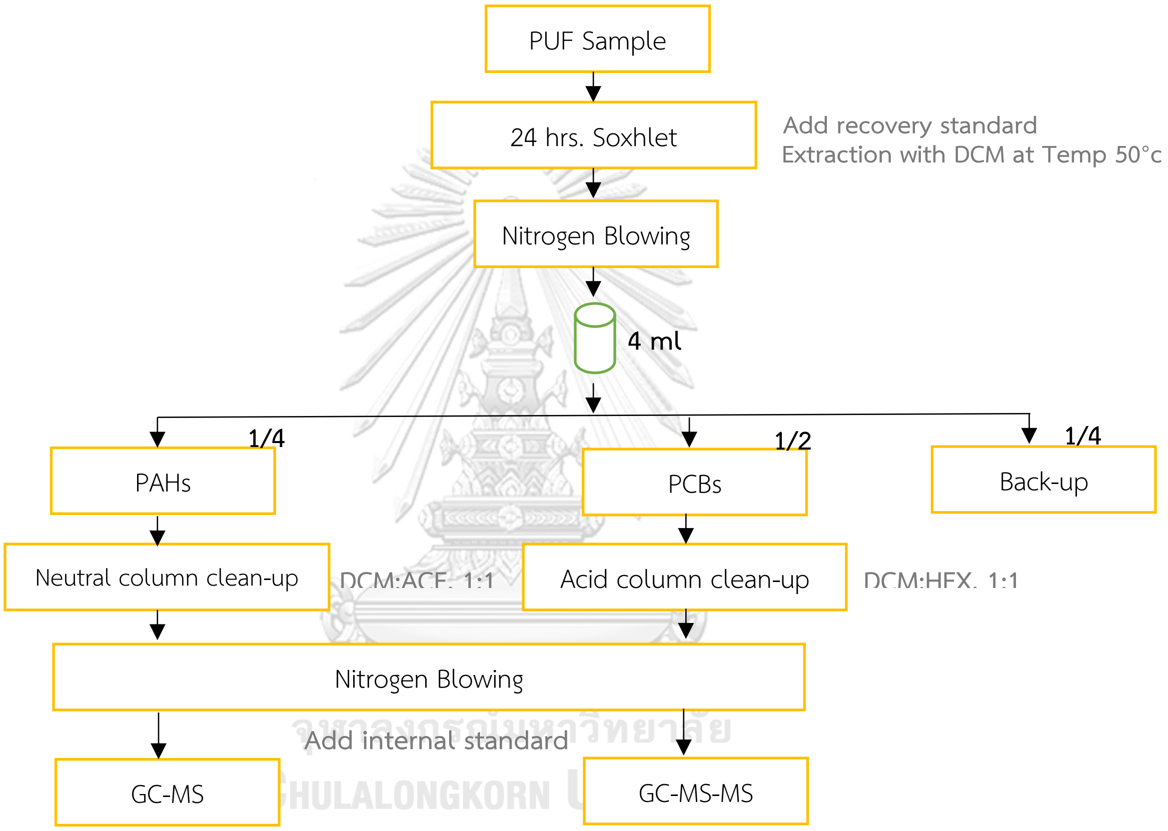


Figure 21 : Schematic overview of the methodology

3.3.2. Extraction and Clean-up

Extraction and cleanup procedure, all the PUF samples were Soxhlet extracted for 24 h with DCM. A known mixture of surrogate standards was added before the extraction. To remove the elemental sulfur, activated copper granules were added into the solvent in the collection flask. The extracts were concentrated through nitrogen blowing (XT-NS1 Nitrogen blowing instrument) and the solvent phase was exchanged to hexane (hexane obtained from Merck and Co., Inc.). Cleanup/purification of PAHs and PCBs were obtained through the alumina/silica column (a 9 mm i.d. glass column), packed from the bottom to top. PAHs column was packed with neutral alumina (3 cm, 3% deactivated), neutral silica gel (3 cm, 3% deactivated), and anhydrous sodium sulfate (1cm). The column was eluted with 50 ml of DCM/hexane (1:1), while PCBs packed with neutral alumina (3 cm, 3% deactivated), neutral silica (2 cm, 3% deactivated), sulfuric acidic silica (3 cm), and anhydrous sodium sulfate (1cm). Column packing ingredients i.e. neutral alumina, neutral silica gel, and anhydrous sodium sulfate were washed with Hexane through Soxhlet-extraction assembly for 48 h, heated at 450 °C for 10-12 hours. The purified fraction of the solvent was further subjected under a gentle nitrogen stream to concentrate up to 0.2 ml after adding Isooctane as a solvent keeper. A known quantity of internal standard was added before GC-MS and GC-MS/MS analysis. (Mao et al., 2019; Zhao et al., 2020)

3.3.3. Chromatographic Analysis

The GC/MS operated under optimal preset GC-MS conditions most suited for the target compounds (Appendix). In general, the mode of ionization will be the positive electron impact (EI^+) while the selected ion monitoring (SIM) mode will be used for detection. The target POPs will be identified based on their relative retention times (RRT) which should match that of the corresponding standard. Quantification will be performed using internal standards and the isotopic dilution technique: peak areas were compared directly with those of congeners used as internal standards and added to the samples in known quantities.

The standard mixture of 16 USEPA PAHs including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), ben[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[ah]anthracene (DahA), benzo[g,h,i]perylene (BghiP) , and indeno[1,2,3-c,d] pyrene (IcdP) was adopted in this study. Naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12 was added as an internal standard for GC-MS (Shimazu-QP2010) injection. The target compounds were separated on an HP-5MS column (30 m×0.25 mm, film thickness 0.25 μm), and the instrumental conditions were as follows: injector temperature, 280 °C; ion source temperature, 230 °C; and temperature program, 60 °C (5 min), 60– 290 °C at 3 °C/min, and 290 °C (30 min). The carrier gas was helium at a constant flow rate of 1.2 mL/min, the mass selective detector operated in the electron impact mode (-70 eV), and a 1-μL sample was injected in spitless mode. Mass range m/z 50 to 500 was used for quantitative determinations. For PCBs analysis, this study was focused on dioxin-like PCBs for health risk assessment. The 13C^{12}-Labeled PCBs were used as internal standard and analyzed by GC-MS/MS Agilent 7693, CP-Sil 8 CB (50 m x 0.25 mm, film thickness 0.12 μm; Agilent, Santa Clara, CA, USA) column was used and operated under electron-ion (EI) source (-70 eV) in multiple reaction monitoring (MRM). The temperature of the injector, interface, and ion sources were set at 280°C, 290°C, and 230°C, respectively. The temperature program of the oven was as follows: 100°C for 0.5 minutes, then 10°C/min to 160°C, 3°C/min to 250°C, and 10 °C/min to 295 °C for 10 minutes and hold for 10 minutes at 300 °C. A 1-μL sample was injected in spitless mode. The congeners of PCB were identified based on a specific MRM parameter.

3.3.4. Quality control and quality assurance (QC/QA)

A quality control procedure was strictly followed for the entire analysis to ensure the quality of results. Calibration standards were used daily for instrument calibration. Analytical grade chemicals were used during the experimentation. Field, procedural, and solvent blanks were analyzed and disposed of using the same procedure as for other samples according to the methodology. Glassware was double washed with deionized distilled water and heated at 450 °C for >6 hours. Agilent Mass Hunter software and Shimazu Post-run software were used for data acquisition and analysis were conducted at the State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Science. The analytical method was adopted in the processing. All sample preparation and present study following institute methodology (Mao et al., 2019).

3.3.5 Sample and Data analysis

All the sample were used Postrun and MassHunter for data analysis. Parameter and conditions of GC-MS/MS analysis as in table appendix 1,3. For air concentation calculation this study, equations and parameters for estimation were used as shown in table 7. They retrieved from literature or derived from octanol-water partition coefficient. PCBs (Harner & Bidleman, 1998), and PAHs (Pozo et al., 2015). Log KOA values depend on compounds’ nature and temperature and were calculated by using the template from (Lee et al., 2016)

Table 7 : Equations and parameters for estimation of air concentrations

$C_{air} = M_{PUF} / V_{air}$

$V_{air} = K_{PUF} \times V_{PUF} \times \{1\text{-}\exp [- (t \times k_A) / (K_{PUF} \times D_{film})]$

$K'_{PUF} = K_{PUF} \times \rho_{PUF}$

$\log K_{PUF} = 0.6366 \times \log K_{OA} - 3.1744$ (for PCBs)

$\log K_{PUF} = 0.7370 \times \log K_{OA} + 1.0982$ (for PAHs)

$k_A = R / A_{PUF}$

Parameter		**Value and notes**
C_{air}	Air concentration of pollutant	Expressed in pg/m^3 , ng/m^3
M_{PUF}	Amount of pollutant accumulated in PUF disk	Derived from instrumental analysis and expressed in pg, ng
V_{air}	Effective air volume	Compound specific and as a function of PUF parameters, sampling duration, and meteorological conditions
K_{OA}	Octanol-air partition coefficient	Retrieved from literature or derived from octanol-water partition coefficient: PCBs (Harner & Bidleman, 1998), PAHs (Pozo et al., 2015). Log KOA values depend on compounds' nature and temperature and were calculated by using the template from (Lee et al., 2016)
K_{PUF}	PUF-air partition coefficient	Dimensionless
K'_{PUF}	PUF-air partition coefficient adjusted by PUF disk density	Dimensionless
ρ_{PUF}	Density of PUF disk	$21000\ g/m^3$
V_{PUF}	Volume of PUF disk	$2.10\times 10^{-4}\ m^3$
t	Sampling duration	Expressed in days
K_A	Air-side mass transfer coefficient	108 m/d
R	Sampling rate	$4\ m^{3}/d$
A_{PUF}	Exposed surface area of PUF disk	$3.70 \times 10^{-2}\ m^2$
D_{film}	Effective film thickness	5.67×10^{-3} m

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 PAHs and PCBs Concentration

To characterize and quantify the PCBs and PAHs from the passive air sampler in the ambient air. Resulting in pollutants profiles compared between two big cities, Bangkok and Chiangmai were discussed in this chapter.

4.1.1 Concentrations and profile of PAHs

The concentrations of 16 USEPA PAHs were sampled in the dry season of Thailand. A total of 15 PAHs was obtained in Bangkok and Chiang Mai from December 2018 to June 2019 the approach of passive air samplers was investigated for over 60 days per period. This approach was invented for alternatively sampling atmospheric pollutants in remoting. In this study, we have discussed the concentration in gas phare of PAHs. Various studies in Thailand were focusing on PAHs concentration that obtains from the fine particle such as PM_{10} or $PM_{2.5}$. Particulate bound to PAHs conducted in a major city that had a serious issue of atmospheric pollution, then the differences in this study were conducted and quantify PAHs concentration in the gas phase. As a result, conducting by the passive air sampler approach was collecting gas phase of pollutants. From 16 target USEPA PAHs, Naphthalene was eliminated because of the high volatility of low molecular weight. In general, low molecular weight PAHs 2-3 rings (LMW) and High molecular weight PAHs 5-6 rings (HMW) is dominant in the gas phase. Medium molecular weight (MMW) PAHs 4 ring is distributed in both particle and gas phase in the atmosphere (Lai, Tsai, Chen, & Chang-Chien, 2017). In this study, two major cities are found Phe, Fl, Flu, and Pry as a dominant species. PAH concentration in Bangkok and Chiangmai was differently ranged in three periods (Figure 22-23). As the result, the highest PAH concentration was found at Khwaeng Wang Mai (B5). At this sampling site were found Phenanthrene (Phe), Fluorene (Fl), Fluoranthene (Flu), and Pyrene (Pyr) as dominant species and, all species were ranged from 0.12 to 20.10 ng/m^3. In all three periods of samplings, high also concentration found from February to April 2019. At 4 sampling site, Khwaeng Tha Raeng (B1), Khwaeng Thung Song Hong (B2), Khwaeng Phaya Thai (B3), and Khwaeng Wong Sawang (B4) were ranged 0.15 to 35, 0.02 to 19.5,0.06 to 92.9, and 0.05 to 15.2 ng/m^3, respectively.

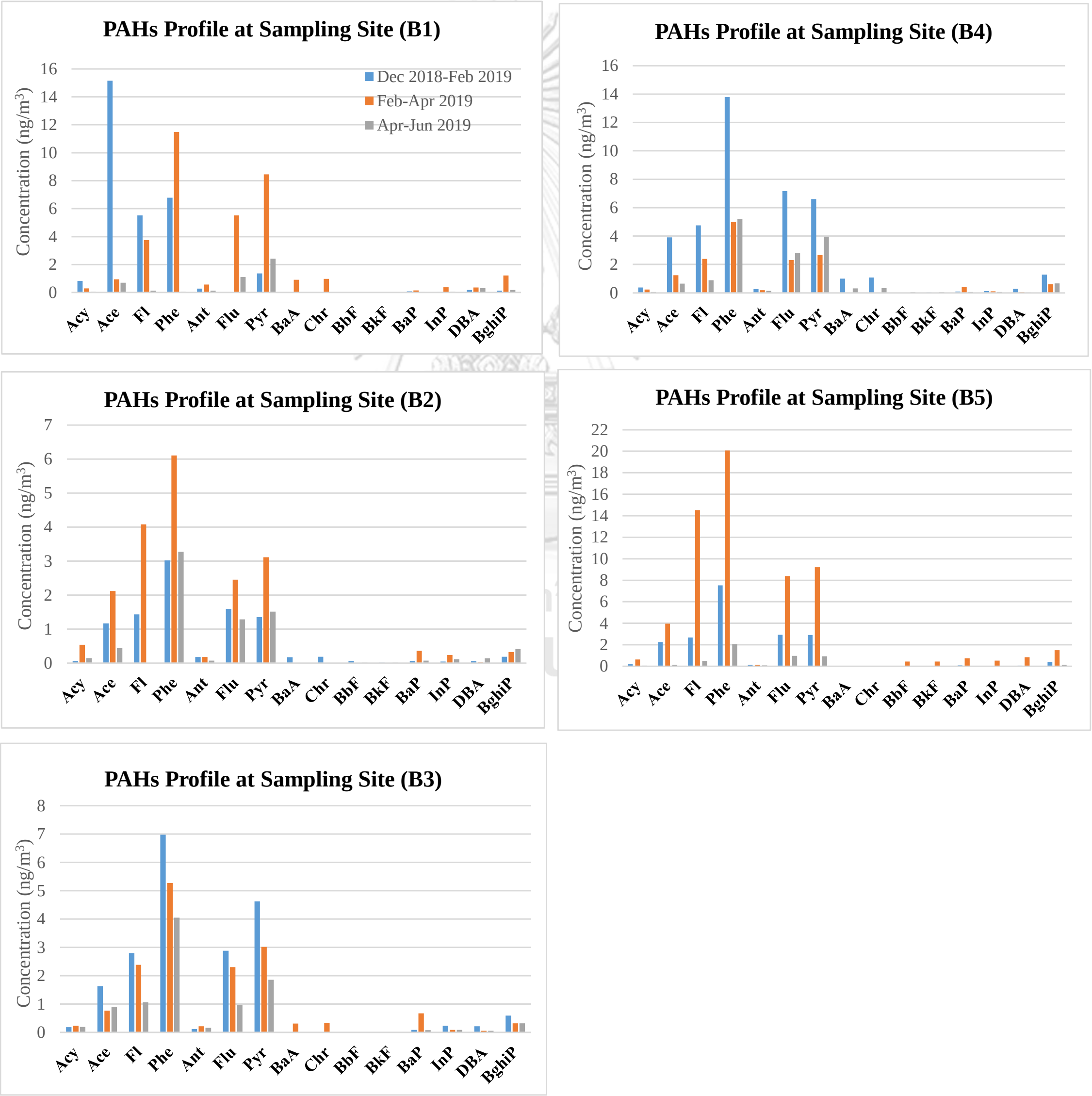


Figure 22 : PAHs profiles in each sampling site in Bangkok

Similar to Chiang Mai, the highest concentration PAHs were detected from February to April. At Tambon Hai Ya (C1) sampling site were found Phe, Flu, Fl, and Pry as a dominate species, PAHs concentration was ranging from 358 to 0.09 ng/m^3. At the other sampling site, Tambon Nong Han (C2) also found a high concentration which is ranging from 0.08 to 115 ng/m^3. The concentration PAHs at the reference site, Tambon Su Thep (C3) was ranging from 0.008 to 2.15 ng/m^3. As a result, Phenanthrene (PA), Fluorene (Fl), Fluoranthene (FL), and Pyrene (Pyr) were shown to be dominant PAHs species of both major. Phenanthrene is a species that is dominant in this study that mostly emits diesel vehicles and coal-burning (Liu et al., 2015). The small molecular weight PAHs (Ace, AcPy, Flu, Phe, and Pry) were the dominants species that emitted from heavy diesel vehicles and organic burning (Cao et al., 2017; de Souza & Correa, 2016). Furthermore, the vehicles using gasoline mostly emit BghiP, Daha, and BaP. However, BaP, Daha, and BghiP are the high molecular weight PAHs which can exist in the atmosphere and environment for a longer time than the low molecular weight PAHs. The reason why high molecular weight PAHs were not much found in this study because of the low molecular weight species were a dominant species of passive air sampling approach. A gas phase of PAH concentrations were found in this study were associated with the gasoline vehicle emission and organic burning.

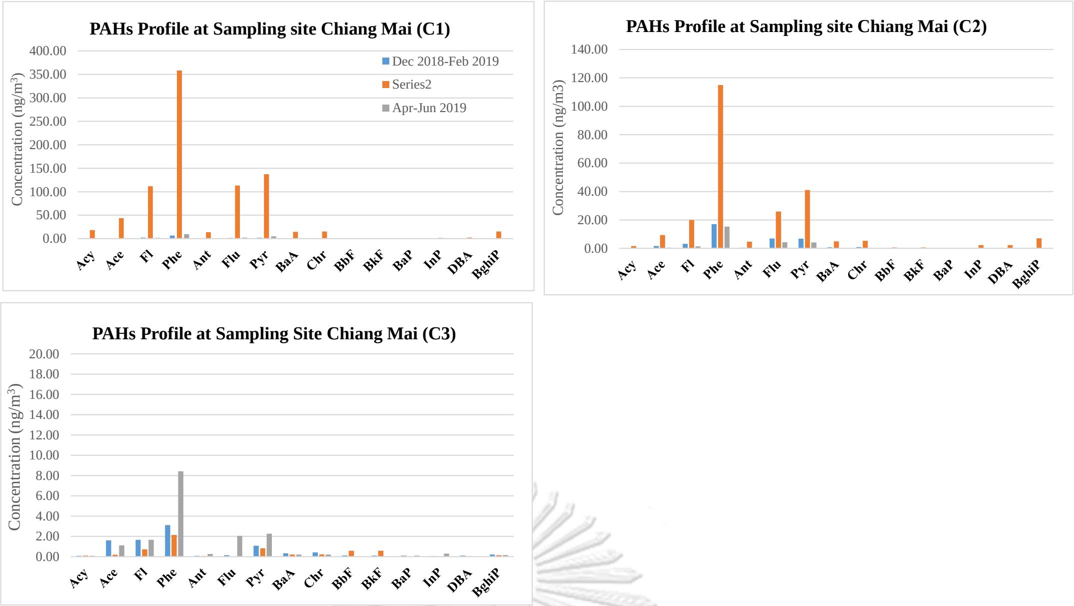


Figure 23 : PAHs profiles in each sampling site in Chiang Mai

4.1.2 Concentrations and profile of PCBs

Among 12 initial POPs regulated by Stockholm Convention, polychlorinated biphenyls are listed under Annex C which is an unintentional production. PCBs have many studies because of their high toxicity and bioaccumulation. However, to evaluate health risk assessment, this study was only focusing on 12 dl-PCBs. 7 PCBs congeners were conducted in every sampling site in both Bangkok and Chiang Mai (Figure 24- 25). The highest concentration was found at and Khwaeng Wong Sawang (B4), from April to June, ranging from 0.05 to 11.96 pg/m^3. There was no signification of PCBs between site sampling. As a result, April to June is the period that found a higher concentration than the other period. PCBs concentration at Bangkok sampling site, Khwaeng Tha Raeng (B1), Khwaeng Thung Song Hong (B2), Khwaeng Phaya Thai (B3), and Khwaeng Wang Mai (B5) were ranging 0.06 to 1.43, 0.05 to 0.7, 0.2 to 1.5, and 0.05 to 0.98 pg/m^3, respectively.

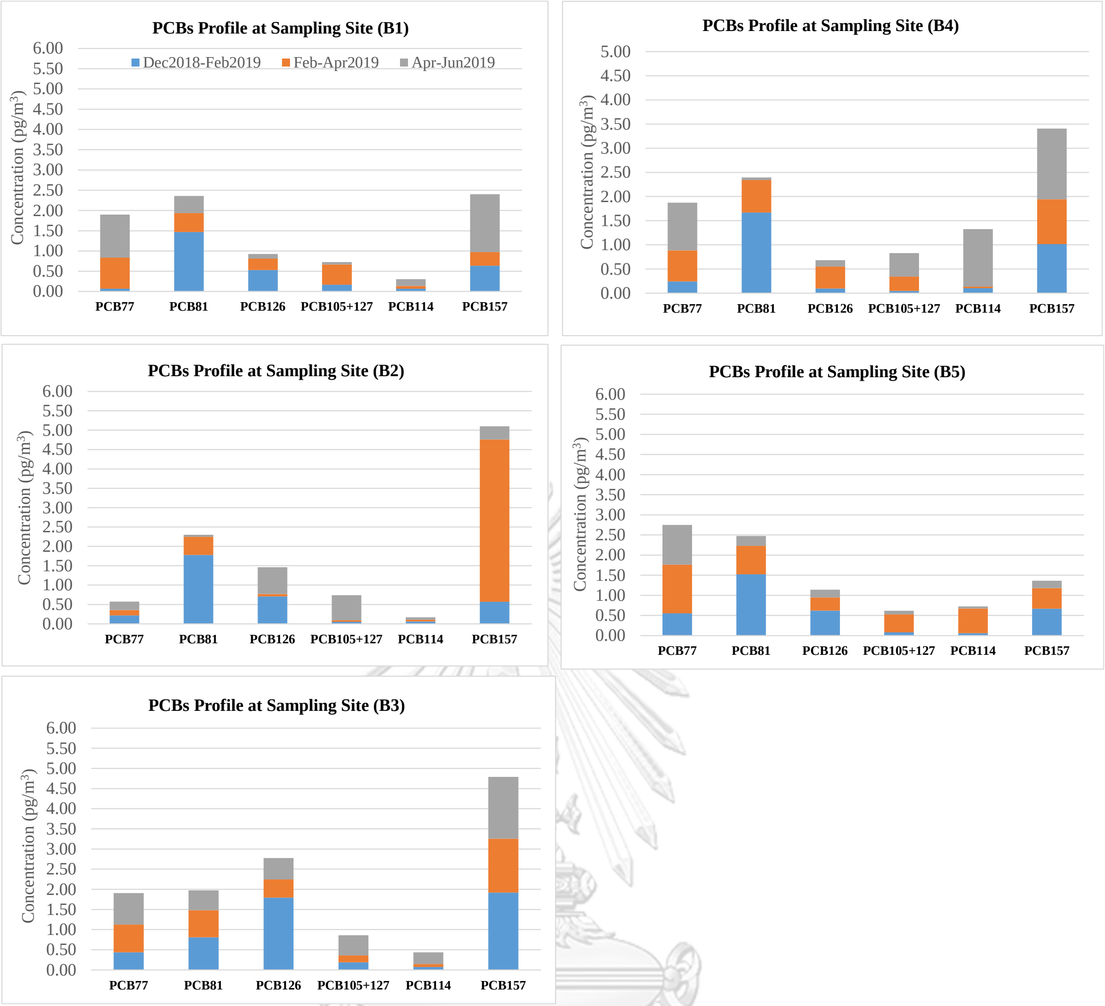


Figure 24 : PCBs profiles in each sampling site in Bangkok

Three sampling sites in Chiang Mai, Tambon Hai Ya (C1), Tambon Nong Han (C2), and Tambon Su Thep (C3). PABs concentrations were ranged from 0.006 to 0.56, 0.04 to 1.39, 0.07 to 0.19 pg/m^3, respectively. PCB 77, 81, and 157 congeners are shown to be a dominant compound of both Bangkok and Chiang Mai. PCBs and dl-like PCBs concentration and congener distribution in the environment are strongly affected by distance to nearby emission sources. Major PCBs emission sources, possibly can be a long-range atmospheric transport (LRAT). The sources emission of PCBs includes combustion activity such as fossil combustion municipal, hazardous, and medical waste incineration, open burning, and metal smelting chemical production (Chi et al., 2016; Chi et al., 2010; Thuan et al., 2013).

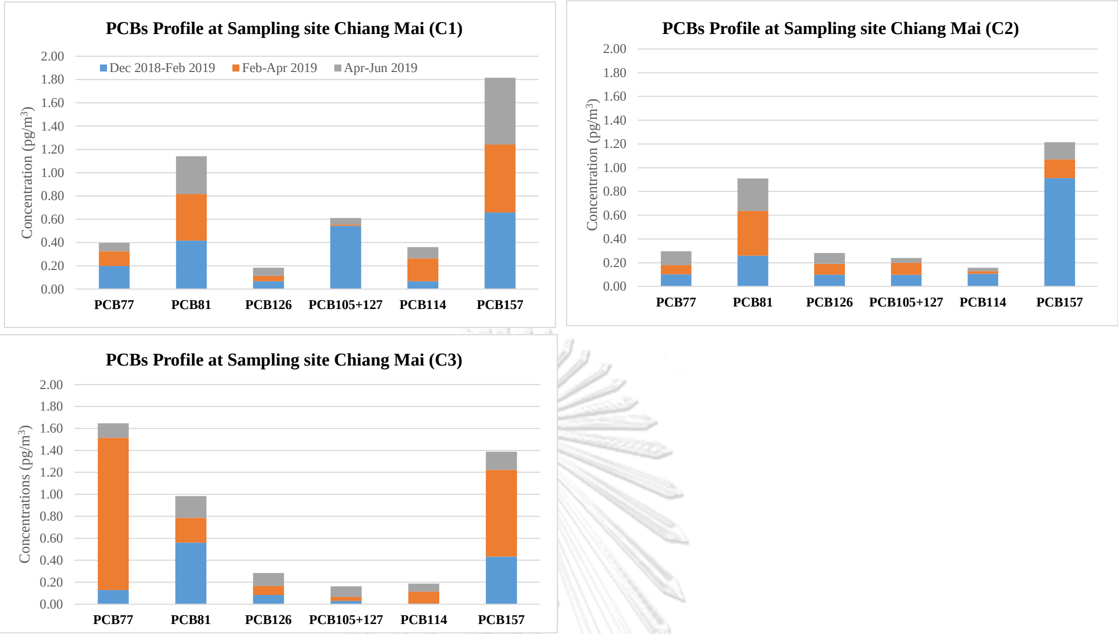


Figure 25 : PCBs profiles in each sampling site in Chiang Mai

4.2 Comparison of total concentration between Bangkok and Chiang Mai

4.2.1 Total PAHs and PCBs concentration in Bangkok and Chiang Mai.

The concentrations of 16 USEPA PAHs and 12 dl-like PCBs were sampled in the dry season of Thailand. A total of 15 PAHs was obtained in Bangkok and Chiang Mai from December 2018 to June 2019, as shown in (a) and (b) in Figure 26. The approach of passive air samplers was investigated for over 60 days per period. The statistical summary in Table 8, shows the total PAHs, the mean, maximum and minimum concentration. Naphthalene was eliminated because of the high volatility of low molecular weight PAH. As a result, a total PAH concentration in Chiang Mai has found to be ranged from 588 to 848 ng/m^3, which is higher than Bangkok, which ranged from 4.87 to 455 ng/m^3. The highest concentration PAHs of all sampling sites were increased during the second period from February to April 2019.

Table 8 : Concentration of PAHs and PCBs in polyurethane disk samples during December 2018-June 2019

Pollutants	Bangkok				Chiangmai			
	Min^{1}	*Max*^{2}	*Avg*^{3}	*SD*^{4}	*Min*^{1}	*Max*^{2}	*Avg*^{3}	*SD*^{4}
AcPy ^{a}	4.30×10^{-2}	8.35×10^{-1}	2.74×10^{-1}	2.32×10^{-1}	7.85×10^{-2}	1.83×10^{1}	2.34	6.02
Acp ^{a}	1.36×10^{-1}	1.52×10^{1}	2.40	3.71	1.83×10^{-1}	4.38×10^{1}	6.64	1.42×10^{1}
Flu ^{a}	1.33×10^{-1}	1.45×10^{1}	3.35	3.59	7.18×10^{-1}	1.12×10^{2}	1.60×10^{1}	3.63×10^{1}
PA ^{a}	5.54×10^{-2}	2.01×10^{1}	6.71	5.06	2.15	3.58×10^{2}	5.95×10^{1}	1.18×10^{2}
Ant ^{a}	7.44×10^{-2}	5.66×10^{-1}	1.89×10^{-1}	1.20×10^{-1}	7.61×10^{-2}	1.36×10^{1}	2.24	4.53
FL ^{a}	9.57×10^{-1}	8.39	3.05	2.33	8.07×10^{-3}	1.13×10^{2}	1.74×10^{1}	3.68×10^{1}
Pyr ^{a}	9.30×10^{-1}	9.20	3.60	2.58	8.24×10^{-1}	1.37×10^{2}	2.23×10^{1}	4.50×10^{1}
BaA ^{a}	1.73×10^{-1}	9.96×10^{-1}	5.41×10^{-1}	3.83×10^{-1}	1.90×10^{-1}	1.45×10^{1}	2.45	4.78
CHR ^{a}	1.83×10^{-1}	1.07	5.79×10^{-1}	4.13×10^{-1}	2.04×10^{-1}	1.54×10^{1}	2.62	5.07
BbF ^{a}	1.01×10^{-2}	4.43×10^{-1}	1.14×10^{-1}	1.85×10^{-1}	1.10×10^{-2}	7.86×10^{-1}	3.26×10^{-1}	3.01×10^{-1}
BkF ^{a}	1.01×10^{-2}	4.43×10^{-1}	9.15×10^{2}	1.73×10^{-1}	4.32×10^{-3}	7.86×10^{-1}	3.18×10^{-1}	3.00×10^{-1}
BaP ^{a}	1.12×10^{-1}	7.41×10^{-1}	2.00×10^{-1}	2.35×10^{-1}	1.63×10^{-2}	2.69×10^{-1}	9.52×10^{-2}	7.37×10^{-2}
IND ^{a}	5.68×10^{-3}	5.18×10^{-1}	1.39×10^{-1}	1.45×10^{-1}	2.94×10^{-2}	2.37	5.53×10^{-1}	8.73×10^{-1}
DBA ^{a}	3.39×10^{-3}	8.34×10^{-1}	1.78×10^{-1}	2.15×10^{-1}	1.21×10^{-2}	2.40	6.27×10^{-1}	9.78×10^{-1}
BghiP ^{a}	1.25×10^{-1}	1.51	5.49×10^{-1}	4.45×10^{-1}	1.42×10^{-1}	1.53×10^{1}	2.67	5.26
Σ_{15}PAHs ^{a}	4.87	4.55×10^{2}	8.95×10^{-1}	1.30×10^{2}	5.88	8.48×10^{2}	1.69×10^{2}	2.82×10^{2}
PCB77 ^{b}	7.14×10^{-2}	1.21	6.00×10^{-1}	3.68×10^{-4}	7.20×10^{-2}	1.39	2.60×10^{-1}	4.24×10^{-4}
PCB81 ^{b}	5.23×10^{-2}	1.78	7.67×10^{-1}	5.73×10^{-4}	1.98×10^{-1}	5.60×10^{-1}	3.37×10^{-1}	1.13×10^{-4}
PCB126 ^{b}	5.98×10^{-2}	1.79	4.66×10^{-1}	4.29×10^{-1}	4.65×10^{-2}	1.18×10^{-1}	8.33×10^{-2}	2.06×10^{-5}
PCB114 ^{b}	3.26×10^{-2}	1.19×10^{1}	9.10×10^{-1}	3.04	5.80×10^{-3}	1.97×10^{-1}	7.83×10^{-2}	5.82×10^{-5}
Σ_{4} dl-PCBs ^{b}	7.15×10^{-1}	1.31×10^{1}	2.74	2.93	6.94×10^{-1}	2.63	1.36	4.07×10^{-1}
Σ_{7}PCBs ^{b}	1.75	1.50×10^{1}	4.13	3.15×10^{-3}	5.09×10^{-1}	1.81	7.59×10^{-1}	6.24×10^{-1}

15 PAHS compounds: Acenaphthylene (AcPy), Acenaphthene (Ace), Fluorene (Fl), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (FL), Pyrene (Pyr), Ben[a]anthracene (BaA), Chrysene (CHR), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Indeno[1,2,3-c, d] pyrene (IND), Dibenz[ah]anthracene (DBA), and Benzo[g,h,i]perylene (BghiP)

a PAHs (ng/m3)

b Dl-PCBs (pg/m3)

The potential sources of PAHs were found as the combined emission of diesel and gasoline vehicles and biomass combustion. Moreover, the dominant species of using the PAS approach were mostly due to the low molecular weight of PAHs species (Bohlin, Jones, Levin, et al., 2010; W. J. Hong et al., 2016; Wang et al., 2010). According to the results, which indicates the increase of total PAHs concentration was related to the excess increase of $PM_{2.5}$ concentration episodes in Bangkok from January to March 2019, and the forest fire episode in Chiang Mai from February to April 2019.

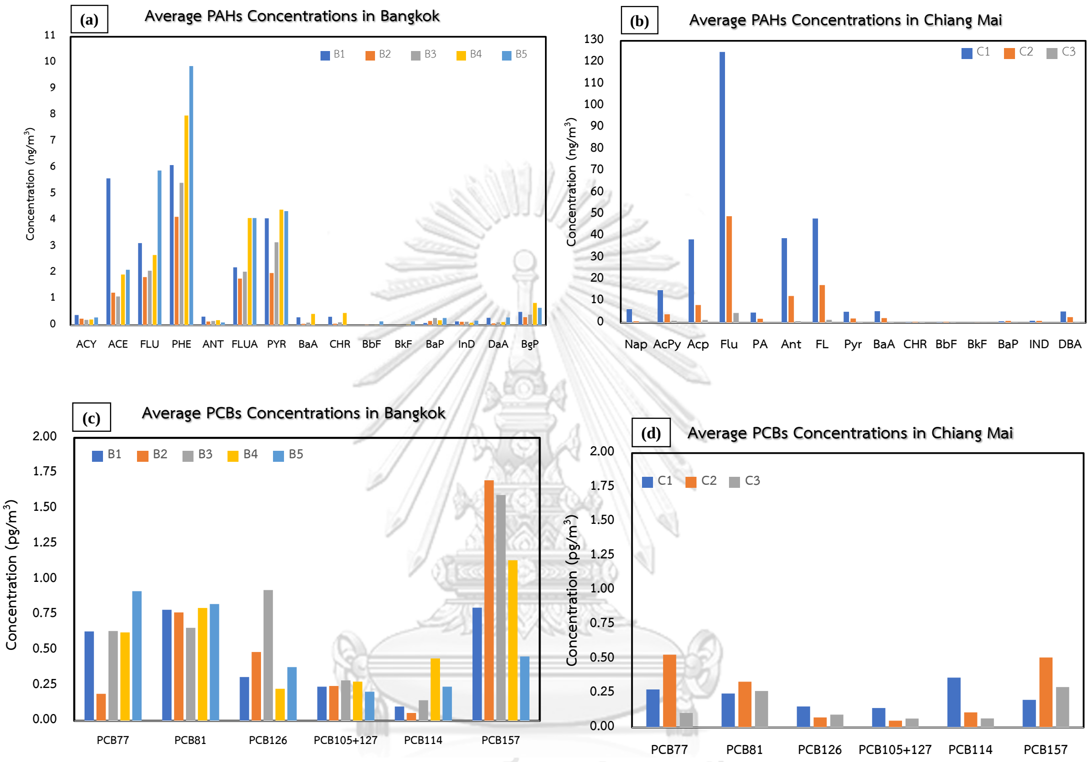


Figure 26 : The average total PAHs and PCBs concentration

Figures 26, (c), and (d) presented the average PCBs concentration collected in the same period of PAHs. A total of 7 congeners of PCBs concentration was obtained in Bangkok which ranged from 1.75 to 15 pg/m^3, in which the maximum of total PCBs was higher than Chiang Mai, which ranged from 0.51 to 1.81 pg/m^3. The highest total PCBs concentration in Bangkok air was not much different from the study of POPs in Vietnam. The study was done in the electronic waste landfill and urban areas. A total of 12 dl-PCBs congeners ranged from 0.95-10 pg/m^3 in the urban area. The highest concentration of dl-like PCBs obtained from the electronic waste landfill was in the range of 3.36-20 pg/m^3 (Anh et al., 2019). Furthermore, Table 4.1 shown total PAH and PCB concentrations compared with other studies that derived by passive air sampling.

Table 9 : Comparison of PAHs and PCBs concentration with other studies

Country	Location, Sampling year	Concentrations	References
PAHs (ng/m^3)			
Thailand	Bangkok, urban 2018 - 2019	0.09 - 6.71	This study
	Chiang Mai	0.10 - 59.50	
Vietnam	Hanoi, urban, 2013 - 2015	0.01 - 0.04	(Anh et al., 2020)
	Bac Giang and Thai Nguyen, vehicle waste processing, 2013 - 2015	0.01 - 0.10	(Anh et al., 2020)
China	Shanghai, urban and rural, 2006 - 2007	0.02 - 0.05	(Wang et al., 2010)
India	Urban, suburban, rural areas of 3 cities Kolkata, Mumbai, Chennai, 2006	0.06 - 0.55	(Cheng et al., 2013)
PCBs (pg/m^3)			
Thailand	Bangkok, urban 2018 - 2019	1.75 – 15	This study
	Chiang Mai	0.51 -1.81	
Vietnam	Hanoi, urban, 2013 - 2015	0.95 - 10	(Anh et al., 2019)
	Bac Giang and Thai Nguyen, vehicle waste processing, 2013 - 2015	3.36 - 20	(Anh et al., 2019)
China	Tianjin, industrial zones, living areas, and background areas, 2008–2009	30.8 - 301	(Ding et al., 2013)

4.3 Health Risk Assessment

To evaluate the risk of PCBs and PAHs on human health. The excess cancer risk was calculated using Eq. 11 followed by the USEPA method recommended. The total concentration of 15 PAHs and 7 PCBs are shown in Table 4.3. The mean of lifetime excess cancer risk of total PAHs in Bangkok and Chiang Mai were 7.11x10^{-8} and 1.07x10^{-7}, while the mean of total PCB was 3.16x10^{-3} and 1.25x10^{-7}, respectively. The PCBs excess cancer risk values of Bangkok in this study are a bit higher than that of the other research, which was done in the Yangtze River Delta, China (Zhang et al., 2013). The research investigated the cancer risk of inhalation of PCBs in urban and rural areas. The lifetime cancer risk was found to be 0.77x10^{-5}, 0.83x10^{-6}, and 0.54x10^{-6} for urban, urban-rural, and rural, respectively.

In comparison, the value of this study was lower than the total risk of inhalation PAHs and PCBs of the municipal solid waste landfill in Novi Sad, Serbia. The PAHs and PCBs mean calculation was 3.72x10^{-7}, and 4.51x10^{-7}, respectively (Petrovic et al., 2018). Moreover, the mean concentration of total PAHs and PCBs in the industrial area of Kutahya, Turkey were found to be 4.03x10^{-6} and 1.39x10^{-7}, respectively, which is greater than this study (Dumanoglu, Gaga, Gungormus, Sofuoglu, & Odabasi, 2017). In conclusion, the acceptable level of excess cancer risk defined by USEPA ranged from 10^{-6} to 10^{-4} (USEPA, 2011). As a result, Table 4.3 shown that the excess cancer risk from the inhalation of both the pollutants for the people living in Bangkok and Chiang Mai was lower than the limit value, therefore, there has been a negligible effect on human health from the inhalation of these pollutants.

Table 10 : The excess cancer risk calculations of PAHs and PCBs in Bangkok and Chiang Mai

Excess cancer risk	*Range*		*Avg*	*Median*	*SD*
	Min	*Max*			
Σ15PAHs Bangkok	3.51×10^{-9}	2.80×10^{-7}	7.11×10^{-8}	3.56×10^{-8}	7.76×10^{-8}
Σ15PAHs Chiangmai	1.22×10^{-8}	3.24×10^{-7}	1.07×10^{-7}	5.06×10^{-8}	1.15×10^{-7}
Σ7PCBs Bangkok	9.62×10^{-13}	2.70×10^{-2}	3.16×10^{-3}	6.96×10^{-12}	7.38×10^{-3}
Σ7PCBs Chiangmai	6.94×10^{-8}	1.70×10^{-7}	1.25×10^{-7}	1.31×10^{-7}	2.80×10^{-8}

CHAPTER 5

CONCLUSIONS

5.1 Research conclusions

PAHs and PCBs concentration were observed in Bangkok and Chiang Mai by using Polyurethane disk passive samplers, collected during the dry season from December 2018- June 2019. A total of 24 samples were extracted and further quantitatively analyzed by the standard method using GC-MS. Both PAHs and PCBs concentrations increased during the second period of sampling in Bangkok and Chiang Mai. As a result, Chiang Mai PAHs concentration was higher than Bangkok, the maximum values of PAHs were found to be 848 ng/m^3 and 455 ng/m^3, respectively. On the other hand, the maximum value of PCBs was found in Bangkok to be 15 pg/m^3 which is higher than in Chiang Mai. The maximum value was 1.81 pg/m^3 during the high PM$_{2.5}$ concentration episode in Bangkok. Chiang Mai sites had more dominant species of PAHs than in Bangkok, particularly during forest fire episodes from February to April 2019. The carcinogenic risk associated with inhalation exposure to PAHs and PCBs was in the range of acceptable levels at all the sampling points. The calculated risk values were lower than the limit value ($<10^{-6}$) defined by USEPA. The estimation of exposure to these pollutants is negligible for health effects. Nevertheless, in early 2020, due to the COVID-19 pandemic, Bangkok city was under lockdown situation, with very little traffic movement, as a result, the concentration of air pollution has decreased considerably, and the haze episode has also disappeared. Air pollutants monitoring is needed in both major Bangkok and Chiang Mai.

5.2 Recommendations

For further research, the source of PAHs and PCBs may be undertaken to understand the contribution of trans-boundary pollutants and local pollutants in developing total PAHs and PCBs in Bangkok and Chiang Mai. The seasonal investigation would be investigated in the season to compare the concentration, and use of statistic models for predicting PAHs and PCBs. Nevertheless, the concentration distribution of the investigation after the COVID-19 pandemic would be very interesting in the continual pollutant monitoring. Meanwhile, from February to April 2020, in Chiangmai, the forest fire and smoke from organic waste burning due to agriculture activities have led to an increase in a considerable amount of air pollution again as well and hence has resulted in an increase in the concentration of PAHs in Chiang Mai compared to Bangkok. Thus, it reflects the major source of these pollutants was biomass burning. Therefore, air quality management is an essential issue for both cities of Thailand, which needs to be monitored

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APPENDIX

Experimental Procedural

Figure A. 1: Glassware using in laboratory

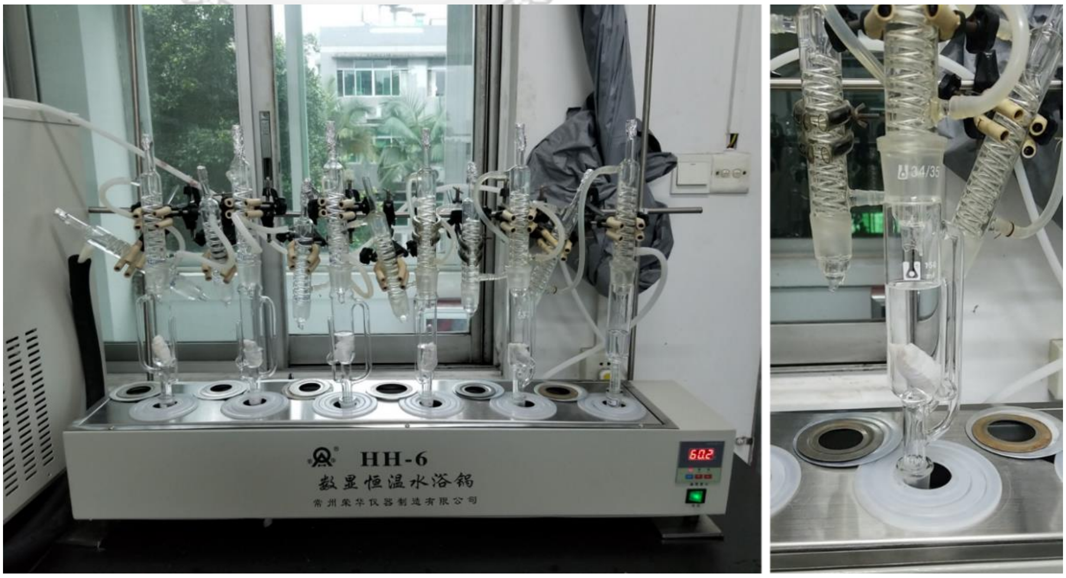


Figure A. 2: Soxhlet extractor and Water bath

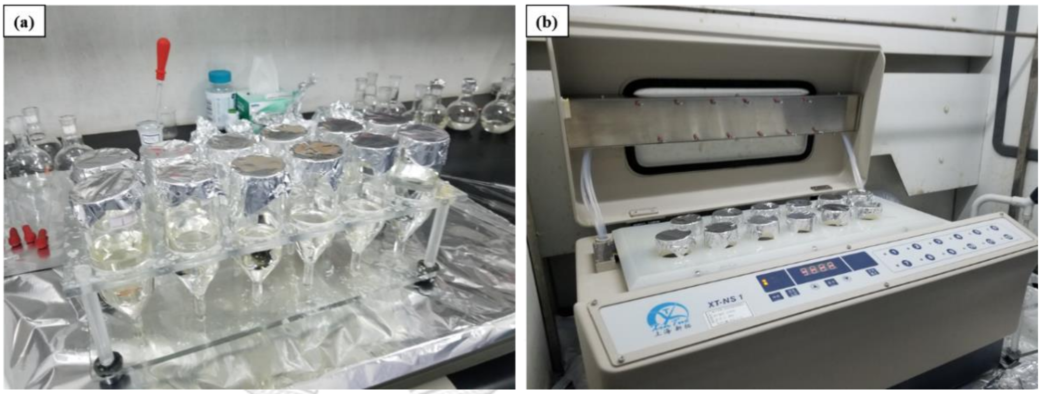


Figure A. 3: (a) Cylinder tube for nitrogen blowing

(b) *XT-NS1, Nitrogen blowing instrument*

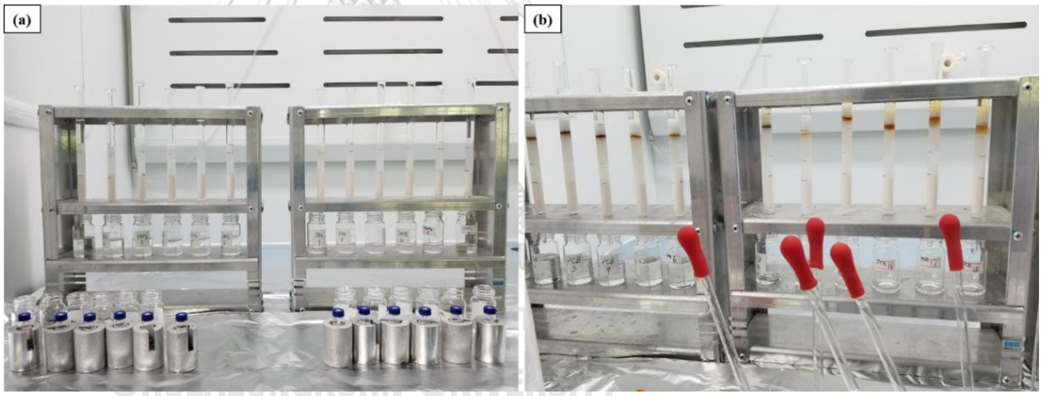


Figure A. 4: (a)Column packing for PAHs and PCBs compound

(b)Cleaning-up procedure.

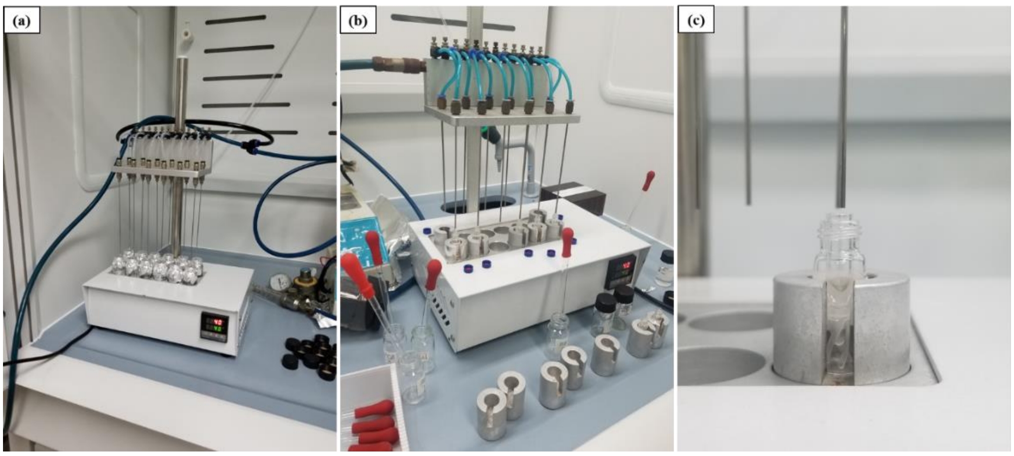


Figure A.5:(a) Sample were subjected under a gentle nitrogen stream (b)Concentrated samples up to 0.2 ml (c)Preparation before GC-MS analysis

Figure A.6: GC-MS, Shimazu-QP2010 for PAHs analysis

Figure A.7: GC-MS-MS, Agilent 7693 for PCBs analysis

Table A.1: Retention time of PAHs compounds by using GC-MS

<table>
<tr><th colspan="3">PAHs</th></tr>
<tr><th>Parameter</th><th colspan="2">Condition/setting values</th></tr>
<tr><td>Instrument</td><td colspan="2">Shimazu-QP2010 (PostRun Data Analysis)</td></tr>
<tr><td>Column</td><td colspan="2">HP-5MS column (30 m×0.25 mm, film thickness 0.25 µm)</td></tr>
<tr><td>Injection</td><td colspan="2">Spitless mode, injection volume 1-µL, temperature 280 °C</td></tr>
<tr><td>Carrier gas</td><td colspan="2">Helium, flow rate of 1.2 mL min^{-1}</td></tr>
<tr><td>Oven temperature program</td><td colspan="2">110 °C (hold 1 min), to 170 °C (20 °C/min), to 220 °C (4 °C /min), to 270 oC (3 oC /min), to 310 oC (20 oC /min, hold 10 min).</td></tr>
<tr><td>Interface temperature</td><td colspan="2">310 °C</td></tr>
<tr><td>Ion source temperature</td><td colspan="2">230 °C</td></tr>
<tr><td>Ionization mode</td><td colspan="2">Electron impact, electron 70 eV</td></tr>
<tr><th>Compound</th><th>Abbreviation</th><th>m/z</th></tr>
<tr><td>Naphthalene</td><td>NAP</td><td>128</td></tr>
<tr><td>Acenaphthylene</td><td>ACY</td><td>152</td></tr>
<tr><td>Acenaphthene</td><td>ACE</td><td>153</td></tr>
<tr><td>Fluorene</td><td>FLU</td><td>166</td></tr>
<tr><td>Phenanthrene</td><td>PHE</td><td>178</td></tr>
<tr><td>Anthracene</td><td>ANT</td><td>178</td></tr>
<tr><td>Fluoranthene</td><td>FLUA</td><td>202</td></tr>
<tr><td>Pyrene</td><td>PYR</td><td>202</td></tr>
<tr><td>Benzo(a)anthracene</td><td>BaA</td><td>228</td></tr>
<tr><td>Chrysene</td><td>CHR</td><td>228</td></tr>
<tr><td>Benzo(b)fluoranthene</td><td>BbF</td><td>252</td></tr>
<tr><td>Benzo(k)fluoranthene</td><td>BkF</td><td>252</td></tr>
<tr><td>Benzo(a)pyrene</td><td>BaP</td><td>252</td></tr>
<tr><td>Indeno(1,2,3-c,d)pyrene</td><td>InD</td><td>252</td></tr>
<tr><td>Dibenzo(a,h)anthracene</td><td>DaA</td><td>278</td></tr>
<tr><td>Benzo(g,h,i)perylene</td><td>BgP</td><td>276</td></tr>
</table>

Table A.2: Retention time of PAHs compounds by using GC-MS

PAHs Compound	Abbr.	Retention time
Naphthalene	NAP	7.16
Acenaphthylene	ANY	10.91
Acenaphthene	ACE	11.34
Fluorene	FLU	12.60
Phenanthrene	PHE	14.90
Anthracene	ANT	15.03
Fluoranthene	FLUA	17.78
Pyrene	PYR	18.30
Benz[a]anthracene	BaA	21.23
Chrysene	CHR	21.31
Benzo[b]fluoranthene	BbF	23.65
Benzo[k]fluoranthene	BkF	23.71
Benzo[a]pyrene	BaP	24.32
Indeno[1,2,3-cd]pyrene	InD	26.64
Dibenz[a,h]anthracene	DiB	26.72
Benzo[g,h,i]perylene	DghiP	27.25

Table A.3: Parameter and conditions of GC-MS/MS analysis.

PCBs		
Parameter	**Condition/setting values**	
Instrument	GC-MS-MS Agilent 7693 (MassHunter Data Analysis)	
Column	CP-Sil 8 CB (50 m x 0.25 mm, film thickness 0.12 μm) and DB-5MS (30m x 0.250 mm, film thickness 0.25 μm)	
Injection	Spitless mode, injection volume 1-μL, temperature 280 °C	
Carrier gas	Helium, flow rate of 1.2 mL/min	
Oven temperature program	100 °C for 0.5 min, then 10 °C /min to 160 °C, 3 °C /min to 250 °C, and 10 °C /min to 295 °C or 10 min and hold for 10 min at 300 °C	
Interface temperature	280 °C	
Ion source temperature	290 °C	
Ionization mode	Electron impact, electron -70 eV	
Homolog dl-PCBs	**Precursor**	**Product**
PCB77	290	220
PCB81	290	220
PCB126	326	256
PCB169	360	290
PCB105+127	326	256
PCB114	326	256
PCB118+106	326	256
PCB123	326	256
PCB156	360	290
PCB157	360	290
PCB167	360	290
PCB189	394	324
PCB11	222	152
PCB28+31	256	186
PCB52+73+69	290	220
PCB101+89+90	326	256
PCB138+164+163	360	290
PCB153+132+168	360	290
PCB180	394	324

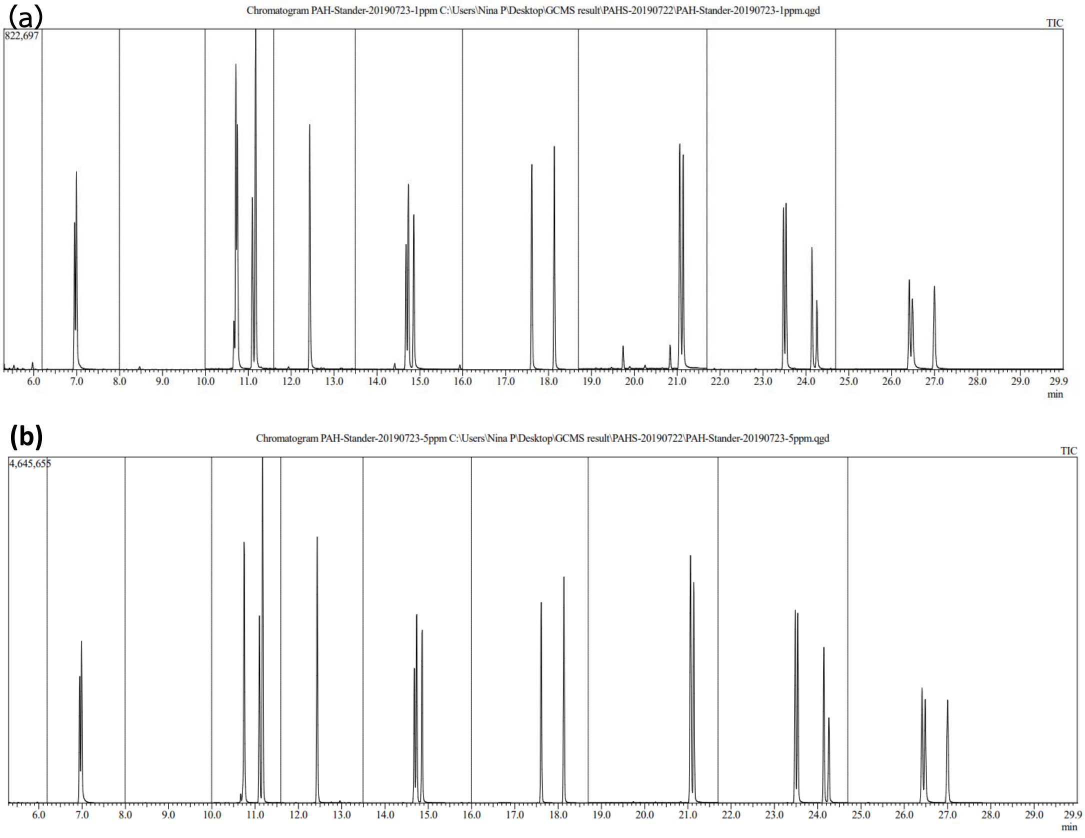
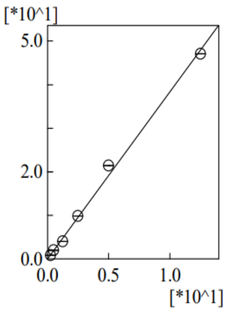


Figure A. 8: (a) Sample of PAHs standard Chromatogram at 1 ppm

(b) Sample of PAHs standard Chromatogram at 5 ppm

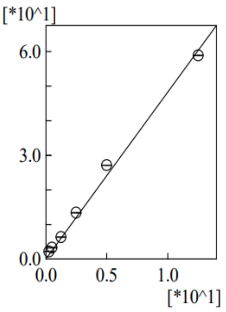
Calibration

ID#:1 Mass:136.00 Name:NAP-d8
f(x)=3.835007*x+0.000000
rr2=0.996027



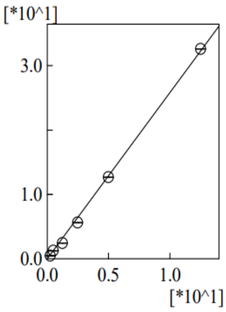
#	Conc. Ratio (ng)	Mean Area Ratio
1	0.250	0.83
2	0.500	2.00
3	1.250	4.07
4	2.500	9.87
5	5.000	21.43
6	12.500	47.05

ID#:2 Mass:128.00 Name:NAP
f(x)=4.832180*x+0.000000
rr2=0.996850



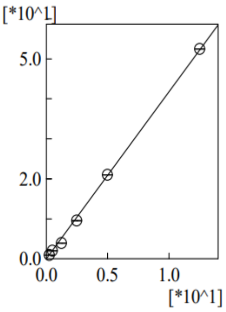
#	Conc. Ratio (ng)	Mean Area Ratio
1	0.250	2.14
2	0.500	3.26
3	1.250	6.38
4	2.500	13.42
5	5.000	27.08
6	12.500	58.88

ID#:5 Mass:162.00 Name:ACE-d10
f(x)=2.581081*x+0.000000
rr2=0.999118



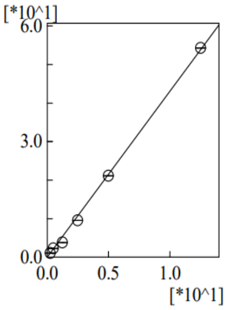
#	Conc. Ratio (ng)	Mean Area Ratio
1	0.250	0.48
2	0.500	1.28
3	1.250	2.43
4	2.500	5.64
5	5.000	12.70
6	12.500	32.59

ID#:6 Mass:153.00 Name:ACE
f(x)=4.176738*x+0.000000
rr2=0.999308



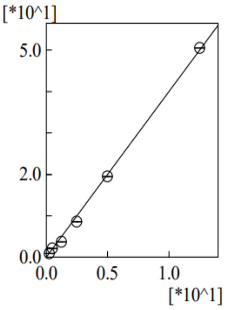
#	Conc. Ratio (ng)	Mean Area Ratio
1	0.250	0.95
2	0.500	2.04
3	1.250	3.97
4	2.500	9.58
5	5.000	20.98
6	12.500	52.47

ID#:7 Mass:166.00 Name:FLU
f(x)=4.301759*x+0.000000
rr2=0.998799



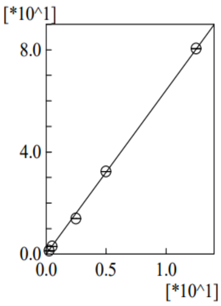
#	Conc. Ratio (ng)	Mean Area Ratio
1	0.250	1.08
2	0.500	2.27
3	1.250	3.84
4	2.500	9.56
5	5.000	21.12
6	12.500	54.32

ID#:8 Mass:188.00 Name:PHE-d10
f(x)=3.994946*x+0.000000
rr2=0.998662



#	Conc. Ratio (ng)	Mean Area Ratio
1	0.250	0.96
2	0.500	2.14
3	1.250	3.71
4	2.500	8.60
5	5.000	19.49
6	12.500	50.53

ID#:4 Mass:152.00 Name:ANY
f(x)=6.414538*x+0.000000
rr2=0.999239



#	Conc. Ratio (ng)	Mean Area Ratio
1	0.250	1.39
2	0.500	3.00
4	2.500	13.96
5	5.000	32.35
6	12.500	80.50

Figure A. 9: The example of standard calibration of PAHs compounds

Table A. 4 : Retention time of PCBs by using GC-MS/MS

Homogus	PCBs NO.	RT	Homogus	PCBs NO.	RT	PCBs NO.	RT	Homogus	PCBs NO.	RT
CBs	1	10.381	Tetra-CBs	44	21.261	111+117	26.253	Hexa-CBs	162	32.395
	2	11.649		59	21.38	87+116+115	26.341		128	32.613
	3	11.791		42	21.441	85+109	26.544		167	32.717
Di-CBs	4+10	12.603		72	21.725	110	26.859		156	33.958
	9+7	13.599		71	21.851	82	27.46		157	34.272
	6	14.036		64+41	21.909	124	27.851		169	36.054
	8+5	14.327		68	21.978	108+107	28.039	Hepta-CBs	188	29.23
	14	14.894		40	22.326	123	28.181		184	29.605
	11	15.76		57	22.426	11+106	28.315		179	30.387
	12+13	16.036		67	22.66	114	28.912		176	30.785
	15	16.289		58	22.828	122	29.062		186	31.272
Tri-CBs	19	15.173		63	22.951	105+127	29.782		178	31.632
	30	15.56		74+61	23.185	126	31.595		175	31.939
	18	16.196		70	23.361	155	24.372		182+187	32.096
	17	16.296		76	23.434	150	2554		183	32.375
	27+24	16.698		80+66	23.537	152	25.95		185	32.946
	16+32	17.089		55	24.008	145	26.31		174	33.368
	34+23	17.568		56+60	24.457	148	26.536		181	33.437
	29	17.737		79	25.211	136	26.694		177	33.667
	26	17.963		78	25.767	154	26.95		171	33.912
	25	18.089		81	23.1	151	27.567		173	34.234
	31	18.369		77	26.84	135+144	27.812		172+192	34.605
	28	18.438	Penta-CBs	104	21.046	147	285		180	34.927
	21+33+20	18.917		96	22.153	139+149	28.222		193	35.084
	22	19.292		103	22.376	143	28.395		191	35.31
	36	19.584		100	22.667	140	28.736		170+190	36.575
	39	20.02		94	23.1	134	28.793		189	37.966
	38	20.526		98+102	23.475	133	28.927	Octa-CBs	202	33.892
	35	21.04		93+95	23.594	131+142	29.058		201	34.325
	37	21.427		88+121	23.77	165	29.173		204	34.417
Tetra-CBs	54	17.74		91	23.943	146	29.268		197	34.724
	50	18.384		92	24.556	161	29.372		200	35.59
	53	183958		84	24.728	153	29.606		198	36.866
	51	19.207		89+101+90	24.87	132+168	29.74		199	37.027
	45	19.56		113	25.058	141	30.295		203+196	37.302
	46	19.962		99	25.154	137	30.667		195	38.601
	69	20.112		119	25.514	130	30.82		194	39.398
	52+73	20.223		112	25.617	164+163+138	31.104		205	39.594
	43+49	20.41		120+83	25.751	160+158	31.234	Nona-CBs	208	38.571
	47+75+48	20.302		97	26.035	129	31.552		207	38.892
	65	20.778		86	26.096	166	31.912		206	40.678
	62	20.847		125	26.173	159	32.088	DecaCBs	209	41.624

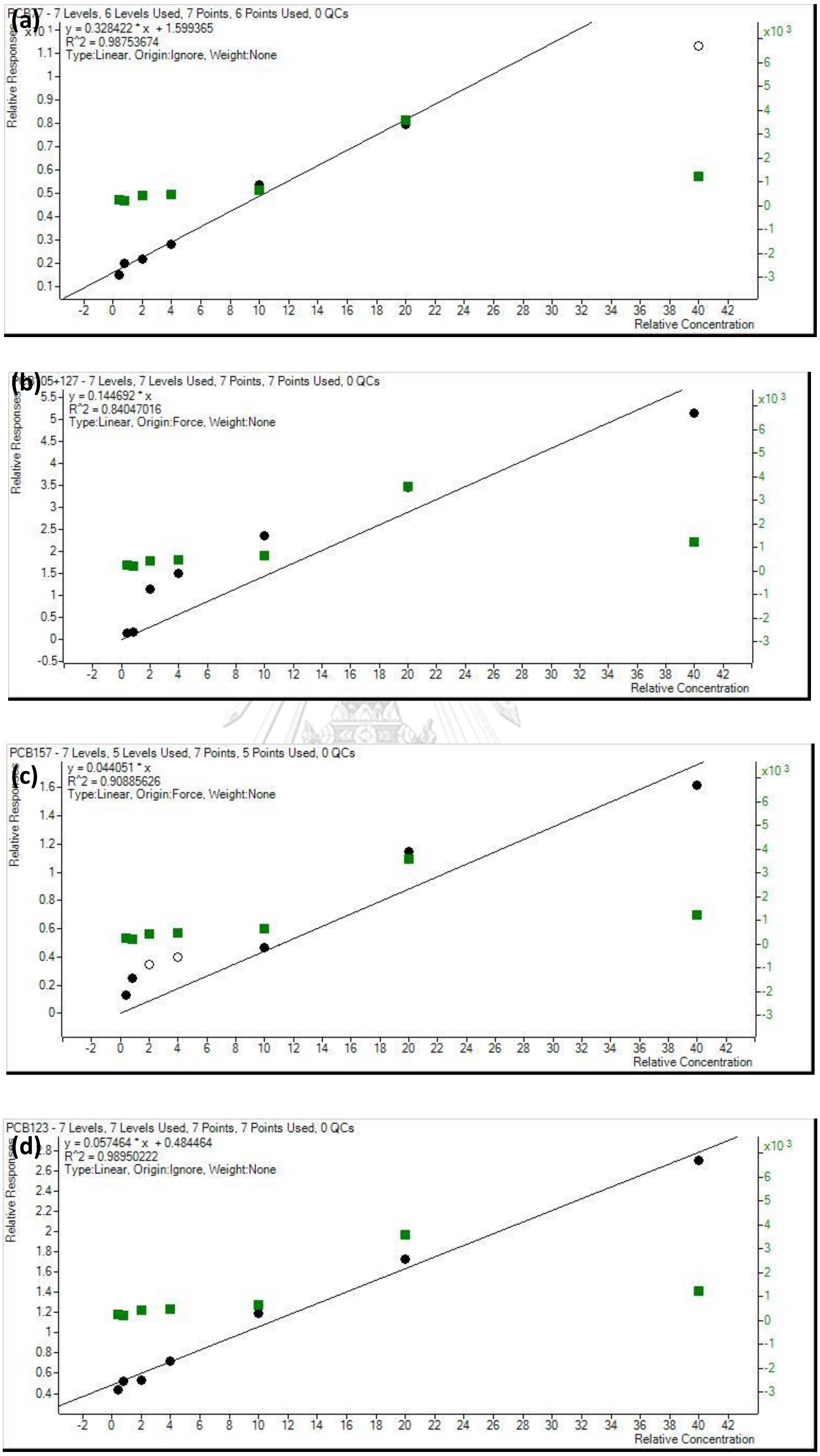


Figure A. 10: The sample of PCBs congener calibration curve

Health Risk Assessment

Table A.5: The parameter using for health risk assessment

Parameter	**Value**	**Unit**	**Reference**
Body Weight (BW)	70	kg	(USEPA, 2011)
Inhalation rate (IR)	16	m^3/day	
Exposure duration (ED)	70	year	
Exposure Frequency (EF)	180	days/year	(Pongpiachan et al., 2015)
Average time (AT)	70×365	day/year	For non-carcinogen: ED ×365 days and for carcinogen used 70 years × 365 days

Compounds	Bangkok														
	Period 1 Dec 2018-Feb 2019					Period 2 Feb-Apr 2019					Period 3 Apr-Jun 2019				
	B1	B2	B3	B4	B5	B12	B22	B32	B42	B52	B13	B23	B33	B43	B53
PAHs															
AcPy	8.35E-10	6.91E-11	1.84E-10	3.80E-10	1.65E-07	3.00E-10	5.40E-10	2.34E-10	2.32E-10	6.32E-10	4.30E-11	1.47E-10	1.93E-10	5.68E-11	6.28E-11
Acp	1.52E-08	1.17E-09	1.63E-09	3.91E-09	1.97E-10	9.49E-10	2.12E-09	7.67E-10	1.25E-09	3.96E-09	7.05E-10	4.37E-10	9.02E-10	6.54E-10	1.36E-10
Flu	5.52E-09	1.43E-09	2.80E-09	4.75E-09	2.25E-09	3.75E-09	4.08E-09	2.38E-09	2.38E-09	1.45E-08	1.33E-10	nd	1.06E-09	8.97E-10	5.15E-10
PA	6.78E-09	3.02E-09	6.97E-09	1.38E-08	2.68E-09	1.15E-08	6.11E-09	5.27E-09	4.99E-09	2.01E-08	5.54E-11	3.27E-09	4.05E-09	5.21E-09	2.04E-09
Ant	2.83E-09	1.81E-09	1.21E-09	2.59E-09	7.54E-08	5.66E-09	1.82E-09	2.12E-09	1.90E-09	1.17E-09	1.36E-09	7.44E-10	1.62E-09	1.42E-09	7.83E-10
FL	nd	1.59E-09	2.88E-09	7.17E-09	1.31E-10	5.52E-09	2.46E-09	2.30E-09	2.32E-09	8.39E-09	1.11E-09	1.29E-09	9.57E-10	2.79E-09	9.66E-10
Pyr	1.37E-09	1.35E-09	4.62E-09	6.61E-09	2.92E-09	8.45E-09	3.11E-09	3.01E-09	2.65E-09	9.20E-09	2.42E-09	1.51E-09	1.86E-09	3.96E-09	9.30E-10
BaA	nd	1.73E-08	0.00E+00	9.96E-08	2.91E-07	9.14E-08	nd	3.13E-08	nd	nd	nd	nd	nd	3.10E-08	nd
CHR	nd	1.83E-09	nd	1.07E-08	nd	9.75E-09	nd	3.32E-09	nd	nd	nd	nd	nd	3.29E-09	nd
BbF	nd	6.55E-09	nd	nd	nd	nd	nd	nd	nd	4.43E-08	nd	1.01E-09	nd	4.08E-09	nd
BkF	nd	1.20E-09	nd	3.21E-09	1.12E-09	nd	nd	nd	nd	4.43E-08	nd	1.01E-09	nd	4.08E-09	nd
BaP	7.46E-08	6.58E-08	8.76E-08	8.54E-08	1.12E-08	1.53E-07	3.60E-07	6.69E-07	4.19E-07	7.41E-07	3.01E-08	7.13E-08	7.54E-08	6.53E-08	1.12E-08
IND	2.50E-09	4.72E-09	2.30E-08	1.27E-08	8.75E-09	3.72E-08	2.41E-08	8.54E-09	1.11E-08	5.18E-08	5.56E-09	1.15E-08	8.49E-09	5.89E-09	5.68E-10
DBA	1.85E-07	5.74E-08	2.18E-07	2.89E-07	7.82E-09	3.51E-07	2.18E-08	5.79E-08	4.47E-08	8.34E-07	3.14E-07	1.38E-07	5.74E-08	3.34E-08	3.39E-09
BghiP	1.25E-09	1.85E-09	5.90E-09	1.29E-08	5.90E-10	1.22E-08	3.25E-09	3.18E-09	6.02E-09	1.51E-08	1.79E-09	4.15E-09	3.19E-09	6.67E-09	1.29E-09
Total Bapeq	2.96E-07	1.67E-07	3.54E-07	5.53E-07	5.70E-07	6.90E-07	4.29E-07	7.90E-07	4.96E-07	1.79E-06	3.57E-07	2.34E-07	1.55E-07	1.69E-07	2.18E-08
PCBs															
PCB77	7.14E-14	2.16E-13	4.35E-13	2.43E-13	5.53E-13	7.67E-13	1.39E-13	6.89E-13	6.45E-13	1.21E-12	1.06E-12	2.17E-13	7.82E-13	9.87E-13	9.87E-13
PCB81	4.70E-04	5.69E-04	2.59E-05	5.35E-04	4.87E-13	1.50E-13	1.50E-13	2.15E-13	2.15E-13	2.27E-13	1.34E-13	1.68E-14	1.57E-13	1.68E-14	7.80E-14
PCB126	5.31E-02	7.09E-02	1.79E-01	9.88E-03	6.20E-11	2.81E-11	5.98E-12	4.49E-11	4.54E-11	3.29E-11	1.16E-11	6.91E-11	5.30E-11	1.29E-11	1.92E-11
PCB105+127	5.01E-06	1.62E-06	5.64E-06	1.41E-06	2.45E-15	1.50E-14	1.08E-15	5.16E-15	8.95E-15	1.33E-14	1.81E-15	1.95E-14	1.50E-14	1.46E-14	2.79E-15
PCB114	2.14E-06	1.77E-06	2.20E-06	3.12E-06	1.77E-15	2.03E-15	1.45E-15	2.08E-15	9.77E-16	1.85E-14	5.00E-15	1.77E-15	8.83E-15	3.57E-13	1.54E-15
PCB157	1.92E-05	1.70E-05	5.75E-05	3.04E-05	2.01E-14	1.00E-14	1.26E-13	4.02E-14	2.79E-14	1.53E-14	4.28E-14	1.02E-14	4.60E-14	4.39E-14	5.61E-15
Total PCB-TEQ	5.36E-02	7.15E-02	1.80E-01	1.04E-02	6.31E-11	2.91E-11	6.40E-12	4.59E-11	4.63E-11	3.44E-11	1.29E-11	6.93E-11	5.40E-11	1.43E-11	2.02E-11

*nd refer to not detected, the concentration has less amount to detected.

Table A.7: Total Bap$_{eq}$ and Total PCBs-TEQ in Chiang Mai

Compounds	Period 1 Dec 2018-Feb 2019			Period 2 Feb-Apr 2019			Period 3 Apr-Jun 2019		
	C1	C2	C3	C1	C22	C32	C1	C23	C33
PAHs									
AcPy	3.37E-10	1.92E-10	8.97E-11	1.83E-08	1.73E-09	9.41E-11	1.18E-10	8.23E-11	7.85E-11
Acp	9.31E-10	1.73E-09	1.61E-09	4.38E-08	9.45E-09	1.83E-10	4.64E-10	5.50E-10	1.11E-09
Flu	2.19E-09	3.25E-09	1.65E-09	1.12E-07	2.00E-08	7.18E-10	1.61E-09	1.50E-09	1.66E-09
PA	6.53E-09	1.71E-08	3.10E-09	3.58E-07	1.15E-07	2.15E-09	9.61E-09	1.54E-08	8.42E-09
Ant	2.82E-09	5.70E-09	9.34E-10	1.36E-07	4.78E-08	7.61E-10	1.94E-09	2.66E-09	2.61E-09
FL	1.50E-09	6.95E-09	1.38E-10	1.13E-07	2.59E-08	8.07E-12	2.37E-09	4.30E-09	2.04E-09
Pyr	1.97E-09	6.84E-09	1.08E-09	1.37E-07	4.11E-08	8.24E-10	4.83E-09	4.24E-09	2.26E-09
BaA	1.92E-08	8.64E-08	3.39E-08	1.45E-06	4.94E-07	2.15E-08	5.66E-08	1.90E-08	2.15E-08
CHR	2.04E-09	9.16E-09	4.17E-09	1.54E-07	5.31E-08	2.28E-09	5.12E-09	3.84E-09	2.16E-09
BbF	8.61E-09	2.73E-08	1.29E-08	7.86E-08	7.11E-08	5.85E-08	1.10E-09	3.37E-08	1.13E-09
BkF	1.03E-08	2.73E-08	9.45E-09	7.86E-08	6.90E-08	5.81E-08	1.10E-09	3.16E-08	4.32E-10
BaP	1.63E-08	2.69E-07	1.05E-07	8.75E-08	7.79E-08	1.65E-08	8.76E-08	8.64E-08	1.11E-07
IND	5.46E-09	1.02E-08	4.46E-09	1.75E-07	2.37E-07	2.94E-09	2.48E-08	8.49E-09	2.93E-08
DBA	5.05E-08	2.30E-07	1.11E-07	2.40E-06	2.27E-06	2.96E-08	4.16E-07	1.20E-07	1.21E-08
BghiP	2.37E-09	4.97E-09	2.10E-09	1.53E-07	7.17E-08	1.42E-09	1.59E-09	1.69E-09	1.52E-09
Total Bap$_{eq}$	1.31E-07	7.06E-07	2.91E-07	5.50E-06	3.61E-06	1.96E-07	6.15E-07	3.34E-07	1.97E-07
PCBs									
PCB77	1.98E-13	1.27E-13	7.20E-14	1.03E-13	7.73E-14	1.16E-13	1.28E-13	1.39E-12	1.31E-13
PCB81	1.33E-12	1.28E-13	1.04E-13	8.31E-14	1.20E-13	8.79E-14	1.79E-13	7.25E-14	6.34E-14
PCB126	6.65E-12	4.65E-12	7.08E-12	9.92E-12	9.13E-12	9.08E-12	8.35E-12	8.27E-12	1.18E-11
PCB105+127	1.63E-14	3.19E-16	1.72E-15	2.94E-15	3.05E-15	1.23E-15	9.03E-16	1.09E-15	2.91E-15
PCB114	2.00E-15	5.91E-15	2.91E-15	3.19E-15	7.05E-16	8.38E-16	1.74E-16	3.28E-15	2.15E-15
PCB157	1.97E-14	1.75E-14	1.72E-14	2.74E-14	4.73E-15	4.32E-15	1.30E-14	2.37E-14	4.93E-15
Total PCB-TEQ	8.22E-12	4.92E-12	7.27E-12	1.01E-11	9.34E-12	9.29E-12	8.67E-12	9.76E-12	1.21E-11

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