Analysis and monitoring of odour and semi-volatile organic compounds in different environmental matrices via gas chromatography-mass spectrometry

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**ANALYSIS AND MONITORING OF ODOUR AND SEMI-VOLATILE
ORGANIC COMPOUNDS IN DIFFERENT ENVIRONMENTAL MATRICES
VIA GAS CHROMATOGRAPHY-MASS SPECTROMETRY**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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**A thesis submitted to Nanyang Technological University
in partial fulfillment of the requirement for the degree of
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2017

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Table of Contents

ABSTRACT	1
CHAPTER 1. PARTICULATE BOUND ATMOSPHERIC POLYCYCLIC AROMATIC HYDROCARBONS AND POLYCHLORINATED BIPHENYLS	1
1.1 THEORY AND BACKGROUND	1
1.2 PARTICULATE MATTER.....	3
<i>1.2.1 Health effects of particulate matter.....</i>	<i>4</i>
<i>1.2.2 Sources of particulate matter</i>	<i>6</i>
1.2.3 PARTICULATE MATTER REGULATION	7
1.3 POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)	9
1.3.1 Physical and chemical properties	10
1.3.2 Environmental fate, markers and sources of PAHs.....	11
1.3.3 Health effects and regulation control.....	14
1.4 POLYCHLORINATED BIPHENYLS (PCBs).....	19
1.4.1 Physical and chemical properties	19
1.4.2 Human exposure health effect and regulations	22
1.5 RECENT STUDIES ON ATMOSPHERIC PROFILES OF PAHs AND PCBs IN SOUTHEAST ASIA..	25
1.6 SCOPE OF THE PROJECT	27
CHAPTER 2: DEVELOPMENT OF A QUANTITATIVE ASSESSMENT METHOD FOR ATMOSPHERIC SEMI-VOLATILE ORGANIC POLLUTANTS USING SOLID PHASE EXTRACTION COUPLED TO GAS CHROMATOGRAPHY MASS SPECTROMETRY	29
2.1 INTRODUCTION.....	29

2.2 EXPERIMENTAL	31
2.2.1 Chemicals and standard solutions.....	31
2.2.2 Solid phase extraction	32
2.2.3 Instrumentation.....	33
2.2.4 Tuning of mass spectrometer.....	33
2.2.5 Quality control and assurance	34
2.3 RESULTS AND DISCUSSION	35
2.3.1 GC-MS parameters optimization (method development).....	35
2.3.2 Filter handling.....	43
2.3.3 Extraction of the PM ₁₀ bound PAHs.....	44
2.3.4 Extraction of the PM _{2.5} bound PCBs.....	47
2.4 CONCLUSION	49
 CHAPTER 3. CONCENTRATIONS, SOURCE DETERMINATION, TREND PROFILES AND HEALTH RISK ASSESSMENT OF ATMOSPHERIC SEMI VOLATILE ORGANIC POLLUTANTS IN SINGAPORE’S TROPICAL CLIMATE.....	 51
3.2 EXPERIMENTAL	51
3.2.1 Sampling Site	51
3.2.2 Sample Collection.....	53
3.3 RESULTS AND DISCUSSION	55
3.3.1 Air mass backward trajectory classification analysis.....	55
3.3.2 Concentration trend and profiles of the PM ₁₀ bound PAHs	59
3.3.3 PAHs molecular and ring size distribution	63
3.3.4 Seasonal variation and source apportionment.....	65
3.3.5 Source diagnostic ratios DRs	67
3.3.6 Principal component analysis (PCA)	70

3.3.7 <i>PM₁₀ bound PAHs health risk assessment analysis</i>	72
3.4. CONCENTRATION TRENDS AND TEMPORAL VARIATION PROFILES OF THE PM _{2.5} BOUND PCBs	77
3.4.1 <i>Molecular composition and profiles of PM_{2.5} bound PCBs</i>	80
3.4.2 <i>Source factor assessment of airborne PCBs in Singapore coastal environment using Principal component statistical analysis (PCA)</i>	83
3.5 CONCLUSION	87
CHAPTER 4. SPE-GC-MS ANALYSIS OF THE SVOCs IN DIFFERENT WATER SAMPLES COLLECTED IN LOWER HIMALAYAS IN THE TRASHIGANG DISTRICT IN BHUTAN	90
4.1 INTRODUCTION.....	90
4.2 ORGANOCHLORINE PESTICIDES (OCPs): PHYSICOCHEMICAL PROPERTIES, ENVIRONMENTAL OCCURRENCE AND HEALTH IMPACT	93
4.3 PAHs: PHYSICOCHEMICAL PROPERTIES, ENVIRONMENTAL OCCURRENCE AND HEALTH IMPACT	96
4.4 NEW TRENDS IN SVOC ANALYSIS USING SPE-GC-MS	96
4.5 SVOC PROFILES AND OCCURRENCE IN HIMALAYAS AND POLAR REGIONS.....	99
4.4 PRINCIPLES OF THE SOLID PHASE EXTRACTION (SPE) FOR SVOCs ANALYSIS IN AQUEOUS SAMPLES	100
4.5 NEW TRENDS IN SVOC ANALYSIS USING SPE-GC-MS	102
4.6 SVOC PROFILES AND OCCURRENCE IN HIMALAYAS AND POLAR REGIONS.....	105
4.6 MATERIALS AND METHODOLOGY	101
4.6.1 PRINCIPLES OF THE SOLID PHASE EXTRACTION (SPE) FOR SVOCs ANALYSIS IN AQUEOUS SAMPLES	101
4.6.2 <i>Chemicals and Standard Solutions</i>	103

4.6.3 Instrumentation and tuning procedure	104
4.6.4 GC-MS method development for OCPs analysis.....	104
4.6.5 Quality control and quality assurance (QA/QC).....	106
4.7 OCPs EXTRACTION FROM THE SPRING WATER SAMPLES COLLECTED FROM THE LOWER HIMALAYAS IN THE TRASHIGANG DISTRICT (BHUTAN)	109
4.7.1 SOLID PHASE EXTRACTION OF THE PAHs FROM THE S LAKE TEYMINUS AND HIMALAYAS GLACIERS SAMPLES IN THE EASTERN BHUTAN REGION	112
4.8 CONCLUSION	114
CHAPTER 5. SAMPLING METHODOLOGY AND CONCENTRATION PROFILES OF SVOCS ANALYSED IN WATER SAMPLES COLLECTED IN LOWER HIMALAYAS IN BHUTAN.....	115
5.1 SAMPLING LOCATION	115
5.2 SAMPLE COLLECTION	118
5.3 CONCENTRATION TRENDS AND PROFILES OF THE OCPs AND PAHs IN VARIOUS AQUEOUS SAMPLES COLLECTED IN LOWER HIMALAYAS IN BHUTAN	119
5.3.1 Organochlorine pesticides (OCPs) concentration profiles in various water samples collected in lower Himalayas in Bhutan	119
5.3.2 Polycyclic aromatic hydrocarbons (PAHs) concentration profiles in Lake Teyminus and Himalayas glaciers samples in the Eastern Bhutan region.....	123
5.4 CONCLUSION	127
CHAPTER 6. THERMAL DESORPTION GAS CHROMATOGRAPHY MASS SPECTROMETRY ANALYSIS OF THE VOLATILE ORGANIC SULFUR COMPOUNDS IN SINGAPORE’S ATMOSPHERE.....	128
6.1 INTRODUCTION.....	128
6.2 SOLID SORBENT SAMPLING METHODOLOGY	130

6.2.1 Sorbent materials.....	133
6.2.2 Physicochemical properties of the sampling sorbent materials.....	134
6.3 SAMPLING METHODOLOGY OF VOLATILE COMPOUNDS	148
6.4 RECENT STUDIES ON ATMOSPHERIC PROFILES OF THE VOSCs	143
6.5 ATMOSPHERIC VOSCs PROFILES IN DIFFERENT COUNTRIES	149
CHAPTER 7. METHOD DEVELOPMENT FOR THE ANALYSIS OF THE VOLATILE SULFUR ORGANIC COMPOUNDS USING THERMAL DESORPTION GAS CHROMATOGRAPHY MASS SPECTROMETRY	151
7.1 INTRODUCTION.....	151
7.1.1 Chemicals.....	152
7.1.2 Sorbent sampling materials.....	153
7.1.3 Instrumentation.....	154
7.1.4 Qualification/Quantification parameters	156
7.1.5 Method validation.....	158
7.1.6 Performance evaluation of sorbent tubes in samples.....	162
7.2 CONCLUSION	168
CHAPTER 8. TREND PROFILES AND CONCENTRATION PATTERNS OF THE VOLATILE SULFUR COMPOUNDS IN THE LARGEST INDUSTRIAL COMPLEX IN SOUTHEAST ASIA FROM A SEMI URBAN SAMPLING SITE.....	170
8.1 INTRODUCTION.....	170
8.2 SAMPLING LOCATION	171
8.3 SAMPLE COLLECTION	174
8.4 RESULTS AND DISCUSSION	174
8.4.1 General patterns of VOSC distribution in the study area	174
8.4.2 Derivation of odor intensity (OI).....	182

8.5 CONCLUSION	183
CHAPTER 9. SUMMARY AND CONCLUSION	185
REFERENCES:.....	189
APPENDIX 1.	221
APPENDIX 2.	251

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ABSTRACT

Gas Chromatography Mass Spectrometry (GC-MS) combined with Thermal Desorption (TD) and solid phase extraction (SPE) methodologies were developed for the quantification and qualification of:

- Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) bound on airborne particulate matter (PM) (different sizes of 10 and 2.5 μm).
- The PAHs and organochlorine pesticides (OCPs) in various water samples collected in lower Himalayas in Bhutan.
- The volatile organic sulfur compounds (VOSCs) in air.

At a Nanyang Technological University (NTU) rooftop sampling site, airborne particulates were sampled in two different sizes of 10 and 2.5 μm between May 2015 to May 2016 and April 2016 to September 2016 for analysis of PM_{10} bound PAHs and $\text{PM}_{2.5}$ bound PCBs, respectively. The same sampling site was used for collecting air samples for the analysis of odour VOSCs.

One of the findings of this project is that when comparing PAHs abundances in Singapore to the other countries in the SEA and Asia in global Singapore has some of the lowest values of airborne PAHs, likely due to strict emission regulations for both traffic and industry sectors. In spite of this observation, the main problem for Singapore is trans-boundary pollution when the PM_{10} concentrations increased from a typical average reading of approximately 25 $\mu\text{g}/\text{m}^3$ up to a concentration reaching over 300 $\mu\text{g}/\text{m}^3$ during the high haze events, while PAH concentrations approximately doubled.

In terms of the PCBs monitored when comparing data to the literature review reports on

airborne PCBs in the region results showed there were not significant changes in the last 15 years. PCA analysis of factor loadings for every component extracted and compared to the work previously conducted in neighbouring countries suggested possible contribution of the emissions from electronic waste (incineration plant in Tuas) [62] and ship-dismantling activities [146].

Furthermore, SPE-GC-MS analysis of OCPs and PAHs were performed on water samples from 9 spring water sources, 7 storage facilities, 11 end user taps and water samples collected from the Lake “Teyminus” together with a glacier inlet sample collected in close proximity.

This sampling campaign was conducted in and around Yonphula, Kanglung and Rongthung areas located in Lower Himalayas in Trashigang District of Eastern Bhutan.

One of the major outcomes of this project is that out of 23 OCPs monitored, 8 were detected in concentrations within allowed admissible concentration for pesticides of $0.1 \mu\text{g L}^{-1}$. Comparing to the OCPs quantified, PAHs detected in lake samples including glacier and an inlet stream showed higher concentrations. All 16 targeted PAHs were detected and quantified in every sample. The most abundant PAHs were NAPH and ACP representing lighter PAHs and BbF, BkF, BaP, IcP, DhA and BghiP for the heavier PAHs. Dominance of this specific congeners suggested domestic heating and long distance transport from countries such as India, Nepal and China as a sources of the PAHs in this sampling site.

At the end detailed study on volatile organic sulfur compounds including: dimethyl sulfide, carbon disulfide, propyl mercaptan, dimethyl trisulfide and 1-buthanethiol was performed to help to fill some data gap in the understanding of air quality in Singapore semi-urban atmosphere in terms of odour compounds since there hasn't been any work done related

tot his topic in Singapore. The occurrence of the VOSCs in semi urban ambient air was examined in terms of diurnal, inter-day and intra-day variations. Throughout all the sampling campaign, BuSH and PrSH were not detected in any samples. However, other 4 compounds (EtSH, DMS, DMTS and CS₂) were detected with 100% detection frequency. All results were in a ppbv range and above instrumental and method detection limits. Overall, 4 months of statistical data calculated for all target VOSCs revealed that DMS and CS₂ were the most dominant organosulfur compounds in the atmosphere.

Chapter 1. Particulate bound atmospheric polycyclic aromatic hydrocarbons and polychlorinated biphenyls

1.1 Theory and background

Singapore is a heavily industrialized country with extensive operations in oil refining, petro-chemical and chemical industries and major power plants that are all located in the west side of the country in the Tuas region and Jurong Island. Therefore, the western region of Singapore is an ideal location to place a monitoring station to collect air samples to determine pollution levels brought about by industrial activities. Furthermore, parts of SEA suffer trans-boundary air pollution due to peat and forest fires in Indonesia resulting in the air quality index (AQI) regularly reaching unhealthy ($AQI > 150$) and sometimes hazardous ($AQI > 300$) levels of $PM_{2.5}$. These regional haze episodes are caused by land clearing activities in Kalimantan, South Sumatra and Borneo and have occurred almost annually, especially during the dry season for the past 15 years. [73-78] In 2015, the PM levels caused by the haze were particular high and prolonged due to the El Niño effect. The atmosphere in Singapore is usually affected during the southwest monsoon season when strong winds blowing from the southwest over the equator towards the northern hemisphere transport dense smoke from peat-land fires in Indonesia.

Monitoring and characterization of PM is of significance because of its unique and complex chemical structure. It has always been challenging to characterize and quantify all the constituents related to the PM, and it is categorized as one of the five crucial pollutants (ozone, particulate pollution, carbon monoxide, sulfur dioxide and nitrogen dioxide) and

possibly the most important in terms of adverse effects on human health such as respiratory and cardiovascular diseases. [28, 79-84] Recently, a number of studies have reported on the PM composition in SEA. [57, 85-90]

Due to health concerns, it is of vital importance to perform thorough and detailed characterization and quantification studies on PM, as well as to study its effects on the environment. This can be partially achieved by considering the environmental fate of the volatile (VOCs) and semi-volatile (SVOCs) organic compounds such as *n*-alkanes, PAHs, organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) that are ubiquitously present in all environmental matrices, including PM. Various SVOCs are recognized to have large carcinogenic and mutagenic potential and many other deleterious impacts on human health such as endocrine disruption, cardiovascular and pulmonary diseases (ASTDR, 2009; WHO, 2003) [84, 91-93]

This study focuses on quantification and characterization of the PAHs and PCBs related to the PM by utilizing gas chromatography mass spectrometry (GC-MS) because it has been shown that heavier PAHs (rather than the gas phase molecules) have a greater carcinogenic and mutagenic potential than lighter ones. [27, 30, 94, 95] Gas chromatography mass spectrometry (GC-MS) was used to characterize and quantify PAHs (PM₁₀) and PCBs (PM_{2.5}) respectively. Subsequently, statistical analysis of all data were performed to identify the main source contributors and to investigate the effect of the regional smoke haze episode on the abundance and distribution of PAHs and PCBs and PM within Singapore's atmosphere based on long term sampling. Since there are a very few studies concerning PAHs and PCBs in the South East Asia region, [57, 66, 81, 96, 97] this new work provides improved analytical sampling methodology and detailed one year

monitoring data, including source apportionment analysis together with a health risk assessment.

1.2 Particulate matter

Airborne particulate matter (PM) is thought to be one of the most harmful atmospheric pollutants due to its complexity in chemical composition.[1] PM represents suspended solid materials and liquid aerosols in the atmosphere that occur in different sizes and chemical compositions. Structure of the airborne particulate matter is mainly a complex mixture of organic and inorganic substances, and have strong deleterious effects on the environment, climate, visibility, health and life quality. Airborne particulates can be primary emitted to the atmosphere directly from the various natural or anthropogenic sources or secondary formed in the atmosphere from gaseous precursors.[2] PM ranges in size from 0.01 up to 100 μm in diameter. The size distribution of particulate matter varies depending on its sources. Natural sources such as sea salt and volcanoes for instance emits coarse particles usually larger than 2.5 μm , while all varieties of combustion processes that are the main anthropogenic sources of PM, emit fine particles with a diameter in the range of 0.1 up to 2.5 μm . [3] Figure 1-1 illustrated by the United States Environment Protection Agency (USEPA) clearly describes size distribution of the airborne particulate matter by comparing human hair (70 microns) with fine and coarse airborne particles.

Figure 1-1. Size comparison of the human hair (70 microns) to the fine (PM_{2.5}) and coarse airborne particles (PM₁₀)

* Graphic provided from the US Environmental Protection Agency *

1.2.1 Health effects of particulate matter

Airborne particulate matter has a wide range of effects on human health due to its complex composition that comprises organic compounds such as aromatic hydrocarbons, biphenyls, pesticides, alkanes as well as inorganic elements like heavy metals.[4] A wide range of serious cardiovascular and respiratory diseases, more specifically chronic bronchitis and asthma, myocardial infarction, anemia, decreased lung function can be associated with high PM levels. More seriously, PM can have carcinogenic and mutagenic potentials depending

on its particle morphology and chemical mineralogy composition.

Many recent epidemiologic studies propose that tens of thousands of excess deaths per year occur due to prolonged exposure to PM and rapidly increasing cases of illness among populations with chronic respiratory and cardiovascular symptoms. [5]

Figure 1-2 illustrates how PM can enter and affect the human body. It starts with our respiratory system (nose and throat) where airborne particulates (coarse and fine) enter our body and depending on the size, it is distributed in different ways. PM₁₀ particles usually do not cause problems because they are eliminated from our body via coughing, sneezing and swallowing while fine particles as PM_{2.5} can infiltrate deeper into the lungs thereby penetrating into the alveoli and entering the vascular system and spreading harmful chemicals into organs such as the liver, kidneys, spleen or the brain. The smaller the particles are, the larger is their relative total surface area leading to more damage caused. The world health organisation (WHO) conducted a study recently that showed that excessive exposure to PM_{2.5} has the potential to cause premature births, respiratory diseases in children as well as arteriosclerosis, neurological development and cognitive skills as well as diabetes. [6-17]

Figure 1-2. How particulate matter enters the body 1. Through the nose and mouth while breathing 2/3. Body eliminates larger particles when inhaled 4. Fine particles (PM_{2.5}) penetrate deeper to the lungs where infiltrates into the alveoli and enters the bloodstream.

1.2.2 Sources of particulate matter

Due to its complex physicochemical properties such as diversity in size and shape, inorganic and organic composition and severe health effects that it has, studies on source identification/contribution of airborne particulate matter have been extensively conducted. Components of particulate matter (PM) include finely divided solids or liquids such as dust, fly ash, soot, smoke, aerosols, fumes, mists and condensing vapors. The main classification of the PM sources are: primary (natural and anthropogenic) and secondary (precursors pollutants that can help form particulate matter). Primary sources are mostly combustion of fossil fuels and organic matter, industrial processes, agricultural operations, construction and demolition activities, volcanoes, sea salt, windblown dust, and wildfires.

The most common secondary pollutants include ammonia, sulfur oxides (SO_x), nitrogen oxides (NO_x) and volatile organic compounds (VOCs). The aforementioned pollutants are considered as precursors for PM formation.[11, 18]

1.2.3 Particulate matter regulation

Many studies have shown strong correlations between rising atmospheric pollution causing an increase in hospital admissions of patients with respiratory symptoms and even premature deaths caused by heart and respiratory problems. To this day, no safe limits of atmospheric particulate matter were established that cause no health effects to people. Mature people, people with cardiovascular and heart disease, and people with respiratory problems, such as acute bronchitis and asthma, are at greatest risk from short-term exposure to PM. [19-22]

In Europe, public concern about PM toxicity on human health began from the great smoke episode in Great Britain, London, in 1952 caused by excessive coal burning. In the period of 1970s to 1980s, vast industrialization followed by lack of emission regulations, caused severe air pollution problems affecting tens of millions of people. This pollution epidemic led to the first main regulatory emission legislation being implemented. The first EU Directive 80/779/EEC on air quality aimed at suspended particulates set limit values for PM in terms of total suspended particles (TSP) that included fine (PM_{2.5}) and coarse (PM₁₀) particles. Airborne PM₁₀ regulatory thresholds are 40 µg m⁻³ (annual average) and a daily limit of 60 µg m⁻³ that should not exceed this value more than 35 days of the year. The aforementioned limits were legally implemented on 1st of January 2005. Additionally, in 2010 new more strict thresholds took effect with a less allowed TSP annual average

concentration of $20 \mu\text{g m}^{-3}$ and $50 \mu\text{g m}^{-3}$ for the daily average. [23] Table 5-1 summarizes particulate matter regulatory history from the 1971s up to the last legislation in 2012.

Table 1-1. Regulatory legislatives for the particulate matter with thresholds levels for a different source contributors and target groups

Final Rule	Primary/ Secondary	Indicator	Averaging Time	Level	Form
1971	Primary	TSP	24-hour	$260 \mu\text{g/m}^3$	Not to be exceeded more than once per year
			Annual	$75 \mu\text{g/m}^3$	Annual geometric mean
	Secondary	TSP	24-hour	$150 \mu\text{g/m}^3$	Not to be exceeded more than once per year
			Annual	$60 \mu\text{g/m}^3$	Annual geometric mean
1987	Primary and Secondary	PM ₁₀	24-hour	$150 \mu\text{g/m}^3$	Not to be exceeded more than once per year on average over a 3-year period
			Annual	$50 \mu\text{g/m}^3$	Annual arithmetic mean, averaged over 3 years
1997	Primary and Secondary	PM _{2.5}	24-hour	$65 \mu\text{g/m}^3$	98th percentile, averaged over 3 years
			Annual	$15.0 \mu\text{g/m}^3$	Annual arithmetic mean, averaged over 3 years
		PM ₁₀	24-hour	$150 \mu\text{g/m}^3$	Initially promulgated 99th percentile, averaged over 3 years; when 1997 standards for PM10 were vacated, the form of 1987 standards remained in place (not to be exceeded more than once per year on average over a 3-year period)

Table 1-1. (Continued) Regulatory legislatives for the particulate matter with thresholds levels for a different source contributors and target groups

Final Rule	Primary/ Secondary	Indicator	Averaging Time	Level	Form
2006	Primary and Secondary	PM _{2.5}	24-hour	35 µg/m ³	98th percentile, averaged over 3 years
			Annual	15.0 µg/m ³	Annual arithmetic mean, averaged over 3 years
		PM ₁₀	24-hour	150 µg/m ³	Not to be exceeded more than once per year on average over a 3-year period
2012	Primary	PM _{2.5}	Annual	12.0 µg/m ³	Annual arithmetic mean, averaged over 3 years
	Secondary		Annual	15.0 µg/m ³	Annual arithmetic mean, averaged over 3 years
	Primary and Secondary		24-hour	35 µg/m ³	98th percentile, averaged over 3 years
	Primary and Secondary	PM ₁₀	24-hour	150 µg/m ³	Not to be exceeded more than once per year on average over a 3-year period

1.3 Polycyclic aromatic hydrocarbons (PAHs)

PAHs are organic substances comprised of two or more fused aromatic rings and are found in the gas phase or adsorbed onto airborne PM. Generally, PAHs with three or four rings are found in both gas phase and PM due to their intermediate vapor pressures but those that contain more than four rings are mainly found in PM in the atmosphere. [24, 25] There are hundreds of individual PAHs present in the environment but only the 16 that are classified as priority pollutants by the US Environmental Protection Agency [26] are the focus of this

study. The 16 PAHs compounds along with their vapor pressures are summarized in Table 2.1.

1.3.1 Physical and chemical properties

PAHs are a large and ubiquitous group of organic solid compounds that are mostly either colorless or white to pale yellow shades. There are around 500 chemically related compounds associated with PAHs that, depending on their physicochemical properties, are usually classified as environmental persistent compounds with varying toxicity.[27] PAHs consist of only H and C atoms structured in one or more fused aromatic rings (benzene) in linear clusters or angular arrangements. PAHs can be formed from a minimum of 2 fused benzene rings with a pair of H and C atoms shared amongst two rings in the molecule. These compounds have high boiling and melting points, hence exist in solid form, and they poses low vapor pressure and low water solubility that decreases with increasing molecular weight (number of rings) of the PAHs. The more benzene rings are fused together, the more stable PAH is, which results in higher resistance to oxido-reduction processes in environment. Most of the PAHs are also light sensitive, highly resistant to corrosion and heat. Every benzene ring that PAHs are comprised of adsorbs UV light at a specific wavelength making them quite easy to detect using absorbance detectors since every isomer absorbs radiation at different wavelengths.[28] A summary of the major physicochemical properties of the PAHs monitored in this study is presented in table 1-2.

1.3.2 Environmental fate, markers and sources of PAHs

PAHs are typically generated as by-products from the incomplete combustion and pyrolysis of fossil fuels and wood as well as the release of petroleum products. PAHs predominantly result during the burning of fossil fuels and are also found in coal tar, crude oil, creosote and roofing tar, as well as being used in manufacturing dyes, plastics and pesticides.[29] Their specific sources can be divided into the following categories: [29-32]

- Natural (non-anthropogenic fires caused by lightning strikes, volcanic emissions, diagenesis of sedimentary organic material and biosynthesis by microbes and plants. Accidental e.g. spillage of petroleum products).
- Domestic (burning of wood, coal and other fuels for space heating and cooking).
- Mobile (exhaust emissions from vehicles including automobiles, trains, ships, aircraft, and machinery).
- Industrial and power plants e.g. aluminium production, coke production (e.g. in iron and steel works), creosote and wood preservation, cement production, incineration of waste, fossil fuel and biomass burning for commercial heat and electricity production.
- Agricultural sources, biomass burning (crops, forests, residue disposals, land clearing activities...)

PAHs are abundant and widespread organic environmental contaminants that are usually found in atmosphere in mixtures rather than sole compounds. Therefore, it has always been challenging to trace the specific source of the PAHs in the atmosphere. However, by monitoring concentration profile analysis and diagnostic ratios statistics of specific PAH isomers, some are proven to be markers for certain specific sources of pollution. PYR, PHE and FLT are reported to be markers for incineration processes, [33, 34], while abundances

of B(k)F and CYR suggests dominant influence of coal combustion. [29, 35] Coal combustion together with traffic are considered as the major sources of PAHs globally, [25] while the dominance of the heavier PAHs in environmental samples as DhA, B(ghi)A, COR and IcP is a sign that traffic is the major source contributor.[36] PAHs environmental fates, including deposition (wet/dry), transport, chemical transformation to the even more potent Oxy-PAHs or Nitro-PAHs is strongly correlated to the gas/phase partitioning. [27, 37]

As PAHs are semi-volatile compounds they tend to partition between the gas phase or to become adsorbed on particulate matter in the atmosphere. This process is strongly dependent on temperature, humidity, precipitation and on molecular weight of the compounds itself. The heavier the compounds are, they more they will tend to partition in solid phase as adsorbed on PM.[38] Nevertheless, heavier PAHs adsorbed on particles (>4 benzene rings) are classified as low mobile pollutants that tend to deposit in close vicinity to the source, while lighter PAHs (<4 benzene rings) are more mobile pollutants that can undergo long range transport depending on the meteorological conditions and are commonly trapped and accumulated in polar regions and high mountain peaks such as the Himalayas. [39, 40]

In the following chapters in this thesis, analytical methods were developed for performing quantification and qualification analysis on PAHs that occur in different environmental matrices (water, glaciers, particulate matter) in both the tropical coastal environment in Singapore and polar regions of lower Himalayas in the Trashigang District of Bhutan.

Table 1.2 USEPA priority list of 16 PAHs with their formulas, structures and boiling points

No.	PAH	Abbreviation	Formula	Structure	Molecular Weight	Boiling Point (°C)
1	Naphthalene	NAP	C ₁₀ H ₈		128.171	218 (Alfa Aesar)
2	Acenaphthylene	ACY	C ₁₂ H ₈		152.192	280 (Oxford University Safety Data)
3	Acenaphthene	ACP	C ₁₂ H ₁₀		154.208	278 (Alfa Aesar)
4	Fluorene	FLR	C ₁₃ H ₁₀		166.219	295 (Alfa Aesar)
5	Phenanthrene	PHE	C ₁₄ H ₁₀		178.229	340 (Alfa Aesar)
6	Anthracene	ANT	C ₁₄ H ₁₀		178.229	340-342 (Alfa Aesar)
7	Fluoranthene	FLT	C ₁₆ H ₁₀		202.251	375 (Oxford University Safety Data)
8	Pyrene	PYR	C ₁₆ H ₁₀		202.251	393 (Alfa Aesar)
9	Benz(a)anthracene	BaA	C ₁₈ H ₁₂		228.288	438 (Biosynth)
10	Chrysene	CYR	C ₁₈ H ₁₂		228.288	448 (Biosynth)
11	Benzo(b)fluoranthene	BbF	C ₂₀ H ₁₂		252.309	467.5±12 (ACD/Labs)
12	Benzo(k)fluoranthene	BkF	C ₂₀ H ₁₂		252.309	480 (Oxford University Safety Data)

Table 1.2 (Continued) USEPA priority list of 16 PAHs with their formulas, structures and boiling points

No.	PAH	Abbreviation	Formula	Structure	Molecular Weight	Boiling Point (°C)
13	Benzo(a)pyrene	BaP	C ₂₀ H ₁₂		252.309	495 (Alfa Aesar)
14	Indeno(1,2,3-cd)pyrene	IcP	C ₂₂ H ₁₂		276.331	497.1±12.0 (ACD/Labs)
15	Benzo(g,h,i)perylene	BP	C ₂₂ H ₁₂		276.331	500 (Oxford University Safety Data)
16	Dibenz(a,h)anthracene	DhA	C ₂₂ H ₁₄		278.347	524 (Oxford University Safety Data)

1.3.3 Health effects and regulation control

Based on biomedical research results, the USEPA classified 16 PAHs (table 1-2) as carcinogenic, mutagenic and endocrine disruptive compounds that need to be monitored in all samples related to human health.[41] However, not all PAHs have same health effects on humans so they are further classified by the International Agency for Research on Cancer as carcinogens with known, possible or probable tendencies.[42] Due to their persistency in the environment and many different remote pollution sources, PAHs can be found in all environmental matrices, as well as in food products. Hence, human exposure to PAHs comes from many routes such as ingestion through food and beverage consumption, inhalation through breathing polluted air or dermal exposure through occupational or non-occupational exposure. Furthermore benzo(a)pyrene is classified as the most carcinogenic PAH is found as abundance in cigarette smoke.[43, 44] The intensity and types of possible symptoms due to exposure to PAHs depend on concentration of the

PAHs and length and routes of exposure. Nevertheless possible symptoms of short-term (acute) exposure to PAHs are digestive problems (diarrhea, nausea, vomiting) eye and skin irritation with possible confusion. Furthermore, long-term (chronic) exposure results in anemia, damage and reduced functioning of organs such as kidneys, liver and lungs. Most common problems with high exposures are chronic breathing problems including asthma and bronchitis followed by lung function anomalies.[41] However, one major abundance of PAHs is in ambient air, where they are spread to other environmental matrices (water, soil, crops) through dry and wet deposition atmospheric processes (Figure 1-3). Hence, the most prominent source of human exposure to PAHs comes from ambient air.

Figure 1-3. Environmental fate and cycle of PAHs in nature

Gas-phase pollutants are likely to be inhaled and exhaled more easily and will tend to associate with the mucus lining of the lung, while PM is more likely to settle on the lung surface and be absorbed more readily. Hence it is suggested that heavier molecular weight (HMW) PAHs are associated predominantly with particulates and these will pose the greater health risk.[45] Upon absorption into the body from the lungs, gut or skin, PAHs can deposit in fatty tissues and have been observed in most internal organs (WHO, 2000). The International agency for research and cancer (IARC) has categorized 16 USEPA priority listed PAHs according to their mutagenic and carcinogenic properties as presented in table 1.4. [28, 29, 43]

Due to all the abovementioned concerns, PAHs are controlled by many legislative regulations and measures are in place on national and international levels with the goals of reducing the PAHs emissions. A detailed summary of main legislative bodies responsible for setting up allowed emission levels and regulations in terms of PAHs are presented in the table 1-5.

BaP is often used as a toxicity indicator for all the PAHs as it is proven to be the most toxic compounds of all tested. The last European Community directive (2005/107/EC) fixed a target threshold for BaP of 1 ng m^{-3} as the annual mean concentration as a marker for all other PAHs. It is estimated that 20-29% of the urban populations in the EU are exposed to BaP levels higher than the 1 ng m^{-3} EU limit and 93-94% are exposed to levels higher than the 0.12 ng m^{-3} WHO guide level (EEA, 2012).

Table 1.4 Mutagenic and/or carcinogenic categorization of PAH compounds studies in the present investigation

a – Durant et al. (1996) - (+) indicates compound is mutagenic; (-) indicates compound is not mutagenic at the doses tested; ND indicates the compound was not tested.

b – IARC (1983, 1989, 2010) : 1 = carcinogenic to humans ; 2A = probably carcinogenic to humans ; 2B = possibly carcinogenic to humans ; 3 = not possible to classify ; ND = not determined

No.	PAHs	Human cell mutagenicity ^a	IARC classification ^b	Relative human cell mutagenicity (ratio to BaP) ^a
1	Naphthalene	+	ND	0.00056
2	Acenaphthylene	ND	ND	n/a
3	Acenaphthene	ND	ND	n/a
4	Fluorene	-	ND	n/a
5	Phenanthrene	ND	ND	n/a
6	Anthracene	-	ND	n/a
7	Fluoranthene	-	ND	n/a
8	Pyrene	+	2B	0.082
9	Benz(a)anthracene	+	3	0.017
10	Chrysene	+	2B	0.25
11	Benzo(b)fluoranthene	+	2B	0.11
12	Benzo(k)fluoranthene	+	2B	0.0017
13	Benzo(a)pyrene	+	2B	1
14	Indeno(1,2,3-cd)pyrene	+	2B	0.31
15	Benzo(g,h,i)perylene	+	2B	0.19
16	Dibenz(a,h)anthracene	+	2A	0.29

Table 1.5 Summary of standards and regulations to PAHs exposure

* TLV: threshold limit value. TWA (time-weighted average REL (recommended exposure limit) PEL (permissible exposure limit),

<i>Organization</i>	<i>Matrix</i>	<i>Thresholds</i>	<i>Comments</i>
American Conference of Governmental Industrial Hygienists	Air: workplace	0.2 mg m ⁻³ for benzene-soluble coal tar pitch fraction	Advisory: TLV* (8-hour TWA [†])
National Institute for Occupational Safety and Health	Air: workplace	0.1 mg m ⁻³ for coal tar pitch volatile agents	Advisory: REL* (8-hour TWA)
Occupational Safety and Health Administration	Air: workplace	0.2 mg m ⁻³ for benzene-soluble coal tar pitch fraction	Regulation: (benzene soluble fraction of coal tar volatiles) PEL [§] (8-hour workday)
U.S. Environmental Protection Agency (2000)	Water	0.0001 mg L ⁻¹ 0.0002 mg L ⁻¹ 0.0003 mg L ⁻¹ 0.0004 mg L ⁻¹	MCL* for B(a)A MCL for B(a)P B(b)F, B(k)F, CRY MCL for DhA MCL for IcP
World Health Organization (WHO) (2003)	a) Air b) Air	87 x 10 ⁻⁶ ng m ⁻³ 0.1-1.3 ng m ⁻³	Lung cancer unit for a lifetime exposure Guidance value for BaP for a lifetime exposure

1.4 Polychlorinated biphenyls (PCBs)

PCBs are a class of organic compounds comprising hydrogen, carbon and chlorine atoms predominately synthesized by industry. There are 209 individually produced compounds also known as congeners. Up to the present date, there are not proven possible natural sources of any of the PCBs. PCBs are generally liquids with oily texture or solid compounds either colorless or pale yellow color and are known not to have either taste or smell. Another popular synonym for PCBs is the trade name Aroclor, mostly utilized in the United States.[46]. They were firstly produced in the early 19th century until first signs of their toxic effects started to appear in late 1960's. One of the most severe cases is when more than 14,000 people were poisoned in Japan from eating rice contaminated with PCBs. As a result, PCBs were officially banned in 1980. Even though manufacturing stopped almost 30 years ago, PCBs are still of major concern as environmental pollutants that can be toxic to humans and animals due to their chemical stability and high persistency in food and all environmental matrices.[47]

1.4.1 Physical and chemical properties

The component of the chemical structure is a biphenyl molecule that forms a base for the attachment of chlorine atoms (2-10 atoms). The general chemical structure of chlorinated biphenyls is presented in figure 1-4. It can be seen that many levels of variations of chlorinated species are possible depending on the chlorination level and substitution that can be made in ortho, meta and para positions. Furthermore, the aromatic ring can rotate

around the bond that connects the phenyls assuming either planar or non-planar configurations depending on the number of substituents in the ortho positions.

Figure 1-4. General chemical structure of the chlorinated biphenyl with labeled ortho (2 – 2'), meta (3 - 3') and para (4 - 4') positions.

The main property of the PCBs is their chemical and thermal stability and inertness towards acids and alkalis. This is why they were manufactured and applied in a wide range of industries and used mostly as lubricants, dielectric and heat transfer fluids, thermo isolation materials, adhesives, insulators, electrical equipment and oil based paints. High hydrophobic properties make them very persistent leading to accumulation in the environment and human tissue. The hydrophobic character increases gradually with increasing chlorination level of the biphenyl group. However, PCBs are soluble in organic solvents and biological lipids. Combustion of the PCBs (waste treatment) can lead to the production of even more toxic and hazardous materials than themselves, such as polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and hydrogen chloride (HCl).

The list of PCBs selected as a target analytes following the USEPA method 8082A are shown in table 1-6, together with the structure, molecular weight and boiling point information regarding each analyte.

Table 1-6. Summary of the target PCBs monitored in this study together with their IUPAC names, formulas, molecular weight and boiling point information.

No.	IUPAC Name	Formula	Structure	Molecular Weight	Boiling Point
1	2-Chlorobiphenyl	C ₁₂ H ₉ Cl		188.653	274 °C (SynQuest)
2	2,3-Dichlorobiphenyl	C ₁₂ H ₈ Cl ₂		223.098	307.8±22.0 °C (predicted ACD/Labs)
3	2,2',5-Trichlorobiphenyl	C ₁₂ H ₇ Cl ₃		257.543	317.6±27.0 °C (predicted ACD/Labs)
4	2,4',5-Trichlorobiphenyl	C ₁₂ H ₇ Cl ₃		257.543	65 °C (Jean-Claude Bradley)
5	2,2',3,5'-Tetrachlorobiphenyl	C ₁₂ H ₆ Cl ₄		291.988	348.8±37.0 °C (predicted ACD/Labs)
6	2,2',5,5'-Tetrachlorobiphenyl	C ₁₂ H ₆ Cl ₄		291.988	344.9±37.0 °C (predicted ACD/Labs)
7	2,3',4,4'-Tetrachlorobiphenyl	C ₁₂ H ₆ Cl ₄		291.988	361.4±37.0 (predicted ACD/Labs)
8	2,2',3,4,5'-Pentachlorobiphenyl	C ₁₂ H ₅ Cl ₅		326.433	326.433 (predicted ACD/Labs)
9	2,2',4,5,5'-Pentachlorobiphenyl	C ₁₂ H ₅ Cl ₅		326.433	374.9±37.0 °C (predicted ACD/Labs)
10	2,3,3',4',6-Pentachlorobiphenyl	C ₁₂ H ₅ Cl ₅		326.433	374.9±37.0 °C (predicted ACD/Labs)
11	2,2',3,4,4',5'-Hexachlorobiphenyl	C ₁₂ H ₄ Cl ₆		360.878	400.0±37.0 °C (predicted ACD/Labs)
12	2,2',3,4,5,5'-Hexachlorobiphenyl	C ₁₂ H ₄ Cl ₆		360.878	400.1±40.0 °C (predicted ACD/Labs)

Table 1-6. (Continued) Summary of the target PCBs monitored in this study together with their IUPAC names, formulas, molecular weight and boiling point information.

1.4.2 Human exposure health effect and regulations

13	2,2',3,5,5',6- Hexachlorobiphenyl	C ₁₂ H ₄ Cl ₆		360.878	383.7±37.0 °C (predicted ACD/Labs)
14	2,2',4,4',5,5'- Hexachlorobiphenyl	C ₁₂ H ₄ Cl ₆		360.878	396.2±37.0 °C (predicted ACD/Labs)
15	2,2',3,3',4,4',5- Heptachlorobiphenyl	C ₁₂ H ₃ Cl ₇		395.323	428.1±40.0 °C (predicted ACD/Labs)
16	2,2',3,4,4',5,5'- Heptachlorobiphenyl	C ₁₂ H ₃ Cl ₇		395.323	424.3±40.0 °C (predicted ACD/Labs)
17	2,2',3,4,4',5',6- Heptachlorobiphenyl	C ₁₂ H ₃ Cl ₇		395.323	407.2±40.0 °C (predicted ACD/Labs)
18	2,2',3,4',5,5',6- Heptachlorobiphenyl	C ₁₂ H ₃ Cl ₇		395.323	408.2±40.0 °C (predicted ACD/Labs)
19	2,2',3,3',4,4',5,5',6- Nonachlorobiphenyl	C ₁₂ HCl ₉		464.213	458.6±40.0 °C (predicted ACD/Labs)

PCBs are pollutants broadly distributed in the environment, detected in every environmental matrix including: soil, sediment, water, in aquatic and terrestrial biota as well as human tissue.[48] Unfortunately, many cases in history have shown how PCBs can be harmful to human wellbeing upon exposure. [49]

One of the most severe cases happened in 1968 in Japan and Taiwan where people became poisoned by consuming contaminated food. The main indications of the disease included acne-like eruptions, skin and nail pigmentation, conjunctivas followed by increased discharge from eyes, and numbness in the limbs. [50, 51] Furthermore, the epidemic was confirmed later in 1969 and these symptoms received their own classification called “Yusho” disease. Nearly 15,000 people were reported with abovementioned symptoms and 1867 diagnosed as Yusho victims. However, analogous accident of PCBs poisoning took place in Taiwan 10 years later by consuming cooking oil. [50] Extensive and long-term

biomedical studies were conducted to monitor Yusho victims for generations and the results indicated that harmful symptoms of the disease were sustained for two generations.[50]

Few more cases of direct human exposure to PCBs/Dioxins/PCDF were reported in Vietnam and Italy (Seveso). The United States military in the period of 1962 to 1971 contaminated southern Vietnam land by spraying large forest areas and crops with 80 million liters of the defoliant herbicides (Agent Orange, a 50:50 mixture of 2,4,5-T and 2,4-D). [52-54] Byproducts of PCBs such as dioxins and furans were reported to be even more harmful and toxic to the environment and human body with effects on nervous and immune system, hepatotoxicity, carcinogenicity and metabolic and enzyme toxicity. [53, 54] Major World's regulatory bodies (OSHA, NIOSH, EPA, FDA and WHO) have published legislation regarding allowable concentration levels in different environmental matrices including water, air and food. Summary of the published legislations are presented in table 1-7.

Table 1-7. Summary of standards regulations and recommendation for PCBs

OSHA = The Occupational Safety and Health Administration,

FDA = United states food and drug administration,

NIOSH = National Institute of Occupational Safety and Health,

FAO = Food and Agriculture Organization of the United Nations,

Regulatory Body	Sample	Limits	Comments
OSHA*	Ambient Air Work related exposure	1.0 mg / m ³ PCBs with (42% Cl) loading 0.5 mg / m ³ PCBs with (54% Cl) loading	40h working week
NIOSH*	Ambient Air Work related exposure	1.0 µg/m ³	Advisory; time average (10-hour)
EPA	Drinking water	0.0005 ppm	Enforceable maximum level
FDA*	Food and beverages	0.2-3.0 ppm (all food products) 2.0 ppm (all fish and seafood) 10 ppm (paper food- packaging materials)	Enforceable tolerance limits
WHO and FAO*	Food and beverages	6.0 µg/kg per day	Allowable daily intake

However the European Commission's Committee of Experts on Food proposed a limit called "tolerable weekly intake" (TWI) given by the total of dioxins and PCBs of 14 pg TEQ/kg of body weight, which is an average of 2 pg TEQ/day/kg of body weight where TEQ stands for toxicity equivalency factor.[55] The main goal of establishing new strict regulatory policies is to reduce environmental contamination of the PCBs and its bio-products (dioxins, furans) leading to decreasing accumulation in the food chain leading to lower levels of human exposure (intake) to PCBs.

1.5 Recent studies on atmospheric profiles of PAHs and PCBs in Southeast Asia

Air quality monitoring in Southeast Asia (SEA) is of considerable interest from both scientific and governance perspectives due to the continuous air pollution problems occurring in this region. In recent years, SEA countries have undergone vast economic development and industrialization. Hence, rising problems with atmospheric pollution is a regular subject of concern. Regional trans-boundary pollution occurs in this region almost every year causing serious air pollution episodes due to uncontrolled land clearing activities (burning peat and forest) mostly in Indonesia. This section summarizes concentration profile trends of PAHs and PCBs in various countries in SEA including Singapore, Vietnam, Thailand, Malaysia and Taiwan.

The last published study conducted on SVOCs analysis in Singapore including PAHs and PCB was in 2009 by Balasubramanian and coworkers. [56] The study was conducted with a goal to characterize rainwater and PM₁₀ bounded PAHs and PCBs in Singapore's atmosphere. Results showed that median levels of PAHs and PCBs in air (particle + gas)

were 136.5 ng m^{-3} and 27 pg m^{-3} respectively. PCBs were recognized to be primarily from the commercial mixtures of Aroclors 1248 and 1254. No relevant results were reported on source contributors of the PM bound PAHs. Furthermore, thorough studies were conducted in neighboring Malaysia by Jamhari and Khan et al [57] on PM_{10} bound PAHs in Kuala Lumpur. The results showed that the total PAHs concentrations throughout seasonal monsoons for Kuala Lumpur, ranged from 1.33 ng m^{-3} to 4.84 ng m^{-3} respectively. Heavier, 5-ring and 6-ring PAHs such as BaP, (IcP), (BbF), (BkF) and (BgP) were dominant contributors of all PAHs collected. The abundance of BgP with high concentrations at all sampling sites implied a source marker for traffic emission. Results of running diagnostic ratio (DRs) and principal component analysis (PCA) showed significant influences from traffic emission, while low effects from natural gas emissions and coal combustion.

Kim Oanh et al, [58] conducted very detailed studies in Thailand on PM characterization produced by burning rice straw in laboratory conditions in order to simulate field conditions of the very common haze episodes in this region. Amongst the 16 PAHs and 14 PCBs that were monitored, the most abundant PAHs were BaP and BaA, while out of heavier 6 ring PAHs only BP was detected in small concentrations. Out of all 14 PCBs monitored, 10 were detected in PM_{10} mainly in levels less than 1 ng m^{-3} .

A comprehensive study was reported on the long term monitoring of chlorinated organic compounds including 23 different PCBs in 15 different locations in Vietnam by Wang et al. [59] Concentrations of the monitored PCBs were in range from $136\text{--}736 \text{ pg m}^{-3}$ (summer), and $145\text{--}1518 \text{ pg m}^{-3}$ (winter). These concentrations are much higher than reported in Europe ($2.5\text{--}280 \text{ pg m}^{-3}$) [60] or other Asian countries (China, Japan, South Korea, and Singapore) ($21\text{--}336 \text{ pg m}^{-3}$) [61] but similar with levels reported in India

(coastal and inland sites) ($120\text{--}1080\text{ pg m}^{-3}$). The highest PCB concentrations were detected at suburban sites or sites at close proximity to urban centers. The tri- to penta-PCBs accounted for more than 80% of the total PCBs in Vietnam, regardless of summer or winter. The main source and reason for these high levels of PCBs in Vietnam lies in improper e-waste recycling activities and open municipal waste-dumping sites, confirmed in a study conducted by Tue et al., 2013 [62].

Even though PAHs and PCBs are two of the most widespread and harmful class of pollutants, not many research studies have been performed in SEA in terms of detailed long term monitoring with statistical analysis to determine possible sources and trans boundary air pollution effects on their abundances. Table 1-8 summarizes studies conducted in SEA and major Asian cities related to the PAHs. However, in terms of PCBs there are few studies conducted related to the long term monitoring and possible source identification analysis except those mentioned in the text above.

The common conclusion for all the studies referenced in table 1-8 is that by performing statistical analysis for source contribution such as diagnostic ratio (DRs), principal component analysis (PCA) and positive matrix factorization (PMF), the main source contributor of the PAHs occurrence is pyrogenic in nature (traffic) and coal combustion (domestic heating).

Table 1-8. Mean concentration of particulate bound PAHs in SEA and various major Asian cities.

City/Country	Mean PAHs ng/m ³	No of PAHs	Source	Reference
Southeast Asia (SEA)				
Kuala Lumpur, Malaysia	1.33	12	PM ₁₀	[63]
Ho Chi Min City, Vietnam	7.6	12	PM ₁₀	[64]
Chiang Mai, Thailand	69.52	16	PM ₁₀	[65]
Singapore	4.28	16	PM ₁₀	[66]
Other Asian Cities and Megacities				
Seoul, South Korea	26.6	16	PM ₁₀	[67]
Lhasa, Tibet	20.0	16	PM ₁₀	[68]
Hong Kong	15.9	12	PM ₁₀	[69]
Osaka, Japan	4.0	12	PM ₁₀	[64]
Delhi, India	105	16	PM ₁₀	[70]
Kathmandu Valley, Nepal	155	16	TSP	[71]
Beijing, China	160	16	TSP	[72]

Chapter 2: Development of a quantitative assessment method for atmospheric semi-volatile organic pollutants using solid phase extraction coupled to gas chromatography mass spectrometry

2.1 Introduction

In the last few decades Asian countries have experienced substantially raised concentrations of atmospheric pollution, that not only degrades regional air quality, but also significantly impacts public health and global climate as a direct consequence of a progressive rise of the industrial activities due to the rapid growth of the economies. Countries like China, India and other is the Southeast Asia region have for many years back attracting attention of scientists and policy makers as well as the general public because of severe air pollution that occurs in these regions on a regular basis. One of the major reasons for this is that many of the countries in Asia do not follow the emission regulations. For instance, just recently the Chinese government announced an ambitious goal to reduce the major air pollutants by 30% in its most developed regions by 2017. To achieve such an ambitious goal, it is important to know what are the source contributors and concentrations of all the target air pollutants in all the regions of interest. That is why it is of crucial significance that new, more environment friendly, sustainable and efficient analytical methods for qualification/quantification of different air pollutants are developing to be able to monitor all the changes in the atmosphere and hence to design effective control

strategies. SVOCs including PAHs and PCBs are one of the most harmful atmospheric pollutants known as very persistent organic chemicals that are toxic to the environment and human beings.[98-102]

GC-MS is an affordable and rugged system and it is proven and widely recognized as a state of the art analytical technique for the qualification and quantification analysis of a wide range of thermally stable VOCs or SVOCs organic compounds, such as PAHs, pesticides, PCBs, dioxins, brominated flame retardants, endocrine disruptive compounds and related persistent organic pollutants (POPs) in diverse environmental matrices that presently cannot be analyzed by conventional LC-MS methods. Recently there have been major advancements in developing new instrumentation, comprising tandem mass spectrometry (MS-MS) and time-of-flight (TOF) detectors to the GC or tandem GC×GC with solid phase micro extraction (SPME) pre cleaning systems attached, that opened up and broadened the possibilities of environmental analytical chemistry applications.

In Singapore, regular monitoring and analysis of the SVOCs in the atmosphere has not been carried out, or at least reported in the literature. Only a couple studies have been reported more than 10 years ago regarding the occurrence of PAHs, PCBs and OCPs in Singapore's atmosphere. Comparing with other countries in the region, Singapore's air quality is amongst the best due to strict emission regulation policies for industry and traffic. The problem is that Singapore suffers from trans-boundary pollution caused by land clearing activities mostly in Indonesia where strong monsoons winds carries dense smoke from the peat land fires over Singapore causing severe levels of air pollution. The principal public organization responsible for monitoring the air quality in Singapore, the National Environment Agency (NEA) only reports the PSI, which is calculated based on 5 foremost

atmospheric pollutants comprising PM_{2.5}, SO₂, NO_x, CO and tropospheric O₃ concentration measurements. Only the abovementioned 5 priority pollutants have been regularly reported in Singapore. [103]

This chapter describes and explains how analytical methods were developed and validated for evaluating the quantities of atmospheric SVOCs including PAHs and PCBs that are monitored in the western region of Singapore, which is known as the most industrialized region where one of the largest petroleum refineries in the world is stationed. 16 PAHs and 19 PCBs were selected as target analytes of interest for this study as they were proven to be the most harmful from both perspectives of the environment and health.

2.2 Experimental

2.2.1 Chemicals and standard solutions

All the solvents used in this study were high purity HPLC grade and these included: dichloromethane (VWR), methanol (VWR), hexane (VWR) and acetone (VWR). All the SVOCs standards were purchased from AccuStandard (New Haven, USA). 16 USEPA PAHs mixture of NAP, ACY, ACP, FLR, PHE, ANT, FLT, PYR, BaA, CYR, BbF, BkF, BaP, IND, DhA, BgP in a concentration of 2.0 mg/mL dissolved in dichloromethane:benzene (1:1). Internal standard mixture consisted of acenaphthene-d₁₀, chrysene-d₁₂, naphthalene-d₈, perylene-d₁₂, phenanthrene-d₁₀ (4mg/ml) dissolved in DCM. The standard mix (100µg/ml) of 19 different congeners of PCBs were also purchased from AccuStandard (New Haven, USA) including: 2-chlorobiphenyl, 2,3-dichlorobiphenyl, 2,2',5-trichlorobiphenyl, 2,4',5-trichlorobiphenyl, 2,2',3,5'-

tetrachlorobiphenyl, 2,2',5,5'-tetrachlorobiphenyl, 2,3',4,4'-tetrachlorobiphenyl, 2,2',3,4,5'-pentachlorobiphenyl, 2,2',4,5,5'-pentachlorobiphenyl, 2,3,3',4',6-pentachlorobiphenyl, 2,2',3,4,4',5'-hexachlorobiphenyl, 2,2',3,4,5,5'-hexachlorobiphenyl, 2,2',3,5,5',6-hexachlorobiphenyl, 2,2',4,4',5,5'-hexachlorobiphenyl, 2,2',3,3',4,4',5-heptachlorobiphenyl, 2,2',3,4,4',5,5'-heptachlorobiphenyl, 2,2',3,4,4',5',6-heptachlorobiphenyl, 2,2',3,4',5,5',6-heptachlorobiphenyl and 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl. Internal standards for PCBs were tetrachloro-m-xylene and decachlorobiphenyl, 5.0 µg/mL in hexane mixture.

2.2.2 Solid phase extraction

Sample preparation is always a crucial part in method development, especially in aerosol analysis of SVOCs where the complex matrix that comprises different kinds of organic compounds such as alcohols, esters, alkanes, ketones, phenols, fatty acids, aldehydes as well as nitrogen, oxygen and sulfur hetero compounds can affect analysis or damage the GC-MS causing lesser sensitivity and reproducibility. [104] Hence, a solid phase extraction (SPE) clean-up procedure is necessary prior to chromatographic analysis in order to develop a reliable and accurate method for the qualification and quantification of the targeted particle bound PAHs and PCBs that usually occur in ultra-trace levels. For the PAHs analysis, Strata-X 33µm polymeric reverse phase (PHENOMENEX, USA) cartridges were used, while the analysis of PCBs employed Strata FL-PR Florisil 170µm, 500mg/6mL (PHENOMENEX, USA) cartridges. Optimum conditions for the SPE procedure consisted of 4 main steps: conditioning, loading, washing and eluting, and were developed to meet EPA criteria in terms of recoveries and reproducibility.

2.2.3 Instrumentation

Qualification and quantification of the PAHs and PCBs were performed using an Agilent 7890A gas chromatograph coupled to an Agilent 5975C mass spectrometry system (GC/MS), utilizing a Zebron ZB-5MS Guardian capillary column (30 m + 5 m guardian length $\times$ 0.25 mm i.d. 0.25 μ m film thickness) with high purity helium (99.999%) as the carrier gas applied with a constant 1.5 mL/min flow in the column and at the column inlet. The interface temperature between the GC and MS was kept at 250 °C. The mass spectrometer acquisition parameters for both SIM (selected ion monitoring) and full SCAN mode was set up to the mass range between 35 and 300 amu. The ionization source used was electron Impact (EI) and it operated at 70 eV, while mass spec quadrupole temperature was set at 150 °C and ionization source temperature at 230 °C.

2.2.4 Tuning of mass spectrometer

The GC-MS system was tuned every day using a standard perfluorotributylamine (PFTBA) solution as a system check procedure prior to instrumental analysis at m/z = 69, 219 and 502 as well as air/water leak checks (m/z 18, 32, 44). PFTBA was used to assess the overall condition of the mass spectrometer, while air/water leak checks examined if there is any leak in the general GC-MS system.

2.2.5 Quality control and assurance

Every target SVOC was associated with three ions, one for quantification and two for qualification purposes. The quality of the data in this study was determined by using limits of detection (LOD), limits of quantification (LOQ), and the linearity of the calibration line that was estimated by analyzing a 6 points calibration curve (0.01, 0.1, 0.25, 0.5, 1 and 2 ng μL^{-1}). All calibration curves plotted for all compounds of interest have acceptable linearity with R^2 values higher than 0.99 according to the EPA regulations. Prior to analysis, continuing calibration verification (CCV) tests were conducted in order to verify system stability and calibration curve used for quantification. Depending on the number of samples run, closing calibration verification was conducted after every 20 samples run following standard regulations. To minimize quantification errors, procedural and field blanks were carried out as well as surrogate standard spiking for recovery assessment and error corrections. Procedural and field blank samples analysis showed none of the SVOCs of interest. Recoveries of the sample preparation procedure were in the range from 60-120% and recoveries corrections were made to the measured concentrations. Surrogate standards were chosen to cover all the range of the chromatogram in order to obtain the most accurate and valid quantification; thus the following 7 deuterated standards were used: acenaphthene-d10, chrysene-d12, naphthalene-d8, perylene-d12 and phenanthrene-d10 for the PAHs analysis while tetrachloro-m-xylene and decachlorobiphenyl were chosen as a surrogate standards for the PAHs and PCBs quantification. Plastic wares were not used to avoid any cross-contamination. Analytical grade solvents DCM and Hex in combination with sonication and baking were used for the washing procedure to

quantitatively remove any residual organics and moisture that could affect quantification accuracy and reproducibility.

2.3 Results and discussion

2.3.1 GC-MS parameters optimization (method development)

Three distinct GC methods were developed for separation of the PAHs and PCBs, respectively. The first critical step in GC method development is the injection port temperature due to it having to efficiently and quantitatively transfer all analytes to the GC column for further separation. Temperatures of 200 °C, 230 °C, 250 °C, 270 °C and 300 °C were monitored in order to obtain the strongest analyte response for best sensitivity, while not producing a noisy background due to ghost peaks that might interfere with measurements. The temperature of 250 °C showed the best analyte response with a clear blank. Temperatures below 250 °C showed clear blanks and less sensitivity, while temperatures above 250 °C resulted in relatively higher sensitivity but high background noise originating from degradation of the inlet components such as the septum and liner fillings. The initial temperature gradient of the GC oven was modified for improvements to the analytical resolutions between the isomer pairs of SVOC analyzed.

For PAHs and PCBs, analysis starting temperatures of 40 °C and 60 °C were optimized to give the separation for the most volatile species.[105-108] Since SVOCs are compounds that exist in trace levels, splitless injection mode for all PAHs and PCBs analysis was utilized to enable the optimal performance in terms of sensitivity (LOD and LOQ) of the methods because all the analytes were transferred from the inlet to the column for further

analysis. Optimized parameters for separation and detection of the target PAHs and PCBs including GC and MS are summarized in tables 2-1 and 2-2 accordingly. Furthermore, SIM mode was developed in order to reduce background noise and reach lower detection limits of the instrument. One ion for quantification and two additional ions for qualification purposes were chosen from the mass spectrum by analyzing each target compound separately (appendix 1). Solvent delay was determined to cut the solvent peak from the total chromatogram and to save the ionization source from overloading. Prior to any instrumental analysis, the instrument was auto-tuned to validate that analysis were performed by meeting proposed criteria by following procedures described in the section 2.2.4.

Table 2-1. Summary of the GC-MS parameters optimized for the PAHs analysis

GC parameters (PAHs)	
Initial temperature 40 °C	0.5 min (hold time)
Then 20 °C/min to 138 °C	0.5 min (hold time)
Then 30 °C/min to 300 °C	7 min (hold time)
Total Run Time	18.3 min
Injection Mode	Splitless
Injection Temperature	250 °C
Pressure	13.22 psi
Total Flow	74.5 mL/min
Gas Saver	20 mL/min After 1.25 min
Purge Flow to Split vent	70 mL/min at 1.2 min
Septum Purge Flow	3 mL/min
MS conditions	
Mode	SIM
Tune	PFTBA
Solvent delay	6.5min

Table 2-2. Summary of the GC-MS parameters optimized for the PCBs analysis

GC parameters (PCBs)	
60 °C for	start
then 100 °C/min to 200 °C	0.5 min (Hold time)
then 25 °C/min to 250 °C	0 min (Hold time)
Then 6 °C/min to 300 °C	10 min (Hold time)
Run Time	22.233 min
Injection Mode	Splitless
Injection Temperature	250 °C
Pressure	15.197 psi
Total Flow	74.5 mL/min
Gas Saver	20 mL/min After 1.25 min
Purge Flow to Split vent	70 mL/min at 1.2 min
Septum Purge Flow	3 mL/min
MS Conditions	
Mode	SIM
Tune	PFTBA
Solvent delay	3.0min

Furthermore, after each analysis the column was heated on the maximum temperature (300 °C) for 5 more minutes in order to clean it, which enables less blank runs and reduces the total analysis time. The authentication of the peaks was performed by comparing the retention times (tR), relative abundance of the quantifier and qualifier ions to those of targeted SVOCs standards. Quantification of the SVOCs target compounds from PM samples collected was accomplished using an external calibration procedure. Calibration curves of SVOC standards were constructed by plotting the integrated area under the SVOC quantifier ion signals against varying analyte concentrations. The linear relationship between the two functions was examined using the coefficient of determination, R^2 . The linearity of the multi-point calibration curve of SVOC standards over an extensive range of concentrations was tested.

Instrument sensitivity was evaluated by its limit of detection (LOD) and limit of quantification (LOQ). LOD is the minimum amount of analyte present in a sample that can

be detected but not quantified as an accurate value. LOQ is the minimum amount of analyte found in a sample that can be quantitatively established with reliable precision and accuracy [109]. LODs and LOQs were determined by injecting 7 replicates of the lowest calibration curve standard and calculating standard deviation. 3.3 times standard deviation represents LOD while 10 times standard deviation represents LOQ. Method detection limit determined by dividing these values by the total volume of the sample collected (1500m³ of air) to get MDL values of pg m⁻³ level. Instrumental limits of detection and quantification LOD and LOQ, together with a method limits of detection (MDL) were not calculated for the surrogate standards because they were used only for the recovery analysis.

[110] Figures 2-1 and 2-2 shows the total ion current chromatograms including 16 target PAHs and 4 surrogate standards respectively, while figure 2-3 shows 19 PCBs together with surrogate standards analyzed using the optimized GC-MS procedure. Tables 2-3, 2-4a and 2-4b shows the retention times of the target PAHs and PCBs their quantifier and qualifier ions, the identity and calibration linearity.

Figure 2-1. Chromatographic separation of the 16 EPA listed PAHs

Figure 2-2. Chromatographic separation of the 4 surrogate PAH standards

Table 2-3. Table of target PAHs and their retention times (t_R), quantifier and qualifier ions (Q1) and (Q2), calibration linearity (0.001ng - 2ng), limits of detection (LOD) and limits of the quantification (LOQ).

No.	PAH	Quantitative ion	Q1	Q2	t_R (min)	Linearity R^2	LOD (ng)	LOQ (ng)	MDL ($\mu\text{g m}^{-3}$)
1	NAP	128.1	127.0	129.0	6.66	0.9978	0.0007	0.0021	0.0014
2	ACY	152.1	151.0	153.0	8.44	0.9982	0.0026	0.0078	0.0052
3	ACP	153.0	153.0	152.1	8.62	0.9977	0.0009	0.0028	0.0020
4	FLR	166.0	165.1	167.0	9.11	0.9976	0.0008	0.0025	0.0017
5	PHE	178.1	176.1	179.0	9.98	0.9978	0.0007	0.0022	0.0015
6	ANT	178.1	176.1	179.0	10.03	0.9980	0.0010	0.0032	0.0021
7	FLT	202.0	200.1	203.0	11.09	0.9985	0.0018	0.0054	0.0036
8	PYR	202.0	203.1	200.2	11.20	0.9983	0.0011	0.0033	0.0022
9	BaA	228.1	229.1	226.1	12.28	0.9985	0.0010	0.0031	0.0021
10	CYR	228.1	229.1	226.1	12.32	0.9958	0.0027	0.0082	0.0055
11	BbF	252.1	250.1	253.1	13.64	0.9974	0.0076	0.0230	0.1533
12	BkF	252.1	250.1	253.1	13.68	0.9975	0.0025	0.0077	0.0051
13	BaP	252.1	250.2	253.2	14.17	0.9981	0.0069	0.0208	0.0138
14	IcP	276.1	274.1	277.1	16.52	0.9974	0.0028	0.0084	0.0056
15	DhA	278.1	279.1	277.1	16.59	0.9972	0.0020	0.0061	0.0041
16	BghiP	276.1	264.1	277.1	17.23	0.9966	0.0024	0.0072	0.0048

	PAH	Quantitative ion	Q1	Q2	t_R (min)	Linearity R^2	LOD (ng)	LOQ (ng)
a.	D8-NAP	136.2	137.2	134.2	6.64	0.9932	n.a.	n.a.
b.	D10-ACP	164.1	160.2	162.1	8.56	0.9992	n.a.	n.a.
c.	D10-PHE	188.0	187.0	189.0	9.96	0.9953	n.a.	n.a.
d.	D12-CRY	240.0	241.1	236.1	12.28	0.9973	n.a.	n.a.
e.	D12-PRY	264.1	265.1	260.1	14.29	0.9989	n.a.	n.a.

Throughout this study, surrogate standards were used for quantification purposes to evaluate the method efficiency and to correct for losses during sample preparation. Surrogates were carefully chosen so that they did not co-elute with target analyte peaks. The surrogates are compounds not found in a nature or in the blank runs, which allows representable and valid data corrections and the examination of sample preparation efficiency by monitoring the recoveries.

Figure 2-3 Chromatographic separation of the 19 PCB standards including 2 surrogate standards (a,b)

Table 2-4a. Table of target PCBs and their retention times (t_R), quantifier and qualifier ions (Q1) and (Q2), calibration linearity (0.001ng - 2ng), limits of detection (LOD) and limits of the quantification (LOQ).

PCBs No/(UPAC)		Quantitative ion	Q1	Q2	t_R (min)	Linearity R^2	LOD (ng)	LOQ (ng)	MDL (pg m ⁻³)
1	1	187.9	189.9	152.1	3.286	0.9982	0.0005	0.0047	0.0031
2	5	222.0	223.9	152.2	3.899	0.9977	0.0009	0.0091	0.0066
3	18	186.0	255.9	257.8	4.163	0.9976	0.0004	0.0044	0.0029
4	31	255.9	257.9	186.1	4.493	0.9978	0.0007	0.0067	0.0045
5	44	229.1	290.0	220.1	4.749	0.9980	0.0001	0.0066	0.0044
6	52	291.9	289.0	293.8	4.922	0.9985	0.0002	0.0018	0.0012
7	66	291.8	290.0	219.9	5.303	0.9983	0.0011	0.0111	0.0074

Table 2-4a. (Continued) Table of target PCBs and their retention times (t_R), quantifier and qualifier ions (Q1) and (Q2), calibration linearity (0.001ng - 2ng), limits of detection (LOD) and limits of the quantification (LOQ).

8	87	325.8	323.9	327.8	5.513	0.9985	0.0007	0.0073	0.0049
9	101	325.9	323.9	324.8	5.798	0.9958	0.0010	0.0103	0.0069
10	110	325.9	361.8	289.9	5.894	0.9974	0.0011	0.0113	0.007
11	138	361.8	325.9	290.0	6.012	0.9975	0.0007	0.0075	0.005
12	141	359.8	361.8	289.9	6.449	0.9981	0.0004	0.0044	0.003
13	151	360.0	290.1	261.9	6.619	0.9974	0.0004	0.0043	0.003
14	153	359.8	289.9	361.8	6.807	0.9972	0.0003	0.0030	0.002
15	170	393.8	395.8	324.0	7.001	0.9966	0.0007	0.0069	0.0046
16	180	393.8	395.8	323.9	7.080	0.9932	0.0008	0.0079	0.0053
17	183	393.8	321.9	391.8	7.782	0.9992	0.0008	0.0081	0.0054
18	187	393.8	395.8	324.9	8.252	0.9953	0.0010	0.0096	0.0064
19	206	391.8	321.9	393.9	10.063	0.9973	0.0006	0.0062	0.0041

Table 2-4b. Surrogate standards Tetrachloro-m-xylene and Decachlorobiphenyl for a PCBs analysis

No.	PCBs	Quantitative ion	Q1	Q2	t_R (min)	Linearity R^2	LOD (ng)	LOQ (ng)
1	Tetrachloro-m-xylene	244.1	242.1	245.9	3.64	0.9989	0.001	0.001
2	Decachlorobiphenyl	497.7	495.7	499.7	10.67	0.9948	0.001	0.001

2.3.2 Filter handling

Prior to sampling, filters were baked at 200 °C in glass drying oven (B-585 Buchi) under vacuum for 12h to remove any organic residues from the filter that could interfere with measurements. After which, filters were weighed on an analytical balance and transported to the sampling site. Singapore's climate is very humid, with an annual average of 83.9%, as presented in figure 2-4.[111] Therefore, after sampling, the filters were desiccated for 24h to remove the residual moisture in order to obtain an accurate mass of the net particulate mass sampled. During this study, all the filters were transported, kept and stored in clean polyethylene bags. Due to volatility of the SVOCs, PM samples were stored in the refrigerator at 4°C to avoid any loss of the target analytes. All the samples were extracted and analyzed within 24h of the desiccation.

Figure 2-4. Hourly variation of relative humidity for each month (1982-2016) Singapore meteorological service (<http://www.weather.gov.sg/climate-climate-of-singapore>)

To prevent contamination, all the apparatus and glassware were cleaned with high purity solvents (Ace, DCM) and dried overnight to remove any organic compounds that might contaminate experiments. Since some of the PAHs and PCBs are light sensitive, experimental conditions were maintained under dimmed lights and most of the glassware used was ambered as a preventive measure against loss of any analyte studied.

2.3.3 Extraction of the PM_{10} bound PAHs

The extraction procedure was modified from previous works. [27, 97, 112] The filter was cut in half with solvent rinsed ceramic scissors into small pieces (approximately 1×1 cm). Filters were spiked with 50 μ l of 10 ppm of the calibration standard mixture of 16 PAHs to evaluate extraction efficiency for each target analyte by monitoring the recoveries. PAHs were extracted from the filter by using sonication agitation in mixtures of DCM and MeOH in a 4:1 ratio, which gave the best performance in extracting the whole range of 16 targeted PAHs. Sonication extraction was repeated 3 times in time intervals of the 20 minutes with fresh solvents used each time. The combined extract was then filtered using syringe filtration (0.45 microns) to remove any of the remaining insoluble particles. The extract was rotary evaporated until the remaining solvent reached 1 ml in volume. DCM was used as the solvent due to its low boiling point of the 40 °C, enabling it to be evaporated quickly reducing the losses of volatile PAHs from the sample. The same extraction procedure was repeated 3 times to validate the sample preparation method by assessing the standard deviation of the recoveries as presented in table 2-5.

Table 2-5. Sample preparation efficiency summarized with a average recoveries and relative standard deviation (blank filters)

No.	Compound	Recoveries (%)	RSD (%) n=3
1	NAP	82.24	3.44
2	ACY	82.65	2.19
3	ACP	86.92	4.10
4	FLR	84.09	5.10
5	PHE	87.86	3.98
6	ANT	86.45	4.38
7	FLT	81.57	3.82
8	PYR	89.10	2.88
9	BaA	94.00	3.93
10	CYR	76.44	1.45
11	BbF	90.25	2.88
12	BkF	72.44	3.11
13	BaP	83.82	3.49
14	IcP	78.25	5.42
15	DhA	75.88	5.35
16	BghiP	69.71	5.93

The same extraction procedure was repeated with loaded filters to examine possible matrix effects on recoveries. In this case, filters were spiked with a 50 µl of 10 ppm deuterated surrogate standard mixture of acenaphthene-d10, chrysene-d12, naphthalene-d8, perylene-d12, phenanthrene-d10 where recoveries were monitored for sample preparation efficiency (Table 2-6). Due to chemical complexity of the PM matrix and low concentrations of PAHs, the SPE procedure was employed as a clean-up step to remove any insoluble particles that might damage the GC-MS system while also removing components that

might interfere with target analytes such as alkanes, fatty acids, alcohols, aldehydes, ketones and esters. [104] (refer to 3.2.2. section). Three consequent extraction procedures were conducted in a same way with addition of the SPE procedure to evaluate sample preparation accuracy, efficiency and reproducibility.

Table 2-6. Sample preparation efficiency summarized with a average recoveries and relative standard deviation (loaded filters)

No.	Surrogate standards	Recoveries (%)	STDV (%) n=3
1	D8-Naphthalene	90.76	6.53
2	D10-Acenaphthene	86.14	5.34
3	D10-Phenanthrene	82.80	6.55
4	D12-Chrysene	73.19	4.15
5	D12-Perylene	68.00	4.97

The final SPE procedure developed is a modification from the previous literature.[104, 113] SPE sorbent (polymeric Strata-X from Phenomenex. USA) was conditioned with 8 mL of methanol, followed by 8 mL of DCM and then dried under vacuum for 5 minutes. Next, around 1 mL of the sample extract was loaded onto the cartridge and the cartridge was dried under vacuum for 5 minutes. The PAHs were then eluted from the cartridge using 10 mL of dichloromethane. The flow rate of sample loading and eluting was controlled to approximately 1 mL min⁻¹. The obtained solution was then evaporated to a volume of close to 1 ml using a rotary evaporator. After which, excess solvent was evaporated by a gentle nitrogen gas stream to make sure the samples collected were exactly 1 mL in volume to be able to perform valid calculations later on. The samples were then collected in amber vials,

caped, sealed and stored in the refrigerator for further GC-MS analysis. Samples were always left to warm up to the room temperature prior to injection, since the temperature of the sample affects evaporation efficiency in the GC inlet. Hence, different temperature of the final sample can lead to non-reproducible results.

2.3.4 Extraction of the $PM_{2.5}$ bound PCBs

In order to reach quantification limits for the PCBs that occur in the atmosphere even in $pg\ m^{-3}$ levels, filters were sampled for 48h for trapping, while for the PAHs study, it was found that 24h sampling time was enough to reach $ng\ m^{-3}$ levels. Filters were cut into small pieces and spiked with 50 μl of 10 ppm surrogate standard mixture of the tetrachloro-m-xylene and decachlorobiphenyl for the recovery assessment on loaded filters to investigate PM matrix impact on recoveries, while blank filters were spiked with a 50 μl of 10 ppm calibration standards of target PCBs respectively. PCBs were extracted from the particulate matter by using sonication extraction with an acetone and hexane mixture (3:1 ratio). The sonication process was repeated for 3×20 minutes with fresh solvents each time. The combined extract was then filtered using syringe filtration (0.45microns) to remove any insoluble particles prior to rotary evaporation under vacuum to reach a volume of approximately 1 ml. The concentrated extract was further cleaned up with a FL-PR Florisil 170um, 500mg/6mL cartridge. The cartridge was conditioned with 6 ml of HEX and 6 ml of Ace before the sample extract ~1ml was loaded into the cartridge. 10 ml of Hexane was used as an elution solvent to quantitatively extract PCBs from the SPE sorbent bed. The flows were maintained at $1\ ml\ min^{-1}$ for all the SPE clean

up steps. Finally, the resulting clean extract was evaporated under a nitrogen stream to 0.5 ml for further GC-MS analysis. The final extract was concentrated to 0.5 ml to be able to reach low detection limits for the PCBs accordingly. Tables 2-7 and 2-8 summarize blank filter and loaded filter recoveries together with standard deviations for 3 replicate sample preparation procedures.

Table 2-7. Sample preparation efficiency summarized with average recoveries and relative standard deviation (blank filters) STDV calculated for n=3

PCBs No. / (UPAC)		Recovery (%)	STDV (%)
1	1	93	3.50
2	5	91	3.14
3	18	103	4.47
4	31	105	4.59
5	44	99	5.13
6	52	91	6.19
7	66	89	4.55
8	87	96	3.89
9	101	103	2.87
10	110	105	4.74
11	138	100	2.30
12	141	94	4.59
13	151	87	5.84
14	153	93	6.14
15	170	99	6.35
16	180	102	5.62
17	183	104	4.50
18	187	101	5.37
19	206	91	5.96

Table 2-8. Sample preparation efficiency summarized with average recoveries and relative standard deviation (loaded filters) STDV calculated for n=3

No.	Surrogates	Recovery (%)	STDV (%)
1	Tetrachloro-m-xylene	92	4.35
2	Decachlorobiphenyl	97	3.20

2.4 Conclusion

An SPE-GC-MS method has been developed for the detection and quantification of 16 PAHs and 19 PCBs respectively. Good linearity with a minimum of $R^2=0.99$ was achieved for a wide range of concentrations between 0.001 to 2 ng for all target SVOCs in this study. Detection levels achieved for all SVOCs were in a low ppb range. Different sampling volumes of 24h, 48h and 72h were investigated for reaching desired detection limit of all the SVOC target analytes. For PAHs, 24h sampling was found to be enough while for PCBs, 48h sampling was required. Recoveries and standard deviation of the replicate sample preparation procedures for all SVOCs monitored in this study showed acceptable recovery values to fall within the desired range of 60 % - 120 % proposed by USEPA (EPA TO-13A) regulations.[41]

A SPE enrichment and clean up step was added prior to further GC-MS analysis to remove any insoluble particles and to isolate target compounds from the complex aerosol matrix. Strata-X polymeric phase sorbent was used for PAHs analysis while FL-PR Florisil was used for PCBs.

With a versatile method optimized, developed and validated for detecting PAHs and PCBs, further studies were implemented for the monitoring the air quality in the industrialized

region in western Singapore, understanding the concentration patterns of these compounds that are present in the atmosphere at various time periods, and predicting sources of these compounds. These additional environmental studies are described in Chapter 3.

Chapter 3. Concentrations, source determination, trend profiles and health risk assessment of atmospheric semi volatile organic pollutants in Singapore's tropical climate

3.2 Experimental

3.2.1 Sampling Site

All airborne particulate matter samples (PM₁₀ and PM_{2.5}) were collected from May 2015 to May 2016 and from April 2016 to September 2016. The sampling location was on the roof of the School of Physical and Mathematical Sciences (SPMS) at the Nanyang Technological University campus in Western Singapore, approximately 20 meters above the ground (67 m above sea level) to ensure valid sampling with no interferences to the air inlet. In the western part of Singapore lies the largest Industrial complex in the country and Southeast Asia,[114] which makes this sampling site ideal for characterizing SVOCs related to PM from both urban and industrial areas of Singapore since there are many possible different source contributors. These include emissions from major power plants, incinerators, chemical industries and petroleum refineries located on Jurong Island, Tuas and Jurong Industrial Estate (5.8 kilometres away), the main expressway (150 metres from sampling location) and residential areas (350 metres away). Singapore is a city-state with a tropical climate located on the southern tip of the Malay Peninsula and adjacent to Sumatra in Indonesia. The latitude and longitude of this site are 1°20'31.9"N and 103°40'56.3"E, respectively. Singapore is an island that includes 63 other islets within its

territorial waters. Because of its geographical position (lies near on equator) and maritime coverage, Singapore's climate is uniform with constant pressure temperature intervals, characterized with high humidity and abundant rainfalls. Singapore's climate is divided by two main monsoon periods: Northeast Monsoon and the Southwest Monsoon season divided by two rather short inter-monsoon periods. (Table 3-1)

Figure 3.1 Sampling site and its vicinity

3.2.2 Sample Collection

In this study, two different sampling campaigns were conducted by collecting PM_{2.5} bound PCBs and PM₁₀ Bound PAHs. Since airborne SVOCs occur at very low concentrations in the atmosphere, high volume samplers were used in this study to collect enough air for sufficient quantification of the target SVOCs. Depending on the PM diameter, collection from two different samplers were employed. For the collection of the PM₁₀, a TE-PNY1123 Mass Flow Controlled High Volume Air Sampler was used figure 3-2. This instrument samples large volumes of air and is based on aerodynamic principles which result in the collection of particles 10 microns and less. The sampler consists of an anodized aluminum shelter, aluminum blower motor assembly, stainless steel filter holder with probe hole, 7 day mechanical timer, mass flow controller, elapsed time indicator and 6" round PUF spool piece. A Whatman® QM-A quartz microfiber filter (QFF-TE-QMA4/Tish Environmental and 20.3 cm × 25.4 cm filter) was used to collect PM₁₀ particles.

To collect PM_{2.5} particles, the high volume sampler (EcoTach HiVol 3000) was used. The filter medium for the PM trapping was polytetrafluoroethylene (ECO- 200010 100 × PTFE 200 × 250 mm Pallflex). The sampler used a gravimetric method to collect PM_{2.5} using a size selective inlet capable of trapping particles larger than 2.5 µm. The flow rate was maintained using a volumetric flow controller incorporating a variable speed drive, which corrected for water and pressure conditions to maintain a constant flow rate (Figure 3-3). The samplers were regularly maintained and calibrated to operate at a flow rate from 1.1 to 1.7 m³ min⁻¹ according to the EPA regulations [115]

Figure 3-2. PM₁₀ High volume sampler (photo taken during haze period)

Figure 3-3. a) PM_{2.5} high volume sampler including photos taken b) prior loading and after loading c)

Sampling was conducted usually once a week for each of the PAHs and PCBs. More extensive sampling was carried on only during the unforeseen environmental hazards, including Haze periods, in order to get more detailed data for studying its environmental impact.

3.3 Results and discussion

3.3.1 Air mass backward trajectory classification analysis

The origins of the air masses arriving at the sampling site during the sampling period were determined by constructing and analyzing backward air trajectories (Figure 3-5) using the 4.9 Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) developed by the National Oceanic and Atmospheric Administration (NOAA). [116, 117] Data used in the calculations were obtained from the National Centers for Environmental Prediction (NCEP) Global Data Assimilation System (GDAS, global, 2006-present). Backward air trajectories were generated at 4 starting times every 6 h during each sampling event for 96 h back in time with 500 m–agl (above ground level) ending level, which ensures that each trajectory starts in the atmospheric boundary level. [85, 118] The one-year sampling study includes 2 monsoon seasons (SW-Southwest, NE-Northeast) and 2 inter-monsoon periods (Table 3-1). Sampling data collected during the SW monsoon starting from June until late October showed a significant impact on Singapore's atmosphere especially in the period (September-October). During this time strong winds blew (partly terrestrial and oceanic in origin) through islands of southern Indonesia such as Lombok, Saba, Sumbawa, Java Sea, and southwestern Sumatra and Kalimantan, where vast peat and forest fires created a dense

smoke that was carried to Singapore causing hazardous ranges of AQI values (table 3-2).

Figure 3-4. Indonesia peat and forest fire (a) Haze in Singapore (b) Haze in Singapore
(c).[119]

Table 3-1. Singapore tropical climate information (Monsoon seasons)

<i>Classification</i>	<i>Duration</i>	<i>Wind direction</i>	<i>Rainfall</i>
Northeast Monsoon	December - late March	From land towards the see	Continuous heavy rain
Southwest Monsoon	Late May-Late October	From the sea towards the land	Isolated to scattered rain
Pre Southwest monsoon	March – Late May	Light and variable winds	Isolated showers with thunder
Pre Northeast Monsoon	October– November	Light and variable winds	Scattered showers with thunder

Table 3-2. AQI categorization reporting scheme. Resource:

<https://airnow.gov/index.cfm?action=aqibasics.aqi>

Air Quality Index (AQI) Values	Levels of Health Concern	Colors
0 to 50	Good	Green
51 to 100	Moderate	Yellow
101 to 150	Unhealthy for Sensitive Groups	Orange
151 to 200	Unhealthy	Red
201 to 300	Very Unhealthy	Purple
301 to 500	Hazardous	Maroon

Figure 3-5. Computed air mass backward trajectories arriving at the study site during May 2015 to May 2016 categorized in four types (a. Pre-SW; b. SW; c. Pre-NE; d. NE).

Diurnal variations in heights of mixing boundary layers are strongly dependent on wind speed, humidity and temperature. Since this study is conducted in an equatorial tropical region (low diurnal fluctuation in temperature) and during monsoon seasons (strong winds), the diurnal variation of layers mixing is smaller. Generally, during the day the sun's radiation warms the surface, and air masses start rising and mixing with the surrounding air, hence, the boundary layer is well mixed and reaches its deepest during this time. As a result, the dispersion of pollutants is high during this time. At night PBL is much shallower due to lower mixing of the atmospheric layers.[120]

Running a back trajectory, the starting height is the arriving altitude. Hence, the best and most common practice to determine the height when sampling 24h samples is to use the middle of the PBL. Since the PBL is ~1000 m, the most common practice is 500 m which ensures that each trajectory starts in the atmospheric boundary level. [116, 117]

3.3.2 Concentration trend and profiles of the PM₁₀ bound PAHs

Over the course of this study, one year monitoring of PM₁₀ bound PAHs was conducted to investigate concentration trends, molecular distribution, possible sources and health risk assessment. The PM₁₀ concentrations were found to vary from 32 to 323 $\mu\text{g m}^{-3}$. The higher concentrations were detected during the haze period (September-October) when large amounts of smoke were carried by strong southwest monsoon winds from the forest and peat fires in Indonesia. Results show that PM₁₀ concentrations on "normal" days were much lower, ranging from 32 to 70 $\mu\text{g m}^{-3}$ compared to the haze period (September-October) where PM₁₀ concentrations ranged between 72 $\mu\text{g m}^{-3}$ to 323 $\mu\text{g m}^{-3}$. In Singapore, the reported AQI levels are predominantly derived from the PM_{2.5} readings, thus our studies show that measured PM₁₀ concentrations are in strong correlation with the corresponding AQI values as indicated in Figure 3-6a. Furthermore, strong correlation is shown in Figure 3-6b between the total concentration of the PAHs and PM₁₀ concentration throughout the sampling period. Table 3-3a provides the minimum, the mean and the maximum concentrations of PM₁₀ bound 16 (USEPA) PAHs analyzed in 54 samples collected from May 2015 to May 2016 at the sampling site in Singapore. The results obtained in this study were also used to evaluate how biomass burning from Indonesian peat and forest fires impacted the USEPA 16 priority listed PAH concentrations in the atmosphere. The PM₁₀

bound PAH concentration varied from 0.68 ng m⁻³ to 3.07 ng m⁻³ with a median value of 1.83 ng m⁻³ (non-haze) and 1.07 ng m⁻³ to 5.97 ng m⁻³ with a median concentration of 2.45 ng m⁻³ (for the haze period from September to October 2015).

The more volatile and lighter PAHs (NAPH, ACY, ACP and FLR) were not detected because they mostly occur in the gas phase due to their high vapor pressures, especially at the relatively high ambient temperatures at the equator, which are observed throughout the year. This has also been reported in other studies in the region [57, 81, 97, 121-123].

Table 3-3. Mean concentration with minimum and maximum values of PM₁₀ bound PAHs during haze (n=40) and non-haze (n=14) periods and the total concentration of PAHs in Singapore atmosphere. nd. = not detected; n = the number of samples used for computing the statistical data.

No.	ng m ⁻³	Non-Haze period n=40			Haze Period n=14		
		Min.	Med.	Max.	Min.	Med.	Max.
	[PM ₁₀] µg/m ³	32	46.5	70	71	116	323
1	Naphthalene(NAP)	nd.	nd.	nd.	nd.	nd.	nd.
2	Acenaphthylene(ACY)	nd.	nd.	nd.	nd.	nd.	nd.
3	Acenaphthene(ACP)	nd.	nd.	nd.	nd.	nd.	nd.
4	Fluorene(FLR)	nd.	nd.	nd.	nd.	nd.	nd.
5	Phenanthrene(PHE)	0.05	0.12	0.20	0.13	0.26	0.44

Table 3-3. (Continued) Mean concentration with minimum and maximum values of PM₁₀ bound PAHs during haze (n=40) and non-haze (n=14) periods and the total concentration of PAHs in Singapore atmosphere. nd. = not detected; n = the number of samples used for computing the statistical data.

6	Anthracene(ANT)	0.01	0.02	0.04	0.02	0.03	0.07
7	Fluoranthene(FLT)	0.03	0.07	0.19	0.05	0.08	0.13
8	Pyrene(PYR)	0.03	0.09	0.16	0.07	0.11	0.23
9	Benzo(a)anthracene(BaA)	0.06	0.12	0.23	0.12	0.17	0.39
10	Chrysene(CYR)	0.08	0.12	0.23	0.003	0.16	0.41
11	Benzo(b)fluoranthene(BbF)	0.08	0.25	0.43	0.25	0.42	1.33
12	Benzo(k)fluoranthene(BkF)	0.03	0.14	0.28	0.08	0.18	0.31
13	Benzo(a)pyrene(BaP)	0.06	0.22	0.30	0.07	0.26	0.76
14	Indeno(1,2,3-cd)pyrene(IcP)	0.08	0.22	0.35	0.11	0.26	0.68
15	Dibenzo(a,h)anthracene(DhA)	0.10	0.21	0.28	0.04	0.22	0.42
16	Benzo(g,h,i)perylene(BgP)	0.06	0.22	0.34	0.15	0.30	0.82
	ΣPAHs	0.68	1.83	3.07	1.07	2.45	5.97

Figure 3-6. Temporal variations in a) PM₁₀ concentrations and Air Quality Index (AQI) and b) PM₁₀ concentrations and total PAHs concentration throughout annual sampling period.

As PAHs are formed during incomplete combustion and pyrolysis they cannot be used as exclusive indicators of biomass combustion. Nevertheless, the results in Tables 3-3 showed that the levels of PAHs associated with PM₁₀ during the high haze period were significantly higher compared to the regular days. The results indicate that atmospheric configuration in

Singapore was influenced by long-distance pyrogenic, biomass combustion processes occurring at that time in Indonesia (forest and peat fires).

3.3.3 PAHs molecular and ring size distribution

The PAHs in this study can be classified into groups by the number of aromatic rings: two rings (Naph), three rings (Acp, Acy, Phe, Ant, Flr), four rings (Pyr, Flt, Chry, BaA), five rings (BkF, BbF, Bap, DhA) and six rings (IcP, BgP). Figure 3-7 shows the percentage distribution of PAHs during hazy b) and non-hazy a) periods as well as molecular distribution of 12 detected PAHs throughout the complete sampling study. For both periods, the heavier 5 ring PAHs made up close to half of the total amount of PAHs. The middle molecular weight 4 ring species contributed around 20% and the small 3 ring species only around 10%. The reasons for such distribution of the PAHs [70% of heavier PAHs (5 and 6 rings) compared to the 30% of the lighter ones (3 and 4 rings), lies in higher vapour pressures of the lighter ones (e.g. Naph: 10^{-2} kPa). This causes the lighter PAHs to be extensively distributed in the atmosphere between the gas and particulate phases and more prone to degradation, especially in tropical environments, resulting in their inefficient trapping with GFF filters used in this study. [71, 124]

Figure 3-7. Ring number distribution of PM₁₀ bound PAHs during (a) non-haze and (b) haze sampling periods of PM₁₀ together with (c) a molecular distribution based on the total concentrations from collected samples during haze (14 samples) and regular (14 samples) days.

Our results have shown that the molecular distribution of PAHs was very similar for hazy and non-hazy conditions, suggesting that during the haze period only the atmospheric concentration of these species changed, without significantly affecting the PAH's molecular distribution. There are a few reasons affecting such phenomena. Firstly, biomass burning causes chemicals that are previously deposited into the vegetation being re-released into the atmosphere, hence affecting the specific source determination accuracy that are based on using a mean values of PAHs abundance. Furthermore, results in this

study showed that the major source contributor of PAHs in Singapore atmosphere during the normal episode days is fuel combustion (traffic) that is high temperature process as well as biomass burning, resulting in similar PAHs compounds released, hence leading to the similar molecular distribution. [35, 57, 85, 96, 122, 125]

In addition, ring size distribution needs to be used with caution because PAH profiles in sampling locations can be different from those in the sources' sites [126], since they can be altered due to the chemical reaction with other atmospheric pollutants, such as NO_x and O₃. [127] In addition, degradation that may occur during the sampling process can also modify the atmospheric PAHs levels and thus the ratios between PAHs. [127]

However, confirmation of these claims are observed in figure 3-7, where molecular distribution is plotted together with concentration abundances for all PAHs monitored, where even though distribution stays the same, concentration differences and impact of haze are clearly observable. Nevertheless, this also provides more confirmation that during regular days the main source of PAHs in Singapore comes from high temperature processes such as combustion of fuels in engines as previously reported in Singapore [85, 128] From a perspective of human health, the total concentration of PAHs were above the recommended guideline concentrations of 1 ng m⁻³ (USEPA) [41] throughout the hazy period and around this concentration for low-hazy conditions.

3.3.4 Seasonal variation and source apportionment

Singapore lies just north of the Equator near Latitude 1.5 deg N and Longitude 104 deg E. Due to its geographic position and maritime exposure its climate is almost uniform throughout all the year with a constant temperature, pressure, high humidity and abundant

rainfall. Singapore's climate consists of two main monsoon seasons: the Northeast Monsoon and the Southwest Monsoon season that are divided by two shorter inter-monsoon periods (Table 3-1) The monthly variations in the atmospheric total PAHs mean concentrations are plotted in the figure 3-8 and shows that the PAHs concentrations remain relatively constant throughout the year.

Figure 3-8. Seasonal variations of total of 16 atmospheric USEPA PAHs based on the total concentrations measured twice per month

The explanation for this consistency is due to Singapore being a small but well industrialized country with uniform tropical climate and narrow temperature and pressure variations throughout the year resulting in constant gas/particle partitioning of emitted PAHs. The significant increase in monthly mean total PAH value in September was likely influenced by the SW monsoon season when winds carried the dense smoke from the forest and peat fires in Sumatra and Kalimantan (Indonesia) over Singapore. In contrast to the haze period, there appeared to be a small decrease in the average concentration of PAHs

detected for the rainy months (November-January and March), which likely caused more PAHs to be washed out from the atmosphere. [90]

3.3.5 Source diagnostic ratios DRs

It has been reported that diagnostic ratio (DR) analyses have some limitations [109] such as intersource similarity as well as intrasource variability of different PAHs isomer ratios and particle/gas partitioning. This because PAHs are semi-volatile compounds and they tend to partition under different atmospheric conditions between gas/particle phases resulting in different composition of results. Furthermore, particle deposition and precipitation scavenging are listed as one of the possible limitations in performing DRs analysis. Nevertheless, they have been used extensively for source identification and apportionment of PAHs found in atmospheric matrices. [29, 31, 129-131] Calculations are based on comparing ratios of pairs of most frequently identified PAH isomers to characterize the origins of PAHs in ambient air. In this study, DRs were calculated to distinguish between two main sampling events (hazy vs. regular sampling days) covered in one year of monitoring. From the results in Figure 3-7c it could be seen that some PAH congeners (Phe, BaA, BbF, BaP, IcP, BgP) show large increases from non-haze to haze periods, while the other congeners show limited variation. Diagnostic ratios including those species (BbF/BkF, BaP/BgP, IcP/BgP, BaP/IcP, IcP/(IcP+BgP)) were chosen to investigate and assign the ratios to specific contributors of PAHs in PM₁₀ during the haze period. The most common and recently reported DRs of ANT/(ANT + PHE), FLT/(FLT + PYR), BaA/(BaA + CRY) and IcP/(IcP + BgP) were used to investigate the contributors of PAHs in Singapore's air during the regular sampling days. [128, 132, 133]

Figure 3-9 clearly illustrates how chosen DRs are affected by different concentrations of the haze, by sorting data into 4 different groups: $<50 \mu\text{g}/\text{m}^3 \text{PM}_{10}$; $50\text{-}100 \mu\text{g}/\text{m}^3 \text{PM}_{10}$; $100\text{-}200 \mu\text{g}/\text{m}^3 \text{PM}_{10}$; $200\text{-}300 \mu\text{g}/\text{m}^3 \text{PM}_{10}$. A strong trend was observed for BbF/BkF, BaP/BgP and IcP/BgP suggesting that these three DRs could be used as fingerprint DRs for biomass burning (peat and forest fires) even though BbF/BkF has not been previously reported. The most common DR used for identifying biomass burning source is IcP/(IcP + BgP) with a threshold of >0.5 . Our results for this DR during the regular days values were below 0.49 and raising proportionally with haze intensity to 0.59-0.62-0.70 as can be seen from Figure 3-9, and supporting that biomass burning in Indonesia affected the occurrence of PAHs in Singapore's ambient air.

Figure 3-9. Diagnostic ratio values of PAH congeners during the haze period computed for different levels of haze intensity.

The DRs for PAHs in Singapore's ambient air were calculated for source identification and apportionment during the "normal" (non-hazy) sampling days, with the results summarized in Table 3-4 using typical DR recommendations from the recent literature. Sampling site vicinity (main express highway and industrial, petrochemical complexes within 5 km range) proved to be main contributors of the PAHs by interpreting DRs such as FLT/(FLT + PYR) and ANT/(ANT + PHE) that are normally used to characterize the origin of the PAHs from pyrogenic or petrogenic sources. Previous studies [57, 132] indicated that the PAH source is pyrogenic in nature, and more specifically from burning gasoline and motor oil which is suggested by FLT/(FLT + PYR) ratio values. Furthermore, the claim that PAHs are majorly contributed from pyrogenic sources, for example: petroleum fuel incomplete combustion and vehicular exhaust emission is also supported from the BaP/BgP, ICP/(ICP + BgP) and BaA/(BaA + CHR) ratios listed in Table 3-4.

Table 3-4. Diagnostic ratios of the PAH isomers with their proposed standard values used in this study.

PAH Ratio	Value Range	Source	Results (non-haze)	Reference
ANT/(ANT+PHE)	<0.1	Petrogenic	0.23	(Pies et al., 2008)
	>0.1	Pyrogenic		(Jamhari et al., 2014)
FLT/ (FLT+PYR)	<0.4	Petrogenic	0.47	
	0.4-0.5	Fossil Fuel		(Kaur et al., 2013)
	>0.5	Grass, wood coal		(Jamhari et al., 2014)
BaA/ (BaA+CHR)	>0.5	Grass, wood, coal	0.5	
	0.2-0.35	Fresh particles		(Yunker et al., 2002)
	0.4-0.5	Traffic		(Samara et al., 2005)
IcP/ (Icp+BgP)	<0.2	Petrogenic	0.49	
	0.2-0.5	Petroleum		(Jamhari et al., 2014)
	>0.5	Grass, wood, coal		
BaP/BgP	<0.6	Non-traffic	1.09	(Jamhari et al., 2014)
	>0.6	Traffic		(Kaur et al., 2013)

3.3.6 Principal component analysis (PCA)

PCA is one of the most common used multivariate statistical technique to identify the major sources of air pollutants [36]. Analysis were conducted using a statistical software (IBM, SPSS 24.0) by the method of varimax rotated factor matrix, based on the orthogonal rotation criterion maximizing the variance of the squared elements in the column of a factor matrix. [134] Variables with similar characteristics are grouped into specific factors, which indicate the correlation between pollutant species. [30] The principal components that show the maximum percentage of total variance of the data set are used as factors. Loading determines the most representative PAHs compounds in each factor and generally a value > 0.5 is selected. However, these factors indicate more than one possible cause. The

significance of the factors impact are measured by % of initial and cumulative variance. In this study, each factor was associated with a source characterized by their(s) PAH marker(s). Factor loadings report derived from PCA analysis is showed in Table 3-5 for whole sampling campaign. Component 1 (factor 1) explained 51.77% of the total variance, with high loadings of PHE, BbF, BaP, IcP, DhA and BgP. Previous studies suggested that BbF, BkF, BaP, IcP, BgP and DhA are markers of vehicular such as diesel and gasoline combustion sources. Furthermore, high molecular weight PAHs, such as BaP, BkF, InP, BghiP were widely used as tracers for high temperature processes such as burning of gasoline and diesel or biomass combustion as previously explained in sections 3.2.3 and 3.3.5. Component 2 contributed only 13 % of the total variance. The most loaded PAHs were Ant and FLT, which are lower molecular weight PAHs. A high factor loading of lighter PAHs including ANT and FLT points to stationary emission sources such as steel and refinery industries. [29, 34, 135, 136]

Table 3-5. Factor loadings of PCA analysis including initial and cumulative variance %PC1 >0.75 and PC2 >0.7 factor loading limits for data extraction

<i>No.</i>	<i>ID.</i>	<i>PC Component 1</i>	<i>PC Component 2</i>
1	PHE	0.607	0.155
2	ANT	-0.236	0.714
3	FLT	0.180	0.716
4	PYR	0.744	0.320
5	BaA	0.742	0.397
6	CRY	0.626	0.374
7	BBF	0.955	-0.067
8	BkF	0.557	0.442
9	BaP	0.793	-0.191
10	IcP	0.885	0.105
11	DhA	0.785	0.409
12	BgP	0.837	-0.094
	Initial % of variance	51.770	13.091
	Cumulative %	51.770	64.861

Figure 3-10. Scree plot showing eigenvalues for all 12 components (variables) analyzed with significant variance for 2 components statistically analyzed further.

3.3.7 PM_{10} bound PAHs health risk assessment analysis

USEPA and the International Agency for Research on Cancer (IARC) have classified some of the PAHs as carcinogenic compounds. People can be exposed to PAHs via ingestion, dermal exposure and inhalation (USEPA, 1989). However, the health risks of PAHs in this study were performed based on human exposure through inhalation and its correlation between the concentration in air and their epidemiological effects. There are three approaches that exist to evaluate carcinogenic risk assessment of PAHs and all three were evaluated in this study:

- Use of toxic equivalency factor (TEFs)
- Use of BaP as a surrogate

- Comparative potency of mixtures using BaP_{eq}

There are 16 EPA classified PAHs that are regularly measured and are considered to be toxic, and out of these 16 PAHs, BaP is the most toxic and hence a compound that is the most widely used as a surrogate for assessing the risk from PAHs. [137] To account for all the PAHs, a toxic equivalency factor (TEF) for each of the PAHs relative to BaP can be used to compare their relative toxicity. This can be achieved by summing each of the contributions of the individual components to achieve a BaP equivalent concentration of the PAHs and analysed using equations 1 and 2. [43]

$$(1) \quad B[a]P_{eq} = 0.001(Phe + Fluo + Pyr) + 0.01(Ant + B[g,h,i]P + Chry) + 0.1(B[a]A + B[b]F + B[k]F + Ind) + B[a]P + D[a,h]A$$

$$(2) \quad \sum B[a]P_{eq} = \sum_{i=1}^n C_i \times TEF_i$$

In most countries, the maximum acceptable yearly concentration of BaP in the atmosphere is in a range of 0.7 ng m⁻³ - 1.0 ng m⁻³. [138] Since BaP is not the only carcinogen, a mixture of PAHs are included in the calculations, although they do not have the same carcinogen properties. Thus, the establishment of the TEFs for all the PAHs provides more accurate testing for the carcinogenic properties of the PAHs mixtures.

Table 3-6 Concentration of ambient PAHs and their relative toxicity comparison to BaP_{eq}

No.	Compound	TEFs	Ambient ng m ⁻³	BaP _{eq} Pg m ⁻³	Ambient (Haze) ng m ⁻³	BaP _{eq} (Haze) Pg m ⁻³
1	NAP	0.001	nd.	nd.	nd.	nd.
2	ACY	0.001	nd.	nd.	nd.	nd.
3	ACP	0.001	nd.	nd.	nd.	nd.
4	FLR	0.001	nd.	nd.	nd.	nd.
5	PHE	0.001	0.20	0.2	0.44	0.44
6	ANT	0.01	0.04	0.4	0.07	0.7
7	FLT	0.001	0.19	0.19	0.13	0.13
8	PYR	0.001	0.16	0.16	0.23	0.23
9	BaA	0.1	0.23	23	0.39	39
10	CHY	0.01	0.23	2.3	0.41	4.1
11	BbF	0.1	0.43	43	1.33	133
12	BkF	0.1	0.28	28	0.31	31
13	BaP	1	0.30	300	0.76	760
14	IcP	0.1	0.35	35	0.68	68
15	DhA	1	0.28	280	0.42	420
16	BgP	0.01	0.34	3.4	0.82	8.2
	Total		3.07	715.65	5.97	1464.80

The calculations indicate that a potential risk based on BaP_{eq} is in the range of 0.715 ng m⁻³ to 1.465 ng m⁻³, showing that during the haze period the BaP_{eq} concentration is above the allowed limit of 1.0 ng m⁻³, while during the normal days is within an acceptable range. When inhaled, particulate matter has been shown to cause serious health effects including lung cancer (USEPA, 2103) [1]. Health risk assessment can be achieved by estimating the lifetime average daily dose (LADD) calculated using equations 3 and 4. The calculations are based on the intake of a chemical per body weight per day and a BaPs corresponding incremental lifetime cancer risk (ILCR), which is shown to be suitable when assessing chemicals absorbed into the body over long periods [57, 139].

$$(3) \quad LADD = C \times IR \times ED \times EF / (BW \times ALT)$$

$$(4) \quad ILCR = LADD \times CSF$$

In equation 3, C is the PAH concentration in air particles (ng m^{-3}), IR is the air inhalation rate, ED is the lifetime exposure duration (years), EF is the exposure factor (days per year) that was set at 349 for non-hazy days and 16 for hazy days (where the AQI was above 100), BW is the body weight (kg) and ALT is the average lifetime for carcinogens (days). CSF is the cancer slope factor ($\text{per mg kg}^{-1} \text{ day}^{-1}$) in equation 4. Parameters used for calculations are shown in Table 3-7 and the results given in Table 3-8. [43, 57]

The value for $ILCR$ under hazy and non-hazy conditions can be found in Table 4 for a range of different age groups. The acceptable $ILCR$ range indicated by the USEPA is between 10^{-6} and 10^{-4} , meaning that complete safety was denoted with an $ILCR$ value 10^{-6} or less and potentially high risk was estimated by an $ILCR$ value greater than 10^{-4} . The obtained $ILCR$ values during the sampling period indicate that the daily inhalation dose of particle bound PAHs and cancer risk to human adults and children residing in the sampling areas are mostly lower than the minimum acceptable levels.

Table 3-7. Parameters used for calculating LADD value

Parameter	Unit	Infant 0-1year	Toddler 1-6 years	Children 6-12 years	Adolescent 12-18 years	Adult 18-30 years	Adult 18-80 years
(IR)	m ³ /day	5.4	9	12	15.7	15.7	15.7
(ED)	years	1	5	6	6	12	52
(EF)	days/year	349 (16 for the haze period, >100 AQI)					
(BW)	kg	7	15	32	38	66	66
(ALT)	days	29200					

However, these ILCR values obtained are slightly higher compared to other studies in the region [63, 140] and we see an increased risk during haze conditions. The highest estimated ILCR value is 3.95×10^{-7} for adult residents (18-80 years) obtained during the haze episode.

There have been some concerns if health risk assessments from PAHs absorbed on PM results are fully representative of the risks since gas phase PAHs are not taken into account in calculations. However, it has been reported that more than 90% of BaP is absorbed onto PM as well as all of the heavier PAHs that are monitored in this study, which are also the most toxic compounds [99, 100, 141].

Table 3-8. Health risk assessment for total BaP_{eq} for different age groups.

<i>Non-Haze</i>	<i>Units</i>	<i>Infant</i>	<i>Toddler</i>	<i>Children</i>	<i>Adolescent</i>	<i>Adult</i>	<i>Adult</i>
LADD	LADD mg kg ⁻¹ 1 day ⁻¹	4.66E-09	1.81E-08	1.36E-08	1.50E-08	1.72E-08	7.47E-08
CSF	CSF mg kg ⁻¹ day ⁻¹	7.30	7.30	7.30	7.30	7.30	7.30
ILCR	ILCR	3.40E-08	1.32E-07	9.92E-08	1.09E-07	1.26E-07	5.46E-07
<i>Haze</i>	<i>Units</i>	<i>Infant</i>	<i>Toddler</i>	<i>Children</i>	<i>Adolescent</i>	<i>Adult</i>	<i>Adult</i>
LADD	LADD mg kg ⁻¹ 1 day ⁻¹	3.38E-10	1.31E-09	9.86E-10	1.08E-09	1.25E-09	5.42E-09
CSF	CSF mg kg ⁻¹ day ⁻¹	7.3	7.3	7.3	7.3	7.3	7.3
ILCR	ILCR	2.46E-09	9.6E-09	7.2E-09	7.93E-09	9.13E-09	3.95E-07

3.4. Concentration trends and temporal variation profiles of the PM_{2.5} bound PCBs

The sampling campaign was conducted for a 6 month period (April 2016 to September 2016), collecting PM_{2.5} for PCBs analysis with a total of 24 samples collected to investigate concentration trends profile in Singapore's coastal environment. Sampling frequency was usually one sample per week. In order to reach method detection limits, 48h sampling

intervals were conducted. Throughout the sampling period no significant alternation in $\text{PM}_{2.5}$ concentrations were observed. The $\text{PM}_{2.5}$ concentration varied between $6.31 \mu\text{g m}^{-3}$ to $22.31 \mu\text{g m}^{-3}$ with a median value of $12.27 \mu\text{g m}^{-3}$. Out of 19 PCBs monitored 10 were detected with a 100 % frequency of detection. Other 9 PCBs were not detected throughout all of the study. Table 3-9 summarizes concentration levels of the detected PCBs for the complete sampling campaign.

Table 3-9. Minimum, median and maximum concentrations of $\text{PM}_{2.5}$ bound PCBs and the total concentration of PCBs in Singapore's atmosphere. Results are based on complete 6 months sampling study (24 samples)

No.	PCB ($\mu\text{g m}^{-3}$) (IUPAC)	Minimum	Median	Maximum
1	$\text{PM}_{2.5} \mu\text{g/m}^3$	6.31	12.27	22.31
2	18	1.10	1.71	2.99
3	31	0.18	0.89	1.55
4	138	0.13	0.53	1.51
5	101	0.05	0.33	1.60
6	151	0.18	0.54	1.09
7	153	0.45	1.07	1.83
8	170	0.58	1.21	1.90
9	180	0.57	1.13	1.80
10	183	0.89	1.84	3.21
11	187	1.08	1.78	2.69
	Σ PCBs	5.21	11.01	20.17

The PM_{2.5} bound PCBs concentrations varied from 5.21 pg m⁻³ to 20.17 pg m⁻³ with a median value of 11.01 pg m⁻³. The occurrence of PCBs studied in other Asian countries varied between tens to a few hundreds of picograms per cubic meter, with values in the range of 21–336, 7–247, and 12–84 pg m⁻³, for China, Japan and South Korea, respectively.[61] According to the chronological data on PCBs studied for the Java Sea (36 pg m⁻³), Celebes Sea (22 pg m⁻³) and the Strait of Malacca (30 pg m⁻³) [50], when compared to this study, the PCBs occurrence in the region did not undergo significant changes over the last 15 years. Figure 3-12 plots total mean concentrations of PCBs for each month throughout the complete sampling campaign of 6 months.

Figure 3-12. Temporal variations of total of 14 atmospheric PCBs collected throughout six months sampling campaign based on total concentration measured 4 times a month.

Comparing relative abundances of PCBs in different months, close correlations of abundances compared to weather conditions such as rainfall and temperature are observed. April and September were the months with highest precipitation and lowest temperature

amongst other months studied, thus the total summation of the PCBs concentrations (4 samples per month) are almost half than the concentrations in Jun, July and August that are dry months with highest temperatures. This observation implies that higher temperatures might fasten the reemission of PCBs into the atmosphere because these compounds have been accumulated in Singapore for decades including reemission from soil, sediment and vegetation. Furthermore, atmospheric deposition (wet precipitation) is one of the reasons for lower abundances of the PCBs during raining periods (April and September).

3.4.1 Molecular composition and profiles of PM_{2.5} bound PCBs

The PCBs in this study can be classified into groups by the levels of chlorination of the biphenyl group: three chlorines (18 and 31), six chlorines (138, 101, 151 and 153) and seven chlorines (170, 180, 183 and 187). In this study PCBs comprising of 2, 4 and 5 chlorine atoms were not detected. The IUPAC numbering nomenclature pattern for PCBs identification was used in description. Figure 3-13 shows the percentage distribution of PCBs during complete 6 months sampling period.

Figure 3-13. Percentage molecular distribution of the PCBs molecular composition regarding a number of chlorine atoms attached to biphenyl group.

The most dominant PCB congeners were the most saturated ones with a 7 chlorine atoms attached partitioning in 54% to the total PCBs monitored followed by 6 and 3 chlorinated species with a 22 % and 24 % partitioning, respectively.

Figure 3-14 shows abundances for each PCB detected, based on sum of the mean values sampled throughout all 6 months sampling campaign giving further information on molecular composition of the PCBs detected and monitored.

Figure 3-14. Molecular composition of the all atmospheric PCBs sampled based on average concentration for each PCB congener throughout whole sampling period of 6 months

Figure 3-14 shows higher values for more chlorinated species accounting for 76 % of the total PCBs concentration while lower chlorinated PCBs accounted for 24 % respectively. The reason for this distribution is that the lower the level of chlorination, the PCBs have higher K_{OA} (octanol-air partition coefficient) and hence partition more towards the gas phase, while more chlorinated PCB congeners have lower vapor pressures and a tend to be more easily adsorbed onto particulate matter.[85, 142, 143]

A possible main source of PCBs in Singapore's atmosphere is electronic waste including electronic waste recycling activities (incineration) and open municipal waste discarding sites.[62, 144] The main waste incineration plant is located on Jurong Island and is in close vicinity to the sampling site as previously described in the section 3.2.1 (Sampling Site).

Although there is expected to be lower impact on the abundance of PCBs coming from a house dust, it is a medium considered as a basin of pollutants transferring from consumer

electronics, consistent with their principal use in industrial applications and old electrical products rather than in electronics currently in use.[59] Furthermore, a potentially significant source of PCBs in Singapore's coastal environment might be inadequate handling during ship processing activities (also suggested to as ship breaking or ship wreckage) because Singapore is one of the world's most busy and developed marine centers and the main industry in Singapore. Older ships contain significant amounts of PCBs in paints, transformer and capacitor oils and sealants. [59]

3.4.2 Source factor assessment of airborne PCBs in Singapore coastal environment using Principal component statistical analysis (PCA)

PCA is a statistical analysis mainly used in environmental sciences for source apportionment studies. [29, 34, 49, 59] Detailed description of PCA analysis was previously described in the section 3.3.6. Analysis were conducted to try to elucidate the probable source factors of PCBs in Singapore's atmosphere. The datasets of PCB congeners monitored were each standardized to their percentage compositions and then subjected to PCA in normalized varimax rotation mode. Only the major principal components (PCs) were extracted, with significant clusters defined by factor loading coefficients > 0.7 . Three major principal components – PC1 and PC2 – were extracted as affecting PCBs emissions in Singapore.

Table 3-10. Extraction summary of rotation sums of squared loadings with cumulative and variance % values for 2 extracted Principal components

Component	Cumulative %	Total	% of Variance	Cumulative %
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1	59.477	5.948	59.477	59.477
2	71.777	1.230	12.300	71.777

Kaiser-Meyer-Olkin Measure (KMO) of sampling adequacy statistics was performed to assess how suited data is for factor analysis. The test measures sampling adequacy for each variable in the model and for the complete model. The statistic is a measure of the proportion of variance among variables that might be common variance. The lower the proportion, the more suited the data is to Factor Analysis. KMO returns values between 0 and 1. A rule of thumb for interpreting the statistic:[145]

- 0.00 to 0.49 unacceptable.
- 0.50 to 0.59 miserable.
- 0.60 to 0.69 mediocre.
- 0.70 to 0.79 middling.
- 0.80 to 0.89 meritorious.
- 0.90 to 1.00 marvelous.

Our results showed KMO value of 0.8 that confirms data validity for performing PCA factor analysis. Also a scree plot of factor loading coefficients is shown in figure 3-15 where it is shown that out of 10 components only 2 passed the proposed limit of loading factor > 1 .

Figure 3-15. Scree plot of 10 components examined

A scree plot shows the eigenvalues on the y-axis and the number of factors on the x-axis. It always displays a downward curve. The point where the slope of the curve is clearly leveling off (the “elbow”) indicates the number of factors that should be generated by the analysis. Running a factor analysis is to reduce the large number of variables that describe a complex concept such as large sampling data to a few interpretable latent variables (=factor). In other words, we would like to find a smaller number of interpretable factors that explain the maximum amount variability in the data, hence to extract most prominent PCBs congeners out of the mixture.[145]

Table 3-11. Summary of the PCA factor loading rotated component matrix for all 14 monitored PCBs with significant clusters defined by factor loading coefficients > 0.7

(bolded numbers represents high loading factors)

PCBs		Extracted components	
No. /(IUPAC)		1	2
1	18	.402	.138
2	31	.832	-.204
3	138	.197	.815
4	101	.675	-.228
5	151	.848	.422
6	153	.931	-.070
7	170	.757	-.346
8	180	.891	.176
9	183	.915	.193
10	187	.900	-.285

PC1 correlated highly with PCBs 31, 151, 153, 170, 180, 183 and 187, indicating emissions from electronic waste [62] and possible ship-dismantling activities [146]; PCBs 138 correlated closely with PC2, suggesting possible uses as paint and plastic additives.[147]

3.5 Conclusion

Regular monitoring of the SVOCs including 16 PAHs and 19 PCBs was performed for a one year period between May 2015 and May 2016 collecting PM₁₀ particulate matter and six months sampling of PM_{2.5} from April 2016 to September 2016, respectively. A total of 78 samples were acquired and the SVOC concentration measurements were evaluated using different statistical calculations and risk assessment analysis. A total of 78 particulate samples collected include 2 different sampling campaigns.

1. One year monitoring of PM₁₀ bound PAHs occurrence (54 samples collected).
2. Six months monitoring of PM_{2.5} bound PCBs occurrence (24 samples collected).

The possible effects of environmental conditions on the fate of atmospheric SVOCs were accounted and the impact of certain SVOC concentrations on public health was determined. Diagnostic ratio analysis (DRs), correlation regressions and principal component analysis (PCA) were carried out to determine the source profiles and concentration proportions associated to each source. By observing the PAHs molecular distributions and comparing two sets of data (haze and non-haze), significant increases were observed for the Phe, BaA, BbF, BaP, IcP, BgP congeners during the haze period. In addition, DR analysis and PCA were conducted to identify sources with the results showing dominance (with significant level of confidence) of heavier PAHs originating from high temperature processes including petroleum and diesel combustion.

Comparing to the literature review on PAHs abundances in atmosphere, Singapore has some of the lowest values of airborne PAHs, likely due to strict emission regulations for both traffic and industry sectors. In spite of this observation, the main problem for Singapore is trans-boundary pollution when the PM₁₀ concentrations increased from a

typical average reading of approximately 25 $\mu\text{g}/\text{m}^3$ up to a concentration reaching over 300 $\mu\text{g}/\text{m}^3$ during the high haze events, while PAH concentrations approximately doubled.

A health risk assessment was performed following the USEPA guidelines. The BaP_{eq} values for the haze dataset were slightly above the allowed concentration threshold and double the values calculated for the normal sampling days. However, the estimated incremental life-time cancer risk (ILCR) from exposure to airborne BaP_{eq} is negligible for both haze and normal sampling data. This suggests a low carcinogenic risk to human adults and children residing in the sampling areas in terms of exposure to PM bound PAHs.

Comparing to the PAHs that showed strong correlation with the PM abundances, a six months study on PCBs bounded to $\text{PM}_{2.5}$ showed very low correlation with the $\text{PM}_{2.5}$ concentration patterns, but strong correlation with a weather conditions including precipitation and temperature levels. Furthermore, regarding the literature review reports on airborne PCBs in the region, the present results showed there were not significant changes in the last 15 years. PCA analysis of factor loadings for every component extracted and compared to the work previously conducted in neighboring countries suggested possible contribution of the emissions from electronic waste (incineration plant in Tuas) [62] and ship-dismantling activities [146].

The present studies have been focused mainly on various fractions of PM including characterization of the physio-chemical composition and long-term monitoring. The future work that could improve these findings is to develop a new analytical method for qualification and quantification analysis of the SVOCs occurring in a gas phase to obtain a fully picture of these persistent pollutants in Singapore's atmosphere.

The following chapter is a study conducted for chemical analysis of the same SVOCs in a

region of lower Himalayas in Bhutan, performed on aqueous samples (glaciers, spring water, pipelines, lakes) to obtain a wider understanding of SVOCs occurrence in different environmental matrices in different climate regions including tropical area of SEA and cooler region of Himalayas.

Chapter 4. SPE-GC-MS analysis of the SVOCs in different water samples collected in lower Himalayas in the Trashigang District in Bhutan

4.1 Introduction

Alleviation of the poverty and improving of the wellbeing are two main goals for most of the South Asian countries. However, every nation has their own strategies, means and developing plans to achieve these objectives. Since 1960s, modernization of Bhutan started to rise after borders to the outside world were opened and self-imposed isolation terminated. The economy started to slowly rise with establishment of basic infrastructure developments such as: power, telecommunications and road transport. Over the past 50 years of being a free non-isolated economy, Bhutan has many developing opportunities. [148-150] Transition from the non-monetized traditional approach to wage based exchange economy occurred in 1981. [151] Agriculture, livestock and forestry are three main sectors that 80% of the Bhutanese population depends on for their livelihood. [152] Managing water sources and water quality in Bhutan is one of the most important keys in sustaining agriculture, forestry and livestock as well as providing s safe drinking water supply for people. The main source of electricity comes from hydropower since Bhutan is rich in river systems. Bhutan has four major river systems (the Ammochu, the Wangchu, the Sankosh, and the Mansa) with their estimated total length being about 7200km [153] with enormous potential for hydropower because of drops of height from 7000 to 100 m. Up to date, there are no specific policies and laws concerning the use of water resources in Bhutan.

However, a national water policy currently is being formulated by the Ministry of Agriculture.[154] In the last few decades, due to increasing industrialization and low regulatory management of the environmental, there has been a deterioration of the water quality. Non-monitored use of pesticides, herbicides in agriculture, land clearing activities to raise fields for cattle and crops as well as mining activities are one of the main sources that lead to water pollution with a main focus on drinking water quality. Streams, springs and rivers are the major sources of the supply of drinking water in Bhutan. In developing countries such as Bhutan, there are very pronounced differences in safe drinking water availability to people, that depends on their economic status. Wealthier households in urban areas are using water from the pipeline systems while poor households in rural areas are using drinking water from the various self-made wells connected to the various springs in their vicinity. [155]

There are many cases of water poisoning in rural areas due to uncontrolled and unregulated water supply despite there being several policies, guidelines and regulations, namely: the Environmental standard (2010), the Rural Water Supply Scheme policy, the Water Act of Bhutan (2011), the Water Regulation and watershed management guidelines (2014), Bhutan Drinking Water Quality Standard (2016), enacted to ensure the quality of drinking water and sustainability of the water sources. Very common water poisoning, especially in rural areas suggests that the quality of drinking water in Bhutan is of concern. [150, 155]

Semi-volatile organic compounds such as PAHs, PCBs, OCPs are some of the most dangerous water pollutants even though they are usually found in trace levels (ppb-ppt), due to their carcinogenic and mutagenic potential and tendency to accumulate in water and the human body. In the last two decades the discovery of the “grasshopper effect” model

has confirmed that POPs can move from the warmer to polar regions through the 3 mechanisms: repeated-evaporation, atmospheric transport, and deposition.[156-158] Polar regions and high mountains such as Himalayas are increasingly important for analytical chemists to investigate the POPs including PAHs, PCBs and pesticides because the Himalayas are the main source of fresh water for the most populated countries in the world (India and China) and there has been only a few studies on the occurrence of these compounds in such regions. However, it has also been shown that high mountains can act as condensation and accumulation sites for the SVOCs [159] thus, mountain glaciers are important sites used for studying historical trends of the SVOCs. [40, 160-162] It has been reported that the main contributors of the SVOCs in fresh water systems are melting glaciers that also effect water downstream quality by 50–97%.[146]

SPE pre-concentration and cleaning steps in combination with LC-MS and GC-MS are the most common methodologies for analysis of the SVOCs in water matrices that allows the detection of trace elements such as PAHs, PCBs and OCPs. The SPE pre-concentration procedure has been successfully used to extract a wide range of trace level SVOCs from different environmental matrices (particulate matter, soil, sediment and water) including PAHs, PCBs and OCPs. [59, 163-166] In this chapter, SPE pre-concentration of the organic contaminants will be discussed as well as the occurrence of the PAHs and OCPs in the region of the Himalayas in different water matrices, supplemented with a detailed literature review related to this topic. In addition, the latest analytical developments of the SPE-GC-MS system for screening SVOCs will be reviewed.

4.2 Organochlorine Pesticides (OCPs): physicochemical properties, environmental occurrence and health impact

Organochlorine pesticides (OCPs) are an important group of environmentally persistent organic contaminants with varied toxicity that are classified together according to their chemical-related structures. They are chlorinated compounds that have two or more single or fused aromatic rings. This ubiquitous group of OCPs includes (1) compounds of cyclodiene structure such as aldrin, dieldrin, endrin, heptachlor, endosulfan, and chlordane, (2) halogenated aromatic compounds such as DDT, methoxychlor, (3) cycloparaffins such as hexachlorocyclohexane (HCH). OCPs have a wide variety of physicochemical properties for individual compounds though they are similar in terms of low aqueous solubility and low reactivity to the surroundings with the exception of when in contact with strong alkali. OCPs are primarily found in solid phase at prevailing ambient temperature.[167, 168]. OCPs can be found in soil or aquatic environments primarily from agricultural through rainfall or runoff, erosion and infiltration processes and transported all over different parts of the world through the water cycle. (Figure 4-1) [169, 170] They are endocrine disrupters in wildlife and humans as they have been shown to cause carcinogenic, mutagenic, neurological and even teratogenic effects.

Figure 4-1. Environmental cycle of the pesticides

Prolonged exposure to OCPs will have serious repercussions on health, which include breast cancer, abnormal sperm counts, birth defects, immunity dysfunctionality, cognitive impairment, Parkinson's disease, respiratory illness and behavioral changes. The various toxicity characteristics of OCPs, coupled with their perpetual and extensive distribution has sparked a concern over the water quality around the world. [171, 172].

In this study, 23 OCPs were monitored in 28 different aqueous samples collected from the various springs, dwells and pipelines in lower Himalayas in the Trashigang District in Bhutan. List of target 23 OCP analytes together with the individual compounds molecular formulas and molar masses are presented in the table 4-1.

Table 4-1. List of target OCPs including molecular formulas and molar masses of the every OCP compound listed accordingly.

No.	OCPs	Chemical Formula	Molar Mass (g/mol)
1	Oxychlordane Isomer	C ₁₀ H ₄ Cl ₈ O	423.8
2	δ-hexachlorocyclohexane	C ₆ H ₆ Cl ₆	290.8
3	Pentachloroanisole	C ₇ H ₃ Cl ₅ O	280.4
4	α-hexachlorocyclohexane	C ₆ H ₆ Cl ₆	290.8
5	β-hexachlorocyclohexane	C ₆ H ₆ Cl ₆	290.8
6	γ-hexachlorocyclohexane	C ₆ H ₆ Cl ₆	290.8
7	Heptachlor	C ₁₀ H ₅ Cl ₇	373.3
8	Aldrin	C ₁₂ H ₈ Cl ₆	364.9
9	Endosulfan	C ₉ H ₆ Cl ₆ O ₃ S	406.9
10	Heptachlor epoxide	C ₁₀ H ₅ Cl ₇ O	389.3
11	γ -Chlordane	C ₁₀ H ₆ Cl ₈	409.8
12	α -Chlordane	C ₁₀ H ₆ Cl ₈	409.8
13	p p'-DDE	C ₁₈ H ₈ Cl ₄	318
14	Dieldrin	C ₁₂ H ₈ Cl ₆ O	380.9
15	Endrin	C ₁₂ H ₈ Cl ₆ O	380.9
16	Endosulfan II	C ₉ H ₆ Cl ₆ O ₃ S	406.9
17	p p'-DDD	C ₁₈ H ₁₀ Cl ₄	320
18	cis-Nonachlor	C ₁₀ H ₅ Cl ₉	444.2
19	Endrin aldehyde	C ₁₂ H ₈ Cl ₆ O	380.9
20	Endosulfan I	C ₉ H ₆ Cl ₆ O ₃ S	406.9
21	p p'-DDT	C ₁₈ H ₉ Cl ₅	354.5
22	Endrin ketone	C ₁₂ H ₈ Cl ₆ O	380.9
23	Methoxychlor	C ₁₆ H ₁₅ Cl ₃ O ₂	345.7

4.3 PAHs: physicochemical properties, environmental occurrence and health impact

Detailed description of the physico chemical properties, health effects, environmental cycle and regulations of the PAHs is described in detail in the previous section 1.3.

4.4 New trends in SVOC analysis using SPE-GC-MS

SVOCs also known as persistent organic contaminants including PAHs, PCBs, pesticides, dioxins are the most widespread environmental pollutants that are found in all the matrices (water, soil, sediment, water, glaciers, aerosols). As SVOCs are classified as endocrine disruptive compounds with carcinogenic and mutagenic properties and their tendency to accumulate in living organisms, research about developing new improved analytical methodologies for qualification and quantification of these compounds in complicated matrices is of the top priority in environmental sciences. [187-189]

The major problem when performing direct GC or LC analysis of SVOCs is complexity of the sample and low concentration that these compounds usually occur in the environment. Therefore, sample pre-concentration steps are required prior to further instrumental analysis to reach detection limits. To date, many different sample pre-concentration techniques have been developed for the enrichment and extraction of the SVOCs in complex environmental matrices.[185, 190] Techniques developed by now are: Solid-phase extraction (SPE) [191], liquid–liquid extraction (LLE) [192], microwave-assisted extraction (MAE) [193], dispersive liquid–liquid micro extraction (DLLME) [194], ultrasonic extraction (USE) [195], liquid-phase micro extraction (LPME) [196] and solid-

phase micro extraction (SPME). [197] The LLE extraction procedure was first developed, but it had drawbacks as large solvent waste generation and time consuming. SPE brought revolution in sample preparation procedures as simple, selective, effective, low solvent waste generation and high enrichment factors. Since then, many different sorbent materials for SPE packing have been developed and tested and it is still ongoing and popular research area.

The most recent study was performed by the Lei Wang research group [185] on developing multi walled carbon nanotubes (MWCNTs) as a sorbent material for SPE. MWCNTs are very popular in analytical chemistry due to their outstanding properties such as large surface area, high porosity and lightweight. Performance of the carbon nano tubes was investigated for the first time as a sorbent material for the extraction of the PCBs. GC-MS was employed for quantification analysis. Results showed competitive results compared to other sorbent materials: low limits of detection ($0.72 - 1.98 \text{ ng L}^{-1}$), wide range of linearity ($10\text{--}1000 \text{ ng L}^{-1}$) and good repeatability ($2.69\text{--}6.85\%$, $n = 5$). Nevertheless, under optimized conditions, CNT materials showed higher extraction performance than other adsorbent materials. Experiments were conducted on water samples with recoveries of $81.1\text{--}119.1\%$ showing that CNT materials are suitable for analysis of the POPs such as PCBs for trace level analysis. [185]

In recent years, there have been many new advances in developing magnetic solid-phase extraction (MSPE) and functionalized magnetic adsorbents that have been utilized for the extraction of POPs including magnetic graphene composite, MWCNT, palpitane and oleate coated magnetic nano-particles and Fe_3O_4 chitosan-poly(m-phenylenediamine).[198-202]

However, the complexity of the synthesis for most of the materials is a drawback from routine usage.

Yu-Han Fan and coworkers [190] developed hexadecyl-functionalized magnetic core-shell microspheres ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-C16}$) successfully prepared by a one-pot sol-gel method and used for magnetic solid-phase extraction of polychlorinated biphenyls (PCBs) in environmental water samples. Gas chromatography-triple quadrupole mass spectrometry (GC-MSMS) was used to evaluate the MSPE extraction performance. The study showed competitive results compared to other extraction materials. A good linearity range of 1–100 ng L^{-1} with correlation coefficients (R^2) of 0.9989–0.9993. Limits of detection (LODs) and limits of quantification (LOQs) were in the range 0.14–0.27 and 0.39–0.91 ng L^{-1} , respectively. The absolute recoveries of PCBs in spiked real water samples were in the range of 75.17 to 101.20%.

Ednei Primel et al. [203] developed and evaluated a method for pesticide extraction from water samples using vortex-assisted Matrix Solid Phase Dispersion (MSPD) by using GC-MS to evaluate performance of the extraction procedure. Recoveries ranged from 70 to 120% with RSD below 20% for all analytes. Limits of quantification (LOQ) of the method ranged from 5 to 500 mg kg^{-1} whereas linearity of the calibration curves showed correlation coefficients above 0.997. Method showed advantages over other extraction methods in speed, simplicity and low-cost material.

José A. López and coworkers [204] developed a solvent bar micro-extraction (SBME) procedure for extraction of the 16 EPA listed PAHs from seawater. Extraction was conducted using hexane as a solvent. Enrichment factors from 45 to 163 were obtained after 60 min at a stirring rate of 500 rpm in the sample. The limits of detection were in the

range from 0.21 to 0.82 ng L⁻¹. The method showed a linear response up to 500 µg L⁻¹, and the average relative standard deviation for seawater samples spiked with 5 ng L⁻¹ PAHs was 11.6%.

4.5 SVOC profiles and occurrence in Himalayas and polar regions

As SVOCs such as PAHs, PCBs, pesticides are a class of persistent organic chemicals that can migrate long distances via atmospheric processes of repeated-evaporation, atmospheric transport and deposition they can be found in the cleanest environments such as high-altitude mountains and polar regions.[205] These environmental sites are gaining attention in recent years because these cold environments are able to accumulate POPs by condensation of the semi volatile pollutants. As such, glaciers can be analyzed as POPs contributors in the fresh water systems (melting glacier supplies 50–97% of the organochlorine inputs to the water system downstream) and can be used as “natural archives” for studying historical trends of pollution.[160]

Xiaoping Wang's research group [206] published a work on analyzing POPs deposition in ice cores from Dasuopu Glacier in Mt. Xixiabangma, central Himalayas. 28 different PCBs were detected in a range of 0.09–0.3 ng/l. Concentrations of hexachlorobenzene (HCB) ranged from 0.04 to 0.07 ng/l, and total DDTs were in the range of 0.15–0.3 ng/l. Total glacier PAHs were below 26 ng/l. PCBs did not show a variation in occurrence in different seasons while all the target PAHs showed higher values in summer periods.

The same research group [39] studied the occurrence of OCPs and PAHs in Himalayan spruce needle samples from Zhangmu–Nyalam region (central-Himalayas) and the altitudinal gradient of these pollutants was investigated. Total HCHs and DDTs

concentration in needles were in the range of 1.3–2.9 ng g⁻¹ dry weight and 1.7–11 ng g⁻¹ which were lower than concentrations reported in spruce needles from the Alps. Fluorene, phenanthrene and acenaphthene were abundant PAHs found in all the spruce needle samples while total PAHs were not below 600 ng g⁻¹ levels

Yoon-Seok Chang and coworkers [207] performed a case study on monitoring levels of OCPs and PCBs in a high-altitude mountain region, by analyzing a 2.1 m snowpack sample collected from the East Rongbuk Glacier at 6572 m.a.s.l. on Mt. Everest. The most abundant compounds detected in the snow samples were γ -HCH and α -HCH with mean concentrations of 123 pg L⁻¹ and 92 pg L⁻¹, respectively. Furthermore among the seven marker PCB congeners quantified, PCB 28 and PCB 52 were the only dominant PCB congeners detected, with mean concentrations of 17 pg L⁻¹ and 6 pg L⁻¹. Seasonal differences were observed only for α - and γ -HCH concentrations increasing from the non-monsoon season to the monsoon season, while detected PCBs had uniform concentration trends.

Licia Guzzella et al [208] published a study on assessing sediments and soils collected on the southern slopes of Mt. Everest (Himalaya, Nepal) for PAHs, PCBs and PBDEs contamination. Based on the results obtained from 30 different samples analyzed, most of them were close or below the detection limits, it was possible to confirm that this area was characterized by a very limited contamination due to POPs, and, as expected, the southern slope of the Himalayas can generally be considered a pristine area on a global scale.

4.6 Materials and methodology

4.6.1 Principles of the Solid phase extraction (SPE) for SVOCs analysis in aqueous samples

There are three main challenges analyzing environmental samples for organic contaminants:

1. Complexity of the sample matrix (isolation).
2. Dirty samples (filtering).
3. Trace levels (retaining / pre-concentration).

Solid Phase Extraction (SPE) is the most effective, environmental friendly and sensitive procedure that overcomes all three mentioned features. There is wide range of commercially available SPE cartridges that are able to isolate and concentrate target compounds of interest from the sample matrix by retaining them on the sorbent bed while insoluble particles and sample matrix are flushed away or retained on the sorbent depending on the application procedure.[173] Also, the SPE extraction procedure allows changes in the organic phase and/or to separate it from the aqueous phase. The SPE procedure can be conducted on the micro scale known as Solid Phase Micro Extraction (SPME). SPME cartridges are connected on-line to the GC or LC system where the extract is injected directly and quantitatively for further analysis, allowing low detection limits on the micro scale.[113, 174] To perform the SPE procedure, it is necessary to modify and develop four basic steps of solid phase extraction: (Figure 4-2)

1. Conditioning

2. Loading
3. Washing and
4. Elution

Figure 4-2. Illustration of the main solid phase extraction procedure steps

Conditioning is the step where the sorbent bed is wetted and contact sites activated by choosing an appropriate solvent or solvent mixture to enable effective interactions with a sample in the solution. Depending on the application sorbent, it can be conditioned in a way to retain target analytes while the sample matrix goes through the sorbent bed or to trap the impurities while target analytes go through the SPE cartridge unretained. For the analysis of aqueous samples, conditioning is performed by passing MeOH and/or ACE through the sorbent bed due to strong hydrophobicity of the most of the sorbent materials making it more hydrophilic and more compatible to interact with an aqueous sample.

Loading of the sample onto the sorbent bed is performed under slow flow rate ~1 ml/min

regulated by the pump to provide enough time for the sample or sample matrix interaction (depending on the application) with an active surface of the SPE sorbent.

The washing procedure has to be performed in a way that target analytes are retained while unwanted sample matrix and impurities are eluted as effectively as possible by matching solubility with an appropriate solvent. For analysis of organic contaminants in water samples, the best washing solution is ultrapure water (UPW) or mixtures of ultra pure water containing low percentages (5-15%) of an organic solvent.

The last step of the SPE procedure is elution of the target analytes where target compounds are extracted from the sorbent bed to the liquid phase suitable for further analytical measurements (GC-MS/LC-MS). It is important to remove water as much as possible from the cartridge prior to elution, which is usually done by using a vacuum, centrifuge, nitrogen stream or combination of each because water vapor can damage the GC column and the effluent can contain two phases that effects further analytical measurements. [104, 113, 173, 175-179]

Furthermore, many different sorbent materials were developed and utilized for SPE extraction procedures of organic contaminants such as C18- bonded silica, [180] bamboo charcoal, [181] magnetic nano-porous carbon, [182] expanded graphite, [183] multi walled carbon nanotubes [184, 185] and hydrofluoric acid etched sand particles. [186]

4.6.2 Chemicals and Standard Solutions

All the solvents used for sample processing and analysis including hexane (VWR), dichloromethane (VWR), acetone (VWR) and methanol (VWR) were of high purity pesticide free HPLC grade. Standard chlorinated pesticide mix solution for 23 OCPs used

in this study were provided by AccuStandard (New Haven, USA), including aldrin, dieldrin, endosulfan, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, α -BHC, β -BHC, γ -BHC, δ -BHC, oxychlordane, pentachloroanisole, heptachlor, heptachlor epoxide, γ -chlordane, α -chlordane, p p' -DDE, p p' DDD, p p' DDT, cis-nonachlor and metoxychlor. Due to similar properties tetrachloro- m -xylene and decachlorobiphenyl, 5.0 $\mu\text{g/mL}$ in hexane were used as surrogate standards. In addition, the chemicals including standard solution of PAHs used in this study are previously detailed described in the section 2.2.1

4.6.3 Instrumentation and tuning procedure

Instrumentation (GC-MS) details used in this study including developed tuning procedure are previously described in the sections 2.2.3 and 2.2.4 respectively. SPE cartridges used in this study were polymeric sorbents Strata® X (Phenomenex. USA).

4.6.4 GC-MS method development for OCPs analysis

GC and MS parameters were optimized for separation and quantification of the 23 different organochlorine pesticides including two surrogate compounds used for quantification and recovery efficiency assessment listed in the table 5-1.

Injection port temperature was maintained at 250 °C as this temperature showed the best performance in terms of transferring efficiency of the target OCP analytes to the column for further analysis while producing a clear blank with no co-eluting/interfering peaks that might affect chromatogram due to release of various silica interferences from the injection port materials such as the inlet septum or liner fillings. Furthermore, cold trap focusing at

the start of the column (60 °C) was a method of choice for semi-volatile target analytes due to better separation (resolution), especially for the early eluting peaks. SIM mode was developed to be able to reach low detection limits by specifying the masses that MS is analyzing, thus lowering background noise and reaching higher sensitivity of the instrument.

Table 5-1 summarizes GC and MS parameters optimized for quantification and qualification analysis of OCPs.

Table 5-1. Summary of the GC-MS parameters optimized for the OCPs analysis

GC parameters (OCPs)	
60 °C for	1 min
then 15 °C/min to 200 °C	1 min
then 3 °C/min to 234 °C	0 min
then 50 °C/min to 300 °C	10 min
Run Time	25.403 min
Injection Mode	Splitless
Injection port Heater	250 °C
Pressure	9.1128 psi
Total Flow	74 mL/min
Gas Saver	20 mL/min After 1.2 min
Purge Flow to Split vent	70 mL/min at 1 min
Septum Purge Flow	3 mL/min
MS Conditions	
Mode	SIM
Tune	PFTBA
Solvent delay	3.0min

As a result of parameters optimized in table 5-1, chromatographic separation of 23 OCPs and 2 surrogate standards was performed by meeting all chromatographic criteria including separation time, peak resolution and peak shape. Total ion current chromatograms are shown in the figure 5-1.

Figure 5-1. Total ion current chromatogram showing a separation of 23 OCPs together with a 2 surrogate standards (Peaks 2 and 25). Labeled chromatographic peak IDs are shown in a table 5-2. (50ng injection)

4.6.5 *Quality control and quality assurance (QA/QC)*

The main guidelines in choosing an internal standard (tetrachloro-m-xylene and decachlorobiphenyl) are that it has to have similar interaction with a GC column due to similar chemical structure with the OCPs and cannot be found in the real sample. To ensure quality control, relevant standards were analyzed to check instrumental performance, peak height, and resolution.

Table 5-2. Method development summary for OCPs analysis including retention time (t_R min), quantification (ion I) and qualification (Ion II and Ion III) ions, instrumental limits of detection (LOD) and quantification (LOQ), together with a method limits of detection (MDL) and quantification (MQL). Limits are presented in $\mu\text{g/L}$ and ng/L respectively.

No.	OCPs	t_R (min)	Ion I	Ion II	Ion III	LOD [$\mu\text{g/L}$]	LOQ [$\mu\text{g/L}$]	MDL [ng/L]	MQL [ng/L]
1	Oxychlordane Isomer	10.544	129.1	183.0	218.0	0.0180	0.1802	0.0901	0.9009
2	Tetrachloro-m-xylene	11.329	206.9	208.9	243.9	n.a.	n.a.	n.a.	n.a.
3	d-BHC	12.150	180.9	182.9	218.9	0.0032	0.0322	0.0161	0.1611
4	Pentachlorideanisole	12.342	236.8	264.8	279.8	0.0030	0.0300	0.0150	0.1502
5	a-BHC	12.644	109.0	182.9	218.9	0.0078	0.0778	0.0389	0.3888
6	b-BHC	12.874	109.0	182.9	218.9	0.0069	0.0695	0.0347	0.3475
7	g-BHC	13.505	180.9	182.9	218.9	0.0064	0.0641	0.0320	0.3203
8	Heptachlor	14.776	100.0	271.8	273.8	0.0016	0.0164	0.0082	0.0820
9	Aldrin	15.877	262.8	264.8	292.9	0.0015	0.0147	0.0073	0.0735
10	Endosulfan	16.853	192.8	194.8	262.8	0.0042	0.0424	0.0212	0.2119
11	Heptachlor epoxide	17.170	352.8	354.8	388.8	0.0021	0.0212	0.0106	0.1060
12	g-chlordane	18.036	271.8	372.8	374.8	0.0019	0.0190	0.0095	0.0952
13	a-chlordane	18.529	236.8	372.8	374.8	0.0019	0.0192	0.0096	0.0962
14	p p'-DDE	19.409	224.6	248.0	317.9	0.0058	0.0577	0.0288	0.2883
15	Dieldrin	19.629	79.10	262.8	276.9	0.0018	0.0176	0.0088	0.0879
16	Endrin	20.503	244.9	262.8	278.8	0.0017	0.0173	0.0087	0.0867
17	Endosulfan	20.964	165.0	194.9	206.9	0.0018	0.0176	0.0090	0.0880
18	p p'-DDD	21.208	235.0	236.8	408.9	0.0019	0.0190	0.0095	0.0950
19	cis -nonachlor	21.208	235.0	236.8	408.9	0.0019	0.0190	0.0505	0.5052
20	Endrin Aldehyde	21.609	67.10	249.8	344.9	0.0101	0.1010	0.0125	0.1254
21	Endosulfan I	22.677	228.8	271.6	386.8	0.0025	0.0251	0.0133	0.1328
22	p p' DDT	22.929	165.0	235.0	237.0	0.0027	0.0266	0.0157	0.1574
23	Endrin Ketone	23.940	67.00	316.8	318.7	0.0031	0.0315	0.0184	0.1843
24	Metoxychlor	24.179	227.3	228.3	274.1	0.0037	0.0369	0.0034	0.0343
25	Decachlorobiphenyl	26.885	356.0	427.9	497.9	n.a.	n.a.	n.a.	n.a.

With each set of samples to be analyzed (reference standard mixture, actual environmental samples), method blanks were run every single time thereafter to check for instrumental performance, peak identification as well as quantification. Procedure blanks were run after a few samples, to ensure there is no contamination or remnants of OCPs in the system that could affect quantification accuracy. No OCPs were detected in the procedure blanks. All glassware used in this experimental procedure was clean and rinsed with acetone followed by hexane. Linearity was determined for the instrumental response by using the targeted OCPs standard stock solution. The calibration curve was plotted using a least-square regression method with analyzing reference standard solutions at six concentration levels 0.001, 0.005, 0.1, 0.25, 0.5, 1 ng μl^{-1} . Good linearity was shown in the chosen working range for the standards with correlation coefficient (r^2) values from 0.994 to 1. Continuing calibration verification standards (CCVs) were performed once every few samples to ensure that the calibration of the GC-MS system is still in the acceptable range by monitoring analyte response to be within a 15% of the calibration range. [214]

Instrument sensitivity was evaluated by its limit of detection (LOD) and limit of quantification (LOQ). LOD is the minimum amount of analyte present in a sample that can be detected but not quantified as an accurate value.[110] LOQ is the minimum amount of analyte found in a sample that can be quantitatively established with reliable precision and accuracy. [110] The LOD and LOQ calculations were carried out using signal to noise approaches. As all compounds of interest were absent from blanks, LOD represented the amount of analyte that produces a signal-to-noise ratio of 3, while LOQ is the amount of analyte that generates a signal-to-noise ratio of 10 [110]. The method and instrumental detection and quantification limits, retention times and qualification and quantification ions

of the target 23 OCPs are summarized in Table 5-2. The MDL of target analytes was calculated based on the sample volume. The LOD in Table 5-2 was divided by the chosen sampling volume to obtain the method detection limit (MDL) and LOQ divided by sample volume to obtain the method quantification limit (MQL).

4.7 OCPs extraction from the spring water samples collected from the lower Himalayas in the Trashigang district (Bhutan)

The Strata® X of 6cc, 500 mg is a polymeric SPE sorbent of unique selectivity that has been developed to cover a diverse spectrum of analytes and simplify the method development process for fast and efficient sample preparation. It is a reverse-phase sorbent and is commonly used to remove polar interferences from the extract prior to GC or GC-MS analysis. In this SPE procedure, the organo-chlorine analytes such as OCPs are retained and concentrated on the cartridge; the analytes are then eluted with suitable solvent while polar interferences remain in the cartridge. It is of primary significance that the sorbent bed is cleaned prior to the extraction procedure because the introduction of any interfering compounds resulting from leaching of extractables from the cartridge defeats the purpose of the procedure.

The extraction method procedure used is modified and upgraded from Angello et al. [215] SPE cartridges were first conditioned with 10 mL of DCM, followed by 10 mL of MeOH and 10 mL of ultrapure water was used for equilibration. All solutions were passed through the cartridges at a controlled flow-rate of 1 mL min⁻¹. After which samples were loaded and extracted at a flow rate of 1 mL min⁻¹. Furthermore, the cartridges were left to dry under nitrogen flow and vacuum for 30 min to remove any residing moisture. The analytes

were then eluted with a combination of 5 mL of DCM and 5 mL of acetone (ACE) at a flow rate of 1 mL/min and trace amount of water was removed with an anhydrous salt. The solvents were then reduced to near dryness via a rotary evaporator and dried under a gentle flow of nitrogen to a final volume of 1 mL. 1 µL of the sample was then injected and analyzed by GC-MS system. For recovery testing and method validation, 100 µL of pesticide mix was spiked in 200 mL of ultrapure water and loaded into the cartridge for further extraction analysis. Standard deviation of the recovery was examined by performing 3 replicate extraction procedures repeated under the same experimental conditions.

Table 5-3. Summarized SPE method development parameters for OCPs and surrogate standards (bolded) extraction efficiency (STDV % calculated form 3 repeated measurements)

Table 5-3. (Continued) Summarized SPE method development parameters for OCPs and

No	OCPs	Recovery (%)	STDV (%) n=3
1	Oxychlorthane Isomer	115.9	6.45
2	Tetrachloro-m-xylene	93.5	5.33
3	d-BHC	91.6	5.89
4	Pentachlorideanisole	86.1	4.32
5	a-BHC	101.6	7.45
6	b-BHC	119	9.53
7	g-BHC	105.3	6.44
8	Heptachlor	69.5	3.49
9	Aldrin	68.2	3.31
10	Endosulfan	72.3	4.43

surrogate standards (bolded) extraction efficiency (STDV % calculated form 3 repeated measurements)

No.	OCPs	Recovery (%)	STDV (%) n=3
11	Heptachlor epoxide	73.4	5.31
12	g-chlordane	74.5	5.44
13	a-chlordane	69.8	5.19
14	p p'-DDE	82.3	4.17
15	Dieldrin	91.2	6.68
16	Endrin	62	5.62
17	Endosulfan	82.2	6.39
18	p p'-DDD	82.2	5.32
19	cis -nonachlor	82.2	7.23
20	Endrin Aldehyde	118.4	6.22
21	Endosulfan I	103.1	8.37
22	p p' DDT	77.4	4.11
23	Endrin Ketone	105.3	8.54
24	Metoxychlor	86.3	4.22
25	Decachlorobiphenyl	79.8	3.19

Results showed good recoveries and standard deviation meeting USEPA guidelines for the OCPs extraction procedures. Recoveries were in a range from 62 % to 119 % (60 % to 120 %) and standard deviations in a range from 3.19 % to 9.53 % ($\pm 15\%$) [214, 216, 217]. Developed SPE procedures were further utilized for OCPs quantification analysis performed on non-monsoonal spring water samples from the Lower Himalayas in Trashigang District of Eastern Bhutan described in the further chapters.

4.7.1 Solid phase extraction of the PAHs from the s Lake Teyminus and Himalayas glaciers samples in the Eastern Bhutan region

The extraction procedure used is modified form the literature[163, 218]. Sorbent material was first conditioned with a 10 ml of the DCM followed by 10ml of MeOH and equilibrated with a 10ml of ultra pure water (UPW). 200ml of UPW was spiked with the target PAHs standards including 4 surrogate standards and loaded for extraction. All the conditioning and loading steps were maintained on $\sim 1\text{ml min}^{-1}$. After loading, the cartridge was left under vacuum and blown by the gentle stream of nitrogen gas for 30 min to remove moisture. Analytes were eluted with 10 ml of DCM $\sim 1\text{ml min}^{-1}$. Moisture residue was removed by adding anhydrous salt then filtered and evaporated to exactly 1 ml of volume. This procedure was repeated 3 times for recovery and standard deviation analysis presented in table 5-2. Results showed good recoveries ranging from 65 % to 101 % following acceptance criteria (60 % - 120 %) and standard deviation varying from 3.44% to 9% following criteria of ($\pm 15\%$) established by the USEPA.[218] Described SPE procedure was not further modified and it was used for analysis of water samples collected from the from Lake Teyminus and Himalayas glaciers samples in the Eastern Bhutan region.

Table 5-4. Summarized SPE method development parameters for PAHs and surrogate standards (bolded) extraction efficiency (STDV % calculated from 3 repeated measurements)

No.	Compound	Recoveries (%)	RSD (%) n=3
1	NAP	84.39	4.55
2	ACY	81.22	8.32
3	ACP	83.33	7.44
4	FLR	81.02	5.89
5	PHE	77.21	4.15
6	ANT	81.45	6.81
7	FLT	101.41	9.01
8	PYR	91.23	5.66
9	BaA	95.01	5.13
10	CYR	75.41	7.44
11	BbF	88.98	5.30
12	BkF	72.41	6.90
13	BaP	81.13	7.11
14	IcP	69.48	8.10
15	DhA	70.91	7.41
16	BghiP	65.41	5.13
a.	D8-NAP	88.90	3.44
b.	D10-ACP	81.31	4.89
c.	D10-PHE	78.13	6.17
d.	D12-CRY	66.58	4.10

4.8 Conclusion

Chromatographic separations of 23 OCPs including 2 surrogate standards (figure 5-1) and 16 EPA listed PAHs including 4 surrogate standards (figures 2-1 and 2-2) were developed by meeting all chromatographic criteria including separation time, peak resolution and peak shape. (Figure 5-1) The calibration curve was plotted using reference standard solutions at six concentration levels 0.001, 0.005, 0.1, 0.25, 0.5, 1 ng μl^{-1} . Good linearity was shown in the chosen working range for the standards with correlation coefficient (r^2) values from 0.994 to 1. Continuing calibration verification standards (CCVs) were performed once every few samples to ensure that the calibration of the GC-MS system is still in the acceptable range by monitoring analyte response to be within a 15% of the calibration range. [214] MDL and MQL of the method reached low ng L^{-1} detection and quantification limits.(Table 5-2)

The Strata® X of 6cc, 500 mg is a polymeric SPE used in this study as a pre-concentration step prior further GC-MS analysis. A total of 39 compounds including 16 PAHs and 23 OCPs were evaluated for recovery assessment to meet criteria of 60% - 120% including maximum of 15 % standard deviation when performing replicate analysis. Table 5-3 and 5-4 shows the final summarized SPE results for OCPs and PAHs respectively. Results obtained showed good recoveries ranging from 65 % to 101 % with standard deviation falling under 15 % EPA criteria ranging from 3.19 % to 9.53 % and 3.44% to 9% for OCPs and PAHs analysis respectively.[214, 216, 217]

Developed analytical procedures were further used for analysis of water samples collected from the from Lake Teyminus and Himalayas glaciers samples in the Eastern Bhutan region as discussed in the following chapter 6.

Chapter 5. Sampling methodology and concentration profiles of SVOCs analysed in water samples collected in lower Himalayas in Bhutan

5.1 Sampling location

Kanglung Gewog (a village block) is situated under Tashigang Dzongkhag, Eastern Bhutan, at an elevation of 1930m above sea level. The summer temperature ranges from 16 to 24 °C while winter temperature varies from 3 to 13 °C. Kanglung Gewog has a total land area of 63.3 km² with 5 chiwogs (village clusters) and population of about 10,282 people. The Gewog has 4 Primary Schools, 2 Lower Secondary Schools, Jampeling High School, Shedra, Yonphula Domestic Airport, Bhutan Power Corporation sub-station, Royal Education Council, Sherubtse College and several other government, corporate and private establishments. Recently, Kanglung is identified as the regional Educational Hub because of its existing infrastructures, strategic location and favorable climatic conditions. Over the years, Kanglung has seen increasing population partly due to the increase in student intake of the Sherubtse College and partly due to the establishment of new government, corporate and private facilities in the town. This has led to water shortage in the community as the per capita use of water has increased. Moreover, availability of clean drinking water is another issue in the community as the existing water supplied to the people is untreated. The area of study comprises of two sub-watersheds viz. Bodhidrang and Namshing. It is located in the south eastern part of Kanglung Gewog under Trashigang District between 27°14'26.9"N and 27°17'46.3"N latitude and 91°30'41.7"E and

91°34'1.9"E longitude. Sub-watersheds within the study area cover an area of approximately 15 sq. km (Figure 5-1).

Figure 5-1. Study area where sampling was conducted including topography and water streams information

The area has wide variation in elevation due to irregular nature of the terrain (Figure 5-2b). The average elevation of the basin is 2056 m, with highest and lowest of about 2978 m and 1081 meters respectively. The slope gradient of the project area ranges from about 0.3° to 63° (Figure 5-2c). About 70 percent of the project area has more than 20 degree slope. Bodidrang watershed (figure 5-2d) is a very important catchment for the people living within the catchment as well as for the people living outside the catchment. The majority

of the streams flowing in the Bodidrang catchment are being tapped by the people living outside the catchment such as Sherubtse College, Shedra, Jampleling School, Yonphula School and the nearby villages. Rongthung village receives its water from both Bodhidrang and Namshing watersheds for domestic purposes including irrigation of their paddy. The streams flowing in the Namshing sub-catchment viz., Namshing, Omshayri and Setshangri provide water for people living in the nearby villages such as Jomri, Omshayri and Setshangri villages respectively for the domestic use.

a) Land use land cover

b) Contour

c) Slope

d) Watershed

Figure 5-2. Map of the study area including: a) land use and land cover b) costour c) Slope and d) watershed

5.2 Sample collection

Water samples were collected from stream source, storage tank and end user taps using standard protocol. Water samples were collected in triplicates into sterile polyethylene bottles 80 ml in volume. The bottles were further rinsed three times with sample water at the time of collection. Bottles were sealed stored on cold and then transferred to Nanyang Technological University, Singapore for the analysis of OCPs and PAHs. Sample IDs and source location for each of the sample is presented in a table 5-1. Appendix 2 includes detailed sampling location information including pictures from the each sampling site in specific.

Table 5-1. Summary of the sample information including sample ID and location where it is sampled.

Sample ID	Sample Description	Sample ID	Sample Description
1A	Sherubtse (Source)	5C	Upper Market (End User)
1B	Sherubtse (Storage)	5D	Upper Market (End User)
2A1	Yonphula (Source)	5E	Upper Market (End User)
2A2	Yonphula (Source)	6A	Kanglung (Source)
2B	Yonphula (Storage)	6B	Kanglung (Storage)
2C	Yonphula (End User)	6C	Kanglung (End User)
2D	Yonphula (End User)	7A1	Rongthung (Source)
2E	Yonphula (End User)	7A2	Rongthung (Source)

3A	Shedra (Source)	7B	Rongthung (Storage)
3B	Shedra (Storage)	7C	Rongthung (End User)
4A	Jampeling (Source)	7D	Rongthung (End User)
5A	Upper Market (Source)	8A	Rongthung School (Source)
5B	Upper Market (Storage)	8C	Rongthung School (End User)
4B	Jampeling (Storage)	7E	Rongthung (End User)

5.3 Concentration trends and profiles of the OCPs and PAHs in various aqueous samples collected in lower Himalayas in Bhutan

5.3.1 Organochlorine pesticides (OCPs) concentration profiles in various water samples collected in lower Himalayas in Bhutan

The developed SPE-GC-MS method was applied to the analysis of 23 organochlorine pesticides in real spring water samples collected from twenty-eight various different sites in Trashigang district in Bhutan. Using the optimized conditions described above, water samples were extracted by the developed SPE method. Analysis of the water samples have shown that there are no particular high pesticide concentrations to be found. With reference to the European Union Directive on drinking water quality (98/83/EC), which states that the admissible concentration for pesticides is $0.1 \mu\text{g L}^{-1}$ for each individual substance and $0.5 \mu\text{g L}^{-1}$ for the sum of pesticides, there were only 8 pesticides detected and at very low concentration, below $0.1 \mu\text{g L}^{-1}$ in the 28 spring water samples.[219] They are mainly

oxychlordan, heptachlor epoxide, γ -chlordan, α -chlordan, p,p' -DDE, p,p' DDD, cis-nonachlor and metoxychlor as shown in Table 6-2.

Traces of these 8 pesticides can be found in Bhutan's springwater, most likely because these glaciers are prone to airborne persistent OCPs, which ultimately reaches the springwater via cold condensation, thin soil layers as well as sparse vegetation. [220] It was noted that oxychlordan, γ -chlordan and α -chlordan were detected in almost all of the 28 samples analyzed. Chlordan is mainly used to control termites and is used on many agricultural crops and vegetation, and on non-food, injected into foundations of buildings. Its association with high persistency of up to more than 20 years, wet or dry deposition via long-range transportation and tendency to leach in many soils might be the potential reasons as to why they are still detectable in almost all of the 28 samples analyzed.[221] Among DDT metabolites, p,p' -DDE was more prevalent as the main contaminant followed by p,p' -DDD with the absence of p,p' DDT among the 28 samples but p,p' -DDD is present in relative higher amount (by a factor of 10) as compared to p,p' -DDE which coincides with historic facts and data of heavy utilization of pesticides DDTs in surrounding countries like India, Bangladesh, Nepal and China which suggested contamination from abroad. [222, 223] The absence of DDT might be due to the fact that most of the DDT has been broken down into its major metabolites or p,p' -DDE and p,p' -DDD. DDE only enters the environment through the breakdown of DDT whereas DDD enters the environment as a result of both breakdown and its use in killing pests. This might explain the occurrence of a relative higher concentration of DDD as compared to DDE. [224]

Table 5-2. Summary of the OCPs detected and quantified in the Bhutan sampling campaign *ND stands for not detected and NA=Not analyzed due to contamination

ID	Sample Description	Oxy chlordane (ng/l)	Heptachlor epoxide (ng/l)	g- chlordane (ng/l)	a- chlordane (ng/l)	p p'-DDE (ng/l)	p p'- DDD (ng/l)	cis – nonachlor (ng/l)	Metoxychlor (ng/l)
1A	Sherubtse (Source)	78.69	6.31	0.90	0.80	0.24	1.62	3.56	8.46
1B	Sherubtse (Storage)	90.71	ND	0.90	1.10	0.20	ND	ND	ND
2A1	Yonphula (Source)	65.39	43.00	1.80	1.80	1.04	2.88	5.51	11.57
2A2	Yonphula (Source)	64.08	24.93	1.10	1.00	0.26	1.82	3.36	8.38
2B	Yonphula (Storage)	117.32	26.93	1.10	1.10	0.18	1.96	3.68	8.48
2C	Yonphula (End User)	75.37	ND	0.80	1.00	0.48	ND	ND	ND
2D	Yonphula (End User)	259.85	ND	0.80	0.70	0.40	ND	ND	ND
2E	Yonphula (End User)	80.62	ND	0.40	0.80	0.53	ND	ND	ND
3A	Shedra (Source)	113.53	ND	0.90	0.80	ND	ND	ND	ND
3B	Shedra (Storage)	70.86	ND	0.80	0.80	0.35	ND	ND	ND
4A	Jampeling (Source)	2.37	ND	ND	ND	ND	ND	ND	ND
4B	Jampeling (Storage)	139.75	ND	0.80	1.10	0.56	ND	ND	ND
5A	Upper Market (Source)	ND	ND	ND	ND	ND	ND	42.40	ND
5B	Upper Market (Storage)	19.73	ND	0.80	0.80	ND	ND	ND	ND
5C	Upper Market (End User)	30.70	ND	0.90	0.80	ND	ND	ND	ND
5D	Upper Market (End User)	NA	NA	NA	NA	NA	NA	NA	NA
5E	Upper Market (End User)	54.20	ND	0.30	0.70	0.45	ND	ND	ND
6A	Kanglung (Source)	73.25	ND	0.80	1.00	0.39	ND	ND	ND
6B	Kanglung (Storage)	79.08	2.57	0.90	1.00	0.19	ND	ND	7.81
6C	Kanglung (End User)	168.67	ND	0.80	0.70	0.34	ND	ND	ND
7A1	Rongthung (Source)	86.51	ND	0.80	0.80	0.45	1.49	2.99	ND
7A2	Rongthung (Source)	9.17	7.14	0.80	0.80	0.36	1.53	3.23	ND
7B	Rongthung (Storage)	114.93	20.68	0.80	0.80	0.13	1.49	3.08	7.32
7C	Rongthung (End User)	82.88	19.63	0.80	0.80	0.20	1.42	2.98	7.24
7D	Rongthung (End User)	50.66	ND	0.80	0.80	0.49	ND	ND	ND
7E	Rongthung (End User)	116.05	ND	0.90	0.90	0.54	ND	ND	ND
8A	Rongthung School (Source)	NA	NA	NA	NA	NA	NA	NA	NA
8C	Rongthung School (End User)	46.60	ND	0.80	ND	ND	ND	ND	ND

5.3.2 Polycyclic aromatic hydrocarbons (PAHs) concentration profiles in Lake Teyminus and Himalayas glaciers samples in the Eastern Bhutan region

The developed analytical SPE-GC-MS method was applied to the analysis of 16 PAHs in different water samples collected from the Teyminus lake, including the shallow and middle parts. Samples were also collected from the glacier in close proximity and inlet stream that leads to the lake. Using the optimized SPE conditions described above, water samples were extracted and the results are shown in table 5-3 and 5-4 and indicated that all 16 monitored PAHs were detected and quantified respectively.

Table 5-3. Summary of the PAHs detected and quantified in the Teyminus lake, lake inlet stream, and glacier in close proximity. All concentrations are presented in µg/L levels.

<i>No.</i>	<i>PAHs</i>	<i>LakeTeyminus</i>	<i>Lake (Middle)</i>	<i>Lake inlet</i>
1	Naphthalene	0.0362	0.0422	0.1697
2	Acenaphthylene	0.0066	0.0067	0.0051
3	Acenaphthene	0.0642	0.0926	0.0843
4	Fluorene	0.0028	0.0027	0.0027
5	Phenanthrene	0.0073	0.0037	0.0071
6	Anthracene	0.0040	0.0007	0.0015
7	Fluoranthene	0.0121	0.0022	0.0051
8	Pyrene	0.0140	0.0020	0.0076
9	Benzo(a)anthracene	0.0288	0.0039	0.0146
10	Chrysene	0.0306	0.0034	0.0159
11	Benzo(b)fluoranthene	0.0330	0.0010	0.0207
12	Benzo(k)fluoranthene	0.0382	0.0031	0.0205
13	Benzo(a)pyrene	0.0402	0.0027	0.0278
14	Indeno(1,2,3-cd)pyrene	0.0318	0.0020	0.0264
15	Dibenz(a,h)anthracene	0.0499	0.0040	0.0300
16	Benzo(g,h,i)perylene	0.0432	0.0041	0.0231

Higher water solubility of low molecular weight PAHs compared to the heavy PAHs may explain their comparative high abundance detected in water. Partitioning towards water is also favored by the low octanol–water coefficients of the lighter PAHs. In Figure 5-3 the compositional profile of PAHs, in terms of concentration according to the every PAH congener at each sampling site, is illustrated. Water solubility of PAHs is not favored by the low temperatures in these regions. Solubility and potential mobility of the PAHs in water, especially lighter PAHs increase with a higher temperature.[162, 163, 220, 225, 226] Thus it can be seen from the Figure 6-3, that higher concentrations for lighter PAHs such as NAP and ACP are observed for all water samples collected compared to the heavier ones.

Figure 5-3. Correlation trends comparing abundances of the all 16 PAHs detected between samples taken from the shallow, middle and inlet part of the Teyminus lake.

By comparing concentration profiles of the PAHs, it can be seen that the concentration trends do not vary substantially between samples collected from the shallow and middle part of the lake including an inlet stream. Slightly higher concentrations are observed in the shallow part of the lake compared to the inlet and middle part suggesting low mobility of the PAHs due to low solubility and low temperatures at the sampling site.

In addition, two glacier samples were collected in close proximity. One sample was filtered at the site and one was not, and they were analyzed separately to see effect of the suspended particles on PAHs occurrence in the aqueous samples. Results on concentration abundances are summarized in a table 5-4. All PAHs were detected in low ppb levels.

Table 5-4. Summary of the PAHs concentration collected from the 2 replicates of the glacier sample one filtered and one not filtered that were analyzed separately

No.	ID.	Glacier (µg/L)	Glacier filtered (µg/L)
1	NAP	0.0877	0.0993
2	ACY	0.0036	0.0006
3	ACP	0.0612	0.0431
4	FLR	0.0045	0.0018
5	PHE	0.0127	0.0038
6	ANT	0.0128	nd
7	FLT	0.0208	0.0003
8	PYR	0.0212	0.0011
9	BaA	0.0484	0.0002
10	CYR	0.0551	0.0004
11	BbF	0.0440	nd
12	BkF	0.0591	nd
13	BaP	0.0550	nd
14	IcP	0.0418	nd
15	DhA	0.0553	nd
16	BghiP	0.0514	nd

Results showed smaller concentration of the PAHs in filtered samples for the lighter PAHs, while heavier PAHs samples (BbF, BkF, BaP, IcP, DhA, BghiP) were not even detected in filtered glacier sample, compared to the regular sample where all PAHs were detected in low ppb levels. This result indicates that due to low solubility in water, PAHs tend to adsorb and accumulate on the suspended solids, especially the heavier PAHs.[220, 227] Comparing concentration profiles of all samples analyzed for PAHs, a uniform trend in individual PAHs abundances was observed.

Among all 16 PAHs detected and quantified, the most abundant PAHs can be classified in two groups: NAPH and ACP (lighter PAHs) and BbF, BkF, BaP, IcP, DhA, BghiP (heavier PAHs). Dominance of this specific congeners suggests domestic heating and long term transport from neighbouring countries (India, Nepal, China) as a sources of the PAHs in this sampling site.[156, 161, 189, 208, 220, 228]

5.4 Conclusion

Analytical method was developed for the quantification of 23 OCPs and 16 PAHs in various water samples including 9 spring water sources, 7 storage facilities, 11 end user taps and water samples collected from Lake “Teyminus” together with glacier inlet samples collected in close proximity in the lower Himalayas in Bhutan. A SPE method that was used followed acceptable criteria with recoveries in a range 60%-120% with a standard deviation of 3 replicate analysis within 15%.

Out of 23 OCPs monitored, 8 were detected in concentrations within allowed admissible concentration for pesticides of $0.1 \mu\text{g L}^{-1}$. Comparing to the OCPs quantified, PAHs detected in lake samples including glacier and an inlet stream showed higher concentrations. All 16 targeted PAHs were detected and quantified in every sample. The most abundant PAHs were NAPH and ACP representing lighter PAHs and BbF, BkF, BaP, ICP, DhA and BghiP for the heavier PAHs. Dominance of this specific congeners suggested domestic heating and long-distance transport from countries such as India, Nepal and China as a sources of the PAHs in this sampling site.

Chapter 6. Thermal desorption gas chromatography mass spectrometry analysis of the volatile organic sulfur compounds in Singapore's atmosphere

6.1 Introduction

The presence of volatile organic sulfur compounds (VOSCs), often known as odor compounds, in the environment causes a wide range of health, social and environmental problems.[229] Therefore, interest in the quantification of such compounds in the atmosphere is increasing constantly. The most known effects of the VOSCs on the environment, is that they contribute to the formation of acid rain, which leads to corrosion of metallic structures, as well as damage to the natural environment. Furthermore, these compounds have a strong effect on atmospheric chemistry due to their strong potential of oxidation to secondary pollutants contributing to global warming. [230, 231] Environmental and health effects of volatile organic sulfur contaminants have been reported in a number of previous investigations.[229, 232] When acute exposure to the some of the VOSCs, human health can be affected by an increase in the risk of asthma, irritation of mucous membranes, and nausea. Furthermore, nervous, immune and reproductive systems can be also be affected. [232-235] The most common sources of the natural volatile sulfur compounds such as dimethyl sulfide (DMS), hydrogen sulfide H_2S and dimethyl disulfide (DMDS) are oceans, soils, flora, volcanic and geothermal activities.[236]

Although natural emissions constitute roughly 24% of total sulfur emissions, [237] VOSCs are commonly emitted to the atmosphere during industrial processes such as degradation of organic matter that includes pulp milling, landfilling, slaughtering, sewage treatment, waste incineration, biogas production, etc.[238]

Up to the present date, there have been no reports on the occurrence of the VOSCs in Singapore's atmosphere. The western coast of Singapore is the most industrialized part of the country where all the oil refineries and waste incineration plants are situated as well as the agriculture facilities including various farms, slaughter and wastewater treatment plants. Therefore, people residing in that area often have problems with strong unpleasant odors in the atmosphere, hence the sampling location for VOSCs was placed in close proximity to the abovementioned sources. (Refer to the Figure 8-1)

Thermal desorption (TD) coupled to gas chromatography mass spectrometry (GC-MS) is by far the best and the most used analytical method for determining the amounts of VOSCs present in the air. VOSCs can be collected using various types of sampling vessels such as sorbents, canisters or polymer bags. These sampling vessels can be connected to the GCMS via a TD system, which has a focusing mechanism to concentrate the VOSCs before transferring them into the GC-MS for analysis. The TD process employs high purity inert gas, usually helium, for high temperature extraction. There are two main stages in TD for sorbent-based sampling techniques. The first stage involves transferring the VOSC analytes from the air sample to the pre-concentrator. The pre-concentrator is either an electrically cooled Peltier or a cryogenic trap. High temperature and a stream of helium are applied to the tube to desorb VOSCs and transfer them into the trap for pre-concentration. The final stage involves the inversion of helium flow through the trap and the heating of

the cold trap rapidly to a high temperature at the maximum rate to transport the VOSCs into the GCMS. Figure 6-1 shows the TD mechanism for sorbent-based sampling.[239]

Figure 6-1.Two stage (a) primary and (b) secondary thermal desorption processes for solid sorbent based sampling[239]

6.2 Solid sorbent sampling methodology

Solid sorbent adsorption is solvent free and one of the most efficient and environmental friendly techniques extensively utilized for concentration of large group of VOSCs. The principle of the sorbent-based sampling procedure is retaining the target analytes (VOSCs) present in the air onto the various kinds of solid sorbent materials, which are usually packed in glass or stainless steel tubes. Analytes of interest can be trapped onto sorbent material by two mechanisms: Adsorption and/or chemical interaction. Porosity and surface area are the main characteristics that affect sampling performance. Large surface area sorbents with

the pores in molecular size scale have strong trapping affinity for VOSCs.[240] By the IUPAC definitions, pore dimensions are classified as micropores (2 nm in width), mesopores (2 nm up to 50 nm in diameter) macropores (more than 50 nm wide).[241-243] Physical adsorption processes that occur on microporous particles are the strongest as the forces are in proximity to numerous sides of the inner pore surface and can be explained by interpreting the Langmuir or Dubinin–Radushkevich equation, while for the other pore sizes Freundlich or Langmuir isotherm equations can be used.[244] Adsorption occurring on the macropore levels are referred to molecular monolayers that can be accumulated into multilayers. [245] Depending on the ambient concentrations of the target VOSCs, the Freundlich isotherm may show linear or curved regression trends. In our study a linear regression line is observed when trace and low levels of the ambient VOSCs are analyzed [246-250] Chemical adsorption represents a form of interaction where the sorbent material supports chemicals to react with each other to produce a stable product. Reducing the activation energies of these reactions is possible during chemisorption that results in a chemical reaction.[249] Analytes are desorbed from the sorbent materials by heating the sorbent tubes to high temperatures enhanced by a stream of high purity helium (99.9997%) to transfer the VOSCs onto a cryogenic trap at -10°C where the analytes are pre-concentrated. The trapped pre-concentrated analytes are again desorbed under high temperatures during a second desorption step with a back flush of the He stream to transfer the compounds to the GC-MS system for further analysis. The second cryogenic desorption step is introduced as an intermediate process to enhance the chromatographic results in terms of peak shape and resolution by focusing the stream of analytes prior entering a GC column.[239] A schematic representation of desorption and sampling flow pathways, of

the sorbent tube and its filling methods can be seen in figure 6-2.

Figure 6-2. Schematic representation of the sorbent tube with its sampling and desorption flows pathways.[239]

Sorbent tubes can be filled with only one sorbent, but this is usually insufficient for analyzing a broad range of compounds due to varying physical and chemical properties of the target analytes, such as polarity and volatility. [251] Therefore, the most common practice in packing the tubes is to fill the tubes with multiple types of sorbent materials so that they can efficiently trap a wide range of compounds. It is common practice to pack the tubes with sorbents in the order that the sorbent strength increases from the sampling end in order to prevent less volatile compounds being entrapped by the strong retention sorbent.[240, 252, 253] Less volatile compounds generally get trapped first by the weaker sorbent so they do not reach the strong retaining sorbent. There are many commercial available sorbent materials for air sampling TD-GC-MS applications. [239, 240, 254] Two main methods of sampling, active and passive via solid sorbent adsorption, will be discussed in the following sections as well as detailed descriptions of the physical and

chemical properties of various types of sorbent materials presently available.

6.2.1 Sorbent materials

Different sorbent materials, such as molecular sieves, activated charcoal, graphitized carbon black, silica gel, aluminum oxide, and porous polymers have been used for sampling (trapping) a wide range of volatile and semi-volatile species. Porous polymer materials are the most commonly used for the collection of volatile sulfur compounds due to efficient desorption, comparing to some strong retaining sorbents like activated charcoal.[239] Furthermore, porous polymer materials such as Tenax TA are hydrophobic, thus have low affinity towards water vapor in the atmosphere such that breakthrough is not strongly dependent on the humidity of the sampling site and so makes it an ideal sampling material in regions such as SEA. Also, high thermal stability of the porous polymers allows efficient desorption at high temperatures of 375 °C without damaging the sorbent. Porous polymers are polymeric resins that are formed by suspension polymerization where a mixture of monomers and crosslinking reagents are polymerized in the presence of an inert solvent.[255, 256] Present porous polymer materials available for VOC sampling are Tenax (GA and TA) Chromosorb (102 and 106) and Porapak (N and Q) series. The chemistry behind Tenax involves polymerization by oxidation of 2,6-diphenylphenol to form a polymer 2,6-diphenyl-p-phenylene oxide. [249, 257] Chromosorb materials are derived from styrene and divinyl-benzene and the Propak series are polymers synthesized from styrene, ethylene glycol, vinylpyrrolidone, ethylvinylbenzene, vinylpyridine, divinylbenzene, and dimethyl adipate. [258, 259]

Graphitized carbons represent a wide range of sorbent materials that are usually non-porous

and non-specific with a sorbent strength varying from very weak (Carbotrap C/Carbopack C/ Carbograph 2TD) to very strong, as represented by products from the groups of Zeolite molecular sieves and activated charcoal. The graphitization process removes selective sites for adsorption of small and polar compounds such as water so that they are not able to interact through hydrogen-bonding with the sorbent material. This leads to polar compounds not being retained resulting in hydrophobicity of the materials.

Zeolite molecular sieves are derived from alkali metal aluminosilicates. They come in two series for sampling: molecular sieve 5A and M\molecular sieve 13X, depending on the particle and interior pore surfaces. Zeolite materials are extremely hydrophilic, thus not recommended for use in humid environments. [260]

Carbonaceous molecular sieves are characterized by a large surface area and are manufactured via pyrolysis of sulfonated polymers known as Carboxens and polyvinylidene chlorides.[261, 262] Carbonaceous molecular sieves have very disordered cavity aperture structure due to microscopic size graphite crosslink crystallization. These types of microporous sorbents are suitable for analyzing very volatile and very low molecular weight organic compounds due to their high surface area. [259, 262]

6.2.2 Physicochemical properties of the sampling sorbent materials

As there is a broad variety of the commercially offered sorbent materials for thermal desorption applications, evaluations of the advantages and limitations of different sorbent materials are essential for defining the ultimate sorbent materials for an analytical procedure. Tables 6-1, 6-2 and 6-3 summarize all their physical and chemical properties such as hydrophobicity, thermal stability, sorbent adsorption strength, surface area,

applicable volatility range and chemical composition. One of the most important characteristics of the sorbent is its adsorption strength defined as the ability of the material to retain analytes during the sampling processes and efficiently release them upon heating. Breakthrough analysis (amount of the target analytes that were lost or not retained from the sorbent tube) is the most common validation methodology, also identified as percentage breakthrough, breakthrough volumes and as well as safe sampling volumes analysis. The breakthrough procedure is conducted in such a way so that a second sorbent tube is connected in series to the back end of the first tube. Two types of breakthrough analyses have to be conducted in order for the method to be considered valid, including analytical standard injection breakthrough (under constant flow of nitrogen and fixed duration) and breakthrough volume analysis via real sampling of the air. Nevertheless, the amount of the sulfur volatile components detected in the back tube should not be above 5% of the amount in the first tube following EPA guidelines.[239] Although breakthrough information of some sorbent materials are also available from commercial suppliers, it is important for each laboratory to validate data by performing its own breakthrough experiments under the same environmental conditions that are used during sampling. Safe sampling volumes can be calculated and have two definitions; either half of the chromatographically evaluated breakthrough volume, or two-thirds of the experimentally evaluated breakthrough volume. [260, 263] This project was carried out in the humid atmosphere of Singapore where average relative humidity is 84% and it has been proven that increased relative humidity results in higher breakthrough percentages and analyte leakages from the material. Therefore, it is important that sorbent materials used are hydrophobic in order to prevent the water vapor in the air from influencing analyte breakthrough. One of the methods to

prevent retention of the water vapor on the sorbent materials is an extensive dry purging of the hydrophilic materials including Carboxens, Unicarb, Carbosieves, Propak N and molecular sieves.[256, 259, 264]

Table 6-1. Physical and chemical characteristics of porous organic polymers [259]

Sorbent	Hydrophobicity	Sorbent strength	Surface area (m ² /g)	Maximum temperature (°C)	Applicable volatility range	Chemical Composition	Example of analytes
Chromosorb 102	Hydrophobic	Medium	~350	250	50°C - 200°C	Styrene-divinylbenzene co-polymer	Extensive spectrum of VOCs such as volatile oxygenated analytes, haloforms and chlorinated pesticides with bp of 40 °C
Chromosorb 106	Hydrophobic	Medium	~750	225 - 250	50°C - 200°C n-C ₅ to n-C ₁₂	Polystyrene	Volatile labile and oxygenated hydrocarbon compounds
HayeSep D	Hydrophobic	Medium	~800	290	50°C - 200°C n-C ₅ to n-C ₁₂	Divinylbenzene polymer	GB/GE derivatives of VX (Chemical warfare agents), light compounds including acetylene, halogen-containing and sulfur-containing compounds. CO and CO ₂ .
Porapak N	Hydrophilic. Dry-purging is required.	Medium	~300	190	50°C - 200°C n-C ₅ to n-C ₈	Polyvinylpyrrolidone	Volatile nitriles (acrylonitrile, acetonitrile and propionitrile), pyridine, low-boiling alcohols, ethanol and 2-butanone.
Porapak Q	Hydrophobic	Medium	~550	250	50°C - 200°C n-C ₅ to n-C ₁₂	Ethylvinylbenzene-divinylbenzene co-polymer	Wide range of VOCs such as oxygenated compounds, but unsuitable for amines, anilines and nitric oxides.
Tenax TA	Hydrophobic	Weak	~35	350	100°C - 400°C n-C ₇ to n-C ₂₆	Poly (2,6-diphenyl- <i>p</i> -phenylene oxide)	All aromatics except benzene, non-polar compounds (bp 100 °C), and semi-volatile polar compounds (bp 150 °C).
Tenax GR	Hydrophobic	Weak	~35	350	100°C - 450°C n-C ₇ to n-C ₃₀	Poly (2,6-diphenyl- <i>p</i> -phenylene oxide) + 23% graphitized carbon	Alkylbenzenes, polycyclic aromatic hydrocarbons, polychlorobiphenyls and as above for Tenax TA. Replaced by Tenax TA for lower background interferences.

Table 6-2. Physical and chemical characteristics of graphitized carbon blacks, zeolite molecular sieves and activated charcoal [259]

Sorbent	Hydrophobicity	Sorbent strength	Surface area (m ² /g)	Maximum temperature (°C)	Applicable volatility range	Chemical composition	Example of analytes
Zeolite molecular sieve							
Molecular sieve 5A	Significantly hydrophilic	Very strong	1200	350 - 400	-60°C - 80 °C	-	Nitrous oxide and permanent gases
Molecular sieve 13X		Very strong	1200	350 - 400	-60°C - 80 °C	-	1,3-butadiene and permanent gases
Graphitized carbon blacks							
Carbotrap C Carbopack C Carbograph 2TD	Hydrophobic	Very weak	~12	>400	n-C ₈ to n-C ₂₀	Graphitization of the surface of carbon blacks. Different degree of graphitization would result in surface area variations.	Hydrocarbons to C20, alkyl benzenes, heavy organics: polychlorobiphenyls, polynuclear aromatics
Carbotrap B Carbopack B Carbograph 1TD		Medium weak	~100	>400	n-C _{5/6} to n-C ₁₄		Broad specs of VOCs including ketones, alcohols and aldehydes (Bp 75 °C), and all polar compounds within the volatility range specified, and perfluorocarbon tracer gases
Carbopack X		Medium	~240	>400	n-C ₅ to n-C ₈		Low molecular mass hydrocarbons, benzene, toluene, ethylbenzene, xylene isomers, 1,3-butadiene.
Carbograph 5TD		Medium	~100	>400	50°C - 150°C n-C _{3/4} to n-C _{6/7}		Low molecular mass hydrocarbons between C3 to C8, 1,3-butadiene

Table 6-3. Physical and chemical characteristics of carbon molecular sieves [259]

Sorbent	Hydrophobicity	Sorbent strength	Surface area (m ² /g)	Maximum temperature (°C)	Applicable volatility range	Chemical composition	Example of analytes
Carbon molecular sieves							
Carbosieve S- III	Significantly water-retentive – avoid usage in high humidity.	Very strong	~800	> 400	-60°C - 80°C Ethane to n-C5	Generated from the thermochemical decomposition of organic polymers such as poly(vinylchloride) or corresponding copolymers. Elimination of hydrogen chloride occurs at 180°C and the remainder from the reaction is the porous carbon backbone. Non-friable.	Ultravolatile hydrocarbons such as C2 to C4 hydrocarbons, chloromethane. Also suitable for permanent gases such as hydrogen (H2), oxygen (O2), argon (Ar), CO, CO2.
Carboxen 569	Less hydrophilic compared to other carbon molecular sieves. Dry-purging may still be needed.	Strong	~485	> 450	-30°C - 150 °C n-C3 to n-C8		Volatile hydrocarbons
Carboxen 1000	Prone to water retention – unsuitable for high humidity environments. Dry-purge extensively prior to usage.	Very strong	>1200	>400	-60°C - 80 °C n-C2 to n-C3		Ultravolatile hydrocarbons such as C2 to C4 hydrocarbons, vinyl chloride. Good for permanent gases e.g. H2, O2, Ar, CO, CO2.
Carboxen 1003	Hydrophilic. Dry-purging maybe necessary.	Very strong	1000	>400	Ethane to n-C5		Ultra-light compounds such as C2 to C5 hydrocarbons, permanent gases such as H2, O2, Ar, CO, CO2
Sphero-car Unicarb	Hydrophilic. Dry-purging is required.	Strong	~1200	> 400	-30°C - 150°C n-C3 to n-C8		Very volatile and small analytes (Vinyl chloride, ethylene oxide, carbon disulfide, dichloromethane, chloroform). Very volatile and spatially large molecules such as sulfur hexafluoride. Low-boiling polar compounds such as methanol, ethanol and acetone.

It is also very important to know the thermal stability of the sorbent materials before use because desorption and conditioning temperatures can reach values of 300 °C and even 400 °C depending on the application. The thermal stability varies between different sorbent materials. The most thermally stable sorbent materials commonly used are carbon-based that can be heated up to 400 °C without any degradation or any artifacts released. Sorbent materials such as Porapak series and Chromosorbs, which are porous polymers easily degrade on temperatures higher than 225 °C, with Tenax as the exception as it is the only thermally stable porous polymer that can be desorbed above 225 °C with ability to be heated up to 350 °C.[240, 260, 261]

6.3 Sampling methodology of Volatile compounds

Because the TD-GC-MS technique is very sensitive (ppb) levels, collection of VOSCs require very small quantities of compounds to be retained by the sorbent. To be able to stay within desired calibration range of the MS detector and avoid high breakthroughs of analytes/standards, small volumes are needed to be sampled, thus allowing very low flow rates for longer sampling periods. Sampling can be conducted in a way so that the flow rate and volume of air that is collected are controlled by calibrated pumps, while between sampling the sorbent material is kept free of air by using diffusion locking caps (so-called “Difflok”). This type of collection is called active sampling, while passive sampling simply allows diffusion of the gasses onto the sorbent sampling material. The total net target analytes collected by a sorbent bed comes from either when an equilibrium is reached or when sampling is discontinued by the operator.[254]

The ranges of the final sampling volume and air flow for active sampling are between 0.1 to 150 litres and 10 mL/min to 1000 mL/min, respectively [252]. However, recent innovations in technology have allowed low active sampling flow rates of between 0.5 mL/min to 1 mL/min with minimal or no influences from diffusion uptake. The sorbent is encased in a Safelok tube, which has a specially designed diffusion lock inserted in the air gaps at both ends of the tube [252, 259, 265].

The optimum volume and flow have to be determined for the analytical application. While higher volumes would enhance the sensitivity of analytical methods, it could increase the risk of breakthrough of analytes through the sorbent materials.[266] The breakthrough values are calculated as percentages of the target compounds detected at the back tube when two similar tubes are attached in sequence with a calibrated pump attached to the back tube.[251]

Kristin Andersen and coworkers [267] published a work on optimizing a methodology for sampling thiols, with eliminating artifact formation by investigating various types of sorbent materials by using TD-GC–MS. Breakthrough, desorption rate, the effects of storage and desorption temperatures were investigated and different drying methods were established with respect to quantitative sampling. The study showed that multi-sorbent tube filled with Tenax TA and carbonised molecular sieve or Tenax TA cooled to ≤ 0 °C gave the best results.

However, compared to active sampling that is the most commonly utilized technique, there are no reports yet published on passive sampling of volatile sulfur compounds. [268] The mechanism of concentrating volatile analytes including sulfur volatiles on sorbent beds in passive dosimetry is by diffusion of gaseous molecules from the exposed side of the sample

tube. The net transport of volatile species being trapped onto the sorbent material coming from the outer sampling environment ceases when equilibrium is reached or discontinued by the user. [259]

Gallego et al. [266] evaluated the passive sampling in comparison to active sampling by analyzing volatile organic compounds and found that there were significant differences in the majority of the concentrations obtained from the two different sampling procedures in spite of having comparable analytical characteristics during method validation. The concentrations measured using radial-type sampling tubes were higher than pumped sampling. Hence, calculation of the real diffusion sampling rate is essential to prevent overestimation of the value that was determined by suppliers via exposure chambers. Due to the distinct direction of diffusion in radial samplers as compared to axial samplers, sampling times could be a factor that affects the uptake rates.

Gallego et al. [269] in another study how the duration of sampling and atmospheric VOC concentrations could influence the uptake performance of the passive samplers. Radial-type diffusive tubes with 4 replicates were sampled for different periods (3, 4, 7 and 14 days) during each sampling experiment. The results revealed that more than half of the measurements show significant differences between the total mass of VOCs collected in two short sampling intervals and in one equally long sampling period. Longer sampling durations introduce more uncertainties to the results as it can lead to back diffusion especially when weak sorbents were utilized for sampling.

6.4 Literature review on sorbent materials properties

It has always been challenging to analyze sulfur compounds in the atmosphere because they mainly occur in trace levels. Most of the volatile sulfur compounds exists in low concentrations, even at parts per trillion (ppt) levels, hence analyzing complex mixtures can lead to problems with interferences between major and minor constituents. Furthermore, a second major problem is that sulfur compounds are highly reactive in nature with metal catalytic oxidative, photo-oxidative absorptive and adsorptive properties meaning that they can degrade during sampling. Their reactive properties leads to catalytic reactions, irreversible adsorption, self-reactions between molecules, reactions catalyzed by different materials as well as reactions with substances they come in contact with. Hence, during the analysis all the steps need to be conducted with special precautions such as pre-concentration, sampling, chromatographic analysis, storage and isolation.[270, 271] There are different types of pre-concentration methods available. Atmospheric VOSCs can be collected in vessels such as glass bulbs, canister bags, polymer bags, and Tedlar film bags or collected on solid sorbent materials usually packed in glass or stainless steel tubes. Sampling on solid sorbent is the most common technique used for collection of volatile sulfur compounds. This methodology provides a wide range of different sorbent materials such as activated charcoal, silica gel, aluminum oxide, graphitized carbon black, molecular sieves, and porous sorbents (Tenax series) as discussed in sections (6.2.1 and 6.2.2). A number of materials have been tested and found to be useful in collecting volatile sulfur species.[272-275] However the most popular sampling material for trapping the VOSCs is Tenax and it has been widely used for the collection of ketones, esters, volatile aromatics, aldehydes, alcohols and aliphatic hydrocarbons. For humid areas such as Singapore, Tenax

as a primary sorbent is a material of choice due to its hydrophobic properties and high thermal stability. [237, 239, 276] Although Tenax has shown limitations in terms of collection of the low boiling points organosulfur compounds (e.g., H₂S, MeSH, etc), this can be overcome by adding one more backup sorbent, usually sorbents from the Carboxen series that increase the sampling capacity (boiling point range of the target analytes).[230, 263, 271, 277-281]

A study by Przyjazny et al. [282] investigated the adsorption efficiency and capacity by analysis of the breakthrough volumes of different sorbent materials (Chromosorb 102, XAD-2, XAD-4, XAD-7, and Tenax) for eleven organo-sulfur compounds including sulfides, thiols, thiophenes and disulfides. XAD-4 porous resins were found to have the largest breakthrough volume, due to bleeding and efficiency limitations.

Lestremat et al. [283] studied sorbent material sampling efficiency using nine volatile sulfur compounds including thiols, sulfides and disulfides. Tenax TA, molecular sieves 5A and Carboxen 569 were the sorbent materials that were investigated. Carboxen 569 showed a tendency to convert all the thiols and hydrogen sulfide into SO₂, hence was not studied further, while 5Å molecular sieve showed limitations due to low temperature stability (artifact formation) caused by a catalytic effect. Tenax TA showed the best performance especially with more volatile VOSCs.

A study by Baltussen et al. [284] investigated performance of the Carbotrap 300, polydimethylsiloxane (PDMS) and Tenax for sampling of nine VOSCs. Recoveries of ~ 100% were reported for all 9 compounds only with Tenax TA, while for PDMS and Carbotrap 300 three thiols showed very low recovery values in a range of 2-10%.

The most recent study by Borrás et al. [230] used activated coconut solid-phase sorbent for

active sampling of the nine VOSCs (H_2S , EtSH, DMS, CS_2 , BuSH and DMDS) The method has been developed for analysis of ambient air on close vicinity to three landfills processing urban and industrial solid wastes. Recovery efficiency varied from 75% to 97% with no artifact formation during the desorption process that could interfere with measurements. No losses were found during the storage at -20°C .

Gallego et al. [285] published a study on TD-GC-MS analysis of the indoor malodor air coming from a waste treatment facility. Carbotrap, Carbopack X, Carboxen 569 multi sorbent tubes and Tenax TA were evaluated respectively for the trapping of the wide range of VOCs and RSCs. One hundred and thirty chemical compounds were determined qualitatively. Alcohols, esters, terpenoids and carboxylic acids showed the higher concentrations, however, esters, carboxylic acids and aldehydes contributed in a greater part to OU in all studied locations of the facility

Andersen et al. [267] reported an extensive study on various sorbent materials such as Tenax (35/60) combined with sieves (CMS) (60/80), Tenax TA (35/60) combined with Carbograph 5TD (40/60) multi sorbent tubes, and single sorbent tubes packed with Tenax TA and silica gel. Also different tubing material (stainless steel and silanized glass) were investigated. The best performance found were for stainless steel tubes packed with Tenax TA and CMS where no breakthroughs were detected during all experiments, while for silica gel even though it has large adsorption capacity, breakthrough happened after short time. Merlen, et al. [268] studied breakthrough volumes for ppb levels analyzing six different VOSCs (diethylsulfide, methylmercaptan, dimethylsulfide, ethylmercaptan, isopropylmercaptan, tertbutylmercaptan,) conducting active sampling on tubes packed with Tenax TA. For a constant flow of 25 mL min^{-1} , the breakthrough volumes ranged

between 1 L to 5 L except for methylmercaptan, for which it was estimated to be 0.2 L for 20 ppb and around 2 L for 1 ppb.

A literature review summary on pre-concentration methods commonly employed for the sampling of VOSCs in ambient air together with a most common detection techniques employed are summarized in Tables 6-4 and 6-5, respectively.

Table 6-4. Summary of preconcentration methods commonly employed for the analysis of the RSCs in ambient air Sample

Method	RSC type	Collection media	Source
Sorptive metals	DMS	Gold-coated glass wool	Curran et al. [286]
	DMS	Gold coated glass beads	Braman et al. [282]
	DMS	Gold plated sand	Braman et al. [282]
	Total sulfur	Metal foils	Farwell et al. [287]
Sorption on solid sorbent	DMS	Activated charcoal	Lewis et al. [273]
	COS, DMS	Molecular sieve	Wylie et al. [274], Davison et al. [272], Bruyn et al. [288]
	DMS	Tenax TA	Pio et al. [276]
	EtSH, DMS, CS ₂ , PrSH, DMDS, and PeSH	Tenax TA	Rosa Ras et al. [237]
	DMS	Tenax TA	Bruyn et al. [275]
Cryogenic trapping	H ₂ S, MeSH, DMS, CS ₂ , and DMDS	Cryofocusing on cold trap packed with silica gel + carbopack B	Kim [289], Pandey and Kim [290]
	DMS and CS ₂	Cryogenic trap	Ivey and Swan [291]
	COS, MeSH, and CS ₂	Silanized glass-lined	Hobe et al. [292]
Solid phase microextraction (SPME)	H ₂ S, MeSH, EtSH, DMS, and DMDS	100 µm PDMS, 65 µm DVB-PDMS, and 75 µm CAR-PDMS fibers in a Tedlar bag	Lestremau et al. [293]
	MeSH, BuSH, i-PrSH, and i-BuSH	100 µm PDMS and 75 µm carboxen-PDMS fibers from permeation tubes	Haberhauer-Troyer et al. [175]
Other methods (non-GC)	RSC (Not specified)	PTFE tubes	Dincer et al. [294]
	H ₂ S, MeSH, EtSH, and PrSH	Trapping/ preconcentration in alkaline aqueous phase	Bramanti et al. [295]
	Sulfide, methanethiolate, sulfite, and sulfate	Collection on diffusion scrubbers	Ohira and Toda [296]

Table 6-5. Summary of the main detection methods for RSC analysis in ambient air samples

Method	Target Rscs	Analytical condition	Source
		[A] GC-methods	
FID	DMS	Field (natural)	Lewis et al. [273]
FPD	DMS	Field (natural)	Davison et al. [272], Wylie et al. [274], Bruyn et al. [275], Pio et al. [276]
	H ₂ S, MeSH, DMS, and DMDS	Laboratory	EPA [297]
	COS, MeSH, and CS ₂	Laboratory + field (natural)	Hobe et al. [298]
PFPD	H ₂ S, MeSH, DMS, CS ₂ , and DMDS	Laboratory	Pandey and Kim [271]
	H ₂ S, MeSH, DMS, CS ₂ , COS, SO ₂ , and DMDS	Laboratory	Kim [289, 299, 300], Catalan et al. [301]
	H ₂ S, MeSH, DMS, CS ₂ , and DMDS	Laboratory	Kim [299], Pandey and Kim [290]
	H ₂ S, MeSH, EtSH, DMS, and DMDS	Laboratory + field (industrial samples)	Lestremau et al.[293]
SCD	Dimethyl sulfide and carbon disulfide	Field (natural)	Ivey and Swan [291]
	H ₂ S, MeSH, EtSH, 1-PrSH, 2-PrSH, DMS, CS ₂ , DMS, COS, and SO ₂	Laboratory	SCAQMD [302]
AED	MeSH, BuSH, i-PrSH, and i-BuSH	Laboratory	Haberhauer-Troyer et al. [175]
MS	Not specified		Dincer et al. [294]
	EtSH, DMS, CS ₂ , PrSH, DMDS, 1-PeSH	Field (bioindustry)	RosaRas et al. [237]
ASD	Not specified		Perkin-Elmer [303]
SCS	H ₂ S, MeSH, and DMS	Oral malodour measurement	Hanada et al. [304]
		[B] Methods other than GC	
LC-AFS	H ₂ S, MeSH, EtSH, and PrSH	Field (industrial)	Bramanti et al.[295]
IC	Sulfide, methanethiolate, sulfite, and sulfate	Field (natural)	Ohira and Toda [296]

6.5 Atmospheric VOSCs Profiles in different countries

Based on reports on monitoring VOSCs in recent years, the most common technique used for analysis is TD-GC with active sampling on solid sorbent materials. The most effective and used sorbent materials are Tenax TA or multi sorbent tubes containing Tenax TA/Carbopack. Several of the most widely reported VOSC contaminants of interest that have been monitored as a malodor contributors are hydrogen sulfide (H_2S), ethanethiol ($\text{CH}_3\text{CH}_2\text{SH}$) methanethiol (MeSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS), propyl mercaptan ($\text{C}_3\text{H}_8\text{S}$) and carbon disulfide (CS_2). As the main sources of the odour pollutants come from industrial zones, landfills, sewers and water treatment plants, many countries conduct studies by monitoring emissions of the VOSCs at these characteristic sampling sites to determine how these processes affect the ambient air quality. Table 6-6 summarizes concentrations of the most common VOSCs (H_2S , DMS, DMDS, MeSH and CS_2) in different samples in the vicinity to sewers, landfills, industrial complexes, wastewater treatment plants (WWTPs) and sewage treatment sludge in eight different countries (Australia, Taiwan, China, Spain, United States, Sweden, South Korea and Turkey). From the concentrations listed in the table 7-6, it can be seen that there are large variations in results between different countries or regions due to the nature and magnitude of sewage-driven odour emissions, which depends on environmental and hydraulic conditions of wastewater and the design of treatment systems. Nevertheless, there are few reports to date about long term monitoring of the air quality in terms of volatile sulfur compounds from any of the abovementioned sources. Most published research has been based on developing analytical methods to improve sampling by studying different sorbent materials and improving collection and desorption processes.

Table 6-6. Ambient concentrations of the most common VOSCs in different countries sampled in close vicinity to different sources such as: sewers, waste water treatment plants, landfills and industrial complexes.

Study Country	Source	H ₂ S (µg/m ³)	MeSH (µg/m ³)	DMS (µg/m ³)	CS ₂ (µg/m ³)	DMDS (µg/m ³)	Reference
Taiwan	Sewers	-	-	-	6.39–7.5	-	{Huang, 2012 #761}
US	WWTPs	17–446.9	8–8.7	3.8–26.4	6–5.7	-	{Khan, 2012}
Sweden	WWTPs	40.3	13.7	114.1	1.9	<0.1	{Nielsen, 2002}
Australia	Sewers	0.3–13.9	19.6–98.1	25.3–126.7	-	-	{Wang, 2015}
Spain	sludge	-	-	0.4–608.5	nd–658.5	1.0–857.8	{Borrás, 2016}
Spain	Landfill	608	-	-	139	41	{Borrás, 2016}
China	Landfill	31–867	12–113	24–40	-	60–149	{Duan, 2014}
South Korea	Industrial Complex	7.887	0.128	3.421	-	0.064	{Pal, 2009}
Turkey	Sewers	47.1	-	59.1	-	-	{Muezzinoglu, 2003}

Chapter 7. Method development for the analysis of the volatile sulfur organic compounds using thermal desorption gas chromatography mass spectrometry

7.1 Introduction

Anthropogenic VOSC emissions into the atmosphere can become conceivably harmful to all living organisms due to continuous global industrial activities. The quantification of VOSCs present in ambient air is therefore very important for developing regulations needed to control pollution. Environmental and health effects of some of these contaminants have been established in a number of previous investigations. [229, 232, 264, 309] Acute exposure to VOSCs can induce irritation of mucous membranes, nausea, increase the risk of asthma and affect the nervous, immune and reproductive systems. [229, 235, 309, 310]

TD-GCMS is a solvent-free analytical technique that has become widely recognized and utilized for studying outdoor environmental pollution, indoor air quality and organic gases in different types of microenvironments. Applications of the analytical technique have been expanded further in recent years. For example, several toxic organic compounds were incorporated as target analytes that were not previously analyzed. Albert Tangerman and coworkers optimized and validated a sensitive TD-GC-MS procedure for screening trace amounts of H₂S, COS, CS₂, thiols, sulfides, disulfides present in air samples.[279] Andersen and colleagues [267] discovered the optimum analytical and storage conditions

for sampling and determining methanethiol, a highly volatile and reactive organic compound via TD-GC-MS.

The determination of safe sampling and breakthrough volumes of different types of multi sorbent tubes for an extensive range of organic contaminants were also carried out in recent studies.[240, 266, 271] This is because commercial suppliers of sorbent materials provide breakthrough information of limited types of VOSCs, which are only applicable to single sorbents.

In this chapter, an analytical method was developed and validated for evaluating the amounts of atmospheric VOSCs that are commonly found in the western industrialized region of Singapore, which is the home to one of the largest petroleum refineries in the world, waste treatment factories and paper, food and beverage and farm industries. Ethanethiol (EtSH), dimethyl sulfide (DMS), carbon disulfide (CS₂), propyl mercaptan (PrSH), dimethyl trisulfide (DMTS) and 1-buthanethiol (1-BuSH) compounds were selected as target analytes after identification from air samples collected by active sorbent-based sampling and evaluated using TD-GCMS prior to method optimization.

7.1.1 Chemicals

All the chemicals ethanethiol, dimethyl sulfide, carbon disulfide, propyl mercaptan, dimethyl trisulfide and 1-buthanethiol were purchased from Sigma-Aldrich (St Louis, USA) in the forms of analytical standards dissolved in high purity HPLC grade MeOH (VWR) and neat chemicals with a purity no less than 99 %. All the neat chemical standards were prepared by dissolving in MeOH after which standard stock solutions were subsequently prepared. All the stock standard solutions were then individually transferred

to a volumetric flask diluted with MeOH to make a mixture of the 1000 ng/μl concentration. Further dilution of the mixture was carried out to make calibration standard solutions, with various concentrations ranging from 0.1 to 100 ng/μL. The 500 ppm stock standard solution mix was confirmed by experiments to be stable and last at least for 14 days when properly stored at 4 °C in darkness.

7.1.2 Sorbent sampling materials

In this study, stainless steel sorbent tubes (3.5 in. (89 mm) length × 0.25 in. (6.4 mm) o.d.) were used with different packing materials such as Tenax, Carbopack X, Carboxen obtained from (Markes International Limited, Llantrisant, U.K.) used for the collection of samples and injection of analytical standards. Multi sorbent tubes Tenax/Carbopack X and Carbopack X/Carboxen were also investigated for their adsorption efficiencies by studying both, calibration standard injection and sampling breakthroughs. It has been previously reported that multi sorbent tubes are more efficient of adsorbing a wide range of compounds with different boiling points (BPs) and polarities when compared to the single sorbent tubes. Carbopack X selectivity is increased towards more volatile analytes with BPs between 50 °C to 150 °C, while Tenax is a weak sorbent more selective for the sampling of the aromatics and non polar VOCs with BPs above 100 °C [239]. Low hydrophobicity of the both materials makes them suitable for the analysis in humid areas such as Singapore and as such reduces breakthroughs related to humidity. [259]

Carbopack X/Carboxen tubes were conditioned for 1 hour at 100°C, followed by 1 hour at 200 °C, followed by 1 hour at 300 °C, followed by 4 hours minimum at 380 °C. Tubes

were reconditioned for 15 min at 100 °C, followed by 15 min at 200 °C, followed by 15 min at 300 °C, followed by 15 min at 380 °C.

Tenax tubes were conditioned for 2 hours at 320 °C, followed by 30 min at 335 °C. Tenax tubes were reconditioned for 30 min at 335 °C, while Tenax/Carbopack X were conditioned for 2 hours at 320 °C, followed by 4 hours minimum at 335 °C and reconditioned every time for 30 min at 335 °C. Conditioning procedures were followed by the manufacturers guidelines (Markes International Limited, Llantrisant, U.K.) and always maintained under 99.999% pure nitrogen flow of 70 mL/min. Calibration standards were transferred onto the sorbent beds by injecting 1 µL of the standard solution into the sorbent tube connected to a calibration loading ring using a GC manual syringe which was kept connected for 20 seconds to confirm that target analytes were completely vaporized. The stream of the nitrogen gas 99.999% purity aids the adsorption of the VOSCs onto the sorbent material and purges the solvent (i.e. methanol which is only very weakly retained) from the tube. For all the conditioning processes in this study, a TC-20 (Markes International Limited, Llantrisant, U.K) tube conditioner system was used with a nitrogen flow of 70 mL/min.

7.1.3 Instrumentation

TD-GC-MS was used in this study for quantification and qualification analysis of the target VOSCs. Thermal desorption inlet “UNITY” series 2 and Ultra auto sampler were from (Markes International Limited, Llantrisant, U.K.) are shown in figure 7-1. The thermal desorption unit was attached to an Agilent 7890A gas chromatograph coupled to an Agilent 5975C mass spectrometry system (GC/MS). Pre desorption purge was set at 1 minute with a flow of 45 ml/min with a split flow of 6 ml/min. Sorbent tube desorption was conducted

in two stages. Sorbent tubes were heated at 200 °C and 300 °C, each for a 5 minute hold time. High purity (99.999%) helium gas was continually passed through the sorbent tubes at the rate of 35 ml/min to simultaneously desorb and focus the analytes onto a cold trap (Tenax/Unicarb) held at -10 °C by a Peltier cooler. The cold trap was then heated to 200 °C at a rate of 40 °C s⁻¹ for 3 minutes to desorb the analytes onto the GC column. A =split flow of 20 ml min⁻¹ was optimized for both stages of desorption. Mass spectrometer tuning was performed as previously described in section 2.2.4.

Figure 7-1. TD-GCMS system used in this study

7.1.4 Qualification/Quantification parameters

Mass certified GC column (1-ms 60m 0.32mm Zebron, Phenomenex, USA) was used for separation of the 6 target VOSCs (ethanethiol, dimethyl sulfide, carbon disulfide, propyl mercaptan, dimethyl trisulfide and 1-buthanethiol). The GC oven was programmed at 36 °C and kept for 5 minutes then increased to 240 °C at a rate of 80 °C/min. The temperature of 240 °C/min was kept for 6 minutes to allow the analytes of interest to elute. The carrier (inert) gas in all experiments was 99.999% pure Helium maintained at the flow of 2 ml/min. Final separation results are shown in the chromatogram in the figure 8-2.

The temperature of the interface that connects the GC to the MS was kept on 250 °C. Scan mode acquisition was in the mass range of 35 up to 300 amu. The ionization source used for this study was electron impact (EI) with an applied voltage of 70 eV. Quadrupole temperatures of 150 °C and 230 °C were correspondingly set. Qualitative analysis of the VSOCs were conducted by matching the retention times (tR) as well as relative abundance of the qualifier and quantifier ions to the external standards of the target VSOCs compounds. Quantification analysis from the real samples collected, were performed using an external calibration curve procedure. Table 7-1 represents a sum up of the GC-MS development showing qualification and quantification ions for all the VOSCs analyzed together with the retention times of eluting peaks.

Figure 7-2. TIC Chromatogram of the 6 target VOSCs

Table 7-1. Sum up of target VSOCs retention times (t_R), qualifier ions (Q1 and Q2) and quantifier ions.

VOSCs reference number	Target Analyte name	Quantificatio n Ion	Qualification ions		Retention time t_R (min)
			Q1	Q2	
1	Ethanethiol	62.1	32.1	47.1	3.26
2	Dimethyl Sulfide	62.1	45.1	47.1	3.51
3	Carbon Disulfide	76.0	44.0	78.0	3.85
4	Propyl Mercaptan	76.1	47.1	61.1	5.40
5	1-Buthanethiol	90.1	41.1	56.1	6.75
6	Dimethyl Trisulfide	126.1	79.0	111.0	8.25

7.1.5 Method validation

Method validation was performed to inspect the performance of the developed TD-GC-MS procedure for VOSCs analysis for the following criteria: precision, selectivity, linearity, sensitivity, breakthrough, tube desorption accuracy and efficiency. Table 7-2 summarizes all the method validation data obtained for the abovementioned analytical features.

Selectivity of the method was evaluated by assessing the developed temperature gradient for peak separation at high concentrations. The analytical resolutions obtained between all compounds of interest were calculated from a total ion chromatogram that was generated from a sorbent tube injected with 100 ng of standards. Excellent chromatographic separation was observed for all target VOSCs (refer to the figure 7-2). Evaluation of the precision was performed by analyzing five sorbent tubes (n=5) loaded with 100 ng of VOSCs standards and calculating the percentage relative standard deviation (%RSD) of the RSC quantifier ion signals found in the chromatograms obtained from these tubes. Excellent repeatability was achieved for all target compounds. The %RSD values for all VOSCs (Table 7-3) were below 5% and complied within the EPA TO-17 performance criteria of 25%.

Calibration curves of standards were constructed by plotting the integrated area under quantifier ion signals against varying analyte concentrations [110]. The linear relationship between the two functions was examined using the coefficient of determination, R^2 . The linearity of the multi-point calibration curve of VOSC standards over an extensive range of concentrations was tested. All target analytes exhibited good linearity between 0.01 ng to 100 ng, with R^2 values ≥ 0.99 , for signal to noise ratios ≥ 10 (i.e. the limit of quantification). Table 7-3 shows the R^2 values for each compound that is between the limits

of quantification and up to 100 ng.

Instrument sensitivity was evaluated by its limit of detection (LOD) and limit of quantification (LOQ). LOD is the minimum amount of analyte present in a sample that can be detected but not quantified as an accurate value [110]. LOQ is the minimum amount of analyte found in a sample that can be quantitatively established with reliable precision and accuracy [110]. The LOD and LOQ calculations were carried out using the signal to noise approach. All compounds of interest were absent from blanks, thus, LOD is the amount of analyte that produces a signal-to-noise ratio of 3, while LOQ is the amount of analyte that generates a signal-to-noise ratio of 10 [110]. LOD and LOQ values for each VOSC's analytes are summarized in Table 7-2.

Tube desorption efficiency examines the recovery of analytes from tube desorption and investigates whether there are any remaining target analytes in the sorbent tube after the first analysis. In other words, it is used to evaluate whether the tube desorption parameters (i.e. temperature, time and flow) are efficient for maximal transfer of analytes into the GC-MS. The sorbent tube, spiked with 100 ng of the analyte mixture via a calibration loading ring was analyzed twice by TD-GC-MS. The tube desorption efficiency is reported as the percentage of VOSC quantifier ion peak area during the first TD-GC-MS analysis over the sum of quantifier ion peak areas obtained for the analyte in both TD-GC-MS analysis. Complete recovery efficiency of 100% was obtained for all target analytes that were tested. Method accuracy was calculated as the percentage recovery of the integrated area under the analyte quantifier ion signal obtained using TD-GC-MS, compared to the analyte quantifier ion response area obtained by direct injection under the same split conditions. Triplicate analysis of 100 ng of VOSC's was conducted for both methods to determine the

average response. Recoveries between 86 % to 92 % were achieved for the compounds of interest (refer to Table 7-2).

Table 7-2. Summary of method validation data for standards where %RSD stands for Percentage relative standard deviation, R^2 stands for linear regression coefficients for concentrations between LOQ to 500 ng, LOD is Limit of Detection, LOQ is Limit of Quantification. %RSD rounded to nearest whole number.

RSC Reference no.	Target compound	%RSD (n=5)	R^2	Breakthrough (%)	LOD (ng)	LOQ (ng)	Tube desorption efficiency (%)	Accuracy (%)
1	Ethanethiol	2	0.9973	0	0.04	0.07	100	89
2	Dimethyl Sulfide	1	0.9977	0	0.03	0.06	100	92
3	Carbon Disulfide	3	0.9982	0.65	0.001	0.009	100	88
4	Propyl Mercaptan	1	0.9929	0	0.01	0.04	100	91
5	Buthanethiol	1	0.9991	0	0.01	0.06	100	93
6	Dimethyl Trisulfide	2	0.9910	0	0.06	0.08	100	86

Breakthrough was investigated to determine the retention capacity limits of selected sorbent materials during air sampling and injection of standards. It is defined as the percentage of VOSC mass detected in the back sorbent tube when two sorbent tubes of the same type are connected in series. While breakthrough information of certain compounds in single sorbents are available from commercial suppliers, it is important to determine the breakthrough under the present sampling conditions where multi-sorbents are used. Carboxen/Carboxen 5TD, Tenax TA and Tenax TA/Carboxen were sorbent materials investigated for breakthrough results. Two types of breakthroughs were evaluated in this

study: during the loading of VOSC standards via a stream of nitrogen gas for trapping compounds onto the sorbent materials (Table 7-2 and 7-3), and during the collection of air samples using calibrated air pumps (Tables 7-4 and 7-5). The latter will be elaborated further under the next section. The former was carried out by injecting a 1 μ L aliquot of the 100 ng/ μ L standard mixture into the front end of the tubes connected in series. A stream of nitrogen gas (99.999% purity) was concurrently flowing into the connected tubes at 100 mL/min for 5 minutes during the loading of standards. The experiment was carried out at 25 °C and 55% relative humidity. Both tubes were analyzed and the peak area of the target compounds were quantified using the calibration curve established at concentrations between 0.01 ng to 500 ng. Breakthrough values for each VOSC was calculated as a percentage of the mass of VOSC analyte present in the back tube, over the total mass of VOC detected in both tubes [311]. All sorbent materials examined demonstrated excellent breakthrough values of < 4 % during the injection of VOSC standards, except for Carbopack/Carboxen that showed relatively high breakthroughs for Carbon Disulfide 10.67 % and Dimethyl Trisulfide 7.45 %, respectively, as shown in Table 7-3. The breakthrough data reveals that there were minimal leakages of analytes from the front sorbent tube during the preparation of sorbent tube standards for a nitrogen gas flow of 100 mL/min for all the sorbent materials studied.

Table 7-3. Breakthrough percentage values of VOSCs for different types of sorbent materials used (Calibration loading ring set up on 100 ml/min flow rate)

Sorbent material	Ethanethiol	Dimethyl Sulfide	Carbon Disulfide	Propyl Mercaptan	Buthanethiol	Dimethyl trisulfide
Tenax TA	0	0	0.65	0	0	0
Carbopack/Carboxen	0	3.12	10.67	1.12	0	7.45
Tenax TA/ Carbopack	0	0	1.41	0	0	0.83

7.1.6 Performance evaluation of sorbent tubes in samples

The performance of sorbent tubes under real sampling conditions was investigated by a series of air sampling experiments, at different sampling flow rates (i.e. 30 mL/min, 50 mL/min and 70 mL/min) and sampling volumes (i.e 1 L, 5 L and 10 L). Reproducibility and breakthrough of target VOCs detected in air samples were calculated for each combination of sampling volume and flow rate utilized. This is to establish the optimal sampling volume and flow rate for real sample collection. Two tubes were connected in series with a portable pump attached to the sorbent tube at the back end. All sampling pumps were calibrated with a flow meter prior to use. The summary of percentage breakthrough measurements obtained for all sampling volumes and flow rates are tabulated in Table 7-4 and 7-5. The value of zero indicates that no analyte was detected in the back tube, while n.d. means that no analyte was detected during sampling. The percentage breakthrough values of the target RSCs found in samples were calculated the same way as the percentage breakthrough values for standards in section 8.2.2. A triplicate setup was made to investigate the reproducibility of the sampling procedure using portable sampling

pumps. %RSD was used to express the reproducibility of the sampling. The percentage breakthrough values were found to be $\leq 5\%$ over all flow rates and volumes for all the target analytes except for carbon disulfide sampled with a multi sorbent tube TenaxTA/CarbopackX with a breakthrough value of 6.04 %. A uniform increment in breakthrough was expected when the sampling volume and flow rate increased. However, this was not always the case, such as for carbon disulfide where irregular trends were observed.

Table 7-4. Table of percentage breakthrough values (Tenax) for all sampling volumes and flow rates. 0 stands for no VOSC detected in the back tube and n.d. represents not detected in sampling. RH stands for relative humidity.

No.	Compound name (VOSC)	1 L sample volume			5 L sample volume			10 L sample volume		
		55% RH 30 °C	55% RH 31 °C	55% RH 32 °C	55% RH 32 °C	55% RH 31 °C	55% RH 31 °C	55% RH 30 °C	55% RH 30 °C	55% RH 30 °C
		30 mL/min	50 mL/min	70 mL/min	30 mL/min	50 mL/min	70 mL/min	30 mL/min	50 mL/min	70 mL/min
1	Ethanethiol	n.d.	n.d.	n.d.	0	0	0	0	0	0
2	Dimethyl Sulfide	0	0	0	0	0.52	0.67	0.87	0.98	1.3
3	Carbon Disulfide	0	0	0	0.61	0.88	0.66	1.34	2.63	3.8
4	Propyl Mercaptan	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	Buthanethiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6	Dimethyl Trisulfide	n.d.	n.d.	n.d.	0	0	0.44	0.52	0.68	0.83

Table 7-5. Table of percentage breakthrough values (Tenax/Carbopack X) for all sampling volumes and flow rates, 0 stands for no VOSC detected in the back tube and n.d. represents not detected in sampling. RH stands for relative humidity.

No.	Compound name (VOSC)	1 L sample volume			5 L sample volume			10 L sample volume		
		55% RH 30 °C	55% RH 31 °C	55% RH 32 °C	55% RH 32 °C	55% RH 31 °C	55% RH 31 °C	55% RH 30 °C	55% RH 30 °C	55% RH 30 °C
		30 mL/min	50 mL/min	70 mL/min	30 mL/min	50 mL/min	70 mL/min	30 mL/min	50 mL/min	70 mL/min
1	Ethanethiol	n.d.	n.d.	n.d.	0	0	0	0.45	0.77	1.39
2	Dimethyl Sulfide	0	0	0	0.33	0.67	0.91	1.54	2.01	2.54
3	Carbon Disulfide	0	0	0.38	0.80	1.35	1.11	3.54	4.21	3.04
4	Propyl Mercaptan	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	Buthanethiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6	Dimethyl Trisulfide	0	0	0.29	0.45	0.85	1.34	2.57	3.51	4.52

There are a few possible reasons for the observed anomalous breakthrough data. Natural variations in temperature could potentially influence the breakthrough values. It is widely known that breakthrough values are dependent on temperature and relative humidity of the sampling environment [312]. Because the time period for the collection of air samples are different due to different sampling flow rates, significant changes in the combination of both factors (i.e. temperature and relative humidity) during the different time spans could affect the breakthrough values obtained. Therefore Tenax TA as hydrophobic material [251] showed better performance comparing to Carbonized materials as Carboxen and Carboxen series.

Another possible explanation for the non-uniform variation in breakthrough readings with sampling volume and flow rate is the natural variation in the concentration of atmospheric VOCs at different times of the day. Errors from breakthrough calculation could happen when low amounts of analytes were detected in the front tube even though trace amounts were found in the back tube. 50 mL/min was chosen as the sampling flow rate because the majority of the compounds of interest demonstrated excellent breakthrough (i.e. 5%) at that flow rate. Another reason is that the mentioned breakthrough anomalies were observed in samples obtained at flow rates from 70 mL/min. Sampling volume of 5 L at 50 mL/min flow rate using a Tenax TA sorbent material are the optimum sampling conditions developed that produce best detection limits and acceptable breakthrough criteria (i.e. 5%) with all parameters summarized in Table 7-6.

Table 7-6. Summary of the Tenax TA sorbent tube performance in sampling at 50 mL/min, with a 5 L final volume. n.d. = not detected.

No.	Compound name (RSCs)	Breakthrough (%)	% RSD (n=3)	MDL (ng m ⁻³)	MQL (ng m ⁻³)
1	Ethanethiol	0	2	0.008	0.014
2	Dimethyl Sulfide	0.52	3	0.006	0.012
3	Carbon Disulfide	1.35	2	0.0002	0.0018
4	Propyl Mercaptan	n.d.	n.d.	n.d.	n.d.
5	Buthanethiol	n.d.	n.d.	n.d.	n.d.
6	Dimethyl Trisulfide	0.85	2	0.012	0.016

5 L would be an advantageous choice as the optimal sampling volume because a high sampling volume reduces the method detection and quantification limit for all target compounds. The sensitivity of the analytical procedure could be enhanced when the higher sampling volume was used for pre-concentration of VOCs on sorbent materials. In addition, more pre-concentration is necessary for some compounds to be detected. Compounds such as ethanethiol and dimethyl trisulfide were not detected in 1L and 3L samples or were below the detection limits.

Sorbent trapping of atmospheric VOSCs using calibrated portable pumps was shown to be highly reproducible for all compounds of interest at sampling volumes of 1 L, 5 L and 10 L at 50 mL/min. All 6 target VOSCs present in samples met the EPA TO-17 guidelines for reproducibility and have %RSD values under 20% (Table 7-6) for n=3. The MDL of target

analytes was calculated based on the sampling volume. The LOD in Table 7-2 was divided by the chosen sampling volume to obtain the MDL. The MQL of target analytes was determined by division of the LOQ found in Table 7-2 and the selected sampling volume.

7.2 Conclusion

A TD-GCMS method has been developed for the detection and quantification of 6 atmospheric VOSCs (ethanethiol dimethyl sulfide carbon disulfide propyl mercaptan buthanethiol dimethyl trisulfide) frequently present in the western semi-urbanized region of Singapore, located in close proximity to petrochemical and heavy industries (figure 8-1). All 6 VOSCs were assessed and validated for several analytical method characteristics. Excellent repeatability with %RSD values $\leq 3\%$, good linearity with R^2 0.99 for a wide range of concentrations between 0.01 to 100 ng, percentage breakthrough values 5% or lower, tube desorption efficiencies 100% and good recoveries between 86% to 93% were noted for all analytes. Different sampling volumes and flow rates were utilized for evaluating the performance of the multi-sorbent tubes. 50 mL/min was selected as the optimal flow rate while a sampling volume of 5 L showed the best results in analytical performance (i.e. reproducibility and sampling breakthrough). The majority of the VOSCs of interest demonstrated acceptable breakthrough 5%, reproducibility 10% deviation and method detection limits (table 7-3). Criteria established by the EPA for sorbent tube sampling (EPA TO-17) were complied with for all analytes of interest. propyl mercaptan and buthanethiol were not detected in the environment during sampling breakthrough experiments thus the selection of sampling volume, breakthrough, reproducibility, MDL and MQL values remain unknown.

With a versatile method optimized, developed and validated for detecting VOSCs, further studies were implemented for the monitoring the air quality in the industrialized region in western Singapore, understanding the concentration patterns of these compounds that are present in the atmosphere at various time periods, and predicting sources of these compounds. These additional environmental studies are described in Chapter 8.

Chapter 8. Trend profiles and concentration patterns of the volatile sulfur compounds in the largest industrial complex in Southeast Asia from a semi urban sampling site

8.1 Introduction

Air pollution has been a major concern for Singapore over the last two decades. Rapid industrialization in the city-state nation has been ongoing since its independence and there is a growing necessity to monitor the levels of gaseous emissions generated by industries, motor vehicles and other urban anthropogenic activities. In addition, Singapore suffers from severe trans-boundary haze pollution annually due to the smoke from forest fires in neighboring countries that were started to create areas for palm oil plantations [73]. The NEA, Singapore's primary government organization in charge of monitoring the air quality nationwide, regularly reports six major atmospheric contaminants: CO, NO_x, O₃, PM₁₀, PM_{2.5} and SO₂. An air quality indicator known as the PSI is calculated by the agency as well, based on all monitored pollutants. There are a total of 14 monitoring stations located island-wide that are recording these measurements [313]. Other than biomass burning studies, air quality investigations have been carried out for monitoring trace metals, ions, PAHs, water-soluble organic compounds, elemental composition and organic carbon present in outdoor PM_{2.5} [3, 38, 86, 259]. Some of the constituents found in particles were determined in specified microenvironments. Kalaiarasan et al. assessed the amounts of PAHs within particulates in multi-story public housings [314]. See and various coworkers have quantified the organic compounds, ions and metals of PM_{2.5} from cooking techniques

in a residential kitchen [315] as well as investigated PAHs in particulates emitted from diesel vehicles [316]. There are only a few publications, which describe monitoring ambient organic contaminants in Singapore even though the class of compounds is considered as one of the major criteria pollutants by environmental agencies around the world [74, 317, 318]. He and colleagues monitored gaseous emissions of semi-VOCs, as well as those found in water [85]. As far as we know, there is no information about the volatile organic sulfur compounds (VOSCs) found in the atmosphere as previous reports were associated with monitoring particulates and heavier organic molecules.

The objective of this study is to monitor ambient VOSCs present in a semi-urban sampling site that lies between one of the largest industrial estates in Southeast Asia and several livestock farms that are situated in western Singapore. In this chapter, the concentration trend profiles, weekly and monthly statistics for 6 target VOSCs were determined. The analytical method that was described in Chapter 8 is used for this study.

8.2 Sampling location

The collection of air samples was performed on the roof of the School of Physical and Mathematical Sciences building (SPMS) within Nanyang Technological University, situated in the western region of Singapore. Vicinity of the potential VOSCs sources related to the sampling site is illustrated in the figure 8-1. Although, sampling site is the same as previously explained in the section 3.2.1, some specific potential sources closely related to odor species in the western area of Singapore are described. All the farming activities (more than 10) are situated in the western part of Singapore just 6 km away from the sampling site, also 4 waste water treatment plants (WWTP) are situated just 1-4 km away. Various

types of manufacturing industries such as petrochemical refining, rubber vulcanizing and plastic molding process plants, food and beverages factories, pharmaceuticals and medical technology companies are found in Tuas all located within two kilometers from the SPMS. Two main waste incineration plants are also located in the Tuas industry zone. The vicinity in the south and east direction of the school building comprises of a portion of the Pan-Island Expressway (PIE) and residential estates. Both are located 100 m and 260 m away from the SPMS, respectively.[259]

A forest borders the north and west of the university, in contrast to the industries and residential neighborhoods situated to its south and east. The geographical proximity of the sampling site, residential areas, the natural forest and industries present in Tuas and Jurong Island makes it ideal for investigating the VOSCs concentration patterns in such a complex environment. Regular monitoring at this semi urban sampling location can potentially provide valuable information on the concentration levels and patterns of atmospheric volatile organics emitted from several sources.

Sampling sites description

Figure 8-1. Sampling site and its vicinity

8.3 Sample Collection

Atmospheric VOSCs ethanethiol (EtSH), 1-butanethiol (BtSH), dimethyl sulfide (DMS), dimethyl trisulfide (DMTS), carbon disulfide (CS₂) and propyl mercaptan (PrSH) were collected using multi-sorbent tubes [3.5 in. (89 mm) $\times$ 0.25 in. (6.4 mm) o.d.] packed with 400 mg of Tenax TA (Markes International Limited, Llantrisant, U.K). A total of 112 air samples, collected at a sampling volume of 5 L, were acquired between 9th of March 2017 to 25th of Jun 2017 using a MTS-32TM sequential tube sampler equipped with a SKC Pump set at a flow of 50 mL/min. In addition one week of exhaust sampling campaign was performed for studying intraday and diurnal concentration trends of target VOSCs.

8.4 Results and discussion

8.4.1 General patterns of VOSC distribution in the study area

Throughout this study, BtSH and PrSH were not detected, while EtSH, DMS, CS₂ and DMTS were detected in every sample above detection limits. Prior to continuous monitoring, an initial study of 3 days of sampling was performed for different time intervals to determine the sampling frequency. Results showed significant variation in concentration between daytime and nighttime samples collected. Hence, monitoring was performed by collecting 2 samples per day, once during the daytime (10am) and once at nighttime (7.30pm) usually once a week for 4 months. A concentration summary of the target VOSCs analytes monitored are shown in table 8-1. Results are shown for daytime and nighttime respectively.

Table 8.1 Concentration summary (ppbv) of the target VOSCs analyzed during 4 months sampling campaign

Date	Daytime samples (ppbv)				Nighttime samples (ppbv)			
	Ethanethiol	Dimethyl Sulfide	Carbon Disulfide	Dimethyl trisulfide	Ethanethiol	Dimethyl Sulfide	Carbon Disulfide	Dimethyl trisulfide
09/03/17	0.0800	0.9390	0.3241	0.0132	0.1134	0.1417	0.1241	0.0132
13/03/17	0.0632	2.3111	0.5768	0.0058	0.8134	0.1963	0.3768	0.0281
15/03/17	0.1267	3.3110	0.9477	0.0095	0.2401	0.1469	0.2477	0.0095
22/03/17	0.1045	1.1310	0.3572	0.0357	0.0849	0.1811	0.1572	0.0572
30/03/17	0.0828	0.8317	0.3189	0.0032	0.1290	0.7531	0.3319	0.0889
04/04/17	0.0957	0.8131	0.6929	0.0193	0.3942	0.0660	0.0929	0.0093
08/04/17	0.0866	0.9131	0.3522	0.0352	0.2932	1.2000	0.1522	0.0052
12/04/17	0.1101	1.4131	1.5210	0.0210	0.1130	1.3445	0.4391	0.0450
18/04/17	0.0722	0.9310	0.4596	0.0046	0.0920	0.2431	0.2736	0.0396
23/04/17	0.0686	2.3130	0.3810	0.0381	0.3512	0.2600	0.3810	0.0081
28/04/17	0.0550	0.7321	1.2281	0.0393	0.3392	0.3834	0.3481	0.0393
02/05/17	0.0821	0.8134	0.4347	0.0043	0.1420	0.8598	0.2927	0.0266
05/05/17	0.1259	1.3142	0.8317	0.0033	0.1923	0.4013	0.5133	0.0093
08/05/17	0.0720	1.4000	0.3494	0.0035	0.1432	0.7980	0.1249	0.0085
12/05/17	0.1142	0.9423	0.9305	0.0131	0.5312	0.8600	0.5131	0.0075
22/05/17	0.3042	0.6133	1.0022	0.0219	0.2321	0.0757	0.3219	0.0059
28/05/17	0.1794	3.5315	0.4308	0.0024	0.1530	0.2772	0.2228	0.0094
01/06/17	0.0720	0.6411	0.3518	0.0352	0.0859	0.1955	0.3518	0.0156
03/06/17	0.0825	0.7241	0.8212	0.0021	0.3333	0.3920	0.4212	0.0062
07/06/17	0.1465	2.2310	0.9014	0.0014	0.0930	1.7923	0.7429	0.0214
25/06/17	0.0874	1.3143	0.6057	0.0057	0.5139	0.4591	0.4457	0.0094

Among all VOSCs detected, DMS was most prominent in terms of magnitude during both daytime and nighttime sampling campaigns with a mean ppbv values of 1.3888 and 0.5251, respectively. Other VOSCs including EtSH, CS₂ and DMTS occurred in considerably lower concentrations as shown in table 8-2.

Table 8-2. Mean, Minimum, maximum and standard deviation of the target VOSCs monitored in this study for daytime and nighttime samples collected.

(ppbv)	Ethanethiol	Dimethyl Sulfide	Carbon Disulfide	Dimethyl trisulfide
Day time				
Mean	0.1053	1.3888	0.6580	0.0151
Min	0.0550	0.6133	0.3189	0.0014
Max	0.3042	3.5315	1.5210	0.0393
Stdv	0.0546	0.8551	0.3384	0.0138
Night time				
Mean	0.2564	0.5251	0.3274	0.0221
Min	0.0849	0.0660	0.0929	0.0052
Max	0.8134	1.7923	0.7429	0.0889
Stdv	0.1878	0.4685	0.1584	0.0215

Moreover, the maximum DMS value (3.5315 ppbv) was significantly higher as those of the other compounds such as 0.0889 ppbv (DMTS), 0.8134 ppbv (EtSH) and 1.5210 ppbv (CS₂). Hence, at this stage, DMS represents a substantial component of malodor phenomenon in this study area. Results presented in table 8-2 showed significant variations of the mean values for daytime and nighttime sampling periods for all the target compounds monitored. Comparing the relative mean abundances of the monitored VOSC during the

day time and night time it can be seen that for DMS (1.3888 ppbv - 0.5251 ppbv) and CS₂ (0.6580 ppbv - 0.3274 ppbv) daytime values are 3 times and 2 times higher respectively, while the EtSH results (0.1053 ppbv – 0.2564 ppbv) showed more than double higher average abundances during nighttime, although DMTS data (0.0151 ppbv - 0.0221 ppbv) showed only slightly higher values for samples collected during the nighttime. When the daytime and nighttime dominance of the particular compounds were statistically analyzed by performing a *t*-test at a confidence level of 99% and critical value of $p=0.01$, the results obtained showed values less than the critical value for: CS₂ 0.00024, DMS 0.00036 and EtSH 0.00105 hence, significant differences between daytime and nighttime sampling dataset were confirmed. Only DMTS with a calculated value of 0.02227 was higher than the critical values of 0.01, which suggested insignificant differences in diurnal variations. More detailed and extensive studies were performed to evaluate intraday status of VOSCs as well as to try to determine possible influences of anthropogenic sources on VOSC ambient daily distribution. Thorough sampling campaign was performed by collecting 10 samples per day with 5L of volume each. Sampling timetable was: 8.00am - 9.30am - 12.00pm - 14.30pm - 17.00pm - 19.30pm - 22.00pm - 12.30am - 3.00am-5.30am. Results presented in figure 8-2 shows relatively good correlation trends for all 4 monitored VOSCs. These results confirmed the previous findings (table 8-2) about diurnal variations that during daytime occurrence of the DMS and CS₂ are significantly higher comparing to the nighttime and EtSH and DMTS showing the opposite trend. Further statistical analysis on data set of 70 samples collected for this sampling campaign was performed to evaluate significance and validity of the results.

Figure 8-2. 24h intra day variations of VOSCs data across all week in the study area

Linear coefficient matrix analysis were performed to determine inter-day correlation values. Mean values (n=21) of the correlation coefficient (R) were relatively acceptable for all VOSCs monitored: DMS (0.64 ± 0.12), DMTS (0.67 ± 0.19), CS₂ (0.61 ± 0.12) and EtSH (0.63 ± 0.24) respectively. Negative vales are considered as offsets and were not included in statistical analysis as shown in table 8-3.

Table 8-3. Correlation coefficient matrix statistical summary for intensive one week study with a data set of 70 samples collected

a) Negative values are interpreted as offset and were not included in statistical analysis

Correlation coefficient (R) N=21	Ethanethiol	Dimethyl Sulfide	Carbon Disulfide	Dimethyl trisulfide
Min	0.29	0.41	0.17	0.29
Max	0.93	0.92	0.83	0.93
Mean	0.63	0.70	0.61	0.67
Stdev %	0.24	0.16	0.12	0.19
Offsets ^a	3	0	6	4

The relative abundance of EtSH during the nighttime could be explained by a tendency to undergo photodecomposition and reacting with OH radicals during the day time or being converted into other forms of reduced sulfur compounds (VOSCs), most commonly dimethyl disulfide (DMDS) under aerobic conditions.[309] Dimethyl sulfide is a potentially key sulfur source in tropical atmospheres such as Singapore, since the main natural source is oceanic where it is produced by algae and corals. [319, 320] Most of the DMS contributions to the atmosphere come from the marine environment, as large

concentrations of DMS were found over the surface of the ocean by Lovestock et al. [321]. Andreae et al. [307] confirmed concentrations of DMS over the oceanic surface and found that the volatile DMS was produced by marine algae. Sulfate is taken up by algae and then reduced and incorporated into organosulphur compounds.

There are many studies reporting on ocean/air transport of dimethyl sulfide. Results showed higher abundance of the DMS and DMDS during the day compared to the nighttime due to enhanced evaporation of the sulfur compounds from the algae and coral reefs. [320, 322] The main source of the DMTS in the atmosphere comes from livestock and farming activities. [323] Furthermore it has been reported previously that the main anthropogenic source of CS₂ appears to be associated with the strong emissions occurring from waste water treatment plants (WWTP).[324, 325]

As the study area can be subject to the influence of diverse anthropogenic processes such as petrochemical, food and beverage industries, farming, WWTP, sewage systems and incineration plants (Figure 8-1) the status of VOSCs pollution is worth diagnosing with respect to the legislative criteria for VOSCs control. According to various air quality guidelines, the RSC levels in this study are still within the acceptable range of ambient air concentration levels. [326, 327]

The relative composition (%) of VOSCs, if computed as the (v/v) percentage of a particular component over the sum of all RSCs, showed that the most abundant VOSCs during the day was dimethyl sulfide (62%) followed by carbon disulfide (32%) ethanethiol (5%) and dimethyl tyrisulfide (1%), while for the night sampling period ethanethiol becomes 20% more abundant with a final partitioning of 25% while DMS reduces by 23% and CS₂ stays relatively the same (Figure 8-3). Even though it has been statistically proven that CS₂

undergoes diurnal variation, the daytime and nighttime relative percentage (v/v) composition stays the same. The reason for this lies in the contribution of the anthropogenic sources and also high reactivity of the CS₂ with other chemicals in the atmosphere. Several industries use carbon disulfide as a raw material to make such materials such as rayon, paper products, cellophane and carbon tetrachloride. Currently, the largest user of this chemical is the viscose rayon industry. Thus it could be said that 5 paper product factories together with 4 WWTPs located in close vicinity to the monitoring site (Figure 8-1) contribute significantly to the distribution and occurrence of the CS₂ in Singapore's west coast atmosphere.

Figure 8.3 VOSCs molecular distribution in total sample collected a) Daytime and b) nighttime

EtSH has been widely used in petrochemical industry as an additive to odorless gases such as butane, propane and petroleum processing catalysts. This could explain the dominance of these two sulfur components as the monitoring site is located on the island in close vicinity

to the largest petrochemical industrial complex in SEA.[328] Comparing to other VOSCs monitored, DMTS occurs in significantly smaller amounts, suggesting that impact of farming activities (main source of the DMTS) on malodor is very small.

8.4.2 Derivation of odor intensity (OI)

As VOSCs constitute to one of the major malodorous substances with rather small threshold values, assessment of their relative strength as odorous components is an essential step to evaluate their malodor potential. Odor intensity (OI) is used as a means to measure malodor intensity of the VOSCs in ambient air. The main principle is to convert concentration data into OI values by employing empirical relationships that are previously established via human sensory methods [309, 329, 330] Among those VOSCs monitored, DMS was found to be the most abundant and as previously reported, it is a compound that has the highest malodor intensity.[324] Hence, the DMS data were only converted into OI via the following conversion formula (1):

$$\text{OI (DMS)} = 0.784 \log X + 4.06 \quad (1)$$

Here, X stands for the concentrations of the VOSCs in units of ppm. The resulting OIs were analogous to those established by the sensory method: 0 - no odor; 1 - very weak; 2 - weak; 3 - distinct; 4 - strong; 5 - very strong; 6 – intolerable [331].

Results showed that OI for DMS throughout all study had a mean value of 1.82, minimum of 1.54 and maximum of 2.14. The odor intensity computed for the DMS is in good

accordance with previous studies outside Singapore made either in ambient air at industrial sites [309, 324, 332, 333] or in urban background air.[294, 334, 335]

8.5 Conclusion

Regular monitoring of 6 atmospheric VOSC (EtSH, DMS, DMTS, CS₂, PrSH and BuSH) pollutants was performed over a 4 months period between March 2017 and Jun 2017. A total of 112 samples were acquired and the VOSC concentration measurements were evaluated using different statistical calculations. The occurrence of the VOSCs in semi urban ambient air was examined in terms of diurnal, inter-day and intra-day variations. Throughout all the sampling campaign, BuSH and PrSH were not detected in any samples. However, other 4 compounds (EtSH, DMS, DMTS and CS₂) were detected with 100% detection frequency. All results were in a ppbv range and above instrumental and method detection limits. Overall, 4 months of statistical data calculated for all target VOSCs revealed that DMS and CS₂ were the most dominant organosulfur compounds in the atmosphere. Results also showed significant variations in the abundance of VOSCs for daytime and nighttime sampling periods for all the target compounds monitored. Inter-day variation of the VOSCs showed relatively high correlation trends with a mean value of R in a range from 0.61 to 0.67, indicating consistency in VOSCs occurrence in the atmosphere. A few offsets were observed due to the influence of anthropogenic sources such as the petrochemical industry for EtSH, WWTP and paper product industry for CS₂ and farming activities for DMTS. DMS showed no offsets in terms of correlation efficiency most likely due to the dominant impact of the marine environment at the monitoring site. The relative composition (%) of VOSCs, computed as the (v/v) percentage of a particular

component over the sum of all RSCs, were calculated for daytime and nighttime sampling respectively. Only CS₂ showed constant composition for both data sets even though diurnal studies showed relatively higher ambient occurrence in daytime, proving that out of all VOSCs monitored CS₂ is the most impacted by the anthropogenic sources.

However, the low concentration (0.001 - 3.5 ppbv) range of the target VOSCs monitored shows that there is no significant impact of the anthropogenic sources that are in close vicinity to the sampling station that could possibly cause stronger ambient malodor. Odor intensity (OI) data conversion was performed for DMS to determine the malodor intensity. Results showed that odour intensity tended to vary between very weak and weak values (OI=1-2).

Chapter 9. Summary and conclusion

Semi-volatile organic compounds are one of the most widespread environmental pollutants very persistent in nature due to their high resistance to photolytic, biological and chemical degradation. They can be accumulated in human and animal tissue, resulting in chronic and (eco) toxicological effects. [166] In addition, due to being semi-volatile, they are able to exist in the vapor phase of the atmosphere or be ad/ab-sorbed by atmospheric particles, thereby facilitating transport over long distances through the atmosphere. [189] In this study, different analytical methods including gas chromatography - mass spectrometry were utilized for qualification and quantification of the SVOCs in different environmental matrices (water, glacier and particulate matter) in different climates including Singapore's tropical atmosphere and a region of lower Himalayas in Bhutan.

A study of 16 United States Environmental Protection Agency (USEPA) priority listed PAHs associated with particulate matter (PM₁₀) was conducted in Singapore during the period May 2015 to May 2016. The sampling period coincided with an extensive, regional smoke haze episode (5th September to 25th October) that occurred as a result of forest and peat fires in neighboring Indonesia. Throughout this study, 54 atmospheric PM₁₀ samples were collected in 24 h periods using a high volume sampler (HVS) and quartz fiber filters (QFF) as the collection medium. Hysplit software for computing 3-D backward air mass trajectories, diagnostic ratio analysis and ring number distribution calculations were used to examine the sources of PAHs in the atmosphere in Singapore. Under normal conditions the total PAH concentrations were in a range from 0.68 ng m⁻³ to 3.07 ng m⁻³, while for the high haze period the results showed approximately double the concentrations with a

maximum value of 5.97 ng m^{-3} . Diagnostic ratio (DR) and principal component analysis (PCA) were conducted and indicated the contribution of the traffic as a dominant pyrogenic source of PAHs during normal periods, while results from the haze dataset showed relatively strong influence of smoke from peat and forest fires in Indonesia. Environmental and health risk from PAHs were assessed for both regular and hazy days.

6 months sampling campaign (April 2016 to September 2016) of PCBs bounded to $\text{PM}_{2.5}$ showed very low correlation with the $\text{PM}_{2.5}$ concentration patterns, but strong correlation with weather conditions including precipitation and temperature levels. Comparing the literature reports on airborne PCBs related to PM in the region, the present results showed there was not significant changes in the last 15 years. Out of 19 PCBs monitored, 10 were detected with a 100 % frequency of detection. Other 9 PCBs were not detected throughout all the study. The $\text{PM}_{2.5}$ bound PCBs concentrations varied from 5.21 pg m^{-3} to 20.17 pg m^{-3} with a median value of 11.01 pg m^{-3} . Molecular distribution (chlorination levels) showed high domination of the most chlorinated compounds comparing to the less chlorinated ones. PCA analysis of factor loadings for every component extracted and compared to the work previously conducted in neighbouring countries showed possible contributions of the emissions from electronic waste (incineration plant in Tuas) [62] and ship-dismantling activities [146].

A case study was conducted on pesticides and PAHs present in water samples collected in Bhutan in December 2015. The water samples were from 9 spring water sources, 7 storage

facilities, 11 end user taps and water samples collected from the Lake “Teyminus” together with a glacier inlet. Out of 23 OCPs monitored, 8 were detected in concentrations within allowed admissible concentrations for pesticides of $0.1 \mu\text{g L}^{-1}$. Comparing to the OCPs that were quantified, the PAHs detected in lake samples including glacier and an inlet stream showed higher concentrations. All 16 targeted PAHs were detected and quantified in every sample. The most abundant PAHs were NAPH and ACP representing lighter PAHs and BbF, BkF, BaP, IcP, DhA and BghiP as heavier PAHs. Dominance of these specific congeners suggested domestic heating and long distance transport from countries such as India, Nepal and China as a sources of the PAHs in this sampling site.

An analytical method was developed employing thermal desorption (TD) coupled to the GC-MS system for the analysis of the volatile organic sulfur compounds (VOSCs) in Singapore’s industrial and semi urban atmosphere. Four months monitoring over a period between March 2017 and Jun 2017 was conducted and statistical analysis performed to analyze VOSCs concentration trends and identify possible source contributors. Overall, 4 months of statistical data calculated for all target VOSCs revealed that DMS and CS₂ were the most dominant organosulfur compounds in the atmosphere. Results also showed significant variations in the abundance of VOSCs for daytime and nighttime sampling periods for all the target compounds monitored. Inter-day variation of the VOSCs showed relatively high correlation trends with a mean value of R in a range from 0.61 to 0.67, indicating consistency in VOSCs occurrence in the atmosphere. Low concentration (0.001 - 3.5 ppbv) range of the target VOSCs monitored shows that there is no significant impact of the anthropogenic sources that are in close vicinity to the sampling station that could

possibly cause stronger ambient malodor. Odor intensity (OI) data conversion was performed for DMS to determine the malodor intensity. Results showed that odour intensity tended to vary between very weak and weak values (OI=1-2).

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Appendix 1.

It includes mass spectrums obtained for quantification and qualification purposes of the all SVOCs stuided comprising PAHs, PCBs and OCPs

a)

b)

c)

d)

Figure A-1. (PAHs) Mass spectrums obtained for: a) NAP; b) ACE; c) ACY and d) FLO

a)

b)

c)

d)

Figure A-2. (PAHs) Mass spectrums obtained for: a) PHE; b) ANT; c) FLT and d) PYR

a)

b)

c)

d)

Figure A-3. (PAHs) Mass spectrums for: a) BaA; b) CRY; c) BbF and d) BkF

a)

b)

Figure A-4. (PAHs) Mass spectrums for: a) BaP; b) IcP; c) DhA and d) BgP

a)

b)

c)

d)

Figure A-5. (PCBs) Mass spectrums obtained for: a) 1; b) 5; c) 18 and d) 31

a)

b)

c)

d)

Figure A-6. (PCBs) Mass spectrums obtained for: a) 44; b) 52; c) 66 and d) 87

a)

b)

c)

d)

Figure A-7. (PCBs) Mass spectrums obtained for: a) 101; b) 110; c) 138 and d) 141

a)

b)

c)

d)

Figure A-8. (PCBs) Mass spectrums obtained for: a) 151; b) 153; c) 170 and d) 180

a)

b)

c)

Figure A-9 . (PCBs) Mass spectrums obtained for: a) 183; b) 187 and c) 206

a)

b)

c)

d)

Figure A-10 . (OCPs) Mass spectrums obtained for: a) Chlordane; b) d-BHC; c) Pentachloroanisole and d) a-BHC

a)

b)

Figure A-11. (OCPs) Mass spectrums obtained for: a) b-BHC; b) g-BHC; c) Heptachlor and d) Aldrin

a)

b)

Figure A-12 . (OCPs) Mass spectrums obtained for: a) Endosulfan; b) Heptachlor Epoxide; c) g-Chlordane and d) Chlordane

a)

b)

c)

d)

Figure A-13 . (OCPs) Mass spectrums obtained for: a) p,p'-DDE; b) Dieldrin; c) Endrin and d) Endosulfan

a)

b)

Figure A-14 . (OCPs) Mass spectrums obtained for: a) p,p'-DDD; b) Cis-nonachlor; c) Endrin aldehyde and d) Endosulfan 1

a)

b)

c)

Figure A-15 . (OCPs) Mass spectrums obtained for: a) p,p'-DDT; b) Endrin ketone; and c) Metoxichloro

Appendix 2.

Samples IDs and pictures taken from the all sampling locations related to the case study done in Bhutan

*Pictures are provided from the Mr Tshewang (Sherubtse College, Bhutan)

Sherubtse College

1A

1B

Yonphula Village

2A1

2A2

2B

2C
Photo not available

2D

2E

Shedra

3A

3B

Jampeling

4A

4B

Upper Market

5A

5B

5C

5D

5E

Kanglung School

6A

6B

6C

Rongthung Village

7A1

7A2

7B

7C

7D

7E

Rongthung Primary School

8A

8C

Photo not available