Applications of purge-and-trap gas chromatography - Mass spectrometry for the determination of volatile organic compounds in water

Ng, Shu Jun

2018

Ng, S. J. (2018). Applications of purge-and-trap gas chromatography - Mass spectrometry for the determination of volatile organic compounds in water. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/73329>

<https://doi.org/10.32657/10356/73329>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**Applications of Purge-and-Trap Gas Chromatography-Mass
Spectrometry for the Determination of Volatile Organic
Compounds in Water**

NG SHU JUN

**SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES
NANYANG TECHNOLOGICAL UNIVERSITY**

2017

This page has been intentionally left blank.

**Application of Purge-and-Trap Gas
Chromatography – Mass Spectrometry for the
Detection of Volatile Organic Compounds in
Water**

NG SHU JUN

School of Physical and Mathematical Sciences

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2017

This page has been intentionally left blank.

Acknowledgements

First and foremost, I would like to express my gratitude towards NTU for the Nanyang President's Graduate Scholarship and all the kind, thoughtful and caring souls that I had met during my times at NTU. Special thanks to Associate Professor Richard David Webster for his guidance and support throughout my undergraduate and postgraduate studies. I would also like to thank my mentors Dr. Bahareh Khezri and Dr. Gwendeline Wong for teaching me everything I know about analytical instruments. And to my oxytocin tribe and lunch buddies, Dr. Serena Tan, Dr. Diane Tiong, Maria Laurentia Novianti Prananto, and Dr. Nisha Khanizeman, thank you for your unwavering encouragement and faith. The last four years had been enjoyable because of my lab mates Dr. Malcolm Eugene Tessensohn, Dr. Sherman Lauw, Dr. Jazreen Lee, Dr. Kwok Kiong Chan, Sher Li Gan for willing to go an extra mile, Dr. Ying Shan Tan, Dr. Ya Yun Chan, Dr. Yanni Yue, Dr. Xiuhui Xu, Dr. Dejan Urbancok and Maja Budanovic for making lab experience exciting. I would also like to acknowledge and thank my students, Rachel Sim, Rayna Tan, Esther Tay, Natalie Sims and Brenda Chong for their contributions and laughs that they had brought to the lab. Last but not least I would like to let my family know how much I appreciate their complete understanding and support (not forgetting my nieces and nephews who kept me smiling). I love you all.

This page has been intentionally left blank.

Tables of Contents

Acknowledgements.....	5
Tables of Contents	7
Abstract.....	15
List of publications	18
Chapter 1.....	19
Introduction – Water, Volatile Organic Compounds (VOCs) Contamination, Purification, and Quantification	19
1.1. Water	19
1.1.1. Water resources in Singapore	19
1.2. Volatile organic compounds (VOCs)	21
1.2.1. VOCs in water – Rainwater, water treatments, and leaching	22
1.3. Water purification methods targeting VOCs	26
1.3.1. Adsorption	27
1.3.1.1. Granular activated carbon (GAC)	27
1.3.1.2. Nano-sorbents	28
1.3.2. Reverse Osmosis, nanofiltration, and ultrafiltration	29
1.3.3. Redox reaction	30
1.3.4. Vacuum membrane distillation (pervaporation)	31
1.3.5. Membrane-assisted solvent extraction (pervaporation)	31
1.4. Methods measuring VOCs in water	32
1.4.1. Gas chromatography (Direct injection)	33
1.4.2. HPLC (Functionalization).....	35
1.4.3. Calculation	35
1.4.4. Sample treatment	36
1.4.4.1. Purge-and-Trap (PAT)	36

1.4.4.2.	Headspace (HS).....	40
1.4.4.3.	Thin-layer headspace (TLHS).....	42
1.4.4.4.	HS-SPME (solid-phase microextraction).....	42
1.4.4.5.	Stir bar sorptive extraction (SBSE).....	44
1.4.4.6.	Liquid-liquid extraction (LLE).....	44
1.4.4.7.	Liquid-phase microextraction (LPME)	45
1.5.	Scope of work	46
1.6.	Reference	48
Chapter 2		63
Method development – Analysis of Volatile Organic Compounds (VOCs) in rainwater using Purge-and-Trap Gas Chromatography-Mass Spectrometry		63
2.1.	Introduction	63
2.1.1.	Rainwater	63
2.1.2.	Quantification methods	63
2.1.2.1.	Gas chromatography-mass spectrometry (GC-MS).....	63
2.1.2.2.	Thermal-desorption gas chromatography-mass spectrometry (TD GC-MS) 64	
2.1.2.3.	Purge-and-Trap Gas Chromatography-Mass Spectrometry (PAT GC-MS) 65	
2.1.3.	Rainwater sampler	66
2.1.3.1.	Commercial sampler	66
2.1.3.2.	Makeshift sampler	66
2.1.4.	Objective	67
2.2.	Experimental, Method Development, and Validation	67
2.2.1.	Instrumentation	67
2.2.2.	Sampling location and samplers	68
2.2.3.	Syringe filters.....	68
2.2.4.	Method development	69

2.2.4.1.	Identification of plausible VOCs candidates.....	69
2.2.4.2.	Materials.....	70
2.2.4.3.	Verification of retention time and mass spectrum	70
2.2.4.4.	GC parameter studies	71
2.2.4.5.	Selective Ion Monitoring (SIM) mode study	71
2.2.4.6.	PAT parameter studies	72
2.2.5.	Method Validation	72
2.2.5.1.	Precision and Accuracy.....	72
2.2.5.2.	Minimal Reporting Level (MRL) and Detection Limit (DL)	73
2.2.5.3.	Rainwater sampler study	73
2.3.	Results and Discussion	74
2.3.1.	Preliminary studies – Identification of potential analytes	74
2.3.2.	Syringe filters.....	77
2.3.3.	Optimization	79
2.3.3.1.	Analyte Confirmation.....	79
2.3.3.2.	GC-MS parameters.....	80
2.3.3.2.1.	Oven temperature programming	80
2.3.3.2.2.	Flow rate.....	82
2.3.3.2.3.	Split ratio.....	82
2.3.3.3.	Selective Ion Monitoring (SIM) mode.....	83
2.3.3.3.1.	SIM dynamic calibration.....	83
2.3.3.4.	PAT parameters.....	85
2.3.3.5.	Method Validation	88
2.3.3.5.1.	Precision and Accuracy of SIM mode	88
2.3.3.5.2.	MRL and DL determination of SIM mode	89
2.3.3.5.3.	Method validation for Scan mode.....	91
2.3.4.	Rain Sampler.....	93

2.4. Conclusion	96
2.5. References	99
Chapter 3	103
Analysis of Aqueous Leachable Contaminants from Syringe Filters	103
3.1. Introduction	103
3.2. Experimental.....	104
3.3. Materials	105
3.3.1. Chemicals.....	105
3.3.2. Syringe filters and sample preparations	106
3.4. Results and Discussion	107
3.4.1. Preliminary screening	107
3.4.2. Further investigation of nylon filters	110
3.4.3. Further investigation of syringe filters having housing materials other than PP	111
3.4.4. Compatibility investigation (CI) of PP filter membrane and water containing aromatic compounds	115
3.4.5. ICP-MS	116
3.5. Conclusion	119
3.6. References	121
Chapter 4.....	123
Analysis of Volatile Organic Compounds (VOCs) in Rain Water of Western Singapore – Trends, Correlations, and Source Apportionment studies.....	123
4.1. Introduction	123
4.1.1. Climate of Singapore and haze	126
4.1.1.1. Climate of Singapore.....	126
4.1.1.2. Haze.....	127
4.1.2. Objective	128

4.2.	Experimental.....	129
4.2.1.	Sampling location and sample collection	129
4.2.2.	Chemical Reagents and Standards	131
4.2.3.	Data collection	131
4.2.4.	Data Analysis	132
4.2.4.1.	Statistical and trend analysis	132
4.2.4.2.	Positive Matrix Factorization (PMF)	133
4.2.4.2.1.	Modelling	134
4.3.	Results and Discussion	137
4.3.1.	Rain Samples	137
4.3.2.	Yearlong statistical analysis.....	138
4.3.3.	Trend study	142
4.3.3.1.	Yearlong analysis	143
4.3.3.2.	Haze trend analysis (September to October 2015).....	149
4.3.3.3.	Monsoon analysis.....	152
4.3.4.	Correlation calculations	155
4.3.4.1.	Yearly correlation.....	156
	Table 4.5. Yearly correlation between VOCs pairs from August 2015 to July 2016	156
4.3.4.2.	Haze correlation	158
4.3.4.3.	Monthly correlation.....	161
4.3.4.4.	Monsoon Correlation	163
4.3.5.	PMF	165
4.3.6.	Significant implications of VOCs in Rainwater	173
4.4.	Conclusion.....	174
4.5.	References	177
	Chapter 5.....	189

Removal of Volatile Organic Compounds (VOCs) from Water Using Mixtures of Olive Oil, Lecithin, and Vitamin E as Phase Transfer Agents.....	189
5.1. Introduction	189
5.2. Experimental.....	190
5.2.1. Materials	191
5.2.2. Sample preparation	191
5.2.2.1. Lecithin with olive oil	191
5.2.2.2. Lecithin with vitamin E	192
5.2.3. Sample analysis.....	193
5.3. Results and discussion	193
5.3.1. Lecithin with olive oil.....	193
5.3.1.1. Preliminary studies	193
5.3.1.2. Optimization.....	196
5.3.2. Lecithin with vitamin E	199
5.3.2.1. Preliminary studies	199
5.3.2.2. Optimization.....	201
5.4. Conclusion	203
5.5. References	204
Chapter 6.....	209
Conclusion.....	209
Appendix A.1. Information of VOCs studied.....	215
Appendix A.2. Quantifier and qualifier ions, MRL and DL for VOCs with internal standard reference and monitoring window.....	217
Appendix A.3. Probable identity of chromatographic peaks in rain samples.....	219
Appendix A.4. Duplicate analysis of GC parameter effect on peak resolution. ...	221
Appendix A.5. Duplicate analysis of PAT parameter effect on Response Factor.	222

Appendix A.6. Chromatograms of filtered and unfiltered ultrapure water and rainwater	224
Appendix B.1. Sample solution preparation	224
Appendix B.2. Reproducibility test of VOCs leachable contaminants in ultrapure water.....	226
Appendix B.3. Preliminary screening of VOCs leachable contaminants in different filtrate.....	228
Appendix B.4. Decrement in aromatic VOCs in filtered water	230
Appendix B.5. Concentration of metals in ultrapure water filtrates	231
Appendix C.1. Box plots of VOCs from August 2015 to July 2016	234
Appendix C.2. PMF Calculation.....	241
Appendix C.3. Trend graphs between VOCs from August 2015 to July 2016	244
Appendix C.4. Trend graphs of all VOCs (Monsoon).....	245
Appendix C.5. Monthly correlation distribution	246
Appendix C.6. Monsoon correlation distribution	247
Appendix D.1. Concentration of metals in ultrapure water filtrates.....	248
Appendix D.2. NIST library match of unknown compounds from sonication of lecithin with vitamin E samples	249
Appendix D.2. Table 1-2. NIST library match of unknown compounds from sonication of lecithin with vitamin E samples	249
Appendix D.3. Optimization of vitamin E encapsulation for VOCs removal	250

This page has been intentionally left blank.

Abstract

Volatile organic compounds (VOCs) enter water systems through rainfall, through intentional or unintentional industrial or domestic releases as well as through leaching of (from) contaminated sources. The adverse effects of VOCs on health, the environment, and scientific experiments has led to monitoring of VOCs in various aqueous media. Purge-and-trap gas chromatography-mass spectrometry (PAT GC-MS) was applied to three applications of monitoring VOCs in water; (i) to the yearlong monitoring of VOCs present in rainwater collected in the western region of Singapore, (ii) in the qualification and quantification of leachable VOCs from syringe filters, and (iii) in the assessment of the efficiency of water purification with natural materials (lecithin, olive oil, and vitamin E) for the removal VOCs.

A PAT GC-MS method for the detection and quantification of VOCs in rainwater was developed for 28 VOCs and described in Chapter 2. Method 524.4 from the Environmental Protection Agency (EPA) of the United States was used as a guideline for the method development of the list of potential VOCs to be monitored in rainwater. Some of the VOCs from the potential list had not been validated or tested by the original method but were proven to be quantifiable via the method with good reproducibility and precision found after the optimization. The concentration of VOCs in rainwater were known from the literature to be low in concentration. Therefore, development of Selective Ion Monitoring (SIM) detection mode was performed. Through the study, a suitable collection set-up was tested and shown not to introduce VOC contaminants while the act of filtering was found to potentially introduce contaminants into the samples collected.

The contamination of VOCs from syringe filters was further explored in Chapter 3, and the different filtrates were tested to determine if any one condition may trigger the

introduction of VOCs contaminants. A list of different syringe filters with different housing material and filter membrane were tested, and it was determined that housing material significantly affects the type and amount of VOCs detected in the filtrate. Several VOCs such as nonanal could be removed from the syringe filter through pre-filtration while some VOCs such as styrene and methyl methacrylate were found to be persistently present in the filtrate after substantial volume of water had been passed. Henceforth, filtration was not used as a sample preparation step to the rainwater collection, but the particulate matter in the samples were allowed to settle down before introduction to the PAT system to reduce the contamination issues to the frit in the sparger of the PAT.

A yearlong monitoring of VOCs in rainwater was performed in the western region of Singapore. The sources of emission, as well as the seasonal monsoon, were found to affect the concentration of VOCs determined. One of the most severe haze period in Singapore due to the biomass clearing in the neighboring countries occurred during this yearlong monitoring of VOCs in rainwater and the impact of haze was found to be not limited to particulate matter, but also the increase in VOCs detected in rainwater. A Positive Matrix Factorization (PMF) analysis of the yearlong result deconstructed that 8 factors traceable to the sources of emission in the vicinity of the sampling site contributed to the VOCs detected in rainwater.

The traditional methods of water treatment often require the use of methods or materials that may be hard to maintain or expensive, moreover, the goal of water treatments are often not focused on the removal of VOCs that can have much effect on human health. Therefore, the concept of water purification with food safe and readily available material for the removal of VOCs was explored with lecithin and other natural materials. The combination of lecithin and olive oil was found to be efficient in removing VOCs from

water through a phased exchange enhanced by the presence of a small amount of lecithin.

The results obtained were optimistic in providing a foundation of natural materials as an alternative exploration of a water purification treatment method.

List of publications

1. Ng, S.J., Sims, N.F., Tay, E.X.Y., and Webster, R.D., *Removal of Volatile Organic Compounds (VOCs) from Water Using Mixtures of Olive Oil, Lecithin, and Vitamin E as Phase Transfer Agents*. Journal of Water Process Engineering, 2017. **18**: p. 58-64.
2. Tessensohn, M.E., Ng, S.J., Chan, K.K., Gan, S.L., Sims, N.F., Koh, Y.R. and Webster, R.D., *Impurities in Nitrile Solvents Commonly Used for Electrochemistry, and their Effects on Voltammetric Data*. ChemElectroChem, 2016. **3**(11): p. 1753-1759.
3. Wong, G.K.S., Ng, S.J. and Webster, R.D., *Quantitative analysis of atmospheric volatile organic pollutants by thermal desorption gas chromatography mass spectrometry*. Analytical Methods, 2013. **5**(1): p. 219-230.

Introduction – Water, Volatile Organic Compounds (VOCs) Contamination, Purification, and Quantification

1.1. Water

Water covers around 71% of the Earth's surface, and it is essential for life. However, freshwater supplies only make up 2.5% (35,029,000 km³) of the 1,385,984,000 km³ volume of water surface and subsurface existing on planet Earth [1]. Furthermore, only 0.26% (90,000 km³) of the fresh water reserves are readily available in freshwater lakes and rivers while the rest are stored in less accessible locations such as ice caps, permanent snow, glaciers and underground. The distribution of freshwater reserves within reach are regrettably imbalanced throughout various nations, therefore, it is not unusual for countries or states to face water scarcity. Singapore, an island nation, ranks number one alongside six other countries in the projection of the most water-stressed countries by the year 2040, in a water scarcity study performed by the World Resources Institute [2].

1.1.1. Water resources in Singapore

Singapore faces physical water scarcity as the small nation does not own much groundwater nor natural freshwater bodies but it is one of the most overpopulated countries based on the population size to land area ratio. However, as Singapore lies within the equatorial rain belt and receives an average of 2,358 mm of rainfall annually (abundant by most standards), the amount of rainwater could satisfy Singapore's water needs if the country had a more extensive landmass [3]. A landmass area of 710 km² places a limit on the amount of land that can be allotted to store, and capture rainwater

given that land space is also required for the expanding and growing economy of Singapore. To meet the demand of water, an agreement was signed between Singapore and its neighboring country, Malaysia, in 1927 to allow Singapore to import water from Johor, Malaysia [4]. Two more agreements were signed in 1961 and 1962 to give Singapore the exclusive right to import water from Gunong Pulai and Pontian Catchment, Tebrau and Scudai Rivers [5] as well as Johor River with a cap of 250 million gallons per day [6].

Although water treaties had been signed to sustain the water demands in Singapore, insufficient water supplies led to water rationing in the 1960s. Thereafter, smaller river streams (Kranji, Pandan, Murai, Poyan, Sarimbun, and Tengeh) were dammed to create more reservoirs while the original reservoirs such as Pierce and Seletar were expanded to increase the amount of rainwater collected [7]. To safeguard the integrity of rainwater collected at reservoirs, less pollutive land use (residential estates and light industry) were allowed up to 34% (urbanization cap) of the unprotected catchment areas [4]. In 2001, Malaysia threatened to cut the supply of water to Singapore in addition to raising the cost of water from RM 0.03 to RM 8 per gallon as Malaysia faces the possibility of water rationing in early 2000 following periods of low rainfall [4]. Consequently, to defuse the threat, more reservoirs were created, and desalination, as well as NEWater (recycled sewage water) systems, were introduced to increase the self-reliance in Singapore's own water supply. A system of pipelines and pumps were introduced to various reservoirs to transfer catchments from reservoirs with a smaller capacity to more massive reservoirs for the reduction of overflows and wastage. The efforts placed towards preservation on the reliability of rainwater collected and care to reduce wastage highlights the importance of rainwater as the primary domestic source of water in Singapore. However, the study of contaminants in rainwater gathered in Singapore had been limited to inorganic

contaminants and some organic compounds [8-11] while more consideration and analysis should be assigned to understand the quality of rainwater regarding other contaminants before processing to drinking water.

1.2. Volatile organic compounds (VOCs)

The United States Environmental Protection Agency (US EPA) defines volatile organic compounds (VOCs) as organic compounds with low boiling points ($<260\text{ }^{\circ}\text{C}$) and noteworthy vapour pressure ($>10\text{ Pa}$) at standard atmospheric pressure (101.3 kPa) and temperature ($25\text{ }^{\circ}\text{C}$) with 15 or less carbon atoms [12, 13]. VOCs may originate from both natural (plants, oceans, and soils) [14, 15] and anthropogenic sources (combustion of fossil fuels and production of consumer products) [16, 17] as seen in Figure 1.1 and their release into the atmosphere or surroundings is inevitable as VOCs are highly mobile in the gaseous phase [18].

Figure 1.1. Illustration of VOCs cycle.

Once in the atmosphere, VOCs can undergo oxidation reactions with hydroxyl radicals and other reactive species [19-21] which in turn increases their solubility in water or

proceed to the complete oxidation product (CO_2 and H_2O) as a form of sink (a means to reduce and/or remove VOCs from the atmosphere).

Physical removal such as dry deposition on vegetation [22, 23] or aerosol [24] and wet deposition [25, 26] with rain can also act as sink processes. Physical removal usually occurs more readily with intermediate oxidation products with lower vapor pressures and higher polarity as larger alkane ($>\text{C}_{20}$) [27] and multi-functional organic compounds such as oxalic acid [28] have been reported to be readily adsorbed and removed through aerosol particles. Despite being detected at relatively low concentrations in the environment, VOCs have been a subject of interest because of their unfavorable effects on the environment and health. VOCs can become involved in the production of secondary pollutants such as ozone in the troposphere [29, 30] and some VOCs such as chlorofluorocarbons cause stratospheric ozone depletion [31] when released into the atmosphere. Damage to organs and disorders to immune, nervous and reproduction systems or even cancer can occur with excessive exposure to some VOCs [32-34]; VOCs such as benzene and bromodichloromethane are known carcinogens while chloroform is cytotoxic in nature. [35, 36]

1.2.1. VOCs in water – Rainwater, water treatments, and leaching

The detection of VOCs is not limited to the atmosphere as VOCs enter the water systems through rain (sink of VOCs from the air), intentional or unintentional discharge into water sources as well as leaching [37-40]. Table 1.1 to 1.3 displays the concentration of VOCs detected in several sources of water. Halogenated and aromatic VOCs [41, 42] were found in groundwater at μM concentration while trihalomethanes (THMs), a subclass of VOCs and halogenated VOCs, are more commonly perceived in surface water due to microbial activities [43] (Table 1.2). In modern society, water purification processes to

water sources (groundwater, surface water, and rainwater) are often implemented to safeguard the interest of consumers at the receiving end.

Table 1.1. VOC concentration in the tap water of Spain and Kuwait and bottled water of Kuwait.

Samples	Range detected	VOCs detected	Reference
Tap water in Spain	N.D.-66.5 $\mu\text{g L}^{-1}$	Trichloromethane: 1.0-40.8 $\mu\text{g L}^{-1}$ Tribromomethane: N.D.-24.7 $\mu\text{g L}^{-1}$ bromodichloromethane: N.D.-55.3 $\mu\text{g L}^{-1}$ Dibromochloromethane: N.D.-66.5 $\mu\text{g L}^{-1}$	[53]
Tap water in Kuwait	0.10-82.32 $\mu\text{g L}^{-1}$	Tribromomethane: 0.66-82.32 $\mu\text{g L}^{-1}$ Dibromochloromethane: 0.58-37.99 $\mu\text{g L}^{-1}$ Bromodichloromethane: 0.10-5.57 $\mu\text{g L}^{-1}$ Trichloromethane: 0.10-1.23 $\mu\text{g L}^{-1}$ Dibromomethane: 0.10-3.18 $\mu\text{g L}^{-1}$ Toluene: 0.10-1.85 $\mu\text{g L}^{-1}$ 1,2-Dichloropropane: 0.10-1.71 $\mu\text{g L}^{-1}$ Naphthalene: 0.10-0.60 $\mu\text{g L}^{-1}$ 1,2,4-Trichlorobenzene: 0.10-0.92 $\mu\text{g L}^{-1}$ Xylene _{total} : 0.27-0.58 $\mu\text{g L}^{-1}$ 1,2,3-Trichlorobenzene: 0.13-0.16 $\mu\text{g L}^{-1}$ Benzene: 0.64-0.91 $\mu\text{g L}^{-1}$ 1,2-Dibromo-3-chloropropane: 0.14-0.14 $\mu\text{g L}^{-1}$	[54]
Bottled water from Kuwait	0.10-46.40 $\mu\text{g L}^{-1}$	Tribromomethane: 0.11-37.55 $\mu\text{g L}^{-1}$ Dibromochloromethane: 0.10-1.76 $\mu\text{g L}^{-1}$ Bromodichloromethane: 0.10-0.58 $\mu\text{g L}^{-1}$ Chloroform: 0.10-1.85 $\mu\text{g L}^{-1}$ Dibromomethane: 0.10-0.74 $\mu\text{g L}^{-1}$ Toluene: 0.10-1.18 $\mu\text{g L}^{-1}$ Ethyl benzene: 0.10-5.17 $\mu\text{g L}^{-1}$ Xylene _{total} : 0.20-0.77 $\mu\text{g L}^{-1}$ 1,2,4-Trimethylbenzene: 0.11-0.13 $\mu\text{g L}^{-1}$ 1,3,5-Trimethylbenzene: 0.41-0.41 $\mu\text{g L}^{-1}$ Naphthalene: 0.10-0.75 $\mu\text{g L}^{-1}$ Styrene: 0.50-46.4 $\mu\text{g L}^{-1}$ 1,2-Dichloropropane: 0.12-0.40 $\mu\text{g L}^{-1}$ Trichloroethene: 0.13-0.13 $\mu\text{g L}^{-1}$ <i>iso</i> -Propylbenzene: 0.11-0.11 $\mu\text{g L}^{-1}$ 1,3-Dichlorobenzene: 0.10-0.10 $\mu\text{g L}^{-1}$	[54]

While the disinfection processes destroy pathogens present in water, the process may introduce disinfectant byproducts (DBPs) such as THMs. The addition of ozone, chlorine, chlorine dioxide or chloramines during the disinfection process react with naturally occurring organic matters (NOMs) for instance humic substance to produce THMs [44, 45]. Maximum contaminant level (MRL) of THMs had been established by governing bodies [46, 47] to control the quality of drinking water as chloroform and bromodichloromethane of THMs are known to be carcinogenic or cytotoxic [36].

Table 1.2. VOC concentration in rivers, lakes, and rainwater from different countries.

Samples	Range detected	VOCs detected	Reference
Lake water from Swiss	0.29-2.05 $\mu\text{g L}^{-1}$	Methyl tertbutyl ether: 0.29-1.40 $\mu\text{g L}^{-1}$ BTEX*: 0.39-2.05 $\mu\text{g L}^{-1}$	[55]
River water from Northern Greece	N.D.-40.0 $\mu\text{g L}^{-1}$	Trichloromethane: N.D.-0.417 $\mu\text{g L}^{-1}$ Tetrachloromethane: N.D. 0.314 $\mu\text{g L}^{-1}$ Trichloroethylene: N.D.-40.0 $\mu\text{g L}^{-1}$ Dichlorobromomethane: N.D.-0.063 $\mu\text{g L}^{-1}$ Tetrachloroethylene: N.D.-0.190 $\mu\text{g L}^{-1}$ Chlorodibromomethane: N.D.	[43]
Lake water from Northern Greece	N.D.-0.221 $\mu\text{g L}^{-1}$	Trichloromethane: N.D.-0.174 $\mu\text{g L}^{-1}$ Tetrachloromethane: N.D. 0.221 $\mu\text{g L}^{-1}$ Trichloroethylene: N.D. Dichlorobromomethane: N.D.-0.063 $\mu\text{g L}^{-1}$ Tetrachloroethylene: N.D. Chlorodibromomethane: N.D.-0.042 $\mu\text{g L}^{-1}$	[43]
Rainwater in Kanagawa, Japan	N.D.- 10191.60 ng L^{-1}	Dichloromethane: <47.56-10191.60 ng L^{-1} Trichloromethane: <42.98-4178.30 ng L^{-1} Tetrachloromethane: <58.45-1045.98 ng L^{-1} 1,2-Dichloroethane: <21.77-3067.76 ng L^{-1} 1,1,1-Trichloroethane: <50.69-1053.86 ng L^{-1} Trichloroethylene: <49.93-564.98 ng L^{-1} Tetrachloroethylene: N.D. 1,2-Dichloropropane: N.D. <i>p</i> -Dichlorobenzene: <30.87-1911.00 ng L^{-1} Benzene: <1015-859.21 ng L^{-1} Toluene: <16.59-2579.92 ng L^{-1} <i>m,p</i> -Xylene: <11.68-127.39 ng L^{-1} <i>o</i> -Xylene: <25.48-127.39 ng L^{-1}	[56]
Rainwater in Portland, OR	N.D.-260.00 ng L^{-1}	Trichloroethylene: 0.78-9.70 ng L^{-1} Tetrachloroethylene: 0.82-9.20 ng L^{-1} Tribromomethane: N.D.-4.00 ng L^{-1} 1,4-Dichlorobenzene: N.D.-7.00 ng L^{-1} 1,2-Dichlorobenzene: N.D.-0.62 ng L^{-1} 1,2,4-Trichlorobenzene: N.D.-0.45 ng L^{-1} α -hexachlorocyclohexane: 8.20-15.00 ng L^{-1} γ -hexachlorocyclohexane: N.D.-3.10 ng L^{-1} Toluene: N.D.- 220.00 ng L^{-1} Ethyl benzene: 3.90-72.00 ng L^{-1} <i>m,p</i> -Xylene: 34.00-260.00 ng L^{-1} <i>o</i> -Xylene: 12.00-110.00 ng L^{-1} 1,3,5-Trimethylbenzene: 2.10-10.00 ng L^{-1} 1,2,4-Trimethylbenzene: 16.00-44.00 ng L^{-1} 1,2,4,5-Tetramethylbenzene: 1.10-5.20 ng L^{-1}	[57]
Rainwater in Los Angeles, CA	9-250 ng L^{-1}	1,2-Dichloroethene: 230 ng L^{-1} Trichloromethane: 250 ng L^{-1} 1,1,1-Trichloroethane: 69 ng L^{-1} Tetrachloroethylene: 21 ng L^{-1} Toluene: 76 ng L^{-1} Ethyl benzene: 9 ng L^{-1} <i>m,p</i> -Xylene: 11 ng L^{-1}	[58]

Table 1.3. VOC concentration in rainwater from Camarillo, CA.

Samples	Range detected	VOCs detected	Reference
Rainwater from Camarillo, CA	7-60 $\mu\text{g L}^{-1}$	Formaldehyde: 60 $\mu\text{g L}^{-1}$ Acetaldehyde: 10 $\mu\text{g L}^{-1}$ Hexanal: 7-10 $\mu\text{g L}^{-1}$	[59]

To date, many reports on the cancer risk assessments [33, 48-52] with regards to drinking chlorinated tap water and bottled water were reported, and these calculations require the quantification and identification of VOCs in water.

It was noted that some tap water analysed in Kuwait (Table 1.1) contained total THM concentrations over the limit determined by governing bodies ($80 \mu\text{g L}^{-1}$) [46, 47] while lower concentrations were detected in bottled water which could be attributed to the treatments that may have been applied to the bottled water in comparison to tap water. Water purification methods can be introduced to reduce the amount of THMs produced during the disinfection process or decrease the existing THM concentrations in the water after disinfection to safeguard the consumers from drinking disinfected water. Other than THMs, VOCs with adverse effects when consumed such as formaldehyde and styrene have also been detected in drinking water due to leaching or migration from storage materials [60-62].

Halogenated and aromatic VOCs were also found in studies of rainwater conducted in Portland [57] and Los Angeles [58] in the United States as well as that in Kanagawa, Japan [56] at low concentrations of ng L^{-1} (Table 1.2). In addition, carbonyl VOCs were also detected in the rainwater of Camarillo, USA [59] while volatile organic carbon was observed in rainfalls of Wilmington (USA) [63] and Brazil [64] measured in ranges of μM or $\mu\text{g L}^{-1}$. Although the lethal dosage of VOCs is often much higher in comparison to the amount present in water, the long-term and additive effects of these compounds are still not fully understood and could be hard to determine [26, 65]. Furthermore, the risk of VOCs present in drinking water is not restricted to drinking intake alone as contact through inhalation is probable when taking part in activities like showering [66-68] and the dosage of chloroform and cancer risk from 10 minutes of showering can be greater than or equal to that from daily water intake [68].

The problem of VOCs present in water supplies does not end with the probable health effects faced when consumed but also with the possible side reactions/effects it holds when used in scientific experiments. A small amount of impurities can have a significant effect on experimental results, as before the use of ultrapure water; electrochemical experiments had been plagued by organic, surface-active contaminants [69]. Also, VOCs can be introduced into aqueous solutions employed in experiments through leaching through laboratory consumables such as syringe filters, which have been shown to contain extractable VOCs concentration up to mg g^{-1} of VOCs in syringe membrane filter [70].

1.3. Water purification methods targeting VOCs

Before the widespread use of disinfection process on drinking water, millions of people died from waterborne diseases due to the pathogens present in raw water sources. A new set of problems, however, plagues drinking water through the formation of DBPs (which possess some health hazards) from the reaction of chemical oxidants used in the disinfection process with NOM (from decaying leaves and other plant matters) and anthropogenic contaminants (treated wastewater and agricultural run-off) [44]. Anthropogenic contaminants such as antibacterial agents, textile dyes, pharmaceuticals, pesticides, bisphenol A, ultraviolet (UV) filters used in sunscreens, alkylphenol surfactants, and diesel fuel can also react with chemical disinfectants to form contaminant DBPs [71]. The introduction of coagulation, flocculation, sedimentation, and filtration before chemical disinfection treatments can remove chlorine sensitive organic compounds which would reduce the formation of DBPs or THMs in drinking water [72]. The nonchemical (reverse osmosis and UV light) means of disinfecting drinking water may also reduce the levels of DBPs formed, but such disinfectants have their limitations. Higher levels of certain DBPs could be formed when NOM react with medium-pressure

UV [73] while reverse osmosis faces problems with the disposal of brine resulting from the treatments. Water purification techniques targeting the removal of DBPs have been explored to maintain the regulations set on drinking water as the formation of DBPs may not be entirely prevented in the disinfection stage. THMs were first discovered in chlorinated drinking water in 1974 [74], and subsequently, the carcinogenic properties of some THMs were brought to light which has led to the strict control of their concentrations in drinking water. The use of granular activated carbon (GAC), pervaporation and even reverse osmosis after chlorination can lower the concentration of THMs in drinking water and such techniques as well as new approaches which make use of membrane and non-toxic materials targeting the removal of VOCs (THMs) from water will be discussed further in the following sections.

1.3.1. Adsorption

Adsorption using sorbent materials for the purification of water is often employed to remove inorganic and organic pollutants from contaminated water. Most of the sorbent materials used are carbonaceous, but other organic or inorganic sorbent materials may also be applied, and modifications can be performed to improve their efficiency as sorbent materials.

1.3.1.1. Granular activated carbon (GAC)

Granular activated carbon (GAC) has been used in water treatment process to control taste and odor of water for many years, and GAC is perhaps the most commonly used method of the removal or reduction of THM concentrations in drinking water [75]. The high surface area (500 to 1500 m² g⁻¹) and the presence of a broad spectrum of surface functioning groups are some of the reasons that make activated carbon an attractive sorbent for water treatment [76]. Acidic and basic treatments can be performed on

activated carbon to modify its affinity for specific contaminants [77]. In 1978, USPEA specified the use of the GAC treatment to source waters that were considerably contaminated, for the control of the synthesis of other organic contaminants, with GAC typically lasting 3 to 22 weeks before exhaustion (effluent concentration nearly equaled influx concentration) dependent on the types of contaminants in the water feed [78]. The adsorption system typically uses stationary beds with water flowing downward through the GAC where the adsorbed material accumulates at the top of the bed until exhaustion [78] and the freshness of GAC can affect the efficiency of THMs removal [79]. However, the problem with pathogen growth on GAC filters poses as a problem when applying GAC in water filtration processes as *Yersinia enterocolitis* O:8, *Salmonella typhimurium* and enterotoxigenic *Escherichia coli* were found to colonize readily on sterile GAC [80]. Therefore, instead of removing contaminants, GAC can possibly become a breeding ground for harmful pathogens and once again introduce the need of disinfection.

1.3.1.2. Nano-sorbents

Nanoparticles make good sorbents as they have surface areas much more abundant than bulk particles, and can behave as high capacity selective sorbents for VOCs in aqueous solutions. VOCs such as 1,2-dichlorobenzene had been found to be adsorbed onto carbon nanotubes (CNTs) in 40 min with maximum sorption capacity of 30.8 mg g^{-1} [81] which is a lot faster than the equilibration time (20 h) required for the adsorption of phenol on activated carbon [82]. Similarly, acid-treated commercially available CNTs were demonstrated to be more hydrophilic which in turns makes them more suitable for the adsorption of THMs (low molecular weight and relatively polar) at pH below 7 and above 3, with shorter equilibrium time and higher adsorption capacity for chloroform in comparison to powdered activated carbon [83].

Synthetic nonporous coated-glass activated carbon fibers (ACFs) with an average pore size of 1.16 nm and surface areas ranging from 171 – 483 m² g⁻¹ have been reported to have much higher organic sorption equilibrium constants at 20 °C for benzene, toluene, *p*-xylene, and ethyl benzene than GACs [84]. Functionalization can be performed on nanomaterials to increase their affinity towards different contaminants present in water, such as for halogenated VOCs including tetrachloroethylene, and trichloroethylene, which has been demonstrated to have higher sorption capacity in sodium dodecyl sulfate (SDS) functionalized magnesium-aluminum layered double hydroxides in aqueous solutions than organoclays [85]. Although nanomaterials perform better than conventional bulk materials as sorbents, their cost and availability remain the primary challenge in the application of nanotechnology to water purification. Moreover, the environmental fate, transport, and toxicity of nanomaterials have not been well established in current studies which make the application of nanomaterials impractical at this point in time.

1.3.2. Reverse Osmosis, nanofiltration, and ultrafiltration

The use of membranes in reverse osmosis, nanofiltration and ultrafiltration are budding essential constituents of advanced water purification and desalination technologies. The three types of filtration are not fundamentally different with the exception being the size of molecules retained [86]. The use of membrane filtration is not common for the removal of VOCs or THMs but more on the removal of precursors of THMs (NOMs). Reverse osmosis uses membranes with pore sizes of 0.1-1.0 nm and rejects dissolved organic solutes with molar mass above 200 Da in the feed water, and the efficiency is measured via the rejection ratio [87]. Nanofiltration membranes are very efficient in removing organic solutes with molar mass between 200 – 3000 Da [87] and the use of nanofiltration on groundwater and surface water samples have been proven effective in the removal of

NOMs organic pollutants and other inorganic and biological contaminants [88] as well as large water distribution systems [89]. The efficiency of removing trichloroethylene, tetrachloroethylene and chloroform were tested out with nanofiltration, and it was determined that rejection factors between 65% to 90% could be obtained [90]. However, the efficiency was limited by the absorption and desorption of the halogenated VOCs tested on the membrane which would require periodic replacement or the use of the organic solvent resistant membrane. A study was also conducted on the removal of chloroform using reverse osmosis, nanofiltration and ultrafiltration and ultrafiltration (pore rating range from 1000 to 500,000 Da) were found to be the most efficient even though the membrane used in ultrafiltration was more susceptible to fouling [91]. Fouling is a condition in which a membrane undergoes plugging or coating by some components in the water feed which is the primary limiting factor in membrane filtration applications [92, 93]. Fouling requires the frequent replacement of the membrane which can be costly in addition to the cost of setting up membrane filtration systems.

1.3.3. Redox reaction

The photocatalytic properties of nanoparticles such as titanium dioxide (TiO_2) have shown great potential in the application of water purification due to their ability to act both as a reductive and oxidative catalyst for organic pollutants [94]. The activation of the catalytic properties of TiO_2 with UV light has been demonstrated to enhance the removal of total organic carbon from water [95] and in particular the degradation of chlorinated alkanes, benzenes, and furans [96]. Similar to the use of other nanomaterials in the application of photocatalytic nanoparticles in the water purification process, the availability, and cost, as well as the impact of the nanomaterials to the environment and health, are points of concern when considering their replacement with current technologies.

1.3.4. Vacuum membrane distillation (pervaporation)

Vacuum membrane distillation makes use of a hydrophobic porous membrane to physically separate the feed (contaminated water) and the permeate side where a low pressure or vacuum is applied, and permeate condensation takes place outside of the system [97, 98]. The transport mechanism of VOCs in vacuum membrane distillation includes evaporation of VOCs in the feed, diffusion of the vapor through the membrane pores and the condensation of the vapor stream outside of the module. This combination of actions allows the removal of VOCs including benzene and MTBE occurring at high concentrations ($0.12\text{--}28\text{ g L}^{-1}$) in water with separation factors up to 307 [99, 100]. The separation factor compares the mass fraction in the permeate side and in the feed. Halogenated compounds such as chloroform, trichloroethylene, and tetrachloroethylene have been demonstrated to be removed with very high separation factors (up to 860) at lower concentration ($400\text{ }\mu\text{g L}^{-1}$) in water using vacuum membrane distillation [101]. Although the idea of using vacuum membrane distillation is appealing, the energy consumption, cost, as well as the ease of applying vacuum membrane distillation at a water processing plant scale can make application of vacuum membrane distillation hard to achieve.

1.3.5. Membrane-assisted solvent extraction (pervaporation)

Liquid-liquid extraction or solvent extraction can be used to transfer VOCs between two immiscible liquid (organic phase and water). However, problems with the formation of emulsion and challenges with solvent wastage have prevented the widespread usage of solvent extraction as a form of VOCs removal technique in water. To solve these problems, membrane-assisted solvent extraction coupled (MASX) with membrane-assisted distillation stripping (MADS) was developed to decontaminate groundwater

[102]. In place of an organic solvent, sunflower oil was employed and recycled with distillation stripping where the efficiency of VOCs extraction greatly depends on the diffusivities of VOCs in water and sunflower oil while distillation of sunflower oil depends on the concentration of VOCs present in the oil. Although the concept and lab-scale experiments of MASX and MADS of VOCs removal from water are feasible, pilot-scale units have to be tested out before the application of such new methods in real water purification plants. Nonetheless, the use of food-grade material makes such methods attractive as safety issues on the consumption of water from such processes and the impact on the environment are known.

1.4. Methods measuring VOCs in water

Figure 1.2. Analysis techniques for VOCs in water.

Techniques in bold are further discussed in the following sections. DAI – direct aqueous injection, MIMS – membrane-introduction MS, LLE – liquid-liquid extraction, LPME – liquid-phase microextraction, HS – headspace, PAT – purge-and-trap, TLHS – thin-layer headspace, SPE – solid-phase extraction, SPME, solid-phase microextraction, SBSE – stir-bar sorptive extraction, SCMS – supported capillary membrane sampling, CMS – capillary membrane sampler, CMS-FIA – CMS-flow injection analysis.

For the determination of VOCs, gas chromatography (GC) along with different types of the detector such as flame-ionization detector (FID), electron capture detector (ECD), photoionization detector (PID) and mass-selective detector (MSD) are often top choices. Nonetheless, other methods such as high-pressure liquid chromatography (HPLC) can be employed with functionalization of targeted groups while calculations can be performed to determined VOCs concentration as a sum. The following section provides an in-depth discussion on the advantages and disadvantages of some analytical techniques developed to measure VOCs in different sources of water.

1.4.1. Gas chromatography (Direct injection)

GC separates a mixture of the gaseous or liquid sample (later vaporized) based on the individual compounds' interaction with the column, hence the rate it is carried towards the detected by the carrier gas. Direct injection as the name suggests does not require any sample pre-treatment, and the aqueous samples are directly injected into the GC in the DAI analysis method, and this idea was first proposed in 1962 and 1965 [103]. In most DAI analysis, a guard column (paired with a capillary column) is required in the GC setting for the trapping of water and other compounds (high molecular weight or non-volatile compounds) that are not suitable for analysis with the column installed or clog the front of the GC column. This method allows the introduction of selective analytes and the guard column regeneration through the split vent removal of trapped water and other compounds as shown in Figure 1.3 after a split-less injection of sample. Chromosorb P-NAW [104] and lithium chloride [105] were used as guard columns to retain mainly water and the optional non-volatile compounds from drinking water samples to give detection limits of $0.6 - 1.1 \mu\text{g L}^{-1}$ and quantitation limit of around $1 \mu\text{g L}^{-1}$, which are relatively high.

The use of Chromosorb P-NAW allows injection of up to 250 μL and the analysis of aromatic VOCs while lithium chloride allows the injection of up to 120 μL and the analysis of polar VOCs. DAI is usually applied to clear samples or samples of small organic matter concentration, and possible limitation of matrix effect may exist, however, this method of analysis allows the preservation of thermally unstable VOCs as the inlets are not heated and permits the analysis of VOCs with a broad range of volatility as the partition is not part of the sample preparation process. The lack of sample preparation would eliminate the possibility of contamination, and no other solvents are used.

Membrane introduction MS (MIMS), although not a GC method, is another direct injection method, can be employed to study the VOCs present in aqueous samples. The system makes use of the diffusion or evaporation of analytes through the thin membrane and into the MS system [103, 106] that skips the chromatographic separation. However, identification of VOCs can be problematic when isomers are present as isomers possess similar ions and ratios between ions in a mass spectrum.

Figure 1.3. DAI guard column introduction of analyte into the capillary column and the removal of water with the split flow.

1.4.2. HPLC (Functionalization)

Functionalization can be used on VOCs to improve their suitability for analysis using HPLC, by increasing their molecular mass and visibility when ultraviolet (UV) detectors are used. Depending on the types of functional groups on the target VOCs for study, different types of derivatives can be employed for the functionalization. HPLC functionalization was used to detect carbonyl containing VOCs in rainwater through the derivatization of carbonyls to hydrazones using 2,4-dinitrophenylhydrazine (DNPH) [59].

Figure 1.9. DNPH reaction with carbonyl groups to form derivatives.

The analysis of the derivatized samples was then conducted via injection of the sample into the HPLC system with UV detection at 360 nm after organic extraction and concentration. HPLC functionalization is both flexible and restrictive at the same time for selective chemicals are required for various functionalization. The necessary treatment steps can often lead to the introduction of errors towards the detection process. Moreover, the identity of VOCs would only be confirmed through retention times comparison, and overlapping peaks can cause false positive or false negative results.

1.4.3. Calculation

The sum of the VOC concentrations in water samples can be determined through calculations if the components of the samples are well understood. It was hypothesized that volatile organic carbon or the sum of VOCs would be equivalent to the subtraction of all other types of carbon (inorganic carbon (IC) and non-purgeable dissolved organic

carbon (NPDOC)) from the total carbon (TC) concentration measured (Equation 1.1) and it was applied in a study of volatile organic carbon in rainwater of Brazil [64].

$$\text{Volatile organic carbon} = TC - IC - NPDOC \quad (1.1)$$

Calculating the sum of VOCs may be straightforward and easy to obtain, however, the assumption is not foolproof as errors in the detection of TC, IC and NPDOC could lead to inaccurate determination of volatile organic carbon concentrations. It was perceived in the study of rainwater in Brazil that negative sum of VOCs was found through the hypothesized equation which leads to a question on the reliability of such an assumption. Moreover, the potency of each individual VOC needs to be taken into account as the sum of VOCs does not represent the effect on the environment nor human health. Nonetheless, the calculation in Equation 1.1 can prove to be a straightforward estimation in times when quick analysis of VOCs is required.

1.4.4. Sample treatment

1.4.4.1. Purge-and-Trap (PAT)

Figure 1.4. Purge process in PAT sparger.

The working principle of PAT or dynamic headspace is based on the constant removal of headspace by passing an inert gas through the sample, was pioneered by Bellar and

Lichtenberg in 1979 [107]. The VOC concentrations in the liquid and vapor phase reach equilibrium (Dalton's law) when left to equilibrate, however, in a PAT system, the headspace or vapor phase is continuously removed. As shown in Figure 1.4, high purity nitrogen or helium gas is passed from one end of the sparger through the sample causing the formation of bubbles which sends the VOCs present in the vapor phase into the trap.

Therefore, more VOCs continually migrate into the vapor phase as the continual purging causes the concentration in the headspace to be essentially near zero, which would maximize extraction and reduce the volume of samples required for detection [108, 109]. The VOCs adsorbed on the trap (sorbent tube) which could include cryo-trapping are then desorbed through heating into the GC system with nitrogen or helium gas flowing in the opposite direction of adsorption. The efficiency of purging is controlled by varying purge volume, purge flow and the temperature in which samples are kept at during the purge process. Polar VOCs may require a larger purge volume while less polar VOCs face elution from the trap if the purge volume is over the breakthrough volume of VOCs for a specific trap sorbent material.

PAT is widely used because the sample treatment method has good recoveries and high sensitivity. Moreover, samples with a different matrix such as human blood [110], analysis of drinking water [111, 112], and analysis of offshore waste gas in crude oil production [113] can be prepared for GC analysis using PAT. Table 1.4 displays some examples of publications using PAT GC hyphenated systems for the analysis of VOCs in different sources of water. The sample treatment step allows analysis of a wide range of VOCs with average concentration from ng L^{-1} to $\mu\text{g L}^{-1}$. Seeing that the concentration of VOCs present in water can be in the ng L^{-1} range, it is essential that the methods used for VOC quantification have detection limits low enough for analysis. A variety of PAT GC hyphenated systems have been reported for the analysis of different sources of water

(Table 1.4), and lower detection limits were obtained when an MS detector was matched with PAT GC in comparison with FID (Flame ionization detector) or AED (Atomic emission detector). MS provides the possibility of the lower detection limit of ng L⁻¹ as selective ion monitoring (SIM) mode can be applied to increase the sensitivity by monitoring certain ion in the short time frame of analysis.

Table 1.4. Publications using PAT sample treatment for the detection of VOCs in water. *On-line – On-line monitoring.

Analysis method	Analytes	Samples	Detection limit	Reference
PAT GC-AED	Halogenated VOCs	Tap/mineral water	0.05-0.5 µg L ⁻¹	[114]
PAT GC-FID	Halogenated, aromatics and carbonyl VOCs	Wastewater	0.32-2.39 µg L ⁻¹	[115]
PAT GC-MS	Halogenated and aromatic VOCs	Surface water	0.56-28 ng L ⁻¹	[116]
PAT GC-MS	Halogenated and aromatic VOCs	Tap/bottled water	0.01-0.10 µg L ⁻¹	[54]
PAT GC-MS	Halogenated VOCs	Seawater	0.05-0.5 ng L ⁻¹	[117]
PAT GC-MS	THMs	Tap water	0.02-0.12 µg L ⁻¹	[118]
[On-line]				
PAT GC-MS	THMs	Tap/mineral water	1 ng L ⁻¹	[119]
PAT GC-MS	Halogenated and aromatic VOCs	Drinking water	0.002-0.2 µg L ⁻¹	[120]

Modifications can also be made to the different components of PAT to improve further the sensitivity. Trap temperature of PAT systems is usually kept near 25 °C or 1-2 °C above of ambient room temperature (rarely over 30 °C) during the purging process as trapping adsorbents generally displayed optimal efficiency at lower temperature [108]. A cooling system (cryo-trapping) with the use of liquid nitrogen to maintain the trap's temperature at -100 °C has been reported to improve the detection limit to 1 ng L⁻¹ for the monitoring of contaminated water with a low concentration of VOCs in MS-SIM mode analysis [119]. However, at such low temperature, complications can take place and a second condenser had to be introduced to condense water vapor at -10 °C with ethylene glycol as a coolant to avoid blockage from the formation of ice on the trap. The study also highlighted the need to increase the trap temperature to -70 °C when analyzing samples containing high CO₂ concentration (e.g., sparkling water), or NaOH could be added to form CaCO₃ that precipitates before analysis.

Innovation in PAT studies has led to the development of more cost-effective in-tube extraction (ITEX) processes for the extraction of VOCs from aqueous samples. Instead of purchasing a PAT unit, ITEX can be installed into a regular auto-sampler where the needle (attached to a gas-tight syringe with side-port) is packed with a sorbent, and the headspace is dynamically removed while the sample undergoes stirring to encourage transfer from the liquid phase into the gaseous phase [121]. The trapped VOCs are then heated for release into the GC column and cleaning takes place by withdrawing the syringe above the side-port for flushing with an inert gas (Figure 1.5). Method detection limit of 1-10 ng L⁻¹ of individual VOCs was obtained through scan mode analysis from the GC-MS and requires lesser sample volume with fewer problems with contamination in comparison to PAT sample preparation.

Figure 1.5. ITEX working principle [121].

The use of PAT GC hyphenated techniques produces reliable analytical information, however, the purging process can be time-consuming. A typical PAT system is set to purge at 11 min with a purge flow rate of 40 mL min⁻¹ [108, 112] for optimal purging of VOCs which is exclusive of the time required for chromatographic separation which can be as long as 30 min with a 60 m column. Therefore, an analysis of water sample using

PAT GC-hyphenated techniques could take up to an hour when cooling and preparation time are considered; not accounting for the blank runs required between samples. Moreover, if the PAT system is not equipped with an auto-sampler, the analysis is labor intensive. The scope of VOCs analyzed using PAT is limited by the VOCs' response to purging (purgeability), and hence some VOCs may not be suitable to be analyzed using PAT [112], and aqueous samples with the tendency to foam (such as those containing detergents) may not be suitable for PAT sample treatment process.

1.4.4.2. Headspace (HS)

Figure 1.6. Partition of VOCs in HS sample preparation.

Unlike PAT, headspace (HS) or static headspace samples the headspace when an equilibrium is reached between the concentration of VOCs in the liquid and vapor phase [122]. The equilibrium follows the partition coefficient of individual VOCs, and a larger coefficient value would indicate a lesser tendency of migration into the gaseous phase (headspace). Through modification of temperature of equilibration, sample matrix, and sample volume, the partition coefficient can be lowered to obtain higher concentrations in the headspace. Matrix effects can be decreased with the addition of salts (ammonium chloride, ammonium sulfate, sodium chloride, sodium citrate, sodium sulphate and potassium carbonate) which is also known as 'salting out', where the increase in salt content in the aqueous sample would decrease the solubility of polar VOCs hence

promoting VOC's transfer into the gaseous phase. The analysis of VOCs containing reactive hydrogens (acids, alcohols, and amines) can be complicated as they can react with the surfaces of the analytical column or injection port resulting in tailing peaks and low responses. Derivatization of such reactive hydrogen VOCs to volatile species of lower solubility (e.g., esters) can be performed to improve analysis using HS sample preparation techniques. HS sample preparation technique is popular for the analysis of consumer products containing high concentrations of VOCs for a fast and clean method of analysis.

As shown in Figure 1.7 and 1.8, HS can remove compounds that are not analyzed or may not be suited to the analysis using GC which can lead to the contamination of the system otherwise reacting with the stationary phase of the column [123].

Figure 1.7 & 1.8. Chromatogram of direct injection of perfume (left) and the chromatogram of perfume analysis using HS sample preparation [123].

In comparison to PAT, fewer reports on the determination of VOCs in aqueous samples have been published using HS GC-MS even though the detection limits were almost comparable or slightly higher than that of PAT GC-MS in both SIM and scan modes, as indicated in Table 1.5. This observation could be due to the concentration of VOCs detected in aqueous samples. Even though HS GC-MS can obtain lower detection limits

(ng L⁻¹) with the use of SIM mode analysis, the amount of modification to improve the partition of VOCs between liquid and gaseous phase can be limited, and a larger volume of aqueous sample may be required. However, the source of water samples may not be infinite which limits the use of HS GC-MS for VOCs analysis in aqueous samples.

Table 1.5. Publications using HS sample treatment for the detection of VOCs in water.

Analysis method	Analytes	Samples	Detection limit	Reference
HS GC-MS	Halogenated and aromatics VOCs and alkenes	Wastewater and River samples	0.1 µg L ⁻¹	[124]
HS GC-MS	Aromatic VOCs	Drinking water	10 ng L ⁻¹	[125]
HS GC-MS	Aromatic VOCs	Spiked drinking water	Not reported	[126]

1.4.4.3. Thin-layer headspace (TLHS)

Thin-layer headspace (TLHS) utilizes a special TLHS column where the sample passes through a spiral thermostatic glass tube as the purging gas passes through the sample in the opposite direction [103]. The small amount of water vapor generated through this purging process along with the VOCs extracted by the purge gas is then condensed as the purging gas enters a second column which can be analyzed using DAI-GC. The application of TLHS had been reported on biological fluids such as urine [127] while not many publications have been on its implementation on water (drinking water or water sources). DAI-GC analysis has been known to produce slightly higher detection limits, therefore, a combination method of TLHS and DAI-GC may not be as commonly used because other analytical methods have better sensitivity and shorter processing times.

1.4.4.4. HS-SPME (solid-phase microextraction)

HS can be paired with solid-phase microextraction (SPME) and a GC-hyphenated detection system to improve sensitivity and detection limits (Table 1.6). SPME was proposed by Pawliszyn and Arthur in 1990 [134] with emphasis placed on the sorbent material coated on the extraction fiber which is attached to a syringe. During the sampling

process, the fiber is pushed out of the needle and exposed to the headspace for a set period of time, while simultaneously stirring or heating of the water sample to increase the amount of VOCs partitioning into the gaseous phase. The fibers are retracted into the needle, and the syringe containing the fibers is then transferred immediately for desorption in the heated injection port of the GC [129]. HS-SPME technically makes use of dynamic headspace analysis instead of static headspace for the increment of sensitivity, and the lowering of detection limits as the extraction of the VOCs onto the fiber decreases the concentration of VOCs in the gaseous phase which promotes the partitioning of VOCs into the gaseous phase. The effectiveness of SPME extraction relies on the extraction fiber, and commercially available fibers may have a high cost, lower thermal and chemical stability, less reusability (<100 use) and lower stability towards non-polar VOCs [130, 135]. As shown in Table 1.6, with the utilization of an MS-MS detector, the detection limit of VOCs in aqueous samples can go as low as pg L^{-1} .

Table 1.6. Publications using HS-SPME sample treatment for the detection of VOCs in water.

Analysis method	Analytes	Samples	Detection limit	Reference
HS-SPME GC-FID	Aromatic VOCs and oxygenated VOCs	Lake water	$0.01\text{-}1.0 \mu\text{g L}^{-1}$	[55]
HS-SPME GC- μ FID	Aromatic VOCs	Wastewaters	$<1.5 \mu\text{g L}^{-1}$	[128]
HS-SPME GC-ECD	Halogenated VOCs	Wastewater and water	$0.08\text{-}23.8 \text{ ng L}^{-1}$	[129]
HS-SPME GC-MS	Halogenated VOCs	Water	$106\text{-}195 \text{ ng L}^{-1}$	[130]
HS-SPME GC-MS	Halogenated VOCs	Groundwater	$0.9\text{-}50 \text{ ng L}^{-1}$	[131]
HS-SPME GC-TOF-MS	Aromatic VOCs	Drinking water	$0.015\text{-}0.477 \mu\text{g L}^{-1}$	[132]
HS-SPME GC-MS-MS	Halogenated Aromatic VOCs	River water and sewage	$0.03\text{-}0.33 \text{ pg L}^{-1}$	[133]

The HS-SPME GC hyphenated technique displays good detection limits towards VOCs and the scope of VOCs studied is dependent on the types of fibers used in the SPME sampling. However, like in the case of the PAT GC hyphenated techniques, HS-SPME GC hyphenated techniques can be time-consuming depending on the optimized exposure time of SPME to the headspace and is labor intensive if a non-automated system is employed. It is also essential to ensure that the fibers used in SPME do not introduce

contaminants into the sample and hence examination on the types of fibers used during the method development stage is an important issue to investigate.

1.4.4.5. Stir bar sorptive extraction (SBSE)

Stirrer bar sorptive extraction (SBSE) was first introduced in 1999 where a stirrer bar coated with sorbent material (polydimethylsiloxane – PDMS) is used to stir the aqueous sample, and the VOCs present in the sample is adsorbed onto the sorbent material similar to that of SPME [103]. The stirrer-bar can then be thermally desorbed for analysis or extraction with the use of an appropriate solvent. The concentration of halogenated VOCs in water and human urine samples were examined using SBSE coupled with thermal desorption (TD)-GC-HRMS (high-resolution MS) and detection limits $<1.7 \text{ ng L}^{-1}$ with good repeatability for all 4 (bromodichloromethane, dibromochloromethane, bromoform, and tetrachloroethylene) VOCs were found. The stirrer-bars used in the extraction were conditioned through heating with the inert gas flow before sampling [136]. The analysis does not require drying of the stirrer bar which reduces the chance of the VOCs eluting off the sorbent material before analysis. However, automation is not yet possible for this method which may account for the relatively small number of publications on the use of SBSE on the analysis of VOCs in aqueous samples. Moreover, the use of PDMS is usually applied to VOCs with good to high thermal stability and volatility which may restrict the scope of VOCs studied using SBSE sample preparation technique.

1.4.4.6. Liquid-liquid extraction (LLE)

Liquid-liquid extraction (LLE) is a technique commonly used for sample extraction as it is straightforward to perform and does not require the addition of other equipment than the GC system, hence, decreasing the cost of using this method. The isolation of VOCs in LLE is based on the partition between the aqueous phase (sample) and an organic solvent

which are immiscible, and for maximum extraction, the analytes would need to have better solubility in the organic solvent [103]. However, the large amount of solvent required for LLE often deters researchers from using this method as the solvents used may be analytes (VOCs) present in the samples and further concentration of the extracted solvent into a smaller volume is frequently required for injection into GC column for analysis. LLE was reportedly used in the detection of geosmin and 2-methylisoborneol in drinking water in Shanghai using hexane as the extraction solvent [137]. The sample recovery of 2-methylisoborneol was not ideal (>50%), however, the detection limits of both VOCs were low (1.0-5.0 ng L⁻¹).

1.4.4.7. Liquid-phase microextraction (LPME)

Liquid-phase microextraction (LPME) using hollow fibers was introduced into the sample preparation step where the solvent used for extraction resides within the hollow fiber which separates the two liquid phases and reduces the volume of sample used as well as decreasing the need for solvent concentration after extraction. In one report, LPME was performed using a polypropylene hollow fiber for the extraction of aromatic VOCs from water and good reproducibility (relative standard deviation: 2.02-4.61%) was obtained from using octanal as the organic extractor [138]. As the solvent concentration step is not required in LPME, sample loss is minimized, and hence good reproducibility can be obtained from such sample treatment procedures. Similar to SPME, the fiber used in LPME should also be determined not to introduce contaminants into the sample before use, and the grade of solvent utilized in both LPME and LLE should also be sufficiently high to reduce the chances of cross-contamination.

1.5. Scope of work

Facing water scarcity, Singapore highly relies on rainwater catchments as one of its primary sources of domestic water. The quality of the water collected has been carefully preserved by limiting the types of land use surrounding the reservoirs, and past studies had been conducted on the inorganic and certain organic contaminants present in rainwater. However, an emerging contaminant, VOCs, emitted from anthropogenic sources, can contaminate rainwater through sink processes in the atmosphere and their effects on the quality of rainwater collected remain undocumented in Singapore. Being a small island nation, Singapore maximizes land use for the growing economy forcing residential areas to be situated near anthropogenic sources emitting VOCs. These VOCs, in turn, get washed out of the atmosphere into rainwater which can cause contamination to surface water. In addition to anthropogenic sources, cross-boundary events such as biomass burning in neighboring countries can affect the amount of VOCs washout with uniform air mass transport during seasonal monsoons. To understand the effects of VOCs on rainwater and its seasonal variation in the monsoon patterns, a long-term study on VOCs in rainwater of western region of Singapore is conducted with a reliable VOCs quantification method.

PAT GC-MS is one of the several methods capable of measuring VOCs in rainwater as reported in several publications and it is suitable as there are no sample preparation steps that require the use of solvents which could limit the scope of VOCs studied. In comparison to other gas extraction techniques, PAT does not need further enhancement with a combination of microextraction techniques and analysis in SIM mode allows detection down to ng L^{-1} which had been the VOCs concentration level reported in most rain samples. The VOC target analytes for study in the long-term monitoring were determined through the analysis of rain samples with PAT GC-MS in Scan mode, and the

probable identity of individual chromatographic peaks determined through mass spectrum matching with the National Institute of Standards and Technology (NIST) library database. However, seeing that the concentration of most VOCs occurring in rainwater in previous literature was low, 48 VOCs previously detected in the atmosphere in Singapore was also considered as probable VOC target analytes as rain is the sinking process for atmospheric VOCs. Neat chemical standards of individual VOCs were purchased and tested for retention time, and mass spectrum matching as well as purge response to confirm the final list of VOCs monitored using the method developed.

The separation of the mixtures of VOCs was optimized through the variation of GC parameters and the ions used for SIM mode analysis were determined through dynamic calibration. Guidelines for the detection of THMs in water using PAT GC-MS have been well documented by US EPA Method 524.4 and the recommended, an acceptable range of parameters using PAT was employed as guidelines for the optimization of VOCs analysis in rainwater using PAT GC-MS. As Singapore is plagued with particulate matter pollutants, filtration of rainwater was considered in the method development stage to determine a suitable syringe filter for the filtration process. Also, a suitable rain collector that does not introduce contaminants was examined in the method development stage.

Results from the yearlong analysis were expected to provide information on the monsoon variation of VOCs found in rainwater. Source apportionment using statistical tools such as Pearson correlation calculation, and positive matrix factorization (PMF) was used to determine the likely sources of contribution to the VOCs observed in rainwater. Furthermore, meteorological data and special events such as haze were noted for a better understanding of the variation throughout the year and the impact of events on VOCs in rainwater. The risk of contamination of surface water, as well as consumption, can be

examined through comparison of the VOCs concentrations in surface water and the MCL or lethal dosage of VOCs. The current water treatment procedures to reduce or remove THMs from drinking water has its list of advantages and disadvantages. The cost of operation and the types of materials used are often points of concern as most materials used in the water purification methods can have probable adverse health effect and the environmental impact of specific materials have yet to be well established. Therefore, to expand the scope of materials used in water purification, more natural materials such as lecithin, olive oil, and vitamin E were explored for their probable water purification of VOCs and THMs in water through emulsions and phase exchange.

1.6. Reference

1. Shiklomanov, I.A., *Water in Crisis A Guide to the World's Fresh Water Resources*, ed. P.H. Gleick. 1993, New York: Oxford University Press.
2. Maddocks., A., R.S. Young., and P. Reig. *Ranking the World's Most Water-Stressed Countries in 2040*. 2015 [cited 7 November 2016]; Available from: <http://www.wri.org/blog/2015/08/ranking-world%E2%80%99s-most-water-stressed-countries-2040>.
3. Tortajada, C., Y.K. Joshi, and A.K. Biswas, *The Singapore water story : sustainable development in an urban city-state*. 2013: New York, NY : Routledge, 2013.
4. *Water : from scarce resource to national asset*. Singapore's urban systems studies booklet series. 2012: Singapore : Cengage Learning Asia, c2012.
5. Council, S.C. and Johor, *Tebrau and Scudai Rivers Water Agreement*. 1961.
6. *Water agreements*. Singapore: the encyclopedia, ed. T. Koh., et al. 2006, Singapore: Editions Didier Millet in association with the National Heritage Board.
7. *Water Pollution Control and Drainage Bill*. 1975.

8. G.P. Hu, R. Balasubramanian, and C.D. Wu, *Chemical characterization of rainwater at Singapore*. Chemosphere, 2003. **51**: p. 747-755.
9. R. Balasubramanian, T. Victor, and R. Begum, *Impact of biomass burning on rainwater acidity and composition in Singapore*. Journal of Geophysical Research 1999. **104**: p. 26881-26890.
10. R. Balasubramanian, T. Victor, and N. Chun, *Chemical and statistical analysis of precipitation in Singapore*. Water, Air and Soil Pollution, 2001. **130**: p. 451-456.
11. He, J. and R. Balasubramanian, *Semi-volatile organic compounds (SVOCs) in ambient air and rainwater in a tropical environment: Concentrations and temporal and seasonal trends*. Chemosphere, 2010. **78**(6): p. 742-751.
12. Ivan P. Roman Falco and M.N. Moya, *Analysis of Volatile Organic Compounds in Water*, in *Handbook of Water Analysis*, L.M.L. Nollet, Editor. 2007, CRC Press.
13. US EPA, *Method 5035A - Closed-system purge-and-trap and extraction for volatile organics in soil and waste samples*, C. Office of Resource, and Recovery Methods Team, Editor. 2002, United States Environmental Protection Agency (US EPA).
14. Fall, R., *Chapter 2 - Biogenic Emissions of Volatile Organic Compounds from Higher Plants A2 - Hewitt, C. Nicholas*, in *Reactive Hydrocarbons in the Atmosphere*. 1999, Academic Press: San Diego. p. 41-96.
15. Fuentes, J.D., et al., *Biogenic Hydrocarbons in the Atmospheric Boundary Layer: A Review*. 2000.
16. Barrefors, G. and G. Petersson, *Volatile hydrocarbons from domestic wood burning*. Chemosphere, 1995. **30**(8): p. 1551-1556.
17. Friedrich, R. and A. Obermeier, *Chapter 1 - Anthropogenic Emissions of Volatile Organic Compounds A2 - Hewitt, C. Nicholas*, in *Reactive Hydrocarbons in the Atmosphere*. 1999, Academic Press: San Diego. p. 1-39.

18. Claudio, B.-L. and M.M. Stephen, *Volatile Organic Compound (VOC) Analysis in Water, Sediments, and Soils and Its Application in Environmental Forensics*, in *Methods in Environmental Forensics*. 2008, CRC Press. p. 171-194.
19. Atkinson, R., *Gas-phase tropospheric chemistry of organic compounds: a review*. Atmospheric Environment, 2007. **41, Supplement**: p. 200-240.
20. Jenkin, M.E., et al., *Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds*. Atmos. Chem. Phys., 2003. **3**(1): p. 181-193.
21. Saunders, S.M., et al., *Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds*. Atmos. Chem. Phys., 2003. **3**(1): p. 161-180.
22. Doskey, P.V., et al., *Source Profiles for Nonmethane Organic Compounds in the Atmosphere of Cairo, Egypt*. Journal of the Air & Waste Management Association, 1999. **49**(7): p. 814-822.
23. Müller, J.-F., *Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gasses*. Journal of Geophysical Research: Atmospheres, 1992. **97**(D4): p. 3787-3804.
24. Cousins, I.T. and D. Mackay, *Gas-Particle Partitioning of Organic Compounds and Its Interpretation Using Relative Solubilities*. Environmental Science & Technology, 2001. **35**(4): p. 643-647.
25. Fornaro, A. and I.G.R. Gutz, *Wet deposition and related atmospheric chemistry in the São Paulo metropolis, Brazil: Part 2—contribution of formic and acetic acids*. Atmospheric Environment, 2003. **37**(1): p. 117-128.
26. Kieber, R.J., et al., *Dissolved organic carbon and organic acids in coastal New Zealand rainwater*. Atmospheric Environment, 2002. **36**(21): p. 3557-3563.

27. Bidleman, T.F., *Atmospheric processes*. Environmental Science & Technology, 1988. **22**(4): p. 361-367.
28. Mochida, M., et al., *Bimodal size distribution of C2–C4 dicarboxylic acids in the marine aerosols*. Geophysical Research Letters, 2003. **30**(13): p. n/a-n/a.
29. Andersson-Sköld, Y. and L. Holmberg, *Photochemical ozone creation potentials (POCP) and replacement of solvents in Europe*. Atmospheric Environment, 2000. **34**(19): p. 3159-3169.
30. Derwent, R.G., et al., *Photochemical ozone creation potentials for organic compounds in northwest Europe calculated with a master chemical mechanism*. Atmospheric Environment, 1998. **32**(14–15): p. 2429-2441.
31. US DOC, *Scientific assessment of ozone depletion 2006*, WMO/UNEP Assessment. Project, Editor. 2006.
32. Pellizzari, E.D., R.L. Perritt, and C.A. Clayton, *National human exposure assessment survey (NHEXAS): exploratory survey of exposure among population subgroups in EPA Region V*. J Expo Anal Environ Epidemiol, 1999. **9**(1): p. 49-55.
33. Fawell, J., *Risk assessment case study—Chloroform and related substances*. Food and Chemical Toxicology, 2000. **38**, **Supplement 1**(0): p. S91-S95.
34. Morris, R.D., *Drinking water and cancer*. Environmental Health Perspect, 1995. **103**: p. 225-232.
35. US EPA. 2012 [cited 24th January 2014]; Available from: <http://www.epa.gov/>.
36. ASTDR. *Agency for Toxic Substances & Disease Registry*. 2012 [cited 24th January 2016]; Available from: www.atsdr.cdc.gov/.
37. Williams, J. and R. Koppmann, *Volatile Organic Compounds in the Atmosphere: An Overview*. 2007, Blackwell Publishing.

38. Hofer, M. and L. Shuker, *ILSI Europe Workshop on Assessing Health Risks From Environmental Exposure to Chemicals: the Example of Drinking Water. Summary Report. International Life Sciences Institute. Food Chem Toxicol*, 2000. **38**(1 Suppl): p. S3-12.
39. Squillace, P.J., et al., *VOCs, pesticides, nitrate, and their mixtures in groundwater used for drinking water in the United States. Environ Sci Technol*, 2002. **36**(9): p. 1923-30.
40. Line, D.E., et al., *Water quality of first flush runoff from 20 industrial sites. Water Environment Research*, 1997. **69**(3): p. 305-310.
41. Nikolaou, A.D., et al., *Determination of volatile organic compounds in surface waters and treated wastewater in Greece. Water Research*, 2002. **36**(11): p. 2883-2890.
42. Phelan, D.J., et al., *Assessment of Volatile Organic Compounds in Surface Water at Canal Creek, Aberdeen Proving Ground, Maryland, U.S.G. Survey, Editor. 2001, U.S. Geological Survey: Baltimore, Maryland, USA.*
43. Kostopoulou, M.N., et al., *Volatile organic compounds in the surface waters of Northern Greece. Chemosphere*, 2000. **40**(5): p. 527-532.
44. Richardson, S.D. and C. Postigo, *Drinking water disinfection by-products, in Emerging organic contaminants and human health. 2012, Springer. p. 93-137.*
45. Rook, J.J., *Chlorination reactions of fulvic acids in natural waters. Environmental Science & Technology*, 1977. **11**(5): p. 478-482.
46. USPEA, *Title XIV of the Public Health Service Act - Safety of public water systems (Safe drinking water act), EPA, Editor. 2002, US EPA: United States.*
47. WHO, *Guidelines for drinking-water quality, fourth edition, WHO, Editor. 2011, Gutenberg: Malta.*
48. Pinar Kavcar, et al., *Occurrence, oral exposure and risk assessment of volatile organic compounds in drinking water for Izmir. Water Research*, 2006. **40**: p. 3219-3230.
49. Gen-Shuh Wang, Ya-Chen Deng, and T.-F. Lin, *Cancer risk assessment from trihalomethanes in drinking water. Science of the Total Environment*, 2007. **387**: p. 86-95.

50. Uyak, V., *Multi-pathway risk assessment of trihalomethanes exposure in Istanbul drinking water supplies*. Environment International 2006. **32**: p. 12-21.
51. Panyakpo Mallika, Soontornchai Sarisak, and P. Pongsri, *Cancer risk assessment from exposure to trihalomethanes in tap water and swimming pool water*. Journal of Environmental Sciences, 2008. **20**: p. 372-378.
52. Hsu, C.-H., et al., *Estimation of Potential Lifetime Cancer Risks for Trihalomethanes from Consuming Chlorinated Drinking Water in Taiwan*. Environmental Research, 2001. **85**(2): p. 77-82.
53. N. Camillo, et al., *Purge and trap capillary gas chromatography with atomic emission detection for volatile halogenated organic compounds determination in waters and beverages*. Journal of Chromatography A, 2004. **1035**: p. 1-8.
54. Al-Mudhaf, H.F., F.A. Alsharifi, and A.-S.I. Abu-Shady, *A survey of organic contaminants in household and bottled drinking waters in Kuwait*. Science of The Total Environment, 2009. **407**(5): p. 1658-1668.
55. Schmidt, T.C., et al., *Occurrence and fate modeling of MTBE and BTEX compounds in a Swiss Lake used as drinking water supply*. Water Research, 2004. **38**(6): p. 1520-1529.
56. Manabu Igawa, Norhide Nakada, and H. Okochi, *Determination of Volatile Organic Compounds in Rainwater and the Dominant Factors of their Concentrations*. Journal of Japan Society of Atmospheric Environment, 1998. **34**: p. 211-218.
57. Ligocki, M.P., C. Leuenberger, and J.F. Pankow, *Trace organic compounds in rain—II. Gas scavenging of neutral organic compounds*. Atmospheric Environment (1967), 1985. **19**(10): p. 1609-1617.
58. Kawamura, K. and I.R. Kaplan, *Organic compounds in the rainwater of Los Angeles*. Environmental Science & Technology, 1983. **17**(8): p. 497-501.
59. Grosjean, D. and B. Wright, *Carbonyls in urban fog, ice fog, cloudwater and rainwater*. Atmospheric Environment (1967), 1983. **17**(10): p. 2093-2096.

60. Hernandez, R.J. and J.R. Giacini, *Factors affecting permeation, sorption and migration processes in package-product systems*, in *Food Storage Stability*, Irwin A. Taub and R.P. Singh, Editors. 1997, CRC Press.
61. Emma, L.B. and C. Laurence, *Residues of Food Contact Materials*, in *Handbook of Seafood and Seafood Products Analysis*, Leo M. L. Nollet and F. Toldra, Editors. 2009, CRC Press.
62. Sablani, S.S. and M.S. Rahman, *Food Packaging Interaction*, in *Handbook of Food Preservation*, M.S. Rahman, Editor. 2007, CRC Press.
63. Avery, J.G.B., et al., *Assessment of rainwater volatile organic carbon in southeastern North Carolina, USA*. Atmospheric Environment, 2009. **43**: p. 2678-2681.
64. Campos, M.L.A.M., et al., *Dissolved organic carbon in rainwater: Glassware decontamination and sample preservation and volatile organic carbon*. Atmospheric Environment, 2007. **41**(39): p. 8924-8931.
65. Yu, M.-H., H. Tsunoda, and M. Tsunoda, *Environmental toxicology: biological and health effects of pollutants*. 2011: CRC Press.
66. McKone, T.E., *Human exposure to volatile organic compounds in household tap water: the indoor inhalation pathway*. Environmental science & technology, 1987. **21**(12): p. 1194-1201.
67. Tancrede, M., Y. Yanagisawa, and R. Wilson, *Volatilization of volatile organic compounds from showers—I. Analytical method and quantitative assessment*. Atmospheric Environment. Part A. General Topics, 1992. **26**(6): p. 1103-1111.
68. Jo, W.K., C.P. Weisel, and P.J. Liou, *Routes of chloroform exposure and body burden from showering with chlorinated tap water*. Risk Analysis, 1990. **10**(4): p. 575-580.
69. Conway, B.E., et al., *Ultrapurification of water for electrochemical and surface chemical work by catalytic pyrodistillation*. Analytical Chemistry, 1973. **45**(8): p. 1331-1336.

70. Huang, M., et al., *Impact of extractables/leachables from filters on stability of protein formulations*. Journal of Pharmaceutical Sciences, 2011. **100**(11): p. 4617-4630.
71. Richardson, S.D., et al., *Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research*. Mutation Research/Reviews in Mutation Research, 2007. **636**(1–3): p. 178-242.
72. Edzwald, J.K., *Coagulation in drinking water treatment: Particles, organics and coagulants*. Water Science and Technology, 1993. **27**(11): p. 21-35.
73. Liu, W., et al., *THM, HAA and CNCl formation from UV irradiation and chlor(am)ination of selected organic waters*. Water Research, 2006. **40**(10): p. 2033-2043.
74. Bellar, T.A., J.J. Lichtenberg, and R.C. Kroner, *The Occurrence of Organohalides in Chlorinated Drinking Waters*. Journal (American Water Works Association), 1974. **66**(12): p. 703-706.
75. Lykins, B.W., R.M. Clark, and J.Q. Adams, *Granular Activated Carbon for Controlling THMs*. Journal (American Water Works Association), 1988. **80**(5): p. 85-92.
76. Chingombe, P., B. Saha, and R.J. Wakeman, *Surface modification and characterisation of a coal-based activated carbon*. Carbon, 2005. **43**(15): p. 3132-3143.
77. Yin, C.Y., M.K. Aroua, and W.M.A.W. Daud, *Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions*. Separation and Purification Technology, 2007. **52**(3): p. 403-415.
78. James M. Symons, et al., *Treatment Techniques for Controlling Trihalomethanes in Drinking Water*, E.P. Agency, Editor. 1981, US EPA: Washington, DC.
79. Blanck, C.A., *Trihalomethane Reduction in Operating Water Treatment Plants*. Journal (American Water Works Association), 1979. **71**(9): p. 525-528.
80. Camper, A.K., et al., *Growth and persistence of pathogens on granular activated carbon filters*. Applied and Environmental Microbiology, 1985. **50**(6): p. 1378-1382.

81. Peng, X., et al., *Adsorption of 1,2-dichlorobenzene from water to carbon nanotubes*. Chemical Physics Letters, 2003. **376**(1–2): p. 154-158.
82. Daifullah, A.A.M. and B.S. Girgis, *Removal of some Substituted Phenols by Activated Carbon Obtained from Agriculture Waste*. Water Research, 1998. **32**(4): p. 1169-1177.
83. Lu, C., Y.-L. Chung, and K.-F. Chang, *Adsorption of trihalomethanes from water with carbon nanotubes*. Water Research, 2005. **39**(6): p. 1183-1189.
84. Mangun, C.L., et al., *Adsorption of Organic Contaminants from Water Using Tailored ACFs*. Chemistry of Materials, 2001. **13**(7): p. 2356-2360.
85. Zhao, H. and K.L. Nagy, *Dodecyl sulfate–hydrotalcite nanocomposites for trapping chlorinated organic pollutants in water*. Journal of Colloid and Interface Science, 2004. **274**(2): p. 613-624.
86. Nath, K., *Membrane separation processes*. 2008: PHI Learning Pvt. Ltd.
87. Zydney, A.L. and L.J. Zeman., *Microfiltration and Ultrafiltration: Principles and Applications*. 1996, New York: Taylor & Francis.
88. Van der Bruggen, B. and C. Vandecasteele, *Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry*. Environmental Pollution, 2003. **122**(3): p. 435-445.
89. Peltier, S., et al., *Nanofiltration: improvements of water quality in a large distribution system*. Water Science and Technology: Water Supply, 2003. **3**(1-2): p. 193-200.
90. Ducom, G. and C. Cabassud, *Interests and limitations of nanofiltration for the removal of volatile organic compounds in drinking water production*. Desalination, 1999. **124**(1): p. 115-123.
91. Waniek, A., M. Bodzek, and K. Konieczny, *Trihalomethane removal from water using membrane processes*. Polish journal of environmental studies, 2002. **11**(2): p. 171-178.

92. Van Der Bruggen, B., et al., *A review of pressure-driven membrane processes in wastewater treatment and drinking water production*. Environmental Progress, 2003. **22**(1): p. 46-56.
93. Potts, D.E., R.C. Ahlert, and S.S. Wang, *A critical review of fouling of reverse osmosis membranes*. Desalination, 1981. **36**(3): p. 235-264.
94. Adesina, A.A., *Industrial exploitation of photocatalysis: progress, perspectives and prospects*. Catalysis Surveys from Asia, 2004. **8**(4): p. 265-273.
95. Chitose, N., et al., *Radiolysis of aqueous phenol solutions with nanoparticles. 1. Phenol degradation and TOC removal in solutions containing TiO₂ induced by UV, γ -ray and electron beams*. Chemosphere, 2003. **50**(8): p. 1007-1013.
96. Kabra, K., R. Chaudhary, and R.L. Sawhney, *Treatment of Hazardous Organic and Inorganic Compounds through Aqueous-Phase Photocatalysis: A Review*. Industrial & Engineering Chemistry Research, 2004. **43**(24): p. 7683-7696.
97. Bandini, S., C. Gostoli, and G.C. Sarti, *Separation efficiency in vacuum membrane distillation*. Journal of Membrane Science, 1992. **73**(2): p. 217-229.
98. Camera-Roda, G., et al., *Heat and mass transfer boundary layers in radial creeping flow*. International Journal of Heat and Mass Transfer, 1994. **37**(14): p. 2145-2153.
99. Sarti, G.C., C. Gostoli, and S. Bandini, *Extraction of organic components from aqueous streams by vacuum membrane distillation*. Journal of Membrane Science, 1993. **80**(1): p. 21-33.
100. Banat, F.A. and J. Simandl, *Removal of benzene traces from contaminated water by vacuum membrane distillation*. Chemical Engineering Science, 1996. **51**(8): p. 1257-1265.
101. Couffin, N., C. Cabassud, and V. Lahoussine-Turcaud, *A new process to remove halogenated VOCs for drinking water production: vacuum membrane distillation*. Desalination, 1998. **117**(1): p. 233-245.

102. Hutter, J.C., et al., *Removal of VOCs from groundwater using membrane-assisted solvent extraction*. AIChE Journal, 1994. **40**(1): p. 166-177.
103. Marczak, M., et al., *Microanalysis of Volatile Organic Compounds (VOCs) in Water Samples – Methods and Instruments*. Microchimica Acta, 2006. **155**(3): p. 331-348.
104. Kubinec, R., et al., *Gas chromatographic determination of benzene, toluene, ethylbenzene and xylenes using flame ionization detector in water samples with direct aqueous injection up to 250 μ l*. Journal of Chromatography A, 2005. **1084**(1–2): p. 90-94.
105. Pettersson, J. and J. Roeraade, *Method for Analysis of Polar Volatile Trace Components in Aqueous Samples by Gas Chromatography*. Analytical Chemistry, 2005. **77**(10): p. 3365-3371.
106. Pérez Pavón, J.L., et al., *Determination of trihalomethanes in water samples: A review*. Analytica Chimica Acta, 2008. **629**(1–2): p. 6-23.
107. Bellar, A.T. and J.J. Lichtenberg, *Semi-automated head-space analysis of drinking waters and industrial waters for purgeable volatile organic compounds*, in *STP 686 Measurement of Organic Pollutants in Water and Wastewater*, V.H. CE, Editor. 1979, American Society for Testing and Materials.
108. Abeel, S.M., A.K. Vickers, and D. Decker, *Trends in Purge and Trap*. Journal of Chromatographic Science, 1994. **32**(8): p. 328-338.
109. *Optimizing the Analysis of Volatile Organic Compounds*. 2003: Restek Corporation.
110. Ashley, D.L., et al., *Determining volatile organic compounds in human blood from a large sample population by using purge and trap gas chromatography/mass spectrometry*. Analytical Chemistry, 1992. **64**(9): p. 1021-1029.
111. Page, B.D., et al., *Survey of bottled drinking water sold in Canada. Part 2. Selected volatile organic compounds*. J AOAC Int, 1993. **76**(1): p. 26-31.

112. David J. Munch and S.C. Wendelken, *Method 524.4 Measurement of purgeable organic compounds in water by gas chromatography/mass spectrometry using nitrogen purge gas*, U.S.E.O.o. Water, Editor. 2013, U.S. EPA.
113. Sauer, T.C., *Volatile liquid hydrocarbon characterization of underwater hydrocarbon vents and formation waters from offshore production operations*. Environmental Science & Technology, 1981. **15**(8): p. 917-923.
114. Campillo, N., et al., *Purge-and-trap capillary gas chromatography with atomic emission detection for volatile halogenated organic compounds determination in waters and beverages*. Journal of Chromatography A, 2004. **1035**(1): p. 1-8.
115. Liu, H.-W., et al., *Process sampling module coupled with purge and trap–GC–FID for in situ auto-monitoring of volatile organic compounds in wastewater*. Talanta, 2009. **80**(2): p. 903-908.
116. Huybrechts, T., J. Dewulf, and H. Van Langenhove, *Priority volatile organic compounds in surface waters of the southern North Sea*. Environmental Pollution, 2005. **133**(2): p. 255-264.
117. Ekdahl, A. and K. Abrahamsson, *A simple and sensitive method for the determination of volatile halogenated organic compounds in sea water in the amol l–1 to pmol l–1 range*. Analytica Chimica Acta, 1997. **357**(3): p. 197-209.
118. Chen, T.-C. and G.-R. Her, *On-line monitoring of trihalomethanes in drinking water using continuous-flow purge and cryofocusing gas chromatography–mass spectrometry*. Journal of Chromatography A, 2001. **927**(1–2): p. 229-235.
119. Zoccolillo, L., et al., *Improved analysis of volatile halogenated hydrocarbons in water by purge-and-trap with gas chromatography and mass spectrometric detection*. Journal of Chromatography A, 2005. **1077**(2): p. 181-187.

120. Lara-Gonzalo, A., et al., *Critical comparison of automated purge and trap and solid-phase microextraction for routine determination of volatile organic compounds in drinking waters by GC–MS*. Talanta, 2008. **74**(5): p. 1455-1462.
121. Laaks, J., et al., *In-Tube Extraction of Volatile Organic Compounds from Aqueous Samples: An Economical Alternative to Purge and Trap Enrichment*. Analytical Chemistry, 2010. **82**(18): p. 7641-7648.
122. Kolb, B. and L.S. Ettre, *General Introduction*, in *Static Headspace–Gas Chromatography*. 2006, John Wiley & Sons, Inc. p. 1-18.
123. Tipler, A., *An Introduction to Headspace Sampling in Gas Chromatography - Fundamentals and Theory*, PerkinElmer, Editor. 2014, PerkinElmer: USA.
124. Safarova, V.I., et al., *Gas chromatography–mass spectrometry with headspace for the analysis of volatile organic compounds in waste water*. Journal of Chromatography B, 2004. **800**(1–2): p. 325-330.
125. Kavcar, P., et al., *Occurrence, oral exposure and risk assessment of volatile organic compounds in drinking water for İzmir*. Water Research, 2006. **40**(17): p. 3219-3230.
126. Hervás, C., et al., *Multilogistic regression by evolutionary neural network as a classification tool to discriminate highly overlapping signals: Qualitative investigation of volatile organic compounds in polluted waters by using headspace-mass spectrometric analysis*. Chemometrics and Intelligent Laboratory Systems, 2008. **92**(2): p. 179-185.
127. Polkowska, Ż., et al., *Relationship between volatile organohalogen compounds in drinking water and human urine in Poland*. Chemosphere, 2003. **53**(8): p. 899-909.
128. Ji, J., et al., *Field analysis of benzene, toluene, ethylbenzene and xylene in water by portable gas chromatography–microflame ionization detector combined with headspace solid-phase microextraction*. Talanta, 2006. **69**(4): p. 894-899.
129. Antoniou, C.V., E.E. Koukouraki, and E. Diamadopoulos, *Determination of chlorinated volatile organic compounds in water and municipal wastewater using*

headspace–solid phase microextraction–gas chromatography. Journal of Chromatography A, 2006. **1132**(1–2): p. 310-314.

130. Sun, T., et al., *Application of novel activated carbon fiber solid-phase, microextraction to the analysis of chlorinated hydrocarbons in water by gas chromatography–mass spectrometry*. Analytica Chimica Acta, 2005. **530**(1): p. 33-40.

131. Pecoraino, G., et al., *Distribution of volatile organic compounds in Sicilian groundwaters analysed by headspace-solid phase microextraction coupled with gas chromatography mass spectrometry (SPME/GC/MS)*. Water Research, 2008. **42**(14): p. 3563-3577.

132. Niri, V.H., L. Bragg, and J. Pawliszyn, *Fast analysis of volatile organic compounds and disinfection by-products in drinking water using solid-phase microextraction–gas chromatography/time-of-flight mass spectrometry*. Journal of Chromatography A, 2008. **1201**(2): p. 222-227.

133. Regueiro, J., et al., *Development of a solid-phase microextraction–gas chromatography-tandem mass spectrometry method for the analysis of chlorinated toluenes in environmental waters*. Journal of Chromatography A, 2009. **1216**(14): p. 2816-2824.

134. Arthur, C.L. and J. Pawliszyn, *Solid phase microextraction with thermal desorption using fused silica optical fibers*. Analytical Chemistry, 1990. **62**(19): p. 2145-2148.

135. Gonçalves, C. and M.F. Alpendurada, *Comparison of three different poly(dimethylsiloxane)–divinylbenzene fibres for the analysis of pesticide multiresidues in water samples: structure and efficiency*. Journal of Chromatography A, 2002. **963**(1–2): p. 19-26.

136. Jakubowska, N., et al., *Optimization of a Novel Procedure for Determination of VOCs in Water and Human Urine Samples Based on SBSE Coupled with TD-GC-HRMS*. Journal of Chromatographic Science, 2009. **47**(8): p. 689-693.

137. Ma, X., et al., *Detection of geosmin and 2-methylisoborneol by liquid-liquid extraction-gas chromatograph mass spectrum (LLE-GCMS) and solid phase extraction-gas chromatograph mass spectrum (SPE-GCMS)*. *Frontiers of Environmental Science & Engineering in China*, 2007. **1**(3): p. 286-291.
138. Sarafray-Yazdi, A., A.H. Amiri, and Z. Es'haghi, *BTEX determination in water matrices using HF-LPME with gas chromatography-flame ionization detector*. *Chemosphere*, 2008. **71**(4): p. 671-676.

Method development – Analysis of Volatile Organic Compounds (VOCs) in rainwater using Purge-and-Trap Gas Chromatography-Mass Spectrometry

2.1. Introduction

2.1.1. Rainwater

Being a small island nation, Singapore faces physical water scarcity where rainwater is collected as one of the sources of water supply to support the country's daily needs [1]. The dependency on rainwater in Singapore had led to queries on the quality of water supply, with previous research conducted on rainwater collected from the island nation focused on the acidity, ionic concentration of major ions as well as metal concentrations present [2-5]. Nonetheless, other atmospheric pollutants such as volatile organic compounds (VOCs) have yet to be studied in rainwater.

2.1.2. Quantification methods

A variety of quantification methods for the measurement of VOCs in rainwater had been employed in previous research performed in other countries, and the advantages and disadvantages of the techniques used will be discussed in the following literature review.

2.1.2.1. Gas chromatography-mass spectrometry (GC-MS)

In a rainwater study performed in Portland, OR [6], rainwater samples were collected in rain extraction cartridges (Tenax-GC) which were dried using centrifugation and further vacuum dried for 20 min. Extraction was then performed on the cartridges with acetone (9 mL) and hexane (6 mL) for 3 h after the addition of an internal standard solution.

Before on-column injection into the GC-MS system, the extracts were concentrated to 1 mL with a Kuderna-Danish apparatus followed by a reduction of volume to 200 μ L by blowdown with ultrapure helium in a 3 mL vial. GC-MS helps to expand the scope of VOCs studied via reducing the necessity of derivatization, and identification of unknown compounds is made easier with the MS library (available when electron ionization (EI) is employed). However, the extraction process which can be time-consuming requires the use of solvents which are often VOCs themselves. This can limit the types of VOCs studied, and the additional labor can potentially increase the chance of contamination and encourage the possible escape of VOCs through the extraction process.

2.1.2.2. Thermal-desorption gas chromatography-mass spectrometry (TD GC-MS)

Rainwater samples that were collected in Portland, OR [6] through a rain desorption cartridges could be analyzed via thermal desorption (TD) GC-MS with the addition of an internal standard after centrifugation and vacuum drying for 20 min. Purging of the TD cartridge was performed with a backflow of helium for 10 min for the removal of oxygen and most of the methanol (from the addition of internal standard) before desorption for 10 min at 250 °C to release the VOCs for sending into GC-MS for separation and analysis. TD GC-MS is a more efficient method for analyzing VOCs in rainwater in comparison to HPLC and GC-MS as no additional solvents (or VOCs) are required to derivatize or concentrate the VOCs. Nonetheless, the centrifuge and vacuum drying, as well as the purging step in TD, could potentially encourage the escape of VOCs from the sorbent material in the cartridge.

2.1.2.3. Purge-and-Trap Gas Chromatography-Mass Spectrometry (PAT GC-MS)

PAT GC-MS, a different sample concentration method for GC-MS, was employed in the study of VOCs in the rainwater of Los Angeles, CA [7] and Japan [8]. PAT or dynamic headspace extracts the VOCs by passing an inert gas (helium or nitrogen) through the sample and traps the purged VOCs on a sorbent trap before desorbing into the GC-MS system [9]. Instead of trapping the VOCs on a sorbent packed cartridge as in the method using TD GC-MS, the VOCs were removed from the rain samples and onto a sorbent trap using an inert gas which reduces the interference from water and lowers the number of steps required to remove water from the sorbent material. Other gaseous stripping methods of sample concentration such as headspace (static) GC-MS [10, 11] exist commercially. However, reports on the use of headspace GC-MS on the analysis of VOCs in rainwater has not been narrated in the past with probable reasoning from the larger volume of rain sample required in headspace analysis. PAT GC-MS is often used in the analysis of VOCs in aqueous samples and the United States Environmental Protection Agency (US EPA) had published several methods for such analysis with the types of VOCs measured limited by the purge response of the compounds. [12, 13]. Nonetheless, the advantages of using PAT GC-MS for the study of VOCs in rainwater outweighs the limitations. Therefore, US EPA Method 524.4, Measurement of Purgeable Organic Compounds in Water by Gas Chromatography-Mass Spectrometry using Nitrogen Purge Gas, would be used as a basis for method development in this study and the required *p*-bromofluorobenzene (BFB) tune for MS will be performed before all analysis.

2.1.3. Rainwater sampler

Different types of rainwater collectors have been reported in past published studies, and the main aim of such samplers is to collect as many samples as possible without the loss of analyte while reducing the artifacts introduced. The systems can be as elaborate as automated electronic sensors or as simple as a clean bottle for collection, and such systems should be tested out for their suitability in collecting rain samples. Some commercial and makeshift rain samplers that had been used in past research are discussed as follows.

2.1.3.1. Commercial sampler

A commercial sampler with a rain sensor was employed in the study of VOCs in rainwater in Japan, and the design allows the collection of every 1 mm of rainfall sample in an amber glass vial chilled at 4 °C [8]. Other simpler or more complicated rainwater collector designs are also available in the market by companies such as Palmex [14], Digitel [15] and New Star Environmental [16]. The cost of such commercial samplers and the materials used to construct the samplers are often consideration points during acquisition.

2.1.3.2. Makeshift sampler

In the study of organic compounds in rainwater of Los Angeles, CA, a makeshift rain sampler was employed. It was constructed from a galvanized iron rubbish bin with the cover inverted; handle removed, and the center of the cover drilled and soldered with a stainless-steel tube acting as a funnel. The funnel transported the rainwater collected into a 20 L glass carboy inside the rubbish bin. A stainless-steel lid covering the makeshift setup was held in place with polyvinyl alcohol paper which dissolved quickly when in contact with water (rainwater), therefore, allowing the lid to spring open and expose the

collector [7]. Similar to the commercial sampler, the makeshift sampler needs to take into consideration the material selected compared to the species being analyzed and the viability of the design of such collectors. Many commercial rainwater collectors use plastic buckets to collect the water which is not appropriate for VOCs monitoring in rainwater as they can introduce contamination.

2.1.4. Objective

The aim of this study is to develop a method using PAT GC-MS modified from the US EPA Method 524.4 for the detection and quantification of VOCs commonly present in the rainwater collected in Singapore. The method developed would be optimized and validated for the VOCs studied, and a suitable rainwater sampler would be acquired and verified to be free from VOC artifacts introduction before applying it in the long-term rainwater monitoring studies.

2.2. Experimental, Method Development, and Validation

2.2.1. Instrumentation

The instrument, settings, and parts for use in the method development of VOCs analysis in rainwater are displayed in Table 2.1.

Table 2.1. PAT GC-MS instrument and setting used in the method development of VOCs analysis in rainwater.

Instrument	Instrument parts/settings
Atomx PAT (Teledyne Tekmar)	#9 proprietary material trap 5 mL sparger Nitrogen sparging gas (99.999%) - Air products
GC-MS (Agilent 7890A & 5975C)	DB-VRX (Agilent J&W 122-1564 260 °C 60 m x 250 µm x 1.4 µm) Electron ionization mode (EI - 230 °C)) Quadrupole (150 °C) scans from 35 to 300 amu Solvent delay (7 min)

The choice of the PAT trap material and column were decided base on the target compounds in which the method will be developed for. Optimal settings for the PAT GC-MS such as sample temperature, flow rate, flow volume, desorption time, and dry

desorption volume of the PAT and oven program, split ratio, flow rate and SIM (selective ion monitoring) mode in GC-MS were examined. The changes performed on PAT were within the recommended, and acceptable criteria for EPA Method 524.4 and the data obtained from the changes made in the method development were processed via the data analysis program, Environmental data analysis.

2.2.2. Sampling location and samplers

The sampling location was located on the rooftop of School of Physical and Mathematical Sciences (SPMS) in Nanyang Technological University (NTU) of Singapore (Latitude: 1 °, 20' 30.3154", Longitude: 103 °, 40' 53.6772"). Situated close to anthropogenic sources of emission (Jurong island, Tuas industrial area, and an expressway) and some residential areas, the sampling site, enables the study on the effects of anthropogenic activities on residences living close to such sources through a long-term study so as to take varying wind directions into account. Two types of rain sampler, Model APS Acid precipitation sampler from New Star Environment (commercially available) and a makeshift manual sampler (assembled from the readily available material of an aluminum tray and terracotta container) were examined for their aptness for capturing VOCs in rainwater. All of the samples collected were stored in an amber glass vial (40 mL) with a septum cap for easy analysis with PAT GC-MS. Samples were collected as soon as possible, and preservation of samples as mentioned in EPA Method 524.4 was not performed as samples were analyzed immediately without storage.

2.2.3. Syringe filters

Filtration of rainwater samples is one of the sample preparation steps mentioned in a previous study [13]. Filtration is potentially vital in Singapore as relatively high levels of particulate matter (PM) are known to be found in the ambient air of Singapore reported

by the National Environmental Agency (NEA) of Singapore [17]. The presence of PM in the rainwater samples could possibly pollute the frit of the sparger in the PAT system and cause more regular cleaning of the sparger than normal. Contamination or interaction between PM and VOCs are found to be little to none from past literature studies [18]. Table 2.2 lists the types of syringe filters tested for the compatibility of filtering rainwater with VOCs studies. Comparisons were performed between filtered and unfiltered rainwater and ultrapure water (Elga Purelab Option-Q ultrapure water system) for the selection of syringe filters.

Table 2.2. List of filter materials, source, and dimension

Material of Filter	Source and Dimension
Nylon	Agilent (0.2 μm) Environmental Express (0.2 μm)
Polypropylene (PP)	Sun-ri Titan2 (0.2 μm)
Regenerated Cellulose (RC)	Agilent (0.2 μm)
Surfactant-Free Cellulose Acetate (SFCA)	Sartorius Stedim (0.45 μm)
Polyethersulfone (PES)	Agilent (0.45 μm) Sartorius Stedim (0.45 μm , Sterile)

2.2.4. Method development

2.2.4.1. Identification of plausible VOCs candidates

Method development started with the determination of probable VOC analytes found in rainwater by running samples of filtered rainwater through a generic PAT GC-MS method. The identification was performed through NIST (National Institute of Standards and Technology) library matching with the mass spectrum of different peaks in the chromatogram through the environmental data analysis program. Matching of the mass spectrum provided a plausible estimation on the identity of the compound. However, isomeric VOCs produce similar spectra, henceforth, the retention time and mass spectrum of all compounds were required to be tested for verification.

2.2.4.2. Materials

Neat chemicals with purity higher than 90% of possible VOC analytes, internal standards, and surrogate standards were purchased from Alfa Aesar, Sigma-Aldrich, Merck, VWR, Fluka, Acros Organics, Mallinckrodt chemicals and TCI. The use of internal and surrogate standards is a requirement of EPA Method 524.4, and the internal standard is used for calibration purposes is to account for plausible fluctuations in the PAT system. The detailed list of chemicals utilized in the method development is attached as Appendix A.1. Stock solutions of individual compounds were made by diluting neat chemicals with Pestinorm PAT grade methanol from VWR to produce a concentration of 1 mg mL⁻¹, and a similar solution was made with the internal and surrogate standards. The stock solutions were further diluted with methanol before a final dilution by injecting 2 to 10 µL into ultrapure water (determined to contain low to no VOCs contaminants) to make up concentrations recommended by US EPA Method 524.4, 10 ng L⁻¹ to 1000 ng L⁻¹ and internal/surrogate standard at 500 ng L⁻¹ for SIM mode and 0.5 µg L⁻¹ to 40 µg L⁻¹ and internal/surrogate standard at 5 µg L⁻¹ for Scan mode.

2.2.4.3. Verification of retention time and mass spectrum

Retention times and mass spectra of individual VOCs were determined through runs of individual pure compounds. Through the analysis of the mass spectra, a quantifier ion (commonly the base peak) and one to two ion(s) unique to the VOC were chosen, where the selected quantifier ion should be free from interference with any plausible overlapping peaks [19]. Additionally, compounds of interest were also tested for purge compatibility with the PAT GC-MS system.

2.2.4.4. GC parameter studies

The flow rate of carrier gas (helium), split ratio and oven temperature programming were investigated to determine the optimal separation conditions by analyzing a 5 µg L⁻¹ mixture of each VOC standards in Scan mode. Shapes of the chromatography peaks such as tailing and fronting as well as resolution (R_S) were factors considered in the final operating conditions. Resolution was calculated based on the Equation 2.1.

$$R_S = \frac{2[(t_R)_A - (t_R)_B]}{W_A + W_B} = \frac{1.178[(t_R)_A - (t_R)_B]}{W_{A_h} + W_{B_h}} \quad (2.1)$$

where t_R is retention time, W is width of the peak, W_h is width of the peak at half the peak height for continuously eluting compounds A and B. A resolution greater than 1.5 is good for quantitative purposes but, the separation of certain peaks may not be feasible or as ideal in real life situations. Therefore, for cases of poor separation, a quantifier ion unique to the compound may be used for quantification if the quantifier ion is free from interference with overlapping peaks. Other than oven temperature programming, flow rates of 1.4 mL min⁻¹, 1.5 mL min⁻¹ and, 1.6 mL min⁻¹ as well as split ratios of 1:3, 1:4 and 1:5 were tested for comparison in search for optimal peak separation.

2.2.4.5. Selective Ion Monitoring (SIM) mode study

The low quantities of VOCs found in rainwater in previous papers [6, 9] suggests the need for SIM mode analysis. Henceforth, SIM mode monitoring ions were determined with standards at 100 ng L⁻¹ through dynamic calibration by testing $M \pm 0.2$ AMU (atomic mass unit) where M is the ion of interest (quantifier or qualifier ions) for each VOC. A quantifier and one to two qualifier ions were determined for each VOC through the dynamic calibration where the optimal SIM ions produce the highest counts in the mass spectrum of the SIM dynamic calibration analysis. Verified SIM ions were then

categorized into SIM windows where dwell time of each ion is set to allow seven to ten scans across chromatographic peaks [12].

2.2.4.6. PAT parameter studies

Response factor (RF) of VOCs with respect to their respective internal standards (Appendix A.2) were calculated using the Equation 2.2.

$$Response\ Factor\ (RF) = \frac{Integrated\ Area_{Analyte}}{Integrated\ Area_{Internal\ standard}} \quad (2.2)$$

Through RF value comparisons, optimum operating conditions were chosen when the majority of VOCs tested displayed optimal RF values for a test condition within the allowable and recommended range stated by US EPA Method 524.4 as seen in Table 2.3.

Table 2.3. Table of recommended and allowable PAT parameters by US EPA Method 524.4 [19].

Parameter	Recommended		Allowable	
	Minimum	Maximum	Minimum	Maximum
Sample Temperature	Ambient	40 °C	Ambient	60 °C
Purge flow rate	40 mL min ⁻¹	55 mL min ⁻¹	20 mL min ⁻¹	80 mL min ⁻¹
Purge volume	360 mL	520 mL	320 mL	520 mL
Desorb time	1 min	1 min	0.5 min	2 min
Purge volume + dry purge volume	360 mL	720 mL	320 mL	720 mL

Sample temperature, purge volume, purge flow rate, desorption time and dry purge volume were optimized, and standards (mixture at 5 µg L⁻¹ in Scan mode) used in the PAT parameter studies were prepared in the same way as the standards used in the GC parameters studies.

2.2.5. Method Validation

2.2.5.1. Precision and Accuracy

The precision of measurement for each VOC was determined through seven replications of standards in SIM and Scan mode, and relative standard deviations were calculated based on Equation 2.3. Acceptable relative standard deviations (%RSD) must be below or equal to 20% for all method analytes.

$$\%RSD = \frac{\text{Standard Deviation}}{\text{Average concentration}} \times 100\% \quad (2.3)$$

Accuracy was determined through the calculation of percentage recovery (%Recovery) (Equation 2.4) from the same runs as the precision experiments, and the average recovery replicate of each VOC must fall within $\pm 20\%$ of the actual value.

$$\%Recovery = \frac{\text{Average Measured Concentration}}{\text{Fortified Concentration}} \times 100\% \quad (2.4)$$

2.2.5.2. Minimal Reporting Level (MRL) and Detection Limit (DL)

The lowest calibration point must be at or below the concentration of the MRL, and the MRL of each VOC is confirmed through seven replicate measurements at or below the proposed MRL. The mean and standard deviations (S) of these replicates were calculated for determination of the Half Range for the Prediction Interval of Results ($HR_{PIR} = 3.963S$) to confirm the upper ($\leq 150\%$) and lower limits ($\geq 50\%$) of the Prediction Interval of Results ($PIR = \text{Mean} \pm HR_{PIR}$). MRL is validated if both the upper and lower PIR limits meet the criteria described above [19]. DL can be calculated based on Equation 2.5 from the set of data used to determine MRL [12].

$$DL = S \times t_{(n-1, 1-\alpha=0.99)} \quad (2.5)$$

where n is the number of replicates, S is the standard deviation and t is the student's t value for the 99% confidence level with $n - 1$ degrees of freedom ($n = 7, t = 3.143$).

2.2.5.3. Rainwater sampler study

The comparison of commercial and makeshift samplers described in “Section 2.2.2 Sampling location and samplers” was performed, and the materials of the sampler selected were investigated to determine the plausible VOCs emitted under normal usage conditions when exposed to heat. The ease of use of each sampler was evaluated in terms of dust collection and the amount of rain collected.

2.3. Results and Discussion

2.3.1. Preliminary studies – Identification of potential analytes

Six filtered rain samples were collected from April to June 2013, and all plausible VOCs present in rainwater were identified in Scan mode using PAT GC-MS (Appendix A.3). PES syringe filters from Sartorius Stedim was utilized for the filtration, and plausible identity of the chromatographic peaks and their detection frequencies were tabulated in Table 2.5. Not all chromatographic peaks were identified as the abundance of ions for certain peaks was too low for a reasonable match with NIST library, and this reaffirms the need to develop a SIM mode method for analyzing VOCs in rainwater. 38% of the probable VOC target analytes identified were detected in at least three out of six rain samples analyzed. Nonetheless, the possible origins of such VOCs should be examined and taken into consideration before deciding on the list of compounds to be studied in future samples.

Polysiloxane is a common stationary phase material used in capillary columns of GC [19], and the detection of octamethylcyclotetrasiloxane and hexamethylcyclotrisiloxane could be a result of column bleeding. As the column installed was relatively new, some loosely bounded stationary phase could be eluted even with column conditioning. It was observed that the detection of siloxane compounds decreases with the age of the column in blank runs. Therefore, octamethylcyclotetrasiloxane and hexamethylcyclotrisiloxane were removed from the list of VOCs studied in rainwater. In addition to polysiloxane, α -methyl styrene, *p*-bromofluorobenzene and propanenitrile were also identified as temporal contaminants from the system or have been designated as carry over from the trap of the PAT system as the bake out parameters were yet to be fully optimized, and they were also detected in blank runs. VOC contaminants can also originate from sources outside the PAT GC-MS system such as the amber glass vial used to store the samples.

Table 2.5. List of plausible VOCs detected and detection frequency from 6 rain samples in 2013.

Plausible VOCs identified	Detection	Plausible VOCs identified	Detection
1,2,3-Trimethylbenzene	50%	Hexamethylcyclotrisiloxane	83%
1,2,4-Trimethylbenzene	33%	Hexanal	67%
1,3,5-Trimethylbenzene	33%	Indane	17%
1-Ethyl-2-methylbenzene	67%	Methacrolein	50%
1-Ethyl-2,4-dimethylbenzene	17%	Methyl acetate	33%
1-Ethyl-3-methylbenzene	50%	Methyl crotonate	33%
1-Ethyl-4-methylbenzene	67%	Methyl isobutyl ketone	33%
2,2-Dimethyltetrahydrofuran	17%	Methyl methacrylate	67%
2,3-Dihydrofuran	67%	Methyl propionate	17%
2,3,5-trimethylhexane	17%	Methyl vinyl ketone	33%
2,4-Dimethylhexane	17%	<i>m</i> -Xylene	50%
2,5-Dihydrofuran	67%	<i>n</i> -Butyl acetate	100%
2-Butanone	100%	Nonanal	33%
2-Butenal	33%	Nonane	17%
2-Ethyl-1,3-dimethylbenzene	17%	Octamethylcyclotetrasiloxane	100%
2-Hexanone	17%	Octanal	17%
2-Methyl-1-Penten-3-ol	17%	<i>o</i> -Cymene	17%
2-Methyl-3-hexanone	17%	<i>o</i> -Xylene	67%
2-Methyl furan	67%	Propanenitrile	17%
2-Pentanone	17%	Propyl benzene	17%
3-Methyl-2-pentanone	17%	<i>p</i> -Bromofluorobenzene	83%
4-Heptanone	17%	<i>p</i> -Xylene	100%
4-Methyl-3-pentenoic acid	17%	Styrene	83%
Acetone	83%	Succinic acid, Decyl tetrahydro furfuryl ester	17%
Acetophenone	17%	<i>tert</i> -Butyl 3,3-dimethylbutylether	17%
Benzaldehyde	67%	Tetrahydro-2-Furanmethanol	17%
Benzonitrile	17%	Tetrahydro-2-methyl furan	17%
Cumene	50%	Tetrahydro-5-methyl-2-Furanmethanol	17%
Decane	17%	<i>trans</i> -Tetrahydro-5-methyl-2-Furanmethanol	17%
Dibromomethane	17%	Trichloroethylene	17%
Dichloromethane	33%	Trimethylsilanol	17%
Ethyl acetate	17%	Toluene	100%
Ethyl acrylate	50%	Undecane	17%
Ethyl benzene	100%	α -Methyl styrene	50%

Toluene was found to migrate into cleaned amber glass vial when stored in cabinets of the laboratory. As the laboratory was newly established and hence with new furniture, toluene residues could be found from the production of this furniture as past studies had discovered exposure to toluene for workers producing wood furniture [20]. Henceforth, the cleaned amber glass vials were stored outside of the cabinets. Trimethylsilanol was found to be from the septum of the open top cap that had not been sufficiently cleaned. Contaminants of such origins should be removed from the list of VOCs studied in rainwater. However, a previous study on VOCs in atmospheric air of Singapore had discovered high levels of toluene in ambient air samples collected [21], therefore, toluene was kept as a potential candidate for the study. Contamination from the amber glass vials

was maintained at a low level by ensuring that all cleaned vials were used immediately and avoided storage in cabinets.

Other than the VOCs detected in the preliminary samples collected, VOCs studied in the ambient air of western Singapore [21] with the sampling site close to the current sample collection location were also considered. Since VOCs are removed from the atmosphere through wet deposition [22], it would appear logical if similar VOCs were detected in both rainwater and atmospheric air. Although some compounds out of the 48 VOCs tested in the ambient air had not been detected in the preliminary samples collected, they were still considered as probable candidates for the study as some of the concentrations could be too low for detection in Scan mode.

Table 2.6. List of plausible VOC analytes in rainwater.

List of plausible VOCs present in Rainwater			
1,2,3-Trimethylbenzene	Benzaldehyde	Heptane	Nonane
1,2,4-Trimethylbenzene	Benzene	Hexanal	Octanal
1,3,5-Trimethylbenzene	Benzonitrile	Hexane	Octane
1-Ethyl-2-methylbenzene	Cumene	Isoprene	<i>o</i> -Xylene
1-Ethyl-3-methylbenzene	Cyclohexane	Isopropyl alcohol	Phenol
1-Ethyl-4-methylbenzene	Decanal	Methacrolein	Propyl benzene
1-Octene	Decane	Methyl crotonate	<i>p</i> -Xylene
2-Butanone	Dichloromethane	Methyl cyclohexane	Pyridine
2-Methyl furan	Ethyl acetate	Methyl isobutyl ketone	Styrene
2-Methyl heptane	Ethyl acrylate	Methyl methacrylate	Tetrachloroethylene
2-Methyl pentane	Ethyl benzene	Methyl cyclopentane	Toluene
3-Methyl pentane	Ethyl ether	<i>m</i> -Xylene	Trichloroethylene
Acetone	Furfural	<i>n</i> -Butyl acetate	Trichloromethane
Acetophenone	Heptanal	Nonanal	

In general, VOCs were mainly contemplated as candidates if the percentage of detection was greater than 50% based on Table 2.5, however, certain compounds such as 2,3-dihydrofuran and 2,5-dihydrofuran were omitted as slight discrepancies were observed in the spectrum matching and the chromatographic peak was most likely related to methacrolein which had been measured previously in the atmospheric air of western Singapore [22]. The final list of VOC candidates considered is tabulated as Table 2.6

after much consideration of the matching percentage and retention time of each chromatographic peak.

2.3.2. Syringe filters

Five types of syringe filter material [nylon, polypropylene (PP), polyethersulfone (PES), regenerated cellulose (RC) and surfactant-free cellulose acetate (SFCA)] were tested by comparing filtered, and unfiltered ultrapure water for compatibility with VOCs studied in rainwater in terms of probable VOC contamination. The amount of VOCs detected from the filters were ranked as follows: PES^{SS} > PES^A > Nylon^A > Nylon^{EE} ≈ RC^A ≈ SFCA^{SS} > PP^T ≈ unfiltered ultrapure water (probable VOCs identified were recorded in Table 2.7).

Table 2.7. Comparison list of plausible VOCs detected from different filters compared with ultrapure water. Where A denotes Agilent, EE denotes Environmental Express; T denotes Titan2, and SS denotes Sartorius Stedim

Plausible VOCs identified	UPW	Nylon ^A	Nylon ^{EE}	PP ^T	PES ^A	PES ^{SS}	RC ^A	SFCA ^{SS}
1,2,3-Trimethylbenzene					x	x		
1,2,4-Trimethylbenzene					x	x		
1-Ethyl-3-methylbenzene						x		
1-Ethyl-4-methylbenzene					x			
2-Butanone						x		
Acetone		x	x			x	x	
Benzaldehyde						x		
Dichloromethane		x				x		
Ethyl benzene						x		
Hexanal						x		
Methyl methacrylate						x		
<i>m</i> -Xylene						x		
<i>n</i> -Butyl acetate					x	x		
Nonanal								x
Octamethylcyclotetrasiloxane		x						
<i>o</i> -Xylene					x	x		
Propanenitrile	x	x	x	x	x	x	x	x
<i>p</i> -Bromofluorobenzene	x	x	x	x	x	x	x	x
<i>p</i> -Xylene					x	x		
Styrene						x		
Trichloroethylene					x			
Toluene	x	x	x	x	x	x	x	x
α -Methyl styrene	x	x	x	x	x	x	x	x

Although PES syringe filters are frequently used in biological studies due to their low protein binding features [23, 24], Agilent Technologies had previously analyzed filtrates using liquid chromatography (LC) MS from competitor PES syringe filters that led to the detection of supplementary peaks, in comparison to an unfiltered solution [23]. Therefore,

PES membrane materials may not be an ideal filter material for VOCs analysis in rainwater, and the other syringe filters (Nylon^A, SFCA^A, and PP^T) were further tested by comparing filtered and unfiltered rainwater. The amount of VOCs found in the rainwater after it had undergone syringe filtration are ranked in the following order: SFCA^{SS}> Nylon^A> PP^T> unfiltered rain sample as seen in Table 2.8.

Table 2.8. List of plausible VOCs detected in filtered and unfiltered precipitation from 04/06/2013.

Plausible VOCs identified	Rain	PP ^T	Nylon ^A	SFCA ^{SS}
1,2,3-Trimethylbenzene	x		x	x
1,2,4-Trimethylbenzene	x		x	
1-Ethyl-2-methylbenzene				x
1-Ethyl-3-methylbenzene				x
1-Ethyl-4-methylbenzene				x
2-Butanone	x	x	x	x
2-Ethyl-1-hexanol				x
2-Methyl furan				x
3-Methyl furan				x
Acetone	x	x	x	x
Acetophenone		x	x	x
Benzaldehyde			x	x
Cumene				x
Ethyl-4-ethoxylbenzoate		x		
Ethyl benzene		x		x
Heptanal			x	x
Hexanal			x	x
Methyl methacrylate				x
<i>m</i> -Xylene				x
<i>n</i> -Butyl acetate		x	x	x
Nonanal			x	x
Octamethylcyclotetrasiloxane			x	x
Octanal				x
<i>o</i> -Xylene		x	x	x
<i>p</i> -Bromofluorobenzene	x	x	x	x
<i>p</i> -Xylene	x	x	x	x
Styrene			x	
<i>tert</i> -Butyl benzene				x
Tridecan3-yl trichloroacetate				x
Toluene	x	x	x	x
α -Methyls tyrene	x	x	x	x

The small discrepancy between the syringe filter study in ultrapure water and rainwater could be linked to the acidity of the solution. Rainwater in Singapore has an average pH of 4.2 [2] which may be incompatible with cellulose acetate or SFCA^{SS} membranes as a recommended pH range of 4-8 is noted for such materials [25]. The acidity of rainwater could have caused degradation to the CA filter material to form acetic acid through hydrolysis of ester bonds, and acetic acid could, in turn, react with other organic

compounds and form the contaminants observed in SFCA. A more in-depth discussion and study on the elution of VOC contaminants from syringe filter with aqueous filtrate is discussed in Chapter 3 of this thesis. Filtration was removed as a sample preparation step for VOC contaminants was still detected in the ‘cleanest’ syringe filter, PP^T. More regular cleaning of the glass sparger of the PAT system was also conducted to maintain the cleanliness of the analytical instrument.

The detection of VOC contaminants from syringe filters in filtered rainwater could have potentially invalidated the previous experiments carried out to examine potential VOC target analytes in rainwater as PES syringe filter was used for filtration. However, it was perceived that most of the VOC contaminants from the syringe filter studies belonged to the list of 48 VOCs quantified in atmospheric air of Singapore [21] and the unfiltered precipitate also contains compounds such as 2-butanone, 2-methyl furan, and xylenes that were also on the list of potential candidates. Therefore, method development for VOCs monitoring in rainwater proceeded with the list of target analytes in Table 2.6.

2.3.3. Optimization

2.3.3.1. Analyte Confirmation

The list of all plausible analytes from Table 2.6 was purchased and tested for retention time and mass spectrum confirmation. Internal standards (Toluene-*D*₈ and *p*-bromofluorobenzene) were used for quantification and calibration to minimize the effect from sample matrix variances between samples and minute differences in flow rates that may occur during the purging process [19]. Surrogate standard (dibromomethane) was also added to samples and calibration points as a requirement in US EPA Method 524.4 for evaluating the performance of the PAT analysis cycle. Surrogate and internal

standards were selected such that they are extremely unlikely to be found in any samples collected [12].

Through the purgeability study of VOCs with PAT GC-MS, only 35 VOCs (Table 2.14) inclusive of internal and surrogate standards remain as the other VOCs (mainly alkane and alkene) were not as responsive in the purge process. 2-Butanone was removed from the analysis as it was found to be a significant contaminant from methanol during SIM mode analysis. Quantifier ions of compounds and retention time were determined from the chromatograms and mass spectra study using PAT GC-MS analysis in Scan mode of diluted neat chemicals. However, it was noted that the retention times for some VOCs were too close for proper quantitation. Hence, GC parameters (flow rate of helium gas, split ratio, and oven programming) were optimized to improve the resolution of chromatographic peaks. All experiments in PAT GC-MS optimization testing were performed in Scan mode with 5 $\mu\text{g L}^{-1}$ of mixed VOC standards.

2.3.3.2. GC-MS parameters

2.3.3.2.1. Oven temperature programming

Three main clusters were observed to have poor separations in the unoptimized oven temperature programming. Henceforth, a variation of temperature ramping and holding of temperature was tested to determine the best solution for resolution (R_s) between the clusters. Generally, the increase in temperature causes a decrease in retention time which decreases the interaction between the gaseous analyte with the stationary phase hence speeding up elution [26]. However, it should be noted that a change in the temperature program does not solely affect the cluster in question but the elution as a whole, therefore, the optimal oven temperature programming may not provide the best programming for every single VOC but a balance between R_s calculated and duplicates of the experiment

are attached as Appendix A.4. Table 2.10 displays a cluster of VOCs with closely spaced retention times. It was found that the R_s between ethyl acrylate and dibromomethane produced a good separation with R_s greater than 1.5 when the temperature was held at 158 °C, however, seeing that trichloroethylene elutes quickly after dibromomethane, holding at 145 °C was chosen to balance the R_s at around 1 for both pairs of VOCs.

Table 2.10. Effects of oven programming on peak cluster 1.

Name of target analytes	Quantifier Ion	Ramp (158 °C)	Hold (158 °C)	Hold (178 °C)	Hold (140 °C)	Hold (145 °C)
		R_s	R_s	R_s	R_s	R_s
Ethyl acrylate	55.1	1.36	1.53	1.48	0.88	1.07
Dibromomethane	174.0	0.61	0.56	0.37	0.79	0.98
Trichloroethylene	130.0					

Table 2.11. Effects of oven programming on peak clusters 2 and 3

Name of target analytes	Quantifier Ion	Hold (197 °C)	Hold (190 °C)	Hold (150 °C)
		R_s	R_s	R_s
1-Ethyl-3-methylbenzene	105.1	0.86	1.04	1.05
1-Ethyl-4-methylbenzene	105.1			
1-Ethyl-2-methylbenzene	105.1			1.16
Octanal	41.1			0.88
Benzonitrile	103.1			

Table 2.11 displays peak clusters 2 and 3 which are closely eluted clusters. Separation of 1-ethyl-3-methylbenzene and 1-ethyl-4-methylbenzene decreases with increasing temperature and 1-ethyl-2-methylbenzene, octanal and benzonitrile cannot be separated at high temperatures. Since both clusters elute better at lower temperatures, holding of temperature at 150 °C was chosen for the final temperature programming as seen in Table 2.12. It should be noted that separation of xylene isomer peaks (*p*-xylene and *m*-xylene) was not attempted because of the restriction caused by the stationary phase due to its lack of selectivity. Separation of isomers may be plausible with a different type of column or by using high-resolution (HR) MS where a more accurate quantifier ion may be employed.

Table 2.12. Final oven temperature programming

	Ramping rate (°C min ⁻¹)	Temperature (°C)	Hold (min)	Time (min)
Optimized oven temperature programming		30	7.0	7.00
	40	145	3.0	12.88
	40	150	5.6	18.60
	60	225	2.7	22.55

2.3.3.2.2. Flow rate

Other than temperature programming, retention time and resolution can be affected by the flow rate of the helium mobile phase. Table 2.13 displays the effect on the flow rate of helium carrier gas on the Rs calculated for all three groups, and it was determined that a flow rate of 1.5 mL min⁻¹ produces the best Rs balance which was thus chosen for the final method development flow rate.

Table 2.13. Resolution calculation and comparison of flow rates and partially optimized oven programming

Name of target analytes	Quantifier Ion	1.4 mL min ⁻¹	1.5 mL min ⁻¹	1.6 mL min ⁻¹
		Rs	Rs	Rs
Ethyl acrylate	55.1	0.87	1.07	0.76
Dibromomethane	174.0	0.76	0.98	1.04
Trichloroethylene	130.0	0.65	0.91	0.85
1-Ethyl-3-methylbenzene	105.1	1.00	1.05	0.96
1-Ethyl-4-methylbenzene	105.1			
1-Ethyl-2-methylbenzene	105.1	0.87	1.16	0.98
Octanal	41.1	0.89	0.88	0.67
Benzonitrile	103.1			

2.3.3.2.3. Split ratio

Although split ratio does not affect the Rs and retention time of chromatographic peaks as much as oven temperature programming and flow rate, it influences the shape of the chromatographic peaks by changing the amount of sample introduced into the GC column. Excessive sample introduction can cause fronting of peaks which deviates from the ideal Gaussian shape that in turn potentially affects separation between two VOC peaks [19]. On the other hand, unnecessary splitting can cause analytes occurring at a lower concentration to go below the detection limit, hence losing sensitivity.

Figure 2.1 displays a comparison between 1:3, 1:4 and 1:5 split ratios tested and it was observed that split ratio affects VOCs eluting closer to the start of the chromatogram rather than the later eluting VOCs. A split ratio of 1:4 produces sharper peaks in comparison to 1:3 and the split ratio of 1:5 decreases the amount of VOCs introduced into

the system. Therefore, the split ratio of 1:4 is chosen as the optimal split ratio for future GC-MS analysis of the VOCs in rainwater. Optimal separation was achieved through the modification of GC parameters and the final retention time (RT) for each VOC is displayed in Table 2.14.

Figure 2.1. Effects of split ratio on the shape of chromatographic peaks from 8 to 11.5 min.

Table 2.14. The retention time of each VOCs after optimization of GC parameters.

VOCs	RT (min)	VOCs	RT (min)	VOCs	RT (min)
Isoprene	8.633	Methyl isobutyl ketone	12.819	<i>p</i> -Bromofluorobenzene	16.436
Dichloromethane	9.076	Methyl crotonate	13.154	1-Ethyl-3-methylbenzene	17.319
Methacrolein	9.969	Toluene- <i>D</i> ₈	13.346	1-Ethyl-4-methylbenzene	17.418
2-Methyl furan	10.622	Toluene	13.411	1,3,5-Trimethylbenzene	17.646
Trichloromethane	10.777	Hexanal	13.675	1-ethyl-2-Methylbenzene	17.977
Benzene	11.702	<i>n</i> -Butyl acetate	13.783	Octanal	18.047
Ethyl acrylate	12.098	Tetrachloroethylene	14.108	Benzonitrile	18.140
Dibromomethane	12.155	Ethyl benzene	15.030	1,2,4-Trimethylbenzene	18.537
Trichloroethylene	12.212	<i>m,p</i> -Xylene	15.251	1,2,3-Trimethylbenzene	19.439
Methyl methacrylate	12.326	Heptanal	15.494	Nonanal	20.512
Methyl cyclohexane	12.626	Styrene	15.694	Decanal	22.720
		<i>o</i> -Xylene	15.808		

2.3.3.3. Selective Ion Monitoring (SIM) mode

2.3.3.3.1. SIM dynamic calibration

Figures 2.2 and 2.3 display examples of SIM dynamic calibration of ethyl benzene. Through MS analysis, two to three ions (unique and non-overlapping with other peaks) were chosen for the SIM dynamic calibration experiments. Ions with the highest abundance count in the sim dynamic calibration are used in SIM mode as the quantifier ion or qualifier ions. Mass to charge ratio (M/Z) 91.1 (base ion), 106.2 and 78.1 were selected for SIM dynamic calibration where $M/Z \pm 0.2$ were tested.

Figure 2.2. MS of ethyl benzene.

Figure 2.3. SIM dynamic calibration of ethyl benzene.

It was determined that quantifier ion 91.1 and qualifier ions 106.1 and 78.1 had the highest response in the SIM dynamic calibration and therefore, could be used in future SIM mode analysis. The final SIM ions chosen for all VOCs in this method are attached as Appendix A.2 with classification into eight windows of detection periods where the dwell time for each ion was set to achieve seven to ten scans per chromatographic peak.

2.3.3.4. PAT parameters

A recommended range of parameters for PAT was provided by US EPA Method 524.4 as parameters including purge volume can affect the effective concentration of VOCs observed in the test solutions. If the purge volume was too little, the purge could be incomplete while a purge volume that is too high could lead to the breakthrough of VOCs where the compounds elute out of the sorbent trap due to the high volume of purge gas.

The Response factor (RF) was used to determine the efficiency of the different purge conditions and the results (duplicate of the experiments is attached as Appendix A.5) from the PAT study are displayed in Table 2.15. Purge volumes between 360 mL and 520 mL were tested with a flow rate of 40 mL min⁻¹ which was the initial recommended setting. Purge volume was determined before all other settings as it is affected by the interaction between the sorbent trap material and the target analytes. Purge flow rates between 40 mL min⁻¹ to 55 mL min⁻¹ were tested with a 520 mL purge volume, desorption times between 0.5 min to 2 min, as well as sample temperature from ambient to 60 °C, were also examined. The parameters tested with the most significant number of VOCs displaying the highest RF were chosen as the optimal conditions for the PAT method development, and most of the parameters were within the recommended settings with the exception of desorption time. The larger purge volume and higher flow rate during purging showed a better response factor possibly because of the removal of lighter or more polar compounds from the aqueous sample. The recommended desorption time by EPA method 524.4 was stated as 1 min, however, desorption time of 1.5 min displayed a larger number of VOCs with better response factor. Hence, a comparison between 1.5 min desorption at the acceptable range and 1 min was performed (Table 2.16) to ensure that the selected parameter in the acceptable range was truly better performing than the recommended settings.

Table 2.15. PAT parameter tested and the total number of VOCs displaying the highest response factor (RF) for each parameter in yellow

VOCs	Purge flow rate (mL min ⁻¹)					Purge volume (mL)					Desorption time (min)					Temperature (°C)				
	40	45	50	55		360	400	440	480	520	0.5	1	1.5	2		Ambient	40	60		
Isoprene	0.055	0.058	0.060	0.058		0.060	0.063	0.055	0.062	0.067	0.061	0.062	0.063	0.055		0.045	0.045	0.047		
Dichloromethane	0.251	0.252	0.250	0.260		0.264	0.264	0.251	0.247	0.260	0.267	0.251	0.256	0.251		0.220	0.222	0.216		
Methacrolein	0.023	0.023	0.023	0.023		0.021	0.022	0.023	0.025	0.029	0.023	0.025	0.024	0.023		0.020	0.020	0.020		
2-Methyl furan	0.054	0.056	0.056	0.055		0.056	0.057	0.054	0.058	0.062	0.057	0.059	0.059	0.054		0.044	0.046	0.045		
Trichloromethane	0.251	0.257	0.253	0.256		0.263	0.261	0.251	0.261	0.267	0.266	0.251	0.267	0.251		0.223	0.223	0.223		
Benzene	0.258	0.264	0.263	0.266		0.265	0.270	0.258	0.268	0.284	0.271	0.272	0.275	0.258		0.214	0.217	0.219		
Ethyl acrylate	0.079	0.079	0.081	0.080		0.079	0.081	0.079	0.078	0.081	0.063	0.062	0.066	0.079		0.056	0.057	0.055		
Dibromomethane (SS)	0.320	0.313	0.302	0.305		0.310	0.317	0.320	0.328	0.336	0.321	0.312	0.329	0.320		0.334	0.332	0.329		
Trichloroethylene	0.076	0.078	0.079	0.078		0.079	0.080	0.076	0.079	0.083	0.078	0.079	0.081	0.076		0.065	0.066	0.066		
Methyl methacrylate	0.025	0.025	0.028	0.026		0.024	0.025	0.025	0.028	0.031	0.027	0.025	0.028	0.025		0.023	0.025	0.023		
Methyl cyclohexane	0.079	0.080	0.081	0.081		0.081	0.079	0.079	0.079	0.082	0.096	0.079	0.100	0.079		0.060	0.061	0.061		
Methyl isobutyl ketone	0.040	0.042	0.046	0.043		0.039	0.045	0.040	0.047	0.053	0.043	0.042	0.043	0.040		0.038	0.038	0.039		
Methyl crotonate	0.007	0.007	0.008	0.007		0.007	0.007	0.007	0.010	0.011	0.010	0.009	0.008	0.007		0.007	0.007	0.007		
Toluene- <i>p</i> s (IS)	1.000	1.000	1.000	1.000		1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000		1.000	1.000	1.000		
Toluene	0.249	0.260	0.259	0.263		0.258	0.256	0.249	0.251	0.265	0.262	0.257	0.259	0.249		0.215	0.217	0.219		
Hexanal	0.010	0.010	0.010	0.009		0.009	0.009	0.010	0.011	0.012	0.010	0.010	0.011	0.010		0.009	0.009	0.009		
<i>n</i> -Butyl acetate	0.049	0.049	0.054	0.053		0.046	0.047	0.049	0.054	0.057	0.051	0.049	0.048	0.049		0.046	0.043	0.043		
Tetrachloroethylene	0.073	0.075	0.074	0.075		0.075	0.075	0.073	0.075	0.076	0.079	0.076	0.075	0.073		0.063	0.063	0.063		
Ethyl benzene	0.789	0.790	0.813	0.812		0.815	0.802	0.789	0.801	0.813	0.791	0.773	0.821	0.789		0.663	0.681	0.661		
<i>m,p</i> -Xylene	1.229	1.214	1.271	1.270		1.282	1.252	1.229	1.243	1.270	1.243	1.202	1.278	1.229		1.030	1.059	1.017		
Heptanal	0.048	0.041	0.048	0.050		0.039	0.043	0.048	0.051	0.054	0.044	0.042	0.046	0.048		0.033	0.040	0.036		
Styrene	0.305	0.303	0.316	0.314		0.315	0.312	0.305	0.311	0.320	0.312	0.302	0.312	0.305		0.263	0.270	0.257		
<i>o</i> -Xylene	0.667	0.665	0.683	0.666		0.686	0.674	0.667	0.676	0.684	0.667	0.650	0.679	0.667		0.566	0.575	0.557		
<i>p</i> -Bromofluorobenzene (IS)	1.000	1.000	1.000	1.000		1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000		1.000	1.000	1.000		
1-Ethyl-3-methylbenzene	0.676	0.656	0.673	0.669		0.682	0.666	0.676	0.669	0.678	0.669	0.643	0.670	0.676		0.539	0.560	0.541		
1-Ethyl-4-methylbenzene	0.654	0.642	0.644	0.640		0.651	0.628	0.654	0.641	0.649	0.640	0.605	0.646	0.654		0.504	0.540	0.522		
1,3,5-Trimethylbenzene	0.676	0.656	0.561	0.672		0.684	0.666	0.676	0.663	0.675	0.664	0.535	0.675	0.676		0.544	0.574	0.552		
1-Ethyl-2-methylbenzene	0.717	0.712	0.717	0.719		0.734	0.721	0.717	0.707	0.718	0.714	0.686	0.718	0.717		0.591	0.604	0.581		
Octanal	0.075	0.060	0.083	0.066		0.060	0.064	0.075	0.079	0.073	0.060	0.067	0.066	0.075		0.060	0.055	0.053		
Benzonitrile	0.054	0.055	0.064	0.048		0.038	0.049	0.054	0.061	0.070	0.029	0.047	0.054	0.054		0.044	0.044	0.039		
1,2,4-Trimethylbenzene	0.576	0.561	0.573	0.570		0.586	0.570	0.576	0.571	0.573	0.566	0.548	0.579	0.576		0.465	0.473	0.465		
1,2,3-Trimethylbenzene	0.574	0.558	0.574	0.571		0.578	0.579	0.574	0.566	0.578	0.574	0.550	0.569	0.574		0.468	0.492	0.466		
Nonanal	0.084	0.090	0.086	0.081		0.085	0.093	0.084	0.097	0.096	0.074	0.083	0.089	0.084		0.076	0.081	0.074		
Decanal	0.037	0.040	0.039	0.034		0.033	0.035	0.037	0.036	0.039	0.013	0.025	0.037	0.037		0.023	0.030	0.029		
Total number	6	3	17	6		7	2	1	2	20	5	1	17	9		6	20	6		

Table 2.16. Response factor of VOCs with different desorption time and the comparison of response factor between desorption time 1.5 min and 1 min and Response factor of VOCs with different dry purge conditions. *yellow highlight displays the highest RF while the beige highlight displays the highest RF comparison between 25 mL and 50 mL of dry purging.

VOCs	Desorption time (min)			Dry purge volume (mL)		
	1	1.5	RF _{1.5} /RF ₁	0	25	50
Isoprene	0.062	0.063	101%	0.064	0.064	0.055
Dichloromethane	0.251	0.256	102%	0.266	0.258	0.251
Methacrolein	0.025	0.024	94%	0.025	0.024	0.023
2-Methyl furan	0.059	0.059	100%	0.060	0.058	0.054
Trichloromethane	0.251	0.267	106%	0.286	0.273	0.251
Benzene	0.272	0.275	101%	0.277	0.272	0.258
Ethyl acrylate	0.062	0.066	106%	0.069	0.068	0.079
Dibromomethane (SS)	0.312	0.329	105%	0.333	0.328	0.320
Trichloroethylene	0.079	0.081	102%	0.078	0.079	0.076
Methyl methacrylate	0.025	0.028	112%	0.028	0.026	0.025
Methyl cyclohexane	0.079	0.100	126%	0.080	0.081	0.079
Methyl isobutyl ketone	0.042	0.043	102%	0.048	0.044	0.040
Methyl crotonate	0.009	0.008	87%	0.007	0.008	0.007
Toluene- <i>D</i> ₈ (IS)	1.000	1.000	100%	1.000	1.000	1.000
Toluene	0.257	0.259	100%	0.256	0.286	0.249
Hexanal	0.010	0.011	104%	0.017	0.011	0.010
<i>n</i> -Butyl acetate	0.049	0.048	98%	0.056	0.052	0.049
Tetrachloroethylene	0.076	0.075	100%	0.078	0.076	0.073
Ethyl benzene	0.773	0.821	106%	0.807	0.803	0.789
<i>m,p</i> -Xylene	1.202	1.278	106%	1.253	1.252	1.229
Heptanal	0.042	0.046	109%	0.052	0.048	0.048
Styrene	0.302	0.312	103%	0.313	0.314	0.305
<i>o</i> -Xylene	0.650	0.679	105%	0.671	0.664	0.667
<i>p</i> -Bromofluorobenzene (IS)	1.000	1.000	100%	1.000	1.000	1.000
1-Ethyl-3-methylbenzene	0.643	0.670	104%	0.674	0.669	0.676
1-Ethyl-4-methylbenzene	0.605	0.646	107%	0.637	0.645	0.654
1,3,5-Trimethylbenzene	0.535	0.675	126%	0.574	0.676	0.676
1-Ethyl-2-methylbenzene	0.686	0.718	105%	0.723	0.721	0.717
Octanal	0.067	0.066	98%	0.075	0.071	0.075
Benzonitrile	0.047	0.054	115%	0.061	0.053	0.054
1,2,4-Trimethylbenzene	0.548	0.579	106%	0.581	0.583	0.576
1,2,3-Trimethylbenzene	0.550	0.569	103%	0.592	0.579	0.574
Nonanal	0.083	0.089	108%	0.135	0.090	0.084
Decanal	0.025	0.037	146%	0.045	0.035	0.037
Total number	1	17		23	5 (24)	4 (8)

Almost all the VOCs displayed better response with 1.5 min of desorption in comparison to 1 min of desorption with the exception for four VOCs. The slightly longer desorption time ensures complete desorption of the VOCs from the trap to be sent into the column of the GC-MS for separation and minimize the carryover or bake-time required for the trap for the next sample analyzed.

The dry purge volume displaying the largest amount of highest response factor (yellow highlights) with 100 mL min⁻¹ flow rate was found to be at 0 mL as seen in Table 2.16. The slightly lower RF value observed in the other purge volumes could be due to the fact that the dry purge process could elute loosely bounded VOCs from the sorbent material, however, to minimize the introduction of water and to prolong the lifetime usage of the GC column, 0 mL may not be the ideal volume. Henceforth, 25 mL was chosen after a comparison between 25 mL and 50 mL of dry purge volume (beige highlights).

2.3.3.5. Method Validation

2.3.3.5.1. Precision and Accuracy of SIM mode

Precision and accuracy tests were performed as part of method validation of the optimized PAT GC-MS method in SIM mode by analyzing seven repeats of a 100 ng L⁻¹ mixture of 32 VOCs with three internal and surrogate standards at 500 ng L⁻¹. For the validation of the optimized method, the relative standard deviation (%RSD) was used to determine precision where the %RSD should be under 20% while accuracy must be within $\pm 20\%$ of the actual value determined through percentage recovery (%Recovery) calculation (Table 2.17). As all 32 VOCs tested demonstrated good precision and accuracy, all VOCs were kept in the method for further validation.

Table 2.17. Precision (%RSD) and Accuracy (%Recovery) method validation of SIM mode PAT GC-MS.

VOCs	Standard			
	Mean (ng L ⁻¹)	Deviation	%RSD	%Recovery
Isoprene	113.96	3.85	3%	114%
Dichloromethane	117.40	4.71	4%	117%
Methacrolein	111.72	5.37	5%	112%
2-Methyl furan	97.79	2.24	2%	98%
Trichloromethane	119.40	6.26	5%	119%
Benzene	95.67	2.00	2%	96%
Ethyl acrylate	102.69	5.20	5%	103%
Trichloroethylene	94.26	2.41	3%	94%
Methyl methacrylate	111.68	5.36	5%	112%
Methyl cyclohexane	97.25	1.42	1%	97%
Methyl isobutyl ketone	94.82	5.30	6%	95%
Methyl crotonate	79.89	6.77	8%	80%
Toluene	94.52	1.42	2%	95%
Hexanal	97.48	6.31	6%	97%
<i>n</i> -Butyl acetate	93.12	3.61	4%	93%
Tetrachloroethylene	91.55	2.60	3%	92%
Ethyl benzene	105.22	5.36	5%	105%
<i>m,p</i> -Xylene	95.34	3.94	4%	95%
Heptanal	108.16	8.28	8%	108%
Styrene	99.37	3.52	4%	99%
<i>o</i> -Xylene	89.01	2.85	3%	89%
1-Ethyl-3-methylbenzene	98.99	3.07	3%	99%
1-Ethyl-4-methylbenzene	89.93	2.48	3%	90%
1,3,5-Trimethylbenzene	97.52	3.11	3%	98%
1-Ethyl-2-methylbenzene	98.33	3.04	3%	98%
Octanal	95.32	8.18	9%	95%
Benzonitrile	101.31	11.23	11%	101%
1,2,4-Trimethylbenzene	85.35	1.92	2%	85%
1,2,3-Trimethylbenzene	98.78	3.31	3%	99%
Nonanal	116.14	14.72	13%	116%
Decanal	99.95	10.25	10%	100%

2.3.3.5.2. MRL and DL determination of SIM mode

The minimal reporting level (MRL) and detection limit (DL) of this method was determined and displayed in Table 2.18. Firstly, MRL was determined through the lowest concentration MRL (LCMRL) calculator developed by the EPA with the calculated input of seven replicates of four different calibration levels [28] to obtain a graphical determination of LCMRL. From the data, the intercept of the upper recovery bound (150%) at 99% prediction interval with the upper bound (150%) of the data quality objective bound, gives the LCMRL value [26, 28], an example of which is displayed in Figure 2.4.

Figure 2.4. Example of an LCMRL graph [26]

The LCMRL value can then be used as the basis of MRL calculation to determine if the Upper and Lower PIR are within $\pm 50\%$ of the actual value of seven replicate measurements of concentration at or below the MRL of individual VOCs. The mean and standard deviation (STD) calculated from the seven replicate concentrations at a different level for different VOCs were used to determine the suitability of the MRL setting as well as the determination of DL. MRL and DL values were determined for 28 VOCs as the MRL and DL of certain VOCs (octanal, nonanal, and decanal) could not be determined in SIM mode for their detection limits, and purgeability were not suitable in SIM mode of analysis. Moreover, dichloromethane was also removed from the study as the background concentration from the ultrapure water source was not low enough for monitoring in rainwater. From the MRL studies, the lowest calibration point will be set to 2.5 ng L^{-1} to account for VOCs with low MRL levels with maximum range to $50,000 \text{ ng L}^{-1}$.

Table 2.18. MRL and DL determination of SIM mode analysis method of VOCs in rainwater using PAT GC-MS based on the seven repeated measurements of concentration at or below the MRL based on the LCMRL calculated. *STD = standard deviation.

VOCs	MRL (ng L ⁻¹)	Mean (ng L ⁻¹)	STD*	HR _{PIR}	UPPER _{PIR}	LOWER _{PIR}	DL (ng L ⁻¹)
Isoprene	12	10.85	0.77	3.05	139%	78%	2.42
Methacrolein	22	19.47	2.19	8.69	141%	54%	6.89
2-Methyl furan	12	4.81	0.46	1.81	132%	60%	1.44
Trichloromethane	35	30.61	3.02	11.98	122%	53%	9.50
Benzene	5.6	5.46	0.24	0.94	128%	90%	0.75
Ethyl acrylate	22	22.26	1.68	6.64	144%	78%	5.27
Trichloroethylene	9.1	5.23	0.47	1.88	142%	67%	1.49
Methyl methacrylate	17	13.68	1.09	4.33	113%	58%	3.44
Methyl cyclohexane	34	26.55	0.70	2.76	98%	79%	2.19
Methyl isobutyl ketone	26	21.09	0.56	2.22	117%	94%	1.76
Methyl crotonate	28	24.24	1.26	5.00	146%	96%	3.96
Toluene	13	11.15	0.80	3.16	143%	80%	2.50
Hexanal	29	24.48	2.68	10.61	140%	55%	8.41
<i>n</i> -Butyl acetate	17	15.10	0.47	1.88	106%	83%	1.49
Tetrachloroethylene	8.2	8.88	0.68	2.68	145%	78%	2.13
Ethyl benzene	17	13.53	1.36	5.39	126%	54%	4.28
<i>m,p</i> -Xylene	22	20.89	1.09	4.33	126%	83%	3.44
Heptanal	35	37.13	1.81	7.18	127%	86%	5.69
Styrene	20	15.40	0.86	3.42	126%	80%	2.72
<i>o</i> -Xylene	13	7.14	0.27	1.09	82%	61%	0.86
1-Ethyl-3-methylbenzene	9.2	8.36	0.45	1.80	127%	82%	1.43
1-Ethyl-4-methylbenzene	15	14.49	0.81	3.21	118%	75%	2.55
1,3,5-Trimethylbenzene	13	12.07	0.39	1.55	136%	105%	1.23
1-Ethyl-2-methylbenzene	8.9	4.52	0.32	1.27	116%	65%	1.01
Benzonitrile	17	13.66	0.89	3.52	107%	63%	2.79
1,2,4-Trimethylbenzene	20	13.77	0.84	3.34	114%	69%	2.65
1,2,3-Trimethylbenzene	12	8.65	0.69	2.73	114%	59%	2.17

2.3.3.5.3. Method validation for Scan mode

Although a SIM mode analysis is preferred for the determination of VOCs in rainwater, the Scan mode version of the method was also validated in the same way as in the SIM mode to account for possible high concentrations determined in future samples. Precision and accuracy validation of scan mode was determined through seven replicate measurements of standards at 5 µg L⁻¹ as displayed in Table 2.19, while MRL and DL determinations are shown in Table 2.20 and 2.21. The lowest level of calibration will be kept at 0.5 µg L⁻¹ as recommended by US EPA Method 524.4 with the highest calibration point at 80 µg L⁻¹.

Table 2.19. Precision (%RSD) and Accuracy (%Recovery) method validation of Scan mode PAT GC-MS method development for determination of VOCs in rainwater.

VOCs	Mean ($\mu\text{g L}^{-1}$)	Standard Deviation	Precision	Accuracy
Isoprene	4.43	0.09	2%	89%
Dichloromethane	4.94	0.17	3%	99%
Methacrolein	4.56	0.09	2%	91%
2-Methyl furan	4.48	0.08	2%	90%
Trichloromethane	4.94	0.13	3%	99%
Benzene	4.84	0.11	2%	97%
Ethyl acrylate	4.26	0.08	2%	85%
Trichloroethylene	4.94	0.09	2%	99%
Methyl methacrylate	4.62	0.07	2%	92%
Methyl cyclohexane	4.84	0.10	2%	97%
Methyl isobutyl ketone	4.59	0.07	1%	92%
Methyl crotonate	4.56	0.11	3%	91%
Toluene	5.03	0.16	3%	101%
Hexanal	4.62	0.04	1%	92%
<i>n</i> -Butyl acetate	4.31	0.06	1%	86%
Tetrachloroethylene	5.02	0.11	2%	100%
Ethyl benzene	4.32	0.12	3%	86%
<i>m,p</i> -Xylene	4.87	0.14	3%	97%
Heptanal	4.02	0.12	3%	80%
Styrene	4.45	0.12	3%	89%
<i>o</i> -Xylene	4.86	0.16	3%	97%
1-Ethyl-3-methylbenzene	4.61	0.13	3%	92%
1-Ethyl-4-methylbenzene	4.72	0.14	3%	94%
1,3,5-Trimethylbenzene	4.55	0.13	3%	91%
1-Ethyl-2-methylbenzene	4.60	0.13	3%	92%
Octanal	4.27	0.16	4%	85%
Benzonitrile	5.04	0.07	1%	101%
1,2,4-Trimethylbenzene	4.89	0.18	4%	98%
1,2,3-Trimethylbenzene	4.47	0.12	3%	89%
Nonanal	4.37	0.23	5%	87%
Decanal	4.43	0.23	5%	89%

Table 2.20. MRL and DL determination of Scan mode analysis method of VOCs in rainwater using PAT GC-MS based on the seven repeated measurements of concentration at or below the MRL based on the LCMRL calculated (Isoprene to tetrachloroethylene). *STD = standard deviation.

VOCs	MRL ($\mu\text{g L}^{-1}$)	Mean ($\mu\text{g L}^{-1}$)	STD*	HR _{PIR}	UPPER _{PIR}	LOWER _{PIR}	DL ($\mu\text{g L}^{-1}$)
Isoprene	1.1	1.04	0.01	0.04	108%	100%	0.03
Dichloromethane	0.83	0.75	0.07	0.27	137%	64%	0.22
Methacrolein	1.8	1.50	0.04	0.16	111%	89%	0.13
2-Methyl furan	0.88	0.82	0.01	0.03	113%	105%	0.02
Trichloromethane	1.2	0.97	0.05	0.20	117%	77%	0.16
Benzene	0.77	0.81	0.02	0.07	117%	99%	0.05
Ethyl acrylate	1.2	1.07	0.07	0.29	137%	78%	0.23
Trichloroethylene	1.2	1.06	0.05	0.18	124%	88%	0.14
Methyl methacrylate	1.5	1.23	0.04	0.15	92%	72%	0.12
Methyl cyclohexane	0.99	0.73	0.01	0.05	104%	91%	0.04
Methyl isobutyl ketone	2.1	1.56	0.04	0.16	86%	70%	0.13
Methyl crotonate	1.6	1.35	0.03	0.11	97%	83%	0.08
Toluene	0.79	0.76	0.01	0.04	107%	96%	0.03
Hexanal	1.9	1.38	0.03	0.11	100%	84%	0.09
<i>n</i> -Butyl acetate	1.3	1.04	0.08	0.33	138%	71%	0.27
Tetrachloroethylene	0.91	1.00	0.02	0.07	142%	125%	0.05

Table 2.21. MRL and DL determination of Scan mode analysis method of VOCs in rainwater using PAT GC-MS based on the seven repeated measurements of concentration at or below the MRL based on the LCMRL calculated (Ethyl benzene to Decanal). *STD = standard deviation.

VOCs	MRL ($\mu\text{g L}^{-1}$)	Mean ($\mu\text{g L}^{-1}$)	STD*	HR _{PIR}	UPPER _{PIR}	LOWER _{PIR}	DL ($\mu\text{g L}^{-1}$)
Ethyl benzene	0.54	0.52	0.01	0.06	145%	116%	0.05
<i>m,p</i> -Xylene	0.95	0.75	0.01	0.03	104%	95%	0.02
Heptanal	1.2	1.17	0.04	0.15	132%	102%	0.12
Styrene	0.47	0.49	0.01	0.03	130%	115%	0.02
<i>o</i> -Xylene	0.81	0.72	0.01	0.04	101%	91%	0.03
1-Ethyl-3-methylbenzene	0.96	0.75	0.01	0.02	104%	97%	0.02
1-Ethyl-4-methylbenzene	0.68	0.39	0.01	0.05	110%	86%	0.04
1,3,5-Trimethylbenzene	0.63	0.56	0.01	0.04	150%	128%	0.03
1-Ethyl-2-methylbenzene	0.6	0.48	0.01	0.04	130%	110%	0.03
Octanal	2.1	1.87	0.07	0.27	107%	80%	0.21
Benzonitrile	2	1.64	0.11	0.43	104%	60%	0.34
1,2,4-Trimethylbenzene	0.54	0.38	0.01	0.05	107%	83%	0.04
1,2,3-Trimethylbenzene	0.66	0.45	0.01	0.04	123%	102%	0.03
Nonanal	1.3	0.90	0.05	0.18	108%	71%	0.15
Decanal	1.5	1.42	0.09	0.35	118%	71%	0.28

2.3.4. Rain Sampler

Figure 2.5. Automated rain sampler from New Star Environmental.

Figure 2.6. Setup of manual rainwater sampler.

Figure 2.5 and 2.6 displays the commercial automated and self-prepared manual rainwater sampler examined for rainwater collection. The automated rainwater water sampler (Figure 2.5) is equipped with a rain sensor that shifts the cover of the rain sampler from wet to dry during a rain event for rainwater collection in the high-density polyethylene (HDPE) container. The cover then shifts back when the rain event stops to minimize sample lost during rainwater gathering. The manual sampler (Figure 2.6) contains an aluminum funnel attached to a metal scaffolding covering two terracotta pots secured to a wire mesh grid panel. The sample collecting vial is kept under the terracotta pots for protection against strong wind and coverage against dust. It was found that although the automated sampler kept the collector clean of particulate matter, the time taken for the auto-sampler to react to rain decreased the amount of rain collected in comparison to the manual collector. Moreover, the design of the self-prepared collector provided sufficient shielding of the amber glass vials used in the collection of rain and had a faster reaction time which allowed more rain to be collected. It should also be noted that the automated rain sampler uses an HDPE container which has been shown in past studies to emit VOCs [35], hence, it would not be an ideal version of a sampler for VOC research. Therefore, the self-prepared rain sampler was used for the collections.

The self-prepared manual sampler allows a different choice of material to collect the rain which can be more versatile than the HDPE containers used in the automated rain sampler. Therefore, the materials utilized in the self-prepared sampler were examined for emission of VOCs under normal room temperature conditions and warm (heated) conditions. Ultrapure water was ran through the collector under the different conditions and collected in the amber glass vial at the end of the collector as depicted in Figure 2.6. The manual sampler was

heated up by using a heat gun for a few minutes to mimic the heating of the sun when the sampler is placed on the rooftop and when the sampler is warmed. The result from the study is displayed in Table 2.21.

It was determined that the manual sampler did not introduce additional VOCs when ultrapure water was run through the system both under normal and heated conditions. It was also noted that the VOCs found in the ultrapure water sample, trichloromethane, toluene, ethyl benzene and *m,p*-xylene had known origins. Very low (<DL) concentrations of toluene, ethyl benzene, and *m,p*-xylene originated from the plastic squeeze bottle used to store the ultrapure water used in this study while trichloromethane originated from the water used in the experiments. Henceforth, the makeshift manual sampler was concluded to be suitable to be used to collect rainwater for the long-term monitoring of VOCs present in the rainwater.

Table 2.21. VOC emission from manual sampler in comparison to ultrapure water

VOCs	Ultrapure water (ng L ⁻¹)	Manual normal (ng L ⁻¹)	Manual warm (ng L ⁻¹)
Isoprene	N.D.	N.D.	N.D.
Methacrolein	N.D.	N.D.	N.D.
2-Methyl furan	N.D.	N.D.	N.D.
Trichloromethane	88.1	48.27	38.96
Benzene	N.D.	N.D.	N.D.
Ethyl acrylate	N.D.	N.D.	N.D.
Trichloroethylene	N.D.	N.D.	N.D.
Methyl methacrylate	N.D.	N.D.	N.D.
Methyl cyclohexane	N.D.	N.D.	N.D.
Methyl isobutyl ketone	N.D.	N.D.	N.D.
Methyl crotonate	N.D.	N.D.	N.D.
Toluene	<DL	<DL	<DL
Hexanal	N.D.	N.D.	N.D.
n-Butyl acetate	N.D.	N.D.	N.D.
Tetrachloroethylene	N.D.	N.D.	N.D.
Ethyl benzene	<DL	<DL	<DL
<i>m,p</i> -Xylene	<DL	<DL	<DL
Heptanal	N.D.	N.D.	N.D.
Styrene	N.D.	N.D.	N.D.
<i>o</i> -Xylene	N.D.	N.D.	N.D.
1-Ethyl-3-methylbenzene	N.D.	N.D.	N.D.
1-Ethyl-4-methylbenzene	N.D.	N.D.	N.D.
1,3,5-Trimethylbenzene	N.D.	N.D.	N.D.
1-Ethyl-2-methylbenzene	N.D.	N.D.	N.D.
Benzonitrile	N.D.	N.D.	N.D.
1,2,4-Trimethylbenzene	N.D.	N.D.	N.D.
1,2,3-Trimethylbenzene	N.D.	N.D.	N.D.

2.4. Conclusion

Although short-term studies of VOCs in rainwater have been attempted in several other countries, the published studies on the composition of rainwater in Singapore had focused on pH, major inorganic ions, and metal concentrations. Therefore, to increase the understanding of monsoon variation experienced in Singapore on the distribution of VOCs in rainwater, a PAT GC-MS procedure based on US EPA 524.4 method developed, specific for the local environmental conditions. Probable VOC analytes for monitoring in rainwater were investigated through the analysis of six filtered rain samples collected at the sampling site (rooftop of SPMS) with PAT GC-MS in Scan mode. 55 VOCs were listed as possible VOCs for monitoring in rainwater as well as VOCs previously studied in the atmospheric air of Singapore which were also considered as rain is a known mechanism for washing out compounds from the atmosphere.

Filtration of rainwater samples is usually performed to remove particulate matter which can contaminate the PAT system. Therefore, syringe filter materials suitable for rainwater filtration were examined to avoid the possible introduction of VOC contaminants. Five different types of syringe filter material (nylon, PES, PP, SFCA and RC) were tested for probable VOC leachable contaminants by comparing filtered and unfiltered ultrapure water. PES membrane syringe filters were determined to be unsuitable for rainwater filtration as VOC contaminants were found in filtered ultrapure water, and the detection of leachable organic contaminants had been reported in the past using LC-MS analysis. Other syringe membrane materials tested were of acceptable cleanliness, and further investigation was performed by comparing PAT GC-MS analysis of filtered and unfiltered rainwater samples. It was, however, discovered that more VOC contaminants were introduced by nearly all the

syringe filter materials tested when rainwater was filtered which deviates from the study using ultrapure water. A probable explanation of the deviation observed could be linked to the pH compatibility of the tested syringe filter materials. Nonetheless, more testing, described in Chapter 4 of this thesis, was carried out to for investigation.

A list of 35 VOCs, inclusive of internal and surrogate standards (dibromomethane, toluene-*D*₈, and *p*-bromofluorobenzene), were identified as target analytes for future studies through analyte confirmation using individual diluted neat chemicals along with the compatibility study of VOCs using PAT GC-MS. As the concentration of VOCs in rainwater detected in past studies was generally low, SIM mode analysis with the MS was optimized through the identification of quantifier and qualifier ions in a SIM dynamic calibration study. Two to three mass to charge (*M/Z*) ions unique to the VOCs were selected for testing, and the finalized list of quantifier and qualifier ions in specific detection windows as well as the respective internal standard references were concluded and tabulated in Appendix A.2. Three clusters of VOCs were observed in the initial settings used in the GC separation of the mixture of 35 VOCs. Therefore, optimization of the separation of VOCs was enhanced by investigating changes in flow rate, split ratio, and oven temperature programming. The optimal balance in elution of the VOCs was achieved through a series of ramp and holding of oven temperature, the flow rate at 1.5 mL min⁻¹ and a split ratio of 1:4. However, VOCs such as *p*-xylene and *m*-xylene could not be separated with the current column installation, therefore, were not quantified as a group in future analysis.

The PAT method optimization was accomplished by studying the response factor from a range of purge volumes, flow rates, desorption times and dry purge volumes in the recommended or acceptable range stated in US EPA Method 524.4. A purge volume of 520

mL, purge flow rate of 50 mL min⁻¹, desorption time of 1.5 min, 40 °C sample temperature and dry purge volume of 25 mL were determined for use in the optimized PAT method as most of them led to the most significant number of VOCs with the highest response factors. The desorption time of 1.5 min falls within the acceptable range but not the recommended range stated in the base method, therefore, additional confirmation on the performance of 1.5 min of desorption time was required, and it was determined that 29 VOCs (excluding the two internal standards) displayed better response factors in comparison to 1 min. Furthermore, even though the dry purge volume at 25 mL was not an optimal setting for PAT GC-MS analysis, a purge volume of 0 mL led to the highest number of VOCs showing the greatest response factor, but does not allow time for the removal of water from the hydrophobic trap which may result in the introduction of water into the GC-MS system which can be undesirable. Therefore, to account for the need for water removal, the dry purge volume at 25 mL was chosen as it allowed the second highest number of VOCs showing the best response factors.

Method validation was performed through the confirmation of precision, accuracy, MRL and DL values for each VOC. All VOCs displayed good precision and accuracy with relative standard deviations below 20% and percentage recoveries within $\pm 20\%$ of the actual value. MRL and DL values were first determined through the identification of LCMRL through the LCMRL calculator developed by the EPA with seven replicate measurements of four calibration points. After which the upper and lower limit of PIR calculation of seven replicate measurements at or below the LCMRL value were determined for each VOC which were found to be greater than 50% for the lower limit and lesser than 150% for the upper limit for most VOCs. Henceforth, the LCMRL values calculated from the calculator could be used as

MRL levels for the method development. DL was then determined from the standard deviation of the seven replicates performed for the MRL confirmation experiment. It should be noted that MRL and DL of only 28 VOCs were identified for SIM mode analysis as some of the VOCs did not have detection limits low enough for analysis in the low concentration region of SIM mode. In addition to the method validation in SIM mode, Scan mode validation was also performed in similar fashion to SIM mode to account for the plausible high concentration of VOCs found in rainwater and all 32 VOCs was validated.

A comparison of rainwater samplers was performed between a commercial automated system and a self-prepared manual rain sampler, and it was determined that the automated rain sampler had a poor reaction time towards rainwater collection and the material used for the collection in the automated rainwater sampler could potentially cause VOC contamination to the samples collected. Therefore, it was determined that the manual rain sampler was preferably employed, with an additional design to minimize dust collection into the amber glass vial.

2.5. References

1. *Our Water, Our Future*, in *Public Utilities Board of Singapore*, P.U.B.o. Singapore, Editor. 2016, Public Utilities Board of Singapore: Singapore.
2. G.P. Hu, R. Balasubramanian, and C.D. Wu, *Chemical characterization of rainwater at Singapore*. *Chemosphere*, 2003. **51**: p. 747-755.
3. R. Balasubramanian, T. Victor, and R. Begum, *Impact of biomass burning on rainwater acidity and composition in Singapore*. *Journal of Geophysical Research* 1999. **104**: p. 26881-26890.

4. R. Balasubramanian, T. Victor, and N. Chun, *Chemical and statistical analysis of precipitation in Singapore*. Water, Air and Soil Pollution, 2001. **130**: p. 451-456.
5. Khezri, B., *Chemical analysis and statistical study on the composition of airborne particulate matter (PM_{2.5} and PM₁₀), aerosols (PM_{2.5}) inorganic trace gasses and precipitation in Singapore Between 2009 – 2012*. 2012.
7. Ligocki, M.P., C. Leuenberger, and J.F. Pankow, *Trace organic compounds in rain—II. Gas scavenging of neutral organic compounds*. Atmospheric Environment (1967), 1985. **19**(10): p. 1609-1617.
8. Kimitaka Kawamura and I.R. Kaplan, *Organic Compounds in the Rainwater of Los Angeles*. Environmental Science & Technology, 1983. **17**: p. 497-501.
9. Manabu Igawa, Norhide Nakada, and H. Okochi, *Determination of Volatile Organic Compounds in Rainwater and the Dominant Factors of their Concentrations*. Journal of Japan Society of Atmospheric Environment, 1998. **34**: p. 211-218.
10. Ivan P. Roman Falco and M.N. Moya, *Analysis of Volatile Organic Compounds in Water*, in *Handbook of Water Analysis*, L.M.L. Nollet, Editor. 2007, CRC Press.
11. Anastasia D. Nikolaou, S.K.G. Themistokles D. Lekkas, and M.N. Kostopoulou, *Application of different analytical methods for determination of volatile chlorination by-products in drinking water*. Talanta, 2002. **56**: p. 717-726.
12. Raimo A. Ketola, et al., *Comparison of different methods for the determination of volatile organic compounds in water samples*. Talanta, 1997. **44**: p. 373-382.
13. David J. Munch and S.C. Wendelken, *Method 524.4 Measurement of purgeable organic compounds in water by gas chromatography/mass spectrometry using nitrogen purge gas*, U.S.E.O.o. Water, Editor. 2013, U.S. EPA.

14. US EPA, *Method 5035A - Closed-system purge-and-trap and extraction for volatile organics in soil and waste samples*, C. Office of Resource, and Recovery Methods Team, Editor. 2002, United States Environmental Protection Agency (US EPA).
15. *Palmex Rain Sampler RSI*. 2015 [cited 15 December 2016]; Available from: <http://www.rainsampler.com/portfolio-page/rain-sampler-rs1/>.
16. *Wet-only Sampler*. 2016 [cited 15 December 2016]; Available from: <http://www.digitel-ag.com/de/en/products/wet-only-sampler/>.
17. *Acid Precipitation Sampler*. [cited 15 December 2016]; Available from: <http://www.newstarensvironmental.com/air-toxics/acid-precipitation-sampler.html>.
18. Mochida, M., et al., *Bimodal size distribution of C2–C4 dicarboxylic acids in the marine aerosols*. *Geophysical Research Letters*, 2003. **30**(13): p. n/a-n/a.
19. *PSI*. 2014 [cited 8 November 2016]; Available from: <http://www.haze.gov.sg/haze-updates/psi>.
20. Harris, D.C., *Quantitative Chemical Analysis (7th ed.)*. 7th edition ed. 2007, United States of America: W.H. Freeman and Company.
21. Nanna P. Brandorff, et al., *National survey on the use of chemicals in the working environment: estimated exposure events*. *Occupational and Environmental Medicine* 1995. **52**(7): p. 454-463.
22. Wong, G.K.S., S.J. Ng, and R.D. Webster, *Quantitative analysis of atmospheric volatile organic pollutants by thermal desorption gas chromatography mass spectrometry*. *Analytical Methods*, 2013. **5**(1): p. 219-230.
23. Williams, J. and R. Koppmann, *Volatile Organic Compounds in the Atmosphere: An Overview*. 2007, Blackwell Publishing.

24. Technologies, A., *Agilent Captiva Syringe Filters - Raise your sample filtration standards*. 2013, Agilent Technologies, Inc: USA.
25. Corporation, P., *Polyethersulfone membrane (Hydrophilic)*. 2012, Pall Corporation
26. Technologies, A. *Premium Syringe Filters - Chemical Compatibility Chart*. 2014 [cited 13 March 2014]; Available from: <http://www.chem.agilent.com/en-US/products-services/Columns-Sample-Preparation/Sample-Preparation/Filtration/Syringe-Filters/Pages/syringechemicalcompatibility.aspx>.
27. Urias, K.R., *Experimental Studies in Temperature Programmed Gas Chromatography*. 2002, Virginia Polytechnic Institute and State University: Blacksburg, VA.
28. Winslow, S.D., et al., *Statistical Procedures for Determination and Verification of Minimum Reporting Levels for Drinking Water Methods*. Environmental Science & Technology, 2006. **40**(1): p. 281-288.
29. David Munch and P. Branson, *Statistical Protocol for the Determination of the Single-Laboratory Lowest Concentration Minimum Reporting Level (LCMRL) and Validation of Laboratory Performance at or Below the Minimum Reporting Level (MRL)*, E.P. Agency, Editor. 2004, US EPA: United States.
30. Skjevrak, I., et al., *Volatile organic components migrating from plastic pipes (HDPE, PEX, and PVC) into drinking water*. Water Research, 2003. **37**(8): p. 1912-1920.

Analysis of Aqueous Leachable Contaminants from Syringe Filters

3.1. Introduction

Filtration is one of the many separation methods that is used to minimize errors from particulate interferences present in a sample matrix. An ideal filtration minimizes the amount of sample lost while not introducing contaminants into the filtrate. Syringe filters are commonly used in the biological and chemical fields as sample preparation steps for filtration of micro-organism, proteins, and particulates. However, some problems with extractable and leachable (E&L) artifacts found eluted from the filters have been reported in past investigations by syringe filter manufacturers and pharmaceutical researchers [1-6]. E&L compounds are undesired inorganic, and organic artifacts contributed to the filtrate from the filter device (membrane, housing or components introduced during the manufacturing or packaging process) where leachable is a subset of extractable, originating from the actual use or pharmaceutical process conditions [1, 7]. Extractable artifacts such as wetting agents (nonionic detergents), plasticizers, inorganic electrolytes and non-volatile water-soluble organic solutes have been detected in membrane filters using reverse phase high-pressure liquid chromatography (RP-HPLC), atomic absorbance spectroscopy (AAS), ultraviolet (UV) and infrared (IR) spectroscopy [3].

Extractable artifacts are unfavorable in many cases as wetting agents, plasticizers, and organic solutes can cause stability issues with protein formulations resulting from the change in surface tension of the solution [6] while the presence of metal ions may affect protein

folding [8] or catalyze unwanted side reactions. Although reports of organic extractable artifacts have mainly been on non-volatile contaminants, the analysis of volatile organic compounds (VOCs) extractable artifacts from syringe filter has been reported [6]. Extractable VOCs such as hexylene glycol (1.7 mg g^{-1}), 2-butoxyethyl acetate ($6.7 \text{ } \mu\text{g g}^{-1}$), 1-butanol ($2.13 \text{ } \mu\text{g g}^{-1}$) and several other unidentified VOCs were detected in different types of syringe filters using thermal desorption gas chromatography-mass spectrometry (TD GC-MS) [6]. The detection of VOCs in syringe filters is not unexpected as VOCs are often used as solvents in the manufacturing processes and in the starting material of polymers. Low levels of leachable VOCs artifacts may have a significant impact on the surface tension behavior, affecting proteins sensitive to interfacial stress [6]. Other than altering surface tension, leachable VOCs may also jeopardize analytical results through co-elution and extraneous peaks [1], affect solubility or cause an undesirable reaction in chemical systems. To fully understand the inorganic and organic contaminants from syringe filters and the conditions eluting them, more studies should be performed on VOCs and trace metal leachable artifacts using high sensitivity instruments so as to forecast the likely effects of the contaminants as well as to appraise the safe use of different filters.

3.2. Experimental

Advisory information on the working pH range of syringe filters are often provided by manufacturers as biological experiments are usually sensitive to fluctuations of acidity, thus buffer solutions are frequently used. To mimic experimental working conditions for the quantification and identification of leachable VOCs, buffer solutions (pH 2.71, 7.77 and 9.95), ionic mixture solutions (IMS) (Appendix B.1) and ultrapure water (UPW) were tested and compared against unfiltered solutions using purge-and-trap (PAT) GC-MS (Teledyne

Tekmar Atomx and Agilent Technologies 7890A GC, 5975C MS). This provides a better assessment on which VOCs can be leached from syringe filters under the conditions that they are generally used since previous studies performed on leaching from filters made use of organic solvents which are likely to have different leaching properties (and themselves are comprised of or contain VOCs) [1, 2]. Furthermore, filter materials such as polypropylene (PP) are recommended to be incompatible towards the use of aromatic solvents. Therefore, the filtration of a small mixture of aromatic solvents in UPW was tested on PP and nylon filters to determine the effect of PP filters on aromatic VOCs analysis. UPW filtrate of different filters was also analyzed by inductively coupled plasma–mass spectrometry (ICP–MS) (Agilent 7700 series) to widen the scope of contaminant studies for trace metal analysis.

3.3. Materials

3.3.1. Chemicals

Britton-Robinson buffer components, ionic solutions and neat VOCs for the different experiments and quantification were purchased from Acros Organics, Alfa Aesar, Fluka, Merck, Schedelco, Sigma-Aldrich, Sinopharm, TCI, and VWR. UPW from Millipore (Milli-Q Integral 5) was used for testing and dilution of test solutions (Details of chemicals used are available in Appendix A.1). Calibration solutions (internal standards and VOCs) for PAT GC-MS analysis were made from neat chemicals and diluted with Pestinorm PAT grade methanol from VWR while calibration solutions for ICP–MS were made via dilution with 5% nitric acid (JT.Baker) solutions.

3.3.2. Syringe filters and sample preparations

Preliminary screening was performed on all syringe filters (except 5PP) by collecting 40 mL of filtrates from five different types of solution [UPW, Britton-Robinson buffer solutions (pH 2.71, 7.77 and 9.95) and IMS] with no pre-filtering treatment conducted on each filter used. Syringe filters that displayed leachable VOCs contaminants were then singled out for further examination to determine the possible sources of contaminants as well as the viability of pre-treatment filtration.

Table 3.1. Syringe filters specifications and test performed on each filter. (PES – polyethersulfone, PP - polypropylene, PVDF - polyvinylidene fluoride, SFCA - surfactant free cellulose acetate, MCE - mixed cellulose acetate, MA - modified acrylic, MBS – methyl methacrylate butadiene styrene).

Syringe Filters					
Label	Brand	Membrane	Housing	Pore size	Sterile
1PES	Acrodisc	PES	MA	0.20 µm	Yes
2N	Cole-Parmer	Nylon	PP	0.20 µm	No
3N2	Cronus	Nylon	PP	0.20 µm	No
3N45	Cronus	Nylon	PP	0.45 µm	No
4N	Envexp	Nylon	PP	0.20 µm	No
5N	Titan2	Nylon	PP	0.20 µm	No
5PP	Titan2	PP	PP	0.20 µm	No
6PP	Whatman	PP	PP	0.45 µm	No
7N	Xiboshi	Nylon	PP	0.20 µm	No
8N	Millex	Nylon	PP	0.45 µm	No
8PVDF	Millex	PVDF	PP	0.45 µm	No
9N	Nalgene	Nylon	PP	0.45 µm	Yes
9PES	Nalgene	PES	PP	0.45 µm	Yes
9MCE	Nalgene	MCE	PP	0.45 µm	Yes
9PVDF	Nalgene	PVDF	PP	0.45 µm	Yes
10SFCA	Sartorius	SFCA	MBS	0.20 µm	Yes
10PESS	Sartorius	PES	MBS	0.20 µm	Yes
10PES	Sartorius	PES	MBS	0.20 µm	No
10N	Sartorius	Nylon	PP	0.20 µm	Yes

The first further investigation was conducted on three nylon filters (4N, 5N & 7N) where 2 × 40 mL bottles of Britton-Robinson buffer (pH 2.71) filtrate were collected. Five filters (1PES, 9PES, 10SFCA, 10PESS & 10PES) were selected for the second round of further investigation where 160 mL worth of solutions was filtered through each filter. 2 × 40 mL

amber glass vials of UPW filtrate were collected, followed by 2×40 mL of Britton-Robinson buffer (pH 2.71). A compatibility investigation was conducted on two syringe filters (6PP & 8N) by filtering a mixture of diluted aromatic compounds. All leachable VOC contaminant solutions collected were stored in 40 mL amber glass vials sealed with septums and comparisons were performed between filtered and unfiltered solutions using PAT GC-MS. 4 mL of UPW was filtered through all syringe filters for analyses using ICP-MS and details of syringe filters utilized in the investigations are displayed in Table 3.1.

3.4. Results and Discussion

3.4.1. Preliminary screening

Leachable VOC contaminants in 40 mL of five filtrates [UPW, Britton-Robinson buffer solutions (pH 2.71, 7.77 and 9.95) and IMS] from different syringe filters were tested and evaluated against unfiltered solutions using PAT GC-MS. Most of the syringe filters examined were demonstrated to be considerably free from leachable VOC contaminants as similar contents, or very low levels of contaminants were found in filtered solutions in comparison to unfiltered standard solutions. An evaluation between UPW filtrates of different syringe filters showed relative standard deviations (Appendix B.2) of VOC concentrations above minimal reporting level (Appendix A.2) to be within 20%, and eight VOCs (methyl methacrylate, methyl isobutyl ketone, hexanal, heptanal, octanal, nonanal, 1,2,3-trimethylbenzene, and styrene) that were not found in the blank filtrates were detected and identified in some of the five types of filtrates tested. Table 3.2 highlights certain selected syringe filters displayed as a representation of groups of syringe filters with similar leachable contents and several of the detected VOCs.

Syringe filter 9N illustrates the general syringe filters noticeably free from VOCs leachable with aqueous based filtrates. Most syringe filters produced clean filtrates using UPW but leached a small amount of hexanal (usually below the detection limit of the instrument) when buffer solutions were used. However, some nylon filters were found to introduce an unusual amount of nonanal (1.74-4.60 $\mu\text{g L}^{-1}$) into filtrate samples as in the example of 4N in the preliminary screening (Table 3.2). Nonanal and other aldehydes like hexanal are conventional thermal oxidation degradation products from manufacturing processes of polymers such as polypropylene containing unsaturated additives [9-11].

Table 3.2. Preliminary screening of VOCs leachable contaminants in different filtrates * Indicates concentration below detection limit while ^ indicates concentration below minimal reporting level. A space indicates no compound was detected.

Syringe filter	Filtrate	VOCs leachable contaminants ($\mu\text{g L}^{-1}$)								
		Methyl methacrylate	Methyl isobutyl ketone	Hexanal	Heptanal	Octanal	Nonanal	1,2,3-Trimethyl benzene	Styrene	Total VOCs
9N	UPW IMS pH2.71 pH7.77 pH9.95									
4N	UPW IMS pH2.71 pH7.77 pH9.95			0.44*			2.28 4.60 3.78 3.47		0.32^	2.28 5.36 3.78 3.47
10SFCA	UPW IMS pH2.71 pH7.77 pH9.95	0.66* 1.07^ 1.01^ 0.95^ 0.62*		0.75* 1.11^ 1.14^ 1.15^ 0.97^	0.80* 1.17^ 1.06^ 1.23 1.05^	1.08* 2.43 1.80^ 2.05^ 1.64^	9.75 22.26 18.64 21.16 16.99	0.38^ 0.36^ 0.38^ 0.37^ 0.37^	0.72 0.58 0.57 0.53 0.47	14.14 28.98 24.60 27.71 22.38
9PES	UPW IMS pH2.71 pH7.77 pH9.95		0.26* 0.24*							0.26 0.24

It was perceived that nonanal was only detected in filtrates other than UPW of 4N, 5N and 7N nylon syringe filters as the acidic/basic conditions of the buffer solutions could have catalyzed the formation of geminal diols which would increase the solubility of nonanal in the filtrate samples thus causing nonanal to be observed [12].

Syringe filters introducing more VOCs such as 1PES, 10SFCA, 10PES, and 10PESS were also singled out as leachable VOC contaminants were detected even in the UPW filtrate, with 10SFCA containing the highest concentrations ($14.14\text{--}28.98\ \mu\text{g L}^{-1}$) of total leached VOCs of the five types of filtrate tested. There were no apparent trends between leachable VOCs and the various filtrates used except a smaller concentration of VOCs in the UPW filtrate. For the nylon filters, nonanal was also detected at substantial levels with a lower concentration of methyl methacrylate, methyl isobutyl ketone, hexanal, heptanal, octanal, 1,2,3-trimethylbenzene and styrene (Appendix B.3). PES is one of the conventional membrane materials in syringe filters that was found to elute leachable VOC contaminants. However, syringe filters with a PES membrane can also be relatively free from leachable VOC contaminants as shown in the case of 9PES (Table 3.2). Therefore, the exact manufacturing process of the syringe filter is also likely to be important in determining which VOCs are present in the filtrate.

A characteristic feature of 1PES, 10SFCA, 10PES and 10PESS filters that were found to leach VOCs, lied in the housing material being a mixture of polymers other than PP. A closer analysis of the types of VOCs evolved suggested that building blocks or degradation products of the polymers such as methyl methacrylate, styrene, and nonanal were quantified in the various filtrates which may imply incomplete polymerization or breakdown of the housing materials. In several filtrate samples, unidentified VOCs were also detected, but the

concentrations of such VOCs were too low hence poor probability matches to the NIST (National Institute of Standards and Technology) library were given by the data analysis program. The unknown peaks were not further studied by extracting VOCs contaminants from the syringe filter as the primary focus of this study was on leachable contaminants.

Although the quantitated amount of leached VOCs detected for some syringe filters are high and could cause interference problems with some chemical or biological systems, the act of pre-filtration can potentially remove the leachable contaminants thus ensuring that syringe filters are in a clean state before the main filtration process. Pre-filtration treatment or the abandonment of the first few milliliter of filtrates of syringe filters are often advised by syringe filter manufacturers to remove probable leachable contaminants [1, 2]. Henceforth, the viability of pre-filtration of nylon filters to remove nonanal contaminants and the feasibility of pre-filtration treatment on syringe filters of housing other than PP were carried out to gain a better understanding of the conditions for eluting and removing of such leachable VOC contaminants.

3.4.2. Further investigation of nylon filters

Figure 3.1. Leachable nonanal concentration in successive vials of pH 2.71 buffer solutions.

The pH 2.71 buffer solution was chosen for the pre-filtration treatment of 4N, 5N and 7N nylon filters where nonanal had been detected in the initial experiments shown in Table 3.2

indicated that it leached the highest amounts of VOCs for nylon membrane syringe filters. Multiples of 40 mL solutions were collected to minimize VOCs lost through the presence of headspace in the amber glass vial used for the viability study. Marginal differences between the nonanal concentration in preliminary screening and the 1st 40 mL vial were observed with relative standard deviations remaining within 20% for concentrations detected above the minimal reporting level. It was established that nonanal is removable within the first vial of a buffer solution with 4N ($3.61 \mu\text{g L}^{-1}$) eluting the highest amount of nonanal and 7N ($1.20 \mu\text{g L}^{-1}$) eluting the least as shown in Figure 3.1. Nonanal was not detected in any of the second 40 mL aliquots of pH 2.71 buffer solutions passed through each filter. Although the concentrations of nonanal detected from the syringe filters were less than what had been proposed in past studies to cause major effects, such as increases in the number of apoptotic cells, affecting tubulin polymerization and impairing binding activity [13, 14], minor disturbances to such systems can occur and affect quantitative experimental results. The presence of nonanal in some syringe filters but not others could have been due to the different source of raw material (PP) used in the production or a difference in the production methods used to make the filters which may lead to thermal oxidation degradation of the polymer. Therefore, discarding the first few milliliters of filtrate before using nylon syringe filters can aid in the removal of nonanal in experiments which may contain reactants/substrates that are sensitive to aldehyde compounds when acidic/basic conditions are used.

3.4.3. Further investigation of syringe filters having housing materials other than PP

Leachable VOCs were found in different types of filtrates from syringe filters with housing materials other than PP without distinct relations between the types of filtrate used and the

concentration of leached VOCs. An investigation was performed on 10PES, 10SFCA, 10PESS, and 10PES by flushing with 2×40 mL UPW followed by flushing with 2×40 mL pH 2.71 buffer solutions. Three VOC contaminants that were substantially leached (hexanal, methyl methacrylate, and styrene) from the four selected syringe filters are displayed in Figure 3.2 to 3.4. The greatest concentration of leachable VOC contaminants over four successive vials of the filtrate was detected in 10PESS while the least leachable VOC contaminants were detected in 1PES.

Figure 3.2-4. Leachable VOCs concentration in successive vials of 2×40 mL of ultrapure water followed by 2×40 mL of pH 2.71 buffer solution in scan mode PAT GC-MS analysis.

10PES and 10PESS were constructed by the same manufacturer with similar material and processes with the exception of sterilization. 10PESS was subjected to ethylene oxide (EtO) sterilization, however, despite the sterilization process, more leachable VOCs were detected in 10PESS in comparison to 10PES. EtO sterilization makes use of ethylene oxide gas to infuse pores of the syringe filter which could have caused the breakdown of the polymer housing or purging of the starting material more deeply embedded in the housing, assuming a similar amount of incomplete polymerization for both 10PES and 10PESS. The concentration of leachable VOCs appears to decrease in the 2nd flushing for both UPW and pH 2.71 buffer filtrates for both 10PESS and 10PES. Nonetheless, only hexanal was removed after the 1st 40 mL flushing of UPW for 10PES while all three substantial leachable VOC contaminants were

still detected in the 4th flushing (160 mL total) which exceeds the maximum recommended volume of filtrate for syringe filters of 28 mm size. Therefore, a pre-filtration treatment is not entirely successful for 10PESS and 10PES.

The pre-filtration treatment was useful in removing leachable VOCs from 10SFCA as the subsequent filtrate vials after the 1st 40 mL flushing did not contain VOCs. The housing material of 10SFCA is identical to that of 10PESS and 10PES, and interestingly EtO sterilization was also applied to 10SFCA (similar to 10PESS). However, the leachable VOCs detected in each syringe filter filtrate were vastly different. The cellulose acetate membrane in 10SFCA could have a lesser affinity for VOCs which would allow the VOCs to be more easily removed with filtrates in comparison to PES. Also, the surfactant-free treatment might have removed some incomplete polymerization starting materials, or the treatment might have decreased the likelihood of leachable VOCs adsorbing onto the filter membrane thus allowing the leachable VOCs to be flushed out in the 1st vial of filtration.

1PES only appeared to contain leachable VOCs when using the pH 2.71 buffer solution that was readily removed within the first 40 mL of buffer solution flushing. The presence of methyl methacrylate and styrene suggests that the acrylic polymer used for the housing material was modified with these VOCs to achieved better properties. The concentrations of leachable VOCs detected, in general, was low, with some below the detection limits or minimal reporting levels for PAT GC-MS analysis, therefore, to get a better understanding of pre-filtration treatment on the selected filters, selective ion monitoring (SIM) mode on PAT GC-MS was used.

9PES is an example of a relatively clean PES syringe filter which was also tested for comparison to determine if the PES membrane might have contributed to the leachable VOCs

found in 10PES and 10PESS. 9PES displayed minimal to no detectable leachable VOCs in the filtrate solutions tested except for a small amount of hexanal detected in the pH 2.71 filtrate (4th vial) which had exceeded the recommended volume of filtration (Figure 3.5 to 3.7). Therefore, it can be concluded that the PES membrane does not contribute leachable VOC contaminants under the test conditions, while the leachable VOCs detected in 10PESS and 10PES filtrates likely originate from the housing material. Similar to the results in scan mode analysis, 10PESS was found to elute more leachable VOCs than 10PES except for methyl methacrylate in the 4th vial of 40 mL pH 2.71 buffer filtrate (Figure 3.5 to 3.7).

Figure 3.5-7. Leachable VOCs concentration in successive vials of 2 × 40 mL of ultrapure water followed by 2 × 40 mL of pH 2.71 buffer solution in selective ion monitoring (SIM) mode PAT GC-MS analysis.

The pre-filtration treatment was found to be useful for 10SFCA as leachable VOCs were not sensed in the 2nd 40 mL vial of the UPW filtrate. However, a small amount of hexanal was still detected in pH 2.71 buffer filtrates after the 3rd, and 4th 40 mL aliquots had been passed through the filters and when the recommended volume of filtrate was exceeded. The buffer solution could have increased the solubility of hexanal in water as in the case of nonanal in nylon filters, thus, the detection in the 3rd and 4th filtrate. 1PES which were previously assumed only to leach VOC contaminants under acidic conditions eluted leachable VOCs in UPW as well, but the leachable VOCs concentration was much lower when compared with

10SFCA, 10PES, and 10PESS with no trends observed between the filtrates and leachable VOCs.

It can be generalized that the MBS and MA housing material used in 1PES, 10SFCA, 10PES, and 10PESS may not be ideal for preparing samples sensitive to VOC contamination. Additional studies on the optimal polymerization conditions should be conducted to reduce the amount of residual building block VOCs and the removal of such residues. Sterilization with EtO can cause dislodging or breakdown of the polymer into their building blocks hence eluting as contaminants, and surfactant-free treatment can be helpful in reducing the retention of leachable VOCs in the syringe filters.

3.4.4. Compatibility investigation (CI) of PP filter membrane and water containing aromatic compounds

Other than a working pH range of different syringe filter materials, compatibility issues of chemicals with syringe filter materials are also raised by manufacturers. PP, a lightweight polyolefin, is often used to manufacture syringes, syringe filters (housing and membrane filter) with relatively high chemical resistance but has been reported to be incompatible with aromatic solvents. Therefore, filtering aromatic based solvents through such syringe filters is not recommended; however, the behavior of small amounts of aromatic compounds in other solvents compatible with PP is uncertain. To investigate this behavior, a mixture of VOCs ($40 \mu\text{g L}^{-1}$) in UPW were filtered through 6PP as a representative PP type of filter membrane and 8N for a comparison with a filter membrane with no reported compatibility issues with aromatic compounds (Appendix B.4).

A decrease by an average of 45% and 24% with reference to the unfiltered aromatic containing solution were observed in the filtrate when filtered through 6PP and 8N,

respectively (Figure 3.8). The reduction in aromatic VOCs was more significant in the PP filtrates than the nylon filtrates. The reduction observed in the nylon filtrates (even though nylon membrane filters are supposedly compatible with aromatic VOCs) was most probably due to the contact with PP (used as the housing material) along with the turbulence caused by the filtration process which encourages the escape of VOCs from the filtrate. The reduction was not as significant for VOCs such as benzene and benzonitrile which are better retained in UPW because of their higher miscibility with water. Filtering aqueous solutions containing aromatic VOCs with PP membrane filters or PP housing material can cause false negative analysis through the loss of aromatic VOCs from the weak chemical resistance of PP to aromatic compounds. This may be one of the reasons for the development of other housing materials for desirable properties that PP may lack.

Figure 3.8. Percentage decrease in aromatic compounds concentration in filtered water in comparison to blank

3.4.5. ICP-MS

Syringe filtration of samples used for inorganic analysis is also routinely performed for instruments such as AAS and ICP, where samples are transferred through tubes that are susceptible to clogging with particulate matter. A previous study had concluded that calcium salts are a common inorganic contaminant in filters [3]. However, other trace metals can also

be important if they can be leach into the solutions and affect chemical reactions or protein conformations. Therefore, 4 mL of UPW filtrates were collected and analyzed using ICP-MS for the trace metal composition. 57 elements were tested for (Appendix B.5), but only a few of these were detected. Low concentrations of inorganic leachable contaminants were detected in most syringe filters tested except 5N where a high amount of sodium was also found along with other metal contaminants. The lack of secondary packaging might have led to the inorganic contamination experienced by 5N through storage, and the manufacturing process of 5N could have left the filter contaminated with leachable inorganic contaminants.

Table 3.3. Concentration of metals in filtrates in ultrapure water (* indicates concentration below detection limit)

Syringe Filter	Inorganic leachable contaminants (ppb)								
	Cobalt (Co)	Potassium (K)	Magnesium (Mg)	Manganese (Mn)	Sodium (Na)	Antimony (Sb)	Tin (Sn)	Strontium (Sr)	Tungsten (W)
UPW									
1PES	0.006								2.470
2N	0.002*								
3N2	0.003				0.753				
3N45	0.005								
4N	0.005								
5N	0.020	51.787	16.500	0.125	4608			0.762	
5PP									
6PP									
7N	0.003*					0.950			
8N	1.066						0.544		
8PVDF					141				
9N									
9PES									6.360
9MCE		7.007							
9PVDF					27.9				
10SFCA	0.003		0.462		8.35			1.072	
10PESS	0.007								
10PES	0.005								0.311
10N	0.005								

Cobalt was detected in 63% of syringe filter samples at very low concentrations (ppt) which likely comes from the manufacturing process of the polymer or membrane used in the

syringe filter because cobalt is used as a catalyst for the polymerization of polymers like nylon [15]. It was, however, noted that cobalt was absent in PP filters (PP housing and membrane) as well as filters manufactured by certain companies which may have used catalysts other than cobalt. The types of catalyst leached from syringe filters (polymer) of different manufacturers can differ substantially depending on the suppliers for such materials. Other than cobalt, transition metals including manganese and tungsten were also detected as contaminants. Tungsten was detected in the PES filters except for 10PESS. PES filters are known to have low protein binding and excellent flow rate due to their hydrophilic properties. Such properties are achieved by a membrane oxidation process, catalyzed by metals like zinc and iron [16]. Thus, tungsten could have been used as the catalyst or present as a contaminant in the metal catalysts used for this process.

Inorganic metal contamination from the main group elements tended to be higher than the transition metals detected. Sodium was present in a relatively large concentration in selected filters, and since they are found in many compounds in nature, contamination can be hard to avoid. In short, metals are mostly present in a trace amount, and they may have possibly originated from manufacturing processes as catalysts or contaminants in metal compounds used. False positive results may be observed if samples for elemental analysis are subjected to filtration. It is advisable to have reference samples subjected to the same sample preparation to account for metals that may be present in the filters. Also, specific metal ions such as copper are cofactors, which are essential for the biological activity of proteins. Besides, the folding and unfolding processes of proteins can be greatly affected by interactions between proteins and cofactors [8]. This makes the absence metal contaminants crucial to biology studies to attain accurate results.

3.5. Conclusion

E&L contaminants are often present in syringe filters used in biological and chemical sample preparations, and the presence of such contaminants may play a significant role in the stability of proteins, the possibility of side reactions and the probability of false negative/positive results in analytical analysis. The focus of E&L analysis in past research has been on non-volatile organic compounds and main group inorganic contaminants, while this study has focused on leachable VOCs and trace metal contaminants to obtain a better understanding on the contaminants eluted under normal use (leachable contaminants). PAT GC-MS was employed to identify and quantify the leachable VOC contaminants in five different filtrate solutions in the preliminary study. Most of the syringe filters tested were determined to be relatively free from contaminants with low concentrations of hexanal (probable origin from thermal oxidation process of polymer) found in 78% of syringe filters tested with buffer solution filtrates.

Deviation from the general leachable VOC contaminant free syringe filters was found in syringe filters with housing material other than PP and in certain nylon syringe filters. Nonanal, a thermal oxidation degradation product of polymers, was detected in 4N, 5N, and 7N nylon syringe filters from different manufacturers when filtrates other than UPW was used. The presence of H^+ and OH^- can possibly catalyze the formation of geminal diols thus increasing the solubility of nonanal, hence the observed concentration in such filtrates. Nonanal, however, was readily removed with pre-filtration treatment with pH 2.71 filtrate solutions. Therefore, if leachable nonanal is a concern to experiments conducted with filtrates other than UPW, pre-filtering with an acidic/basic solution is highly recommended to remove leachable nonanal contaminant.

Other than thermal oxidation degradation aldehyde products, building blocks (methyl methacrylate and styrene) of the polymer (MBS) were also detected indicating incomplete polymerization or the breakdown of the polymer casing. No apparent trends were observed between the different filtrates used, but lower concentrations of leachable VOCs were found in UPW. To further investigate the leachable VOCs originating from such syringe filters, the possibility of pre-filtration treatment was also tested with UPW followed by pH 2.71 filtrate solutions. 10PESS eluted the highest concentration of leachable VOCs consistently over 160 mL of filtrate solution. Being sterile and packaged in secondary packaging, 10PESS was expected to elute lower leachable VOCs in comparison to its unsterile counterpart, 10PES, with no secondary packaging. However, the higher leachable content detected in 10PESS was most likely due to the EtO sterilization treatment where the gas infuses the pores. By doing so, the level of leachable VOCs can increase by loosening the attachment of the building blocks in the polymer thus eluting more VOCs than their non-sterile counterparts. Therefore, EtO might not be the best sterilization method for VOC-sensitive experimental conditions.

10SFCA was demonstrated to contain leachable VOCs that were removable with pre-filtration (flushing) treatment. The surfactant-free treatment of the filter membranes could have aided in the removal of leachable VOCs in the pre-treatment filtration. In conclusion, housing building block elution can be affected by the sterilization method used as well as the treatments given to the membrane material and the type of filtrate used. Hence, it is of great importance to ensure that the leachable VOCs detected do not affect the purpose/experiment in which the filter is employed. Although syringe filters with PP housing tend to be free from leachable VOC contaminants, PP is susceptible to absorption or retention of aromatic VOCs

which in turn affects its performance with such solutions. Nylon filters with PP housing also reduced aromatic VOCs present in water although to a lesser extent than PP filters. This decrement can possibly lead to a false negative for analysis of aromatic compounds in water when PP is used as the filter or housing material.

To increase the understanding of leachable elemental inorganic contaminants, ICP-MS was employed to investigate UPW filtrates from different syringe filters. Cobalt, a catalysis used for polymerization was found in low concentration in some of the syringe filters analyzed, although it was absent from certain brands of syringe filter as well as syringe filters made of PP membranes and housing. Other transition metals such as manganese and tungsten were also detected with probable origin from the manufacturing process of the polymer used. Main group elements were also identified with unknown origins, however, sodium is ubiquitous in the general environment, therefore, contamination from storage could take place. It is important to understand what types of inorganic leachable contaminants are present in syringe filters used as they can act as co-factors in protein and catalysis for many organic reactions.

3.6. References

1. Pall *Use of Acrodis Syringe Filters for Analytical Sample Preparation; Including HPLC and Dissolution Testing*. Technical Guide, 2006.
2. Technologies, A., *Agilent Captiva Syringe Filters - Raise your sample filtration standards*. 2013, Agilent Technologies, Inc: USA.
3. Olson, W.P., et al., *Aqueous Filter Extractables: Detection and Elution from Process Filters*. PDA Journal of Pharmaceutical Science and Technology, 1980. **34**(4): p. 254-267.
4. Kao, Y.H., et al., *Characterization of filter extractables by proton NMR spectroscopy: studies on intact filters with process buffers*. PDA J Pharm Sci Technol, 2001. **55**(5): p. 268-77.

5. Jiang, T. and M. Phelan, *Extractables from filter components in model solvent streams for pharmaceutical filtration processes*. PDA J Pharm Sci Technol, 2003. **57**(4): p. 287-99.
6. Huang, M., et al., *Impact of extractables/leachables from filters on stability of protein formulations*. Journal of Pharmaceutical Sciences, 2011. **100**(11): p. 4617-4630.
7. Moffatt, F. *Extractables and leachables in pharma*. Whitepaper, 2011.
8. Wittung-Stafshede, P., *Role of Cofactors in Protein folding*. Accounts of Chemical Research, 2002. **35**(4): p. 201-208.
9. Frostling, H., et al., *Analytical, occupational and toxicologic aspects of the degradation products of polypropylene plastics*. Scand J Work Environ Health, 1984. **10**(3): p. 163-9.
10. Skjevrak, I., et al., *Volatile organic components migrating from plastic pipes (HDPE, PEX and PVC) into drinking water*. Water Research, 2003. **37**(8): p. 1912-1920.
11. Rule, M., et al., *Method to decrease aldehyde content in polyolefin products*. 2003, Google Patents.
12. John McMurry, *Organic Chemistry*. 6 ed. 2004, Singapore: Brooks/Cole - Thomson Learning.
13. Miglietta, A., et al., *Effects of some aldehydes on brain microtubular protein*. Chemico-Biological Interactions, 1991. **78**(2): p. 183-191.
14. Choi, H.-S., M.-K. Song, and J.-C. Ryu, *Integrated analysis of microRNA and mRNA expression profiles highlights alterations in modulation of the apoptosis-related pathway under nonanal exposure*. Molecular & Cellular Toxicology, 2013. **9**(4): p. 351-364.
15. Coffey, G.P., R.L. Cepulis, and B.S. Curatolo, *Preparation of nylon polyamide with cobalt salt*. 1984, Google Patents.
16. Mezhirova, M., E.B. Yeh, and R. Sale, *Hydrophilic polyethersulfone membrane and method for preparing same*. 2009, Google Patents.

Analysis of Volatile Organic Compounds (VOCs) in Rain Water of Western Singapore – Trends, Correlations, and Source Apportionment studies

4.1. Introduction

The release of atmospheric pollutants not only plays a negative impact on human health but also on the environment as the increase in contamination of water bodies are often observed through natural fall outs of pollutants with rainfall [1-3]. The presence of VOCs in rainwater has been reported in many studies in the USA as part of the general identification of organic compounds [4, 5], along with the determination of scavenging ratios of aromatic and halogenated VOCs [6]. In addition, carbonyl VOCs were also found in rainwater samples at low concentrations ranging from ng L^{-1} to $\mu\text{g L}^{-1}$ [5]. The concentration of 14 individual VOCs in rainwater was measured in Japan using purge-and-trap gas chromatography-mass spectrometry (PAT GC-MS) with selective ion monitoring (SIM) mode analysis for increased sensitivity [7]. It was determined through the study that the impact of VOCs pollution from rain to surface water can be noteworthy.

Although the concentrations of VOCs were mostly low in rainwater, VOCs can still pose as health hazards considering that the impact of long-term exposures to VOCs at low concentration have yet to be fully understood. The influence is not only limited to drinking VOCs laden water but also from the exposure to evaporated VOCs [8-10] which can increase their potency via contact through skin absorption [11]. However, since the initial studies conducted on VOCs dissolved in rainwater, later attention has shifted to the measurements of

dissolved organic carbons (DOCs). Rainfall is one of the most efficient removal mechanism for DOCs [12], and measurements of DOCs in rainwater can be used for the partial evaluation of carbon flux out of the troposphere, which is a critical component for anthropogenic induced global warming estimates [13]. Countries such as China [14], New Zealand [15] and South Korea [16] have persevered in the study of rainwater quality with an emphasis on carbon level measurements.

Anthropogenic activities such as the burning of fossil fuels and coals have been recognized to be the primary contributing source of DOCs from both locally and/or transboundary transported origins in China and South Korea [14, 16]. Likewise, regions that practice sugar cane burning before harvest, for the reduction of the amount of manual work, such as Ribeirão Preto and Araraquara in Brazil demonstrated a 144% and 62% corresponding increase in the DOCs levels in rainwater collected during sugar cane burning [17]. Henceforth, it could be established that the DOCs levels in wet precipitate were dependent on anthropogenic emissions from both local and surrounding countries. VOCs, being a subset of DOCs, are usually not measured in DOCs studies due to the requirement of a different set of sample preparation procedure [17]. Therefore, the direct measurement of solely VOCs in rainwater is essential to account for the missing data.

The study of volatile organic carbon does not explicitly identify individual compounds but instead studies volatile compounds as a group, and the quantification of volatile organic carbons is determined through the subtraction of non-purgeable DOC (NPDOC), and inorganic carbon (IC) from the total carbon (TC) concentration measured [18]. The investigation performed in Wilmington (USA) on volatile organic carbon in rainwater found one out of six rain events with detectable levels of volatile organic carbons. The rain event

with detectable volatile organic carbon resulted from an air mass back trajectory from Midwestern USA that produced and used ethanol while the other five rain events had air mass from the ocean (absent from production and usage of ethanol) [18]. Also, a rainwater study in Brazil demonstrated that volatile organic carbons were detected in 69% of rain events with volatile organic carbons making up to 8 - 56% of the DOCs sensed with the production and usage of ethanol (biofuel) and the burning of sugar cane fields as probable sources of volatile organic carbon [19]. These studies demonstrate the importance of the specific study of volatile organic carbons in rainwater as the influence on DOCs measurement can be significant and like DOCs, the volatile organic carbons levels were affected by both types of emission sources (biomass/fuel burning) and transboundary air mass transfer.

With the reliance on rainwater as one of the sources of water supply [20], the study of VOC concentrations of rainwater in Singapore is very much valid as Singapore is affected by atmospheric pollutants from the industries. Moreover, periodic haze from its neighboring countries through the slash and burn agriculture practice (biomass burning) which had been known to increase the amount of volatile organic carbon [17, 19] and VOCs [21] could affect the amount of VOCs quantitated in rain as well. While all piped water in Singapore undergoes a centralized treatment process so that it is safe to drink, some rainwater is consumed directly, such as for certain religious practices. Previous research conducted on rainwater in Singapore focused mainly on the ionic concentration, metal content as well as the acidity; nonetheless, the seasonal variation remains poorly understood [22-24]. Other than inorganic analytes, detailed studies were performed on semi-VOCs (SVOCs) in atmospheric air and rainwater in Singapore. The study indicated a positive correlation of

most SVOCs in ambient air with ambient temperature, and negative correlations to wind speed and relative humidity with emission sources both locally and transboundary [25]. Therefore, the climate (monsoon seasons and meteorological conditions) along with anthropogenic sources of emission both locally and cross-border could significantly affect the VOCs detected in the rainfall of Singapore.

4.1.1. Climate of Singapore and haze

4.1.1.1. Climate of Singapore

The geographical location of Singapore produces a uniform climate (uniform temperature, high humidity, and high rainfall) ideal for rainwater collection. Although there are no distinct seasons, Singapore experiences two main monsoon periods where northeast monsoon (NEM) occurs between December to March while southwest monsoon (SWM) takes place between June to September each year [26].

Figure 4.3. Example of back trajectory of air mass in Singapore during different monsoon period: (a) SWM, (b)NEM, (c)Inter-monsoon (pre-NEM), (d) Inter-monsoon (pre-SWM) [25].

Figure 4.3 displays a back trajectory of the air mass in Singapore during different monsoon periods in a yearlong study of SVOCs in Singapore modeled using HYSPLIT modeling using

meteorological data from National Centers for Environmental Prediction (NCEP) Global Data Assimilation System. The backward air trajectories were generated at eight starting times for every 3 h during each sampling event for 96 h back in time with 500 m above ground level. A more uniformed back trajectory air mass pattern was observed during the monsoon seasons while the inter-monsoon period saw back trajectory with different origins. This is a common example of air mass transport experienced annually in Singapore, henceforth, the discussion on source apportionment and suggestion of likely sources of emission during the monsoon periods are examined using wind directions while more information and confirmations are required during the inter-monsoon period.

4.1.1.2. Haze

Figure 4.4 & 4.5. Graphic images from the sampling site during non-haze (PSI: 50-100) with moderate air quality (left) and haze (right) period with hazardous air quality (PSI: 341).

Slash and burn, or biomass burning are illegal practices performed in Indonesia as a farming method for clearing land. The emission from such burning is not localized as the monsoon wind (south/south-western) during the land clearing season transports the dense smoke from the biomass burning region towards other countries including the Philippines, Malaysia as well as Singapore. Figure 4.4 and 4.5 displays the difference in visibility caused by the haze from the burning of biomass in Indonesia during September and October 2015. Many efforts

have been poured in by the Indonesian government as well as neighboring countries to limit the burning. However, peat fires are persistent and difficult to put out due to their invisibility, and it was further worsened by the natural climate phenomenon, El Niño, in 2015 which increases dryness that led to the importunate forest fire [27].

The rainfall during September and October 2015 was low enough for fires to spread underground into drained, degraded peat swamps where they burned longer with two major burning regions located in Sumatra and Kalimantan of Indonesia [28]. Swamp forests are common in Indonesia which accumulates peat from the waterlogged dead vegetation. Peat stores an enormous amount of carbon; therefore, the burning of the peat releases massive amounts of carbon products into the atmosphere [29, 30]. These proceeding series of events led to the highest pollution record in Singapore where PM_{2.5} readings read 471 µg m⁻³ [31] and PSI levels in Kalimantan went over 2000 (PSI over 350 is considered hazardous) [32]. Sampling of ambient air in the affected region during previous haze events displayed significant increments in benzene, toluene, ethyl benzene and xylenes (BTEX) and other VOCs [21, 29, 30, 33]. Henceforth, knowing that rainfall is an effective method for removing VOCs from the atmosphere, the evaluation of VOCs in rainwater during the haze event is performed separately in the yearlong trend analysis and correlation calculations.

4.1.2. Objective

The aim of this study is to understand the variation of VOCs content in rainwater throughout the year with the changing monsoon season and likely local and transboundary sources of emission of VOCs. With an understanding of the VOCs content in rainwater as well as the sources of emission, the consequences of drinking from rainwater can then be postulated. 28 VOCs were selected for this study to enable an in-depth investigation of the sources of

individual VOCs through positive matrix factorization (PMF) calculations and correlation studies. The selection process for these 28 VOCs was discussed in Chapter 2 of this thesis while the sampling site chosen for this study is located in the western region of Singapore which would represent a semi-urban residential area situated close to anthropogenic sources of emission from the industry. Meteorological data and pollutant levels for each rain event were collected for further discussion on the effects of weather conditions on VOCs in rainwater samples.

4.2. Experimental

4.2.1. Sampling location and sample collection

The sampling site for this study is located on the rooftop of School of Physical and Mathematical Sciences (SPMS), Nanyang Technological University (longitude: 103 °, 40' 53.68", latitude: 1 °, 20' 30.32") in the western region of Singapore. The vicinity includes a residential area (260 m), an expressway (Pan Island Expressway (PIE)) (100 m), Tuas industrial park (1.77 km) as well as Jurong Island (5.75 km), home to Singapore's major petrochemical industries (with the distance from the sampling site indicated in the brackets following the mentioned area). A wide variety of industries ranging from pharmaceutical and medical technology companies to petrochemical refining as well as food and beverage factories can be found in the western region of Singapore.

A manual sampler (Figure 4.2) was created through a series of connecting items for the use of rainwater collection. An aluminum platter with a carved hole was molded into a funnel-shaped and attached to a metal scaffolding covering two terracotta pots secured to a wire mesh grid panel to act as the manual sampler. The manual sampler was designed to maximize the collection of rainwater and minimize the interruption of rainwater collection from gusty

wind experienced during rain events along with the reduction of dust accumulation on the rainwater collection vial. The materials chosen were studied to be free from VOCs contamination to the rainwater sampling as discussed in Chapter 2.

Figure 4.1 & 4.2: Sampling location of rainwater for VOCs analysis using PAT GC-MS (left) and manual sampler for rainwater collection (right).

A 40 mL amber glass vial is placed under one of the terracotta pot before the rain event for actual rainwater collection, and subsequent vials of rainwater (up to 3 vials) were collected from the rain accumulated on the aluminum funnel and terracotta pot as soon as the rain event ends. The manual sampler was dismantled for cleaning with ultrapure water (UPW) and reassembled after drying with a disposable industrial roll for the removal of dust collected daily. Amber glass vials used for rainwater collection were washed with detergent and UPW before a final rinse with HPLC grade methanol (Tedia) and air dried in a fume cupboard. Minimal headspace is kept above the sample by filling the sample vials entirely to discourage the equilibration of VOCs into the gas phase. A total of 476 rain samples were collected from 193 rain events that had occurred between 1st August 2015 to 31st July 2016.

4.2.2. Chemical Reagents and Standards

Pure chemical standards of 28 VOCs determined from the method developed for VOCs analysis in rainwater (Chapter 2) were diluted to 1 mg mL^{-1} in a 50 mL volumetric flask with PAT grade methanol (VWR), sealed with parafilm, wrapped in aluminum foil and stored at 4°C . Experiments had shown that the diluted standard was stable for two weeks when stored under such conditions. Purity and information on the individual neat chemicals are available in Appendix A.1. A separate stock solution was prepared for the internal and surrogate standards (toluene- D_8 , *p*-bromofluorobenzene, and dibromomethane) in a similar fashion. Further dilutions were made to the stock solutions to create a calibration curve ranging from 2.5 to 1000 ng L^{-1} with an internal standard solution at 500 ng L^{-1} for each individual point. Additional concentration points (up to $50 \text{ } \mu\text{g L}^{-1}$) were tested for the calibration curve as some VOCs had higher levels of concentration during certain months in the yearlong study.

4.2.3. Data collection

Table 4.1. List of information collected an hour before, during the rain event as well as an hour after.

Pollutant concentrations	Meteorological data
24 h Sulfur dioxide ($\mu\text{g m}^{-3}$)	Rainfall Temperature Humidity Wind direction Wind speed
24 h PM ₁₀ ($\mu\text{g m}^{-3}$)	
1 h Nitrogen dioxide ($\mu\text{g m}^{-3}$)	
8 h Ozone ($\mu\text{g m}^{-3}$)	
8 h Carbon monoxide (mg m^{-3})	
24 h PM _{2.5} ($\mu\text{g m}^{-3}$)	
3 h PSI	
24 h PSI	

Meteorological data and pollutant concentration information were collected from the Meteorological Service Singapore (MSS) and NEA website respectively for the duration of

each rain event collected. Table 4.1 displays the different set of data collected from the various web pages. Readings were averaged for each rain event for Pearson correlation calculations.

4.2.4. Data Analysis

4.2.4.1. Statistical and trend analysis

Statistical calculations and plotting of trend graphs were performed with the Microsoft Excel 2013 program, and data were analyzed over a year to determine the effects of the haze and monsoon seasons in relation to the yearlong averages. The concentrations of the VOCs detected were plotted in a box and whiskers diagram for better visualization of results (Appendix B.1). Calculation such as mean (Equation 4.1) is an example of statistical calculations performed on the yearlong study of VOCs in rainwater from the western region of Singapore.

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n} \quad (4.1)$$

where x_i represents VOC concentration, n , the total number of samples and $\bar{x}$, the mean concentration of VOC. Trend graphs were plotted in 3 different groups namely oxygenated compounds, aromatic compounds and halogenated compounds and alkane/alkene. Compounds showing similar trends were highlighted and further discussed. Correlations between VOCs were determined through Pearson correlation coefficient to further verify the trends between the VOC pairs in comparison. Pearson coefficients calculated ≥ 0.8 & ≤ -0.8 were listed as correlation pairs with good correlations, and calculations on the types of correlations observed per month and over monsoon periods were performed. The calculation for Pearson correlation is as follows in Equation 4.2.

$$\rho = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2} \sqrt{\sum_{i=1}^n (y_i - \bar{y})^2}} \quad (4.2)$$

where x_i and y_i are individual concentration of the two VOCs in comparison while $\bar{x}_i$ and $\bar{y}_i$ are the means of the respective VOCs. Pearson correlations range from -1 to +1 where a positive value indicates a positive trend between the two VOCs in comparison. The more inline the trends are between the two VOCs in comparison, the closer the value of correlation calculated approaches +1; the opposite trend is observed for negative correlation. Effects of meteorological conditions on VOCs were also investigated through correlation calculations for yearlong, monthly, monsoon and haze periods.

4.2.4.2. Positive Matrix Factorization (PMF)

EPA PMF 5.0 multivariate receptor modeling was used for analyzing contribution factors of different sources towards the measured concentrations [34]. PMF is useful when source apportionment is required for a large number of samples with little to no detailed information on the composition of the emission sources. The general equation used for PMF factor analysis is as follows in Equation 4.3.

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (4.3)$$

where x is the data matrix, i is number of samples, j is chemical species, p is the number of factors, f is the species profile of each source, g is the amount of mass contributed by each factor to each individual sample and e is the residual for each sample and species [35]. PMF constraints result such that no negative source contribution is allowed for any sample. Individual data points can be weighed separately thus enables modification of the uncertainty with regards to a particular set of data.

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right)^2 \quad (4.4)$$

The object function Q (Equation 4.4) is minimized by PMF solution and calculation is based upon uncertainties (u) [35]. As PMF does not accept missing values nor values below the detection limit, replacement values were calculated as followed:

$$x_{ij} = \begin{cases} x_{ij}, & x_{ij} \geq DL_j \\ \frac{DL_j}{2}, & x_{ij} < DL_j \\ 4\bar{x}_j, & x_{ij} \text{ missing} \end{cases}$$

where $\bar{x}_j$ is the geometric mean of the samples greater than the method detection limit [36].

Object function Q calculation requires uncertainty values for all the concentrations of individual VOCs measured. Hence, the second file on uncertainty was calculated as follows and a copy of this file was also saved for data input:

$$s_{ij} = \begin{cases} \frac{DL_j}{3} + 0.15x_{ij}, & x_{ij} \geq DL_j \\ \frac{5}{6}DL_j, & x_{ij} < DL_j \\ 4\bar{x}_j, & x_{ij} \text{ missing} \end{cases}$$

where s_{ij} is the uncertainty for the j^{th} species in the i^{th} sample [36]. Detection limit values used in the calculations were determined as in Chapter 2 (Appendix A.2).

4.2.4.2.1. Modelling

Firstly, the files on concentration and uncertainty were input into the system, and the signal to noise ratio (S/N) of VOCs were calculated by the software using Equation 4.5; after which, the values of S/N were examined. As a general guide from the EPA, VOCs with S/N lesser than 0.5 were classified as bad, S/N between 0.5 and 1 was sorted as weak, and S/N above 1 was considered as strong [35].

$$\left(\frac{S}{N}\right) = \sqrt{\frac{\sum_{i=1}^n (x_{ij} - s_{ij})^2}{\sum_{i=1}^n s_{ij}^2}} \quad (4.5)$$

Classification of VOCs as bad removes the compound from PMF modeling while terming VOCs as weak increases the uncertainty of the VOC by three-fold. However, additional uncertainty was taken into account when calculations were made, hence increasing the S/N for most VOCs tested. To account for the increase, VOCs with S/N below 1.5 were classified as bad while S/N between 1.5 and 2.2 were classified as weak. VOCs were also considered as bad if their frequency of detection (FOD) above DL was lesser than 40% (with exceptions) as well as those VOCs whose difference between FOD above DL and FOD above MRL was greater than 50%. Exceptions were made to VOCs with good correlations ($\rho \geq 0.8$) identified in the yearlong analysis as similar potential sources of emission were high. VOCs with good correlations were classified as bad when FOD above DL was greater than 53%.

Base model runs were carried out after the categorization of VOCs, and the number of factors was varied with random seeds. The location of the sampling site is situated close to the previous sampling site of VOCs in ambient air of the western region of Singapore and seven factors were resolved for the vicinity [37]. Henceforth, seven factors were used as a guideline for the solution to this PMF analysis. Base model runs were performed with 20 runs of five to eleven factors with random seed setting. The results were then evaluated based on the Q values obtained, and the optimal solution should have a $Q(\text{Robust})$ within 1% of the $Q(\text{True})$ and 50% of the Q theoretical, calculated based on Equation 4.6.

$$Q_{\text{theoretical}} \approx nm - p(n + m) \quad (4.6)$$

where n represents the number of VOC species included in the model, m represents the number of samples in the dataset and p the number of factors that fitted the model. All possible solutions that attained convergence and a good quality of fit for all the mentioned

criteria of the Q values were inspected further. Base model runs were executed until the following conditions were achieved:

1. All residual values should fall between ± 3 .
2. R^2 values between predicted concentration and observed concentration should be moderately or relatively high for most compounds ($R^2 > 0.6$).
3. Distribution of VOCs in the different factors is logical and sound.

To achieve a good modeling result, methyl isobutyl ketone (which had met all the criteria) had to be removed because a supplementary factor was required, and rotational ambiguity occurred between factors when the bootstrap analysis was performed with methyl isobutyl ketone. Furthermore, ethyl benzene was categorized as weak instead of strong to achieve a more stabilized result. In total nine species of VOCs were classified as strong, six weak and thirteen were classified as bad. Displacement error estimation was used to determine if factor swaps occur with changing Q values and it was determined that no factor swaps nor error occurred for the eight factors modeled. Bootstrap analysis was performed with 100 runs, and a block size of four with all 100 bootstrap factors mapped indicating good stability. F_{peak} analysis was also conducted to control factor rotation, and F_{peak} at 0.1 was found to give a Q value that is relatively constant (Appendix C.2), and a positive F_{peak} value was chosen to obtain a more realistic result [36]. Source identification was then performed on the Factor contribution after F_{peak} adjustments.

4.3. Results and Discussion

4.3.1. Rain Samples

A total of 476 rain samples were collected from 193 rain events that had occurred between 1st August 2015 to 31st July 2016 with an average of 16 rain events per month. Table 4.2 displays the number of rain events; rain samples collected each month and the mean rainfall per month. The highest number of precipitations occurred during January 2016 where 27 rain events were recorded. A total of 69 rain samples were collected during the November while the lowest amount of rain events was observed in September 2015 with a total of 9 precipitations, due to the natural phenomena El Niño. El Niño occurs every 2 to 7 year and causes surface temperature of the ocean to increase which triggers shifts in rain patterns by affecting the temperature of the air above the sea. This, in turn, alters the air mass and wind circulation around the planet [38, 39]. A reverse in weather is observed from El Niño with drought experienced in Australia and South Asia along with a rainy season in the Pacific coast of South America [40].

Table 4.2. Number of rain samples collected per month

Month	No. of Rain events	No. of Rain samples collected	Mean Rainfall (mm)
August 2015	11	30	25.9
September 2015	9	20	18.6
October 2015	14	35	13.2
November 2015	25	69	15.2
December 2015	12	28	29.3
January 2016	27	69	14.3
February 2016	13	29	14.4
March 2016	15	31	18.3
April 2016	18	48	13.8
May 2016	14	35	25.7
June 2016	17	43	26.7
July 2016	18	39	22.8

Although December 2015 had the second smallest number of rain events, it had the highest mean rainfall at 29.3 mm. This observation is in agreement with the monsoon season as

December to January of the NEM is known to be the ‘wet’ period where more rainfall is experienced over Singapore [41]. The mean rainfall each month does not have any relation to the number of rain events nor to the number of samples collected. Singapore tends to experience heavy rain events for short periods (<1 h) rather than long periods of constant rain or light drizzle. In general, SWM saw higher mean rainfall than NEM even though NEM had a significant number of rain events. The inter-monsoon period had varying mean rainfall that tends to be on the lower end of the rainfall spectrum.

4.3.2. Yearlong statistical analysis

28 VOCs were analyzed in the rainwater samples collected between 1st August 2015 to 31st July 2016 using PAT GC-MS. Methacrolein had the highest mean and max concentration at 2072 ng L⁻¹ and 43142 ng L⁻¹, respectively. Other than methacrolein, oxygenated VOCs including 2-methyl furan, ethyl acrylate, methyl isobutyl ketone, hexanal, *n*-butyl acetate, heptanal, and benzonitrile all had mean concentrations above 70 ng L⁻¹.

The two other oxygenated VOCs, methyl methacrylate and methyl crotonate had lower means at approximately 22 ng L⁻¹ and 13 ng L⁻¹, respectively. A large number of oxygenated VOCs showing relatively high concentrations measured in rainwater could be due to their solubility in water as rainfall is known to be a natural fallout for VOCs [3]; the better water solubility in comparison with other VOCs will enhance the washout process from the atmosphere. The water solubility of aldehydes such as methacrolein, hexanal, and heptanal can be strengthened by additional reactions such as the formation of gem diols catalyzed by acidic conditions in rainwater and the formation of enolate ions for hexanal and heptanal similar to that of acetaldehyde uptake by water surfaces [42].

Table 4.3. Quantitation and detection of VOCs in rainwater between 1st August 2015 to 31st July 2016. *DF calculation represents samples with non-zero concentration quantitated while QF calculation represents samples with a concentration above respective MRLs. ^indicates values below the detection limit, 0.00^ indicates values below detection limit given through calibration curve calculation by the data analysis program and #indicates values above detection limit but below MRL. ^astatistical calculation was performed with available non-zero data for a better representation of VOCs in rainwater when present.

VOCs	Mean ^a (ng L ⁻¹)	Min (ng L ⁻¹)	Max (ng L ⁻¹)	Detection Frequency (DF)*	Quantitation Frequency (QF)*
Isoprene	9.05 [#]	0.00	114	98%	10%
Methacrolein	2072	0.00	43143	99%	97%
2-methyl furan	167	0.00	1306	100%	93%
Trichloromethane	59.9	0.00	295	100%	4%
Benzene	17.8	0.00 [^]	142	100%	55%
Ethyl acrylate	75.5	0.00 [^]	310	100%	20%
Trichloroethylene	6.41 [#]	0.00	37.6	89%	6%
Methyl methacrylate	22.0	0.00	151.9	73%	29%
Methyl cyclohexane	5.27 [#]	0.00	17.7 [#]	29%	0%
Methyl isobutyl ketone	203.4	0.00	4430	100%	89%
Methyl crotonate	12.6 [#]	0.00	32.9	5%	0%
Toluene	88.8	0.00 [^]	732	100%	32%
Hexanal	1147	0.00 [^]	12202	100%	92%
<i>n</i> -Butyl acetate	158	0.00	1581	100%	90%
Tetrachloroethylene	13.5	0.00	101	99%	36%
Ethyl benzene	28.2	0.00 [^]	323	100%	40%
<i>m,p</i> -Xylene	16.6 [#]	0.00 [^]	142	100%	17%
Heptanal	299.7	0.00 [^]	2425	100%	85%
Styrene	11.2 [#]	0.00	108	99%	7%
<i>o</i> -Xylene	21.5	0.00 [^]	295	100%	40%
1-Ethyl-3-methylbenzene	8.63 [#]	0.00 [^]	44.9	100%	22%
1-Ethyl-4-methylbenzene	8.59 [#]	0.00 [^]	53.2	100%	6%
1,3,5-Trimethylbenzene	11.2 [#]	0.00 [^]	64.9	100%	19%
1-Ethyl-2-methylbenzene	9.34	0.00 [^]	37.8	100%	34%
Benzonitrile	348	0.00	2112	20%	18%
1,2,4-Trimethylbenzene	13.7 [#]	0.00	111	100%	15%
1,2,3-Trimethylbenzene	9.83 [#]	0.00 [^]	62.6	100%	13%
Total Amount	4183	0.00	53086	100%	100%

Most of the VOCs studied in this yearlong analysis had DF above 70% which quickly declines when instrumental/method detection limit and quantitation confidence were considered. The severe decrement of detection was most likely due to the solubility of VOCs in water, and only six VOCs had QF above 70% which happened to be oxygenated VOCs with a mean concentration above 70 ng L⁻¹. Although the QF for most VOCs in rainwater

were low, they were kept for future discussion as the unique appearance of certain VOCs in different months may provide unique insights and thus give rise to probable ideas/suggestions of the various sources of emission.

In comparison with the available VOC concentrations detected in two rain events of Japan (Kanagawa University) as displayed in Table 4.4, the study performed in Kanagawa University displayed higher mean and max concentration of VOCs in rainwater with exceptions to some VOCs such as the xylene compounds.

Table 4.4. Mean and max VOCs concentration in every 1 mm of rainfall collected for 15 events during 14th March and 8th Dec 1997 in Japan^a [7], range of VOCs concentration in rainwater gathered in Portland, OR^b [6], concentration of VOCs in rainwater of Los Angeles, CA^c [4] and range of VOC concentration in rainwater collected in Camarillo, CA^d [5].

VOCs	Mean ^a (ng L ⁻¹)	Max ^a (ng L ⁻¹)	Range ^b (ng L ⁻¹)	Concentration ^c (ng L ⁻¹)	Range ^d (ng L ⁻¹)
Trichloromethane	250.70	4178.30		250.00	
Trichloroethylene	14.45	564.98	0.78 - 9.70		
Tetrachloroethylene			0.82 - 9.20	21.00	
Benzene	28.90	859.21			
Toluene	221.14	2579.92	N.D. - 220.00	76.00	
Ethyl benzene			3.90 - 72.00	9.00	
<i>m,p</i> -Xylene	6.37	127.39	34.00 - 260.00	11.00	
<i>o</i> -Xylene	7.43	127.39	12.00 - 110.00		
1,3,5-Trimethylbenzene			2.10 - 10.00		
1,2,4-Trimethylbenzene			16.00 - 44.00		
Hexanal					7000.00 - 10000.00

The sampling location in Japan was performed in an area near shopping amenities situated approximately 3-4 km away from factories, petrol and chemical industries akin to that of Singapore. Therefore, the concentration of VOCs in rainwater would perhaps be expected to be similar. However, this assumption was not fulfilled as the anthropogenic sources of VOC emissions were closer to the sampling site in Japan and possibly had different types of emissions. Also, the collection of rainwater in Japan occurred every 1 mm of rainfall with an

automated sampler [7], while the analysis performed in this study collected the samples at the end of the rain event with a manual sampler.

The other studies of VOCs in rainwater conducted in Portland, Los Angeles, and Camarillo were also carried out by collecting rainwater samples at the end of a rain event. Nonetheless, differences were still observed in the VOC concentration detected in the different locations indicating that the sources of emission for VOCs at a specific location can affect the amount of VOCs seen in rainwater. Generally, the mean concentration of VOCs in rainwater was comparable to the study performed in Portland but lower than that of the study conducted in Los Angeles. It was also noted that the concentration of hexanals (both in this study and in Camarillo) were comparatively higher than other classifications of VOCs analyzed in past research, with a possible reason due to the ability of carbonyl VOCs to form gem diols and enolate ions catalyzed by the acidic conditions in rainwater. The natural pH of rainwater is approximately 5.7 due to the dissolution of CO₂ gas, and the mean pH of rainwater collected in this study was 4.4 while previous studies conducted on the pH of rainwater in Singapore reported an average pH of 4.2 [22]. Singapore has relatively high levels of SO₂ and NO_x in the atmosphere that can be easily converted into sulfurous, sulfuric acid and nitrous, nitric acid, which explains the low pH readings.

The sequential collection of rainwater allows the concentration of VOCs at different points of the rain event to be measured, which can be highly valuable in terms of the correlation between VOC fallout and time. Alternatively, the collection at the end of the rain event is more applicable to the study of how VOCs in rainwater can affect the contamination of water collection points. Some species of halogenated and aromatic compounds are commonly found in surface waters as observed in two separate studies performed in Greece [43] and the

USA [44]. The observation of oxygenated VOCs in rainwater and other aromatic VOCs can potentially act as additional contamination towards the surface water. However, the concentrations that have been reported in surface waters are usually in the μM range which is a lot higher than the VOCs found in rainwater of this yearlong study. Therefore, there would be a likely chance of VOCs diluting to lower concentrations when added to the large volume of surface water hence reducing the likelihood of detection using current technology.

Other studies performed on volatile organic carbon concluded that a volatile organic carbon range of $1.3 \mu\text{M}$ to $499 \mu\text{M}$ [18, 19] was present in rainwater, calculated by removing non-purgeable DOCs (NPDOCs) and inorganic carbon (IC) from the total carbon (TC) concentration. This chemical class of volatile organic carbon was also much higher than the nM range found in the total VOC rainwater samples in Japan, USA, and this study. In theory, the difference between the sum of NPDOCs and ICs from TC should produce the amount of volatile organic carbon compounds. However, a negative volatile organic carbon concentration was determined in one of the studies [19] which may indicate a possible flaw in this assumption. Nonetheless, it should be noted that the studies of VOCs in rainwater in Singapore, USA, and Japan have not exhausted the list of plausible VOCs with only selected target VOCs studied which could have led to the lower levels of VOCs found.

4.3.3. Trend study

The studies of trends are often performed in the long-term environmental monitoring of pollutants to identify the plausible shared sources of emission. The identification of similar variations of pollutant concentration may indicate similar sources of emission, however, similar trends do not always prove common sources of emission and the appropriate way of source apportionment are usually conducted through statistical tools such as PMF and tracer

compounds. VOCs were classified into 3 groups for the ease of discussion and trend studies, namely, aromatic compounds, oxygenated compounds and halogenated compounds and alkanes/alkenes. The trends from the yearlong analysis, haze analysis, and monsoon classification were explored and studied.

4.3.3.1. Yearlong analysis

Figures 4.6 to 4.8 display the mean concentration of VOCs in rainwater per month during the yearlong analysis. VOCs with concentrations significantly higher than their counterparts of the same group were plotted on a secondary y-axis for a better visualization of trends. Overall, the distribution of VOCs detected every month varies for the different groups in discussion. Several trends exist between aromatic compounds and oxygenated compounds while halogenated compounds and alkanes/alkenes appeared to have no trend in general. Peaks in concentration were observed for the month of September and November 2015 in the group of aromatic VOCs with an additional spike in concentration for ethyl benzene and xylenes during the month of May 2016.

Figure 4.6. Trend graphs of mean concentration of aromatic VOCs in rainwater from August 2015 to July 2016

Figure 4.7. Trend graphs of mean concentration of oxygenated VOCs in rainwater from August 2015 to July 2016

Figure 4.8. Trend graph of mean concentration of halogenated & alkanes/alkenes for a manual sampler from August 2015 to July 2016.

Higher concentrations of oxygenated compounds were also detected during the months of September 2015, October 2015 and April 2016 with elevated levels of methacrolein detected in March 2016. Such spikes in concentration are usually due to notable events that had occurred during the sampling period. Benzene, toluene, ethyl benzene and xylenes (BTEX) is an essential group of VOCs in petrochemical materials and the increment of these VOCs along with other aromatic VOCs in the month of November 2015 could have been due to the sources of emission in the vicinity of the sampling site. Petroleum refinery and petrochemical industries in Jurong Island as well as the use of petroleum in cars [45, 46] from the

expressway, could have been likely sources of emission for the increment observed. Throughout the months of March to May 2016, renovations on SPMS building (sampling site) might have caused the higher spikes observed during April and May 2016 in the oxygenated VOCs and aromatic VOCs (May 2016).

A sharp chemical odor could be perceived at the sampling site during the renovation period and VOCs emitted from the constructions were vented into the atmosphere with the vents installed at SPMS for climate control as seen in Figure 4.9. The VOCs could then be washed out from the atmosphere with rainfall, and hence the higher amount of VOCs perceived during these months. Ethyl acrylate and methacrolein saw a massive increase during this few months, and this increment was most likely due to the fact that ethyl acrylate is used to manufacture latex paints, binders, polishes and adhesives [45] while methacrolein is found to be emitted from steel-protective paints [46] that may have been used during the renovation. On the other hand, aromatics like ethyl benzene are used to produce paints and varnishes [47] while xylenes are also used to produce paints and coatings [48] that may also have been employed during the construction and renovation process.

Figure 4.9. Climate control vents installed at the sampling site.

The concentration of alkanes/alkenes VOCs remain relatively low throughout the year with the exception of isoprene during March 2016 where constructions/renovations were done at the sampling site. Isoprene has been demonstrated to be emitted biogenically from plants and trees [49], but, isoprene is also emitted from anthropogenic sources such as the production of polyisoprene (synthetic rubber) and other elastomers in the industry [50]. The likelihood of increased emission from biogenic sources is small. Therefore, the usage of synthetic rubber in the renovation of SPMS could have been the main source of emission for isoprene during March 2016. The spike in concentration from the haze event was not the highest recorded throughout the year which could have been due to wind dilution and secondary reactions taking place from the time required for transport across boundaries.

A clearer visualization of trends between individual groups was performed by singling out VOCs showing similar inclinations in separate plots. Figure 4.10 displays similar trends between five aromatic VOCs and such movements detected would suggest a common source(s) of emission for the VOCs on inquiry. However, statistical calculations are required to examine the potential sources of emission further. Most aromatic VOCs arise from crude oil while some are from coals with main use as starting materials for consumer products [51], other probability lies in the production of the aromatic compounds from the petrochemical industries and/or the use of petrochemicals products [52, 53].

Figure 4.10 & 4.11. Trend graphs between Intra and inter groups of VOCs in rainwater.

Figure 4.12. Trend graphs wind speed and VOCs.

From Figure 4.10, it was observed that a small spike in concentration occurred during September 2015 and March 2016 while a dip in concentration was found in May and June 2016. The surge in March 2016 was likely to be caused in a similar fashion as the oxygenated compounds seen in Figure 4.7 from the construction work performed at the sampling site from the usage of such VOCs as solvents [52]. Additionally, a dip in concentration during May and June 2016 could have been due to the transition from the inter-monsoon period and monsoon seasons that could bring about an omission of an emission source for these VOCs. Other alike trends within the same group such as trichloroethylene and tetrachloroethylene and hexanal and heptanal were also detected and attached as Appendix C.3. Aldehydes such as hexanal and heptanal have pleasant odors that are usually used for the production of flavors and fragrances [54, 55] while halogenated compounds like trichloroethylene and tetrachloroethylene are used as degreaser and dry cleaning solvents [56, 57], therefore the

manufacture or usage of such products in a similar setting can lead to the release of such VOCs into the atmosphere and hence washout during rainfalls with comparable trends observed in rainwater analysis.

Trends, however, are not limited to VOCs within the same group but also to VOCs from across other groups as seen in Figure 4.11. *o*-Xylene was plotted on a secondary y-axis as the concentration detected of *o*-xylene was significantly lower than that of methyl isobutyl ketone and *n*-butyl acetate. Depending on the anthropogenic activities, anthropogenic sources may emit more than one type of VOCs hence the observation of inter-group correlations. The increase in concentration during April and May 2016 were likely to be from the construction performed at the sampling site for *o*-xylene, methyl isobutyl ketone, and *n*-butyl acetate is used to produce lacquers which may have been employed during the renovation period [48, 58, 59]. Similar cross-group trends of methacrolein and 1,2,3-trimethylbenzene and methyl methacrylate and 1,2,4-trimethylbenzene are attached as Appendix C.3. Seeing that most VOCs can be used as solvents [46, 52], a mixture of different groups of VOCs would not come as a surprise as the production of most products may require various types of solvent for better solubility.

A study of SVOCs in Singapore had determined that certain meteorological conditions can affect the concentration of SVOCs observed in the ambient air of Singapore [25], henceforth, meteorological data were also collected for the duration of this study to investigate if it were also true for VOCs in rainwater. Figure 4.12 displays an example of the trend observed between VOCs and meteorological data collected. Wind speed was plotted on a secondary y-axis in Figure 4.12 for better visualization. A positive trend between wind speed and aromatic VOCs in the atmosphere is uncommon as the previous investigation indicated that

negative trends exist between VOCs and wind speed due to the dispersion factor of the wind [49]. This could suggest that instead of dispersing VOCs from probable local sources in the atmosphere, the aromatic VOCs could have emissions from the origin of air mass/wind, hence carried from a long distance/transboundary events. Alternatively, a constant source of aromatic VOCs could be available close to the sampling site, hence enhancing the concentration of ethyl benzene and xylenes in the atmosphere which in turns increases the likelihood of washout and thus increase of detection in rainwater.

4.3.3.2. Haze trend analysis (September to October 2015)

During September and October 2015, Singapore experienced the worst haze to date from the slash and burn practice (biomass burning) from its neighboring countries, further worsened by the dry conditions from the El Niño weather phenomenon [27, 39]. Biomass burning has been known to introduce volatile organic carbon [17] and VOCs [21] into the atmosphere which can affect Singapore through transboundary air mass transportation. Moreover, the month of September falls in the SWM period which has back trajectory air mass from regions that had biomass burning such as Indonesia as seen from Figure 4.3. The transport of volatile organic carbon to Singapore could be removed through rainfall and hence the observed spikes during the haze period.

Haze from the forest fires in Indonesia could have caused the increments seen in September and October 2015 for aromatic VOCs and certain oxygenated VOCs such as 2-methyl furan, benzonitrile, ethyl acrylate, hexanal, and heptanal. Further evidence to support the source apportionment of VOCs detected in September and October 2015 to haze from Indonesia was found the trends between VOCs such as 2-methyl furan and styrene to the PSI and PM data collected over the yearlong study, as shown in Figure 4.15. A trend between VOCs with PSI

and PM values may indicate that the anthropogenic sources of 2-methyl furan and styrene could be similar to that of the PSI and PM. A spike in the PSI and PM values in the month of September to October 2015 was due to the transboundary haze event from the burning of biomass from neighboring countries of Singapore, and previous studies had linked PM emission to biomass burning [56-59].

Figure 4.13 & 4.14. Trend graphs of aromatic and oxygenated VOCs during haze period.

Figure 4.15 & 4.16. Trend graphs between PSIs, PMs, and VOCs and carbon monoxide level from Aug 2015 to Jul 2016.

Aromatic compounds such as BTEX were detected in the 1998 haze event in Brunei [21] and also in Australia's peat fire study with the addition of styrene [31]. Hence, the increase of aromatic VOC concentration seen in this study during the haze period would not be alarming.

VOCs such as styrene could be released into the atmosphere through the combustion of styrene-based products (polymer) [53] which may have taken place in Indonesia together with the uncontrolled biomass burning while the observation of other aromatic compounds could be linked to the use of petroleum (for the start of biomass burning). It should be noted that the rise of other aromatic VOCs such as trimethylbenzene and ethyl toluene were low in comparison to BTEX and styrene which may elucidate the lack of detection in previous atmospheric VOCs studies of haze events. The detected elevated levels of oxygenated VOCs though not commonly reported in the VOCs detection from haze could be traced to individual events happening during the forest and peat fires.

2-Methyl furan had been found as a pyrolysis product of carbohydrate (hemicellulose) which makes up to around 50-65% of plant cell walls [63], hence the increased detection during forest fires. Moreover, 2-methyl furan could also be detected through the vapor phase hydrogenation of furfural [64] which had been previously linked to biomass burning [37, 65]. Oxygenated VOCs including alcohols, aldehydes, ketones, carboxylic acids, and esters are emitted through biomass burning during smoldering phases of fires (lower burning efficiency) [66]. Henceforth, the increase in the concentration of ethyl acrylate, hexanal and heptanal could be from the smoldering phase of the peat and forest fires as evident in Figure 4.14 where higher levels of these VOCs were observed during October where the forest fires were coming under control. In addition, ethyl acrylate could be formed from acetylene, carbon monoxide, and ethanol through the Reppe reaction [67] as carbon monoxide is produced during haze due to the incomplete combustion common during biomass burning evident from the increase in carbon monoxide level detected (Figure 4.16). The link of benzonitrile to biomass burning had not been reported formerly, and the hypothesis of the unintentional

combustion of consumer products containing benzonitrile could not account for the significant increase observed. However, benzonitrile was demonstrated to be emitted from the burning of humus (dead plant material) [67] and peat [30, 69] and since more than 50% of fires in Indonesia had occurred in peatland areas [70], the increase of benzonitrile concentration in rainwater could be justified.

4.3.3.3. Monsoon analysis

Trend studies analyses were performed on a monsoon period basis where the yearlong monitoring of VOCs in rainwater was split into 5 classifications of monsoon period for discussion and analysis. The main discussion upon the monsoon analysis is of the influence of changing wind directions/wind speed on the amounts of VOCs observed in the rainwater collected in the western region of Singapore. Starting from August 2015 (SWM) and ending in July 2016 (SWM), the trend plot for the full list of VOCs is attached in Appendix B.4 where the inter-monsoon occurs between the 2 main monsoon periods (which was named after the predominant wind direction in the seasons). Ethyl acrylate, ethyl benzene *m,p*-xylene and *o*-xylene in Figure 4.17 and 2-methyl furan in Figure 4.18 were plotted on the secondary y-axis for better visualization of the trend. As shown in Figures 4.17 and partially in 4.18, peaks in the concentrations of VOCs were observed during inter-monsoon. Lighter winds were experienced during this period which could have led to the lesser dispersion of VOCs [49] in the atmosphere, hence more washout during rainfalls that resulted in the observation of the ‘M’ shaped trend in Figure 4.17.

Figure 4.17. M-shaped monsoon trend graph for Rainwater sampled between August 2015 to July 2016.

Figure 4.18. Partial M-shaped monsoon trend graph for Rainwater sampled between August 2015 to July 2016.

The study of VOCs conducted at Kanagawa University concluded that the concentration of VOCs found in rainwater was dependent on the concentration of VOCs in ambient air with the exception of benzene [7]. Hence the concentration in rainwater should reflect the VOCs in ambient air. The peak observed during August to September 2015 SWM in Figure 4.18 would have been due to the increase in VOCs tested during the haze period where emissions of VOCs were common from the burning of biomass [19] which resulted in the partial ‘M’ shape observed. Biomass burning had been known to emit benzene [19] which could have been from the fuel used to start the forest fire or from the combustion of plastic, synthetic rubber, dyestuff and resins which use benzene as a basis for manufacture [71]. Similarly, 1,2,4-trimethylbenzene is a common component of fuel [52] thus could have been traced

back to the fuel used to start the biomass burning while methyl methacrylate is often used to produce polymers [72] that could have been burnt in the forest fires. Whereas, 2-methyl furan as mentioned for Figure 4.11 could have been from furfural [64] which can originate from biomass burning [37, 65] or through the burning of hemicellulose [63] containing plants.

An opposite trend towards the ‘M’ shape observed in Figure 4.17, and 4.18 was seen in Figure 4.19 and 4.20 where a ‘W’ and partial ‘W’ trend was observed respectively. The ‘W’ trend occurs when a higher concentration of VOCs was detected during the monsoon seasons but lesser during the inter-monsoon region. This could suggest that the direction of the wind during monsoon period had carried more of the VOCs showing ‘W’ trend to the sampling site where rain was collected, and accumulation had taken place instead of dispersion. The dip in VOCs concentration observed in Figure 4.20 was opposite of VOC peak in Figure 4.18 which could indicate that isoprene and tetrachloroethylene had not originated from the transboundary haze event. Also, the levels of both VOCs in the SWM at the start and end of the yearlong sampling were relatively low for isoprene and tetrachloroethylene. Hence, the southwest direction from the sampling site might not carry the anthropogenic sources for these two VOCs.

Figure 4.19. W-shaped monsoon trend graph for Rainwater sampled between August 2015 to July 2016.

Figure 4.20. Partial W-shaped monsoon trend graph for Rainwater sampled between August 2015 to July 2016.

The increase of VOC concentrations in rainwater as seen in Figure 4.19 during August to September 2015 SWM was most likely due to the haze event. Aromatic compounds were observed to show ‘W’ trends that could be traced back to the probable usage of petrochemical products [51] during the haze event. The restriction of results for just the monsoon analysis may provide a more simplified view of the data collected throughout the rainwater collection period, but much unique/useful information could be lost through the condensation. Therefore, more apparent correlations were found between more VOC groupings due to the minor points in comparison to the yearlong analysis.

4.3.4. Correlation calculations

Correlation calculations allow a statistical analysis of concentration, hence a step up from the initial visualization analysis performed for trend analysis, for the determination of probable common sources of emission between the VOC pairs. A good positive correlation has a Pearson Correlation value indicated by a value greater than or equal to 0.8, which could suggest possible similar sources of emissions, while a good negative correlation has a value lesser than or equal to -0.8. VOC pairs with values of good positive and negative correlations

were singled out for discussion in the yearlong study and haze dataset while the monthly and monsoon distribution of correlations will be discussed.

4.3.4.1. Yearly correlation

Table 4.5. Yearly correlation between VOCs pairs from August 2015 to July 2016

Correlation pairs		Correlation
Trichloromethane	Methyl crotonate	-1
Benzonitrile	Trichloromethane	0.88
Benzonitrile	Ethyl acrylate	0.82
<i>m,p</i> -Xylene	Ethyl benzene	0.91
<i>o</i> -Xylene	Ethyl benzene	0.86
<i>o</i> -Xylene	<i>m,p</i> -Xylene	0.92
1-Ethyl-4-methylbenzene	1-Ethyl-3-methylbenzene	0.88
1-Ethyl-2-methylbenzene	1-Ethyl-3-methylbenzene	0.90
1-Ethyl-2-methylbenzene	1-Ethyl-4-methylbenzene	0.83
1,3,5-Trimethylbenzene	1,2,3-Trimethylbenzene	0.84
1,2,4-Trimethylbenzene	1,2,3-Trimethylbenzene	0.82
Benzonitrile	3 h PSI	0.84
Benzonitrile	8 h carbon monoxide	0.93

Good correlations, both positive and negative, were observed in eleven pairs of VOCs in the yearlong analysis of VOCs in rainwater between August 2015 to July 2016. The slight deviation was seen in comparison to the trend analysis as monthly average points were used for comparison while correlations for yearlong analysis used all data points available. Approximately 73% of the strong correlation pairs observed were aromatic VOC pairs while the other correlations were across different groups or oxygenated VOC pairs. Similar to the trend analysis, more aromatic VOCs had a similar pattern (strong positive correlation) while correlations between cross groups also exist. The high positive correlation observed were mostly determined for aromatic VOCs isomer pairs with likely sources of emission from the similar production processes of such isomeric VOCs and usage of chemicals that may contain the isomeric mixtures [48, 52].

The production of aromatic compounds is widely from petroleum refineries [73-75] (where the most extensive production of *p*-xylene is located on Jurong Island of Singapore [76]) as

well as the further reactions from petroleum refinery products [77]. Therefore, the high positive correlation of aromatic VOC isomers observed in the yearlong correlation analysis of VOCs in rainwater suggests a constant source of aromatic VOCs all year round with likely sources of emission from the petroleum refinery industry in Jurong Island, situated close to the sampling site. Although strong correlations exist between benzonitrile, trichloromethane, ethyl acrylate and methyl crotonate, their low frequency of detection above MRL increase the uncertainty involved in probable source apportionment which can lead to errors when trying to relate strong positive correlations with sources of emission. Henceforth, the probable shared sources of emission between these VOCs will be omitted from the discussion.

In comparison, the number of strong correlation VOC pairs found in the study of VOCs in ambient air of the western region of Singapore [37] with sampling sites close to this study is higher than that of the current study of VOCs in rainwater. This decrease in the strength and number of correlations was also observed in the study of VOCs in rainwater in Japan [7] which could have been due to the difference in solubility of VOCs in water thus explaining the lower and weaker correlations found in this study. Nonetheless, more strong correlations were found in this study in comparison to the study performed in Japan. It could be due to the fact that Singapore experiences more uniform weather (at least in terms of average daily temperatures) with predominantly known wind directions while Japan has the four seasons which could affect the VOCs observed in rainwater depending on the season [78]. Similar to Hong Kong, the average concentration of alkylbenzenes was found to be greater in summer than the winter rain samples collected [79].

4.3.4.2. Haze correlation

Table 4.6. Strong positive correlation of VOCs with PSIs, PMs, and carbon monoxide in September 2015

September	Benzene	Ethyl acrylate	Toluene	<i>n</i> -Butyl acetate	Benzonitrile	1,2,3-Trimethylbenzene
3 h PSI	0.96		0.93		0.96	0.82
24 h PSI			0.88	0.82		
24 h PM ₁₀			0.86			
24 h PM _{2.5}			0.88	0.82		
8 h Carbon monoxide	0.81	0.89	0.83		0.84	
Benzene						
Ethyl acrylate	0.87					
Toluene	0.83					
<i>n</i> -Butyl acetate			0.87			
Benzonitrile	0.97	0.91	0.87			
1,2,3-Trimethylbenzene	0.97					

Table 4.7. Strong positive correlation of VOCs with PSIs, PMs, and carbon monoxide in September 2015

October	Ethyl acrylate	Heptanal	1-Ethyl-2-methylbenzene	Benzonitrile
3 h PSI	0.83			0.85
24 h PSI		0.81		
24 h PM ₁₀				
24 h PM _{2.5}		0.81		
8 h Carbon monoxide			0.81	

As mentioned in the haze trend analysis, correlations with the PSI and PM during the haze period could suggest that the VOCs under investigation had sources of emission the same as that of the PM [60-62] and hence probably originated from the biomass burning in Indonesia. Therefore, correlation calculations were performed for the month of September and October 2015. VOCs demonstrating a good correlation to PSI, PM, and carbon monoxide (demonstrated to increase drastically during haze period) were extracted and tabulated in Table 4.6 and 4.7. During the month of September 2015, six VOCs were found to have a strong positive relationship towards the PSI, PM and carbon monoxide, and four VOCs were found to have a good correlation in the month of October 2015. There were more correlations in September when compared to October which could have been attributed to the extent of the biomass burning as well as the stage of combustion. During September, the biomass burning was not as widespread where an increased number of active fires were detected in Indonesia during October as seen in Figure 4.21. Therefore, the origin of such VOCs emitted

from biomass burning could be from a more localized area which would equate to better correlations. Moreover, September falls within the SWM that sees stable air mass back trajectory (Figure 4.3) while October would see a less uniform air mass origin. Hence the correlations would be expected to be less in the month of October.

Figure 4.21. Number of active fire of biomass burning in Indonesia detected [70].

In October, strong correlations only existed between meteorological data collected and the VOCs, but not within VOCs themselves. Hereafter, the theory of non-uniform wind directions affecting VOCs observed in rainwater was validated. In addition, with the political efforts put in by neighboring countries and the Indonesian government to reduce the burning, many fires shifted to the smoldering phase which would produce more oxygenated VOCs [66]. This change of fire phase also alters the types of VOCs emitted, hence the decrease of good correlations observed in October 2015. Although the mean concentration of toluene and benzene were not as high as some oxygenated compounds found in rainwater in September 2015, a greater number of strong correlations were determined for toluene and benzene in comparison to other VOCs. Benzene was noted to have the greatest mean concentration of all aromatic VOCs in September (Figure 4.13), and this observation is not unexpected as benzene is known as one of the most abundant aromatic hydrocarbons emitted from biomass

burning [66, 80]. Much attention has been paid to benzene's release from anthropogenic sources as the health risk and hazard posed by benzene can be significant. It was also noted that more positive correlations of VOCs were detected during the month of September where methyl isobutyl ketone (0.83), *o*-xylene (0.87), 1,3,5-trimethylbenzene (0.91), 1-ethyl-2-methylbenzene, 1,2,4-trimethylbenzene (1) and 1,2,3-trimethylbenzene (0.95) had strong positive correlations with the tropospheric ozone concentration measured by the NEA. The increased concentration of VOCs and NO_x in the atmosphere from the biomass burning in Indonesia could have caused the increase in the formation of tropospheric ozone as seen in the following reaction [81]:

The increase in NO_x concentration in the atmosphere is crucial in the production of tropospheric ozone as NO_x is the primary source of oxygen atoms required for ozone formation, which is observed with forest fires and biomass burning [81]. The transboundary transportation of the pollutants may have provided sufficient time for the formation of tropospheric ozone in comparison with locally emitted VOCs. Therefore, the increased emission of VOCs from biomass burning not only affects Singapore through the increase in concentrations observed in the atmosphere and rainwater but also with the secondary pollutants such as tropospheric ozone.

4.3.4.3. Monthly correlation

Figure 4.22, 4.23 & 4.24. Number of monthly correlation distribution of VOCs in rainwater sampled from August 2015 to July 2016.

The highest counts of good correlations were recorded in the month of September 2015 at 91 while the lowest counts of strong correlations were registered in the month of December 2015 at 21 (Appendix C.5). It was interesting to note that the number of strong correlations observed each month does not have any relation to the number of rain events per month as both September and December 2015 had one of the least numbers of rain events per month. The haze event of 2015 took place during September 2015 and October 2015 which could have accounted for the higher number of strong correlations observed in September. December is at the start of the NEM which could mean a transition of the wind from non-

monsoon to monsoon direction that could have disrupted the trend/ sources of emission for the analysis of rainwater, thus, the low amount of strong correlations.

Along the line of discussion where monsoon seasons affect the number of strong correlation pairs observed, a larger number of strong correlations were also noted at the end of the monsoon period rather than the start of the monsoon period i.e., there are more correlations in February and March than December and January, and more correlations in August and September than June and July. Throughout the yearlong analysis, the aromatic, strong positive correlation was recorded indicating an ever-present anthropogenic source(s) of emission of aromatic VOCs which is expected for the location of the sampling site, which was close to many industries such as the petrochemical and manufacturing industries that could have produced or use aromatic VOCs. The aromatic VOCs could also be traced back to the emissions from the expressway located closer to the sampling site than all other anthropogenic sources. The Pan Island Expressway (PIE) is one of the main motorways in Singapore that transports residents along with heavy transport trucks from Malaysia to either end of Singapore (East to West or West to East). The use of petroleum fuel in cars has been found to emit aromatic VOCs [82], the presence of the PIE close to the sampling site could explain the constant good correlation observed for aromatic compounds.

Oxygenated VOCs in rainwater had strong positive correlations in the monthly analysis of correlations for 8 out of 12 months, with possible origins from solvent usage and production of other chemicals and consumer products. Particular note should be taken that certain oxygenated VOCs like aldehydes and esters have common usage in fragrance and flavor production because of their pleasant-smelling properties. Cross-group correlation between different groups of VOCs was also ever-present in both positive and negative strong

correlations each month. Production of goods in the industries usually involves the use of VOCs (e.g., solvents, starting material) from different group classification, therefore, cross-group correlations observation would be foreseeable.

4.3.4.4. Monsoon Correlation

Figure 4.25, 4.26 & 4.27. Number of monsoon correlation distribution of VOCs in rainwater sampled from August 2015 to July 2016.

It was noted that generally, the monsoon season (Appendix C.6) carries a larger number of strong correlations which could be anticipated as the uniform direction of wind would carry unchanging sources of VOCs found in rainwater. The high number of strong correlations in the SWM in August to September 2015 was mostly due to the haze event in 2015 where the emission of many VOCs was related to the burning of biomass [19, 29, 30, 33]. Similar to

monthly analysis, most of the strong correlations observed were positive with the exception in NEM where around half of the strong correlations observed were negative. The positive correlation was mainly aromatic VOC pairs or cross-group VOC pairs as shown in Figure 4.26. The correlation of oxygenated VOCs was less prominent in the monsoon analysis than in the monthly analysis. The monsoon season may help to explain the origins of the VOC pairs that show strong positive correlations as a prevailing wind direction exists during these periods. During SWM, the general wind direction is from the southwest, which would lead to the detection of emission sources from the Tuas industrial estate, Jurong Island, and the expressway situated close to the sampling site (Figure 4.1).

These sources could explain the strong correlations between aromatic VOCs, which are often from petroleum refineries, motor vehicle fuels, and industrial manufacturing processes. Also, the use of solvent VOCs and/or starting materials for the production process could be traced back to such sources of emission. The NEM period saw a more strongly positive correlation in aromatic VOCs in comparison to the SWM and inter-monsoon season, with little strongly positive correlations in cross-group VOC pairs. Northeastern wind during NEM will see sources of the northern and eastern site of Singapore which would lack in the industrial sources of emission as observed during the SWM. Henceforth, the predominant sources of emission would have to be from the expressways located close to the sampling site and perhaps long-range mass flow from Malaysia. This idea of sources from the NE direction is supported by the fact that lesser strong positive correlations between cross-group VOC pairs were observed in the NEM. Cross-group VOC pairs most likely arise from their use in an industry where manufacturing process may require more than one type of VOC for their different properties.

4.3.5. PMF

Table 4.8. Emission sources of VOCs (methacrolein to *p*-xylene).

VOC	Uses and Emission
Methacrolein	<ol style="list-style-type: none"> 1. Production and use in copolymers and resins [83] 2. Intermediate of methacrylonitrile or methacrylic acid [83, 84] 3. Emission from automobile exhaust [85] 4. Emission from steel protective paints [46] 5. Emission from trees [46]
2-Methyl furan	<ol style="list-style-type: none"> 1. Pharmaceutical intermediate of atropine, sodium acetate, furadantine, anisodamine and thiamine furan, vitamin B1, chloroquine [86] 2. Production of methyl furfural, aliphatic compounds, and sulfur, nitrogen heterocycles [86] 3. Making of pesticides, flavors or fragrances [86]
Benzene	<ol style="list-style-type: none"> 1. Natural constituent of crude oil [87] 2. From forest fires and plant volatile [87] 3. Manufacture of industrial chemicals (polymer, detergents, pesticides, pharmaceuticals, dyes, plastics, resins, oils, natural rubber) [88] 4. Production, storage, transport, venting and combustion of gasoline [87] 5. Solvent [71]
Hexanal	<ol style="list-style-type: none"> 1. Food additive (flavor ingredient) [89] 2. Organic synthesis of plasticizers, rubber chemicals, dyes and synthetic resins [90] 3. Perfumery [91] 4. Exhaust gas from gasoline, diesel engines [92-95]
<i>n</i> -Butyl acetate	<ol style="list-style-type: none"> 1. Occurs naturally in many fruits and plants (plant volatile) [95] 2. Manufacture of lacquer, artificial leather, photographic films, plastics, and safety glass [96]
Ethyl benzene	<ol style="list-style-type: none"> 1. Product of biomass combustion [47] 2. Component of crude oil [47] 3. Use as an intermediate for the manufacture of styrene and other chemicals [88] 4. Use as a resin solvent [88] 5. Component of automotive and aviation fuels [97] 6. Exhaust from internal combustion engines and tobacco smoke [47] 7. Emitted from paint [47]
<i>p</i> -Xylene	<ol style="list-style-type: none"> 1. Occurs naturally in petroleum, natural gas [98] 2. Released during forest fires [99] 3. Occurs in various plants (corn, alfalfa and cereal silage) [100] 4. Synthesis of terephthalic acid for polyester resins and fiber [101] 5. Manufacture of vitamins and pharmaceuticals and insecticides [101] 6. Motor vehicle exhaust [101-103] 7. Solvent [104] 8. Emitted from paint [48]

The source apportionment and suggestion of an identification of a factor were performed through deduction and research on the common use or emission of such VOCs in industry. It should also be noted that due to the lack of land space, many different types of industries and thus sources of emission are clustered together in Singapore which can affect the identification of the sources of emission. Table 4.8 and 4.9 summarizes the possible sources of emission and use of the 15 VOCs modeled in the PMF analysis.

Table 4.9. Emission sources of VOCs (*m*-xylenes to 1,2,3-trimethylbenzene).

VOC	Uses and Emission
<i>m</i> -Xylene	<ol style="list-style-type: none"> 1. Occurs naturally in petroleum, natural gas [98] 2. Released during forest fires [99] 3. Occurs in various plants (corn, alfalfa and cereal silage) [91] 4. Solvent [104] 5. Organic synthesis (especially isophthalic acid) [105] 6. Gasoline blending [98] 7. Motor vehicle exhaust [101-104] 8. Emitted from paint [48]
Heptanal	<ol style="list-style-type: none"> 1. Manufacture of 1-heptanol, organic synthesis, perfumery, pharmaceuticals [106] 2. Flavoring agent [106] 3. Emission from motor vehicles [92, 94] 4. Preparation of alpha-amylcinnamaldehyde (soap perfumery) [107, 108]
<i>o</i> -Xylene	<ol style="list-style-type: none"> 1. Occurs naturally in petroleum, natural gas [98] 2. Released during forest fires [99] 3. Occurs in various plants (corn, alfalfa and cereal silage) [90] 4. Manufacture of phthalic anhydride, in vitamin and pharmaceutical synthesis [109] 5. Motor vehicle exhaust [101-103] 6. Solvent [104]
1-Ethyl-3-methylbenzene 1-Ethyl-4-methylbenzene 1-Ethyl-2-methylbenzene	<ol style="list-style-type: none"> 1. Gasoline blending [110] 2. Manufacture of other chemicals [110] 3. Released from vehicle exhaust fumes [110] 4. Manufacture of plastics and coatings [110] 5. Printing materials and inks [110] 6. Solvents [110] 7. Petroleum refineries and petrol stations [110]
1,2,4-Trimethylbenzene	<ol style="list-style-type: none"> 1. Intermediate of trimellitic anhydride, dyes, pharmaceuticals, and pseudocumidine [111] 2. Chief industrial use as a solvent and paint thinner [112] 3. Component of gasoline [113] 4. Emission from gasoline-powered vehicles [114]
1,2,3-Trimethylbenzene	<ol style="list-style-type: none"> 1. Use as a solvent and in dye, perfume manufacturing [115] 2. Component of gasoline [113] 3. Emission from gasoline-powered vehicles [114]

A total of 8 factors were calculated, and the main contributors to Factor 1 are heptanal (flavor and fragrances) with small contributions of hexanal (flavor and fragrances), *n*-butyl acetate, 2-methyl furan (flavor and fragrances), *o*-xylene (solvent) and 1,2,4-trimethylbenzene (solvent) as seen in Figure 4.28. Companies in flavor and fragrance industry such as Firmenich [116], Givaudan [117] and International Flavors & Fragrances Inc. (IFF) [118] have locations in the western region of Singapore such as Chin Bee Road and Tuas West Road which could account for the VOCs distributed to Factor 1 through PMF modeling of 15 VOCs.

Figure 4.28. Factor 1: Synthesis and manufacture of flavors and fragrances.

Figure 4.29. Factor 2: Petroleum Refining.

The main contributors to Factor 2 are 1-ethyl-3-methylbenzene (petroleum refining), 1-ethyl-4-methylbenzene (petroleum refining), 1-ethyl-2-methylbenzene (petroleum refining), 1,2,4-trimethylbenzene (petroleum refining) and 1,2,3-trimethylbenzene (petroleum refining) with small contributions from ethyl benzene (petroleum refining), *m,p*-xylene (petroleum refining) and methacrolein (vehicle emission) as seen in Figure 4.29. Being the global leader in the petrochemical industry, ExxonMobil is Singapore's leading supplier of liquefied petroleum gas (LPG) and the world's leading supplier of jet fuel as well as the leading producer and marketer of lubricant [119]. ExxonMobil has two plants (Jurong and Jurong island) with a capacity of 592,000 barrels per day to produce fuels, lubricant base stock and chemical

feedstock [120]. Other than ExxonMobil, companies such as Singapore Refining Company [121] and Petrochemical Corporation of Singapore (Private) Limited [122] both have plants located on the Jurong Island as well. It should be noted that due to the concentration of VOCs emitted from such sources and the solubility of the said VOCs in rainwater would affect the ‘effective concentration’ observed through the analysis. Henceforth, some aromatic compounds might appear to have no contribution to the source in the PMF modeling. Methacrolein is known to be emitted from vehicle exhaust, seeing the long distance of Jurong Island to the sampling site, vehicle emission might be observed from the factor as well.

Figure 4.30. Factor 3: Manufacture of lacquers and paint.

The main contributors to Factor 3 are *n*-butyl acetate (lacquer production) with small contributions from ethyl benzene (paint), *m,p*-xylene (paint) and other C₉ aromatic compounds (solvent) as observed in Figure 4.30. Companies such as Trasco Coating Pte Ltd [123] and Nippon Paint Singapore [124] are some of the many lacquer and paint companies present in the Tuas industrial area which can result in the detection of the related VOCs in rainwater.

Main contributors to Factor 4 are ethyl benzene (petrol component), *m,p*-xylene (petrol component), *o*-xylene (petrol component) with smaller contributions from 1-ethyl-3-

methylbenzene (petrol component), 1-ethyl-2-methylbenzene (petrol component), 1,2,4-trimethylbenzene (petrol component), 1,2,3-trimethylbenzene (petrol component) as well as 2-methyl furan (Figure 4.31). ExxonMobil has 2 plants in Jurong and Jurong island [120], henceforth, the closer plant (Jurong) could have caused the evaporative emission observed in rainwater. In comparison to Factor 2, more ‘lighter’ aromatics like ethyl benzene and xylenes were allocated to Factor 4 which would support the idea of evaporative emissions. Other than ExxonMobil, smaller petrochemical companies are also located in the Tuas industrial area such as Neste Oil [125] and AP Oil International Limited [126]. 2-Methyl furan is most likely a ‘contaminant’ to this source because of its low concentration and a low percentage of contribution and with pharmaceutical companies in the area as explained in Factor 6.

Figure 4.31. Factor 4: Evaporative emissions.

The main contributors to Factor 5 are benzene (vehicle emission), ethyl benzene (vehicle emission), xylenes (vehicle emissions), some C₉ aromatic VOCs (vehicle emission, hexanal (vehicle emission), heptanal (vehicle emission), 2-methyl furan with some small contribution from methacrolein (vehicle emission) (Figure 4.32). Similar to Factor 4, 2-methyl furan could have been a ‘contaminant’ to the source of emission, or it is possible for 2-methyl

furan to be emitted from motor vehicles as well although it has not been observed in past research.

Seeing that the sampling site is situated close to the expressway, the detection of VOC vehicle emissions in rainwater would be expected, similar to that of VOCs modeling in the atmosphere previously attempted [37]. In 2014, the average annual kilometers traveled per motorcar in Singapore was 17,500 km, while other types of motor vehicles such as private hire buses can travel up to 54,400 km per year. Moreover, a total of 972,037 vehicles (private cars, other vehicles, taxi, buses, goods and other vehicles and motorcycles) were tabulated in Singapore [127], and there are also many heavy motor vehicles that transport goods from Malaysia into Singapore. Therefore, the emission from all vehicles can be immense in Singapore. Factor 5 was labeled as vehicle emission rather than Factor 4 as other aldehyde VOCs (hexanal, heptanal, and methacrolein) associated with vehicle emission were also detected which would be an indicator of the use of petrochemical products.

Figure 4.32. Factor 5: Vehicle Emission.

Main contributors to Factor 6 (Figure 4.33) are 2-methyl furan (pharmaceutical intermediate), methacrolein (chemical intermediate) with small contribution from benzene (used in pharmaceutical manufacture), 1-ethyl-4-methylbenzene (manufacture of other

chemicals/solvents), *m,p*-xylene (used in pharmaceutical industries/solvent), 1-ethyl-2-methylbenzene (manufacture of other chemicals/solvent), 1,2,4-trimethylbenzene (pharmaceutical intermediate) and 1,2,3-trimethylbenzene (solvent). 2-Methyl furan is the intermediate for manufacturing drugs like atropine, sodium acetate, furadantine, anisodamine, thiamine furan, vitamin B₁, and chloroquine. With several pharmaceutical companies, such as Pfizer [128], Novartis [129], GlaxoSmithKline [130] and Aventis Pharma [131] in the Tuas industrial area, the detection of 2-methyl furan in rainwater could possibly be traced back to these companies, although, the exact production volumes from such companies are not reported. Nonetheless, the other VOCs contributing to this factor could be used in the pharmaceutical process, henceforth, Factor 6 could be emissions from the pharmaceutical industry.

Figure 4.33. Factor 6: Pharmaceutical industry.

Primary contributors to Factor 7 (Figure 4.34) are hexanal (organic synthesis of plasticizer, rubber chemicals and resins) and small amounts of heptanal (organic synthesis), methacrolein (intermediate for polymethylmethacrylate), 2-methyl furan (production of other chemicals), xylenes (polyester resins/solvent/manufacture of other compounds), ethyl benzene (intermediate/solvent), 1-ethyl-2-methylbenzene (manufacture of plastic/solvent), 1,2,4-

trimethylbenzene (solvent) and 1,2,3-trimethylbenzene (solvent). Companies such as Teknor Apex [132], Eveready Manufacturing Pte Ltd [133] and even the Polyolefin Company (Singapore) Pte Ltd [134] produce polymers near the sampling site which may account for the VOCs apportioned to Factor 7.

Figure 4.34. Factor 7: Manufacture of polymer and relates.

Figure 4.35. Factor 8: Monomer production.

Main contributors to Factor 8 are methacrolein (intermediate of methyl methacrylate monomer) with a small contribution from 2-methyl furan (production of other compounds) and heptanal (production of other compounds) (Figure 4.32). Sumitomo Chemical Singapore (SCS), a subsidiary of Sumitomo Chemicals operates the largest integrated production of methyl methacrylate and its polymer (polymethylmethacrylate) in Asia with plants in Jurong

island (south of the sampling site) that produces a total of 223,000 million tons per year [135]. Methacrolein is an intermediate from the isobutylene oxidation to methacrylic acid which is then esterified to form methyl methacrylate [87]. Other companies that produce methyl methacrylate such as Lucite International also has an Alpha 1 MMA (methyl methacrylate) plant located in Jurong island [136]. Therefore, it would not be startling to the observed significant amounts of methacrolein in the rainwater collected in the western region of Singapore.

4.3.6. Significant implications of VOCs in Rainwater

The VOC concentrations in rainwater tested were much lower than the reported maximum contaminant level (MCL) or lethal dosage (LD_{50}) of any chemical tested which would indicate that no immediate risk would be caused by drinking rainwater. Out of the 28 VOCs studied, only trichloromethane (trihalomethanes, $80 \mu\text{g L}^{-1}$), benzene ($5 \mu\text{g L}^{-1}$), ethyl benzene ($700 \mu\text{g L}^{-1}$), styrene ($100 \mu\text{g L}^{-1}$), tetrachloroethylene ($5 \mu\text{g L}^{-1}$), toluene ($1000 \mu\text{g L}^{-1}$), trichloroethylene ($5 \mu\text{g L}^{-1}$) and xylenes ($10,000 \mu\text{g L}^{-1}$) have MCL set by the US EPA (United States Environmental Protection Agency) which are regulated in drinking water [137]. However, other than acute risk (lethal dosage), the hazard can come from the regular daily intake of such contaminated water leading to possible health hazards or even cancer risks with VOCs that are known or potentially carcinogenic. Unfortunately, the current research studies have yet to unveil the potential harm of small dosages VOCs consumed over time.

The maximum amount of VOCs consumed from liquid (water) is likely to be much lower than that taken in through breathing in from atmospheric gaseous sources. Therefore, the

potency of VOCs existing in ambient air possesses more health risks which may explain the more intensive research placed in studying different types of pollutants in ambient air. Nonetheless, the existence or detection of VOCs in rainwater indicates the fallout of VOCs from the ambient air, and it was evident through this study that the events or sources of emission can significantly affect the amount of VOCs measured. The likelihood of contamination of VOCs from rainwater to surface water would be minimal due to the large difference in concentration as discussed in Section 3.3.2 Yearlong statistical analysis, and because all surface water is treated before being consumed. Although much attention has been paid by the public and the government on the transboundary haze event caused by the burning of biomass in neighboring countries of Singapore, the largest concentration of VOCs detected in rainwater was most likely from the construction and renovation period at the sampling site. Therefore, more attention should perhaps be placed into the regulation of personalized anthropogenic activities such as construction that makes use of products that releases VOCs.

4.4. Conclusion

The concentration of 28 VOCs in rainwater of the western region of Singapore was studied through the use of PAT GC-MS during August 2015 to July 2016. A total of 476 rain samples were collected from 193 rain events in the year-long study. The data collected were treated to statistical analysis while trend analysis, correlation studies, and PMF modeling was employed to elucidate the likely sources of emission as well as the VOC's contribution to each individual factor resolved. Through the statistical calculations, methacrolein was found to have the highest mean (2072 ng L⁻¹) and maximum (43143 ng L⁻¹) concentration amongst the 28 VOCs tested. The detection frequency of VOCs above MRL was low for most, with

the exception being oxygenated VOCs which tend to have better water solubilities. Moreover, the acidic rainwater in Singapore can catalyze the formation of gem diols and enolate ions for some oxygenated VOCs which could have further improved their solubility and hence detectability in rainwater analysis. The concentrations determined in this study were mostly lower in comparison studies conducted in Japan and the USA. The difference in concentration was likely due to the different types of emission surrounding the site as well as the method used for VOCs analysis involved. Nonetheless, it was still found that the concentrations determined in the rainwater collected in Singapore were far below those in surface water as well as the total volatile organic carbon determined in previous studies.

The trend analysis revealed spikes in some VOCs with probable major traceable events such as the worst haze (September to October 2015) experienced by Singapore to date and the construction (March to May 2016) and renovation work happening at the sampling site. To simplify the trend analysis, VOCs were grouped into aromatic, oxygenated, halogenated and alkanes/alkenes for discussion and comparison. Similar trends were observed between VOCs within the same group as well as VOCs across different groups. Similar trends would suggest similar sources of emission for the VOCs in comparison, however, more statistical treatment was required to be applied to the data before any conclusion could be made. The different monsoon seasons experienced in Singapore were found to affect the amount of VOCs detected in the wet precipitate, with oxygenated compounds and some aromatic compounds showing higher concentrations during the inter-monsoon season where wind speeds are generally lower. The lower wind speed could decrease the dilution of VOCs in ambient air, hence increasing the concentration detected in rainwater through the fallout. An opposite trend was also observed for most aromatic VOCs where higher concentrations were found

during the monsoon season with larger wind speeds, which may indicate that the aromatic VOCs might have sources of emission from the back trajectory of these wind directions.

In addition, similar trends of VOCs toward meteorological data (PSI, PM, and carbon monoxide levels) during the haze months would suggest the VOCs contributions may have been increased by forest burning in neighboring countries. Detailed literature studies suggested some likely sources of emission for VOCs showing similar trends were from different types of material burning (e.g., peat, hemicellulose). The pollution from biomass burning is not just limited to VOCs but also on the secondary pollutants formed from the emitted VOCs and NO_x (tropospheric ozone). Correlation calculations were conducted to confirm further the trends observed for different VOCs which help in the PMF modeling performed at a later stage. In conclusion, the correlation of VOCs in rainwater was lesser and weaker than correlations calculated for VOCs in ambient air sampled close to the sampling site.

More aromatic VOC pairs and cross-group VOC pairs showed strong positive correlations indicating that shared sources of emission of aromatic VOCs and the cross-group VOCs exist in the vicinity of the sampling site. PMF modeling was performed with the yearlong correlation as a guideline, and eight factors were resolved from the calculation. VOCs found in rainwater could be traced back to petroleum refinery, evaporative emission, vehicle emission, the pharmaceutical industry, monomer production, synthesis of flavor and fragrances, manufacture of lacquers and paints as well as manufacture of polymers. The companies and likely location of such emission were given as examples, and most of the activities were traced back to the anthropogenic sites close to the sampling site such as Jurong Island, Tuas industrial area, and the expressway situated close to the sampling site.

The health implication of the VOCs detected in rainwater was minimal as the concentration detected in rainwater were low and well below the MCL set by EPA for drinking water. However, the risk of long-term exposure to VOCs in water sources has yet to be studied in detail. Therefore, the risk of drinking from such water sources should not be entirely eliminated. In contrast to the attention paid by the general public on transboundary haze, more VOCs were detected in rainwater due to probable localized events (construction and renovation) at the sampling site. The time taken for transport as well as the dilution that could have occurred with transporting across boundaries could have decreased the effective concentration observed in the rainwater samples collected. The contamination of VOCs in rainwater to surface water would also be low due to the low concentration, however, the types of VOCs would increase as most VOCs found in surface water are halogenated or aromatic compounds.

4.5. References

1. Garland, J.A., *Dry and wet removal of sulphur from the atmosphere*. Atmospheric Environment (1967), 1978. **12**(1): p. 349-362.
2. McVeety, B.D. and R.A. Hites, *Atmospheric deposition of polycyclic aromatic hydrocarbons to water surfaces: A mass balance approach*. Atmospheric Environment (1967), 1988. **22**(3): p. 511-536.
3. J. Williams. and R. Koppmann., *Volatile Organic Compounds in the Atmosphere: An Overview*. 2007: Blackwell Publishing.
4. Kawamura, K. and I.R. Kaplan, *Organic compounds in the rainwater of Los Angeles*. Environmental Science & Technology, 1983. **17**(8): p. 497-501.
5. Grosjean, D. and B. Wright, *Carbonyls in urban fog, ice fog, cloudwater and rainwater*. Atmospheric Environment (1967), 1983. **17**(10): p. 2093-2096.

6. Ligoeki, M.P., C. Leuenberger, and J.F. Pankow, *Trace organic compounds in rain—II. Gas scavenging of neutral organic compounds*. Atmospheric Environment (1967), 1985. **19**(10): p. 1609-1617.
7. Manabu Igawa, Norhide Nakada, and H. Okochi, *Determination of Volatile Organic Compounds in Rainwater and the Dominant Factors of their Concentrations*. Journal of Japan Society of Atmospheric Environment, 1998. **34**: p. 211-218.
8. McKone, T.E., *Human exposure to volatile organic compounds in household tap water: the indoor inhalation pathway*. Environmental science & technology, 1987. **21**(12): p. 1194-1201.
9. Tancrede, M., Y. Yanagisawa, and R. Wilson, *Volatilization of volatile organic compounds from showers—I. Analytical method and quantitative assessment*. Atmospheric Environment. Part A. General Topics, 1992. **26**(6): p. 1103-1111.
10. Jo, W.K., C.P. Weisel, and P.J. Liroy, *Routes of chloroform exposure and body burden from showering with chlorinated tap water*. Risk Analysis, 1990. **10**(4): p. 575-580.
11. Brown, H.S., D.R. Bishop, and C.A. Rowan, *The role of skin absorption as a route of exposure for volatile organic compounds (VOCs) in drinking water*. American Journal of Public Health, 1984. **74**(5): p. 479-484.
12. Willey, J.D., et al., *Rainwater dissolved organic carbon: Concentrations and global flux*. Global Biogeochemical Cycles, 2000. **14**(1): p. 139-148.
13. McNall, S.G., *Rapid Climate Change: Causes, Consequences, and Solutions*. 2012: Taylor & Francis.
14. Pan, Y., et al., *Study on dissolved organic carbon in precipitation in Northern China*. Atmospheric Environment, 2010. **44**(19): p. 2350-2357.
15. Robert J. Kieber, et al., *Dissolved organic carbon and organic acids in coastal New Zealand rainwater*. Atmospheric Environment, 2002. **36**: p. 3557-3563.

16. Yan, G. and G. Kim, *Dissolved organic carbon in the precipitation of Seoul, Korea: Implications for global wet depositional flux of fossil-fuel derived organic carbon*. Atmospheric Environment, 2012. **59**: p. 117-124.
17. Coelho, C.H., et al., *Dissolved organic carbon in rainwater from areas heavily impacted by sugar cane burning*. Atmospheric Environment, 2008. **42**(30): p. 7115-7121.
18. Avery, J.G.B., et al., *Assessment of rainwater volatile organic carbon in southeastern North Carolina, USA*. Atmospheric Environment, 2009. **43**: p. 2678-2681.
19. Campos, M.L.A.M., et al., *Dissolved organic carbon in rainwater: Glassware decontamination and sample preservation and volatile organic carbon*. Atmospheric Environment, 2007. **41**(39): p. 8924-8931.
20. *Our Water, Our Future*, in *Public Utilities Board of Singapore*, P.U.B.o. Singapore, Editor. 2016, Public Utilities Board of Singapore: Singapore.
21. Muraleedharan, T.R., et al., *Chemical characterisation of the haze in Brunei Darussalam during the 1998 episode*. Atmospheric Environment, 2000. **34**(17): p. 2725-2731.
22. G.P. Hu, R. Balasubramanian, and C.D. Wu, *Chemical characterization of rainwater at Singapore*. Chemosphere, 2003. **51**: p. 747-755.
23. R. Balasubramanian, T. Victor, and R. Begum, *Impact of biomass burning on rainwater acidity and composition in Singapore*. Journal of Geophysical Research 1999. **104**: p. 26881-26890.
24. R. Balasubramanian, T. Victor, and N. Chun, *Chemical and statistical analysis of precipitation in Singapore*. Water, Air and Soil Pollution, 2001. **130**: p. 451-456.
25. He, J. and R. Balasubramanian, *Semi-volatile organic compounds (SVOCs) in ambient air and rainwater in a tropical environment: Concentrations and temporal and seasonal trends*. Chemosphere, 2010. **78**(6): p. 742-751.
26. MSS. *Climate of Singapore*. 2015 [cited 7 November 2016]; Available from: <http://www.weather.gov.sg/climate-climate-of-singapore/>.

27. Jenner, L. *El Niño Brought Drought and Fire to Indonesia*. 2016.
28. Mersmann, K. *Severe 2015 Indonesian Fire Season Linked to El Niño drought*. 2016 [cited 23 November 2016]; Available from: <https://www.nasa.gov/feature/Goddard/2016/severe-2015-indonesian-fire-season-linked-to-el-nino-drought>.
29. Page, S.E., et al., *The amount of carbon released from peat and forest fires in Indonesia during 1997*. *Nature*, 2002. **420**(6911): p. 61-65.
30. Blake, D., A.L. Hinwood, and P. Horwitz, *Peat fires and air quality: Volatile organic compounds and particulates*. *Chemosphere*, 2009. **76**(3): p. 419-423.
31. Khew, C. *Haze: One-hour PM2.5 reading soars to 442*. *The Straits Times*, 2015.
32. Chan, F. *Indonesia set to evacuate kids in worst haze hit areas*. *The Straits Times*, 2015.
33. Spokas, K.A., et al., *Qualitative analysis of volatile organic compounds on biochar*. *Chemosphere*, 2011. **85**(5): p. 869-882.
34. Paatero, P. and U. Tapper, *Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values*. *Environmetrics*, 1994. **5**(2): p. 111-126.
35. Norris, G., et al., *EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide*. 2014, U.S. Environmental Protection Agency: Washington, DC, USA.
36. Xiang, Y., et al., *Development of a methodology examining the behaviours of VOCs source apportionment with micro-meteorology analysis in an urban and industrial area*. *Environmental Pollution*, 2012. **162**: p. 15-28.
37. Wong., G.K.S., *The analysis and monitoring of atmospheric volatile organic compounds via thermal desorption gas chromatography mass spectrometry*, in *School of Physical and Mathematical Sciences (SPMS)*. 2014, Nanyang Technological University: Singapore.
38. Trenberth, K.E., *The Definition of El Niño* *Bulletin of the American Meteorological Society*, 1997. **78**(12): p. 2771-2777.
39. Cole, S. and E. Gray *NASA Examines Global Impacts of the 2015 El Niño*. 2015.
40. Bromwich, J. *Understanding El Niño*. *The New York Times*, 2015.

41. *Climate of Singapore*. [cited 22 November 2016]; Available from: <http://www.weather.gov.sg/climate-climate-of-singapore/>.
42. Jayne, J.T., et al., *Uptake of gas-phase aldehydes by water surfaces*. The Journal of Physical Chemistry, 1992. **96**(13): p. 5452-5460.
43. Nikolaou, A.D., et al., *Determination of volatile organic compounds in surface waters and treated wastewater in Greece*. Water Research, 2002. **36**(11): p. 2883-2890.
44. Phelan, D.J., et al., *Assessment of Volatile Organic Compounds in Surface Water at Canal Creek, Aberdeen Proving Ground, Maryland*, U.S.G. Survey, Editor. 2001, U.S. Geological Survey: Baltimore, Maryland, USA.
45. *Joint Assessment of Commodity Chemicals No. 28 Ethyl Acrylate CAS No. 140-88-5*, E.C.f.E.a.T.o. Chemicals, Editor. 1994, European Centre for Ecotoxicology and Toxicology of Chemicals Brussels, Belgium.
46. *Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 19*. 2015, Washington, DC, United States: National Academy Press
47. *Toxicological Profile for Ethylbenzene*, U.S.D.o.H.a.H. Services, Editor. 2010, U.S. Department of Health and Human Services: United States
48. *Acute Exposure Guideline Levels for Selected Airborne Chemicals, Volume 9*. 2010, Washinton, DC, United States: The National Academies Press.
49. Reimann, S. and A.C. Lewis, *Anthropogenic VOCs*, in *Volatile Organic Compounds in the Atmosphere*. 2007, Blackwell Publishing Ltd. p. 33-81.
50. *HSDB: ISOPRENE*. [cited 22 November 2016]; Available from: <https://toxnet.nlm.nih.gov/cgi-bin/sis/search2/f?./temp/~FX3QCC:3>.
51. *Aromatics - Petrochemical products*. [cited 17 November 2016]; Available from: http://www.petrochemistry.eu/about-petrochemistry/products.html?filter_id=20.
52. *Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 13*. 2013, Washington, DC, United States: The National Academies Press.

53. *Locating and estimating air emissions from sources of styrenes*, O.o.A.Q.P.a. Standards, Editor. 1993, United States Environmental Protection Agency: United States.
54. *Heptanal (aldehyde C-7)*. [cited 17 November 2016]; Available from: <http://www.thegoodscentscompany.com/data/rw1014291.html>.
55. *Hexanal (aldehyde C-6)*. [cited 17 November 2016]; Available from: <http://www.thegoodscentscompany.com/data/rw1011072.html>.
56. *Tetrachloroethylene (CAS Reg. No. 127-18-4) Interim Acute Exposure Guidelines Levels (AEGLs)*, U.S.D.o. Energy, Editor. 2001: United States.
57. *Toxicological Review of Trichloroethylene Chapter 2*, U.S.E.P. Agency, Editor. 2011, United States Environmental Protection Agency: United States.
58. *HSDB: N-BUTYL ACETATE*. [cited 22 November 2016]; Available from: <https://toxnet.nlm.nih.gov/cgi-bin/sis/search2/f?./temp/~u1OsUU:3>.
59. *Methyl Isobutyl Ketone (Hexone)*. 2016 [cited 22 November 2016]; Available from: <https://www3.epa.gov/airtoxics/hlthef/methyl-k.html>.
60. Simoneit, B.R., *Biomass burning—a review of organic tracers for smoke from incomplete combustion*. Applied Geochemistry, 2002. **17**(3): p. 129-162.
61. Levine, J.S., *The 1997 fires in Kalimantan and Sumatra, Indonesia: Gaseous and particulate emissions*. Geophysical Research Letters, 1999. **26**(7): p. 815-818.
62. dos Santos, C.Y.M., D. de Almeida Azevedo, and F.R. de Aquino Neto, *Selected organic compounds from biomass burning found in the atmospheric particulate matter over sugarcane plantation areas*. Atmospheric Environment, 2002. **36**(18): p. 3009-3019.
63. Pouwels, A.D., et al., *Characterisation of beech wood and its holocellulose and xylan fractions by pyrolysis-gas chromatography-mass spectrometry*. Journal of Analytical and Applied Pyrolysis, 1987. **11**: p. 417-436.
64. Burnett, L.W., et al., *Production of 2-Methylfuran by Vapor-Phase Hydrogenation of Furfural*. Industrial & Engineering Chemistry, 1948. **40**(3): p. 502-505.

65. Thunwadee, S., *Atmospheric chemistry of saccharides and furfural*. 2010, University of East Anglia: United Kingdom.
66. Koppmann, R., K.v. Czapiewski, and J. Reid, *A review of biomass burning emissions, part I: gaseous emissions of carbon monoxide, methane, volatile organic compounds, and nitrogen containing compounds*. *Atmospheric Chemistry and Physics Discussions*, 2005. **5**(5): p. 10455-10516.
67. Wang, Z., *Reppe Carbonylation*, in *Comprehensive Organic Name Reactions and Reagents*. 2010, John Wiley & Sons, Inc.
68. McKenzie, L.M., et al., *Measurement and Modeling of Air Toxins from Smoldering Combustion of Biomass*. *Environmental Science & Technology*, 1995. **29**(8): p. 2047-2054.
69. Hadi, A., et al., *Gas emissions in production and use of biochar in peatlands of Kalimantan*.
70. *Updates - Global Fire Emission Database*. 2015 [cited 30 December 2015; Available from: <http://www.globalfiredata.org/updates.html>].
71. *Benzene (CAS Reg. No. 71-43-2) Interim Acute Exposure Guideline Levels (AEGLs)*, U.S.E.P. Agency, Editor. 2009, United States Environmental Protection Agency: United States.
72. *Methyl Methacrylate (CAS Reg. No. 80-62-6) Interim Acute Exposure Guideline Levels*, U.S.E.P. Agency, Editor. 2008, United States Environmental Protection Agency: United States.
73. Waldemar, L., M.G. Alexander, and S. Harold, *Production of xylene*. 1965, Google Patents.
74. Lien, A.P. and D.A. Mccaulay, *Ethyltoluene production*. 1955, Google Patents.
75. *Chemicals in the Environment: 1,2,4-Trimethylbenzene (CAS NO. 95-63-6)*, U.S.E.P. Agency, Editor. 1994, United States Environmental Protection Agency: United States.
76. Tremblay, J.-F., *MAKING AROMATICS IN SINGAPORE*. *Chemical & Engineering News Archive*, 2011. **89**(38): p. 18-19.
77. Le, Q.N., *Production of ethylbenzene*. 1992, Google Patents.

78. Ho, K.F., et al., *Seasonal and diurnal variations of volatile organic compounds (VOCs) in the atmosphere of Hong Kong*. Science of The Total Environment, 2004. **322**(1–3): p. 155-166.
79. Hart, K.M., et al., *The occurrence and the fate of organic pollutants in the atmosphere*. Water, Air, and Soil Pollution, 1993. **68**(1): p. 91-112.
80. Greenberg, J., et al., *Hydrocarbon and carbon monoxide emissions from biomass burning in Brazil*. Journal of Geophysical Research: Atmospheres (1984–2012), 1984. **89**(D1): p. 1350-1354.
81. *Chemistry in the sunlight*. Earth Observatory - Where every day is Earth Day [cited 30 November 2016]; Available from: http://earthobservatory.nasa.gov/Features/ChemistrySunlight/chemistry_sunlight3.php.
82. Som, D., et al., *Studies on commuters' exposure to BTEX in passenger cars in Kolkata, India*. Science of The Total Environment, 2007. **372**(2–3): p. 426-432.
83. *Methacrolein*, in *Hawley's Condensed Chemical Dictionary*. 2007, John Wiley & Sons, Inc.
84. *Chapter VII Process and Economics Overview*. 2015 [cited 28 November 2016]; Available from: <http://www.methanolmsa.com/wp-content/uploads/2015/07/Chapter-VIII-Process-and-Economic-Overview.pdf>.
85. Verschueren, K., *Handbook of environmental data on organic chemicals*. 1983: Van Nostrand Reinhold Co.
86. *2-Methylfuran Market: Global Industry Analysis and Opportunity Assessment 2016-2026*. 2016 [cited 28 November 2016; Available from: <http://www.futuremarketinsights.com/reports/2-methylfuran-market>.
87. *IARC Monographs on the evaluation of the carcinogenic risk of chemicals to humans: Some industrial chemicals and dyestuff*. Vol. 29. 1982, Lyon, France: World Health Organization International Agency For Research On Cancer.
88. O'Neil, M., *The Merck Index*. 15 ed. 2013, Cambridge, UK: Royal Society of Chemistry.

89. Burdock, G.A., *Fenaroli's Handbook of Flavor Ingredients*. 6 ed. 2010, Boca Raton, FL CRC Press.
90. Helmig, D., et al., *Biogenic volatile organic compound emissions (BVOCs) I. Identifications from three continental sites in the U.S.* Chemosphere, 1999. **38**(9): p. 2163-2187.
91. Duke, J.A., *Handbook of phytochemical constituents of GRAS herbs and other economic plants*. 1992, Florida, USA: CRC Press.
92. Schauer, J.J., et al., *Measurement of Emissions from Air Pollution Sources. 2. C1 through C30 Organic Compounds from Medium Duty Diesel Trucks*. Environmental Science & Technology, 1999. **33**(10): p. 1578-1587.
93. Fraser, M.P., G.R. Cass, and B.R.T. Simoneit, *Gas-Phase and Particle-Phase Organic Compounds Emitted from Motor Vehicle Traffic in a Los Angeles Roadway Tunnel*. Environmental Science & Technology, 1998. **32**(14): p. 2051-2060.
94. Grosjean, D., E. Grosjean, and A.W. Gertler, *On-Road Emissions of Carbonyls from Light-Duty and Heavy-Duty Vehicles*. Environmental Science & Technology, 2001. **35**(1): p. 45-53.
95. Guenther, A., P. Zimmerman, and M. Wildermuth, *Natural volatile organic compound emission rate estimates for U.S. woodland landscapes*. Atmospheric Environment, 1994. **28**(6): p. 1197-1210.
96. *n*-Butylacetate, in *The Merck Index*. 2016.
97. Henderson, R.F., *Aromatic Hydrocarbons—Benzene and Other Alkylbenzenes*, in *Patty's Toxicology*. 2001, John Wiley & Sons, Inc.
98. *Toxicological Profile for Xylenes*. 2007 [cited 28 November 2016]; Available from: <https://www.atsdr.cdc.gov/ToxProfiles/tp.asp?id=296&tid=53>.
99. Graedel, T.E., 3 - *HYDROCARBONS*, in *Chemical Compounds in the Atmosphere*. 1978, Academic Press. p. 50-157.
100. *p*-xylene, in *Hawley's Condensed Chemical Dictionary*. 2007, John Wiley & Sons, Inc.

101. Yao, Z., et al., *On-road emission characteristics of VOCs from diesel trucks in Beijing, China*. Atmospheric Environment, 2015. **103**: p. 87-93.
102. Tang, S., et al., *Unregulated Emissions from a Heavy-Duty Diesel Engine with Various Fuels and Emission Control Systems*. Environmental Science & Technology, 2007. **41**(14): p. 5037-5043.
103. Schauer, J.J., et al., *Measurement of Emissions from Air Pollution Sources. 5. C1–C32 Organic Compounds from Gasoline-Powered Motor Vehicles*. Environmental Science & Technology, 2002. **36**(6): p. 1169-1180.
104. *Xylene*, in *Hawley's Condensed Chemical Dictionary*. 2007, John Wiley & Sons, Inc.
105. *m-xylene*, in *Hawley's Condensed Chemical Dictionary*. 2007, John Wiley & Sons, Inc.
106. *Heptanal*, in *Hawley's Condensed Chemical Dictionary*. 2007, John Wiley & Sons, Inc.
107. Payne, L.S., *Improvements in and relating to aldol condensation*. 1990, Google Patents.
108. Kohlpaintner, C., et al., *Aldehydes, Aliphatic*, in *Ullmann's Encyclopedia of Industrial Chemistry*. 2000, Wiley-VCH Verlag GmbH & Co. KGaA.
109. *o-xylene*, in *Hawley's Condensed Chemical Dictionary*. 2007, John Wiley & Sons, Inc.
110. *Pollutant Fact Sheet*. [cited 25 November 2016]; Available from: <http://www.sepa.org.uk/environment/environmental-data/spri/>.
111. *Pseudocumene*, in *Hawley's Condensed Chemical Dictionary*. 2007, John Wiley & Sons, Inc.
112. *Encyclopedia of Occupational Health and Safety*. 1983, Geneva, Switzerland: International Labor Office.
113. Harley, R.A., M.P. Hannigan, and G.R. Cass, *Respeciation of organic gas emissions and the detection of excess unburned gasoline in the atmosphere*. Environmental Science & Technology, 1992. **26**(12): p. 2395-2408.
114. Jüttner, F., *Emission of aromatic hydrocarbons and aldehydes into the water by a four-stroke outboard motor: Quantitative measurements*. Chemosphere, 1994. **29**(2): p. 191-200.

115. *Firmenich Locations*. 2015 [cited 25 November 2016]; Available from: http://www.firmenich.com/en_INT/locations.html.
116. *Locations*. 2016 [cited 25 November 2016]; Available from: <https://www.givaudan.com/locations>.
117. *Contact Us*. 2016 [cited 25 November 2016].
118. Pohanish, R.P., T, in *Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens (Sixth Edition)*. 2012, William Andrew Publishing: Oxford. p. 2483-2677.
119. *Products and Services*. [cited 28 November 2016]; Available from: <http://www.exxonmobil.com.sg/AP-English/ps.aspx>.
120. *About Us*. [cited 28 November 2016]; Available from: <http://www.exxonmobil.com.sg/AP-English/about.aspx>.
121. *Singapore Refining Company*. [cited 29 November 2016]; Available from: <http://www.src.com.sg/>.
122. *Petrochemical Corporation of Singapore* 2016 [cited 29 November 2016]; Available from: <http://www.pcs.com.sg/home/home.asp>.
123. *Contact Us*. [cited 29 November 2016]; Available from: <http://www.trasco.com.sg/Contact-Us/contact-us.html>.
124. *Nippon Paint Singapore Address*. 2016 [cited 29 November 2016]; Available from: <http://www.nipponpaint.com.sg/information/contact-us/>.
125. *Products*. [cited 29 November 2016]; Available from: <https://www.neste.com/en/companies/products>.
126. *AP Oil International Limited*. 2016 [cited 29 November 2016]; Available from: <http://www.apoil.com.sg/products/prodlist.aspx>.
127. *Singapore Land Transport Statistics In Brief 2015*. 2015 [cited 28 November 2016]; Available from:

<https://www.lta.gov.sg/content/dam/ltaweb/corp/PublicationsResearch/files/FactsandFigures/Statistics%20in%20Brief%202015%20FINAL.pdf>.

128. *About Pfizer*. 2016 [cited 29 November 2016]; Available from: <http://www.pfizer.com.sg/about-pfizer>.
129. *Office Location*. 2016 [cited 29 November 2016]; Available from: https://www.novartis.com/about-us/contact/office-locations?tid=All&name_list=SG.
130. *Sites*. 2015 [cited 29 November 2016]; Available from: <https://sg.gsk.com/en-sg/about-us/sites/>.
131. *Sanofi in Singapore*. 2016 [cited 29 November 2016]; Available from: <http://www.sanofi.com.sg/l/sg/en/layout.jsp?scat=F057F6BD-4556-4D35-9A1A-D2AAADEA0519>.
132. *About Teknor Apex*. 2016 [cited 29 November 2016]; Available from: <https://www.teknorapex.com/about>.
133. *Eveready Manufacturing Pte Ltd*. 2008 [cited 29 November 2016]; Available from: <http://www.eveready-mfg.com/contact.htm>.
134. *Index*. 2015 [cited 29 November 2016]; Available from: <https://www.tpc.com.sg/>.
135. *MMA Monomer*. 2016 [cited 28 November 2016]; Available from: <https://scs-chem.com.sg/our-plants/mma-manufacturing-plant/>.
136. *Lucite International* [cited 28 November 2016]; Available from: <https://www.fgould.com/asia/projects/lucite-international-alpha-1-mma-plant-singapore/>.
137. *Table of Regulated Drinking Water Contaminants*. 2016 [cited 29 November 2016]; Available from: <https://www.epa.gov/ground-water-and-drinking-water/table-regulated-drinking-water-contaminants#one>.

Removal of Volatile Organic Compounds (VOCs) from Water Using Mixtures of Olive Oil, Lecithin, and Vitamin E as Phase Transfer Agents

5.1. Introduction

Approximately 2.5% of the world's water supply is freshwater, but most of it is locked in ice caps, glaciers, permanent snow or stored underground [1]. Water purified from freshwater and alternate sources in areas lacking supplies is strictly regulated to safeguard the quality of drinking water. Although the amount of trihalomethanes (THMs), a type of disinfectant byproduct from the chlorination process, have to meet requirements set out by governing bodies [2, 3], exceptions were found in preceding papers where several tap water samples exceeded the specified limit [4, 5]. THMs that are known to be cytotoxic or carcinogenic include chloroform and bromodichloromethane [6]. They are part of a bigger group, volatile organic compounds (VOCs), characterized by their low boiling point and high mobility, increasing their potency and problems caused. The risk of VOCs present in water for consumption is not limited to ingestion alone as exposure through inhalation is very possible when participating in activities like showering [7-9]. One study demonstrated that the dosage of chloroform and the associated cancer risk from 10 minutes of showering could be greater than or equal to that from the daily water intake [9].

The amount of THMs in drinking water can be reduced by introducing coagulation before chlorination to remove chlorine sensitive organic compounds and the use of granular activated carbon (GAC), air stripping after chlorination for adsorption or purging [10-12].

These methods have since been enhanced, and new approaches targeting THM removal which include membrane nanofiltration, carbon nanotubes, and combination techniques have been explored [13-16]. Systems such as GAC and nanofiltration though effective, have shortcomings associated with bacteria build up, fouling, the relatively high cost of installation and operation [17, 18]. Other than THMs, other VOCs with adverse effects when consumed such as styrene and formaldehyde have also been detected in drinking water due to migration from storage materials [19-21], while industrial chemicals like tetrachloroethylene can make their way into groundwater through improper waste disposal [22]. For these reasons, new methods for removing VOCs including THMs using natural and low-cost materials should be examined. Lecithin, a natural emulsifier that can be obtained from soy and eggs, had been reported to form organogels and microemulsions with aid from co-surfactants under certain conditions and has been used as a form of drug delivery by encapsulating organic compounds [23-25]. The encapsulation ability of lecithin requires the presence of additional compounds as it does not spontaneously form micelles in water but packs into a highly stable lamellar liquid crystalline phase [26]. Nevertheless, the formation of an emulsion with lecithin can be achieved in several different ways. In this research, the possibility of using lecithin assisted with non-toxic natural organic materials such as olive oil and vitamin E to remove different classes of VOCs including THMs from water was investigated.

5.2. Experimental

Two approaches for the removal of VOCs from water utilizing lecithin were examined. The first procedure involved the use of an organic phase (olive oil) in a phase transfer step initially proposed for the transfer of gold nanoparticles [27], while the second method

involved the use of encapsulated vitamin E [28] as a foundation for emulsion formation. These methodologies were considered because the supporting materials involved are food or supplements that are safe for use and relatively low in cost. The effectiveness of the purification processes was ascertained by comparing the amount of VOCs in a blank with the amount of VOCs in samples subjected to the water purification methods, with quantification carried out by purge-and-trap gas chromatography-mass spectrometry (PAT GC-MS).

5.2.1. Materials

Lecithin (refined) and DL- α -tocopherol (vitamin E, 97%) used in the experiments were obtained from Alfa Aesar while olive oil (100%) was purchased from a local food supplier. Neat reference chemicals of internal/surrogate standards and VOCs used to test the efficiency of the purification processes were purchased from Alfa Aesar, Sigma-Aldrich, Merck, VWR, Fluka, Acros Organics, and TCI with purity greater than 95% (Appendix A.1). Two stock solutions of the internal standards and VOCs tested (1 mg mL^{-1}) were made by diluting neat chemicals with Pestinorm PAT grade methanol from VWR. Calibration curves used to quantify the relative integrated areas were prepared by injecting 2 – 10 μL of diluted stock solutions into ultrapure water (Millipore Milli-Q Integral 5) to achieve an internal standard concentration of $5 \text{ }\mu\text{g L}^{-1}$ and calibration range of 0.25 - 100 $\mu\text{g L}^{-1}$. All samples tested contained $5 \text{ }\mu\text{g L}^{-1}$ of the internal standard for quantitative analysis.

5.2.2. Sample preparation

5.2.2.1. Lecithin with olive oil

Samples were prepared by weighing lecithin (0.01 – 100 mg) into a 40 mL amber glass vial with an open top cap sealed with septum before the addition of 20 mL of ultrapure water, 4 μL of diluted stock solution (200 mg L^{-1}), a stirrer bar and 5 mL of olive oil. The vial was

stirred at room temperature for 30 min, and samples were further diluted to their final concentrations of $15 \mu\text{g L}^{-1}$ for preliminary studies and $20 \mu\text{g L}^{-1}$ for optimization studies after removal of the olive oil layer if present. A blank and a control sample were prepared in similar fashion with the absence of lecithin and lecithin/olive oil respectively, for comparison. Samples and blanks in the preliminary studies were centrifuged after the removal of the olive oil layer using a Sorvall Lynx 6000 centrifuge (Thermo Scientific) two times at 23,000 rpm, while no further treatment was performed with samples and blanks in the optimization studies. Analysis of the samples was done by a PAT GC-MS system described in the sample analysis section.

5.2.2.2. Lecithin with vitamin E

Lecithin encapsulated vitamin E micelles were first prepared by slow rotatory evaporation of 2 mL chloroform containing weighed vitamin E (0.01 – 0.10 g) and lecithin (0.05 – 0.10 g) in a 50 mL round bottom flask prior to drying under vacuum overnight. Into the round bottom flask, 20 mL of ultrapure water spiked with 4 μL of diluted stock solution (200 mg L^{-1}) was stirred or sonicated at 40 °C for 1 h in the preliminary studies and only stirred at 40 °C for 1 h for optimization studies. Water samples were centrifuged two times at 23,000 rpm for 20 min using a Sorvall Lynx 6000 centrifuge. Similar treatment was performed on the blank prepared without lecithin and vitamin E while the final dilution was performed on the samples and blank to achieve their final concentrations of $10 \mu\text{g L}^{-1}$ for sonicated samples and $20 \mu\text{g L}^{-1}$ for stirred samples. Analysis of the samples was also performed by a PAT GC-MS system described in the sample analysis section.

5.2.3. Sample analysis

Samples were analysed with the method developed in Chapter 2, and the solvent delay was set to 7 min for lecithin/olive oil samples and 11.5 min for lecithin/vitamin E samples. The data obtained were processed via the Environmental data analysis program.

5.3. Results and discussion

5.3.1. Lecithin with olive oil

5.3.1.1. Preliminary studies

PAT GC-MS analysis of VOC residues remaining in the aqueous layer after treatment with lecithin and olive indicated a reduction of between 66-71% when compared with a control blank without olive oil and lecithin (Table 5.1).

The bulk decrease in the VOC residues concentration below that of the blank was mainly attributed to the presence of olive oil, while a small further increment of 9-14% in the total residual VOCs reduction was caused by the addition of 250 ppm and 5000 ppm of lecithin. Olive oil alone was observed to be effective in lowering the concentration of all VOCs in the aqueous phase through solvent extraction with the exception of hexanal. Hexanal is naturally present in olive oil [29]. Thus it was found to be added to the treated water instead of being removed from the water samples. The proposed use of edible oil for the removal of VOCs, though uncommon, has been reported in the past where sunflower oil was utilized in a membrane assisted solvent extraction (MASX) system for VOCs removal from groundwater with a semi-permeable membrane that acted as a barrier between the contaminated water and oil [30]. The theoretical concentration of residual VOCs in the aqueous layer of the control blank without olive oil and lecithin should have been $15 \mu\text{g L}^{-1}$ after dilution (Table 5.1).

Table 5.1. Preliminary study of VOC residues detected in the aqueous phase after 0.5 h of stirring with lecithin/olive oil.
 * indicates concentration below the detection limit (DL), ^ indicates concentration below minimal reporting level (MRL), N.D. stands for not detected.
 Percentage reduction comparisons were performed by comparing samples with the control blank without olive oil and lecithin.

No.	Control		Olive oil			
	Blank		0 ppm Lecithin		250 ppm Lecithin	
	Residue ($\mu\text{g L}^{-1}$)		Residue ($\mu\text{g L}^{-1}$)	% Reduction	Residue ($\mu\text{g L}^{-1}$)	% Reduction
Aldehydes, ketones and furan						
1	10.65		22.39	(-110%)	15.83	(-49%)
2	9.41		1.29	86%	1.24	87%
3	4.58		0.94*	79%	0.83*	82%
4	2.43		N.D.	100%	N.D.	100%
5	8.98		2.83	68%	2.58	71%
6	10.44		7.27	30%	6.16	41%
7	1.22		0.42^	66%	0.41^	66%
Aromatic compounds						
8	1.26		0.32^	75%	0.30^	76%
9	0.72		0.63	13%	0.64	11%
10	1.08		0.61	44%	0.64	41%
11	0.76^		0.34^	55%	0.35^	54%
12, 13	0.55^		0.47^	15%	0.48^	13%
14	0.73^		0.39^	47%	0.41^	44%
15	7.77		1.72^	78%	1.65^	79%
Esters						
16	7.28		1.36	81%	1.34	82%
17	7.76		3.42	56%	3.1	60%
18	8.92		3.44	61%	3.16	65%
19	7.33		1.92	74%	1.71	77%
Halogenated compounds						
20	2.98		0.29*	90%	0.28*	91%
21	4.12		0.57^	86%	0.56^	86%
22	6.71		0.61*	91%	0.62*	91%
23	2.05		0.28*	86%	0.25*	88%
24	0.54^		N.D.	100%	N.D.	100%
25	0.41^		N.D.	100%	0.37^	10%
Sum of VOCs		105.69	45.16	57%	36.40	66%
					31.08	71%

However, all compounds were detected at concentrations lower than this because of the natural ability of the VOCs to escape from the water during the sample preparation steps.

The subjection of water samples to centrifugation for the removal of lecithin could also have encouraged the discharge of VOCs. The use of centrifugation was essential in the removal of lecithin prior to the aqueous layer analysis as the presence of lecithin residues caused excessive bubbling of water samples in the sparger of the PAT that resulted in pressure build up in the system leading to automated aborting of the sample run. Henceforth, alternative methods of removing lecithin were considered. While exploring other methods for removing lecithin in replacement of centrifugation, it was noted in the investigations that when high concentrations of lecithin were used, some lecithin migrated from the aqueous phase into the olive oil layer causing the olive oil to turn cloudy (Figure 5.1).

Figure 5.1. 5000 ppm lecithin sample (left) and 0 ppm lecithin sample (right) after 0.5 h of stirring.

Since the significant increment of lecithin (5000 ppm) did not substantially aid in the removal of VOCs, lower concentrations of lecithin were considered in the optimization experiments to make use of the migration of lecithin into the olive oil as a form of lecithin removal. Another set of experiments with the same parameters were performed with pentane in place of olive oil, and similar reduction properties of the VOCs were perceived, but visible migration of lecithin into the organic layer only occurred when olive oil was used (Appendix

D.1). The ease of migration in olive oil could be due to the better interaction between the larger molecules of oil and lecithin in comparison with pentane and lecithin. For this reason, olive oil was used in the optimization trials to exploit the migration activity of lecithin with the aim of a more straightforward application procedure in large-scale water purification.

5.3.1.2. Optimization

The VOCs residues in the aqueous layer after stirring for 0.5 h with varying amounts of lecithin and 5 mL of olive oil were found to decrease with smaller quantities of lecithin used. From the optimization experiments shown in Figure 5.2, a concentration of 0.5 ppm of lecithin was found to be the most efficient in the reduction of VOCs from water. An overall decline of 70-89% in the sum of VOCs residues (excluding hexanal) was calculated when comparing samples processed with lecithin/olive oil to the control blank without olive oil or lecithin. This is an improvement over the initial 66-71% reduction obtained in the preliminary studies, with the VOCs removal from water improving from 9-14% to 27-48% with the decrease in the amount of lecithin used.

Figure 5.2. Effect of lecithin concentration on the removal of VOCs by olive oil with 0.5 h of stirring. Spiked with 20 µg L⁻¹ of each VOC. VOCs 2 – 25 are given in Table 5.1. *Control does not contain olive oil and lecithin. Blank sample contains olive oil and no lecithin.

It is hypothesized that the opposite trend of lecithin utilization to the level of VOCs removed from the aqueous phase may be linked to the efficiency of lecithin removal from the water samples by olive oil as well as the water solubility and carbon chain length of individual VOCs. The ease of removing lecithin increases with decreasing amounts present in the aqueous phase, thus, smaller amounts of lecithin (up to 5 ppm) can be entirely taken up into the olive oil phase. Shorter carbon chain length and more water soluble VOCs such as esters and certain ketones prefer to remain in the aqueous phase while lecithin carries the larger and the less water soluble VOCs into the organic layer. This hypothesis was tested by studying the effects of VOC removal on the different types of oxygenated compounds. The elimination of methacrolein, methyl isobutyl ketone, and esters were a lot poorer than their less water soluble oxygenated groupmates, heptanal, octanal, nonanal, and 2-methyl furan that have either a carbon chain length greater than seven or exist in a cyclic ring formation. As a whole, lecithin with olive oil appears to be more efficient in the complete elimination of aromatic and halogenated compounds than shorter chain, more water soluble oxygenated compounds. To further optimize the parameters used for the removal of VOCs from water, different stirring times and shaking were tested with 5 ppm of lecithin. Although 0.5 ppm displayed the greatest effect, the difference in the removal of VOCs with added lecithin amounts between 5 ppm and 0.5 ppm was small, and coupling with the larger error involved when weighing lower amounts, 5 ppm of lecithin was used instead of 0.5 ppm in the optimization trials.

The optimal stirring time was found to be 30 min, as 15 min was insufficient for the VOCs removal from the aqueous phase while 1 h made the removal of olive oil slightly harder as the two phases were better emulsified by lecithin (meaning that more lecithin was left over

from the incomplete organic layer removal). Shaking was also investigated as an alternative to stirring. While stirring is more suitable for large-scale water treatment, shaking is more feasible towards portable water treatment processes that can be used by ordinary consumers on a small scale. However, the removal of VOCs from water using the shaking method was harder to quantify because the VOCs escaped from the spiked solutions more readily (presumably through the lids of the containers). Furthermore, the shaken solutions also faced the same problem of extensive emulsification as the sample stirred for 1 h, therefore, lecithin removal was not as effective.

Table 5.2. Study of mixing methods for removal of VOCs from water with olive oil aided by lecithin
 * indicates concentration below the detection limit (DL), ^ indicates concentration below minimal reporting level (MRL); N.D. stands for not detected. Percentage reduction comparison for shake experiment samples was calculated with control blank without olive oil and lecithin.

		Stir (Residue - $\mu\text{g L}^{-1}$)			Shake (% Reduction)	
		15 min	30 min	1 hour	Blank with olive oil	5 ppm lecithin
No.	Aldehydes, ketones, and furan					
1	Hexanal	43.20	26.12	19.16	(-136%)	(-221%)
2	Heptanal	0.84*	0.80*	0.79*	38%	39%
3	Octanal	0.54*	0.51*	0.51*	47%	46%
4	Nonanal	N.D.	N.D.	N.D.	100%	100%
5	Methyl isobutyl ketone	6.15	3.35	3.59	55%	59%
6	Methacrolein	12.18	5.78	9.19	39%	43%
7	2-Methyl furan	0.53^	0.45^	0.48^	73%	75%
	Aromatic compounds					
8	Benzene	0.43^	0.32^	0.35^	83%	84%
9	Ethyl benzene	0.61	0.61	0.61	14%	14%
10	Styrene	0.59	N.D.	0.58	24%	26%
11	Toluene	0.42^	0.36^	0.36^	83%	84%
12, 13	<i>m,p</i> -Xylene	0.46^	0.45^	0.45^	21%	21%
14	<i>o</i> -Xylene	0.37^	0.37^	0.37^	31%	31%
15	Benzonitrile	1.41^	N.D.	1.39^	16%	16%
	Esters					
16	<i>n</i> -Butyl acetate	2.69	1.50	1.60	76%	78%
17	Ethyl acrylate	6.60	3.51	4.00	47%	51%
18	Methyl crotonate	6.97	3.89	4.24	47%	53%
19	Methyl methacrylate	4.24	2.07	2.45	66%	69%
	Halogenated compounds					
20	Bromodichloromethane	0.69^	0.36*	0.41*	89%	91%
21	Dibromochloromethane	0.91^	0.63^	0.67^	87%	89%
22	Tribromomethane	0.50*	0.48*	0.48*	46%	47%
23	Trichloromethane	0.58^	0.30*	0.35*	87%	89%
24	Trichloroethylene	0.45^	0.37^	0.38^	77%	79%
25	Tetrachloroethylene	0.37^	N.D.	N.D.	72%	100%

In summary, the efficiency of the removal of VOCs using lecithin and olive oil is highly dependent on the balance of phase exchange when using lecithin. Excessive lecithin causes problems with removal of lecithin itself, while the elimination of VOCs plateaus at a low lecithin concentration owing to the nature of the VOCs involved. Aggressive mixing of the solution such as stirring for longer than 30 min and shaking causes unfavorable emulsions to be formed which increases the difficulty of eradicating lecithin from the solution.

5.3.2. Lecithin with vitamin E

5.3.2.1. Preliminary studies

Preliminary studies conducted on the removal of VOCs from water using vitamin E encapsulated in lecithin commenced with the investigation of different mixing methods (sonication and stirring) on the lecithin/vitamin E and water spiked with VOCs to mimic contaminated water (Figure 5.3).

Figure 5.3. Lecithin encapsulated vitamin E (left) and control blank (right) after 1 h of stirring.

The act of sonication surprisingly increased the amount of aldehyde residue in the contaminated water with lecithin/vitamin E compared to a control without vitamin E nor lecithin. Also, additional aldehydes which were not spiked into the solutions were matched by the NIST library with high probability (Appendix D.2). The increase in the amount of

aldehydes observed in the treated water could have been due to airborne VOCs absorbed onto lecithin and then released into the water samples when sonicated.

Table 5.3. Preliminary studies on the efficiency of removal of VOCs with 90% w/w lecithin and 10% w/w vitamin E using different mixing methods for 1 h. Percentage reduction comparison calculation for VOCs removal with encapsulated vitamin E experiments was performed with control blank without vitamin E nor lecithin.

		Sonication % Reduction	Stirring % Reduction
No.	Aldehydes and ketones		
1	Hexanal	(-463%)	80%
2	Heptanal	(-1468%)	83%
3	Octanal	(-89%)	100%
4	Nonanal	(-78%)	100%
5	Methyl isobutyl ketone	(-18%)	(-17%)
	Aromatics		
6	Benzene	(-24%)	(-51%)
7	Ethyl benzene	(-9%)	(-7%)
8	Styrene	(-43%)	8%
9	Toluene	(-28%)	(-22%)
10, 11	<i>m,p</i> -Xylene	(-13%)	(-5%)
12	<i>o</i> -Xylene	(-32%)	(-2%)
13	Benzonitrile	(-3%)	20%
	Esters		
14	Ethyl acrylate	(-62%)	(-49%)
15	Methyl methacrylate	(-87%)	(-44%)
16	Methyl crotonate	(-34%)	(-24%)
17	<i>n</i> -Butyl acetate	(-21%)	(-16%)
	Halogenated compounds		
18	Bromodichloromethane	(-88%)	(-37%)
19	Dibromochloromethane	(-46%)	(-10%)
20	Tribromomethane	(-31%)	16%
21	Trichloroethylene	(-11%)	(-31%)
22	Tetrachloroethylene	(-34%)	0%

Henceforth, sonication was not considered in the future optimization studies of the water treatment process with lecithin encapsulated vitamin E. Table 5.3 indicates that many VOCs displayed negative reduction percentages (indicating increases in concentrations) which are likely due to pre-absorbed VOCs present already within the lecithin. It was also noticed in the preliminary studies that some aldehydes were removed from the contaminated water to a greater extent than other VOCs with lecithin/vitamin E. Since VOCs released into the contaminated water from lecithin through sonication were also aldehyde compounds, the affinity of aldehydes and lecithin could be greater than other types of VOCs. The removal

capability of lecithin/vitamin E towards VOCs was not as prominent as the combination of lecithin with olive oil. This was mainly caused by the problem of lecithin removal from the water samples after the treatment because the interaction between VOCs and lecithin-encapsulated vitamin E reduces the ability of VOCs to escape from the aqueous phase in comparison with control blank without vitamin E nor lecithin. Therefore, the optimization of lecithin and vitamin E encapsulation ratio was studied, in search of a more efficient lecithin to vitamin E ratio for lecithin removal through centrifugation.

5.3.2.2. Optimization

The ratio of lecithin to vitamin E which produced the best encapsulation for the removal of VOCs in the contaminated water was found to be 9:2. At higher ratios of vitamin E, as in the case of 1:2 (lecithin: vitamin E), the elimination of VOCs in the contaminated water was poor because it is hard to mix the contaminated water with the lecithin encapsulated vitamin E. The excess vitamin E was not effectively encapsulated by lecithin, which caused the magnetic stirrer bar to become immobilized in the viscous vitamin E oil (Figure 5.4) that was coated on the bottom of the round bottom flask. The ratio of 9:1 used in the preliminary studies were also problematic because it was difficult to remove the lecithin through centrifugation completely. Therefore, the ratio of lecithin to vitamin E used in the removal of VOCs from contaminated water lies in a delicate balance between the ease of removing the lecithin/vitamin E micelles after the water treatment procedure as well as the ease of mixing the lecithin encapsulated vitamin E with contaminated water.

Hitherto, the ability of lecithin encapsulated vitamin E in the removal of VOCs from contaminated water was still relatively poor after optimization of the lecithin to vitamin E ratio. Therefore, stirring time experiments were performed to determine if the reduction of

VOCs in contaminated water could be improved with time. It was found that a stirring time of 1 h was the most effective because over-stirring caused the lecithin/vitamin E encapsulation to break apart thus increasing the difficulty of removing lecithin through centrifugation, whilst stirring for shorter periods did not provide enough time for VOCs to migrate into the encapsulated vesicle (Appendix D.3).

Table 5.4. Optimization of lecithin and vitamin E ratio for VOCs removal

* indicates concentration below detection limit (DL), ^ indicates concentration below minimal reporting level (MRL) and N.D. stands for not detected

Ratio of Lecithin to Vitamin E		1:1	2:1	9:1	9:2	1:2
Amount of Lecithin (% w/v)		0.25	0.50	0.45	0.45	0.25
Amount of Vitamin E (% w/v)		0.25	0.25	0.05	0.10	0.50
		Residue ($\mu\text{g L}^{-1}$)				
No.	Aldehydes and Ketone					
1	Hexanal	9.67	10.15	14.58	9.70	15.79
2	Heptanal	0.96^	0.93^	1.05^	0.91*	1.16^
3	Octanal	0.54*	0.53*	0.54*	0.53*	0.63*
4	Nonanal	N.D.	N.D.	N.D.	N.D.	N.D.
5	Methyl isobutyl ketone	7.28	6.68	9.95	5.19	11.54
	Aromatics					
6	Benzene	1.08	0.98	1.71	0.95	1.90
7	Ethyl benzene	0.61	0.61	0.62	0.61	0.62
8	Styrene	0.59	0.59	0.60	0.59	0.61
9	Toluene	0.56^	0.55^	0.80	0.53^	0.77^
10, 11	<i>m,p</i> -Xylene	0.46^	0.46^	0.46^	0.46^	0.46^
12	<i>o</i> -Xylene	0.38^	0.38^	0.38^	0.38^	0.39^
13	Benzonitrile	1.55^	1.55^	1.63^	1.48^	1.74^
	Esters					
14	Ethyl acrylate	6.96	6.83	9.87	4.81	11.49
15	Methyl crotonate	7.16	6.90	9.80	5.18	11.26
16	Methyl methacrylate	6.82	6.57	9.47	4.75	11.15
17	<i>n</i> -Butyl acetate	5.34	4.72	7.47	4.10	8.48
	Halogenated compounds					
18	Bromodichloromethane	2.54	2.22	3.85	1.85	4.54
19	Dibromochloromethane	2.78	2.51	4.23	2.27	4.60
20	Tribromomethane	0.69*	0.65*	0.79*	0.63*	0.86*
21	Trichloroethylene	0.55^	0.53^	0.74^	0.51^	0.77^
22	Tetrachloroethylene	0.39^	0.37^	0.40^	0.38^	0.39^

Following the optimization of the ratio of lecithin to vitamin E in the encapsulation and stirring time, the elimination of VOCs from water using lecithin with vitamin E though improved, was still not as efficient in comparison to the combination of lecithin with olive oil in the reduction of VOCs in water. The emulsion formed by lecithin encapsulated vitamin E mixed with water might not be effective enough to remove VOCs, and the main issue of

removing lecithin from the samples still exist. Henceforth, unless a more efficient way of removing lecithin is discovered, lecithin with vitamin E would not be an operational method for removing VOCs from contaminated water sources.

Figure 5.4. Immobilization of stirrer bar in 1:2 lecithin and vitamin E (left) and bottom view (right).

5.4. Conclusion

The enhanced removal of VOCs from water using the natural compounds lecithin combined with olive oil or vitamin E was investigated via analysis with PAT GC-MS. The optimal amount of lecithin required when used with olive oil was as low as 0.5 ppm with 0.5 h of stirring. The contribution from lecithin to the removal of VOCs in the aqueous phase increased with lower amounts of lecithin used, which was rationalized by migration of lecithin coupled with VOCs occurring more readily from the aqueous phase into the organic layer (olive oil) at low concentrations of lecithin. However, the effects were limited by the solubility and size of the VOCs. Lecithin combined with vitamin E can also remove VOCs from water, but the problems with separating lecithin from the water via centrifugation still existed. The optimal ratio of lecithin to vitamin E for the removal of VOCs was found to be 9:2 with stirring for 1 h. In comparison to using olive oil combined with lecithin to remove VOCs, the vitamin E encapsulation method requires more lecithin, and the initial process for lecithin encapsulated vitamin E requires the use of chloroform. Therefore, lecithin combined with olive oil is a better method for the reduction of VOCs in water samples because no

additional step to remove lecithin was required. The disadvantage of the removal of VOCs using olive oil was that hexanal that is naturally present in olive oil was transferred into the water samples, which gave the water samples a fruity scent. Explorations into different types of edible oil such as sunflower oil can be performed to find a suitable oil that does not add VOCs into the samples. In the trials, it was also determined that lecithin had a greater affinity with molecules of larger molecular mass. Therefore, exploration of the removal of less volatile pesticides and polycyclic aromatic compounds (PAHs) from water would be possible for future studies.

5.5. References

1. Shiklomanov, I., *World fresh water resources*. Water in Crisis: A Guide to the World's Fresh Water Resources, ed. P.H. Gleick. 1993, New York: Oxford University Press.
2. USPEA, *Title XIV of the Public Health Service Act - Safety of public water systems (Safe drinking water act)*, EPA, Editor. 2002, US EPA: United States.
3. WHO, *Guidelines for drinking water quality, fourth edition*, WHO, Editor. 2011, Gutenberg: Malta.
4. Ikem, A., *Measurement of volatile organic compounds in bottled and tap waters by purge and trap GC-MS: Are drinking water types different?* Journal of Food Composition and Analysis, 2010. **23**: p. 70-77.
5. Panyakpo, M., S. Soontornchai, and P. Paopuree, *Cancer risk assessment from exposure to trihalomethanes in tap water and swimming pool water*. Journal of Environmental Sciences, 2007. **20**(3): p. 372-378.

6. ASTDR. *Agency for Toxic Substances & Disease Registry*. 2012 [cited 2016 24th January]; Available from: www.atsdr.cdc.gov/.
7. McKone, T.E., *Human exposure to volatile organic compounds in household tap water: the indoor inhalation pathway*. Environmental science & technology, 1987. **21**(12): p. 1194-1201.
8. Tancrede, M., Y. Yanagisawa, and R. Wilson, *Volatilization of volatile organic compounds from showers—I. Analytical method and quantitative assessment*. Atmospheric Environment. Part A. General Topics, 1992. **26**(6): p. 1103-1111.
9. Jo, W.K., C.P. Weisel, and P.J. Lioy, *Routes of chloroform exposure and body burden from showering with chlorinated tap water*. Risk Analysis, 1990. **10**(4): p. 575-580.
10. Edzwald, J.K., *Coagulation in drinking water treatment: Particles, organics, and coagulants*. Water Science and Technology, 1993. **27**(11): p. 21-35.
11. Capar, G. and U. Yetis, *Removal of THM precursors by GAC: Ankara case study*. Water Research, 2002. **36**(5): p. 1379-1384.
12. McCarty, P.L., *Organics in Water - An Engineering Challenge*. Journal of the Environmental Engineering Division, 1980. **106**(1): p. 1-17.
13. Uyak, V., et al., *Removal of trihalomethanes from drinking water by nanofiltration membranes*. Journal of Hazardous Materials, 2008. **152**: p. 789-794.
14. Lu, C., Y.-L. Chung, and K.-F. Chang, *Adsorption of trihalomethanes from water with carbon nanotubes*. Water Research, 2005. **39**: p. 1183-1189.
15. Singer, P.C. and K. Bilyk, *Enhanced coagulation using a magnetic ion exchange resin*. Water Research, 2002. **36**(16): p. 4009-4022.

16. Hooper, S.M., et al., *Improving GAC performance by optimized coagulation*. Journal Americal Water Works Association, 1996. **88**(8): p. 107-120.
17. Camper, A.K., et al., *Bacteria Associated with Granular Activated Carbon Particles in Drinking Water*. Applied and Environmental Microbiology, 1986. **52**(3): p. 434-438.
18. Hilal, N., et al., *A comprehensive review of nanofiltration membranes: Treatment, pretreatment, modeling, and atomic force microscopy*. Desalination, 2004. **170**(3): p. 281-308.
19. Hernandez, R.J. and J.R. Giacin, *Factors affecting permeation, sorption, and migration processes in package-product systems*, in *Food Storage Stability*, Irwin A. Taub and R.P. Singh, Editors. 1997, CRC Press.
20. Emma, L.B. and C. Laurence, *Residues of Food Contact Materials*, in *Handbook of Seafood and Seafood Products Analysis*, Leo M. L. Nollet and F. Toldra, Editors. 2009, CRC Press.
21. Sablani, S.S. and M.S. Rahman, *Food Packaging Interaction*, in *Handbook of Food Preservation*, M.S. Rahman, Editor. 2007, CRC Press.
22. Line, D.E., et al., *Water quality of first flush runoff from 20 industrial sites*. Water Environment Research, 1997. **69**(3): p. 305-310.
23. Kumar, R. and O.P. Katare, *Lecithin organogels as a potential phospholipid-structured system for topical drug delivery: A review*. AAPS PharmSciTech, 2005. **6**(2): p. E298-E310.

24. Paolino, D., et al., *Lecithin microemulsions for the topical administration of ketoprofen: percutaneous adsorption through human skin and in vivo human skin tolerability*. International Journal of Pharmaceutics, 2002. **244**(1–2): p. 21-31.
25. Changez, M., J. Chander, and A.K. Dinda, *Transdermal permeation of tetracaine hydrochloride by lecithin microemulsion: In vivo*. Colloids and Surfaces B: Biointerfaces, 2006. **48**(1): p. 58-66.
26. Shinoda, K., Y. Shibata, and B. Lindman, *Interfacial tensions for lecithin microemulsions including the effect of surfactant and polymer addition*. Langmuir, 1993. **9**(5): p. 1254-1257.
27. Wei, G.-T., et al., *Aqueous–Organic Phase Transfer of Gold Nanoparticles and Gold Nanorods Using an Ionic Liquid*. Journal of the American Chemical Society, 2004. **126**(16): p. 5036-5037.
28. Lefevre, T. and M. Picquart, *Vitamin E-phospholipid interactions in model multilayer membranes: A spectroscopic study*. Biospectroscopy, 1996. **2**(6): p. 391-403.
29. Kiritsakis, A., *Flavor components of olive oil—A review*. Journal of the American Oil Chemists' Society, 1998. **75**(6): p. 673-681.
30. Hutter, J.C., et al., *Removal of VOCs from groundwater using membrane-assisted solvent extraction*. AIChE journal, 1994. **40**(1): p. 166-177.

This page has been intentionally left blank.

Conclusion

Being a small island nation with little freshwater sources, Singapore relies heavily on rainwater as one source of water, and strict regulations are placed on the usage of land surrounding catchment areas for the preservation of quality. Previous studies on the quality of rainwater in Singapore have been limited to the inorganic and some organic contaminants present, while other emerging contaminants such as volatile organic compounds (VOCs) have remained undocumented. The possible adverse effects of VOCs on health and the environment has led to many investigations of VOCs present in the atmosphere, and VOCs can also enter the water system by being washed out (sink) from the atmosphere during rain events. The different monsoon seasons and anthropogenic sources in Singapore can affect the amounts of VOCs observed in the rain, therefore, a long-term monitoring of VOCs in rainwater is required to understand the effects of such variables. Chapter 1 discusses the sources of water present in Singapore and the VOCs contaminants detected in the different types of water sources around the world. Water purification methods targeting the removal of VOCs were also examined along with the various analytical methods that can be employed for the measurement of VOCs in water.

A purge-and-trap gas chromatography mass spectroscopy (PAT GC-MS) method for the detection of VOCs in rainwater based on United States Environmental Protection Agency (US EPA) Method 524.4 Measurement of Purgeable Organic Compounds in Water by Gas Chromatography/Mass Spectrometry using Nitrogen Purge Gas was further developed for a

sampling site located in the western region of Singapore and discussed in Chapter 2. Twenty eight VOCs were identified as analytes for monitoring in rainwater through the mass spectrum matching with National Institute of Standards and Technology (NIST) library and retention time and mass spectrum confirmation of neat standards. GC parameters were optimized for the most favorable separation while ions for monitoring in selective ion monitoring (SIM) mode were determined through dynamic calibration, and the PAT system was optimized within the recommended and allowable range set by US EPA Method 524.4. Minimal reporting level (MRL) and detection limit (DL) was determined for the VOCs in both SIM and Scan mode with good precision (standard deviation $\leq 20\%$) and accuracy (percentage recoveries $\pm 20\%$). A manual sampler was developed for the collection of rainwater with no contamination from the materials used, and the filtration process was removed during the method development stage as leachable VOCs were observed with the use of syringe filters.

The method developed in Chapter 2 was employed in a yearlong monitoring of VOCs in rainwater in the western region of Singapore from August 2015 to July 2016 and discussed in Chapter 3. Methacrolein was determined to have the highest mean concentration at 2071.89 ng L⁻¹ in the 476 rain samples collected from 193 rain events, and most VOCs with good detection frequencies were oxygenated VOCs with better water solubility. The spikes in VOCs measured in rainwater throughout the year could be traced back to probable major events such as haze from September to October 2015 and the construction and renovation work conducted at the sampling site during March to May 2016. Also, higher concentration levels of some aromatic and oxygenated VOCs were also found during inter-monsoon seasons where wind speeds were generally lower, and dilution of VOCs in ambient air was

kept to the minimum. However, most aromatic VOCs displayed a higher concentration in rainwater during monsoon seasons with likely sources of emission in the origin of the air mass transfer. Pearson correlation analysis determined a good correlation (≥ 0.8) for VOCs pairs in the yearlong and haze analysis indicating probable similar sources of emission. The results from Pearson correlation analysis of the yearlong analysis was used as a guideline in positive matrix factorization (PMF) calculation to determine the number of sources for the VOCs observed in rainwater, and eight factors were resolved from the calculation. Petroleum refineries, evaporative emissions, vehicle emissions, the pharmaceutical industry, monomer production, synthesis of flavor and fragrances, manufacture of lacquers and paints as well as manufactures of polymers are the probable identity of the factors resolved. The health risk with regards to the concentration of VOCs in rainwater is low for the lethal dosage, and maximum contaminant level (MCL) is much higher in comparison to the concentration detected in rainwater. Nevertheless, contamination towards surface water may occur as different types of VOCs were determined in rainwater than those commonly detected in surface water.

The presence of extractable and leachable contaminants from syringe filters can potentially affect chemical/biological reactions, qualitative and quantitative analysis of samples and stability of products. Leachable VOC contaminants studied using PAT GC-MS in Chapter 4 were most often detected in disposable syringe filters with housing materials other than polypropylene and in those containing nylon filters. Aldehydes such as hexanal, heptanal, and nonanal (products from thermal oxidation degradation) along with the building blocks of syringe filter housing polymers (methyl methacrylate and styrene) were detected as the primary leachable contaminants, with the greatest sum of leachable VOCs at approximately

30 $\mu\text{g L}^{-1}$. Pre-filtration treatments, sterilization, and surfactant free treatment of membranes can affect the leachable VOCs eluted from the syringe filters under general use conditions. Polypropylene, although ideal as a housing material that has minimal leachable VOCs, can adsorb aromatics that are present in solution. Transition metals including cobalt, manganese, and tungsten were also detected in ultrapure water filtrates at low concentration of individual syringe filters with possible origins from manufacturing processes.

Two methods to remove VOCs from water using the natural food additive, lecithin, assisted by olive oil or vitamin E were explored in Chapter 5. Lecithin combined with olive oil was utilized in a phased exchange and solvent extraction process to remove VOCs from water into the olive oil layer. The addition of 0.5 ppm of lecithin into the olive oil was found to be sufficient to remove halogenated and aromatic VOCs completely; however, the method was less efficient against ketones and esters due to their better water solubility and smaller molecular mass in comparison to other VOCs tested. The second method involved combining lecithin with vitamin E to produce an aqueous suspension of micelles that facilitated the removal of VOCs from water into the micelles, with the optimal ratio of lecithin to vitamin E found to be 9:2. The overall removal of VOCs from water using lecithin/vitamin E micelles was not as effective as lecithin/olive oil layers due to the problems faced when removing lecithin from the samples.

In conclusion, PAT GC-MS method was applied to the analysis of VOCs in rainwater and leachable VOCs from syringe filters as well as the assessment of the efficiency of VOCs removal in the water purification process using natural materials such as olive oil, lecithin and vitamin E. VOCs present in rainwater are affected by monsoon season and notable events in the yearlong analysis while health risk is minimal from consumption and

contamination to surface water is probable. This yearlong analysis of VOCs in rainwater can be extended to other parts of Singapore to get a more in-depth understanding on how the various sources of emission of VOCs can affect the VOCs detected in precipitates at different locations. Although the levels of VOCs detected in rainwater are below toxic levels, the long-term study of low-level exposure are not well documented, further studies can be conducted to verify its effect to safeguard the exposure to such pollution. Leachable VOCs originating from housing materials and thermal oxidation degradation of syringe filters were detected in several syringe filters tested, and they may not be suitable for use in experiments sensitive to organic contaminants. The result of water purification with alternative natural materials determined that VOCs removal is plausible with lecithin assisted with olive oil or vitamin E, however, the effectiveness of lecithin removal (post-VOC removal) can affect the efficiency.

This page has been intentionally left blank

Appendix A.1. Information of VOCs studied

Appendix A.1. Table 1 of VOCs and their retention time, boiling point, density, molecular weight, purity, origin, and volume drawn to make the standard stock solution. ^VOCs only analyzed in scan mode, * VOCs used exclusively in Chapter 4, @VOCs used exclusively in Chapter 5, #Volume drawn to make up 1 mg/mL in a 50 mL volumetric flask, +VOCs indicates internal standards, 'VOCs indicates surrogate standard.

VOCs	Retention time (min)	Company	Boiling point (°C)	Density (g cm ⁻³)	Molecular weight (g mol ⁻¹)	Purity (%)	Volume drawn [#] (μL)
Isoprene	8.633	Merck	34.0	0.681	68.12	99.90	73.495
Dichloromethane [^]	9.076	Merck	39.6	1.330	84.93	99.90	37.774
Methacrolein	9.969	Acros Organics	69.0	0.847	70.09	90.00	65.359
2-Butanone [^]	10.494	Alfa Aesar	79.6	0.805	72.11	99.90	62.174
2-Methyl furan	10.622	Acros Organics	63.0	0.927	82.10	99.00	54.482
Trichloromethane	10.777	Alfa Aesar	61.2	1.483	119.38	99.80	33.579
Benzene	11.702	Merck	80.1	0.877	78.11	99.70	57.380
Ethyl acrylate	12.098	TCI	99.4	0.941	100.12	99.00	53.700
Dibromomethane [']	12.155	Alfa Aesar	97.0	2.477	173.83	99.70	20.246
Trichloroethylene	12.212	Merck	87.2	1.460	131.39	99.50	34.348
Bromodichloromethane ^{^@}	12.26	Alfa Aesar	90.0	1.980	163.80	99.10	25.482
Methyl methacrylate	12.326	Alfa Aesar	101.0	0.940	100.12	99.90	53.472
Methyl cyclohexane	12.626	Alfa Aesar	101.0	0.770	98.19	99.90	65.000
Methyl isobutyl ketone	12.819	Merck	117.4	0.802	100.16	99.50	62.736
Methyl Crotonate	13.154	TCI	119.0	0.944	100.12	99.30	53.339
Toluene- <i>D</i> ₈ ⁺	13.346	VWR	110.0	0.943	100.19	99.90	53.075
Toluene	13.411	Merck	111.0	0.870	92.14	99.50	58.094
Hexanal	13.675	Merck	130.0	0.815	100.16	99.50	61.658
Dibromochloromethane ^{^@}	13.732	Alfa Aesar	120.0	2.451	208.28	98.90	20.627
<i>n</i> -Butyl acetate	13.783	Alfa Aesar	127.0	0.880	116.16	99.80	56.932
Tetrachloroethylene	14.108	Alfa Aesar	121.1	1.622	165.83	99.90	30.838
Ethyl benzene	15.030	Merck	136.0	0.867	106.17	99.90	57.728
<i>p</i> -Xylene	15.251	Alfa Aesar	138.4	0.861	106.17	99.80	58.188
<i>m</i> -Xylene	15.251	Alfa Aesar	139.0	0.860	106.16	99.50	57.893
Tribromomethane ^{^@}	15.495	TCI	151.0	2.890	252.73	99.40	17.405
Heptanal	15.494	Alfa Aesar	152.8	0.809	114.18	97.90	62.284
Styrene	15.694	Alfa Aesar	145.0	0.909	104.15	99.90	55.061
<i>o</i> -Xylene	15.808	Alfa Aesar	144.4	0.880	106.17	99.20	57.342
Cumene [*]	16.350	Alfa Aesar	152.0	0.862	120.19	99.60	58.103
<i>p</i> -Bromofluorobenzene ⁺	16.436	Alfa Aesar	150.0	1.593	175.00	99.80	31.450
Allyl benzene [*]	16.884	TCI	156.0	0.892	118.18	99.90	56.110
Propyl benzene [*]	17.115	TCI	159.0	0.862	120.19	99.90	58.063
1-Ethyl-3-methylbenzene	17.319	Sigma Aldrich	159.0	0.865	120.19	99.00	58.387
1-Ethyl-4-methylbenzene	17.418	Alfa Aesar	162.0	0.860	120.19	97.60	59.500

Appendix A.1. Table 2. List 2 of VOCs and their retention time, boiling point, density, molecular weight, purity, origin, and volume drawn to make the standard stock solution. ^VOCs only analyzed in scan mode, * VOCs used exclusively in Chapter 4, @VOCs used exclusively in Chapter 5, #Volume drawn to make up 1 mg/mL in a 50 mL volumetric flask.

VOCs	Retention time (min)	Company	Boiling point (°C)	Density (g cm ⁻³)	Molecular weight (g mol ⁻¹)	Purity (%)	Volume drawn [#] (μL)
1,3,5-Trimethylbenzene	17.646	Merck	164.7	0.864	120.19	99.50	58.161
1-Ethyl-2-methylbenzene	17.977	Sigma Aldrich	164.0	0.884	120.19	98.60	57.170
Octanal [^]	18.047	Merck	171.0	0.821	128.21	99.20	61.392
Benzonitrile	18.140	Sigma Aldrich	188.0	1.000	103.12	99.99	50.005
2-Methyl styrene*	18.477	Alfa Aesar	171.0	0.914	118.18	97.90	55.878
3-Methyl styrene*	18.477	Alfa Aesar	171.0	0.890	118.18	99.80	56.576
1,2,4-Trimethylbenzene	18.537	Acros Organics	168.0	0.876	120.19	98.50	57.947
1,2,3-Trimethylbenzene	19.439	Sigma Aldrich	175.0	0.894	120.19	90.00	62.143
Nonanal [^]	20.512	Alfa Aesar	191.0	0.827	142.24	99.30	60.886
Decanal [^]	22.72	Alfa Aesar	207.0	0.830	156.20	98.40	61.220

Appendix A.1. Table 3. List of additional VOCs used in the analyte confirmation stage and their boiling point, density, molecular weight, purity, origin, and volume drawn to make the standard stock solution. #Volume drawn to make up 1 mg/mL in a 50 mL volumetric flask.

VOCs	Company	Boiling point (°C)	Density (g cm ⁻³)	Molecular weight (g mol ⁻¹)	Purity (%)	Volume drawn (μL) [#]
1-Octene	Fluka	122.0	0.715	112.21	98.00	71.357
2-Methylbutane	TCI	31.0	0.616	72.15	98.00	82.825
2-Methylheptane	Sigma Aldrich	116.0	0.698	114.23	98.00	73.095
2-Methylpentane	Alfa Aesar	61.0	0.653	86.18	99.00	77.343
3-Methylpentane	Alfa Aesar	64.0	0.663	86.18	99.00	76.177
Acetone	Merck	56.2	0.790	58.08	99.00	63.930
Acetophenone	Fluka	202.0	1.030	120.15	99.50	48.788
Benzaldehyde	Fluka	178.0	1.044	106.12	99.00	48.376
Cyclohexane	Merck	81.0	0.780	84.16	99.00	64.750
Decane	Alfa Aesar	173.0	0.730	142.29	99.00	69.185
Ethyl acetate	Merck	77.0	0.900	88.11	99.00	56.117
Ethyl ether	Merck	34.6	0.706	74.12	99.00	71.537
Furfural	Merck	162.0	1.160	96.08	99.00	43.539
Heptane	Mallinckrodt	98.0	0.684	100.20	99.00	73.838
Hexane	Merck	69.0	0.660	86.18	99.00	76.523
Isopropyl alcohol	Merck	82.4	0.786	60.10	99.00	64.256
Methylcyclopentane	Fluka	72.0	0.749	84.16	97.00	68.820
Nonane	Merck	151.0	0.720	128.25	99.00	70.146
Octane	Fluka	126.0	0.703	114.23	99.70	71.338
Phenol	Alfa Aesar	181.0	1.071	94.11	99.00	4.716 g
Pyridine	Fluka	115.0	0.978	79.10	99.80	51.227

Appendix A.2. Quantifier and qualifier ions, MRL and DL for VOCs with internal standard reference and monitoring window

Appendix A.2. Table 1. List 1 of VOCs and their quantifier ion, qualifier ion 1, qualifier ion 2, window of monitoring in SIM mode, and internal standard reference. ^VOCs only analyzed in scan mode, *VOCs used exclusive in Chapter 4, @VOCs used exclusively in Chapter 5, +(-) represents % ratio of qualifier ion against quantifier ion.

VOCs	Quantifier Ion	Qualifier ion 1 ⁺	Qualifier ion 2 ⁺	Window	Internal standard reference	Scan MRL [~] (µg L ⁻¹)	Scan DL [~] (µg L ⁻¹)	SIM MRL [~] (ng L ⁻¹)	SIM DL [~] (ng L ⁻¹)
Isoprene	67.0	53.1 (82)		1	1	1.10	0.50	12.00	2.42
Dichloromethane [^]	84.0	49.0 (116)			1	0.83	0.34		
Methacrolein	70.1	41.1 (131)		1	1	1.80	1.00	22.00	6.89
2-Butanone [^]	43.1	72.1 (27)			1	2.30	0.87		
2-Methyl furan	82.1	53.1 (73)		2	1	0.88	0.33	12.00	1.44
Trichloromethane	83.0	85.0 (66)		2	1	1.20	0.41	35.00	9.50
Benzene	78.1	77.1 (23)		2	1	0.77	0.21	5.60	0.75
Ethyl acrylate	55.1	45.1 (12)		3	1	1.20	0.75	22.00	5.27
Dibromomethane	174.0	172 (52.5)		3	Surrogate standard				
Trichloroethylene	130.0	95.1 (103)		3	1	1.20	0.37	9.10	1.49
Bromodichloromethane ^{^@}	83.0	85.0 (65)			1	1.30	0.47		
Methyl methacrylate	69.1	41.1 (119)		3	1	1.50	0.78	17.00	3.44
Methyl cyclohexane	83.2	55.1 (81)		4	1	0.99	0.43	34.00	2.19
Methyl isobutyl ketone	43.1	58.1 (39)		4	1	2.10	0.82	26.00	1.76
Methyl crotonate	69.1	85.1 (35)		4	1	1.60	0.85	28.00	3.96
Toluene- <i>D</i> ₈	98.1	100.1 (63)		4	Internal standard 1				
Toluene	91.1	92.1 (56)		4	1	0.79	0.29	13.00	2.50
Hexanal	56.1	72.1 (35)		5	1	1.90	0.89	29.00	8.41
Dibromochloromethane ^{^@}	129.0	127 (76)			1	1.20	0.48		
<i>n</i> -Butyl acetate	43.1	56.1 (41)		5	1	1.30	0.77	17.00	1.49
Tetrachloroethylene	166.0	164.0 (74)		5	1	0.91	0.28	8.20	2.13
Ethyl benzene	91.1	106.1 (31)		6	2	0.54	0.14	17.00	4.28
<i>p</i> -Xylene	91.1	106.1 (45)		6	2	0.95	0.26	22.00	3.44
<i>m</i> -Xylene	91.1	106.1 (45)		6	2	0.95	0.26	22.00	3.44
Tribromomethane ^{^@}	172.9	170.9 (50)			2	1.60	0.88		
Heptanal	70.2	55.2 (113)		6	2	1.20	0.92	35.00	5.69
Styrene	104.0	103.1 (59)	78.1 (60)	6	2	0.47	0.09	20.00	2.72
<i>o</i> -Xylene	91.1	106.1 (42)		6	2	0.81	0.16	13.00	0.86
Cumene*	150.1	120.1 (24)			2	0.64	0.14		
<i>p</i> -Bromofluorobenzene	174.1	95.1 (94)		7	Internal standard 2				
Allyl benzene*	117.1	118.1 (70)			2	0.76	0.23		
Propyl benzene*	91.0	120.1 (25)			2	0.84	0.13		
1-Ethyl-3-methylbenzene	105.1	120.1 (30)		7	2	0.96	0.39	9.20	1.43
1-Ethyl-4-methylbenzene	105.1	120.1 (26)		7	2	0.68	0.31	15.00	2.55

Appendix A.2. Table 2. List 2 of VOCs and their quantifier ion, quantifier ion 1, quantifier ion 2, window of monitoring in SIM mode, and internal standard reference. ^VOCs only analyzed in scan mode, *VOCs used exclusive in Chapter 4, @VOCs used exclusively in Chapter 5, +(-) represents % ratio of quantifier ion against quantifier ion.

VOCs	Quantifier Ion	Quantifier ion 1 ⁺	Quantifier ion 2 ⁺	Window	Internal standard reference	Scan MRL [~] (µg L ⁻¹)	Scan DL [~] (µg L ⁻¹)	SIM MRL [~] (ng L ⁻¹)	SIM DL [~] (ng L ⁻¹)
1,3,5-Trimethylbenzene	105.1	120.1 (44)		7	2	0.63	0.095	13.00	1.23
1-Ethyl-2-methylbenzene	105.1	120.1 (28)		8	2	0.60	0.11	8.90	1.01
Octanal [^]	41.1	55.1 (58)	57.1 (63)		2	2.10	1.40		
Benzonitrile	103.1	76.1 (37)		8	2	2.00	0.94	17.00	2.79
2-Methyl styrene*	117.1	118.1 (83)			2	0.89	0.37		
3-Methyl styrene*	117.1	118.1 (83)			2	0.89	0.37		
1,2,4-Trimethylbenzene	105.1	120.1 (38)		8	2	0.54	0.38	20.00	2.65
1,2,3-Trimethylbenzene	105.1	120.1 (40)		8	2	0.66	0.21	12.00	2.17
Nonanal [^]	57.1	41.1 (115)			2	1.30	0.95		
Decanal [^]	57.1	41.1 (132)	70.1 (57)		2	1.50	0.74		

Appendix A.3. Probable identity of chromatographic peaks in rain samples

Appendix A.3. Table 1. Plausible identify of VOCs detected and their occurrence in rainwater collected on the 04/04/2013, 05/04/2013, 17/04/2013, 19/04/2013, 28/05/2013, and 03/06/2013 (List 1).

Plausible VOCs identified	04/04	05/04	17/04	19/04	28/05	03/06	Occurrence
1,2,3-Trimethylbenzene	x				x	x	50%
1,2,4-Trimethylbenzene	x					x	33%
1,3,5-Trimethylbenzene					x	x	33%
1-Ethyl-2-methylbenzene	x			x	x	x	67%
1-Ethyl-2,4-dimethylbenzene						x	17%
1-Ethyl-3-methylbenzene	x				x	x	50%
1-Ethyl-4-methylbenzene	x			x	x	x	67%
2,2-Dimethyltetrahydrofuran					x		17%
2,3-Dihydrofuran	x		x	x	x		67%
2,3,5-trimethylhexane					x		17%
2,4-Dimethylhexane				x			17%
2,5-Dihydrofuran	x	x		x	x		67%
2-Butanone	x	x	x	x	x	x	100%
2-Butenal			x		x		33%
2-Ethyl-1,3-dimethylbenzene						x	17%
2-Hexanone						x	17%
2-Methyl-1-Penten-3-ol				x			17%
2-Methyl-3-hexanone						x	17%
2-Methyl furan	x	x	x		x		67%
2-Pentanone					x		17%
3-Methyl-2-pentanone				x			17%
4-Heptanone						x	17%
4-Methyl-3-pentenoic acid					x		17%
Acetone	x	x		x	x	x	83%
Acetophenone						x	17%
Benzaldehyde	x		x		x	x	67%
Benzonitrile			x				17%
Cumene	x				x	x	50%
Decane	x						17%
Dibromomethane			x				17%
Dichloromethane				x	x		33%
Ethyl acetate				x			17%
Ethyl acrylate		x	x	x			50%
Ethyl benzene	x	x	x	x	x	x	100%
Hexamethylcyclotrisiloxane	x	x	x	x	x		83%
Hexanal			x	x	x	x	67%
Indane					x		17%
Methacrolein			x	x	x		50%
Methyl Acetate				x		x	33%
Methyl crotonate			x	x			33%
Methyl isobutyl ketone				x		x	33%
Methyl methacrylate	x	x	x	x			67%
Methyl propionate		x					17%
Methyl vinyl ketone			x			x	33%
<i>m</i> -Xylene	x			x		x	50%
<i>n</i> -Butyl acetate	x	x	x	x	x	x	100%
Nonanal	x		x				33%
Nonane			x				17%
Octamethylcyclotetrasiloxane	x	x	x	x	x	x	100%
Octanal				x			17%
<i>o</i> -Cymene	x						17%
<i>o</i> -Xylene	x	x			x	x	67%
Propanenitrile					x		17%
Propylbenzene					x		17%
<i>p</i> -Bromofluorobenzene	x	x		x	x	x	83%
<i>p</i> -Xylene	x	x	x	x	x	x	100%
Styrene		x	x	x	x	x	83%

Appendix A.3. Table 2. Plausible identify of VOCs detected and their occurrence in rainwater collected on the 04/04/2013, 05/04/2013, 17/04/2013, 19/04/2013, 28/05/2013, and 03/06/2013 (List 2).

Plausible VOCs identified	04/04	05/04	17/04	19/04	28/05	03/06	Occurrence
Succinic acid, Decyl tetrahydrofurfuryl ester				x			17%
<i>tert</i> -Butyl 3,3-dimethylbutylether		x					17%
Tetrahydro-2-Furan methanol				x			17%
Tetrahydro-2-methyl furan					x		17%
Tetrahydro-5-methyl-2-Furanmethanol				x			17%
<i>trans</i> -Tetrahydro-5-methyl-2-Furanmethanol				x			17%
Trichloroethylene					x		17%
Trimethylsilanol			x	x		x	17%
Toluene	x	x		x	x	x	100%
Undecane					x		17%
α -Methyl styrene			x		x	x	50%

Appendix A.4. Duplicate analysis of GC parameter effect on peak resolution.

Appendix A.4. Table 1. Effects of oven programming on peak cluster 1 Set 2.

Name of target analytes	Quantifier Ion	Ramp (158 °C)		Hold (158 °C)		Hold (178 °C)		Hold (140 °C)		Hold (145 °C)	
		Rs		Rs		Rs		Rs		Rs	
Ethyl acrylate	55.1	1.37		1.53		1.48		0.88		1.06	
Dibromomethane	174.0	0.60		0.56		0.37		0.80		0.98	
Trichloroethylene	130.0										

Appendix A.4. Table 2. Effects of oven programming on peak clusters 2 and 3 Set 2.

Name of target analytes	Quantifier Ion	Hold (197 °C)		Hold (190 °C)		Hold (150 °C)	
		Rs		Rs		Rs	
1-Ethyl-3-methylbenzene	105.1	0.86		1.04		1.05	
1-Ethyl-4-methylbenzene	105.1						
1-Ethyl-2-methylbenzene	105.1					1.16	
Octanal	41.1					0.89	
Benzonitrile	103.1						

Appendix A.4. Table 3. Resolution calculation and comparison of flow rates and partially optimized oven programming Set 2.

Name of target analytes	Quantifier Ion	1.4 mL min ⁻¹		1.5 mL min ⁻¹		1.6 mL min ⁻¹	
		Rs		Rs		Rs	
Ethyl acrylate	55.1	0.87		1.07		0.76	
Dibromomethane	174.0	0.77		0.98		1.04	
Trichloroethylene	130.0	0.65		0.91		0.84	
1-Ethyl-3-methylbenzene	105.1	0.99		1.05		0.96	
1-Ethyl-4-methylbenzene	105.1						
1-Ethyl-2-methylbenzene	105.1	0.87		1.14		0.98	
Octanal	41.1	0.89		0.88		0.67	
Benzonitrile	103.1						

Appendix A.5. Duplicate analysis of PAT parameter effect on Response Factor.

Appendix A.5. Table 1. PAT parameter tested and the total number of VOCs displaying the highest response factor (RF) for each parameter in yellow Set 2.

VOCs	Purge flow rate (mL min ⁻¹)					Purge volume (mL)					Temperature (°C)				
	40	45	50	55		400	440	480	520		Ambient	40		60	
Isoprene	0.154	0.142	0.160	0.133		2.998	2.891	2.478	3.681		0.079	0.111		0.100	
Dichloromethane	1.078	0.923	1.006	1.062		2.719	3.409	2.374	2.568		0.609	1.001		0.930	
Methacrolein	0.090	0.087	0.099	0.088		0.433	0.457	0.321	0.462		0.080	0.072		0.071	
2-Methyl furan	0.276	0.270	0.281	0.265		0.264	0.256	0.263	0.269		0.191	0.220		0.211	
Trichloromethane	1.813	1.653	1.652	1.815		1.726	1.534	1.679	1.746		1.244	1.439		1.431	
Benzene	1.507	1.480	1.521	1.383		1.594	1.554	1.617	1.634		1.158	1.290		1.248	
Ethyl acrylate	0.233	0.219	0.232	0.231		0.252	0.265	0.349	0.328		0.207	0.193		0.198	
Dibromomethane (SS)	0.568	0.524	0.526	0.578		0.502	0.511	0.582	0.571		0.615	0.602		0.626	
Trichloroethylene	0.544	0.595	0.585	0.594		0.591	0.623	0.684	0.647		0.581	0.609		0.608	
Methyl methacrylate	0.141	0.135	0.139	0.138		0.145	0.155	0.186	0.206		0.128	0.130		0.113	
Methyl cyclohexane	0.209	0.193	0.198	0.163		0.212	0.206	0.173	0.151		0.132	0.154		0.139	
Methyl isobutyl ketone	0.279	0.248	0.284	0.274		0.316	0.303	0.400	0.381		0.232	0.222		0.219	
Methyl crotonate	0.085	0.083	0.091	0.076		0.100	0.100	0.126	0.135		0.085	0.073		0.077	
Toluene- <i>p</i> 8 (IS)	1.000	1.000	1.000	1.000		1.000	1.000	1.000	1.000		1.000	1.000		1.000	
Toluene	1.369	1.457	1.349	1.472		1.738	1.695	1.672	1.786		1.286	1.338		1.292	
Hexanal	0.063	0.059	0.065	0.061		0.080	0.078	0.099	0.096		0.058	0.061		0.055	
<i>n</i> -Butyl acetate	0.394	0.370	0.409	0.407		0.441	0.430	0.541	0.547		0.354	0.319		0.329	
Tetrachloroethylene	0.472	0.483	0.485	0.463		0.436	0.443	0.436	0.449		0.409	0.449		0.435	
Ethyl benzene	2.867	2.598	3.555	2.793		4.558	4.884	4.030	4.886		3.028	2.974		3.280	
<i>m,p</i> -Xylene	4.526	3.976	5.684	4.496		7.648	6.218	6.665	7.795		5.318	5.700		5.238	
Heptanal	0.298	0.330	0.263	0.260		0.452	0.463	0.452	0.395		0.316	0.327		0.312	
Styrene	1.787	1.622	2.241	1.782		2.999	3.167	2.731	3.370		2.187	1.924		2.124	
<i>o</i> -Xylene	2.667	2.335	3.376	2.577		4.390	3.857	4.952	5.241		3.578	3.633		3.266	
<i>p</i> -Bromofluorobenzene (IS)	1.000	1.000	1.000	1.000		1.000	1.000	1.000	1.000		1.000	1.000		1.000	
1-Ethyl-3-methylbenzene	2.710	2.372	3.468	2.533		4.841	5.065	5.050	5.521		3.580	3.640		3.389	
1-Ethyl-4-methylbenzene	2.718	2.330	3.503	2.417		5.170	5.297	5.175	5.624		3.882	3.988		3.400	
1,3,5-Trimethylbenzene	2.386	2.075	3.094	2.181		4.406	4.544	4.622	4.152		3.290	2.988		3.001	
1-Ethyl-2-methylbenzene	2.944	2.608	3.767	2.749		5.272	5.406	4.451	3.856		3.926	3.314		3.675	
Octanal	0.508	0.407	0.590	0.438		1.032	0.992	0.946	0.775		0.665	0.678		0.588	
Benzonitrile	0.383	0.284	0.396	0.290		0.645	0.654	0.697	0.688		0.443	0.351		0.402	
1,2,4-Trimethylbenzene	2.998	3.891	2.478	2.681		6.404	6.401	6.233	6.530		5.233	5.516		4.025	
1,2,3-Trimethylbenzene	2.719	3.409	2.374	2.568		4.774	4.820	4.068	4.542		3.576	3.603		3.336	
Nonanal	0.433	0.457	0.321	0.362		0.688	0.662	0.628	0.616		0.450	0.498		0.438	
Decanal	0.132	0.126	0.093	0.100		0.235	0.200	0.202	0.247		0.133	0.142		0.130	
Total number	5	5	18	4		3	4	7	18		9	21		2	

Appendix A.5. Table 2 Duplicated Response factor of VOCs with different desorption time and the comparison of response factor between desorption time 1.5 min and 1 min and Response factor of VOCs with different dry purge conditions. *yellow highlight displays the highest RF while the beige highlight displays the highest RF comparison between 25 mL and 50 mL of dry purging.

VOCs	Desorption time (min)			Dry purge volume (mL)		
	1	1.5	RF _{1.5} /RF ₁	0	25	50
Isoprene	0.160	0.168	105%	0.458	0.288	0.254
Dichloromethane	1.078	1.082	100%	2.151	2.253	1.863
Methacrolein	0.090	0.083	92%	0.184	0.165	0.160
2-Methyl furan	0.276	0.280	101%	0.340	0.335	0.329
Trichloromethane	1.813	1.920	106%	2.768	2.802	2.531
Benzene	1.507	1.524	101%	1.956	1.960	1.927
Ethyl acrylate	0.233	0.210	90%	0.389	0.362	0.370
Dibromomethane (SS)	0.568	0.587	103%	0.655	0.639	0.603
Trichloroethylene	0.544	0.569	105%	0.765	0.757	0.790
Methyl methacrylate	0.141	0.128	91%	0.223	0.212	0.215
Methyl cyclohexane	0.209	0.153	73%	0.299	0.293	0.297
Methyl isobutyl ketone	0.279	0.282	101%	0.461	0.427	0.404
Methyl crotonate	0.085	0.080	94%	0.173	0.154	0.151
Toluene- <i>D</i> ₈ (IS)	1.000	1.000	100%	1.000	1.000	1.000
Toluene	1.369	1.398	102%	1.890	1.915	1.920
Hexanal	0.063	0.059	94%	0.150	0.141	0.107
<i>n</i> -Butyl acetate	0.394	0.374	95%	0.637	0.617	0.553
Tetrachloroethylene	0.472	0.477	101%	0.610	0.623	0.619
Ethyl benzene	2.867	2.889	101%	3.594	4.240	4.878
<i>m,p</i> -Xylene	4.526	4.679	103%	6.213	7.169	8.472
Heptanal	0.298	0.283	95%	0.533	0.661	0.567
Styrene	1.787	1.844	103%	2.791	3.170	3.589
<i>o</i> -Xylene	2.667	2.673	100%	3.913	4.389	5.176
<i>p</i> -Bromofluorobenzene (IS)	2.710	2.721	100%	1.000	1.000	1.000
1-Ethyl-3-methylbenzene	2.718	2.726	100%	4.095	5.651	5.632
1-Ethyl-4-methylbenzene	2.386	2.397	100%	3.785	5.242	5.153
1,3,5-Trimethylbenzene	2.944	2.988	101%	3.151	4.512	4.320
1-Ethyl-2-methylbenzene	0.508	0.521	103%	4.244	5.716	5.680
Octanal	0.383	0.349	91%	1.088	1.177	0.989
Benzonitrile	2.710	2.721	100%	0.748	0.810	0.858
1,2,4-Trimethylbenzene	2.998	2.959	99%	5.746	4.998	4.137
1,2,3-Trimethylbenzene	2.719	2.775	102%	5.061	4.463	4.153
Nonanal	0.433	0.451	104%	0.928	0.951	0.821
Decanal	0.132	0.159	120%	0.274	0.265	0.225
Total number	10	23		14	11 (23)	7 (9)

Appendix A.6. Chromatograms of filtered and unfiltered ultrapure water and rainwater

Appendix A.6. Figure 1. Chromatogram of filtered and unfiltered ultrapure water.

Appendix A.6. Figure 2. Chromatogram of filtered and unfiltered rainwater (8.9-17.3 min)

Appendix A.6. Figure 3. Chromatogram of filtered and unfiltered rainwater (17.3 to 21.3 min)

Appendix B.1. Sample solution preparation

Appendix B.1. Table 1. Composition of Britton-Robinson buffer at pH 2.72, 7.77 and 9.95

pH	Buffer (mL)	NaOH (mL)
2.71	100	15
7.77	100	53
9.95	100	70

Britton-Robinson buffer of pH 2.71, 7.77 and 9.95 was made with 0.04 M boric acid, 0.04 M phosphoric acid and 0.04 M acetic, diluted with ultrapure water. The base for titration was made with 0.2 M sodium hydroxide, also diluted with ultrapure water.

Appendix B.1. Table 2. Concentration of ions in ion solution used for analysis

Cation	Concentration (ppm)	Anion	Concentration (ppm)
Calcium (Ca^{2+})	0.750	Sulphate (SO_4^{2-})	2.100
Sodium (Na^+)	9.400	Chloride (Cl^-)	4.220
Potassium (K^+)	2.850	Nitrate (NO_3^-)	1.400
Ammonium (NH_4^+)	0.375	Fluoride (F^-)	0.280
Magnesium (Mg^{2+})	0.375	Bromide (Br^-)	1.400
Hydrogen (H^+)	4.250	Nitrite (NO_2^-)	1.400
Lithium (Li^+)	0.075		

Appendix B.2. Reproducibility test of VOCs leachable contaminants in ultrapure water

Appendix B.2. Table 1. Reproducibility test of VOCs leachable contaminants in ultrapure water (UPW) filtrate (Blank to 7N). * indicates concentration below detection limit while ^ indicates concentration below minimal reporting level

Syringe filter	Filtrate	Methyl methacrylate	Methyl isobutyl ketone	Hexanal	Heptanal	Octanal	Nonanal	1,2,3-Trimethyl benzene	Styrene
Blank	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								
1PES	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								0.27^ 0.31^ 0.290 0.028 10
2N	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								
3N2	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								
3N45	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								
4N	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								
5N	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								
6PP	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								
7N	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								

Appendix B.2. Table 2. Reproducibility test of VOCs leachable contaminants in ultrapure water (UPW) filtrate (8N to 10N). * indicates concentration below detection limit while ^ indicates concentration below minimal reporting level

Syringe filter	Filtrate	Methyl methacrylate	Methyl isobutyl ketone	Hexanal	Heptanal	Octanal	Nonanal	1,2,3-Trimethyl benzene	Styrene
8N	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								
8PVDF	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								
9N	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								
9PES	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								
9MCE	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								
9PVDF	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								
10SFCA	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)	1.73 1.46^ 1.595 0.191 12		0.75* 0.69* 0.720 0.042 6		1.56^ 1.62^ 1.590 0.042 3	17.23 17.62 17.425 0.276 2	0.31^ 0.32^ 0.315 0.007 2	0.61 0.56 0.585 0.035 6
10PESS	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)	1.66 1.64 1.650 0.014 1		1.85^ 1.55^ 1.685 0.191 11					0.55 0.60 0.575 0.035 6
10PES	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)	1.60 1.45^ 1.525 0.106 7							0.26^ 0.25^ 0.255 0.007 3
10N	UPW 1 ($\mu\text{g L}^{-1}$) UPW 2 ($\mu\text{g L}^{-1}$) Average ($\mu\text{g L}^{-1}$) SD %RSD (%)								

Appendix B.3. Preliminary screening of VOCs leachable contaminants in different filtrate

Appendix B.3. Table 1. Preliminary screening of VOCs leachable contaminants in different filtrates (Blank to 7N). * indicates concentration below detection limit while ^ indicates concentration below minimal reporting level

Syringe filter	Filtrate	VOCs leachable contaminants ($\mu\text{g L}^{-1}$)								
		Methyl methacrylate	Methyl isobutyl ketone	Hexanal	Heptanal	Octanal	Nonanal	1,2,3-Trimethyl benzene	Styrene	Total VOCs
Blank	UPW Ions pH2.71 pH7.77 pH9.95									
1PES	UPW Ions pH2.71 pH7.77 pH9.95	0.36* 0.33* 0.48* 0.40*	0.34* 0.63* 0.57*						0.47 0.36^ 0.43^ 0.39^ 0.39^	0.83 1.03 1.54 1.36 0.39
2N	UPW Ions pH2.71 pH7.77 pH9.95			0.34* 1.07^						0.34 1.07
3N2	UPW Ions pH2.71 pH7.77 pH9.95			0.28*						0.28
3N45	UPW Ions pH2.71 pH7.77 pH9.95			0.26*						0.26
4N	UPW Ions pH2.71 pH7.77 pH9.95			0.44*			2.28 4.60 3.78 3.47		0.32^	2.28 5.36 3.78 3.47
5N	UPW Ions pH2.71 pH7.77 pH9.95			0.41* 0.28*			3.05 2.50			3.46 2.78
6PP	UPW Ions pH2.71 pH7.77 pH9.95			0.32*						0.32
7N	UPW Ions pH2.71 pH7.77 pH9.95		0.23* 0.25*	0.41* 0.47*			2.28 1.74 2.25			2.92 2.46 2.25

Appendix B.3. Table 2. Preliminary screening of VOCs leachable contaminants in different filtrates (8N to 10N). * indicates concentration below detection limit while ^ indicates concentration below minimal reporting level

Syringe filter	Filtrate	VOCs leachable contaminants ($\mu\text{g L}^{-1}$)								
		Methyl methacrylate	Methyl isobutyl ketone	Hexanal	Heptanal	Octanal	Nonanal	1,2,3-Trimethyl benzene	Styrene	Total VOCs
8N	UPW Ions pH2.71 pH7.77 pH9.95									
8PVDF	UPW Ions pH2.71 pH7.77 pH9.95			0.30*						0.30
9N	UPW Ions pH2.71 pH7.77 pH9.95									
9PES	UPW Ions pH2.71 pH7.77 pH9.95		0.26*							0.26
			0.24*							0.24
9MCE	UPW Ions pH2.71 pH7.77 pH9.95		0.27*							0.27
				0.26*						0.26
				0.37*						0.37
9PVDF	UPW Ions pH2.71 pH7.77 pH9.95			0.68*						0.68
10SFCA	UPW	0.66*		0.75*	0.80*	1.08*	9.75	0.38^	0.72	14.14
	Ions	1.07^		1.11^	1.17^	2.43	22.26	0.36^	0.58	28.98
	pH2.71	1.01^		1.14^	1.06^	1.80^	18.64	0.38^	0.57	24.60
	pH7.77	0.95^	0.27*	1.15^	1.23	2.05^	21.16	0.37^	0.53	27.71
10PESS	pH9.95	0.62*	0.27*	0.97^	1.05^	1.64^	16.99	0.37^	0.47	22.38
	UPW	1.31^	0.25*	1.68^					0.53	3.77
	Ions	0.94^		1.07^					0.45^	2.46
	pH2.71	1.57	0.30*	2.20					0.53	4.60
10PES	pH7.77	1.27^	0.25*	1.53^					0.55	3.60
	pH9.95	0.85^	0.25*	0.79*					0.40^	2.29
	UPW	1.98		0.75*					0.41^	3.14
	Ions	0.94^		0.67*					0.37^	1.98
10N	pH2.71	2.74	0.30*	1.12^					0.45^	4.61
	pH7.77	1.15^		0.64*					0.38^	2.17
	pH9.95	0.98^	0.27*	2.00				0.34^	0.63	4.22
	UPW									
10N	Ions									
	pH2.71									
	pH7.77									
10N	pH9.95			0.46*						0.46

Appendix B.4. Decrement in aromatic VOCs in filtered water

Appendix B.4. Table 1. Decrement in aromatic VOCs in filtered water in comparison to blank.

VOCs	VOCs leachable contaminants ($\mu\text{g L}^{-1}$)				
	Blank	8N		6PP	
Benzene	42.81	41.24	39.10	37.05	36.77
Ethyl benzene	30.19	25.18	25.00	19.82	18.45
<i>m,p</i> -Xylene	34.15	27.30	27.19	21.35	19.72
Styrene	36.55	30.24	30.48	26.69	24.91
<i>o</i> -Xylene	40.04	31.01	30.81	27.09	24.69
Cumene	34.36	26.58	26.17	18.23	16.64
Allylbenzene	39.35	31.41	31.14	23.65	21.91
Propylbenzene	34.82	24.98	24.38	13.41	12.32
1-Ethyl-3-methylbenzene	27.41	20.01	19.51	11.96	11.01
1-Ethyl-4-methylbenzene	33.21	23.74	23.13	12.92	11.97
1,3,5-Trimethylbenzene	37.14	24.89	24.15	16.39	15.16
1-Ethyl-2-methylbenzene	41.14	29.15	28.41	20.90	19.35
Benzonitrile	42.83	42.35	40.37	39.12	37.23
2,3-Methylstyrene	39.92	27.47	25.68	18.99	17.90
1,2,4-Trimethylbenzene	41.41	26.16	25.38	17.57	16.25
1,2,3-Trimethylbenzene	42.91	28.04	27.14	21.23	19.83

Appendix B.5. Concentration of metals in ultrapure water filtrates

Appendix B.5. Table 1. Concentration of metals in ultrapure water (Li-Y).

* indicates concentration below detection limit. A space indicates no element was detected.

Syringe Filter	Inorganic leachable contaminants (ppb)																		
	Li	Be	Na	Mg	Al	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge
UPW																			
1PES																			
2N															0.006				
3N2															0.002*				
3N45			0.753												0.003				
4N															0.005				
5N			4608	16.5		51.8	32.1				0.1				0.005				
5PP					1.64										0.02				0.762
6PP																			
7N	0.382														0.003*				
8N															1.066				
8PVDF			141																
9N																			
9PES																			
9MCE						7.01													
9PVDF			27.9																
10SFCA			8.35	0.462											0.003				1.072
10PESS															0.007				
10PES															0.005				
10N															0.005				

Appendix B.5. Table 2. Concentration of metals in ultrapure water (Zr-Hf).

* indicates concentration below detection limit. A space indicates no element was detected.

yringe Filter	Inorganic leachable contaminants (ppb)																							
	Zr	Mo	Cd	In	Sn	Sb	Te	Cs	Ba	La	Ce	Pr	Nd	Em	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf
UPW																								
1PES																								
2N																								
3N2																								
3N45																								
4N																								
5N	0.362																							
5PP																								
6PP																								
7N	0.95																							
8N	0.006		0.544																					
8PVDF																								
9N																								
9PES																								
9MCE																								
9PVDF																								
10SFCA																								
10PESS																								
10PES																								
10N																								

Syringe Filter	Inorganic leachable contaminants (ppb)									
	Ta	W	Re	Hg	Tl	Pb	Bi	Th	U	
UPW										
1PES		2.47								
2N										
3N2										
3N45										
4N										
5N										
5PP										
6PP										
7N										
8N										
8PVDF										
9N										
9PES		6.36								
9MCE										
9PVDF										
10SFCA										
10PESS										
10PES		0.311								
10N										

Appendix B.5. Table 3. Concentration of metals in ultrapure water (Ta-U).

* indicates concentration below detection limit. A space indicates no element was detected.

Appendix C.1. Box plots of VOCs from August 2015 to July 2016

Appendix C.1. Figure 1-4. Box plot of isoprene, methacrolein, 2-methyl furan, and trichloromethane in rainwater from August 2015 to July 2016.

Appendix C.1. Figure 5-8. Box plot of benzene, ethyl acrylate, trichloroethylene, and methyl methacrylate in rainwater from August 2015 to July 2016.

Appendix C.1. Figure 9-12. Box plot of methyl cyclohexane, methyl isobutyl ketone, methyl crotonate, and toluene in rainwater from August 2015 to July 2016.

Appendix C.1. Figure 13-16. Box plot of hexanal, *n*-butyl acetate, tetrachloroethylene, and ethyl benzene in rainwater from August 2015 to July 2016.

Appendix C.1. Figure 13-16. Box plot of *m,p*-xylene, heptanal, styrene, and *o*-xylene in rainwater from August 2015 to July 2016.

Appendix C.1. Figure 17-20. Box plot of 1-ethyl-3-methylbenzene, 1-ethyl-4-methylbenzene, 1,3,5-trimethylbenzene, and 1-ethyl-2-methylbenzene in rainwater from August 2015 to July 2016.

Appendix C.1. Figure 17-20. Box plot of benzonitrile, 1,2,4-trimethylbenzene, and 1,2,3-trimethylbenzene in rainwater from August 2015 to July 2016.

Appendix C.2. PMF Calculation

Appendix C.2. Table 1. Factors 5-11 and base run results.

No. of Factors	Q(Robust)	Q(True)	Convergence	Residuals
5	12515.7	14322.6	Yes	401
6	7196.8	7781.9	Yes	208
7	3287.6	3405.9	Yes	73
8	766.2	766.2	Yes	0
9	427.1	427.1	Yes	0
10	254.1	254.1	Yes	0
11	113.9	113.9	Yes	0

Appendix C.2. Table 2. VOCs and response in base run of 8 Factors.

VOCs	Category	R ²	Intercept	Slope
Methacrolein	Strong	0.99966	1.19351	0.99645
2-Methyl furan	Strong	0.99995	0.08168	0.99966
Benzene	Strong	0.99975	0.08111	0.99153
Hexanal	Strong	0.99913	-5.14488	1.00549
<i>n</i> -Butyl acetate	Strong	0.99817	0.1541	0.99679
Ethyl benzene	Weak	0.84121	2.71198	0.70237
<i>m,p</i> -Xylene	Weak	0.90569	0.88657	0.83579
Heptanal	Strong	0.99993	0.29225	0.99885
<i>o</i> -Xylene	Strong	0.99553	0.21117	0.98457
1-Ethyl-3-methylbenzene	Strong	0.96439	0.44578	0.88289
1-Ethyl-4-methylbenzene	Weak	0.82963	0.82035	0.70528
1-Ethyl-2-methylbenzene	Strong	0.97646	-0.16086	1.02255
1,2,4-Trimethylbenzene	Weak	0.6033	2.85746	0.466
1,2,3-Trimethylbenzene	Weak	0.80631	1.46958	0.72854

Appendix C.2. Table 3. Bootstrap mapping of 8 Factors.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8	Unmapped
Boot Factor 1	100	0	0	0	0	0	0	0	0
Boot Factor 2	0	100	0	0	0	0	0	0	0
Boot Factor 3	0	0	100	0	0	0	0	0	0
Boot Factor 4	0	0	0	100	0	0	0	0	0
Boot Factor 5	0	0	0	0	100	0	0	0	0
Boot Factor 6	0	0	0	0	0	100	0	0	0
Boot Factor 7	0	0	0	0	0	0	100	0	0
Boot Factor 8	0	0	0	0	0	0	0	100	0

Appendix C.2. Figure 1-2. F_{peak} values of $Q(\text{True})$ and $Q(\text{Robust})$.

Appendix C.2. Figure 1-6. Scaled residuals of methacrolein, 2-methyl furan, benzene, hexanal, *n*-butyl acetate and ethyl benzene from PMF

Appendix C.2. Figure 7-15. Scaled residuals of *m,p*-Xylene, heptanal, *o*-xylene, 1-ethyl-3-methylbenzene, 1-ethyl-4-methylbenzene, 1-ethyl-2-methylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, and calculated sum of all species from PMF

Appendix C.3. Trend graphs between VOCs from August 2015 to July 2016

Appendix C.3. Figure 1-4. Trend graphs of trichloroethylene and tetrachloroethylene, hexanal and heptanal, methacrolein and 1,2,3-trimethylbenzene, and methyl methacrylate and 1,2,4-trimethylbenzene in rainwater from August 2015 to July 2016.

Appendix C.4. Trend graphs of all VOCs (Monsoon)

Appendix C.4. Figure 1. Trend graphs of all VOCs in rainwater from August 2015 to July 2016 (Monsoon).

Appendix C.5. Monthly correlation distribution

Appendix C.5. Table 1. Positive monthly correlation >0.8 between VOC pairs collected from August 2015 to July 2016. *A=Aromatic, O=Oxygenated, AA=Alkane/Alkene, and H=Halogenated. ^Cross is the sum of all X/X VOC pairs.

Period	Positive correlations											
	Aromatics	Oxygenated	Halogenated	Alkane/Alkene	A/O*	A/H*	A/AA*	O/AA*	H/AA*	O/H*	Cross^	Others
August 2015	20	5			18	1				3	22	4
September 2015	23	2			12	10				10	32	9
October 2015	27				9			2			11	8
November 2015	25	3			10	7	2				19	4
December 2015	1		1		4	4				5	13	2
January 2016	15	1			2	2	2	1	1		8	3
February 2016	13	1	1		12	2	1	1		3	19	5
March 2016	16	4			10	6	3				19	3
April 2016	13	2			8	2				6	16	2
May 2016	16				15	1		5		3	24	9
June 2016	5	2			4					2	6	6
July 2016	9				9	4				1	14	6

Appendix C.5. Table 2. Negative monthly correlation >0.8 between VOC pairs collected from August 2015 to July 2016. *A=Aromatic, O=Oxygenated, AA=Alkane/Alkene, and H=Halogenated. ^Cross is the sum of all X/X VOC pairs.

Period	Negative correlations											
	Aromatics	Oxygenated	Halogenated	Alkane/Alkene	A/O*	A/H*	A/AA*	O/AA*	H/AA*	O/H*	Cross^	Others
August 2015					3						3	1
September 2015			1		8	10				4	22	2
October 2015	4				11		1	1			13	2
November 2015	5	1				3	1		1	1	6	1
December 2015					2					2	4	
January 2016	5					4	1			1	6	
February 2016	6		1		8	1	1	1		5	16	4
March 2016	7				8			1	1	1	10	2
April 2016	5				2					1	3	2
May 2016	2	1			7	5		1		4	17	2
June 2016	4	5			6					2	8	2
July 2016	1				5						5	1

Appendix C.6. Monsoon correlation distribution

Appendix C.6. Table 1. Positive monsoon correlation >0.8 between VOC pairs collected from August 2015 to July 2016. *A=Aromatic, O=Oxygenated, AA=Alkane/Alkene, and H=Halogenated. ^Cross is the sum of all X/X VOC pairs.

Period	Positive correlations									
	Aromatics	Oxygenated	Halogenated	Alkane/Alkene	A/O*	A/H*	A/AA*	O/AA*	H/AA*	O/H*
August to September 2015 SWM	8	3			9	5	9	2	2	4
October to November 2015 Inter	12	1				1	3		1	2
December to March 2016 NEM	15				1					2
April to May 2016 Inter	9					9				6
June to July 2016 SWM	6			1		4	3		3	1
										11
										2

Appendix C.6. Table 2. Negative monsoon correlation >0.8 between VOC pairs collected from August 2015 to July 2016. *A=Aromatic, O=Oxygenated, AA=Alkane/Alkene, and H=Halogenated. ^Cross is the sum of all X/X VOC pairs.

Period	Negative correlations									
	Aromatics	Oxygenated	Halogenated	Alkane/Alkene	A/O*	A/H*	A/AA*	O/AA*	H/AA*	O/H*
August to September 2015 SWM			2			5				5
October to November 2015 Inter										0
December to March 2016 NEM				1			11	7	2	20
April to May 2016 Inter					3					2
June to July 2016 SWM						3	6	1		2
										5
										1
										12

Appendix D.1. Concentration of metals in ultrapure water filtrates

Appendix D.1. Table 1. Preliminary study of VOC residues detected in the aqueous phase after 0.5 h of stirring with lecithin/pentane.

* indicates concentration below detection limit (DL), ^ indicates concentration below minimal reporting level (MRL), N.D. stands for not detected.

		Control	Pentane		
		Blank	0 ppm Lecithin	250 ppm Lecithin	5000 ppm Lecithin
		Residue ($\mu\text{g L}^{-1}$)	Residue ($\mu\text{g L}^{-1}$)	Residue ($\mu\text{g L}^{-1}$)	Residue ($\mu\text{g L}^{-1}$)
No.	Aldehydes, ketones, and furan				
	1 Hexanal	8.88	8.98	5.11	4.85
	2 Heptanal	6.03	3.87	2.40	1.11^
	3 Octanal	3.25	1.83^	1.23*	0.64*
	4 Nonanal	1.73	1.43	1.30	1.17^
	5 Methyl isobutyl ketone	5.98	3.81	2.87	1.68^
	6 Methacrolein	4.68	6.13	3.61	2.22
	7 2-Methyl furan	0.88	0.82^	0.62^	0.65^
	Aromatic compounds				
	8 Benzene	0.87	0.71^	0.53^	0.52^
	9 Ethyl benzene	0.57	0.51^	0.48^	0.48^
	10 Styrene	0.84	0.54	0.48	0.45^
	11 Toluene	0.68^	0.53^	0.40^	0.39^
	12, 13 <i>m,p</i> -Xylene	0.40^	0.35^	0.32^	0.31^
	14 <i>o</i> -Xylene	0.55^	0.36^	0.30^	0.28^
	15 Benzonitrile	9.07	5.55	4.01	2.23
	Esters				
	16 <i>n</i> -Butyl acetate	5.47	2.76	2.11	1.19^
	17 Ethyl acrylate	4.22	3.12	2.32	1.52
	18 Methyl crotonate	6.61	4.72	3.58	2.17
	19 Methyl methacrylate	4.31	2.68	1.95	1.17^
	Halogenated compounds				
	20 Bromodichloromethane	1.95	1.03^	0.73^	0.49^
	21 Dibromochloromethane	2.83	1.34	1.00^	0.68^
	22 Tribromomethane	3.91	1.57^	1.14^	0.65*
	23 Trichloromethane	1.24	1.39	0.74^	1.60
	24 Trichloroethylene	0.55^	0.47^	0.38^	N.D.
	25 Tetrachloroethylene	0.35^	0.33^	N.D.	N.D.

Appendix D.2. NIST library match of unknown compounds from sonication of lecithin with vitamin E samples

Appendix D.2. Table 1-2. NIST library match of unknown compounds from sonication of lecithin with vitamin E samples

Scan 2535 (19.741 min)						
Rank	Name	MW	Formula	Qual	MI	CAS #
1	2-Octenal, (E)-	126	C8H14O	90		002548-87-0
2	2-Octenal, (E)-	126	C8H14O	86		002548-87-0
3	2-Octenal, (E)-	126	C8H14O	80		002548-87-0
4	2-Hexenal, (E)-	98	C6H10O	64	*	006728-26-3
5	2-Methylene cyclopentanol 1H-Imidazole, 4,5-dihydro-	98	C6H10O	62	*	020461-31-8
6	2,4-dimethyl-	98	C5H10N2	49	*	000930-61-0
7	2-Cyclohexen-1-ol	98	C6H10O	45	*	000822-67-3
8	2-Cyclohexen-1-ol	98	C6H10O	43	*	000822-67-3
9	1-Propenylaziridine	83	C5H9N	38	*	100019-25-0
10	2-Hexenal	98	C6H10O	38	*	000505-57-7
11	2-Propen-1-amine, N-2-propenyl-	97	C6H11N	35	*	000124-02-7
12	2-Cyclohexen-1-ol	98	C6H10O	30	*	000822-67-3
13	6-Oxabicyclo[3.1.0]hexane	84	C5H8O	30	*	000285-67-6
14	3-Hexene, (Z)-	84	C6H12	27	*	007642-09-3
15	2-Hexyn-1-ol	98	C6H10O	27	*	000764-60-3
Scan 2777 (20.519 min)						
Rank	Name	MW	Formula	Qual	MI	CAS #
1	2-Nonen-1-ol, (E)-	142	C9H18O	38		031502-14-4
2	2-Nonen-1-ol	142	C9H18O	35		022104-79-6
3	2-Hepten-1-ol, (E)-	114	C7H14O	32		033467-76-4
4	1H-Pyrrole, 2,5-dihydro-1-nitroso-	98	C4H6N2O	25	*	010552-94-0
5	2-Nonen-1-ol	142	C9H18O	16		022104-79-6
6	3-Buten-1-ol, 3-methyl-Oxirane, 2,2'-(1,4-butanediyl)bis-	86	C5H10O	10		000763-32-6
7	1-Nonanol	142	C8H14O2	10		002426-07-5
8	1-Nonanol	144	C9H20O	10		000143-08-8
9	1-Nonanol	144	C9H20O	10		000143-08-8
10	(Z)-2-Heptene	98	C7H14	9	*	006443-92-1
11	2-Heptene, (E)-	98	C7H14	9	*	014686-13-6
12	2-Heptene	98	C7H14	9	*	000592-77-8
13	2-Heptene	98	C7H14	9	*	000592-77-8
14	(Z)-3-Heptene	98	C7H14	9	*	007642-10-6
15	3-Heptene, (E)-	98	C7H14	9	*	014686-14-7

Appendix D.3. Optimization of vitamin E encapsulation for VOCs removal

Appendix D.2. Table 1. VOCs residues (lecithin: vitamin E, 9:2) with different stirring time.

* indicates concentration below detection limit (DL), ^ indicates concentration below minimal reporting level (MRL), N.D. stands for not detected. Percentage reduction comparisons were performed by comparing samples with the control blank without olive oil and lecithin.

		Vitamin E encapsulated (Lecithin) 2:9 Residue									
		0.5 h stir (µg L ⁻¹)		1 h stir (µg L ⁻¹)		2 h stir (µg L ⁻¹)		3 h stir (µg L ⁻¹)			
No.		0 ppm Lecithin	5 ppm Lecithin	0 ppm Lecithin	5 ppm Lecithin	0 ppm Lecithin	5 ppm Lecithin	0 ppm Lecithin	5 ppm Lecithin	0 ppm Lecithin	5 ppm Lecithin
Aldehydes and Ketone											
1	Hexanal	7.18	12.54	9.46	9.70	12.59	13.90	10.03	17.53		
2	Heptanal	0.91*	1.20	1.16^	0.91*	1.28	0.95^	1.12^	1.01^		
3	Octanal	0.52*	0.63*	0.62*	0.53*	0.62*	0.52*	0.57*	0.52*		
4	Nonanal	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.		
5	Methyl isobutyl ketone	5.40	8.98	7.18	5.19	10.46	7.77	9.23	10.13		
Aromatics											
6	Benzene	1.18	1.66	1.32	0.95	1.21	1.01	1.01	1.10		
7	Ethyl benzene	0.61	0.62	0.62	0.61	0.61	0.61	0.61	0.61		
8	Styrene	0.59	0.61	0.61	0.59	0.61	0.60	0.60	0.59		
9	Toluene	0.67^	0.90	0.78^	0.53^	0.73^	0.60^	0.59^	0.57^		
10, 11	<i>m,p</i> -Xylene	0.46^	0.46^	0.46^	0.46^	0.46^	0.46^	0.46^	0.46^		
12	<i>o</i> -Xylene	0.38^	0.39^	0.39^	0.38^	0.39^	0.38^	0.38^	0.38^		
13	Benzonitrile	1.44^	1.57^	1.58^	1.48^	1.58^	1.48^	1.52^	1.51^		
Esters											
14	Ethyl acrylate	5.22	8.43	6.91	4.81	8.83	7.18	8.41	9.10		
15	Methyl crotonate	5.71	9.67	7.39	5.18	11.09	8.22	9.83	10.70		
16	Methyl methacrylate	5.10	8.29	6.65	4.75	8.66	6.98	8.21	8.75		
17	<i>n</i> -Butyl acetate	4.31	7.67	6.97	4.10	8.32	6.13	7.10	7.44		
Halogenated compounds											
18	Bromodichloromethane	2.13	3.68	3.11	1.85	3.47	2.46	2.96	2.97		
19	Dibromochloromethane	2.38	4.65	3.84	2.27	5.26	3.29	4.30	3.92		
20	Tribromomethane	0.62*	0.80*	0.81*	0.63*	0.91^	0.70*	0.83*	0.76*		
21	Trichloroethylene	0.55^	0.73^	0.65^	0.51^	0.60^	0.56^	0.51^	0.52^		
22	Tetrachloroethylene	N.D.	0.39^	0.386	0.38^	N.D.	N.D.	N.D.	N.D.		