

Chemical assessment of emissions from sewage collection facilities

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Publication Date: 2014

DOI: https://doi.org/10.26190/unsworks/18130

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Chemical Assessment of Emissions from Sewage Collection Facilities

By

Bei Wang

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy



School of Civil and Environmental Engineering Faculty of Engineering

> The University of New South Wales September 2014

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Surname or Family name: Wang	
First name: Bei	Other name/s:
Abbreviation for degree as given in the Universi	ty calendar: PhD School: Civil and
Environmental Engineering	Faculty: Engineering
Title: Chemical Assessment of Emissions from S	Sewage Collection Facilities

Abstract 350 words maximum: (PLEASE TYPE)

Sewage consists of a wide range of organic and inorganic constituents originating from domestic and trade waste discharges. Of particular interest are the range of odorous volatile organic compounds (VOCs) and volatile sulfur compounds(VSCs) produced by anaerobic reactions (such as fermentation and sulfate respiration) in the sewage, sediments and biofilms on the sewer walls. Complaints due to sewage odour are a major issue for wastewater utilities because the repeated release of unpleasant odours from a sewer network constitutes both a public nuisance and possible regulatory violation. However, the complex nature of sewer odours provides many challenges with regards to the management and control of these emissions.

This thesis aims to improve understanding of the emissions of compounds and odorants from sewage collection facilities by developing and benchmarking analytical methodologies. A highly sensitive and reliable method using gas chromatograph was developed and evaluated for the analysis of full spectra of compounds that present at the headspace of sewer air. While identifying the emitted chemical species provides useful information, the key to understanding the odour is establishing which of the chemical species odorants are. The use of gas chromatograph with simultaneous mass spectrometer and olfactory detection port (GC-MS/ODP) provides a method of prioritising the chemical species present along with their odour potential. The VOCs identified within emissions included alkanes, aromatics, halogenated hydrocarbon and terpenes, esters, aldehydes and alcohols whiles non-H₂S VSCs related were: methyl methanethiol (MeSH), dimethyl sulfide (DMS), Carbon disulfide (CS₂), dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS). The spatial-temporal variability of VOCs and VSCs were clearly identified and evaluated.

A similar range of VOCs and VSCs have been identified in sewer headspace air across diverse countries and climatic regions, demonstrating that the data and conclusions presented in this present work would extend to context out of Australia and is useful for identifying the odour implications of sewer headspace VOCs for the wider industry. However, measured VSC concentrations from the Perth sampling sites were significantly higher than those at the Melbourne and Sydney sites. This indicates the possibly important role of climatic conditions played for VSCs emission at sewer networks.

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Acknowledgements

Over the course of my candidature, I have had many pleasures and joys of meeting and working with many fantastic people. I would like to take this opportunity to express my gratitude to all of them.

First, I would like to thank my supervisor Professor Richard Stuetz for his endless supports, highly valuable opinions and enthusiastic guidance during my research period. In addition, I would like to show my great appreciation for his sympathy and patience during the difficult time of my candidature. Also, many thanks toward my co-supervisor Dr Eric C. Sivret and Dr Gavin Parcsi for his guidance and supervision during the development of my analytical method with GC based instrument. I also would like to thank them for their efforts and time in helping me complete my manuscripts for any publication submission.

I would like to extend my thanks to many staff members of the School of Civil and Environmental Engineering, University of New South Wales for their assistance during my candidature. I would like to express my gratitude to Dr Gautam Chattopadhyay, Dr Xinguang Wang, Mr Kelvin Ong for their valuable advices and assistance during my working in the laboratories. I would also like to acknowledge the valuable assistance from industrial colleagues, Mr Shaun Kenny from Sydney Water Corporation for his providing field samples over the past three years and many assistances and advices particularly when diurnal studies were undertaken at the sewage pump station. Sincerely thanks I would like to express are for my colleagues and friends at UNSW, Hung Le, Dr Nhat Le, Lili Wang, Grace Li, Joyce Yuan for kindness and care during my stay at Australia.

I would like to acknowledge the Australian Research Council to provide funding support for the works under the Linkage Project (LP0882016) "Sewer Corrosion and Odour Research" with industry supports from Barwon Regional Water Corporation, Gold Coast Water, Hunter Water Corporation, South Australian Water Corporation, South East Water limited, Sydney Water Corporation and Water Research Australia. I would also to thank Chinese Scholarship Council (CSC) and UNSW Graduate Research School for supporting met with the Tuition Fee Remission (TFR) and CSC scholarship. Last but not least, a special thanks to my family who have been emotionally supporting me throughout my PhD candidate despite their far distances. I would like to specially thank my parents for their support, love and faith in me.

Abstract

Sewage consists of a wide range of organic and inorganic constituents originating from domestic and trade waste discharges. Of particular interest are the range of odorous volatile organic compounds (VOCs) and volatile sulfur compounds(VSCs) produced by anaerobic reactions (such as fermentation and sulfate respiration) in the sewage, sediments and biofilms on the sewer walls. Complaints due to sewage odour are a major issue for wastewater utilities because the repeated release of unpleasant odours from a sewer network constitutes both a public nuisance and possible regulatory violation. So the effective control of odour emissions is essential for sewage system operators and the potential public receptors. However, the complex nature of sewer odours provides many challenges with regards to the management and control of these emissions.

This thesis aims to improve understanding of the emission of compounds and odorants from sewage collection facilities by developing and benchmarking analytical methodologies. A highly sensitive and reliable method using gas chromatography was developed and evaluated for the analysis of full spectra of compounds that present at the headspace of sewer air. To be specific, gas chromatography coupled with mass selective detector (MSD), chemiluminescence detector (SCD) were developed to detect and quantify VOCs and VSCs, respectively. While identifying the emitted chemical species provides useful information, the key to understanding an odour is establishing which of the chemical species odorants are. The use of gas chromatograph with simultaneous mass spectral and olfactory detection port (GC-MS/ODP) provides a method of prioritising chemical species present along with their odour potential.

Extensive field sampling of a range of sewer site (different sewer structures, sewage types and chemical dosing treatments) was performed to develop an understanding of the emissions of sewage collection facilities representative of conditions present in Australia sewerages system. The VOCs identified within emissions included alkanes, aromatics, halogenated hydrocarbons and terpenes, esters, aldehydes and alcohols whiles non-H₂S VSCs related were: methyl methanethiol (MeSH), dimethyl sulfide (DMS), Carbon disulfide (CS₂), dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS).

Measurements over a 3 year period from 12 field monitoring sites across Sydney allowed for a first evaluation of sewer emission dynamics at different timeframe (annual, seasonal and weekly) and answer the question regarding the spatial and temporal variability at humid subtropical climate area - Greater Sydney. It was revealed the associated temporal component of variation was generally larger than the spatial components although most investigated VOCs still exhibited significant spatial variations, even after accounting for the temporal effects. These results suggest that measured VOCs concentration was highly site dependent and a consideration of monitoring sewer sites with specific upstream discharges (e.g. trade waste) at a proper monitoring frequency would be incorporated into future sampling strategies decision making to improve the monitoring of a sewer odour emission and enhance design/operation of odour abatement processes for sewer emissions management.

The characteristic and observed trends of sewer emissions in Sydney were further confirmed by additional sampling and analyses conducted at other Australia cities (Melbourne and Perth). The inclusion of extra emission data collected at Melbourne and Perth allowed for the understanding and depicting the distribution of specific odorants and VOCs across different climatically distinct regions. A similar range of VOCs and VSCs have been identified in sewer headspace air across diverse countries and climatic regions, demonstrating that the data and conclusions presented in this present work would extend to context out of Australia and is useful for identifying the odour implications of sewer headspace VOCs for the wider industry. However, measured VSC concentrations from the Perth sampling sites were significantly higher than those at the Melbourne and Sydney sites. This indicates the possibly important role of climatic conditions played for VSC emissions at sewer networks.

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List of Acronyms & Abbreviations

1-BusH	1-butanethiol
CS_2	carbon disulfide
CLSA	closed loop stripping analysis
DMS	dimethyl sulfide
DMDS	dimethyl disulfide
DMTS	dimethyl trisulfide
DEDS	diethyl disulfide
EtSH	ethyl mercaptan
EMS	ethyl methyl sulfide
ECD	electron capture detector
FID	flame ionisation detector
FPD	flame photometric detector
GC	gas chromatograph
GC/O	gas chromatography/olfactory
H_2S	hydrogen sulfide
IC	ion chromatogram
MS	mass spectrometer
MSD	mass selective detector
MDGC	Multidimensional gas chromatograph
MeSH	methyl mercaptan
MBTE	methyl tert-butyl ether
ODP	olfactory detection port
OTV	olfactory Threshold Value
РТ	purge and trap

SCD	sulfur	chemilu	uminescence	detector

- THC total hydrocarbon compound
- TD thermal desorption
- TD-GC-MS/O thermal desorption-gas chromatography mass/olfactory
- TIC total ion chromatogram
- VOC volatile organic compound
- VSC volatile sulfur compound
- VO(S)C volatile organic (sulfur) compound

List of Publications

- Wang B., Sivret E.C., Parcsi G., Wang X. and Stuetz R.M. (2012) Characterising volatile organic compounds from sewer emissions by thermal desorption coupled with gaschromatography-mass spectrometry. Chemical Engineering Transactions 30, 73-78 (DOI: 10.3303/CET1230013)
- [2] Wang B., Sivret E.C., Parcsi G., Wang X., Le N.M., Kenny S., Bustamante H. and Stuetz R.M. (2014) Is H₂S a suitable process indicator for odour abatement performance of sewer odours? Water Science & Technology 69 (1), 92 – 98 (DOI:10.2166/wst.2013.559)
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- [4] Wang B., Sivret E.C., Parcsi G. and Stuetz R.M. (2015) Determination of VOSCs in sewer headspace air using TD-GC-SCD. Talanta 137, 71-79 (DOI:10.1016/j.talanta.2014.11.072)
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- [6] Sivret E.C., Le N.M., Wang B., Wang X. and Stuetz R.M. (2014) Impact of sewer emissions dynamics on monitoring campaigns design. Chemical Engineering Transactions 40, 43-48 (DOI: 10.3303/CET1440008)

Chapter 1 Introduction

1.1 The Sewer Emission Monitoring and Management

1.1.1 Odour Formation in Sewer Networks

Sewer network is an important component of urban wastewater treatment system and can greatly influence on the performance and environment of downstream wastewater treatment plants. Sewerage collection system as named is used to collect wastewater flows from households and industries as well as runoff from urban surface and transport for treatment and disposal at WWTPs. Figure 1.1 describes the processes within the sewer network and their relevance with the urban system, including the urban atmosphere, WWTPs and receiving waters.



Figure 1-1 Wastewater transport and processes within and related to the urban wastewater system (Stuetz and Frechen 2001)

Sewage consists of a wide range of organic and inorganic constituents originating from domestic and trade waste discharges. Sewer networks thereby serving as a high rate chemical and biological reactor with aerobic, anoxic, and anaerobic environments the diversity of the sewerage constituents is further increased by the reaction products during transport (Hvitved-Jacobsen et al. 2013). The air composition emitted from sewer networks are complex with mixtures volatile chemicals discharged to sewers and volatile by-products derived from biochemical reactions occurring under anaerobic conditions and possibly include a wide range of industrial chemicals depending on the types of industrial discharge to sewer catchments as well. Of particular interest are the range of odorous volatile organic compounds (VOCs) and inorganic compounds, i.e. primarily hydrogen sulfide (H_2S) produced by anaerobic reactions (such as fermentation and sulfate respiration) in the sewage, sediments and biofilms on the sewer walls (Hvitved-Jacobsen et al. 2002, Rudelle et al. 2011). These volatile compounds are transferred and released to the air in the sewer headspace by diffusive and convective mass transfer. As a result, the air in sewer headspaces is fundamental and only concern for malodour problems and nuisance complains (Figure 1-2).



Figure 1-2 Related reaction and exchange of odorous compounds formation in the sewer atmosphere (Hvitved-Jacobsen et al. 2013)

The major sewer systems that could be associated with odour formation and phenomenon are generally included: 1) Odour formations primarily occurred during anaerobic environment, including rising mains (pressurized sewer), full flowing gravity sewer as well in the area of gravity sewer with low slope; 2) odorous emission could be enhanced under aerobic and anoxic condition, typically found at partly filled gravity sewer and sewer structure, like drops, manhole and pump.

1.1.2 Sewer Odour Monitoring and Management in Australia

The formation of odour nuisance entails the design and implementation of an effective engineering solution leading to management of sewer emissions. The importance of managing odorous emissions from sewer networks has become more significant in the past 10-20 years, mainly due to the increasing number of complaints and the reported failures in the performance of odour abatement systems (Gostelow et al. 2001, Lebrero et al. 2011).

From a perspective of abating sewer odours, a significant number of odour abatement processes have been installed and operated by the wastewater industry at 187 sites throughout Australia (Sivret and Stuetz 2012). Based on the fundamental process mechanisms (Figure 1-3), the majority of the abatement operations are adsorption based processes such as activated carbon and zeolite based filters were dominant (76.5%), followed by biological processes (21.1%). Predominately, the existing odour abatement processes are installed on mixed sewers (60.8%), containing both domestic and industrial wastewater), with the remainder of the processes operating on domestic sewers.



Figure 1-3 Overviews of abatement process types for sewer abatement in Australia

With the objectives of developing and selecting odour abatement strategies to mitigate, abate and eliminate nuisance sewer odours, a solid understanding and assessment of the sources must be established.

Odour assessment approach is typically involved with the chemical analysis of individual chemical such as H_2S and the occasional use of dilution olfactometry that provides a measure of the odour present as odour concentration (OU). Whilst OU does not provide little information with regards to qualitative characters of the odour nor does it provide any information related to the chemical composition, which is essential when designing and selecting an abatement strategy. The optimal use of treatment strategies therefore must be targeted towards the problem causing chemicals.

An environmental odour sample may contain up to thousands of both odorous and nonodorous chemical compounds. In addition, the composition and their magnitudes can vary greatly with different sewer structures or with the background environmental conditions in the sewer atmosphere. The complex nature of sewer odours provides many challenges with regards to the monitoring of these emissions.

The first detailed data of sewer odour composition and concentration in Australia context can be tracked back to 1970s when investigated typical composition of sewer under anaerobic environment at dry weather conditions. However, from an general perspective, in Australia monitoring parameters for the sewer emission management purposes are limited to hydrogen sulfide (H_2S), with limited and infrequent monitoring of non- H_2S sulfur compounds and VOCs (Figure 1-4) for characterisation of emissions from sewers (Sivret and Stuetz 2010) and odour abatement performance monitoring (Sivret and Stuetz 2012).



Figure 1-4 Monitoring parameters for the sewer odour management purposes in Australia (Sivret and Stuetz 2012)

1.1.3 Odour Assessment Approaches

Toward an assessment of an odour sample, its composition can be determined by collecting a field sample and using gas chromatograph combined with different detectors to speciate the analytes within the odour sample, whereas dilution olfactometry analysis represents the odour concentration of the whole sample. Gas chromatography and olfactometry detection often represented the most popular odour measurement techniques (Figure 1-5), commonly applied on different industry processes, including such as wastewater, livestock facilities and food industry. Complementary to one of the two major monitoring techniques, the use of GC-O (Gas Chromatography-olfactory analysis) allows the determination of the odorants within a particular sample.



Figure 1-5 Overviews of odour measurement techniques for site monitoring (Muñoz et al. 2010)

1.2 Research Objectives

The overall aim of the project is to employ chemical and olfactory techniques to acquire detailed data on composition of odorants and Volatile Organic Compounds (VOCs) emitted from sewer systems via extensive sampling and monitoring to enhance our understanding of the composition of odours in sewer systems in order to improve the management and the choice of odour abatement strategy. In achieving this aim, a number of objectives must be achieved, which includes:

(1) Development of sampling and analytical methodology using thermal desorption-gas chromatography (TD-GC) based analysis in order to assess the compositions of odorants from sewer odour emissions;

(2) Apply developed analytical methodology to investigate the composition of odorants and VOCs present at the headspace of sewer networks;

(3) Investigate the impact of sewer operational conditions and geographical conditions on odorant and VOC composition;

(4) Develop a composition database for odorants and VOCs for different sewer systems.

1.3 Thesis Structure

This thesis is present in 8 sections. A brief introduction to the background, the objectives are provided in **Chapter 1**. A review of relevant literature that provides the background material used in the development of this research is present in **Chapter 2**, while a description of the experimental methodologies and instrumentations used in this research is proved in **Chapter 3**. **Chapter 4** and **Chapter 5** presents the GC based analytical methods for VSCs and VOCs determinations and the chemical speciation for VSC and VOC emissions from representative sewer sites is explored correspondingly as well. The results of identification and prioritisation of odorants from sewer emission by GC-MS/ODP analysis are present in **Chapter 6**. An evaluation of consistence and variability of chemical speciation across different climatically distinct regions is provided in **Chapter 7**. Finally, **Chapter 8** summaries the conclusions of this study and provide recommendation for further research.

Chapter 2 Literature Review

2.1 Introduction

Wastewater operations (i.e. collection and treatment systems) produce and emit a complex mixture of chemical species in any permutation of concentrations. The chemical matrix of a sample may contain hundreds or thousands of compounds with a wide range of molecular weights and a variety of physicochemical properties. Of particular interest in terms of environmental and social impact are the volatile organic compounds (VOCs) that contribute to the overall odour/malodour of samples.

Previous studies have reported on increasing frequency and details that describe the detection and emissions of VOCs in wastewater and wastewater treatment processes; however the understanding of the VOCs and odour from many sewage collection systems is still very limited and far from sufficient to develop reliable strategies for emission abatement and mitigation. The focus of published studies to date on sewer emissions has been restricted to overall odour issues (i.e. olfactometeric measurement and assessment of odours) with very few studies investigating VOC speciation and their relationships with odours.

The current chapter aims to summarise information on the different sources of VOC emissions at sewage collection facilities, analytical methodologies to separate and identify the species present, techniques to elucidate which were responsible for triggering an olfactory response, the affecting factors reported to determine the variations and emissions of sewer VOCs as well as an up-to-date overview of management practices for sewer odour regulations.

2.2 An Overview of Research Scope and Scale

Table 2-1 summarise research on VOCs at sewer-related facilities that have been conducted at experimental conditions of different scales, i.e., laboratory, pilot and field studies. The focus of the published reviews to date has been on VOCs and odour-related issues. The major topics covered by the previous works can be divided into five categories:

- Development and establishment of analytical methods/procedures for odourrelated VOC detection and measurements;
- 2) Identification of odour-active components from a volatiles matrix on wastewater or sewage (liquid phase), the overall odour concentration;
- Microbiological and biochemical reaction processes and their effect on odorous VOC production in sewage collection/transportation operations;
- Air-water interface transfer process on VOC emission into headspace and evaluation and mathematic modelling of emission factors;
- 5) Technologies and their efficiencies/treatment performance to abate and mitigate odour and VOCs emissions.

While covering a broader scope, the primary emphasis of previous investigation is on the identity, concentrations, the emissions from sewage collection facilities and the influent of WWTPs and relevant assessment technologies to fulfil the different research objectives.

Sample type	Study area	Scope ^a	Compounds ^b	Method ^c	References
Air in wastewater drainage system	Taiwan	IC;C	63	GC-MS/FID	Wu et al. (2006)
Air in the atmosphere at different points of sewer	Germany	М	3 chlorinated hydrocarbons	GC- MS/FID/ECD	Hvitved- Jacobsen et al. (2013)
Air in the headspace of sewers	Southern Taiwan	IC;C	71	GC-MS	Huang et al. (2012)
Raw sewage and WWTPs	Spain	IC	47	CLSA-GC-MS	Escalas et al. (2003)
Headworks Air of WWTPs	US	А	1(MBTE)	GC-FID	Converse et al. (2003)
Air from a manhole of sewer and in-sewer sewage (liquid)	Canada	E;M;C	7 Aromatics	TD-GC-MS	Corsi et al. (1995)
Headspace air of sewers and sewage samples at the drop structure in a sewer	Canada	E;C	5	TD-GC-MS and Portable Photoionization detector	Quigley and Corsi (1995)
Liquid samples from inlet and outlet of pressurised main	Denmark	IC;C; R	5(VFAs)	IC-SCD	Hvitved- Jacobsen et al. (1995)
Air at the inlet works of WWTPs	Singapore	A; O	Total Hydrocarbons	THC Analyzer	(Koe and Tan 1990)
Air at the atmosphere of sewers	Sydney Australia	T;C	12	TD-GC-MS	Wang et al. (2012d)
Influent of WWTPs	Spain	T; IC; O	9	SPME-GC-MS	Godayol et al. (2011)
Air at the atmosphere of sewers	Australia	IC;C	>30		Thistlethway te and Goleb (1972)
Influent of a WWTP	Japan	IC;C	10	GC-FPD/FTD	Hwang et al. (1995)
Overflow of combined sewers	Paris, France	IC;C	12	GC- MS/ECD/MSM S	Gasperi et al. (2011)
Air at polluted creek ¹	Turkey	C;O;E	5(VSCs)	GC-FPD/FID	Muezzinoglu (2003)
Air at the headwork of WWTPs	Finland	O;A;C ;IC	19	PT-TD-GC- MS/O	Lehtinen and Veijanen (2011)

Table 2-1 Overview of studies of VOCs and odorants at sewage collection networks

Table 2-1 (cont.)

Sample type	Study	Scope ^a	Compounds ^b	Method ^c	References
*	area				<u>a</u> . 1
In-sewer wastewater in both lab and filed- scale sewer pipes	Queensla nd Australia	T;C	3(VSCs)	Static headspace-GC- SCD	Sun et al. (2014)
Sewage samples in the pump influent of WWTPs	Belgium	IC;	95	GC-MS	Van Langenhove et al. (1985)
Air collected from manholes of sewerage networks	Taiwan	C;H	>20	TD-GC-MS and NMHC monitor	Yeh et al. (2011)
Sewer gas and sewage	Germany	M;C	3 chlorinated compounds	GC-MS/ECD	Haas and Herrmann (1996)
Headspace air of a pump station	Greece	IC; O; C	2(VSCs)	Portable GC- FID	Lasaridi et al. (2010)
Off-gas samples from inlets to pilot WWTP	Vienna	I; C; E	13 hydrocarbons	TD-GC-FID	Sree et al. (2000)
Liquid and gas samples from junction boxes and drop structures	Canada	M; E	5 aromatics	TD-GC-FID	Corsi and Quigley (1996)
Overflow of combined sewers	Chicago	IC;C	26	GC-MS	Zhang et al. (2004)
Influent of WWTPs	Greece	T;C;IC	31	PT-GC-MS	Nikolaou et al. (2002)
Air and liquid samples from wastewater holding bay	UK	M;E;C	20	TD/PT-GC- FID/MS	Bianchi and Varney (1997)

Note: MBTE: Methyl tert-butyl ether; SCD: suppressed conductivity detector; THC:

Total hydrocarbon concentration; NMHC: Non-methane hydrocarbon compound

a A: abatement of emissions; C: concentration measurement; E: emission measurement; H: health risk and toxicity; IC: identification and characterisation of compounds; M: modelling; O: odour-related or odour-motivated; R: reductions of VOCs in sewer; T: technique and methodology development;

b Number of compounds identified or studied

c The definitions of acronyms refer to the list of acronyms & abbreviations

¹ The polluted creek served as open sewers carrying wastewater

2.3 Sources of VOCs at Sewage Collection Facilities

Form previous studies (Table 2-1), four major sources of VOCs at sewer collection facilities have been identified and have been the focus of this research:

- Organic discharges within municipal or an industrial wastewater flushing into the sewer catchment;
- Volatile by-products derived from biochemical reactions under the anaerobic conditions;
- Source- and site- specified waste discharges into the sewer system, e.g. industrial chemicals and pre-chemical dosing into the upstream of sewers for sulfide control (Ganigue et al. 2011);
- 4) Volatilisation or evaporation between aqueous and air phase (Atasoy et al. 2004).

The identified sources covered the volatile compounds majorly presenting in the air as well as liquid phase. The air phase sources include: 1) Air in the headspaces of sewer networks and headworks of WWTPs; 2) Air in the open atmosphere above wastewater treatment facilities and 3) Ambient air surrounding the sewage collection or treatment systems. The liquid phase sources were comprised of: 1) municipal or industrial sewage and 2) Urban runoff water or storm water (Siebert et al. 2010), whereas the composition of VOCs present in the solid phase such as in sediments and/or biofilms of sewer is not widely studied, compared to wastewater treatment facilities (e.g. sludge and biosolids).

2.4 Sampling and Analytical Methodology

2.4.1 Overview

Due to the variable composition and concentration of VOCs (temporal and spatial variations) in sewer environment, adequate sampling and accurate analytical methods are critical for obtaining reliable and representative results. Additionally, analytical instrumentations allow the qualification and quantification of the VOCs that are present in different environmental sources (Ni et al. 2012). Although sampling and analysis of VOCs from both aquatic and atmospheric sources have been developed and successfully employed for many real cases, the existing techniques and procedures are still challenging when they are applied to characterise the VOCs at the sewer matrix. It is
important be note that most analytical methodologies have been benchmarked for a range of gaseous emissions from industrial to waste management processes, and not specifically optimised for the analysis of odorous emissions from wastewater sources.

The majorities of the published reviews to date has been on VOCs sampling and analysis in wastewater or in-sewer sewage (Ketola et al. 1997, Jakubowska et al. 2009), whereas the focus of this section will be reviewing the existing monitoring and sampling techniques for volatile chemicals in gaseous emission from sewers and WWTPs.

2.4.2 Sampling Methodologies and Scheme

Sample Collection Method

Most VOCs present in odour emission are mostly existing at trace level with typical concentration in the range of ppb-ppt (v/v), so sample pre-concentration is commonly undertaken for sample enrichment to satisfy the requirement of detect limits of the instrument and comply with the sensitivity of the instrument. Investigations of sampling method for gas and/or liquid VOCs, including the sorbent/sorption materials selections, optimisation of sampling conditions have been widely published in the literature. The pre-sampling methods selected for representative sample collections were primarily depend on the type of samples been analysed (i.e. air or wastewater). The technologies involved included the following:

- 1) Wastewater VOCs: purge and trap (Van Langenhove et al. 1985), solid-phase extraction (SPE) or SPME (Cervera et al. 2011, Godayol et al. 2011);
- Gas VOCs: cryogenic sampling (Wu et al. 2006), sorbent tube sampling (Quigley and Corsi 1995, Leach et al. 1999, Wang et al. 2012c), SPME (Wu et al. 2006, Ras et al. 2008b), canister/bag (tedlar or nalophan)/gas-tight vessels sampling (Schweigkofler and Niessner 1999, Bokowa 2012).

Sampling Strategies

The majority of the published studies regarding the determination of VOCs from sewage and WWTPs has used discrete sampling of samples collected over assigned periods of time. This method allows for the collection of representative samples from the sewer sources (such as air, in-sewer wastewater or sediment) and storage and transportation of the samples. A disadvantage with regards to discretely sampling strategy is that published results are limited on the number of samples thereby providing restricted insights into the dynamics (i.e. diurnal and temporal) and viabilities of VOCs under different variables that maybe encountered from the sources. As a result, previous studies using discretely sampling methods were only able to collect and analyse limited number of samples.

An alternative is the continuously and real-time VOCs sampling and analysis on sites. With this method, water samples/gas were collected periodically (e.g. 1 hour) from the sampling site with in-situ analytical instrumentation. However, the applications of on-site sampling and analysis at sewer and WWTPs were fairly limited due to inadequate availability and lacked specificity (e.g. measurements based on the total VOCs rather than individual species) of online instruments. Wu et al. (2006) conducted a semicontinuous study (24 hrs) at an WWTPs and investigated the diurnal variation of 12 selected VOCs (ambient air near the WWTPs) with a portable GC-MS coupled with automatic sampling equipment.

Sampling Technology Restrictions

For this study the logistical limitations resulting from the extensive distances between field sampling locations (typically found in Australia) and the analytical laboratory dictate the use of a robust, easily transportable media for sample collection. Among all the sampling technologies, thermal desorption tubes provide a reliable and robust method for the collection, transport and analysis of VOC and odorant samples from wastewater sources; however careful attention should be given to the selection of sorbent to maximise the representation of the source. The ability to apply a suitable methodology to provide routine calibration for sorbent tubes allows for the chemical species identified within a sample to be accurately quantified. Sorbent tubes may be sampled by collecting a known sample volume to accurately determine source concentrations, or they can be passively collected to assess the general background level of a target chemical.

2.4.3 Chemical Analysis Instruments

Analytical Instruments

To gain knowledge on the fate and behaviour of VOCs and other odorants in sewage collection facilities, precise and accurate analytical techniques are necessary. Odour assessment program can be conducted on the basis of reliable analysis techniques that allows the qualitatively identification of odorants present in or off the sewers. A variety of analytical techniques have been tested and applied in VOCs analysis at sewer networks and other wastewater treatment facilities, including the gas chromatography, electrochemical sensors, and fluorescence spectrometry (Hobbs et al. 1995, Hobbs 2001, Bourgeois and Stuetz 2002).

Two major groups of instruments that have been widely used for VOC identification and quantification at sewers and WWTPs are electrochemical sensors and chromatography, including gas (GC) or liquid chromatography (LC). However, in very limited cases, LC was applied for full spectral identification of VOCs present in the sewer environment but particularly for analysing carbonyl compounds (Kot-Wasik et al. 2004), such as aldehydes, ketones (Grote et al. 1999, Uchiyama and Hasegawa 1999).

In most cases, the determination of trace volatile organic compounds (VOCs) or volatile sulfur compounds (VSCs) by GC coupled with mass spectrometer detector (MSD) or a series of chemical detectors, including FID (flame ionization detector), (P)FPD (pulse flame photometric detector) and ECD (electron capture detector)(Escalas et al. 2003, Li and Shooter 2004, Wu et al. 2006, Muñoz et al. 2010) as well as SCD (sulfur chemiluminescence), which is specifically applied for volatile sulfur compounds (Fox 1999, Siebert et al. 2010). Although a variety of detectors have been employed for analysing VOCs, the most frequent used is MSD due to their simultaneousness on VOCs and VSCs identification and quantification (Muñoz et al. 2010).

ttions of GC based analytical methods for determination of VO(S)Cs from wastewater source
ole 2-2 Applic
Tab

References	Nielsen and Jonsson (2002)	Grote et al. (1999)	Ras et al. (2008a)	Wu et al. (2006)	Sheng et al. (2008)	Escalas et al. (2003)	Sun et al. (2014)	Ras et al. (2008b)	
LOD (μg/m3)	3.1-652	<100-5000	0.01-0.04	0.61-9.88	0.03-0.06	I	0.15-0.81	0.10-0.25	
Detectors	MSD (SIM)	FID	MSD	MSD/FID	MSD	MSD	SCD	MSD	
Recoveries (%)	ı	100 ± 20	98	$100 \pm (0.1-23.2)$	ı	ı	83-103	4 -25	
Preconcentration Method	SPEM 85um CAR- PDMS (fiber)	SPEM 75um PA (fiber) 30 mins	Sorbent tube (400mg Tenax and Unicarb),3L	Canisters, Cryogenic trapping	Canisters, Cryogenic trapping	CLSA-AC filter	Static headspace	SPEM	
Matrix and Source location	Gas/Sewage treatment plant	Water/wastewater treatment plant	Air/Sewage treatment plant	Air/wastewater drain system	Air and Water/wastewater treatment plant	Water/sewage treatment plant	Sewage field/pilot sewer pipes	Air/Sewage treatment plant	and the second and the second se
Target Compounds	VSCs	VOCs	VSCs/odorants	C ₂ -C ₄ VOCs C4-C10 VOCs	VSCs	VOCs	VSCs	VSCs	CDENT. Collid abr

SPEIM: Solid phase micro-extraction

CAR-PDMS: Carboxen@/Polydimethylsiloxane PA: Polyacrylate fibers

CLSA-AC: closed-loop stripping analysis-activated carbon filter

2.4.4 Sensorial Analysis Instruments

Overview

Sensory techniques allow for the qualitative and quantitative evaluation of the sensorial component of odours using the human nose as a detector, and as a result measures the total effect of the target odour on human perception (Gostelow et al. 2001). Unlike analytical analyses, sensorial techniques have lower accuracy and repeatability due to their subjective nature, and their results must be carefully interpreted. These techniques can be applied to determine odour concentrations quantitatively through dynamic olfactometry, or to describe them subjectively in terms of parameters such as hedonic tone, quality and intensity (Suffet and Rosenfeld 2007).

Qualitative Sensorial Odour Analysis (Odour Profile Method)

Recently there has been a concerted effort to apply qualitative sensorial analysis techniques in more a rigorous manner to enhance our understanding of odorant emissions, most notably in the form of the Odour Profile Method (OPM). The OPM utilises a panel that has been trained to characterise the individual components of an odour sample using odour descriptors and intensity ratings (Burlingame et al. 2004). Individual odour descriptors can be associated with typical odorants.

Due to the subjective nature of these methods and the observed variability in dilution olfactometry results (Van Harreveld et al. 2009), comparison and interpretation of data collected by different laboratories (or even between different analysts) can be difficult. Towards resolution of this issue, odour wheels for environmental impact odours have recently been introduced to standardise the basis on which to classify, communicate and identify odour qualities (Burlingame et al. 2004, Suffet et al. 2004, Suffet and Rosenfeld 2007).

Quantitative Sensorial Odour Analysis

Odour detection thresholds and intensities can be measured with olfactometry technique. Training human olfactory panels have been used to provide information on detection thresholds and odour intensity of individual odorants and odour mixtures. The approach involves using a panel of trained individuals who are exposed through sniffing

port to the diluted mixed air stream of odour-free air and the odorous gas. The concentration of the sample in the air stream is increased until all the panel members can detect the odour. The work by (Agnew et al. 2006) showed the use of trained odour assessors and field panellists are suitable techniques to obtain odour intensity and dispersion measurement at manure application sites. However, the limitations of sensory analysis are variability between panels and lack of compound specific information. In the review on the sampling techniques for olfactometric measurement of odours (Bockreis and Steinberg 2005) reported that the use of a reference material such as n-butanol may incur the inaccuracy in measurements because the majority of panellists are too sensitive to this odorant and the maximum period of 30 h between sampling and olfactometry may lead to lower results. (Both et al. 2004) suggests the measurement of odours in terms of pleasant and unpleasant because the increasing odour intensity does not necessarily mean the increasing degree of annoyance.

Alternative to olfactometry technique, such as the electronic noses (or sensor arrays) has been increasingly used to analyse, recognise and identify low-level gaseous emissions for continuous monitoring of environmental odours (Bourgeois et al. 2003, Nake et al. 2005, Capelli et al. 2008, Rock et al. 2008). Electronic noses are gas sensor based instruments that either use conducting metal oxide, conducting polymers and other sensors to detect odour-causing chemical molecules and determine an odour measurement from trace chemical concentrations. Like the human perception of odours, electronic noses can be used to directly characterise an odour without reference to its chemical composition. Many studies on odour measurements with olfactometry and electronic nose have highlighted the potential for using electronic noses as a substitute for olfactometry since there are good correlations between two responses within the same sampling site (Stuetz et al. 1998, Fuchs et al. 2008). Although, sensor systems seem to be working in technical analogy with the human sense of smell, there are some important differences, which can lead to a bad correlation. One principle difference is the functioning of the brain by building up an odour impression for any specific odour composition (Haas et al. 2008). Therefore, the electronic sensor response for odour tends to be source or site specific, requiring different calibrations using olfactometry as a function of the type of source and provides only the characteristic information to

classes of compounds rather than establishment of thresholds for every odour component (Bruno et al. 2007).

2.4.5 Combined Sensorial and Analytical Techniques

Gas chromatography can be coupled with olfactory analysis (GC-O) to determine the odour characteristics of each odorous chemical. This technique brings together the high selectivity and sensitivity of human olfaction with the analytical precision of gas separation and detection using a range of detectors. Delahunty et al. (2006) has provided a detailed review on gas chromatography-olfactometry technique covering the important aspects such as analytical principles, method classifications, extraction methods, instrument conditions, methods of recording data and controlling the potential human assessor bias.

GC-O has been primarily applied for studying odour-active volatiles from food (Pham et al. 2008), beverages (Rega et al. 2003, Plutowska and Wardencki 2008) and perfume research (Fuller et al. 1964, d'Acampora Zellner et al. 2007), but recently with increased but still limited applications to environmental analysis. Table 2-4 lists recent publications representing the most relevant GC-O analysis in the environmental field. These references are characterised with identification of odorants from the emission of livestock operations, the monitoring of indoor air and water and wastewater quality. The selected studies all capture the significance of only a limited number of odour active compounds within a larger matrix of non-odour active compounds. In most of studies, a typical GC-O system is equipped with additional chemical detectors (i.e. GC-FID/O) and GC-MS/O) for odorant identification and quantification from different environmental emission samples. However, there reminds a knowledgeable gap with respects to the GC-MS/O application on characterisation of sewers and WWTPs as to the best of our knowledge, no published data are available up to date.

Sample matrix	Pre concentration	Methodology	Odour Active Chemical Classes	References
Wastewater	Dynamic headspace using Tenax TA	GC-FID/MS/O	Sulfur compounds, ketones, aromatic, volatile fatty acids and alcohol, terpenes	Zarra et al. (2008)
Treated water	Close loop stripping	TD-GC-MS/O	Phenolics, phthalates, diacid esters, aliphatic alkenes, benzothiazole, aliphatic hydrocarbons	Bruchet et al. (2007)
Drinking water	Solvent extraction	GC-MS/O	Methylnaphthalene, geosmin, diisopropylnapthalene	Hochereau and Bruchet (2004)
Swine barn particulates	SPME (PDMS, Carboxen/PDMS and Carbowax/DVB)	TD-MDGC- MS/FID/O	Alkanes, alcohols, aldehydes, ketones, volatile fatty acids, furans, sulfur compounds, nitrogen compounds	Cai et al. (2006)
Air samples from livestock facilities	Headspace sorbent tubes using Tenax TA	TD-MDGC-MS/0	Volatile fatty acids, phenol, skatole, indole, ketone	Zhang et al. (2010)
Air samples from WWTPs	Headspace sorbent tubes using Tenax GR	TD-GC-MS/O	Prioritized: Sulfur compounds, aldehydes, aromatics and terpenes and aromatics	Lehtinen and Veijanen (2011)
Air samples of building products	Headspace sorbent tubes using Tenax TA	TD-GC-MS/O	Aldehydes, ketones, volatile fatty acids, alcohols. Alkanes, aromatics, furans	Clausen et al. (2008)
Wastewater effluent	SPME	GC-MS/O	2,4,5-trichloroanisole, geosmin, vanillin, methyl naphthalene, 2-pyrrolidone	Agus et al. (2011)
Waste gas from a fat refinerv factorv	SPME (CAR/PDMS)	GC-MS/FID/O	Aldehydes, ketones, hydrocarbons, fatty acid methyl esters, alcohols, ternenes, furans	Kleeberg et al. (2005)

Table 2-3 Recent application of chemosensory analysis for environment studies

2.4.6 Summary

A review of existing and emerging odour assessment techniques was conducted. Through this review, strengths, limitations and existing knowledge gaps for a range of odour/odorant monitoring techniques have been identified and assessed. A summary is provided in Table 2-4.

With each technique having different strengths and limitations, and considering the variability in chemical character of odorous emissions, there is no universal analytical technique that can be applied for the measurement of odours from environments such as sewers. For the best outcome, both sensory and analytical techniques currently used to characterise odours must be used as complementary analytical approaches since the information provided by each technique will cover different monitoring needs for odour/malodor assessment.

Based upon the literature, GC and dynamic olfactometry represented the most widely used odorant monitoring techniques for different applications, suggesting a disconnect between monitoring conducted for research purposes and more practically oriented monitoring conducted by the wastewater industry, where specific H_2S sensor monitoring is by far the most dominant monitoring technique employed for odour assessment. While specific sensor are available for H_2S monitoring, which are cost effective and performs well in many applications, not all environmental situations have H_2S as the dominant odorant therefore this form of specific monitoring is of limited benefit. The necessity therefore exists to provide more information through enriching monitoring techniques (particularly those allowing the identification of key odorants) to the industry in a cost effective manner to enhance odour emission assessment and their abatement process selection, design and performance assessment to reduce community impact by nuisance odours.

Technique	Strengths	Limitations	Knowledge gaps
GC	 Identifies VO(S)Cs and odorants Quantitative analysis Flexible 	 Does not provide confirmation of odour-active compounds High expertise requirements and equipment cost 	 Degradation and transformation during analysis Sorbent performance (range of odorants captured and capture efficiency) Limited information on odorants loss during sample collection and storage Guidelines for sample collection and storage
GC-O	 Allows identification and confirmation of odorants Quantitative analysis Flexible technique 	 High expertise requirements and equipment cost Lack of standardized method 	 Degradation and transformation during analysis Sorbent performance (range of odorants captured and capture efficiency) Guidelines for sample collection and storage Limited information on odorants loss during sample collection and storage Standardised analysis methodology
Dynamic Olfactometry	 Allows verification of compliance with standards/regulation Standardized analysis technique 	 Low accuracy Dose not provide character information or identification of odorants Not applicable for ambient sampling 	 Limited information on odorants transformation/loss during sample collection and storage Guidelines for sample collection and storage
OPM	Odour character information provided	• Limited records of application in wastewater industry	• Database of observations and linkage of key odorants/descriptors to common sources for wastewater industry

Table 2-4 Summary	common technique	es for VO(S)Cs and	odour assessment
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2.5 VO(S)Cs and Odorants

2.5.1 Number of Compounds Identified

Various concentrations and compositions of VOC compounds have been reported by different researchers. In general, larger number of VOCs has been reported recently with advanced chemical speciation instrumentations. Early in the 1970s, Thistlethwayte and Goleb (1972) identified more than 30 VOCs compounds including hydrocarbons and chlorinated hydrocarbons, amines, aldehydes and sulfides and mercaptans in the sewer air samples. Similar number of VOC (>20) had been identified in sewage gas samples in Germany (Schweigkofler and Niessner 1999). Most recent works showed that up to hundreds of VOCs were able to be screening out from field sampling and chemical analysis. In Taiwan, a total number of 63 VOCs in the air samples from the wastewater drainage system from an industrial science park were identified by Wu et al. (2006). The recent analysis of sewer gas samples carried out in southern Taiwan also revealed about 71 VOCs, including Alkanes, Alkenes, Chlorinated VOCs, Ketone, ester as well as carbon disulfide (Huang et al. 2012).

2.5.2 VO(S)Cs Species

Classification of VO(S)Cs

Among the available studies, VOCs that are detected in the sewage collection system were generally classified into VFAs, alcohols, aldehydes, aromatics, esters, ethers, terpenics, halogenated compounds, hydrocarbons, ketones, nitrogen-containing compounds and sulfur compounds. In some studies, all the oxygen-containing compounds (i.e. alcohols, ketones, aldehydes acids) were classified as one single group-oxygenated compounds (Wu et al. 2006).

In the review of VOC families as discussed, it was found that the similar classification of sewer VOCs was identified between the studies, however, when it comes to the individual species within the same group, the diversity of species were observed by different researchers depending on the sample types and analytical methodologies (Table 2-2).

Carboxylic acids were commonly detected in the liquid phase with C2-C5 acids being the species most often identified (Hvitved-Jacobsen et al. 1995, Gutierrez et al. 2009), but they were seldomly determined from gas samples within sewer environment. In these gas phase samples, the VFA species were often identified under assistance of GC-MS-olfacotmeter as they were generous odorous with relatively low odour threshold values (OTVs).

Amongst the aromatic groups, BTEXs compounds (such as benzene, toluene, ethyl benzene and xylene) were mostly measured in all of published works at various locations, which includes ambient air surrounding the sewage collection facilities, the headspace air of sewer networks (Corsi et al. 1995, Wang et al. 2012a), the raw wastewater in the sewer catchment (Fatone et al. 2011) as well as the sediment/deposits of sewer. In addition, the alkylbenzene (C_2 - C_4) with their isomers were also widely reported in the published studies (Wu et al. 2006).

Among the subclass of aromatic family, the polycyclic aromatic hydrocarbons (PAHs) were identified as another major component. The PAH compounds were generally characterised with relatively higher molecular weight (or lower boiling point, B.P.), so they were more determined in the in-sewer deposits and liquids than in the air samples. Results from air-phase VOCs emission studies have indicated that naphthalene and its derivate (e.g. methylnaphthalene) were among the most commonly identified species.

Chlorinated organics were the essential species identified from both off or in sewer samples as they are identified as the by-products of disinfection process (Haas and Herrmann 1998, Rodenburg et al. 2010). Table 2-5 shows that the most frequently detected chlorinated organics were polychlorinated hydrocarbon (i.e. C1-C3 alkanes and alkenes) as well aromatics (i.e. chlorobenzene, dichlorobenzene, Dichlorobiphenyl). In addition to the chlorinated VOCs, the bromide and fluoride containing compounds were also identified and reported by (Leach et al. 1999).

Terpenes are generally associated the use of aroma compounds like fragrance additives and liquid cleansers. With this group, most commonly detected species were α -pinene and limonene which are odorous compounds. A study using GC-MS/O also identified

these two compounds featured with "woody-green" or "lemon" like odour characters (Lehtinen and Veijanen 2011).

The alkenes and alkanes families are mostly associated with petroleum solvent discharged upstream. A wide range of branch and chain components were identified and reported from published studies (Wu et al. 2006, Dincer and Muezzinoglu 2008, Huang et al. 2012). From an general prospective, compounds with the carbon number of C2-C10 were most frequently identified from a sample and are generally non-odorous or having relatively high odour threshold values (Van Gemert 2003).

Sulfur-type VOCs including dimethyl sulfide, dimethyl disulfide and mercaptan are another major group that were identifying from the sewage-related sources and are reported as a significant contributor to the malodour smell, generally characterised with the "rotten egg" smell. Among the published studies, up to 12 individual sulfur species has been ever identified from different process in wastewater collection and treatment systems (Muezzinoglu 2003, Ras et al. 2008a, Ras et al. 2008b). Hydrogen sulfide and sulfur dioxide are listed as inorganic fixed gases but also being classified as sulfur-type VOCs by some of studies (Thistlethwayte and Goleb 1972, Muezzinoglu 2003).

Characterisation of Identified Compounds

The detection of VOCs in sewer environment (including the ambient air surrounding the sewage collection facilities) were characterised by a wide range of physicochemical properties. Identified VOCs have a relative low boiling points (<250°C), lighter molecular weight and high vapours pressure relative to their low water solubility, lower odour threshold values (OTVs), and variable atmospheric life reactivity. Compared with other environmental sources for VOC productions and emissions, a major difference was distinguished regarding the characteristics of VOC species, which is that the identified VOCs were less composited of heavier VFAs particularly in emission samples.

2.6 Quantification of VO(S)Cs and Odorants

2.6.1 Overview of VO(S)Cs in Air

Compared with identification of VO(S)Cs, the quantification of VO(S)Cs is more technically challenging not only because it requires better procedures in sampling and analysis, but also because the concentrations of many odorous VO(S)Cs are too low to be quantified by chemical detectors. The earliest VO(S)C quantification at wastewater collection facilities was in liquid phase samples, which actually are the raw sewage samples before discharging into WWTPs. In the 1970s, Thistlethwayte and Goleb (1972) determined the concentrations of sewer air compositions (Table 2-1) and the author measured the concentration levels over 30 VOCs. Increasing number of VO(S)Cs concentrations was by Huang et al. (2012) using TD-GC-MS in 16 samples from headspace of sewer networks. The measurement of 70 VO(S)Cs concentration results in a total concentration of $689 \sim 1173 \,\mu g/m^3$.

It is also essential to understand, which compounds are dominant at sewer emissions to improve the monitoring of odours and mitigate of odour emissions. However, because there was only small portion of the quantified compounds among different publications that provided comparable data, it is impossible at this time to definitely determine the most abundant VO(S)Cs at wastewater facilities as shown in Table 2-5, the most abundant VOCs in air sample that have been confirmed in two independent studies including acetone, toluene, dimethyl sulfide, xylene, chloroform, tetrachloroethane. The abundance of VO(S)Cs would be differed, depending on the types of industrial discharge to sewer catchments as well as the operational characteristics. For example, the concentration level of VOCs determined by Yeh et al. (2011) in a sewer line was up to tens of mg/m³, which are generally the 3-4 magnitude higher than what ware reported by other works (e.g. in the level of μ g/m³) in Table 2-5. Data present in other works are measured from municipal wastewater dominant sewers while sites they sampled are with a record of significant trade waste discharges and produced a distinctly higher level of volatile compounds.

2.6.2 Spatial (and Geographical) Variations

Unlike a large number of investigations about spatial variability of VOCs concentrations at wastewater treatment facilities (Pincince 1995, Escalas et al. 2003), the information regarding VO(S)Cs gradients at different sewer networks, either in the liquid phase or gas phase were very limited due to insufficient sampling sites. In these studies, large VOC spatial variation was observed and concentrations gradients were subject to three primary factors: climatic conditions, hydraulic conditions as well as conditions of upstream discharge. Comparing various gaseous VOCs data from different sampling locations along the wastewater collection and treatment systems, Wu et al. (2006) found higher VOCs concentration emitted at the raw sewage and wastewater discharge pressurised station than treatment processing sites. Also, in this study, the researchers compared the VOCs concentration present at 10 residential sites approximately 100-1000m downwind of sewage drain system. It was observed that higher sewage related VO(S)Cs (e.g. dimethyl sulfide, DMS) were determined from the sampling sites closer to the drain system although other VOC species, like acetone did not exhibit constantly decreasing concentrations with distances from the source (which was ascribed to acetone concentration was affected by not only the wastewater but nearby industrial sources). The DMS concentration measured at residential sites near the sewage drainage facility was up to 1pptv whereas other sites were only 0.64 pptv on average.

In another study, Huang et al. (2012) measured airborne VOCs at two sewer sites located over 2 km apart from each other and the spatial VOC variations were clearly illustrated (Table 2-5) with measured TVOCs concentration differing by 40% between the two sewer sites. The only exception was for some aromatic compounds, such as toluene, styrene, xylene and ethylbenzene. The concentration of all of the detected VOCs were higher in heavier wastewater loaded site (sewer A in this study) compared to lighter concentrated site (sewer B).

2.6.3 Temporal Variations

Compared with spatial variability, temporal variations (both diurnal and seasonal variations) in airborne or aqueous VOC and VSC concentrations are reported by different researchers. Using an in-situ GC-MS with an autosampling device, Wu et al.

(2006) obtained data that clearly demonstrated the diurnal variation of 12 major VOC species in the wastewater drain system where the peak TVOCs concentration (between 01:00–02:00 pm) was about four times that of the minimum concentrations (between 02:00–05:00 am). In addition to diurnal variation, the rough temporal variations were able to be illustrated by single seasonal sampling and analysis (n=4) and it was found that higher VOC concentrations were detected at summer and autumn whereas the non-detectability were observed on the winter period. In a recent study, Huang et al. (2012) observed a prevailing seasonal trend of hydrocarbon at two sampled sewer sites where the significantly higher concentration were measured in dry weather than in wet weather. The effect of rainfall dilution was considered as the primary or determining reason for lower VOCs concentration at the headspace of sewer atmosphere during wet seasons. The similar seasonal patterns of VOCs were confirmed by other researchers in different regions and countries (Wang et al. 2012a).

Various studies have discussed the temporal and/or seasonal variation of VOCs in sewer environment, a define limitation was still reminds due to the lack of a truly systematic time series at the sample location to represent the reliable results on temporal variations in sewer environments. For example, despite previous temporal studies being performed seasonally, the number of samples measured for each season was limited in terms of ranging from 4-9, so that the representativeness of seasonal condition was not able to be achieved. In addition, reported temporal variations of VOC concentrations were sampled within a given monitoring period in a season (e.g. consecutive several days sampling and analysis within a certain month of the season), which may experience meteorology that is not consistent seasonal average. To minimise the effect of meteorological variations between seasons, some studies of discrete VOCs concentration measurements were conducted monthly throughout the year, but the variability were still expected since the weather conditions can change significantly from year to year. In this context, multiple sampling allows for the generation of large quantity of data with high temporal resolution within a wastewater collection system and represents the need of the future research in this area.

1 able 2-2 Comparison		entrauons (µ	g/III) al sew	er air sampie	s (and amole	nt air surrounui	ing sewers) ir	om selected
publications								
Compounds	Wu et al. (2006) ¹	Wang et al. (2012a) ²	Huang et al. (2012) ³	Corsi et al. (1995) ⁴	Muezzinoglu (2003) ⁵	Lehtinen and Veijanen (2011)	Bianchi and Varney $(1997)^7$	Yeh et al. (2011) ⁸
Terpenics								
Alpha-Pinene		13.9				37.2(59.4-21.0)		
D-Limonene		79.5				93.4(194 -13.1)		
S compounds								
Dimethyl sulfide	225 ± 204				56800-11800	43.4(6.3-117)	69.7/50.2	
Dimethyl disulfide						69.6(4.1-216)	67.4/42.3	
Methyl mercaptan							58.3/30.1	
Carbon disulfide	10.2 ± 4.90		6.39-3.92					
2-Propanethiol					18000-n.d.			
Dimethyl trisulfide						5.1(33.1-n.d.)		
Aromatics								
Xylene	2.86 ± 3.89	51.3-23.5	500-54.1	168989-n.d.		38.5-12.7	53.7/20.4	350978-3900
Benzene	1.43 ± 0.41		6.05-n.d.				41.9/15.0	473123-1275
Toluene	35.5 ± 25.6	67.5	148-94.2	172922-n.d.		375 (879-64)	60.7/22.3	324182-6017
Ethylbenzene	3.08 ± 6.98		53.2-19.0	21632-n.d.		11.7(42.5-n.d.)	58.3/23.5	
Trimethylbenzene	2.06 ± 0.54		18.8-2.9				45.6/19.3	
Ethylmethylbenzene		17.6-10.9						
Halogenated								
Dichlorobenzene	4.38 ± 0.96		3.6-n.d					
Tirchloroethylene							44.5/24.3	155535-3218
Chloroform	18.6 ± 22.8		13.8-10.7	9714-n.d.		23.1(92.5-n.d.)	80.0/39.3	1594819-4873
Tetrachloroethane			90.5-4.0					1533943-4111
Bromodichloromethane	9.69 ± 2.14		1.9-n.d					
Dichloroethene			55.0-4.87					56191-8706

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Compounds	Wu et al. (2006) ¹	Wang et al. (2012a) ²	Huang et al. (2012) ³	Corsi et al. (1995) ⁴	Muezzinoglu (2003) ⁵	Lehtinen and Veijanen (2011)	Bianchi and Varney (1997) ⁷	Yeh et al. (2011) ⁸
Alkanes and alkenes								
Butane	2.92 ± 1.61		12.0-6.38					
Decane							11.4/4.7	
Hexane	1.58 ± 0.32		13.5-6.79				18.9/9.8	
2-Methylpentane	1.86 ± 0.98		12.8-4.51					59095-1055
Methylcyclohexane							17.1/5.0	
1-Butenen								31376-1832
Ketones								
Acetone	145 ± 148		61.2-30.9					598105-11142
2-Butanone			8.75-n.d.			11.4(26.9-4.1)	5.2-2.1	
Aldehyde								
Hexanal						36.3(142-n.d.)		
Heptanal						12.6(50.2-n.d.)		
Others								
Diethyl ether						272 (648-47)		
Napthalene							20.3/11.1	
n.d.: Non-detected; Conce	ntration values	were recalculat	ted (at 273 K) a	and present ir	the same unit (μg/m ³);		
¹ The values represented a	s mean ± SD ov	ver measureme	nts of four sea	sons; ² The V	/OC concentrati	ons were the may	cimum values o	determined in
the study; ³ Concentration	ı values were re	presented as th	ne range of ave	srage concent	ration from two	sampled sites; ⁴	The range of n	neasured data
were obtained from four e	vents within the	e period of 48	sampling camp	oaign; ⁵ These	creeks were lik	e open sewers tra	insporting wast	tewaters from
the industry and residentia	al areas. The vi	alue represents	the range of r	neasured con	centration from	different sample	d creeks; ⁶ Me	easured in the

Table 2-5 (cont.)

headwork of the WWTPs. The value represents the mean (concentration range) and Xylene is the averaged concentration ranges measured between two isomers o-xylene and p-xylene;⁷(summer/winter) concentration measured in the headspace of constructed wastewater holding bay

in 1995; 8Concentration obtained among 8 monitoring sites along a sewer networks in an industrial park

2.7 Summary and Knowledge Gaps in Sewer Emission Data

Numerous odorous assessment studies have been performed at wastewater operations with only a handful within sewer collection systems. The lack of sewer odour emission rates and their compositions across a long-term cycle in different climates at different sewer sources makes the management and regulation of emission very challenging. Data obtained from different studies are often incomparable between studies conducted at different geographical locations due to large variation in climatically conditions, sewage characteristics and the design and operation of collection processes. Compared with identification of VOCs, quantification data for VSCs are more difficult to acquire due to technique challenges resulting in it been unfeasible to quantify all known components of VOCs and VSCs at a single location. So the number of VOCs measured with known concentrations is much smaller than that identified at sewer networks in the available literatures. Within those available sewers VOC and VSC data, significant concentration difference were reported amongst the studies conducted at different countries as they can be viewed as both temporal and spatial variations, but were not able to evidently explained by spatial-temporal factors or sources origin difference with discretely and limited sampling events.

2.8 Managements of Odour Emissions at Sewage Collection Facilities

2.8.1 General Practices

The demands for the effective control of VOCs production and emission are increasing among the public and industry operators. However, so far, the reductions of VOC emissions from such emitting facilities have always been related to abating the VOCs and odorous emissions from the different environment sources. Investigations with regards to different abatement technologies treating VOCs emissions either under full or laboratory scale conditions are widely published. Mudliar et al. (2010) has reviewed the technical aspects (of process configuration and design, operation and maintenance as well as process performance) for VOCs emissions abatement techniques regardless the sources the VOCs emitted and produced. Among these studies, there has been fairly limited number of studies that specifically targeted the reduction of VOC emissions from wastewater sources (Koe and Tan 1990, Estrada et al. 2010, Sivret and Stuetz 2012). In their experiments, the techniques for VOC emissions treatment involved:

- Pretreatment on-site of sewers (e.g. dilutions with clean air, addition of chemical upstream (Zhang et al. 2008);
- Physical-chemical treatment of off-sewage VOCs i.e. adsorption (Koe and Tan 1990), chemical scrubber (Sanchez et al. 2006) and incineration (Estrada et al. 2010);
- Biofiltration of off-gas from sewer networks i.e. biofilter (Chitwood et al. 1999, Converse et al. 2003), biotrickling filter (Cox and Deshusses 2002);
- 4) Other treatment, including the hybrid techniques (e.g. activated carbon adsorption combined with biotrickling filter) (Stuetz and Frechen 2001, Duan et al. 2007).

The following section concentrates on the potential emission abatement techniques developed and employed in Australia typically used to control sewer emissions. As introduced in **Chapter 1** of this thesis, adsorption-based processes such as activated carbon and zeolite based filters were dominant (76.5%), followed by biological processes (21.1%) in Australia wastewater industry. Therefore, the discussion will be focused on activated carbon, biotrickling filter and biofilter odour abatement processes.

2.8.2 Comparative Performances of Abatement Processes

Through this review, strengths, limitations and existing knowledge gaps for the three major odour abatement techniques have been identified and assessed. A summary is provided in **Table 2-6**.

Activated Carbon

Activated carbon is the most widely used adsorbent in many industrial sectors due to its excellent adsorptive properties. Activated carbon has high surface area, a microporous structure and a high degree of surface reactivity that allows it to effectively adsorb a variety of chemical groups, including hydrophilic, hydrophobic, acidic and basic chemicals (Schnelle Jr and Brown 2001, Estrada et al. 2010). With high operation and maintenance costs associated with replacement and regeneration, activated carbon is often used for low contaminant loads to ensure acceptable carbon life. Its advantages lies on consistent performance and a mechanically simple process. Whilst, the issues regarding the use of activated carbon for sewage odour control is that premature odour breakthrough can occur and the granular activated carbon replacement is frequently required that can cause high costs for operating these system in sometimes remote locations.

Biofilter

In biofiltration processes, contaminated air passes through a bioreactor filled with porous packed medium that supports a thriving population of microorganisms. Air pollutants are firstly transferred from the air into the water/biofilm phase surrounding the packing materials and then aerobically degrade to various end products, such as CO_2 , H_2O and other inorganics, and incorporated into biomass (Mudliar et al. 2010). Biofilters offer high gas/liquid surface area with relatively easy operation and start-up, and low operating costs. The application of biofilter is a process effective in the reduction of low concentration VOCs and odorants and provided high potential removal efficiency for H_2S (>99%) and significant removal of sulfur compounds. The primary limitations associated with biofilters included the medium deterioration and clogging, reduced efficiency at high odour concentrations, limited removal of chlorinated hydrocarbons and sensitivity to large fluctuations inlet component concentrations.

Biotrickling filter

Similar to biofilters, biotrickling filter are configured with fixed biofilm process in which microorganisms are immobilised on a porous media, through which the contaminated gas stream passes. Biotrickling filters differ in that they are continuously watered thereby providing improved wash-out of acid metabolites and hence better pH control. The major limitation of biotriclking filter is that there are not suitable and effective for treating compounds that are not soluble in water, as the target gaseous compounds must be dissolved in liquid phase to interact with biologically active media (Muñoz et al. 2007).

2.8.3 Summary and Knowledge Gap

Effective design and management strategies allow for efficient odour control in sewer collection systems. There are many different options available for odour abatement at sewage collection works, and many abatement processes have been applied. The approach (i.e. biofilter, biotrickling filter and activated carbon adsorption) are being continuously developed and widely applied within the Australian climate. However, there is no universally suitable treatment process and the best option is usually site specific, highly depending on odour loadings, variability of loading, composition of the odour, availability of and operation and capital cost constraints.

Knowledge gaps exist with regards to process mechanisms as stated in Table 2-6, in both the adsorption and biodegradation processes on the packing material. Understanding the removal mechanism is essential to optimise process selection, design and operation of a particular odour control application. The activated carbon adsorption mechanism, particularly on non-H₂S odorants removals as well as competition in multicomponent adsorption was the key points with very limited information. While in the biofiltration processes, biodegradation mechanism in particular the adsorption process (first step) in the packing material, and understanding of the biodegradation pathways and reaction kinetics for specific contaminant is not well investigated. The performance limitations are due to poor characterisation of emissions in terms of chemical constituents and the lack of a non-process monitoring of abatement procedures (i.e. with of H₂S and odour as dominant parameters), particularly lack of solid data from direct field measurements and characterisation of emission from sewer operations.

Treatment	Strengths	Limitation	Knowledge Gaps
Activated	• Relatively low	• Frequent material	• Lack of
carbon	investment and	replacement	understanding of
	operation cost	 Large footprint 	mechanistic/kinetic
	 Broadly applicable 	required	removal of
	for removing a wide	 Not effective for 	malodorous
	range of gaseous	treating high inlet	organics(non-H ₂ S)
	compounds	concentration of	and VOCs
	 Robust technology 	H_2S	• Lack of full scale
	against operational		field data to justify
	failures		the effects of
			variations in
			operating conditions
			on adsorber
			performance
			• Lack of standard
			guidelines for design
			and operation of
			activated carbon
			adsorbers for odour
			control application
Biofilter	• Low operation cost	• Not suitable for less	• Insufficient
	• Effective for treating	water-soluble	understanding of
	high inlet H_2S	compounds (high	biodegradation
	stream	hydrophobic	mechanisms /
	• No secondary waste	compounds i.e.	kinetics
	streams	chlorinated	• No data available on
		hydrocarbons)	removal of VOCs
		• Sensitive to	found in sewers
		operational changes	• Lack of full scale
		• Only effective for	investigative work
		treating low	for wider ranges of
		pollutant	odorants
D:	T	Concentration	No. 1.4
Biotrickling	• Low operation cost	• Not suitable for less	• No data available on
inter	• Add nutrients	water-soluble	found in services
	and add nutrients	bydrophobio	• Look of full coole
		compounde)	• Lack of full scale
		• Sensitive to	• Lack of standard
		• Selisitive to	• Lack of standard
		operational changes	guidilitie for design
			and operation

Table 2-6 Summary common techniques for VOCs and odour abatement

2.9 Summary and Knowledge Gaps

An odour is often composted of thousands of chemical compounds (containing both odorous and non-odorous components) and there is a dominance of VOCs frequently identified within the emission samples as being critical contributors to the overall odour of a sample. In recent years, there has been considerable number of studies investigating the knowledge of VOCs associated with wastewater operation, however, the understanding of the VOCs and odorants from wastewater operations is primarily limited to WWTPs (Lebrero et al. 2011) and its surrounding atmosphere; compounds in relation to VOCs at wastewater collection systems are rarely studied and reported. From an environment-related perspective, aerial VOCs in and from sewers are the most important because they are directly perceivable by human noses and presumably contribute to exposure hazards for human healthy and quality of life.

Research on VOCs, VSCs and odorants from wastewater sources has demonstrated that it is technically challenging because of the large number of compounds and wide ranging concentrations amongst the compounds. Technical restrictions and high costs of the sampling and sequentially instrumental assessment are often constraints to the advancement of the research in this area. The use of combination of human nose detector and chemical assessment will provide the most promising methodology on measurement and characterisation of sewer odour emissions.

Research at other wastewater operations is generally thought to yield similar mass spectrum of VOCs and odorants to sewer networks, based upon similar bio-generic source of production. However, VOC concentrations and emissions are reported to vary significantly from the studies undertaken in different regions. The variations can be explained and attributed to the specific designs, operation condition and upstream of individual facilities and WWTPs. Thus, it would pertinent to assume that the emissions from sewers could have differential emission matrices and that the difference in the design and construction of sewer systems (i.e. rising mains vs gravity sewers) will also provide areas of possibility in comparing and contrasting the emissions amongst different sewer structures. To date, only a small number of short-term studies in relation to VOCs and odour assessment from sewer networks are available in literature. The quality and quantity of data are far from sufficient to characterise odorous emissions, adequately, explain and relate their variations to affect factors, design and implement reliable techniques and strategies for mitigation and abatement purposes. An large data pool from an extensive field sampling and measurement campaign is needed to improve our understanding and regulation of the release of sewer odours before dispersing into atmosphere or reaching the sensitive receptors.

The purpose of this research is therefore to substantially increase the knowledge of the chemical composition of the gas phase emissions from sewer collection systems. Toward this objective, more effective analytical and instrumental techniques and methodologies are needed to be developed and established allowing us to monitor concentrations, compositions and emissions at higher resolutions in terms of time, space in order to characterisese the release of VOCs, VSCs and odorants from sewer networks. This knowledge will provide and objective criteria for the design and implementation of odour abatement systems or mitigation strategies for the better management of the sewer odour emissions.

Chapter 3 Experimental Design and Instrumentation

3.1 Overview

To ascertain an understanding of odorous emissions from sewer networks, it is necessary to collect samples from a range of different sewage collection facilities. The research work presented henceforth represents data accumulated from VOCs and odorants field samples that have been collected throughout different climatic seasons and at different geographical locations within Australia.

In total, 21 different locations were sampled during the duration of the project for representations of conditions present in Australian sewerage systems. The primary sampling sites were located in Sydney and consisted of 12 sites located in different parts of the sewer network. An additional 7 sites were located in sewer sites in Melbourne and 2 in Perth, these formed a secondary sampling campaign targeted at assessing consistency in different climatically distinct regions of Australia, determined from the results of sampling in the Sydney sewer system. To improve our understanding of the sewer emission dynamics, all sites were designed to be monitored for at least one year, representing temporal variability over the four seasons (winter, spring, summer and autumn). Diurnal emission programmes was developed for sewer sites to provide additional data on short-term dynamics.

Chemical speciation of the samples collected was carried out using thermal desorption coupled to gas chromatograph to provide chemical separation, with a mass selective detector, sulfur chemiluminescence detector and olfactory detection port for the identification and quantification of the VOC, VSC, and odorants in the samples, respectively.

3.2 Site Selection and Field Monitoring Program

Site Selection

The monitoring campaign consisted of 12 sewer locations operated by Sydney Water Corporation, Sydney (Australia). Figure 3-1 illustrates the approximate locations of the field sites across Sydney. The locations of site were distributed in five major sewerage catchments, namely I, II, III, IV and V, receiving 327 ha (IV) and ~ 35,000 ha (II) upstream wastewater discharges.



Figure 3-1 Map of Sydney sewage catchment with approximate field Sites

The selection of sites was intended to be representative of conditions present in Australian sewerage systems. These sites consisted of a range of sewage types (domestic-containing residential, residential and commercial sewage, and mixed-domestic sewage containing industrial wastewater), sewer structures (rising mains, pumping stations, mixing chambers, sewer lines, and sewage treatment plant headworks) and chemical dosing treatments (Ganigue et al. 2011). The main conditions of monitored sites are summarized in Table 3-1.

C:to	Decemintion	Sewage	Chemical	ADWF	Diameter	Catch
Site	Description	Туре	Dosing	(ML/day)	(m)	No.
S 1	Upstream of a siphon	Mixed	dosed ^a	312	0.6	Ι
S 2	Pumping station wet well	Mixed	undosed	0.13	0.4	II
S 3	merging chamber	Mixed	dosed ^a	311	0.6	Ι
S 4	Downstream of a siphon	Mixed	undosed	9.48	0.5	Ι
S 5	Rising main	Mixed	dosed ^a	131	0.6	Ι
S 6	Sewer line	Mixed	dosed ^a	134	0.6	Ι
S 7	Sewer line	Mixed	dosed ^a	163	0.6	Ι
S 8	STP Headworks	Domestic	dosed ^{a,b}	0.28	0.15	IV
S 9	STP Headworks	Mixed	dosed ^b	16.0	0.35	V
S10	STP Headworks	Domestic	undosed	0.95	0.3	III
S11	Sewer line	Mixed	undosed	34	0.4	Ι
S12	Sewer line	Mixed	dosed	230	0.6	II

Table 3-1 Main characteristic of monitored sewer networks in Sydney

a: ferrous chloride; b: magnesium hydroxide

Domestic: containing residential and commercial sewage; Mixed: domestic sewage

containing trade waste (~5%-10% trade wastes)

ADWF: Average Dry Weather Weather Flow

Diameter: Sewer pipe diameter

Catch No.: indicated to which catchment a sewer site belongs

To confirmed the intended representations and investigate any variations between climatic distinct regions, additional field sites were selected at two cities (Melbourne and Perth) within Australia (Figure 3-2). Sites in Melbourne were selected to represent a more temperate climate with cooler ambient temperate and lower relative humidity while sites in Perth were chosen to represent sewers located in tropical climate, with typically higher ambient temperate and relative humidity. Throughout the monitoring program, the temperature, relative humidity and barometric pressure for the sewer air was recorded for each sample collected.



Figure 3-2 Map of field monitoring locations in Australia

Field Monitoring Program

The field sampling commenced between January 2011 and June 2013. Throughout the project the temperature, relative humidity and barometric pressure for the ambient air was recorded for each sample collected. During the project, there were three different sampling campaigns focussed upon different research aims.

1) Initial series of samples were gathered from Sydney sites only to verify methods and revised field techniques for optimal efficiency. This monitoring period captures the summer period (January to March 2011) in which peak odour emissions are commonly observed. It was the results of this initial sampling that led to identify odorants and VOCs present in sewer gases from a range of sites;

2) The second segment of field sampling focussed upon the intensive sampling at the selected Sydney sites over a two year period. This sampling commenced in June 2011 and concluded in March 2013. This allows for gathering a significant amount of sewer emission data to evaluate the variability inherent in sewer odorant emissions (long term/seasonal, spatial). Also conducted during the second sampling was a short-term study. The sampling was carried out on a monthly basis from each site and each month sampling was conducted within a two-week integrated period for 12 sites to minimize

variations of meteorological conditions that would occur over monthly period. Samples were collected at different times during a 24 hour period to observe any diurnal variations. Similarly, samples were collected at consecutive days to reveal any daily variations. This short-term study took place during the spring sampling in Sydney during 24th and 28th of October 2013;

3) The third and final field sampling campaign for this project took place in Melbourne and Perth. The intention of this sampling was to assess consistency or/and variability in different climatically distinct regions of Australia. All region sites were monitored for a one year period to assess variability under a same temporal scale. Seven different sites were sampled during June 2011 and May of 2012 at Melbourne, whilst two sites were collected between July 2012 and June 2013 at Perth.

Whilst these were the intended representations, the number of samples collected for individual sites during each season was not identical, not comply with the proposed scheme due to unavailability on sites. To conserve the integrity and comparability of the data collected, the sites remind the same for the each season within a given year to provide similar representation and equivalent spatial coverage for further data assessment and interpretation.

3.3 Analyte Collection

3.3.1 VSCs Analyte Sampling Apparatus

Gas samples were collected from 12 sewer locations (S1~S12) using custom-made 4L Nalophan bags (UNSW Odour Laboratory) (Figure 3-3). Bags were flushed with ultrapurified N₂ gas (BOC, Australia) to ensure that the bags were contaminant free before sampling. Sulfur samples were collected using a lung sampler at a constant flowrate of 1000 mL/min for 4 mins to ensure that the correct sampling volume (4L) was collected. The internal vacuum pump (SKC Inc., USA) of the system draws air directly into the bag by evacuating the tightly closed atmospheric press vessel, in which a bag was placed. To prevent contamination and absorption of odour substance onto the sampling equipment, only Teflon tube lines and stainless steel fittings were used as connectors.

3.3.2 VOCs Analyte Sampling Apparatus

VOC samples from the sewer emissions through absorption into Tenax TA sorbent tubes (Markes International, UK). The tubes are being pumped from a calibrated air sampling pump (SKC Inc., USA) with the flow rate individually controlled by low flow controllers (Figure 3-4 b). Samples were collected at a constant flow rate of 100 ml/min for 20 mins (2L sampling volume) using a calibrated air sampling pump (SKC Inc., USA). To maintain the scientific integrity throughout the project a number of replicates were collected to allow the application of representative sampling; a manifold (Figure 3-4c) was used to distribute the emissions sourced from the polyethylene duct between the sorbent tubes being collected simultaneously. All sorbent tubes were conditioned and carefully sealed with 2-piece brass screw caps with polytetrafluoroethylene (PTFE) ferrules and verified contaminant free prior to use.



(a)



(b)

Figure 3-3 Equipment used VSCs sampling (a) Tedlar bags in a home-made PVC canister; (b) the sampling with a lung sampler in place



(c) Figure 3-4 Equipment used VOCs sampling (a) Tenax TA sorbent tube; (b) The SKC pump used for pumping sorbent tubes; (c) The sampling manifold with sorbent tubes in place; Arrow indicating the sampling flow direction

11/2011

3.4 Laboratory Analytical Instrumentation

3.4.1 Overview

The comprehensive monitoring was performed based on a thermal desorber (TD for thermal liberation and pre-concentration) coupled with a gas chromatograph (GC for chemical separation) using a variety of detectors for identification and quantification of different targeted analytes:

- 1) Volatile sulfur compounds (VSCs) using a sulfur chemiluminescence detector (SCD);
- 2) Volatile organic compounds (VOCs) using a mass selective detector (MSD);
- 3) Odorants using olfactory detection port (ODP).

The sampling and instrumental analysis procedures were optimized for different analytes targeted and details of optimization will be discussed in **Chapter 4** for VSCs and **Chapter 5** for VOCs.

3.4.2 TD-GC-SCD Analysis for VSCs Samples

Thermal Desorption

Sampled bags were attached to an Air Server (AS) quipped (CIA 8, Markes International, UK) – Thermal Desorber (TD) (Series 2, Markes International, UK) and pre-concentrated onto a U-T6SUL-2S cold trap (Markes International, UK) prior to injection. The CIA 8 thermal desorber has four principle stages of operation:

1) Adsorption mode: In this stage, air sample in the sample bag is concentrated into the low-temperature cold trap, using a vacuum pump;

2) Desorb mode: The samples from stage (1) are desorbed and the carrier gas passes through the adsorption trap of a certain temperature;

3) Samples that filled the trap injected inside GC;

4) System cleaning mode: This cleans out all the paths that the samples pass through by using carrier gas.
To minimize the uncertainty of analysis by reducing the thermal decomposition of analytes and the contamination of the systems followed by VSCs desorption, the temperature of all the paths inside thermal desorption system were maintained at 80 °C.

Gas Chromatography - Sulfur Chemiluminescence Detector

Samples analysis was performed using a gas chromatograph (GC) equipped with a (SCD) (7890N GC and 355 Sulfur Chemiluminescence Detector, Agilent Technologies, USA) using a DB-VRX (30 m \times 0.25 mm \times 1.4 um) column (Agilent Technologies, USA).

Sulfur chemiluminescence detector (SCD) is a relatively new gas chromatographic sulfur-selective detector. It converts the sulfur compounds to sulfur chemiluminescent species and detects the chemiluminescence from the reactions between ozone and sulfur chemiluminescent species. This detector, coupled with GC offers a superior analytical tool for sulfur chemical speciation with advantages of excellent sensitivity, high selectivity and easy operation. The SCD was operated according to the manufacturer's guidelines. The SCD were operated with 800°C burner temperatures with air flow rate of 60 ml/min and hydrogen flow rate of 42.5 ml/min, respectively. The configuration of the instruments, including the detectors can be seen in Figure 3-5.



Figure 3-5 The TD-GC-SCD instrumental setups in UNSW Odour Laboratory

3.4.3 TD-GC-MSD for VOCs Analysis

Thermal Desorption

Collected VOC samples were first thermally desorbed using a Unity thermal desorber (Markes International, UK) coupled with an Ultra automatic sampler (Markes International, UK). A general purpose cold trap (U-T11PGC, Markes International, UK) was used to collect the sample prior to sample injection into a gas chromatograph. This instrument performs a series of sample preparation procedures, focuses the VOCs and then injects them as an analyte into the gas chromatogram. For the analysis of VOCs from sorbent tubes the Standard 2(3) stage desorption is applied. The Unity thermal desorber has three principle stages of operation:

1) Tube Purge: In this stage, Tube pre-purge is an essential parameter to remove humidity and oxygen from tube before reaching the cold trap using the carrier gas. The tube is held at ambient temperature and the cold trap kept at the low-temperature end;

2) Tube Desorb: The analytes are desorbed from tube where they are captured and focused and the carrier gas continues to pass through the tube to flow the sample onto cold trap;

3) Trap Desorb: The cold trap is heating to allow a focussed analyte quickly injected into the gas chromatogram.

Gas Chromatography - Mass Selective detector (GC-MSD)

Gas chromatograph-mass spectrometer combination is applied as a powerful analytical tool in many fields for the analysis of substance matrix. The selectivity, flexibility, and sensitivity of gas chromatography-mass spectrometer allow itself to the analysis of environmental samples.

The chemical characterisation of the VOCs within the sewer emissions was primarily performed using an Agilent 7890N gas chromatograph coupled to an Agilent 5975MSD mass selective detector (Agilent Technologies, USA). Varying different operating parameters during the course of the research enabled an optimum method to be established for the efficient speciation of the analytes captured on the sorbent tubes and is discussed in **Chapter 5.** The configuration of the instruments, including the detectors can be seen in Figure 3-6.



Figure 3-6 The TD-GC-MS instrumental setups in UNSW Odour Laboratory

3.4.4 Olfactory Detection Port for Odorant Analysis

For the purpose of characterising the odorants within the VOCs, an olfactory detection port (ODP) is necessary (Figure 3-7a). It is the combination of the mass spectrometer and the olfactory detection port that provide the significant and unique data set for the characterisation, prioritisation of the odorants present within the sewer gas emissions. The configuration of the gas chromatograph - mass spectrometer coupled to the olfactory port (TD-GC-MS/ODP) is displayed in Figure 3-7. It's similar to the setup of TD-GC-MS system for VOCs determination, but with a small capillary splitter diverted a calculated amount of the sample to the ODP during the analysis of the samples whilst the remainder of the flow continued to the MSD.

The use of the olfactory detection port is to detect compounds that stimulate a sensorial response from an operator and also to record odour intensity and odorant descriptors to both quantitatively and qualitatively characterise the particular odour using a control pad (Figure 3-7b). The ODP results are recorded using the Gerstel ODP Recorder, which integrates with the Agilent ChemStation to provide chromatographic spectra for both the Total Ion Chromatogram (TIC) and the odorant profile or olfactory stimulus chromatogram.









(c)

Figure 3-7 (a) Olfactory detection port; (b) The control pad to record an odorant and rate its hedonic density; (c) The TD-GC-MS/O instrumental setups in UNSW odour laboratory

Chapter 4 Volatile Sulfur Compounds (VSCs) Speciation

4.1 Introduction

A wide variety of trace gases can potentially be formed during sewage transport within aerobic, anoxic, and anaerobic environments (Vincent 2001). Of particular interests, are odorous volatile sulfur compounds (VSCs) produced via the conversion of sulfate by reduction microorganism (Nielsen et al. 1998, Hvitved-Jacobsen et al. 2002) causing environmental impacts on nearby residents and local receptor annoyance (Choi 1997, Nielsen and Keiding 1998, Schiffman and Williams 2005). Odour nuisance may occur even at trace concentrations of those compounds as well as cause serious concrete corrosion when transferred to the sewer structure surface (Stuetz and Frechen 2001, Nielsen and Jonsson 2002). In the past 10-20 years, population growth and increased number of complaints has raised the awareness of VSC emissions requiring sewerage system operators to better manage odorous emissions from sewers. However, the complex composition of sewer odours challenged the monitoring and control of these emissions, which is likely associated with insufficient sampling and the analytical limitations for the analysis of gaseous VSCs matrices that are present at trace levels and over wide-ranging concentrations (Kim 2005b, Muñoz et al. 2010).

H₂S is typically present with the highest content in sewer odours and the monitoring approach for H_2S is well developed for both on-site and off-site. Therefore, from an odour perspective, in Australian the VSCs monitoring the only focus has been upon hydrogen sulfide (H_2S), with limited and infrequent monitoring of non- H_2S sulfur compounds for both characterisation of emissions from sewer and odour abatement performance monitoring (Sivret and Stuetz 2012). However, a range of non-H₂S VSCs can be emitted from sewers that also contribute considerably to malodour complains due to their lower odour threshold values (OTVs)(Van Gemert 2003). Sampling and determination of VSCs has been limited due to reactive nature and trace abundance level of these sulfur compounds at complex matrices (Ras et al. 2008b), which eventually leads to inadequate identification and quantitative assessment of gaseous sulfur compounds. One of the most practical and reliable technique for measuring sulfur compounds is to couple thermal desorption (TD) with gas chromatography-sulfur chemiluminescence detection (GC-SCD) and successfully applied in monitoring campaigns (Khan et al. 2012, Le et al. 2013). The TD-GC-SCD analysis has been proven to be advantageous for trace sulfur gas determinations due to its high sensitivity (e.g. sub pictogram range of determination), selectivity and uniform response for all sulfur compounds (Yan 2002), low sampling volume required (10-400 ml) in sulfur gas analysis (Khan et al. 2012).

Sewer VSC concentrations can vary significantly between the time of day, seasons and year or from one catchment to another (Atasoy et al. 2004, Wang et al. 2013). Also, annual variations in background environmental conditions (i.e. temperature, rainfall and climate) and wastewater characteristics (i.e. sewage compositions and hydraulic conditions and design of collection facilities) can affect concentration levels (Hvitved-Jacobsen et al. 2013, Sun et al. 2014). It thus arise the necessity to more frequently collection and analysis of sulfur gas samples to account for all variables it could be encountered. The reliable monitoring and chemical analysis of dense sewer emission sample are expensive. As a consequence, to date only a small number of studies are available from sewer networks to provide limited insights into the VSCs emission dynamics with discretely sampling on limited number of sites, seasons and years (Thistlethwayte and Goleb 1972, Lasaridi et al. 2010, Huang et al. 2012). While the remaining published sewer VSCs data are based on liquid phase e.g. sewage and influent of sewage treatment plants sampling (Hwang et al. 1995, Sun et al. 2014).

A two-year monitoring program was performed at 12 sewer monitoring sites in Sydney, which were representative of typical sewerage conditions for Australia. The primary aim is to provide detailed information on measured concentrations of the VSCs appearing in the different sewers atmospheres. The monitoring program enables seasonal and year to year variability of VSCs concentrations to be assessed as well as spatial variability by comparing the concentrations measured at the different sewers. Spatial and temporal trend analysis also allows for the determination (i) as to whether any single season best represents an annual mean for the whole sewer networks; (ii) and how well any single site (sites group) represent the seasonal and temporal trends. In addition, correlations matrices between seasons were examined to investigate interspecies relationships and potential emission sources. This advanced characterisation will further improve the field sampling strategies for VSC emissions in sewers and enhance the design and operation of odour abatement processes for better sewer emissions management.

4.2 Materials and Methodology Developments

4.2.1 Overview

The monitoring, management and control of VSCs emissions from sewers are still a challenge due to the lack of an effective (e.g. reliable, fast and cheap) method of measuring/quantifying VSC odorants. The determination of VSCs is difficult in the ambient phase, due to their complex sample matrices, trace concentrations at a wide range and potentially storage losses during sampling and analysing procedures (Pandey and Kim 2009). To this end, some recent studies have focused on VSCs measurements of in-sewer sewages and raw wastewaters (Godayol et al. 2011, Sun et al. 2014) in order to understand and/or estimate VSCs concentrations in sewer atmospheres as their build-up can result in odour (and corrosion) problems (Stuetz and Frechen 2001) for wastewater utilities.

Gas chromatographic analysis coupled with flame photometric detector (FPD), pulsed flame photometric detector (PFPD) and the mass spectrometer (MS) and sulfur chemiilumescence detector (SCD) are frequently used techniques for measuring VSCs in different matrices as reviewed by Kim (2005b) and (Muñoz et al. 2010). Among these detectors, SCD provides higher sensitivity (e.g. sub pictogram range of determination) and selectivity, a more uniform response for all sulfur compounds (Yan 2002) and a low sampling volume (10-400 ml) (Khan et al. 2012). GC-SCD analysis has been successfully applied for the detection of sulfur containing compounds in petroleum (Lopez Garcia et al. 2002), atmosphere (Khan et al. 2012), food (Mussinan and Keelan 1994), wines (Siebert et al. 2010) and recently sewage analysis (Sun et al. 2014). The technical advantages and successful application of SCD in other environmental monitoring suggest its potential for measuring VSCs in complex sewer emission matrices. To our knowledge, no study has been reported to date on the use of SCD to detect atmospheric VSCs in sewer networks and/or WWTPs.

In sewer emissions, most sulfur compounds relating to wastewater, unlike H_2S , are present at trace concentrations (e.g. below ppb) so a pre-concentration step is required to reach the sensitivity of the instruments. Solid sorbent capture is among the most commonly used technique when volatile organic compounds are sampled and analysed. Sorbent tube sampling (using a combination of Tenax TA and Unicarb) equipped with GC-MS has been developed to determine 7 VSC species form sewage (Ras et al. 2008a). However, this approach has limitations due to the high selectivity in capturing airborne sulfur compounds, resulting from the limited capture of small molecular size sulfur compounds that are thermal unstable (such as H_2S , MeSH, carbonyl sulfide), which are typically found in the wastewater related odour emissions. Additionally, the moisture in humid sewer atmospheres can be trapped onto hydrophilic sorbents causing inaccurate sampling of sulfur compounds. To capture the entire sample matrices, solid phase microextration (SPME) has been applied as an alternative technique (Ras et al. 2008b), however the extraction process is time-consuming, fiber selective and the possibly formation of artefact products (e.g. mercaptan decayed into sulfides) are observed during SPME analysis (Lestremau et al. 2004). The coupling of GC-SCD analysis with thermal desorption (TD) has enabled lower sampling volumes to be applied as well as the use of inexpensive gas sample bags as a preferred direct method for collection and storage of the entire air sample. VSCs are however reactive in nature and trace concentrations can undergo storage losses due to sorption (Hansen et al. 2011) and catalytic oxidation with different materials into which they have been sampled (Trabue et al. 2006) as well as large sampling volumes are often required. A recent study by Le et al. (2013), indicated that a broad range of VSCs compounds (10 sulfur compounds) can be stored and analysed within a 24 hour storage period at temperatures of less than 20oC for three types of bag material (Tedlar, Mylar, Nalophan). Most discrete VSCs sampling campaigns would satisfy these analytical conditions. Therefore, the use of this method (for investigating temporal and diurnal variability) would be a suitable and reliable technique to analyse a full spectrum of VSCs over a broad concentration range.

This study aims to characterise VSCs in the atmospheres of different sewer systems using TD-GC-SCD. To achieve this, an analytical method was developed and examined in terms of linear ranges, detection limits, reproducibility for the determination of a broad range of VSCs e.g. methanethiol, dimethyl sulfide and dimethyl disulfide. The method was then applied to measure a full spectrum of VSCs concentrations and their emission dynamics collected from sewer atmospheres.

4.2.2 Materials and Method Developments

Ten VSCs were selected as representative of VSCs emissions from sewer networks, including H_2S , thiols and sulfides, which covered most typical VSCs could find in wastewater or wastewater related sources. A custom-made standard of H₂S and MeSH were purchased in a cylinder at concentration of 10ppmv and 5ppmv (CAC Gas & Instrumentation Pty Ltd, Australia), respectively. Liquid sulfur standard were all obtained from Sigma-Aldrich (Castle Hill, NSW, Australia), which includes EtSH (\geq 97%), DMS (≥ 99%), 1-BuSH (≥ 99%), EMS (≥ 99%), 1-BuSH (≥ 99%), DMDS (≥ 99%), DEDS (\geq 99%), and DMTS (\geq 98%) were obtained from Sigma Aldrich, Australia. Stock solutions of the liquid standards, all with the concentration of 500 ppm (v/v) were firstly prepared in pentane and stored under refrigerated conditions in gastight vials, which were further diluted to 5 different levels (1-50 ppm) for calibration purpose. The working standard of gaseous and liquid phase were all prepared by diluting the primary standard into 4 litre bags using a ultra-purified N₂ gas (BOC, Australia), via dynamic injections, which has been described previously (Wang et al. 2012b). The performance of methanol and n-pentane were evaluated to determine the optimal extraction solvent (e.g. better volatilisation efficiencies) and this assessment was undertaken by loading roughly ~10 ng of VSCs standard mixture, which was previously prepared in two different solvents. All experiments were conducted in triplicates and the samples were then subjected to the full adsorption/desorption extraction and analysis procedure.

4.2.3 Air server-Thermal desorption (AS-TD)

The experiments were undertaken with regards to sampling optimisation, the AS-TD breakthrough flow/volumes were determined to ensure the optimal sample extraction volume and method sensitivity. Sample flow rates of 10-50 ml/min were tested in fixed durations of 5 mins to allow the sampling volume between 50-250 ml, which were generally within the safe sampling ranges suggested by Khan et al. (2012). Triplicate samples were prepared by spiking roughly 5 ng of standard mixture at variable TD loading durations of 2-16 min, corresponded to the volumes of 20-160 ml (i.e. 10 ml/min as determined previously) to achieve optimum recovery of AS-TD sampling.

Optimisation of AS-TD sampling inlet

To optimise the desorption process for the AS-TD sampling system, the influence of adsorption temperature (°C), desorption temperature (°C), desorption flow (ml/min) as well as desorption time (min) were assessed (Figure 4-1). A low-end temperature (during adsorption) is a crucial variable as it has a noticeable influence on the targeted sulfur analytes and the response was maximised when the trap temperature was set at the lowest allowable level (-30 °C). Enhanced responses were achieved when an optimum temperature was applied to facilitate the minimal loss of analytes from the gas samples. A peak area difference for H₂S of up to 45% was achieved for the tested temperatures whereas for other analytes, the increase was no more than 10%. An adsorption temperature of -30 °C was selected for the cold trap in order to efficiently extract the targeted VSCs at the same time.

The parameter for the desorption time was examined in a same way (as adsorption) by adjusting the temperature between 200°C to 300°C. Figure 4-1, shows that the peak areas with most the analytes reaching a maximum value at around 270°C~280°C, therefore 270°C was chosen to ensure the best desorption as well as greater recoveries for more reactive compounds, as very high desorption temperature suppressed the responses of these compounds due to thermal degradation (i.e. pyrolysis). The desorption time was set between 2-10 min to determine the optimal desorption condition, and results showed that desorption time was not significantly affecting the peak area but for times greater than 5 min, relatively greater mass response were achieved. With only a small marginal increase in responses, 5 min was selected as the desorption time.



Figure 4-1 Dependence of analytes recovery on desorption temperature (Top); Dependence of analytes recovery on adsorption temperature (Bottom). The peak areas have been normalised to maximum value for each individual compound

Desorption Flow

Desorption flow is a critical parameter to determine the resolution of GC chromatogram and the response level (e.g. method detection limits) being the sum of the column flow and the split flow (if applicable) in the AS-TD configuration. Desorption flow must provide sufficient time to desorb all the analytes into the chromatographic column. In this step, the split flow strongly influences the shape of the chromatographic peaks, three split flows setting were tested including no-split, 5 ml/min and 10 ml/min. In the splitless mode, considering the high content of H₂S in the sewer samples, its peak generate a greater tail on the chromatogram that suppressed the detection of MeSH as the MeSH peak is eluted in the tail of H₂S. To avoid the tails of H₂S peak and its impact on separation of adjacent peaks, such as MeSH, the split flow was increased (column flow was fixed at 1 ml/min) resulting in reduced response levels. Therefore, the desorption flow or split flow should be made at the lowest possible temperature as no significant change in term of the sharpness and shape of analyte peaks were observed, so 5 ml/min was chosen for further method development as well as field sampling studies.

The experimental studies to determine the optimal sample loading volume/flow (Figure 4-2) shows normalized responses of VSCs collected at between 5 ml/min to 50 ml/min, with maximum sampling volume being less than 250 ml. These results were similar to instrumental settings under various VSCs concentration (Khan et al. 2012), but a marked unit response (instrumental signal) decrease was observed for most of VSCs at a higher flow rate. This suggests that after a sample flow of 10 ml/min passed through the cold trap, breakthrough of VSCs can start to occur. At a sampling flow of 10 ml/min, the response factors (area per ml sample) were increased with increasing sample volume for most of targeted VSC analytes, except H₂S and MeSH. In cases of other VSCs (excluded H₂S and MeSH), the response factors (sensitivities) were relatively constant (variability less than 7%) over tested sampling volumes, with a small increase occurring at higher loading volumes. For H₂S and MeSH, there is a larger discrepancy on the response factors in the instrument with changing sample volume injected and the relative variability was measured up to 10% and 22% for MeSH and H₂S, respectively. The decreased sensitivity were generally observed after around 50~80 ml of two highly reactive compounds and this could either relate to loss of sample (decomposition and/or contaminations from analytical line) or breakthrough on the cold trap at longer sampling durations (e.g. 160 ml required 16 min at 10 ml/min sampling flux). Considering the wide spectrum of VSCs and high concentration of H_2S and MeSH that are supposed to be present in the sewer gases, the sampling volume was limited to 50-100 ml to make a compromise between best possible methods detection limits (MDLs) and optimum retentions of all targeted analytes.



Figure 4-2 Effects of sampling flow (Top) and volume (Bottom) on recovery of VSCs in sample bags

4.2.4 GC-SCD Analysis

Sample analysis was performed using a GC equipped with a sulfur chemiluminescence detector (SCD) (7890N GC and 355 Sulfur Chemiluminescence Detector, Agilent Technologies, USA) using a DB-VRX ($30m \times 0.25mm \times 1.4 \mu m$) column (Agilent Technologies, USA). In order to optimise GC separation of targeted sulfur compounds in working standards and real air samples, the oven program was optimised in terms of

oven temperature (starting from 35 °C, 37 °C, 40 °C and 50°C, respectively) and flow rates (ranging from 1 ml/min to 1.5 ml/min). The SCD were operated with 800°C burner temperatures with air flow rate of 60 ml/min and hydrogen flow rate of 42.5 ml/min.

Optimisation of the GC

Optimisation of the sulfur separation was undertaken by systemically varying oven temperature ramp rates and linear velocity of the helium carrier gas, which are the main parameters that influence separation ability. Adjustments to the carrier gas flow rate (1.0 ml/min to 1.5 ml/min) did not have a significant effect on sulfur peaks resolution. While, the oven temperature did have an impact with lower initial temperature performed better, achieving good separation and magnitude of peaks of the less volatile compounds (e.g. H_2S , MeSH). The peak resolutions (R_s) were determined as 1.18(t_{R_2}) $-t_{R1}$ / (w_{0.5,1} + w_{0.5,2}), where t_R is retention time and w_{0.5} is the width at the half-height. H_2S and MeSH were not resolved (Rs = 1.39 and Rs= 1.71, respectively) under higher initial temperatures (i.e. 40° C and 50° C), but good resolutions were achieved under the relatively lower tested temperature i.e. 30 °C (Rs=6.17) and 37 °C (Rs=5.79). However, when the GC was operated under relatively lower temperatures, around or below room temperature (≤30 °C), more time it required to cool and equilibrate the system for following runs. Therefore, the oven temperature was finalised at 37 °C for 3 min, then raised at a rate of 15 °C/min to 225 °C and held for 2 minutes with a total retention time of 17.3 min. Using the optimised analytical and desorption, the chromatograms (Figure 4-3) shows excellent peak separation and sharpness for the targeted VSCs in both standard solutions and sewer emission samples method) without interference (e.g. (overlapping) between compounds.



Figure 4-3 Chromatogram of VSCs in standard solution of each compound (A) and chromatogram of VSCs in a real sewer gas sample (B)

4.2.4 Quality Assurance and Quality Control

Calibration Linearity

To fully calibrate the AS-TD-GC-SCD system, a series of calibration experiments were conducted. Liquid stock standards (flask) used in this work were prepared at five concentration levels of 1, 5, 10, 25 and 50 ppm (volume/volume). Bag samples for calibration curve tests were then prepared by injecting 40 μ l of the corresponding liquid stock standards, different volumes (5, 10, 20, 25 and 50 ml of 10 ppmv H₂S and 10, 20, 40, 50 and100 ml of 5 ppmv MeSH) gas standard into 4 litre sample bags under calibrated flow using a custom-made calibration solution loading apparatus at a flow rate of 400 ml/min for 10 minutes. Each of these sampled bags was then analysed to extract the calibration data points by loading the TD unit from 1-10 min at a fixed flow rate of 10 ml/min. This corresponds to a sample loading volume range of between 10-100 ml, the absolute quantities of standard supplied into AS/TD were calculated and

present in Table 4-1. The linearity of analytical instrument used in this study was compensated (i.e. different loading volume of a sample) as too concentrated standards may saturate the retention capacity of the cold trap even at shorter supply durations (or at a lower flow rate).

-	Concentration		Theoretical amount (ng)nl20 ml50 ml80 ml100 ml20 2520 2520 2520 25					
Compounds	(ppb)	10 ml	20 ml	50 ml	80 ml	100 ml		
H ₂ S	12.5	0.17	0.35	0.87	1 39	1 73		
1120	25	0.17	0.69	1 73	2 78	3 47		
	29 50	0.55	1 39	3 47	5 55	6 94		
	62.5	0.87	1.32	4 34	6 94	8.67		
	125	1 73	3 47	8 67	13.9	17.4		
MeSH	12.5	0.24	0.49	1.22	1.96	2.45		
	25	0.49	0.98	2.45	3.92	4 90		
	20 50	0.98	1.96	4 90	7.84	9.80		
	62.5	1.22	2.45	6.12	9.80	12.2		
	125	2.45	4 90	12.2	19.6	24.5		
EtSH	34	0.17	0.34	0.43	0.69	0.86		
20011	17	0.43	0.86	2.15	3 45	4 31		
	34	0.86	1.72	4.31	6.89	8.62		
	85	2.15	4.31	10.8	17.2	21.5		
	170	4.31	8.62	21.5	34.5	43.1		
DMS	3.3	0.17	0.34	0.42	0.68	0.85		
	16.7	0.42	0.85	2.12	3.38	4.23		
	33.4	0.85	1.69	4.23	6.77	8.46		
	83.4	2.12	4.23	10.6	16.9	21.2		
	166.8	4.23	8.46	21.2	33.8	42.3		
CS_2	4.1	0.25	0.50	0.63	1.01	1.26		
-	20.3	0.63	1.26	3.15	5.04	6.31		
	40.6	1.26	2.52	6.31	10.1	12.6		
	101	3.15	6.31	15.8	25.2	31.5		
	203	6.31	12.6	31.5	50.4	63.1		
EMS	2.7	0.17	0.34	0.42	0.67	0.84		
	13.5	0.42	0.84	2.11	3.37	4.21		
	27.1	0.84	1.68	4.21	6.74	8.42		
	67.7	2.11	4.21	10.5	16.8	21.1		
	135	4.21	8.42	21.1	33.7	42.1		
1-BusH	2.3	0.17	0.33	0.42	0.67	0.84		
	17.1	0.42	0.84	2.09	3.35	4.19		
	34.1	0.84	1.67	4.19	6.70	8.37		
	85.3	2.09	4.19	10.5	16.7	20.9		
	114	4.19	8.37	20.9	33.5	41.9		

Table 4-1 Theoretical amount ofVSCs supplied into TD over tested samplingloading conditions at 5 prepared concentration levels

Compounds	Concentration		The	oretical amou	nt (ng)	
	(ppb)	10 ml	20 ml	50 ml	80 ml	100 ml
DMDS	2.7	0.21	0.42	0.52	0.84	1.05
	13.6	0.52	1.05	2.62	4.18	5.23
	27.2	1.05	2.09	5.23	8.37	10.5
	68	2.62	5.23	13.1	20.9	26.2
	136	5.23	10.5	26.1	41.8	52.3
DEDS	2	0.20	0.40	0.50	0.79	0.99
	10	0.50	0.99	2.48	3.97	4.97
	20	0.99	1.99	4.97	7.94	9.93
	50	2.48	4.97	12.4	19.9	24.8
	99.5	4.97	9.93	24.8	39.7	49.7
DMTS	2.3	0.24	0.48	0.60	0.96	1.20
	11.7	0.60	1.20	3.01	4.81	6.01
	23.3	1.20	2.40	6.01	9.62	12.0
	58.3	3.01	6.01	15.0	24.0	30.1
	117	6.01	12.0	30.1	48.1	60.1

Table 4-1 (cont.)

Mixture of VSCs standard as loaded into TD at a fixed flow rate of 10 ml/min with 5 different durations of 1, 2, 50, 80 and 100 min to obtain corresponding sampling volume of 10 ml, 20 ml, 50 ml, 80 ml and 100 ml

Calibration linearity was evaluated through the analysis of a series of samples containing 5 concentration levels of the compounds. Samples were loaded into TD unit with the duration of 1~10 min at a fixed flow of 10 ml/min. This corresponds to a sample loading volume range of 10-100 ml and a supply of, i.e. 0.16 ng (12.5 ppb at 10 ml) to 17 ng (125 ppb at 100 ml) of H₂S, accordingly to calculations (Table 4-1). Therefore, 25 response factors (5×5) were derived from 5 points calibrations (i.e. 5 TD loading duration) for each VSC standard (Table 4-2). The SCD response was linear for the specific compound concentration range, with excellent correlations (R^2 values greater than 0.99 were found at the 5 tested concentration levels). The linearity was then determined by pooling all the data (25 data points for each analyte) for the 5 concentration standards at variable TD loading volumes. Table 4-3 shows the identified linear ranges and linear fit quality. The linearity of heavier compounds (i.e. CS₂, DMDS, DMTS and DEDS) were slightly shorter over the tested concentration ranges and can be maintained around ~100 ppb at less than 80 ml of sample volume. The calibrated ranges covered the possible concentration range of these substances in sewer emissions (see Section 3.3), with a broad dynamic range (2-3 orders of magnitude).

Method Detection Limits

Method detection limits (MDLs) were determined using compound standards, with the mass of the analyte being sequentially decreased until the detector response fell below the limit of detection (3 times the baseline noise, S/N=3). For the ranges of compound studied, the MDL determined from 0.009 ng (DMTS) to 0.263 ng (MeSH) in absolute mass term. If expressed into concentration units, they correspond to 0.10 μ g/m³ to 5.26 μ g/m³ when 50 ml of sampling volume was applied for analysis, and were typically less than 1 μ g/m³. Comparably, the GC-SCD detection limits under our configuration offered lower MDLs than that achieved by GC-FPD (Campos et al. 2010) and GC-PFPD (Kim 2005a) but about one order of magnitude higher than that derived by GC-SCD (Khan et al. 2012). But considering our split mode on the AS-TD system, the absolute detection limits for the sulfur compounds in our methods with bag samples were quite comparable with their canister sampling of gaseous VSCs. The determined MDLs were generally lower than the reported OTV ranges for the compounds studied,

which confirms that the analytical approach would be suitable for monitoring odorous VSCs present in sewer and WWTPs emissions.

Recovery Rates

Recovery rates (RR) (%) are considered one of most important parameter to evaluate the performance of an analytical method. In our study, recovery rations were evaluated via two ways as suggested by Kim (2011): (i) by comparing quantities of VSCs detected between direct injection into the GC injector and AS-TD application (overall methodology assessment) and (ii) comparing the theoretical amount of VSCs standard supplied into the TD and amount of VSCs detected by the TD (thermal desorption efficiency assessment). RR (%) from both methods were obtained by spiking ~2 ng and ~25 ng (liquid mixture) and ~2 ng and 16 ng (H₂S and MeSH gas standards) of the target analytes into VSC-free Tedlar bag. The bags used for recovery test were flushed with ultrapure N_2 several times to remove any background VSCs. The average recovery rates for the different VSCs varied from $25 \pm 1\%$ (DEDS in low concentration level) to $95 \pm 2\%$ (EtSH in high concentration level) in the former method. The poorest recovery of $25\% \sim 43\%$ was observed for heavier VSCs at both test concentration levels of the standards while in contrast the results of the relatively lighter (i.e. EtSH, DMS and EMS) yielded higher RR (>50%). The results (Table 4-3) show that heavier VSCs experienced the most significant loss in this method, while this was not the case for the lighter VSCs. However, the overall recoveries rate achieved under our analytical method was generally higher than the SPME sampling method reported by Ras et al. (2008b), indicating the superior potential of sampling via AS-TD over SPME. In the latter methodology, the mean recovery rate was obtained from $87 \pm 1\%$ (1-BuSH in low concentration end) to $112 \pm 12\%$ (MeSH in high concentration level), indicating great desorption efficiency of this TD application for capturing sulfur compounds from gas samples. However, in this method, significant variation on recovery rates were observed for H₂S between 66 \pm 1% (at high concentration level) and 125 \pm 12% (at low concentration level). An increase in the relative standard deviation was generally observed from high concentration (~ 2 ng) to low concentration (~ 25 ng) for the two highly reactive compounds (i.e. H_2S and MeSH), also suggesting larger measurement uncertainties could happen with TD-GC-SCD configuration at a lower concentration level. A similar observation was also observed by Khan et al. (2012) where they used gas VSC standards for tests. Considering the results obtained from both approaches, it infers that the substantial reduction in method sensitive could inevitably occurred if operating of the TD system compared with direct injection onto the GC column, but the TD recovery efficiencies can be maintained for a wide range of VSCs, allowing to trap all sulfur analytes onto GC column.

	Spike	C	nc.1	Con	c.2	C	nc.3	C ₀₁	nc.4	Co	nc.5
Compounds	method	RF	r ²	RF	\mathbf{r}^2	RF	\mathbf{r}^{2}	RF	r²	RF	\mathbf{r}^2
H_2S^1	Gas	972	09660	910	0.9974	1310	0.9971	1576	0.9994	1752	0.9994
MeSH ¹	Gas	2362	0.9991	2359	0.9997	2354	0.9996	2512	0.9985	2284	0.9919
$EtSH^{2}$	Liquid	2050	0.9985	1968	0.9985	2086	0.9987	2114	0.9987	2100	0.9976
DMS^2	Liquid	2709	0.9992	2655	0.9992	2570	0.9992	2405	0.999	2341	0.9985
CS_2^2	Liquid	4434	0.9910	3440	0.9954	3897	0.9889	3818	0.9989	3461	0.9977
EMS^{2}	Liquid	2179	0.9989	2089	0.9970	2310	0.9955	2238	0.9996	2059	0.9969
$1-BuSH^2$	Liquid	1320	0.9988	1188	0.9988	1411	0.9969	1526	0.9996	1477	0.9977
$DMDS^2$	Liquid	4368	0.9904	3057	0.9904	3601	0.9995	4029	0.9991	3611	0.9963
$DEDS^2$	Liquid	4366	0.9992	3973	0.9992	3781	0.9995	3155	0.9992	2692	0.9994
$DMTS^2$	Liquid	4409	0.9985	3333	0.9985	3072	0.9989	3326	0.9992	3302	0.9917
1: H_2S and M	leSH were pr	epared as	gas standard	at 5 concen	itration (12.5	, 25, 50, 62	.5 and 125 pp	b) at differe	nt sample vol	ume of 10-	~100 ml
		;		l		•			-	0 F J	

Table 4-2 Response factors derived from calibration of each VSC standard prepared by AS-TD analysis

2: Other VSCs were prepared as liquid standard at 5 concentration(between ~2 ppb and ~166 ppb) at different sample volume of 10~100 ml:

RF: Response factor (area/ng)

 \mathbf{r}^2 : Determined Coefficient of linear relationship

Conc.1~ Conc.5: Represent the standard concentration at 1^{st} to 5^{th} level

Commenda	oTVs	IM	IC	Linearity	TD Rec	overy (%)	Method re	covery (%)
Compounds	$(\mu g/m^3)^1$	ng	μg/m³	(ng)	High	Low	High	low
H_2S	0.21 - 270	0.26	5.26	0.35 - 13.8	66 (±1)	125 (±12)	NA	NA
MeSH	0.0003 - 38	0.04	0.82	0.24 - 24.5	87(±2)	112 (±9)	NA	NA
EtSH	0.046 - 21	0.15	3.00	0.09 - 43.1	102 (±2)	94 (±2)	95 (±2)	87 (±2)
DMS	0.3 - 160	0.06	1.10	0.09 - 42.3	103 (±1)	91 (±1)	59 (±1)	52 (土1)
CS_2	70 - 180	0.03	0.62	0.13 - 63.1	98 (±1)	$104 (\pm 1)$	90 (±1)	88 (±1)
EMS	62	0.03	0.68	0.09 - 42.1	102 (±1)	91 (±1)	38 (±1)	33 (±1)
1-BuSH	1.5 - 3.0	0.29	5.84	0.09 - 41.9	102 (±2)	87 (±1)	61 (±2)	52 (土2)
DMDS	1.1 - 78	0.01	0.14	0.11 - 52.3	101 (±1)	96 (±3)	43 (±1)	41 (±3)
DEDS	0.3 - 23	0.01	0.10	0.10 - 49.7	101 (±1)	97 (±1)	26 (±1)	24 (土1)
DMTS	0.06 - 7.5	0.01	0.18	0.12 - 60.1	102 (±2)	90 (±1)	37 (±2)	32 (土2)
1: OTVs (odour	threshold values)	present were	according to	(Van Gemert 2003				
NA: data were n	ot available as no	tests were ur	idertaken to i	nject gas standard i	nto GC column			

Standard deviations are showed in parenthesis.

Table 4-3 Quality parameters for the ten VSCs analytes

Chapter 4 Volatile Sulfur Compounds (VSCs) Speciation

Instrument reproducibility

Instrument reproducibility for each compound studied was assessed through the analysis of a series of 3 replicate samples for hydrogen sulfide and methyl mercaptan, and a series of 5 replicate samples for all other compounds. The relative standard deviation (RSD, %) ranged from 1.8 - 6.1% over the compound range studied, without significant differences between both intra-day and inter-day analyses but slightly higher RSD were achieved on weekly analyses, 5.2% (DMDS) ~15.1%. This suggests that the calibration standards need to be prepared at least weekly at the concentration range for measuring atmospheric VSCs accurately. Precision in real samples was determined by the collection of six simultaneous samples from three emission sources representing typical emissions encountered during the monitoring campaign. The inlet, post-heater, and outlet of one of the activated carbon odour abatement processes was used as a site representing typical emission concentrations and compound distribution. The relative standard deviation (RSD) values varied from 2.3-15.1%, higher than those observed under laboratory conditions. The results obtained for each of the sites and under laboratory conditions utilising pure standards are compared in Table 4-4.

			Field evaluat	ion (n=6)				Lab evaluatio	U
Communda	Inlet of	f AC	Post-He	eater	Outlet	ofAC	Inter (n=6)	Intra (n=3)	Weekly (n=3)
Compounds	Conc.	RSD	Conc.	RSD	Conc.	RSD	RSD	RSD	RSD
	(μg/m ³)	(%)	(μg/m ³)	(%)	(μg/m ³)	(%)	(%)	(%)	(%)
H ₂ S	4677	4.4	4041	4.6	20.0	6.3	6.1	8.9	15
MeSH	1094	7.8	857	3.6	6.5	5.8	2.5	5.4	6.5
EtSH	ND	NA	QN	NA	QN	NA	3.1	3.4	<i>T.T</i>
DMS	71.1	4.9	6.99	3.5	80.5	2.3	3.1	4.9	6.6
CS_2	11.6	9.5	9.70	13.5	10.0	2.5	3.3	6.6	7.1
1-BuSH	33.2	12.0	QN	NA	QN	NA	1.8	2.3	6.8
EMS	ND	NA	QN	NA	QN	NA	5.0	4.5	6.3
DMDS	16.8	15.1	12.4	6.5	203	2.3	3.5	6.6	5.5
DEDS	ND	NA	QN	NA	QN	NA	3.0	7.6	6.2
DMDS	10.5	13.8	9.80	7.2	4.40	12.6	4.8	7.8	10.9
ND: not detected (<	MDL); NA: d	lata were no	t available du	e to non-de	tection of a c	i punoduto	n field condition	S	

Table 4-4 Evaluation of sulfur analytical method reproducibility

4.3 Data Analysis Approach

VSCs concentrations below the method detection limit (MDL) were substituted with one-half MDL (1/2 MDL) and extreme observations defined as mean values \pm six standard deviations were excluded from further statistical analysis. Seasonal means for each VOC were calculated using average data from all sites mean over a three-month period (one season), which are expressed in equation (4-1). Similarly, mean values for each year were calculated using average data derived from all seasonal means (e.g. an annual mean = averages of winter, spring, summer and autumn).

$$\overline{Y} = \frac{1}{n} \sum_{1}^{n} \left(\frac{1}{Ki} \sum_{j=1}^{Ki} Y_{ij} \right)$$
Equation 4-1

Where \overline{Y} =the season concentration, n_i =the number of sites sampled, K_i =the number of days sampled at site i. Y_{ij} = the concentration on day j at site i.

The coefficient of variation (CV), the ratio of the standard deviation to the mean, was calculated to compare the distributions of each season (across ~ 10 sites) as well as the differences of each site (amongst 4 seasons). Spearman correlation coefficients amongst seasons were calculated for each species in each sampling year using the season mean values of each site. Correlation analysis was also conducted on all measured concentration data to assess the inter-species relationship. Cluster analysis (CA) was conducted on log-transformed VSCs concentrations to distinguish the similarity or dissimilarity between multiple sampling sites. Normal distributions were examined by the D'Agostino and Pearson omnibus normality test. The analysis of variance (ANOVA) was performed on the VSC concentrations (log-transformed) to determine which compounds had significant concentration difference between sewer sites as classified by the cluster analysis. All experimental data were tested using the SPSS v.21 package (Statistics 2012).

4.4 Result and Discussion

4.4.1 General Patterns of VSCs Detected in Sewer Emissions

Totally, 12 unique VSCs were detected and measured in more than one sewer sites during the studied period between June 2011 and March 2013. The measured VSC components in the headspace of sewer networks included: hydrogen sulfide (H₂S), methyl mercaptan (MeSH), ethyl mercaptan (EtSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS), ethyl methyl sulfide (EMS), carbon disulfide (CS₂), diethyl sulfide (DES), diethyl disulfide (DEDS), diethyl trisulfide (DETS) and 1-butanethiol (1-BuSH).

Six out of twelve sulfur compounds were concurrently detected in the headspace of sewer networks in Sydney during the 24-month monitoring period with appearance frequency over 30% in the pool of samples. Table 4-5 summarizes the average, minimum and maximum concentrations of the six VSCs across the different sewer sites along with associated OTVs. Two-year concentration datasets excluded S11 indicated that all the six VSCs were frequently detected or measured above their corresponding detect limits (MDLs) with over 90% detection frequency for most of targeted VSCs during the two-year sampling. The compound with the highest concentrations was H₂S, being detected in all the sites and found at the levels of up to several millions $\mu g/m^3$. H₂S is traditionally reported as the dominative sulfur compounds emitted from sewage and STPs (Thistlethwayte and Goleb 1972, Al-Shammiri 2004) as H₂S is a major biodegradation products from wastewater organics via sulfur reduction bacteria. The measured H₂S concentration in this study ranged from 290 μ g/m³ to 30780 μ g/m³ (site means) with an arithmetic mean of 6078 μ g/m³ among total 245 sampling events. MeSH was the second most abundant VSCs component collected from all the locations with lower concentrations than H₂S in all the samples, which were generally present in hundreds to thousands of $\mu g/m^3$ with the lowest and highest average site concentration of 6.06 μ g/m³ and 2187 μ g/m³, respectively. Similar or slightly higher concentrations of these two compounds have been reported in the emission samples from either raw sewage or collection systems (Kabir et al. 2010, Sarria and Belanger 2010).

The concentration level of DMS was determined to be between tens to hundreds of $\mu g/m^3$ (18.9 $\mu g/m^3$ to 231 $\mu g/m^3$) across all sampling sites, which is generally the same

magnitude of previous studies that carried out in the city of Izmir, Turkey (Muezzinoglu 2003). A similar concentration range (88.72 \pm 80.50 ppbv) in samples also observed by Wu et al. (2006) collected from a drainage system in Taiwan and large variations on the concentration have been observed subject to the season they were sampled. In Finland, the similar concentrations (between 6.3-117 μ g/m³) for DMS was also detected from waste gas emitted from influent to a municipal STPs (Lehtinen and Veijanen 2011). The occurrence of DMS was well documented as a major VSC in wastewater environment as it is reported to be formed by several mechanisms (i) discharging of industrial DMSO, (ii) the conversion of precursor (DMSP) under anaerobic conditions (Bentley and Chasteen 2004, Cheng et al. 2005) and (iii) the conversion from methanethiol via biological methylation reaction (Lomans et al. 1997).

Carbon disulfide (CS_2) , dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS)were also frequently detected in the sewer emission samples, which is in accordance with previous publications, however the magnitude of these VSCs were reported to vary and was dependent on the sample locations and sewage characteristics (Dincer and Muezzinoglu 2008, Ras et al. 2008a). The presence of DMDS and DMTS, like DMS, could also related with decayed products of methyl mercaptan (Higgins et al. 2006, Van Leerdam et al. 2011) and/or originate from the discharging of industrial wastes. Trace concentrations of the three compounds were determined from sewer gas emissions in the range of ~ tens $\mu g/m^3$ which was generally one order of magnitude lower than DMS. DMDS was found at an average concentration of 20.7 μ g/m³ whereas CS₂ is 17.5 μ g/m³ when the whole dataset was statistically analysed. The level of measured CS_2 concentration in this study is similar to what reported by Lasaridi et al. (2010). They measured the CS₂ concentration in the headspace of a pump station up to 22 μ g/m³. But the DMDS (all sites average) concentration in this study is lower than results measured by Sun et al. (2014) < 2 ppb (corresponding to 126 µg/m³ if calculated by Henry's law assuming gas-liquid equilibrium) at a wastewater pump station but our measured DMDS concentration at S2 (pump station) is close to their results. DMTS was the least detected compounds in terms of both occurrence frequency and abundance with its mean concentration ranging from 4.96 μ g/m³ to 35.9 μ g/m³. To our knowledge, the DMDS and DMTS concentrations at sewerage gas have not been reported to date. DMTS is rarely reported as a component of odour emissions from wastewater source rather than its wide delectability in aqueous phase (Van Langenhove et al. 1985, Gun et al. 2000) due to its relative poor volatilization potential. Volatilization potential of a chemical can be indicated by Henry's law constant (H). The reported DMTS has the lowest Henry's law constant (air-water) value $H_{air/water}$ of 0.022 (atm (kg m⁻³/kg m⁻³ dimensionless) amongst the investigated sulfur compounds, which is three times lower than DMDS (0.065) (Gascons Viladomat et al. 2006). Less volatilization potential of DMTS during the sewage transportation process might reduce its concentrations in the headspace of sewer networks.

Site	Statistic		Co	mpounds	s (μg/m ³)		
Sile	summary	H_2S	MeSH	DMS	CS_2	DMDS	DMTS	Total-S
S 1	Minimum	104	5.74	7.60	7.60	3.19	1.8	116
n=22	Maximum	19474	4698	244	37.3	58.3	87.9	20603
	Mean	6764	1315	117	18.5	22.6	21.4	7323
	Median	4451	1225	105	18.6	21.0	12.7	5195
	Freq $(\%)^{a}$	100	100	100	100	100	100	NA
S2	Minimum	116	5.90	11.4	4.19	3.80	6.09	133
n=20	Maximum	4451	660	207	69.8	85.7	141	4684
	Mean	1281	211	66.1	14.1	24.5	35.9	1426
	Median	821	152	59.4	10.4	18.7	26.8	1112
	Freq (%)	100	100	100	95.0	100	100	NA
S 3	Minimum	1448	352	93.0	11.1	4.47	4.20	3319
n=10	Maximum	13492	1473	196	24.7	24.8	38.9	138817
	Mean	5342	893	142	18.6	12.9	17.2	6840
	Median	3964	937	133	19.4	10.4	16.2	5884
	Freq (%)	100	100	100	100	100	100	NA
S 4	Minimum	86.9	27.7	17.4	3.96	3.65	3.08	154
n=20	Maximum	4729	1596	99.9	15.1	26.4	37.5	5001
	Mean	1628	484	64.7	9.05	12.4	15.5	1906
	Median	1203	371	65.6	9.30	12.8	16.1	1439
	Freq (%)	100	100	100	80	100	100	NA
S 5	Minimum	65.4	3.06	16.7	9.37	1.97	2.11	85.0
n=20	Maximum	19474	2053	183	54.6	88.7	83.7	19829
	Mean	4343	655	81.2	22.8	21.0	18.9	4595
	Median	2156	337	77.6	21.0	12.1	14.7	2729
	Freq (%)	100	100	100	80	100	95	NA
S 6	Minimum	25.0	2.00	8.47	3.23	1.09	1.35	37.4
n=22	Maximum	6260	1260	154	60.2	49.8	90.5	6859
	Mean	2002	444	72.3	14.2	10.3	12.9	2250
	Median	1774	342	73.3	11.2	5.96	7.20	2083
	Freq (%)	100	100	100	90.9	100	95.5	NA
S 7	Minimum	44.5	13.2	20.7	6.94	2.21	2.47	62.4
n=19	Maximum	3199	886	156	35.5	97.4	107	3597
	Mean	1393	357	92.5	15.6	15.5	20.3	1619
	Median	1057	361	92.2	15.1	6.68	8.90	1356
	Freq (%)	100	94.4	100.0	90.9	100.0	100.0	NA
S 8	Minimum	46.6	15.7	4.63	4.10	4.34	1.30	74.1
n=18	Maximum	62596	13609	983	131	126	86.1	68547
	Mean	6758	1921	171	21.7	41.0	26.3	7420
	Median	2295	591	36.2	7.51	35.8	20.3	2455
	Freq (%)	100	94.1	100	92.9	94.1	100	NA

Table 4-5 Summary of measurement data for sewer VSCs from June.2011 toMay.2013

Site	Statistic			Comp	ounds ($\mu g/m^3$)		
	summary	H_2S	MeSH	DMS	CS_2	DMDS	DMTS	Total-S
S9	Minimum	23.0	3.2	7.89	3.00	1.62	3.00	34.9
n=20	Maximum	23647	914	65.0	22.9	17.3	10.7	22467
	Mean	2246	223	24.5	5.79	7.58	4.96	2285
	Median	1043	178	22.8	4.17	6.18	4.46	1134
	Freq (%)	100	100	100	65	100	100	NA
S10	Minimum	237	20.8	5.31	4.31	1.08	1.73	240
n=22	Maximum	17388	5582	55.3	282	34.2	41.8	17762
	Mean	7660	1518	19.7	83.3	11.7	12.9	8273
	Median	6886	1329	12.4	70.7	9.57	10.8	7656
	Freq (%)	100	100	73.7	100	100	94.7	NA
S 11	Minimum	4.17	2.07	2.27	3.44	0.86	1.62	6.29
n=15	Maximum	1544	334	106	8.47	12.4	23.1	1619
	Mean	290	85.1	21.5	6.06	3.40	7.45	235
	Median	23.6	67.8	9.13	10.2	2.10	3.77	11.7
	Freq (%)	68.2	50	50	12.5	45.8	25.0	NA
S12	Minimum	34.8	3.42	3.06	9.08	2.2	3.11	45.8
n=21	Maximum	69551	8276	547	332	602	38.7	71290
	Mean	30780	2188	231	67.8	79.1	14.9	30569
	Median	31994	1919	186	47.0	32.0	12.7	31496
	Freq (%)	100	95.5	100	90.1	95.5	90.1	NA
OTV	Minimum	0.21	0.0003	0.3	70	1.1	0.06	NA
	Maximum	270	38	160	180	78	7.5	NA

Table 4-5 (cout.)

^a Freq(%) is the precent of measured VSCs > MDL(method detect limit); Total-S: Total sulfur concentrations and it is calculated by summary of sulfur mass concentration of six targeted compounds; NA: data are not applicable; OTV: Odour Threshold Value in the unit (Van Gemert 2003); n: Number of samples collected per site

4.4.2 Seasonal and Annual Distributions Patterns

An attempt was made to examine seasonal variations in the occurrence of VSCs. The seasonal and annual variations of the individual VSCs during the two sampling years at the different sewer sites are shown in Figure 4-4. The whiskers in the plots represent 1.5 times of interquartile concentrations while the boxes represent the 25th and 75th percentile concentrations. Odour threshold values (OTVs) are present in each plot as a range based upon the data presented in Van Gemert (2003). The seasonality was examined after excluding datasets acquired from S3 and S11 as large number of measured VSCconcentrations at S11 were found to be below the MDLs and samples were only collected and analyzed for S3 during the second sampling year (July 2012-June 2013). For annual trends, the first sampling year (2011-2012) had slightly higher concentrations than the second year (2012-2013) for all the investigated sulfur

compounds. The seasonal gas VSC concentrations (three month averages over 10 sites) varied from 5671 to 8493 μ g/m³ for H₂S, from 619 to 1336 μ g/m³ for MeSH, from 85.8 to 139 μ g/m³ for DMS, from 12.8 to 26.3 μ g/m³ for CS₂, from 18.0 to 24.0 μ g/m³ for DMDS and from 14.9 to 20.0 μ g/m³ for DMTS, respectively. On average, the highest seasonal mean concentrations were about 1.5-2 times higher than lowest seasonal means.

Measurements from the two-year sampling campaign reveal concentrations of all sulfur species exhibited a similar seasonal trend with cold season lows, warm season (summer, autumn) highs and spring falls in between. Similar seasonal effects on VSCs were observed in previous studies. Sekyiamah et al. (2008) observed major seasonal variations in VSCs emitted from secondary wastewater treatment system in Washington, D.C. (US) and they measured the highest and lowest concentration during autumn and winter varied by a factor of 10. Wu et al. (2006) observed higher gaseous DMS and CS₂ concentrations either in the summer or autumn whereas in winter they were not detected in sewage systems in Taiwan. The seasonal trends observed in our study are consistent with findings from liquid pollution studies in literature (Huang et al. 2012, Rodriguez et al. 2012) that higher concentration of volatile compounds are detected in cold water as they are more stable and concentrated in cold weather lowering the evaporation into air (e.g. low concentrations at air phase). However, when compared with previous studies, the VSCs seasonality in our study was relatively minor and most of inter-season differences on mean VSCs concentrations were not statistically significant (p > 0.05). The differences were only significant between winter and either of summer, spring, winter (i.e. winter vs summer, winter vs spring, winter vs autumn). This may be attributed to the corresponding meteorological conditions for each samplings season. Sydney is not that distinctive for the four seasons, particularly for spring, summer and autumn. For example, the average temperature over 20 years (Bureau of Meteorology 2013c) for the three seasons in Sydney were not varied as distinguishable as other cities, having maximum to minimum of 26.2 °C ± 0.6 to 19.2 ± 0.8 °C for summer, 22.6 ± 1.3 °C to 14.2 ± 2.2 °C for spring, 23.1 ± 2.4 °C to 15.3 ± 2.8 °C for autumn, whereas winter is significantly lower between 18.1 ± 0.8 °C and 9.4 ± 0.6 °C. Rainfall is another meteorological factor affecting the concentrations of sewer VSC, as heavy rainfall dilutes the sewage, shortens the hydraulic retention time (HRT) due to increased pumping events and destroys sewer biofilms as a result of increased flow rate and shear

in the sewer pipes. However, a comparison of seasonal variability with seasonal rainfall data showed that higher concentrations of VSCs were seen in the wet seasons (summer and autumn) rather than the dry seasons (winter and spring) as expected. This observation is most likely due to Sydney being a wetter city than other major Australian cities (e.g. Perth and Melbourne with annual rainfall means being 725mm and 603 mm where Sydney is 1223 mm) with less variations in rainfall data between the seasons $(104 \pm 29.4 \text{mm}, 121 \pm 14.2 \text{mm}, 96.8 \pm 19.0 \text{ mm} \text{ and } 85.4 \pm 18.0 \text{mm} \text{ for summer},$ autumn, winter and spring, respectively). Although our site sampling was performed within two weeks in a month, the monthly or seasonal rainfall averages may be less representative to the rainwater effects on the sampling sessions as the influence of rainfall on sewer flow dynamic could be varied from day to day (short-term) and be dependent on the HRTs of different sewer systems. Additionally, the recovery time on downstream wastewater concentration after a single rainfall event or cumulative rainfall (e.g. 2 days before a sampling event) may better represent the condition of sampling sessions. Previous sewer study has only focused effects of rainfall flushing on dissolved sulfides in sewage (Jiang et al. 2013) without any details on the impact of VSCs emissions. Further studies should therefore consider how rainfall events (direct rainfall, cumulative rainfall) affect VSC concentrations in sewer gas and how such events influence the representativeness of discretely measured concentrations (e.g. two integrated weeks sampling within a month in this study) to the full season of work.



Figure 4-4 Seasonal and annual occurrence of individual VSCs (in μ g/m³) present in sewer emissions (CV: coefficient of variance, % across 12 sites)



Figure 4-4 (Cont.) Seasonal and annual occurrence of individual VSCs (in $\mu g/m^3$) present in sewer emissions (CV: coefficient of variance, % across 12 sites)


Figure 4-4 (Cont.) Seasonal and annual occurrence of individual VSCs (in $\mu g/m^3$) present in sewer emissions (CV: coefficient of variance, % across 12 sites)

Table 4-6 shows the results of spearman correlation analysis and correlation coefficients of each season-annual mean pair in order to determine which single season best represents an annual mean for the sampling sites over 24-month monitoring. The analysis revealed in the majority of cases, autumn had the highest correlations with the annual means of the most volatilized compounds, including H₂S, MeSH, DMS and CS₂ providing the best estimation of the annual average concentrations whereas for the less volatile compounds (i.e. DMDS and DMTS) spring provided a better annual mean. Each seasonal mean was also correlated to the corresponding two-year seasonal averages to identify how well the spatial sampling measurements represented the longterm seasonal means. The seasonal Spearman correlations for each species in each of the sampling years (Table 4-6) showed that significant correlations were consistently observed between seasonal means and long-term mean for a particular season (i.e. 2011-2012: the spring means correlated with corresponding two year spring means) with 2012-2013 having slightly stronger correlations among the four seasons for each of the VSCs species (r > 0.8). The high correlations suggest that the seasonal data collected from 2012-2013 provided a better representative of its corresponding season obtained on long-term sampling networks. Although the other full year VSC concentrations (2011-2012) also provided a fair representation for the two-year measurements (r > 0.6 for most of cases) suggesting that the seasonal patterns remain relatively consistent.

Campaign	VSCs	Season	Winter	Spring	Summer	Autumn	Annual
2011-2012	H_2S	Winter		0.85**	0.39	0.31	0.61
		Spring			0.60	0.50	0.84^{**}
		Summer				0.74*	0.72*
		Autumn					<u>0.93**</u>
	MeSH	Winter		0.87**	0.78*	0.74*	0.85**
		Spring			0.52	0.60	0.65*
		Summer				0.65	0.78
		Autumn					<u>0.93**</u>
	DMS	Winter		0.90**	0.82**	0.35	0.53
		Spring			0.60	0.18	0.38
		Summer				0.42	0.47
		Autumn					0.93**
	CS_2	Winter		0.77*	0.82**	0.45	0.64
		Spring			0.67*	0.55	0.68*
		Summer				0.24	0.62
		Autumn					0.82**
	DMDS	Winter		0.67*	0.55	0.02	0.79**
		Spring			0.62	0.25	0.88**
		Summer				0.30	0.81**
		Autumn					0.42
	DMTS	Winter		0.48	0.70*	0.07	0.73*
		Spring			0.45	-0.15	0.67*
		Summer				0.08	0.73*
		Autumn					0.42
2012-2013	H_2S	Winter		0.42	0.53	0.37	0.72*
		Spring			0.22	0.22	0.41
		Summer				0.87**	0.87**
		Autumn					0.87**
	MeSH	Winter		0.87**	0.48	0.58	0.88**
		Spring			0.23	0.52	0.76*
		Summer				0.63	0.70*
		Autumn					0.82
	DMS	Winter		0.85**	0.43	0.95**	0.93**
		Spring			0.27	0.63	0.81**
		Summer				0.48	0.52
		Autumn					<u>0.95**</u>
	CS_2	Winter		0.90**	0.85**	0.18	<u>0.85**</u>
		Spring			0.71*	-0.01	0.72*
		Summer				0.10	0.68*
		Autumn					0.57
	DMDS	Winter		0.76*	0.70*	0.43	0.85**
		Spring			0.80**	0.83**	<u>0.95**</u>
		Summer				0.57	0.93**
		Autumn					0.67
	DMTS	Winter		0.54	0.25	0.12	0.82**
		Spring			0.62	0.62	<u>0.89*</u>
		Summer				0.37	0.57
		Autumn					0.53

Table 4-6Spearman correlation coefficients between seasonal means forindividual VSCs compounds

*Significant at p<0.05; ** Significant at p<0.01; Underlined numbers indicate highest correlation coefficients between seasonal and annual, among the 4 four seasons in each year.

4.4.3 VSC Spatial Distribution Patterns

The two-year sampling study revealed that VSC concentrations varied significantly across the monitoring sites, having an averaged max/min concentration ratio of up to 24 for H₂S, 10 for MeSH and DMDS, 11 for DMS, 14 for CS₂ and 7 for DMTS between sites (Table 4-7) with the peak mean concentrations for each species being observed in sites: S8, S10 and S12. In order to quantify the difference among sampled sewer points, coefficient of variance (CV) was calculated annually and seasonally across the site locations for each species. Figure 4-4 shows that spatial variability between the VSCs with greatest variability (largest annual CV) being observed for H₂S, followed by $MeSH > CS_2 > DMS > DMDS > DMTS$. For the six VSCs, the greatest inter-site variation was not surprisingly observed for H₂S, as H₂S was most likely affected by upstream odour management conditions, particular chemical dosing. As described previously (Chapter 3), the sewer sites were a mixture of dosed and non-dosed sites with two different chemical dosing (e.g. ferrous chloride and magnesium hydroxide) been applied. Chemical dosing into sewerage catchments for H₂S control has been reported to lower concentration of gaseous H₂S by up to 79%~95% (Padival et al. 1995, Parsons et al. 2003, Ganigue et al. 2011). The spatial variability of the VSCs remained quite consistent from year to year for most of sulfur species, with the exception of methyl mercaptan and dimethyl disulfide. The unstable patterns for DMDS and MeSH could be associated with reactive nature of MeSH having a relative shorter atmospheric lifetime (Smet et al. 1998), and DMDS being either reduced under relatively aerobic conditions or decomposed by photochemical reactions (Toda et al. 2010) that could happened in different sewer site conditions. The observed great spatial variability supports the seasonal distributions (Figure 4-4) in which the concentration of VSCs at S8 and S12 stayed higher for the seasonal and annual means (as observed as outliers and extreme value). Further analysis was conducted to identify whether any single season could be used to represent an annual spatial pattern. Each seasonal derived CV was compared to the corresponding yearly CV and it was observed that that summer season was most representative of the annual spatial variability in the first sampling session whereas both spring and summer were found to be more representative for the second sampling session. Two year results suggest that from a general perspective, the summer period (December ~ February in Australia) best indicates or represents the annual spatial pattern of the studied sewers.

A hierarchical clustering method was employed to classify different sampling points against VSC concentration profiles. The similarity of the sampling locations is described by dendrogram (Figure 4-5), which clearly differentiated the different VSCs content into three major groups as Group A (site 2, 4, 6, 7 and 9), Group B (site 1, 5, 8, 10) and Group C (site 12). Group A comprised of the upstream to midstream sites of catchments (I, II and V) that were all receiving mixed sewage discharges. Group B depicted downstream sewer networks close to STPs at catchment I, III and IV loaded with mixed or domestic containing wastewater whereas Group C was comprised of a single site (S12) that was located at downstream of the catchment II. Sewer VSCs emission samples collected at Cluster A, Cluster B and Cluster C were characterised by the different levels of total sulfur concentration (Table 4-5) and corresponded to low concentrated (1426-2285 $\mu g/m^3$), moderately concentrated (4595-8273 $\mu g/m^3$) and highly concentrated (30569 μ g/m³) sewer sites respectively. The higher concentrations also observed for site 3 (not included in cluster analysis). The S3 is a merging carrier combining two sub streams and located near S1 both close to the STP (downstream of catchment I) and the total sulfur concentration (6840 μ g/m³) is observed very comparable to S1 (7323 μ g/m³). This further confirmed these clusters depend on the geographical location of sampling sites at the studied catchments. Sun et al. (2014) also reported an increased concentration of MeSH and DMS in liquid phase at a sewer site 1100 m downstream of a pump station.



Figure 4-5 Dendrogram of the 10 sampled sewers by cluster analysis: content of different VSCs in sewer gas samples (Wards' Method); Euclidean distance

In group A and B, a division into two subgroups A2 and B2 was clearly distinguished by sewer types. Site 8 and site 9 belonging to subgroup A2 and B2 were headworks of sewage STPs whereas the other sites within groups A and B were pipe lines at the locations prior to STPs. So in addition to geographic locations, the sewer type can attribute to the spatial distribution of sewer VSC concentrations as well. The sampled STP headworks have relative smaller diameters (D) between 0.15 m and 0.35 m whereas the remaining sites had a larger pipe diameter (D \ge 0.4 m). According to Ganigue et al. (2011), sewer pipes with a smaller diameter generally had a more significant biofilm contribution to sulphate reduction resulting in a higher sulfides production in the sewer. So relatively higher concentrations of VSCs at S8 and S10 (cluster B) and S9 (cluster A) than the rest of sites clustered into a same group can be thereby attributed to their significant biofilm effects (or smaller pipe diameter). The ANOVA analysis of each VSC species belonging to the three clusters was further proven at a significant level of α =0.005 for most variables (Table 4-7).

VSCs	SS	DF	MS	F	Р
H_2S	32.27	2	16.14	45.90	P < 0.01
MeSH	13.81	2	6.907	14.04	P < 0.01
DMS	3.210	2	1.605	9.595	P = 0.0001
CS_2	8.196	2	4.098	26.09	P < 0.01
DMDS	4.045	2	2.023	8.404	P = 0.0003
DMTS	0.5422	2	0.2711	1.130	P = 0.3252

Table 4-7 ANOVA analysis of targeted VSCs between Groups (A, B, C)

SS: Sum of squares; DF: Degree of Freedom; MS: Mean square (SS/DF); F: The ratio two mean square values between groups (A, B, C); P<0.01: the null hypothesis is not true and the means between groups are significantly different

Spearman rank correlation coefficients of site-group comparisons were used to assess whether a single site mean could represent the group mean for a VSC concentration cluster (as low, moderate and highly as distinguished in the clustering analysis). The correlation coefficients generated were moderate to high (r > 0.5) but not statistically significant (p > 0.05) indicating that a single site measurement was not able to characterise the overall VSCs concentrations in the sewer atmosphere. Previous results in section 3.2 support that single site monitoring might not adequately represent the longer-term sewer emission, which is largely affected by the wastewater conditions. However, the comparison of site CV and group CV calculated across the four measured seasons for each site (Table 4-8) suggests that seasonal variability on S4 and S10 were more representative of the group variability of Groups A and B. Given this observation, it will further improve seasonal/temporal sampling strategy particularly when resources limited sampling on the entire sewer networks, those two sites monitoring can provide a good snapshot on long term seasonal trends at different VSC concentration levels.

Table 4-8	Seasonal 1	means of	f VSCs in t	the atmospl	here at 10 (different su	ewer sites i	in Sydney	(unit in μg	۰/m ²) from	June 201	1 to June	2013
by group													
2150	100000	H	L ₂ S	Me	HS	DN	AS	Ű	S ₂	DM	DS	DM	SL
olle	Season	AM	S.D.	AM	S.D.	AM	S.D.	AM	S.D.	AM	S.D.	AM	S.D.
S2	Winter	<i>L</i> 6 <i>L</i>	630	88.4	72.6	42.7	16.8	10.1	5.63	22.1	14.9	36.5	26.8
	Spring	1056	1011	235	241	69.0	31.6	27.7	28.6	25.7	13.1	30.4	13.6
	Summer	2061	1519	360	210	93.0	52.7	10.1	2.01	28.1	28.1	41.2	46.3
	Autumn	362	NA	47.0	NA	53.9	NA	5.38	NA	13.6	NA	15.3	NA
	Total ^a	1126	65	201	67	66.5	38	14.1	66	33.1	51	20.6	38
$\mathbf{S4}$	Winter	885	471	271	172	52.3	21.3	5.23	2.45	10.5	5.35	12.7	7.41
	Spring	1122	656	387	238	63.2	30.1	8.04	3.85	13.1	8.79	17.3	12.6
	Summer	2732	1829	783	567	73.4	16.8	10.3	4.40	12.9	6.8	16.3	11.1
	Autumn	2226	NA	570	386	85.3	7.42	7.48	6.51	15.9	1.84	18.7	1.15
	Total ^a	1763	55	515	56	70.0	26	7.85	41	16.7	37	11.7	24
S6	Winter	1334	1008	244	94.6	63.4	30.3	11.1	5.93	12.7	18.2	20.8	34.2
	Spring	3684	2444	836	509	96.2	54.0	21.9	22.2	14.6	9.25	16.0	11.7
	Summer	1232	988	289	255	51.6	36.6	8.14	3.97	6.54	5.87	5.71	5.44
	Autumn	2110	263	526	203	91.7	41.1	13.9	8.13	7.89	4.92	6.47	3.84
	Total ^a	2117	54	494	57	79.8	38	13.4	42	14.5	105	10.2	61
S7	Winter	1069	743	268	228	75.8	43.3	13.2	5.62	25.9	34.1	32.8	38.3
	Spring	2091	1439	387	321	92.1	28.8	21.1	9.21	9.71	8.27	13.8	15.6
	Summer	1172	613	365	120	116	17.7	14.2	4.85	9.77	6.67	13.1	9.42
	Autumn	1057	NA	403	86.2	105	14.5	12.8	7.52	5.09	1.92	6.6	1.95
	Total ^a	1465	56	337	23	94.1	17	15	36	15	93	11	76
S9	Winter	821	586	126	44.5	16.9	4.16	2.93	1.11	8.00	4.37	4.07	0.73
	Spring	1203	1084	240	191	25.3	6.09	4.80	1.87	8.17	3.89	5.53	2.51
	Summer	1494	1971	211	137	22.4	8.27	3.28	1.26	5.21	1.13	4.31	0.90
	Autumn	1252	138	390	364	40.5	16.4	9.53	9.45	10.2	5.85	7.28	3.49
	Total ^a	1126	38	217	60	26.3	36	6.13	112	5.45	36	7.30	34
Group A	Total ^a	1542	31	359.9	30	<u>66</u>	25	11.0	44	16.6	32	12.0	19

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City	Concorr	Η	^{2}S	Me	HS	DI	MS	CS	52	DM	DS	DM	ST
	DCabult	AM	S.D.	AM	S.D.	AM	S.D.	AM	S.D.	AM	S.D.	AM	S.D.
$\mathbf{S1}$	Winter	2937	1182	941	505	107	53.6	15.5	5.88	26.3	16.2	25.6	27.6
	Spring	10403	8119	1327	1131	92.4	46.4	15.72	6.54	19.07	11.9	13.78	11.1
	Summer	7209	4902	1694	1488	151	87.7	24.6	11.0	25.8	16.0	28.8	28.8
	Autumn	5778	3443	1281	436	112	18.3	16.7	5.19	13.2	11.5	9.49	6.16
	Total ^a	6289	49	1278	37	114	25	18.5	26.7	19.9	63	19.3	36
S5	Winter	2812	4353	574	848	54.2	45.7	12.8	3.37	31.2	31.8	16.9	14.0
	Spring	2692	2136	587	684	79.3	11.4	34.1	14.2	13.4	6.59	17.2	10.5
	Summer	5984	7707	941	882	125	43.9	27.4	6.00	28.3	31.0	30.3	32.3
	Autumn	7418	7425	505	377	69.4	23.2	17.9	6.36	5.92	7.07	5.22	6.44
	Total ^a	5247	104	583	99	81.7	38	22.3	43	16.3	67	17.5	65
S8	Winter	2630	2967	613	603	85.2	110	5.86	3.94	26.7	26.6	19.9	17.4
	Spring	2109	1317	519	468	80.3	56.3	9.66	7.15	45.4	11.2	21.0	6.22
	Summer	3681	3457	705	688	62.5	71.2	5.6	3.26	41.9	56.4	22.5	22.0
	Autumn	32272	42885	7388	6732	606	416	65.1	58.1	48.8	28.1	51.1	31.3
	Total ^a	10392	204	1961	187	187	144	20.1	130	28.8	49	36.2	33
$\mathbf{S10}$	Winter	4811	4206	1046	661	56.4	26.8	11.3	15.8	12.2	9.11	13.6	8.37
	Spring	5136	3904	937	1021	52.7	58.2	17.0	22.4	5.31	5.28	5.18	5.13
	Summer	10419	4584	2109	2031	120	99.5	17.7	13.9	18.8	13.4	17.6	15.7
	Autumn	12125	5928	2407	372	127	6.20	14.5	4.33	9.52	4.29	12.0	4.79
	Total ^a	7802	69	1603	57	93.4	44.9	14.5	47	12.3	46	10.3	47
Group B	Total ^a	7508	75	1360	79	119	61	18.8	39	19.3	25	20.8	16
S12	Winter	32689	19692	2334	1050	208	144	40.7	19.1	56.3	39.4	15.7	6.40
	Spring	42600	28696	2704	3261	242	199	124	140	50.0	55.3	9.38	8.32
	Summer	27130	23501	1283	993	212	220	37.3	31.6	121	222	11.6	12.5
	Autumn	19080	13593	2359	2246	237	99.4	65.3	19.0	57.1	40.7	20.5	15.9
Group C	Total ^a	31211	45	1974	60	229	30	64.9	79	13.9	39	62.1	69
NA: Num	ber of meas	surement	on this seaso	on less that	$n \overline{3}$ (n<3) a	nd data are	not available	<u>: AM: arit</u>	hmetic me	ean; S.D.: s	tandard d	eviations;	

Table 4-8 (cont.)

Chapter 4 Volatile Sulfur Compounds (VSCs) Speciation

a: Numbers in S.D. column indicate coefficient of variation values of a site or clustering group

In order to exam if there are any statistically significant inter-species relationships between determined VSCs, correlation coefficients were calculated for all the samples measured for the three Groups (as distinguished earlier in cluster analysis) and the numerical results of correlation analysis for targeted VSCs are compiled in Table 4-9. In general, strong correlation patterns were observed for several VSC pairs from the sewer emission samples (p < 0.05, r > 0.66), confirming the findings by Thistlethwayte and Goleb (1972) that the production of sulfur compounds in sewer environment was more likely a result of anaerobic process rather than upstream inputs. Previous studies have also reported that species belonging to sulfur compounds were closely correlated with each other in many different environmental samples (Kabir et al. 2010, Fang et al. 2012, Rumsey et al. 2014). Among the three groups, inter-species patterns remained very consistent with the highest correlations (r > 0.7, p < 0.01) being observed for two pairs of measured sulfur compounds: H₂S-MeSH and DMDS-DMTS. This observation was further confirmed by examining the inter-sulfur relationships seasonally as to which pairs had the strongest correlations (full data was not shown), with the greatest coefficients being consistently measured for H₂S-MeSH and DMDS-DMTS from season to season. The results also suggest that the emission sources were relatively stable over four seasons for the two-year study over the multiple sewer sites. The strong correlations for the two pairs suggest common emission sources, for example, H₂S-MeSH and DMDS-DMTS. The production of MT under anaerobic conditions is attributed to the sulphate reduction or methylation of sulfide during the degradation of ethoxylated aromatic compounds (Sun et al. 2014), but previous studies have proved that a substantial part of H₂S comes from sulphate reduction (Hvitved-Jacobsen et al. 2013), so the production of H_2S and MeSH in sewer environment are most likely associated with sulphate reduction by SRB (sulfate reducing bacteria) attached on the biofilm of sewer wall. While DMDS and DMTS were produced following a different pathway and would be formed via either anaerobic oxidation or methylation from DMS. This methylation reaction process is common when the sulfur compounds are co-found with hydrocarbons (Cheng et al. 2005, Van Leerdam et al. 2011). Previous characterisation of the emission composition of the same sewer network (Wang et al. 2012c) in Sydney, showed that quite high concentrations of the hydrocarbons were identified. In this context, the detectability of DMDS and DMTS in the present work is likely associated with this process Apart from the two highly correlated pairs, CS_2 was also linked with DMS with a coefficient values between 0.5 and 0.7 (p < 0.01) in most of cases and DMS was also found to be associated with MeSH.

When the properties of individual sulfur species belonging to the three pairs are compared, the pairs can be grouped as relatively high volatile sulfides (H₂S-MeSH), moderated volatiles (DMS- CS_2) and relatively low volatile sulfides (DMDS-DMTS), correspondingly. These observations indicated that VSCs could be released by volatilization of the wastewater. In another word, the source contributing to VSCs in the sewer atmosphere would also result from volatilizations in addition to biodegradations as we and other authors have discussed previously. This conclusion is supported by the seasonal correlation patterns as higher correlation coefficients were obtained during the summer seasons that favours the volatilization processes due to higher temperature as we illustrated in section 4.3.2. It should be noted that aquatic sulfides in the sewage were not monitored during the two-year sampling sessions, so it is not possible to make any conclusion with respect to which source dominates the observed behaviour/trends of the VSCs in sewer atmosphere. However, the patterns of correlation can be used to predict or monitor changing trends of compounds with similar volatile ability (e.g. same or similar K_H value or boiling point). This observation will benefit future monitoring of sewer VSCs emission and the design of abatement system treating sewer emissions by reducing the monitoring targets (VSC analytes) or providing the signal/marker compounds.

VSCs	H_2S	MeSH	DMS	CS_2	DMDS	DMTS
Group A sites (n=10	3)					
H_2S	1.00					
MeSH	0.81**	1.00				
DMS	0.57	0.69*	1.00			
CS_2	0.44	0.43	0.64*	1.00		
DMDS	0.38	0.36	0.50	0.36	1.00	
DMTS	0.41	0.41	0.60	0.49	0.88**	1.00
Group B sites (n=84)					
H_2S	1.00					
MeSH	0.78**	1.00				
DMS	0.60	0.67*	1.00			
CS_2	0.41	0.37	0.48	1.00		
DMDS	0.21	0.36	0.57	0.20	1.00	
DMTS	0.24	0.41	0.60	0.29	0.90**	1.00
Group C sites (n=23)					
H_2S	1.00					
MeSH	0.63*	1.00				
DMS	<u>0.66</u>	0.43	1.00			
CS_2	<u>0.66</u>	0.62*	0.71**	1.00		
DMDS	0.59	0.43	0.78**	0.63*	1.00	
DMTS	0.45	0.63*	0.65**	0.60	<u>0.84**</u>	1.00

 Table 4-9 Inter-VSCs correlation coefficient matrix for VSCs in sewer emssion

 samples

r>0.66 cases were underlined to reflect the strong correaltion; *Significant at p<0.05; ** Significant at p<0.01; Underlined numbers indicate highest correlation coefficients between seasoanl and annual, among the four seasons in each year.

4.4.5 Short-term Study

Diurnal Variation

Diurnal VSCs emission patterns were determined for six sulfur species (H₂S, MeSH, DMS, CS₂, DMDS and DMTS) by collecting bi-hourly integrated samples at a pump station (between 11th and 12th April, 2012). The coefficient of variation (CV) from 12 measurements was calculated for the individual VSCs to represent the diurnal variability. The calculated CV values followed the order of H₂S (46.0%) > CS₂ (30.4%) > DMTS (29.3%) > DMDS (25.2%) > DMS (17.8%) > MeSH (17.1%), indicating that a daily variation was observed in the VSCs concentrations. Figure 4-6 shows the measured average VSCs (n=2) concentrations at a 24-hour period. In general, maximum gas concentrations were measured during the daytime either in the early morning or later afternoon, depending on the compounds. The peak in H₂S and MeSH concentrations were observed between 2:00-4:00 pm, as 5564 μ g/m³ and 398 μ g/m³,

respectively. The maximum concentration was about 2 times higher for MeSH and 4 times for H₂S than the lowest concentration measured at mid-night. The dominance of H₂S occurring in the afternoon is most likely influenced by environmental factors, such as increased temperature and gas flow in the sewers, favouring evaporation processes from the liquids. Biogenic odorous compounds (i.e. DMS, DMDS and DMTS and CS₂) were observed to have peak concentrations between 8-10 am, most likely related to the fact that high concentrations of organic matters are discharged into the sewer catchments in the morning. Following this principle, it would therefore be expected that another peak would elute at the end of the day (i.e. 4:00-8:00 pm), however, in our study, only marginally peaks for dimethyl di-, and trisulfide were observed between 4 and 8 pm whereas CS_2 had two significant higher concentrations measured at 8:00-10:00 and 4:00-6:00 pm. A plausible reason for this observation is that CS_2 is a more stable compound with an atmospheric life of up to 40 days (Smet et al. 1998) and the production of CS_2 was possibly only associated with one dominate source, biodegradation of the sulfur-containing compounds in the wastewater. The diurnal distribution of the other three VSCs is more likely explained by their source properties in sewage and their associated atmospheric behaviour/fate.



Figure 4-6 Diurnal concentration variations of selected VSCs in the pump station (S2): on-line H₂S (top) and other VSCs (bottom) measurements

Weekly Variation

A further sampling campaign at the same site (pump station) was carried out to characterise weekly variations in sewer emissions on 5 consecutive workdays (Wednesday-Tuesday) during the period 24th and 30th November, 2013. Samples were collected and analysed twice a day at 10 am and 2 pm, representatives of peak concentration for most of the VSCs according to the diurnal monitoring. Figure 4-7 shows that a stable daily concentration was observed for the targeted VSCs (during the 5 days), with a variance of 7% (CS_2) - 22% (DMTS) observed. This suggests that similar concentrations of readily biodegradable wastewater were discharged into the sewer catchment during the weekdays.



Figure 4-7 Weekly concentration variations of selected VSCs in the pump station (S2): on-line H₂S (top) other VSCs (bottom) measurements

4.4.6 Evaluation of Odour Implication

Considering the mean values, nearly all of the VSC concentrations were well above their associated OTV range (Table 4-5). The exception was CS_2 in almost all the sampled sites with mean concentrations below its reported low end of OTV ranges (70 μ g/m³) and even considering the a maximum concentrations at different sites, they were generally still below the 70 μ g/m³. Considering the minimum concentrations of the other VSCs (representing conditions that are most likely baseline in nature), they were still present at the level above or within the OTVs in all 12 sites. This suggests from a general perspective, other VSCs in addition to H₂S (a traditional odour maker in sewer emissions) are likely to be a significant contributor to sewer odour phenomena. Frequent non-H₂S sulfur compounds monitoring is required and recommended in order to understanding and abating sewer odours. However, the significance of VSCs as odorants cannot be assessed simply via comparison of their concentration values against the respective OTV values reported in the literature as summarized by Van Gemert (2003). In this study, the OTV values used to assess the contributions of VSCs to odour of were determined from air media, but a threshold still varies considerably due to the difference of measuring and calculating to the same material. The relevant OTVs of targeted VSCs are highly variable and reportedly up to four orders of magnitude of the investigated VSCs (i.e. MeSH). Therefore, It is suggested that more accurate estimates of threshold value would strongly improve this method for estimating odour contribution.

4.5 Summary

An analytical method was developed to optimise the determination of a wide range of VSCs in sewer emissions by TD-GC-SCD. Various factors affecting this technique have been studied in order to achieve high recoveries for most of the VSCs analytes. In the adsorption and desorption process, temperature and flow conditions were determined as: (i) adsorption temperature lower than -20 °C at a sampling flow of 10 ml/min and (ii) desorption temperature at 270 °C at the desorption flow ~ 6 ml/min (split flow: 5ml /min). The optimum GC configuration was determined as an initial temperature of 37 °C, ramping at 15 °C/min with a flow of 1 ml/min to fully resolve all targeted VSCs and enable good TD recoveries. High precision (RSD < 10%) and good linearity ($R^2 > 0.99$) were also observed indicating the methodology is suitable for measuring VSCs at trace levels (sub-pptv). The optimised method was validated using real sewer emission samples, demonstrating good detection limits and precision.

Monitoring of VSCs in sewer headspace air across 12 sewer sites in Sydney identified six of VSCs that were frequently determined in 24 months sampling programs. Among those compounds, hydrogen sulfides, methyl mercaptan and dimethyl sulfides were measured in relatively significant amount, with concentration levels in the order of tens to hundreds of μ g/m³ while other sulfur species were present trace levels, roughly ~ 10 μ g/m³.

Seasonal variations of VSC concentrations were observed to generally follow the trends of cold season low and warm seasons (summer, autumn) high. Significant seasonal differences (p < 0.05) were observed between winter and either of other three seasons, having mean seasonal concentrations differed by a factor of two. The observed seasonal patterns can be explained by climatic conditions (for Sydney) where significant lower average temperature and relatively lower rainfall were measured during winter sampling sessions according to the long-term (20 years) meteorological records. Inter-site comparisons also showed spatial variability across the 12 sampled sewer sites, with peak concentrations of different VSCs up to 7-24 times greater than the other measured concentrations. Hierarchical cluster combined ANOVA analysis, showed that two major observations: (i) that three groups (A, B, C) with similar VSCs concentration content can be were distinguished among ~10 monitored sewer sites as a result of different sewer types (sewer dimensions, sewage flow and retention time) and geographical locations (e.g. upstream or downstream of sewer catchments); and (ii) the level of VSCs concentration belonging to each groups were statistically different that corresponded to relatively low total sulfur concentrated, moderated polluted and high concentrated sewer areas.

Strong correlations between VSC species were generally observed, supporting the previous conclusion that the production of VSCs was more relying on the anaerobic process rather than the wastewater discharge characteristics. Three remarkable pairs (H₂S-MeSH, DMS-CS₂ and DMDS-DMTS) that were moderate to highly correlated, suggests the volatilization process, in addition to biodegradations, may also play a major role to assess the source from that sewer headspace VSCs were originated. Based on the inter-species results obtained for the three correlated pairs, volatility of VSCs could be used as a factor to approximate the changing trends of compounds exhibiting similar volatile properties. This will further benefit monitoring due to the probability of reducing the targeted analytes (VSCs).

Strong and consistent correlations between seasonal and annual values among the measured VSCs indicates that autumn and spring sampling campaigns were more representative of the annual concentrations while comparisons between annual CV with seasonal CV suggested that the spatial variability in the summer season provided the best representation for annual variability. In this study, there is no single sampling site that represented the annual means. This conclusion supports the importance of extensive spatial samplings to better characterize VSCs temporal variability in sewer environment. However, when resources are limited (costs, labors) a single season sampling (spring and autumn) at particular sewer sites (S4 and S10) will provided estimation of long-terms VSCs trends.

Chapter 5 Volatile Organic Compounds (VOCs) Speciation

5.1 Introduction

Wastewater operations (treatment and collections) produce and emit a complex mixture of chemical species in any permutation of concentrations. The chemical matrix of a sample may contain hundreds or thousands of compounds with a wide range of molecular weights and a variety of physicochemical properties. Of particular interest in terms of environmental and social impact are those volatile organic compounds (VOCs) that contribute to the overall odour/malodour of a sample.

An analytical method was developed to characterise VOCs emitted from sewer networks by actively collecting the samples using sorbent tubes followed by chemical analysis using Thermal Desorption coupled with Gas Chromatography-Mass Spectrometry (TD-GC-MS). The method parameters including sorbent tubes materials, tube desorption temperature, desorption time and cold trap desorption temperature were selected and optimised. Validation of TD-GC-MS method showed good precision, linearity and accuracy. Breakthrough tests showed that there is no significant breakthrough when 5000 ppm stock solution was spiked into sorbent tubes (breakthrough volume <1%). The method was evaluated by collecting VOCs from two sewer sites in Sydney. The identification of key chemical groups at individual site is important for monitoring odour annoyance and developing design criteria for odour and VOC abatement systems.

The characterisation of the nature and magnitude of chemicals, which are emitted from sewer networks, is important for health and abatement system design as some VOCs have been shown to be highly toxic and can cause odour annoyance. The objective of this chapter is to characterize the VOC composition of emissions from the sewer networks in Australia. Based on the extensive GC-MS analysis, 585 VOCs were identified from sewer emissions. A selection based on the quantities appearance of organic compounds present in the sampled sites was conducted to screen the key 41 VOC species that were detect in more than 25% of the samples analysed. A quantitative determination of the key organics was also given. The long-term monitoring of selected significant VOCs was made to better understand the temporal and spatial trends and distribution of VOCs. The spatial-temporal variations were further evaluated with random-effects models and principal component analysis.

5.2 Materials and Methodology development

5.2.1 Overview

Studies on VOC emissions derived from sewer network is rarely reported compared to wastewater treatment plants (Atasoy et al. 2004, Ras et al. 2008a). This is most likely due to insufficient sampling and the analytical limitations for the analysis of VOCs that are present at trace level and over a range of concentrations. From previous studies, sorbent-based sampling methods have been successfully used in the collection of a wide range of VOCs from atmospheric environments and/or other industrial processes. Some standardised protocols have been established to sample and analyse air-borne VOCs (McClenny and Colón 1998, Ribes et al. 2007), no methodologies have been optimised for the determination of VOCs from sewers and wastewater treatment plants (WWTPs).

This study aims to characterise chemical species and corresponding amounts present in the gas phase of sewer networks at some representative sites by developing an analytical methodology that actively collects the samples using sorbent tubes followed by Thermal Desorption coupled with Gas Chromatography-Mass Spectrometry (TD-GC-MS). Initially three different sorbent materials will be tested followed by the optimisation of the methodology in terms of thermal desorption parameters.

5.2.2 Materials and Regents

Chemicals and Standard Preparation

All reagents used were of high purity grade and obtained from Sigma-Aldrich. Methanol was used as a solvent for all standard compounds. Standard solutions were prepared for 12 compounds at different concentration, which were considered as representative of VOC emissions from sewer networks. Solutions were prepared in methanol in order to calibrate the methodology and make comparisons among three different sorbent tubes. 1ul liquid standards were loaded onto stainless steel sorbent tubes (Markes, UK) via a Calibration solution loading Ring (Markes, UK) and flushed with clear air (100 mL/min) after liquid injection, the gas stream was applied for 3 min before the tubes was disconnected from the injection port to allow for the VOCs to be fully evaporated and be retained by the sorbent bed. The calibration tubes were analysed under the same analytical conditions as followed for the field samples.

Sample Collection and Thermal Desorption Procedures

Gas phase samples were collected between January to May 2011 from two selected sewer networks sites (S1-S2) operated by the Sydney Water Corporation. Samples were collected using the following adsorbent materials: Tenax TA, Carbotrap 300 and Tenax/Carbongraph1TD (Markes, UK). Prior to sampling, the sorbent tubes were conditioned and tested to ensure that the tubes were contaminant free. VOC samples were collected onto sorbent tubes using a calibrated air-sampling pump (SKC) at a constant flowrate of 100 mL/min for 20 min to ensure that the correct sampling volume (2L) was collected. Samples were analysed within 24 hours after the sampling events.

A thermal desorber (Unity, Markes, UK) coupled with an Ultra automatic sampler (Markes, UK) was employed to desorb the sample from the sorbent tubes. The sorbent tubes were heated at 275°C for 8 min while high purity helium was passed through the sorbent tubes at the flow rate of 50 mL/min to desorb the VOCs and focus them onto cold trap at minus 10 °C by a Peltier cooler. Following the sample transfer, the cold trap was heated to 290 °C at 40 °C/min heat rate for 5 min to desorb the VOCs from the cold trap and then injected into the chromatographic column. A split flow of 20.7 mL/min was applied during tube and traps desorption to prevent column overloading

5.2.3 Sorbent Tube Selection

Lab Performance Evaluation

To determine the most appropriate sorbent material, three types of absorbents (Tenax TA, Carbotrap 300 and Tenax/Carbongraph1TD) were trailed for their capture capacity for VOCs from sewer emissions. All the sorbent materials are described in the literature as general-purpose tubes for capturing a wide range of volatile organics with varied boiling points and hydrophobic characterises. A comparison study has been performed for the three types of sorbent materials by loading the sorbent tubes with 1ul 100ppmv model VOC standard, respectively. Figure 5-1 shows a comparison of peak area for chromatograms. Generally, there was no significant difference observed between the three types of sorbent material for most of tested volatiles, with the exception for Decane and Trichloromethane. The poor retention of these two compounds could be associated with their relatively higher volatile nature (e.g. elution order earlier than

other tested compounds due to lower boiling points) so that moisture captured onto the carbontrap 300 sorbent might saturate the detection of the early eluted compounds.

Field Performance Evaluation

An additional study was conducted to investigate the performance under real sampling conditions. A general overview of the chemical species that were captured from sewer emission sampling is shown in Figure 5-2. As seen in Figure 5-2, the Carbotrap 300 sorbent material had significantly lower capture efficiency than the two other sorbents most likely due to its mildly hydrophilic nature, which allowed a lower efficiency for collecting samples under humid/moister sewer environment. Both Tenax based sorbent materials shows good capture capacity for sewer type emissions. Considering the availability and cost of sorbent tube, Tenax TA was chosen for following method development works as well as field sampling studies.



Figure 5-1 Comparison of capture efficiency between three sorbent materials tested on selected model compounds



Figure 5-2 Chromatograms (TICs) of sewer gas from a sewer line obtained using different sorbent materials: (a) Carbotrap 300; (b) Tenax TA + Carbograph 1TD; (c) Tenax TA

5.2.4 Thermal Desorption

An appropriate tube desorption time and temperature was determined for the analysis methodology to ensure that all volatiles that were retained by the sorbent tubes were completely desorbed in order to reach good recoveries and avoid carryover. Desorption temperature were set from 250 °C to 310 °C to determine the optimal desorption condition using Tenax TA.

Figure 5-3(a) (tube desorption temperature) shows the dependence of the analyte recovery on desorption temperature. It was observed that the recovery increased with enhanced temperature up to 275 °C and clearly decreased from this point for most of target compounds. Thus, the optimal desorption temperature was chosen as 275 °C. The desorption time was set from 2 min to 10 min to determine the optimal desorption condition using Tenax TA. The plots of peak response for the model VOCs versus desorption time is shown in Figure 5-3(b), which shows that tube desorption time was not significantly affecting the peak area but with time greater than 8min resulted in

relatively greater mass response except for one target compound, hexane. This maybe because hexane exhibiting a lower boiling point tend that is decomposed under extend desorption times. The optimum tube desorption time were selected to be 8 min.

The cold trap heating temperature and time were optimised under the initial developed tube desorption method. Various temperatures between 240 to 325 °C and time between 3 min to 8 min were tested to check analyte recoveries and carry-over effect. By analysing blank after each cold trap desorption, tested compounds are all completely or closely desorbed under all the time settings. Therefore, an intermediate time of 5 min was chosen for trap heating. The desorption temperature was selected according to Figure 5-3(c), which shows that most of the compounds had their greatest recovery between the range of 290 and 310 °C, therefore 290 °C was chosen to ensure a better desorption as well as a longer life-span for cold trap as very high heating temperature may destroy the trap resin life.





Figure 5-3 (a) Analyte Response on tube desorption time; (b) Dependence of analyte recovery on tube desorption temperature, the peak area has been normalized to maximum value for each individual compound; (c) Dependence of analyte recovery on trap desorption temperature

5.2.5 Gas Chromatography and Mass Spectrometry Analysis

Sample analysis was performed using a GC-MSD (Agilent 6890N GC, 5973NMSD, Agilent Technologies). The analytical column used for separation was a DB-VRX (30 m \times 0.25 mm \times 1.4 µm). Helium gas was used as the carrier gas at a flow rate of 1.8mL/min. The temperature program for the GC was initially held at 50 °C for 2 min and then raised to 220 °C at a rate of 15 °C/min. The mass spectrometer acquired data in scan mode with m/z interval ranging from 35 to 335. The identity of compounds was verified using reference standard, by matching the mass spectra with a mass spectrum library (NIST02 library) available in the GC-MS system.

5.2.6 Quality Assurance and Quality Control

In the optimised thermal desorption conditions, extensive validation was conducted for the analytical methodology. Table 5-1 provides method detection limit, precision, response factor values for all the target analytes in chromatographic elute order. The method detection limit (MDL) was measured by subsequent dilutions of the working standard when a signal-to-noise ratio is established at 3. The MDL value ranges from 0.43 to 8.05 ng in absolute mass and when those values are converted into concentration MDL using approximate sample collection volumes (2 L), they corresponded to (0.22 μ g/m³ - 4.02 μ g/m³. The precision study was conducted by performing seven replicate measurements of sorbent tubes, which were spiked with the same amount of working solution (with 500ppmv roughly representing about 400 ng for each analyte). All the tested VOCs showed reproducibility less than 10%. The linearity was also assessed with the correlation coefficient (R²)>0.995, almost all the VOCs exhibited linearity ranges from 2 to 3 orders of magnitude.

The desorption efficiency was also evaluated by re-analysing the sorbent tube just after it was analysed and the test was done by loading a 1ul high concentration VOC solution (10000ppmv). The desorption was demonstrated to be efficient for all the target VOCs with desorption percentage over 99%; The retention efficiency was also examined in the laboratory by combining two Tenax TA tubes into series and loading a 2ul 5000ppmv VOCs solution via a calibration rig system flushed with dry air (100 ml/min). The front and back tubes were all analysed and the results demonstrated that no significant breakthrough was observed (<1%). Performance of the GC-MS was controlled by conducted daily autotuning of the mass spectrometer with Perfluorotributylamine (PTFBA) and mid-range standard mixture was checked on each analysis day. Response of the external gas standard (TO-17) was also monitored to ensure no significant changes in the GC-MS response. The filed blanks were collected and analysed throughout the course of the study period and any contaminant compounds were eliminated from calculation.

Compounds	Retention	Response Factor	MDL	MDL	RSD
	Time (min)	(Area/ng Analyte)	(ng)	(µg/m [°])	(%)
Trichloromethane	4.177	15539	2.96	1.48	3.8
2-butanone	4.611	13541	8.05	4.03	7.2
1-butanol	5.421	13827	8.06	4.03	8.3
Benzene	5.685	20032	1.75	0.87	1.3
Toluene	7.304	38336	0.43	0.22	9.7
m,p-xylene	8.775	40263	0.86	0.43	8.8
o-xylene	9.109	38920	0.88	0.44	8.1
alpha-Pinene	9.506	26559	0.86	0.43	5.0
1-ethyl-4-methyl benzene	9.82	42258	1.73	0.87	8.7
Decane	10.003	27073	1.45	0.73	7.7
1-ethyl-2-methyl benzene	10.051	41428	0.89	0.44	9.3
D-limonene	10.515	29806	0.63	0.33	10.0

 Table 5-1 Selected method performance evaluation parameters

Repeatability, expressed as relative standard deviation (RSD %) for the analysis of 100ppmv of VOCs standards (n=7)

5.2.7 Method Validation

In order to evaluate the performance of developed analytical method, gas emission samples were collected from two sewer sites. Samples were collected simultaneously for 20 minutes at a flow of 100 ml/min with six replicates at both sites and no breakthrough of target analyte was observed. Table 5-2 presents averaged concentrations of the target VOCs and their precision as well as total concentration of measured VOCs.

Among all the targeted volatiles, 2-butanone and 1-butanol could not be detected in the sewer emissions whereas the other 10 compounds were all detected with a wide concentration range from 2.41 to 654 μ g/m³, depending on the site. The total VOC concentrations in the two sites were different with S2 (1505 μ g/m³) having a higher concentration than S1 (626 μ g/m³). The difference can be associated with sewage source as S2 being located near an industrial discharg into the sewer. Similarly, the reproducibility test at both sites showed slightly different results although they showed a very acceptable precision (<15 %). The difference may be caused by different sample collection such as humidity, temperature, wind/sewage fluid velocity as they were proved to have a significant influence on precision of methodology (Wu et al. 2006). The field validation tests demonstrated that the sampling and analytical method described in this study was promising for measuring VOCs emission from sewer networks.

Compounds	1	S1	S	\$2
	Conc.	Precision	Conc.	Precision
Trichloromethane	202.0	11.3	654	8.8
2-butanone	nd	-	nd	-
1-butanol	nd	-	nd	-
Benzene	5.52	4.2	8.85	14.1
Toluene	111	4.6	61.2	8.1
m,p-xylene	106	2.7	184	7.0
o-xylene	45.7	2.8	70.6	6.8
alpha-Pinene	2.41	8.8	161	11.8
1-ethyl-4-methyl benzene	18.9	3.9	22.9	9.2
Decane	14.4	4.0	142	7.7
1-ethyl-2-methyl benzene	10.2	3.9	10.6	8.8
D-limonene	110	2.1	191	8.1

Table 5-2 Concentration $(\mu g/m^3)$ of target VOCs measured in two sewer sites

Precision, expressed as relative standard deviation (RSD %) for the analysis of 100ppmv of VOCs standards (n=6)

5.2.8 Summary

In this study, an analytical method has been developed to optimise the determination of VOCs in the sewer gas emission by TD-GC-MS. The thermal desorption method with selected Tenax TA tubes has been optimised to acquire better recoveries of potential target analytes. The method presented high precision and good linearity for all the compounds being tested, which showed it is a suitable and promising method to measure VOCs at a trace level (pptv). Method performance evaluation carried out on real samples collected from two sewer sites showed good reproducibility for most of VOCs being detected. The analysis methodology will enable further characterisation of sewer VOC emissions in terms of composition. This will enable the identification of marker compound and/or groups, which will potentially help to monitor odour annoyance efficiently and develop design criteria for odour and VOC treatment system in order to prevent the dispersion of odorous compounds from such wastewater systems.

5.3 Data Analysis Approaches

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VOCs concentrations below the method detection limit (MDL) were substituted with one-half MDL (1/2 MDL) and extreme observations defined as mean values \pm six standard deviations were excluded from further statistical analysis. The random effect model was used to exam the spatial and temporal variability of the measured individual VOC species. The temporal (day) and spatial (site) were both treated as the random factors in this model:

$$Log(X_{ijk}) = \mu + \alpha_i + b_{ij} + \epsilon_{ijk}$$
 Equation 5-1

Where Log (X_{ijk}) are the measured concentration (log transformed) at the site i on day j, μ =the true mean concentration across all the data, α_i are the variability attribute to effect of sampled site i, b_{ij} are the variability attributed to day j at location i, and ϵ_{ijk} are the residual variability due to the analytical errors and within-day heterogeneity (k) on day j at location i. The variance components ($\sigma^2_{spatial}$ and $\sigma^2_{temporal}$) were obtained from the expected mean square analysis of Equation 5-1 to represent the spatial and temporal variability of selected VOCs, respectively.

The similarity and/or differences of the sample within the range of spatial and temporal variability of VOCs concentrations across the full dataset were further distinguished

using Principle Component Analysis (PCA). This method allows for samples with similar profiles to be identified and clustered together. PCs (principle components) were extracted from the analyses to represent the variances in an order from highest (PC1), the second greatest (PC2) and so on, whereas that of the last one is the lowest. Here, as in the random-effect model, the PCA was performed with a view to assess site and day variations in sewer VOCs emissions samples. All statistical analyses were done with the SPSS statistics package, version 22.0

5.4 Results and Discussions

5.4.1 Overview

Many odour treatment practices have been developed and applied for the management of sewer emissions in Australia (Sivret and Stuetz 2012) with the most common processes being either physical or biological abatement technologies. These abatement systems are typically designed based upon hydrogen sulfide (H_2S) , which allows for the mitigation of sewer odour issues, as H₂S is typically present with the highest concentration in many sewer emissions. Some pre-treatment technologies are also utilised upstream in order to reduce sewer H₂S emissions (Zhang et al. 2008), however, the composition of sewer emissions is complex due to the microanerboic and anaerobic nature (decomposing the organic matters in sewage) of the sewer systems, a range of non-H₂S volatile compounds, such as volatile sulfur compounds (VSCs), volatile organic compounds (VOCs), methane (CH₄) were are also emitted from sewers significantly. The presence of those non-H₂S compounds causes considerable environmental impacts on local receptors and sewer workers, due their odour threshold values and potential toxic effects (Choi 1997, Cheng et al. 2005) as odour annoyance may incur even at a trace concentration level. However, few studies on non-H₂S compound formation in sewer systems have been reported in the literature.

Non-methane VOCs (NMVOCs) is one of most critical group in sewer environment and discharged to sewer catchments from various sources, including industries/commercial facilities (e.g. solvents, cleaning agents, fuel additives), household usage (e.g. cleanser, degreasers, disinfectants), and upstream chemical dosing. The transfer and build-up of NMVOCs from aqueous into the atmosphere via sewage collection and treatment

facilities has incurred growing public concerns and complaints in recent years due to several reasons:

1) Uncontrolled VOCs release may cause detrimental effects: such as toxic pollutants emission and photochemical precursors into atmosphere, explosive gas mixture in confined sewer environments as well as odour nuisance and toxic compounds exposure to local receptor or nearby residents;

2) Most VOCs are malodorous (having relative low odour threshold) and toxic (comprising half of the 129 priority pollutants in USEPA), in order to better manage sewer odour emissions to an acceptable level, the accurately chemical characterisation (e.g. speciation, dynamics and peak concentrations) of sewer emissions is needed to improve development and/or selection of efficient abatement processes. Failure on the performance of odour abatement systems were reported when they were designed and monitored based on one or several compounds (in most case, only H₂S or total VOCs) without considering the individual key compounds present in the complex sewer influent stream;

3) The potential exits for some non-odorous VOCs to have an impact on abatement process performance. Competition and interference between VOCs and other odorants (e.g. reduced sulfur compounds) particularly in the adsorption process (e.g. competitive sorption on active sites, desorption/displacement by other compounds on various sorbent materials) were already observed by and affects the accurate evaluate and predicate the efficiencies and abatement capacities, which is major issue in sewer emission management.

Several published studies on VOCs emissions from sewerage systems have shown that there is a large variation in the results due to the nature and magnitude of sewage-driven odour emissions, which depends on environmental and hydraulic conditions of wastewater and the design of collection systems. Two major limitations of these available studies are: 1) that VOCs emissions derived from sewer networks is rarely reported compared to wastewater treatment plants (WWTPs). Within those published studies, most were focused on several selected VOCs, i.e. BTEX VOCs, chlorinated compounds trying to investigate and model the fate/mass transfer of VOCs between the liquid (in-sewer wastewater) and gas phase with fairly limited number of studies focusing on identifying and quantifying sewer gaseous VOCs. Only recent studies have more studies concentrated on the identification and characterisation of NMVOCs that are present in sewage collection facilities. Huang et al. (2012) employed thermaldesorption (TD) coupled to GC-MS to investigate 71 selected VOCs, present in the headspace of two sewer lines in Southern Taiwan; and 2) Due to the analytical challenges (e.g. absence of reliable, fast and cheap methods) (Muñoz et al. 2010) and high expense for sampling and sequential chemical analysis of gaseous pollutants and most VOCs analysis been performed for sewer emissions has been limited to discrete sampling of a number of sites, seasons and years (Wu et al. 2006, Huang et al. 2012) thereby providing a limited insights into the dynamics of sewer emissions. Previous studies have only obtained data from 1 to 2 sites during one or two-week of a single season (Corsi et al. 1995) or several sampling events in each season (Huang et al. 2012), which does not allow for the systematic comparison of seasonal trends. To the best of author's knowledge, no one sampled in multiple years for same season on sewer networks.

A three-year monitoring program from June 2011 to March 2013 have been performed at 12 sewer networks in Sydney that were representative of sewage conditions of Australia. The primary aim of this chapter is to provide detailed information on the full spectrum of the VOCs appearing in the atmosphere of different Sydney sewer catchments. Within long span time monitoring program, the seasonal and year-to-year variability of VOCs concentrations were firstly characterised. Also, spatial variability was characterised by comparing the concentrations measured at different sampling sites and inter-sites similarity and correlations were identified across multiple sampling locations reflecting different upstream sources of sewers. This spatial and temporal trend analysis will allow to 1) determine whether any single season best represents an annual mean for the whole sewer networks; 2) investigate how well any single site (sites group) represent the seasonal and temporal trends. In addition, potential sources and comparison with relevant existing literature are also explored in this work. This advanced characterisation will further improve the field sampling strategies for NMVOC emissions in sewer and enhance design/operation of odour abatement processes for sewer emissions management.

5.4.2 Non-target Screening of VOCs

GC-MS based non-target screening analyses of sewer emissions from 12 sites have allowed the identification of a large number of VOCs. Substance, that have been screened out were according to 1) frequently detected at individual site with over 25 % detections in each sewer sites and 2) remarkably detected with averaged abundance per unit of sampling volume (chromatographic abundance/ml) > 799.5. All identified compounds are summarised in the Table A-1 (appendix) and arranged in the chemical groups of alcohols, halogenates, aromatics, sulfides, alkanes, terpenes, mono-or polycyclics, alkenes and aldehyde. A high variety of VOC constituents in terms of structural diversity as well as quantitative composition is observed between sites as shown in the Table A-1. Similar chemical groups or VOCs compositions were reported in sewer networks by in previous studies (Huang et al. 2012).

Totally, 112 NMVOCs were detected and measured in more than one sewer sites during the studied period between Octobers 2011 and March 2013 with most detected species presenting in a relative trace level as a result of semi-quantification. However, some of them were detected at the sewer gases at extremely high abundances in at least one sewer, which includes tetrachloroethylene, benzyl alcohol, m, p-xylene, toluene, C_3 - C_5 alkyl benzene and C_4 - C_{10} aliphatic hydrocarbons, and methylcyclohexane. Those compounds were also detected and reported in raw wastewater, WWTPs (Escalas et al. 2003) and their emission samples (Wu et al. 2006).

Considering all sampling campaigns, it shows 41 VOC species with a frequency of detection greater than 25% ever detected in any sites of the sampled sewers, S1~S12 (Figure 5-4). One alkane (2,2-Dimethylbutane), one alkene (2,3-dimethyl-1-Pentene), one halogenate (1,1,1-trichloro-Ethane) were only frequently detected at one site. Other VOCs were characterised as the non-site specific containments in which they were commonly detected among all the studied sewer sites ($n\geq 2$) with regards to the rest of 38 chemicals, classified as aromatics, alkanes, halogenates, monocyclics, sulfides and alkenes.

Aromatics and alkanes, the two largest groups being analysed, are the most detected with 11 compounds and 8 compounds respectively, while aromatics and halogenates present the highest frequency of detection (3 of 11 aromatics and 4 of 7 halogenates were measured greater than 60%). In general terms, there highly presence in the sewer emission samples may be related to high consumptions as petroleum solvents or vehicle washing chemicals (BTEX VOCs) and chlorinated solvents (chloroform, trichloroethylene, tertrachloroethylene and bromodichloromethane). Also, the high presence of one sulfides (up to 75%), DMDS (dimethyl disulfide) was related to the anaerobic decomposition of organic matters containing sulfur (S) or the decay products of mercaptan.


Figure 5-4 Compounds with an averaged frequency of detections higher than 25% in sewer emissions (A*: Aldehyde) along with the number of sites detected (O)

5.4.3 VOCs concentrations in sewer headspace air

Figure 5-5 presents 58 compounds detected at average concentration greater than 50 μ g/m³ in different types of sewer networks. Due to the large variations on the reported OTVs (odour threshold values) (Table 5-3) and the concentration of 50 μ g/m³ was the lower limit of the reported OTVs, this was considered the threshold values for the studied compounds (Van Gemert 2003). Generally, the measured concentration (site means over three year measurements) of 58 targeted compounds were representing a large inter-site variation among S1~S12. However, it is noted that the sulfide compounds (as identified in non-targeted screening analysis at section 5.4.2 were not included in the list of 58 most abundant compounds (reported in Chapter 4 discussion on S–containing compounds). Also, there is a technical limitation of sorbent tube and TD-GC-MS analysis of sulfur compounds (i.e. usage of non-sulfur specific cold trap in the analysis reducing the amount of sulfur compound retained), which affects the accuracy of quantification.

Aromatics and halogenated compounds were most the frequently detected groups in sewer emissions samples (Figure 5-4), having the slightly higher average concentration among all the contaminants of interesting. During the 2011-2013 periods, 13 compounds show concentration greater than 50 μ g/m³ (on average) in at least one site, consisted of 1 alcohols, 3 halogenates, 3 alkanes, 1 terpenes, 1 alkenes, 4 monocyclics. The most commonly detected VOCs were o-xylene, ethylbenzene, C₃₋₄ benzene, and toluene. Aromatic compounds that were present in the highest concentrations (overall means) in the sewer gas samples were trimethylbenzene (179.3-104.0 μ g/m³), Toluene (129.7 μ g/m³), Benzene, 1-ethyl-2-methyl- (122.7 μ g/m³), and o-xylene (61.3 μ g/m³).

In order to better understand the distributions of the measured concentration data and further investigate their viable behaviour in the studied area, it is necessary to select some of the important volatile compounds from the primarily list by frequency and quantitative analyses. The selection and inclusion of key VOCs was based on the following criteria: 1) the VOC is include in the list of frequently detected (Figure 5-4) and quantitative abundant (Figure 5-5); 2) the VOC is potential odorous and there were public perceptions that the chemical may pose a possible odour nuisance; 3) The VOC has previously been detected in sewerage and influent to WWTPs; and 4) the VOC is

listed in Safe Work Australia (2011), European Union (2000) and European Union (2006) as regulated due to OH&S exposure hazard concerns. A detailed statistical summary of 25 selected VOCs concentrations measured in the atmosphere of 12 sampled sewer networks is presented in Table 5-3.

In Table 5-3, the average, 95th percentile, and maximum measured concentrations of each of the 25 VOCs are compared with associated OTVs (Van Gemert 2003) . The average concentrations of VOCs across the 12 sewers ranged between 17 μ g/m³ (for ethyl-cyclohexane) and 1445 μ g/m³ (for toluene). Nearly all of the VOC concentrations were well below their associated OTV range. The exceptions were limonene (105 μ g/m³), m,p-xylene(122 μ g/m³) and toluene (1445 μ g/m³) as well as 1,2,3-trimethylbenzene , if considering its 95th percentile concentration (304 μ g/m³). Compared to the data summarised from Australian and European Union 8-hour time weighted average (TWA) exposure limits, even maximum concentrations observed during the study were generally less than 5% of the exposure limits.



Figure 5-5 VOCs compounds detected at average concentration higher than 50 μ g/m³ (red dash line) in (at least) one sewer site

Tabl	le 5-3 Statistical summary of se	lected VOCs o	concentration	ι (μg/m ³) ο	bserved in	ı sewer sit	tes (Octob	er 2011- J	une 2013)	
	Companyed			May	Moon	0,5 th	CD	Varian	ce (%)	
	Componius			VIAX	INTEALL	R		σ^2_{s}	σ^2_t	10
Ð	Trichloromethane	67-66-3	88.6	932	98.8	378	131	68.4	31.6	500-1350000
ten	Methane, bromodichloro-	75-27-4	71.3	738	54.4	341	106	39.9	60.1	390-145000
ເຈລີ	Trichloroethylene	79-01-6	57.9	360	24.1	117	53.1	84.9	15.1	850-125600
ola	Benzene, 1,4-dichloro-	106-46-7	52.5	812	41.5	216	102	11.5	88.5	730
H	Tetrachloroethylene	127-18-4	75.7	16310	244	999	1317	68.7	31.3	8100-12000
	o-Xylene	95-47-6	50.5	3663	40.4	180	265	19.5	80.5	770-23600
	p-Cymene	99-87-6	38.6	2368	48.7	210	187	23.1	76.9	2700-7200
	Benzene, 1,2,4,5-tetramethyl-	95-93-2	43.1	279	20.0	102	39.0	64.5	35.5	NA
;	Ethylbenzene	100-41-4	82.2	1627	27.8	82.1	151	43.8	56.2	400-78300
oiti	m, p-Xylene	106-42-3	79.2	8467	122	330	732	34.8	65.2	52-86000
em	Benzene, 1,3,5-trimethyl-	108-67-8	55.4	4364	42.8	113	308	20.9	79.1	140-12000
10	Toluene	108 - 88 - 3	91.6	10468	1445	477	754	44.4	55.6	600-590000
V	Benzene, 1,2,3-trimethyl-	526-73-8	65.3	6959	84.1	309	500	33.8	66.2	140-12000
	Benzene, 1-ethyl-2-methyl-	611-14-3	59.9	3630	58.1	200	269	62.7	37.3	NA
Ċ	alpha-Pinene	80-56-8	56.4	299	12.7	63.5	33.2	9.1	90.9	2100-23000
łıə	Limonene	138-86-3	60.4	2495	105	580	264	10.7	89.3	56-55000
T	Eucalyptol	470-82-6	43.1	422	18.3	83.0	44.7	7.9	92.1	45-47000
	n-Nonane	111-84-2	58.9	2474	43.4	203	191	2.8	97.2	60000-108000
əu	n-Dodecane	112-40-3	67.3	1234	35.4	144	115	8.9	91.1	118000-50000
кя	n-Decane	124-18-5	43.1	787	21.1	57.3	90.5	3.1	96.9	11300
IV	Heptane	142-82-5	68.3	1654	44.5	200	140.3	25.6	74.4	23000
	Undecane	1120-21-4	25.2	14494	211	278	1302	1.5	98.5	9600-23000
IJ	Naphthalene, decahydro-	91-17-8	32.7	565	27.6	162	76.4	22	78	NA
эĄ	Cyclohexane, methyl-	108-87-2	46.0	1740	35.7	128	158	48.3	51.7	854000
С	Cyclohexane, ethyl-	1678-91-7	60.0	505	17.0	75.6	53.0	42.4	57.6	NA
N=N	umber of measurements that cor	nplied with QA	/QC demands	;; %> MDI	-=percent (of detected	l values			

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OTV: Odour Threshold Value in the unit (Van Gemert 2003)

5.4.4 Comparison with Other Studies

For a better insight into the environmental behaviour of VOCs, the VOC data collected in this study can be compared with those measured previously in other studies. Information on gaseous VOC levels in the sewage collection system/facilities is however fairly limited. Sewage-driven VOCs data were mostly found in previous studies from 1) emissions from wastewater treatment plants (WWTPs); 2) emissions from raw wastewater or in-sewer wastewater; 3) aqueous phase of sewage (influent, effluent). The measured VOC data from a variety of sewer networks in this study addresses the knowledge gap for sewage collection facilities in Australia.

Gas phase sampling conducted from sewers in Germany (Haas and Herrmann 1996, Haas and Herrmann 1998) and Canada (Corsi et al. 1995) have identified similar key VOCs. Sampling by Haas and Herrmann identified several halogenated hydrocarbons including trichloromethane and tetrachloroethylene (Haas and Herrmann 1996, Haas and Herrmann 1998) along with a range of alkanes, xylenes, and ethylbenzene (Haas and Herrmann 1996). Work by Corsi et al (1995) focused on three aromatic compounds, toluene, ethylbenzene and xylene, with peak concentrations higher (up to 6 times greater in some cases) than those found in the Australian samples.

The remaining published sewer VOC data is based on liquid phase (sewage) sampling, as shown by the work of Haas and Herrmann (1996), studying transport of halogenated hydrocarbons between sewage and sewer headspace air, it is expected that the range of VOCs identified in the sewage will be present in the sewer headspace air. Again a similar range of VOCs as presented in Table 5-3 that have been observed during sewage sampling at the inlets to municipal WWTPs in Spain (Escalas et al. 2003), Italy (Fatone et al. 2011), and Greece (Nikolaou et al. 2002), with toluene being consistently identified as a dominant VOCs along with trimethylbenzene and m,p-xylene. Halogenated hydrocarbons were also identified in these studies (Nikolaou et al. 2002, Escalas et al. 2003).

Given that a similar range of VOCs (and in many cases similar dominant VOCs) have been identified in the sewer headspace air and sewage across diverse countries and climatic regions, the data and conclusions presented in this section are not restricted to the Australian context and is useful for identifying the odour implications of sewer headspace VOCs for the wider industry.

5.4.5 Temporal-Spatial Variations

General Patterns

A total of 97, 85, 79 and 74 species of VOCs were identified (at least in two sampling events over a single season campaign) from sampling in summer, autumn, winter and spring, respectively. The measured chemical families in sewer emissions were consistent from season to season, confirming the previous classification of alcohols, halogenates, aromatics, terpenics, alkenes, cyclic hydrocarbons, alkenes and aldehydes (as discussed on section 5.4.3). Table 5-4 summarises the detected compounds in different samplings.

As seen in Table 5-4, variations in the types and number of VOCs could be observed in the four seasons. Halogenated, aromatics, alkanes as well as cyclic hydrocarbons were dominative species in all sampling campaigns, and more species were detected in summer. These trends of dominance are more significant in summer and autumn samplings. The average concentrations of each chemical group generally follow the ranking as: alkanes > aromatics > halogenates > cyclic hydrocarbons > alkenes > terpenics > aldehydes > alcohols. Whilst this trend differed in winter with an order of aromatics > halogenates > terpenics > Alkanes > cyclic hydrocarbons > aldehyde without the detection of alcohol and aldehyde compounds.

More species and higher concentrations of aromatics, alkanes and cyclic hydrocarbons were detected in either summer or autumn while the concentration and number of most chemical families were being the lowest during the four seasons. The range of VOCs present on the sewer atmospheres are largely determined by several factors, including the wastewater composition, the bioreaction products during the transport, the process of volatilisation i.e. diffusive and convective mass transfer (Hvitved-Jacobsen et al. 2002) as well as meteorological conditions (i.e. temperature, rainfall, atmospheric pressure).

Halogenated compounds are most likely associated with their use as solvents, deodorants, degreaser and fumigants (Golfinopoulos et al. 1998, Jakubowska et al. 2009) as well as disinfection products (Ndon et al. 2000). The alkanes and aromaticcompounds are mostly associated with petroleum solvents (Paxeus 1996, Escalas et al. 2003) and automotive paints. Those chemicals are usually inherent substance of domestic wastewater and therefore their emission are mainly affected by the process of volatility and therefore are more subject to season effects.

Oxygenated species such alcohols, aldehydes are more biogenic and the concentrations of those compounds can be more likely to be affected by the anaerobic/aerobic process during the transport process in the sewer pipes and the seasonality of those compounds is less significant, generally differed by a factor less than 2. Species such as terpenes present in the sewer atmosphere are associated with odour-related compounds (Agus et al. 2011), such as fragrance additives, particularly those used in cleaning products.

Family		Concentratio	n (μg/m ³)		Q	etected compou	und numbers	
	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring
Alcohols	24.6	12.55	na	19.99	2	1	1	0
Halogenated	1145	1066	423	399	6	10	11	10
Aromatic	1954	1842	492	962	24	23	23	23
Terpenes	492	553	310	397.3	9	9	9	9
Alkanes	3543	3012	276	749	27	24	21	19
Cyclic	1038	1002	191	264.9	20	18	13	15
Alkenes	814	469	na	96.9	8	2	3	0
Aldehyde	274	270	159.9	103	1	1	1	1
Total	6859	4394	2653	3951	67	85	62	74

na: data are not available

Spatial and Temporal Variations of VOCs

A one-way ANNOVA analyses (P<0.05) was performed on log-transformed concentrations for the 25 target VOCs at different sewer locations and the results are present in Table 5-5. Most VOCs (i.e. 15 out the 25 species) exhibited significant spatial variations (p<0.05). The exceptions were generally species from terpenes, alkanes as well as 1, 4-dichlorobenzene, o-xylene and 1, 3, 5-trimethylbenzene. A further Turkey's multiple comparisons of individual VOCs among the 12 sampled locations indicated that the less industrial wastes sites (S9 and S11) receiving relatively lower loadings of wastewater into the catchment (as discussed in **Chapter 3**) had significantly lower level of most of the investigated VOCs. Throughout the ANNOVA analysis, the 9 VOC compounds with extremely significant concentration variations (p<0.01) are displayed in Figure 5-6 (a~i) by different sewer sites.

Previous studies were limited to 1 to 2 sewer-monitoring sites, which does not allow for or biases the comparisons of spatial patterns. More discussions were focus on seasonal variations and significant seasonal effects on the air VOCs in the sewer networks were reported previously. Huang et al. (2012) sampled during the wet and dry seasons, however the studies were limited to 2 sewer pipelines in four sampling events.

As shown in the Table 5-3, the temporal variability is generally higher than the spatial variability for most of VOC species. The highest spatial variability was observed for trichloroethylene (84.9 % spatial vs 15.1 % temporal) whereas the highest temporal variability was observed for undecane (98.5% temporal vs 1.5 % spatial). This study presents for the first time the spatial-temporal effects of sewer VOCs, assigning the overall variability and indicating the spatial variation were more dominant than the total variability within the studied period. These results suggest that performing multiple monitoring at several sewer sites over a long-term period of time (i.e. one year) with proper sampling frequency would be a necessary step in understanding the emission loadings for both odour monitoring and odour abatement process design.

	Sum of square	df	Mean square	F	p-value
Trichloromethane	18.910	8	2.364	5.995	< 0.001
Methane, bromodichloro-	16.728	8	2.091	2.866	0.006
Trichloroethylene	43.526	8	5.441	22.931	< 0.001
Benzene, 1,4-dichloro-	5.653	8	0.707	1.018	0.426
Tetrachloroethylene	58.852	8	7.357	13.552	< 0.001
Benzene, 1,2,3-trimethyl-	16.970	8	2.121	2.064	0.044
Ethylbenzene	14.691	8	1.836	3.300	0.002
p-Cymene	20.733	8	2.592	2.164	0.035
Benzene, 1,2,4,5-tetramethyl-	30.389	8	3.799	4.199	< 0.001
o-Xylene	9.862	8	1.233	1.525	0.155
m, p-Xylene	17.224	8	2.153	2.558	0.013
Toluene	11.900	8	1.487	2.179	0.033
Benzene, 1-ethyl-2-methyl-	28.429	8	3.554	3.670	0.001
1,3,5-trimethylbenzene	12.555	8	1.569	1.524	0.155
alpha-Pinene	5.246	8	0.656	0.985	0.451
Limonene	18.561	8	2.320	1.408	0.199
Eucalyptol	8.625	8	1.078	0.966	0.466
n-Decane	1.030	8	0.129	0.151	0.996
Nonane	4.520	8	0.565	0.729	0.665
Dodecane	2.883	8	0.360	0.606	0.771
Heptane	8.923	8	1.115	2.088	0.042
Undecane	3.992	8	0.499	0.770	0.630
Naphthalene, decahydro	10.525	8	1.316	2.315	0.024
Cyclohexane, methyl-	17.923	8	2.240	5.280	< 0.001
Cyclohexane, ethyl-	9.904	8	1.238	3.518	0.001

Table 5-5 Analysis of variance for spatial VOCs concentrations $(\mu g/m^3)$ in the sewer air



Figure 5-6 Comparison of measured concentrations $(\mu g/m^3)$ for selected VOCs by sewer (P>0.01) sites; (a) Trichlomethane; (b) Methane, bromodichloro-; (c) Trichloroethylene; (d) Tercholoethylene (e) Ethylbenzene; (f) Benzene, 1,2,4,5tetramethyl; (g) Benzene, 1-ethyl-2-methyl; (h) cyclohexane, methyl-; (i) Cyclohexane, ethyl-



Figure 5-6 Comparison of measured concentrations $(\mu g/m^3)$ for selected VOCs by sewer (P>0.01) sites; (a) Trichlomethane; (b) Methane, bromodichloro-; (c) Trichloroethylene; (d) Tercholoethylene; (e) Ethylbenzene; (f) Benzene, 1,2,4,5tetramethyl; (g) Benzene, 1-ethyl-2-methyl; (h) cyclohexane, methyl-; (i) Cyclohexane, ethyl-



Figure 5-6 Comparison of measured concentrations $(\mu g/m^3)$ for selected VOCs by sewer (P>0.01) sites; (a) Trichlomethane; (b) Methane, bromodichloro-; (c) Trichloroethylene; (d) Tercholoethylene; (e) Ethylbenzene; (f) Benzene, 1,2,4,5-tetramethyl; (g) Benzene, 1-ethyl-2-methyl; (h) cyclohexane, methyl-; (i) Cyclohexane, ethyl-

5.4.6 PCA Results for Spatial-Temporal Analysis

Principle component analysis (PCA) was applied to the VOCs samples at 8 locations to visually verify the spatial-temporal observations. The measurements of VOCs data from S3, S8, S9 were excluded from the PCA analysis due to the number of samples collected and analysed for the three sites not being as identical to the other sites, while data form S11 was not included in this analysis, since the data had a large proportion of VOC concentrations below the MDL. The analysis was performed on the seasonal average concentrations of 20 VOCs so each data point in this figure represents season average PC scored at each site. Samples with similar characteristics of VOCs profiles appear closely together in the PCA loading figures. Figure 5-7 (a-d) presents the score plots from PCA analysis, yielding two components that explained 64.1%, 60.7 %, 57.5 % and 60.7% of cumulative variance for the summer, autumn, winter and spring, respectively. The percentage of 1st and 2nd principle components (PC) that accounted for most of the total variance in each seasons are provided in Figure 5-7.

As shown in Figure 5-7, PC data point were generally clustered by the seasons rather than sampling sites, indicating temporal effect are more dominant than spatial effect, consistently with the results obtained from random effects models as discussed in the section 5.4.6 (Table 5-3). Nevertheless, the spatial effects were not negligible (i.e. S1 and S12 in the winter and summer samplings). PC 1 distinguishes samples according to the profile or composition of VOCs present at the sewer atmosphere. PC 2 is characterised by the positive loadings of all the sites measured and the higher loading scores of PC2 indicated higher concentration overall in a samples, which indicates the overall concentration of a sample in S1 and S2 are constantly measured higher than the rest of 6 sites among the four measured seasons.

PC scores exhibited comparable results between the measurements of summer (December to February) and winter (June to August) while the observed patterns were more linked between transition seasons, i.e. spring (September to November) and autumn (March to May). The samples from S1 and S12 were distinguishable from other sites by their unique loadings of PC1 and PC2 in winter and summer, suggesting the spatial effect are more apparent in the two seasons, rather than transaction seasons. Given this observation, it will further improve seasonal/temporal sampling strategy

particularly when resources limit sampling of the entire year, as two season monitoring can provide a representative dataset to depict the temporal-spatial variability of VOCs concentrations.



Figure 5-7 Principal component analysis results for 8 sewer sits with VOC samples at summer (PC1 41.7% VS PC2 22.4%); autumn (PC1 43.1 % VS PC 2 17.6 %); winter (PC1 35.2% VS PC2 22.3%); and spring (PC1 42.0%VS PC2 18.7%)



Figure 5-7 (cont.) Principal component analysis results for 8 sewer sits with VOC samples at summer (PC1 41.7% VS PC2 22.4%); autumn (PC1 43.1 % VS PC 2 17.6 %); winter (PC1 35.2% VS PC2 22.3%); and spring (PC1 42.0%VS PC2 18.7%)

To provide a greater understanding of the influence of short-term sewer conditions on emission variability in addition to the knowledge we obtained from long-term emissions monitoring in previous sections. 24 hours atmosphere sewer sampling was undertaken at the pump station (S2) to represent a typical diurnal hydraulic cycle of a sewer networks using 2-hour composition samples.

Figure 5-8 shows the observed variability in selected key VOC components in different chemical classifications. In general, the concentrations of aromatics, terpenes and alkanes varied significantly during the day while halogenated compounds were fluctuated at relatively narrow ranges of concentration. The maximum concentration of all of the species was constantly measured after mid-day. The variations of aromatic compounds (i.e. toluene, ethylbenzene, m,p-xylene and trimethylbenzene) generally followed the same trend, with two significant peak concentrations being measured at 10:00-12:00 and 18:00-20:00. The observed diurnal effects of aromatic compounds are consistent with that previously reported by Corsi et al. (1995) who investigated the 24hr variations in VOCs emissions from a municipal sewer in Canada. Their results indicated that emissions rate of three aromatic compounds peaked at either near noon or late night (22:00). In contrast to the pattern of aromatic VOCs, only one significant peak concentration was observed for two alkane species at late afternoon (16:00-18:00) although their day-night pattern was also significantly observed, with the day/night factor (on averaged concentration) between 4 and 6. The daytime means in $\mu g/m^3$ for decane and nonane were 18.5 ± 13.9 and 17.7 ± 16.8 , while their night time counterparts were 4.6 ± 5.0 and 3.0 ± 3.8 , respectively. Nevertheless, the diurnal pattern is less dominant for the halogenated compounds, with the factor less than 1.5 for the three compounds.

The diurnal distribution of the VOCs is more likely explained by the hydraulic characteristics in sewage and their volatility (i.e. temperature driven) potentials between aqueous-gaseous interfaces. From a general perspective, the dominance of VOCs occurring in the daytime is most likely influenced by environmental factors, such as increased temperature and gas flow in the sewers, favouring evaporative processes from the liquids. The two significant peak concentrations observed for aromatic compounds,

most likely reflected the fact that higher amounts of wastewater loadings discharged into the sewer catchments around those two time points.

These diurnal emission results highlight the importance of timing and understanding the short-term variability for timing sample collection from sewer networks, as the maximum odour and specific odorants concentrations is peaking at early evening, where typical sample collection (during the day) may underestimate the emission loading for odour monitoring and odour abatement process design.



Figure 5-8 Diurnal concentration variations of selected VOCs in the pump station (S2) in different chemical groups: a) terpenes; b) halogenates; c) aromatics; d) alkanes

5.4.8 Evaluation of Odour Implications

Considering the 95th percentile values in Table 5-3, nearly all of the VOC concentrations were observed to be well below their associated OTV range. The exceptions were trimethylbenzene, m,p-xylene and limonene. These concentrations were, however at the low end of the large OTV range, for examples a 95th percentile concentration of 330 μ g/m³ for m,p-xylene in Sydney compared to an OTV range of 52–86,000 μ g/m³.

Maximum VOC concentrations (representing conditions that are most likely episodic in nature) of alkanes in all three cities were below the OTV ranges. Considering the maximum concentrations of the other VOCs, a wide range of aromatic compounds were observed at maximum concentrations within the reported OTV ranges, The maximum measured trichloromethane and 1,4-dichlorobenzene concentrations in Sydney were at the bottom end of the reported OTV ranges, however the maximum concentrations of tertrachloroethylene were well above the OTV range.

From a perspective of understanding sewer odours, VOC monitoring is recommended only for sites with history of significant trade waste discharges or where typical VOC odour descriptors have been identified (for example solvent, sweet, burnt, or musty). Although generally not a significant contributor to sewer odour, the VOCs present in the sewer headspace air may have an impact on the effectiveness (odorant removal and operating cost) of odour abatement processes, for example the potential impact of VOCs on activated carbon based odour abatement processes, which are the dominant odour treatment technology applied in Australian sewer networks (Sivret and Stuetz 2010). VOCs are well known to interact with and be adsorbed by activated carbon (United States Environmental Protection Agency 1988) which may fill up the finite number of adsorption sites in the activated carbon which can lead to premature odour breakthrough (shorter lifespan) and increase operating costs due to the increased frequency of media changes required. Additionally, laboratory based studies have identified competition between VOCs during adsorption (Thoms and Lion 1992, Hepplewhite et al. 2004, Cheng and Tsai 2007). While there is minimal published information on competition between VOCs and known sewer odorants including VSCs and VNCs, the potential exists for similar types of adsorption competition that could negatively impact odorant adsorption.

5.5 Summary

In this study, an analytical method has been developed to optimise the determination of VOCs in the sewer gas emission by TD-GC-MS. The thermal desorption method with selected Tenax TA tubes has been optimised to acquire better recoveries of potential target analytes. The method presented high precision and good linearity for all the compounds being tested, which shows it is a suitable and promising method to measure VOCs at a trace level (pptv). Method performance evaluation carried out on real samples collected from two sewer sites showed good reproducibility for most of VOCs being detected.

Monitoring of VOCs in sewer headspace air across 12 sewer sites in Sydney were performed using the optimised TD-GC-MS method. Non-target screening analyse identified 585 VOCs that were determined during the 24 months sampling program. 25 compounds were selected out (in terms of frequency and abundance of detection, potential malodour and health impacts) and were further quantified. Generally, most measured VOC concentrations were less than 130 μ g/m³, although some VOCs (toluene, t) were present at higher concentrations for some of the sites studied.

Temporal variations of concentration were observed to generally follow the trends of cold season low and warm seasons (summer, autumn) high in different chemical classes (aromatics, halogenates, alcohols, terpenes, alkanes monocyclics, alkenes and aldehyde). These trends can be attributed to the accelerated volatilisation under high ambient temperatures. Aromatics, monocyclics, alkanes and halogenates were observed to be the most significant percentage of total VOC concentrations of a sample.

The temporal-spatial variations of 25 VOCs present in the sewer emissions were elevated using the random effect model and principle component analysis. It was found that the associated temporal component of variation was generally larger than the spatial component and the PCA analysis also confirms that temporal factor was more dominant. However, difference among the sewer types after accounting for the temporal effects

cannot be denied. In another word, the spatial variations of VOC concentrations are also significant for some VOCs, ascertained by one-way ANNOVA analysis. These results suggested the necessity of operating multiple monitoring sites over a significant period of time (e.g. more than one year) for understanding the headspace VOCs composition at sewer networks.

The odour implication assessment results indicate that sewer headspace VOCs are unlikely to be a significant contributor to sewer odours and VOC monitoring is not recommended for characterising these odours. VOC monitoring is, however, recommended for sites with history of significant trade waste discharges or where the odour character descriptors typically VOCs. VOCs may have an impact on the effectiveness of odour abatement processes, but further evaluation is needed to determine their fate in odour abatement technologies and any impacts on performance (particularly with regards to adsorption based systems).

Chapter 6 Odorants Identification and Prioritisation

6.1. Introduction

Of particular interest are the range of odorous volatile organic compounds and volatile sulfur compounds produced by anaerobic reactions (such as fermentation and sulfate respiration) in the sewage, sediments and biofilms on the sewer walls (Rudelle et al. 2011) as well as specific trade waste discharges (Bourgeois and Stuetz 2002, Rodriguez et al. 2012) into sewer catchments. Due to their malodorous characteristics and low odour thresholds (Van Gemert 2003), even at a trace concentration level, these odorous compounds can contribute to significantly odour annoyance. Complaints due to sewage odours are a major issue for wastewater utilities because the repeated release of unpleasant odours from a sewer network constitutes both a public nuisance and potential healthy related concerns. The effective management of odour emissions becomes essential for sewage network operators in order to mitigate their potential impact on public receptors.

Previous research on odour compounds at municipal wastewater have focused on odour at wastewater treatment plants (WWTPs) and their surrounding ambient air that result in nearby public complaints (Gostelow et al. 2001, Zarra et al. 2008). For example, on the anaerobic process (e.g. sludge thickening and digestion process), rotten eggs and decayed cabbage–like odours that relate with anaerobic decomposition of sulfurcontaining compounds were reported (Gostelow et al. 2001), whereas aeration unit treatment processes are more likely characterised by odorants that are originally present at the liquid phase and are dependent on the wastewater compositions. For instance, a large number of lighter (mostly volatile) aliphatic, aromatic, or chlorinated hydrocarbons are prone to volatilise from the wastewater surface due to high turbulence occurring within this unit process.

Odorous compounds derived from sewer networks are rarely reported compared to WWTPs. Given the high potential for volatile by-products being formed in the complex biochemical reactions occurring within different wastewater treatment processes or their tendencies to volatilise via air stripping, the odorants at the sewer networks would be characterised differentially from wastewater treatment processes. More importantly, to develop strategies for effectively manage and minimising the release of these compounds from sewerage collection systems, it would be important to understand the

identities of the most prevalent odorous compounds at the headspace of sewer air. In Australia, the focus on sewer odour monitoring has been on sulfur compounds due to their relative lower odour thresholds, particularly hydrogen sulfide (H_2S) with limited monitoring of non- H_2S sulfur compounds (e.g. mercaptan and sulfides). Additionally, no monitoring of odorous VOCs for olfactory and chemical characterisation of emissions from sewers and odour abatement performance monitoring (Sivret and Stuetz 2012) has been reported and only a limited number of international studies on VOCs emitted from sewer networks or the influent of WWTPs are available (Quigley and Corsi 1995, Haas and Herrmann 1998).

Gas chromatography (GC) coupled with mass spectrometry (MS) and an olfactory detection port (ODP) offers an advantageous technique to simultaneously combine sensory assessment with the identification and quantification of compounds using MS (Delahunty et al. 2006, Muñoz et al. 2010). The GC-MS/O approach also brings together the high resolution of capillary gas chromatography with the high selectivity and sensitivity of human nose olfaction. This method has been initially applied for detecting odour active compounds from food and beverage (Lermusieau et al. 2001, Afoakwa et al. 2009) and perfume(Fuller et al. 1964) and recently expand into the environmental research, such as livestock operations e.g. swine facilities (Zhang et al. 2010), biogas processes (Kleeberg et al. 2005), drinking water (Hochereau and Bruchet 2004), treated effluent (Agus et al. 2011) and nature water (Peter et al. 2009). The advantages and successful application of GC-MS/O in environmental and other fields suggest its potential for detecting odorous VOCs in sewer environments. To our knowledge, no studies have been published on GC-MS/O characterisation of emission from sewers networks.

The aim of this chapter is to develop and apply the combined chemical analysis by GC-O and full scan GC-MS for identifying, prioritising and tracking characteristic odorants present at sewer headspace while at the same time allowing for quantitative analyse of key sewer VOCs in trace concentrations. In addition, temporal-spatial variations of key odorants were further characterised and evaluated by collecting odour samples from 12 representative field monitoring sites across Sydney, Australia. The results of this study will provide further support to sewer odour monitoring decision-making and the design and evaluation of odour abatement processes.

6.2 Materials and Methodology

6.2.1 Thermal Desorption Gas Chromatography-Mass Spectrometry/ Olfactometry (TD-GC-MS/O)

To identify key odorants of concern, a number of samples were analysed via gas chromatography and combined mass spectrometry and olfactory analysis (GC-MS/O). Additional VOC samples collected on Tenax TA sorbent tubes using the methodology described previously were thermally desorbed using a Unity thermal desorber (Markes International, UK) coupled with an Ultra automatic sampler (Markes International, UK). A cold trap (U-T4WMT, Markes International, UK) was utilised to collect the sample prior to sample injection. Sample analysis was performed using a gas chromatograph equipped with a mass spectrometer detector (6890N GC and 5973NMSD, Agilent Technologies, USA) with a DB-VRX (30 m 0.25 mm 1.4 um) column (Agilent Technologies, USA) being utilised in the gas chromatograph for compound separation, using helium as the carrier gas flow rate of 1.6 ml/min. The GC column temperature was initially held at 50°C for 2 mins, then increased at a rate of 15°C/min to 200°C, and held for 3 minutes.

The eluent from the GC was split between a MS operating in scan mode and an olfactory detector port (ODP2, Gerstel GmbH & Co., Germany). Two operators were used for the olfactory analysis. To optimise the use of the operator as an odour detector the split between the MS and ODP was set at 2:3 (MSD: ODP). Split ratios were calculated using the Gerstel Column Calculator (Gerstel GmbH & Co., Germany). All odour stimulus chromatograms were recorded using the Gerstel ODP Recorder software (Gerstel GmbH & Co., Germany).

6.2.2 Description of the Panel and Execution of the GC-O analysis

Duplicate sorbent tubes were assessed by two trained human assessors using the direct intensity technique to record odour descriptors and intensities previously described by van Ruth and O'Connor (2001) and Delahunty et al. (2006). Both analysts were previously screened using n-butanol according to the Australian and New Zealand

Standard (AS/NZS 2001) with one assessor extremely sensitive and the other averagely sensitive. Analysts classified odorants intensities as: 1=low, 2=medium, 3=high and 4=strong. This number (1-4) determined by panellists at the ODP were for a particular odour active VOC were used as a measure of the odour intensity of the VOC. Odour descriptors were recorded according to the wastewater odour wheel (Suffet et al. 2004).

6.2.3 Identification and Recognition of Odour Potential VOCs

The recognised compounds associated with the most frequently detected odours were identified using several tools. Mass spectra were compared with the NIST mass spectral library and the Wiley database library. A percentage is given for the accuracy of the match, for reliability initial matches with greater than 85 % for the NIST library and greater than 70 % for the Wiley were considered as "identified". In addition, odour descriptions and retention times were compared with data for compounds reported on published database. Finally, preliminary screened compounds were further confirmed and verified with reference standards. Since olfactory peaks sometimes lasted for up to 10s, possibly due to presence of multiple compounds with similar odour descriptors,, their retention indices were recorded from the onset to the end of each olfactory peaks.

6.3 Results and Discussion

6.3.1 Prioritisation of Odorants Sewer Headspace Air

GC-MS/O analysis was conducted on samples collected from three representative sewer sites (that were selected based upon observed VOC species) as a screening study to identify odorous VOCs. A sample ion chromatogram with an overlaid odour stimulus chromatogram is provided in Figure 6-1. Where possible, odour descriptors were recorded by the analyst. A summary of the analysis of the samples is provided in Table 6-1, with the identified compounds been provided where applicable. In the event of multiple peaks with the same odour descriptor being observed in a sample, all of the identified peaks are reported for that descriptor. As a result of VOCs speciation in **Chapter 5**, up to a hundred of VOC species from a sample of sewer emission were measured, of which 21 were identified for the odour/aroma characters by GC-MS/O analysis (Table 6-1). Descriptors associated with the samples were chemical (solvent, chemical, burning, melting plastic), sulfury (sulfurous, rotten egg, rotten cabbage), pine,

or citrus/fruit, faecal/sewery and butter/ cheese/pungent. Without the information from the ODP, a reliable detection of three odour-active compounds (acetic acid, indole and geosmin) would not have been possible identified and recognised for a sample emitted from sewer networks. In the mode of GC-MS scanning, those compounds (contributing to buttery/cheese, faecal and earthy-like odour, respectively) were not identified (e.g. below MDLs) or present at lower concentrations due to analytical limitations in analysing these nitrogen or and volatile fatty acids using sorbent tubes sampling and analysis (Kim and Kim 2013).

Descriptor	Compounds	S1	S2	S 3	S4	SS	S6	S7	S8	S9	S10	S11	S12
Solvent/alcohol	Acetone			~				~					✓
Buttery/Cheese	Acetic acid	~	~	~	✓	✓	~	~			~	~	✓
Rotten Egg	Dimethyl sulfide	~	~		~		~	~	~		<	~	~
Solvent	Toluene	✓	✓	✓		✓		✓	✓	✓	~	✓	✓
Faecal	Indole	✓		✓		✓							✓
Rotten Cabbage	Dimethyl disulfide	~	~	~	~	~	~		~	~	~		
Grass/Green	Hexanal		✓	~	✓	✓	✓	~			✓	~	✓
Earthy/Fresh Fruit	Geosmin	✓	✓		✓	✓	✓	~	~	~	<		
Fruit	Unknown	✓	✓		✓	✓	~						
Smoky/Dry manure	m,p-xylene	✓		✓				✓				✓	✓
Yeasty	Ethylbenzene	~	~	~				~					✓
Medicinal	Chlorophenol					✓						~	
Melting plastic	Benzaldehyde	~						~				~	
Citrusy / Methanol	Limonene	~	~	~	~	~		~		~			✓
Mothballs	Dichlorobenzene							~					
Woody/Pine	α-Pinene	~	~	~	~		~	~		✓			✓
Rotten Cabbage	Diethyl disulfide	~	~	~	✓	✓	~	~					✓
Gasoline/Polish	Cumene					~							
Sulfurous	Dimethyl trisulfide			~		~							~
Perfume/ Flora	Unknown			✓	✓		✓						✓
Alkanes	Undecane		✓	✓		✓		~	✓	✓	✓		✓

Table 6-1 Summary of GC-MS/O analyses for samples at 12 sewer sites



Data reduction in terms of the number odorants studied was a necessary next step towards identifying the broad trends in malodorous compounds from the headspace air in different representative sewer sites. The goal of this data reduction step was to prioritise odorants that were present in higher odour intensity rates and ones that appeared more frequently in the dataset (eliminate highly site and episode specific compounds and ones that appear rarely). The prioritisation was performed using the modified frequency MF (%) analysis approach, which combined intensity I (%) and frequency analysis F (%). Data was pooled for each of the 12 sampled sites, and the MF (%) for each VOC was calculated (Equation 6-1).

$$MF(\%) = \sqrt{F(\%) \times I(\%)}$$
Equation 6-1

Where F (%) = the percentage of detection frequency of an VOC attributed; I (%) = the the average in intensity expressed as a percentage of the maximum intensity. An overview of the identified odorants and their relative ranking is provided as Figure 6- 2 (a,b, c).

Odorants with a MF (%) greater than 50 % of the VOC were compiled into a list of priority compounds for the sample of sewer odour emissions. Based upon the modified frequency analysis, a subset of 9 priority odorants was identified as: acetic acid, toluene, hexanal, geosmin, limonene, α -Pinene, dimethyl sulfide, dimethyl disulfide, and diethyl disulphide. Compounds within a family of aromatics, (e.g. ethylbenzene and m,p-xylene and alkanes (e.g. undecane) (Table 6-1) are excluded into the priority list due to their less significant contribution to sewer odours with percent odour intensities less than 20 % (Figure 6-2a), although they were present at a relatively higher detection frequency i.e. > 40% (Figure 6-2b). This agrees well with our pervious results that aromatic and alkane compounds present in the headspace air of sewer networks are unlikely to be a significant contributor to sewer odours (**Chapter 5**).

Table 6-2 lists the odorants prioritised and their descriptors identified in samples from collections at different sewer networks. Many of these peaks have descriptors that appear to be consistent with VOCs (such as sweet, solvent, fruit), however there are a number of peaks with descriptors (fecal/sewery) that related with nitrogen containing compounds and are more indicative of nitrogen based odorants. The presence of sulfur compounds was significant with respect to the odorants being detected as they are

notably nuisance odorants with very low odour detection thresholds characterised by pungent sulfur of dimethyl trisulfide and burning sulfur of dimethyl disulfide. However, it should be emphasised that the methodologies engaged for the assessment of the VOCs and odorants from the sewer networks were not ideally suited to the highly labile sulfur species and the results should be respected as being indicative of volatile organo-sulfur compound presence and the explicitly of any one compound were determined using the results from **Chapter 4 (VSCs speciation)**.



Figure 6-2 An overview the relative rankings (a) Averaged Intensity (I %); (b) Detection Frequency (F %); and (c) Modified Frequency (MF %) for all the odorants identified by GC-O analysis. The red dash line indicated a MF value of 50 %

6.3.2 Sensory Characteristics of Sewer Odours General Pattern

The odour character, intensity and odour event time that were identified and quantified via the olfactory port are presented in Table 6-2 according to the sampling sites. The chemical species identified and characterised by the operators as odorants that were consistently detected within the majority of the samples included a predominance of terpenes and acetic acid and with sulfide species also present. The odorant analysis of the samples collected at the different sites shows that five major aroma groups (consisting of a list of 9 priority odorants) that are attributing to the total sewer odours were identifiedd and included buttery, citrusy, sulfurous, earthy/ fresh fruit and solvent. There was also a consistent dominance of dimethyl sulfide within the odorant profiles, characterised by a rotten egg sulfur odour. The combination of these notably unpleasant odours would probabilistically combine to yield an overall disagreeable odour emission from the respective sewers.

The 5 aroma groups that were identified to attribute to the odorous emissions were evaluated on a scale from 0 to 4 by the two panellists (Figure 6-3). Form a general prospective, the intensity analyses from the GC-O methodology demonstrate the dominance of sulfurous odours within the headspace air of sewer networks. The range of intensity of sulfurous scents, including three components, dimethyl disulfide, dimethyl disulfide, and dimethyl trisulfide were between the ratings of 0-3 (average rating = 2). The second contributing aroma/odour characteristics was reported as buttery by the two ODP panellists with the presence of acetic acids being determined to contribute to the production of odours within sewers system. Whereas the aroma group to be identified to contribute the least to the sewer odours were determined as citrus and earthy characters with a lower average intensity scores of 1, being recognised as weak. The identification of non-sulfurous odours within sewage collection systems are important, as in the cases where sulfides are potentially reduced due to in-sewer pretreatment practices (e.g. chemical dosing) upstream in the sewer networks, the nonsulfurous odour groups may be largely perceived and could then cause serious olfactory nuisance.

At most sampled sites, a wider range of odorants with similar rankings were observed to be present, suggesting the data and conclusions presented in this chapter are not
restricted to just sewer networks in Australia, and could be used for identifying odours and odorants in other global sewer networks.

Variation in Olfactory Panellists

During the olfactory evaluation two panellists were employed with different olfactory sensitivities (based on n-butanol) in order to characterise the emissions. The operator (1) with a greater olfactory sensitivity (i.e. low butanol detection) was able to identify a greater number of odorants than the operator (2) with a normal or average olfactory sensitivity. Figure 6-4 illustrates the two olfactograms that are a result of GC–O analysis of sewer emissions evaluated by two panellists. This resulted in a large variation in the olfactory results obtained of sewer odours olfactory analysis.

The difference in the number of odorants that can be identified in a sample between the two operators was signified, with typically 16 olfactory stimuli compounds by the operator considered to be highly, whilst an identification of 9 compounds was observed from the operator considered to be considered to fall within the range of normal sensitivities.

The intensity rankings between consistently differed by the two panellists in the majority of samples we measured, where the olfactogram from high sensitive panellist were more intense (higher intensity scores) than the lower sensitive panellist as illustrated in Figure 6-4 and Table 6-2. Correspondingly, the descriptors given by the two operators were distinct in detail, whereas the highly sensitive operator characterised the chemical compounds with a higher level of descriptor. In addition, in terms of the aroma/odour profiles of a whole sample, as suggested by Figure 6-3 that while sulfurous-scent compounds are perceived by both panellists as the most important category among the 5 aroma groups, the buttery and citrusy aromas are rich for high sensitive and normal sensitive operators, respectively. This can be partially attributed to training, conditioning and experience with using the olfactory detection port.

More work is required to standardise the descriptors given by different operators in order to increase the validity of the results. The chemical species identified and characterised by the operators as odorants. With such a large percentage of the human genome dedicated to olfactory, it is conceivable that different local receptors may be disturbed by chemicals different to those identified within this project.

	Compounds	Acetic acid	Dimethyl sulfide	Toluene	Dimethyl disulfide	Hexanal	Geosmin	Limonene	a-Pinene	Diethyl disulfide
	Descriptor	Buttery	Rotten Egg	Solvent	Rotten Cabbage	Grass/Green	Earthy/Fresh Fruit	Citrusy / Methanol	Woody/Pine	Sulfurous
	RT (min)	4.95	6.14	7.67	8.36	9.01	9.58	9.86	10.20	11.48
S1	Panellist 1	1	2	2	2	0	1	2	2	2
	Panellist 2	1	3	2	2	0	1	1	2	2
S 2	Panellist 1	1	2	1	2	1	0	1	2	1
	Panellist 2	2	2	1	3	0	1	0	1	1
S 3	Panellist 1	1	0	2	2	1	0	3 1	2	1
	Panellist 1	2	2	0	1	1	1	1	2	1
S4	Panellist 2	1	2	0	2	1	0	2	1	1
~ ~	Panellist 1	1	0	1	2	2	1	3	0	2
S5	Panellist 2	0	0	1	3	2	1	1	0	2
0.0	Panellist 1	2	2	0	2	1	0	0	2	1
50	Panellist 2	1	2	0	2	0	1	0	1	1
\$7	Panellist 1	2	3	1	0	1	1	2	1	2
57	Panellist 2	2	1	1	0	2	1	1	1	3
58	Panellist 1	0	2	1	2	0	2	0	0	0
50	Panellist 2	0	1	1	2	0	0	0	0	0
S 9	Panellist 1	0	0	1	2	0	1	2	2	0
57	Panellist 2	0	0	2	1	0	2	1	1	0
S10	Panellist 1	1	2	1	2	1	1	0	0	0
	Panellist 2	1	2	0	2	1	1	0	0	0
S11	Panellist 1	1	1			1		0	0	0
	Panellist 2	1		0	0	1	1	0	0	0
S12	Panellist I		3	2 1		$\frac{2}{2}$		1	3	2
	Panellist 2	U	4	1	U	2		1	2	3

Table 6-2 Sensory analyses of prioritised odorants in different sewer sites

Column represents odour descriptors and retention times of peaks in GC-O

Rows represent duplicate runs for each sample analysed by two preselected panellists, intensity rating: 0=Non: 1= Low; 2=Media; 3=High; 4=Very high





Figure 6-3 Sensory characterisation of sewer emissions from two ODP panellists. The rankings represent an average odour intensity value (0-4) determined by GC O analysis on the five major odour attributors: Buttery, Citrusy, sulfurous, earthy/ fresh fruit and solvent





6.3.3 Correlation of Intensity with Chemical Concentrations

To assess the accuracy of the intensity scale rating, the results of GC-O for three common potent odorants were compared with concentrations quantified by GC-MS. Considerable variation in response was observed among analysts, which is unavoidable given the subjective nature of the sensory analysis. A comparison between results from quantitative analysis for the three odorants analysed by GC-MS and intensity ratings from GC-O at different sewer sites indicated a good relationship between the two approaches (Figure 6-5). The threshold at which odour compounds were reported as strong (intensity rating = 3) agreed with reported odour thresholds values for the three biogenic sulfur compounds. The relative potency of the solvent scents odorant (e.g. toluene) was also consistent with the olfactory results, eliciting weak-moderate olfactory responses (rating of 1) at average concentrations of 483 μ g/m³, which was significantly greater than the bottom end of the reported OTV ranges (55 μ g/m³). The maximum response for α -Pinene was at a strong intensity rating, which corresponded to average concentration of $345 \ \mu g/m^3$. While, there were also some differences in the results obtained from the two approaches. For example, hexanal had the low-moderate intensity scales (1-2) for the sewer sites we sampled, suggesting that it was the less intense odorant. However, the chemical concentration data indicated that hexanal was generally presented at the concentrations (Table 6-3) above the reported OTVs values $(250 \ \mu g/m^3)$. It is assumed dose response behaviour to chemical concentrations of all volatiles is the same and do not account for the different relative responses for various volatiles, which results in the possibly underestimates or overestimates of odour intensities in ODP analysis.

The major advantage in using OTVs is that it utilizes the better reproducibility of instrumental to determine the accuracy of human responses to determine aroma activity. However, some of the limitations of the use of this approach in determining the accuracy of the intensity scale rating are existed. In this study, the OTV values used to assess the contributions of VOCs to odour of were determined from air media, but a threshold still varies considerably due to the difference of measuring and calculating to the same material. The relevant OTVs of targeted VOCs are highly variable and reportedly up to four orders of magnitude of the investigated VOCs. Therefore, it is suggested that more accurate estimates of threshold value would strongly improve this

method for estimating odour contribution. Also, the OTV approach requires that all aroma/odour active volatiles are known and can be measured. It cannot assess new, unknown aroma components observed in GC-O studies (Table 6-2). The other major limitation of this approach involves potent aroma/odour volatiles present at trace levels. Trace level volatiles are often not quantified. Examples in this study include geosmin and acetic acid listed in Table 6-3 that cannot be assessed in this way as its analytical concentration is unknown. Both volatile were strong odorants present at low levels and could not be easily quantified because of the low signal-to-noise ratios under current developed chromatographic methodology.



Figure 6-5 Concentrations of dimethyl sulfide (DMS), toluene and α -Pinene correlated to odour intensities assigned by GC-O in 12 sewer sites (n=2 for each sites). Intensity rating: 0 = None, 1 = Weak, 2 = Moderate, 3 = Strong and 4 = Strong. Dotted lines depict reported range of odour thresholds

6.4 Summary

The identification and characterisation of odorants within the VOC suite provides an understanding of the chemicals that potentially cause a nuisance to local receptors. In total, approximately 20 odour active VOCs were ever identified in a sample of sewer emissions, predominantly characterised by odour descriptor categories of rancid/putrid (scents of heptanal), solventy/plastics (aromatics), rotten cabbage/garlic (sulfur compounds), and green/fruity/woody (terpenes). Table 6-3 summarises the volatiles with distinct odour characteristics in a sewer emission samples collected. Concentrations of odorous compounds correlated well with the measured intensity, confirming their significant characteristics as odour-active compounds in the sewer emissions. These odorants are known nuisance odorants and would most likely contribute to an overall unpleasant odour in sewer headspace air. Field samples from sewers confirmed that the target compounds quantified included those contributing to an overall characteristic odour.

	Odorants	Concentration ranges (µg/m ³)	Range of odour intensities (1-4)	Comments	
Buttery	Acetic acid	-	1-2	• Observations of acetic acid as an olfactory stimulus and not as an instrumental response reflect that ideology of low odour detection thresholds having a high olfactory response, even if below the instrumental detection	
Green /Citrusy	Hexanal	154-348	1-2	 Chemical concentrations of were not agreed with their olfactory scales Concentration present above the OTVs but less intense olfactory responses elicited Reflect the Dose response to chemical concentrations of different volatiles could be differed 	
nit	Limonene	80-585	2-3	• Chemical concentrations of were agreed with their odour scales for g-Pinene	
Earth/ resh fru	α-Pinene	10-345	1-3	and limonene by GC-O analysis and this groups	
<u> </u>	Geosmin	-	1-2	triggered moderate olfactory stimuli	
	Dimethyl sulfide	31-245	2-4	• Chemical concentrations of the three biogenic sulfur compounds were highly	
Sulfurous	Dimethyl disulfide	12-92	1-3	agreed with their odou ratings • Concentrations well above reported odour threshold	
	Diethyl disulfide	6-32	1-3	in the literature. This confirms their most significant characteristics to sewer odours	
Solventy	Toluene	25-1456	1-2	• The measured concentrations of toluene were all present above the bottom end of OTVs, triggered weak-moderate odour responses.	

Table 6-3 Odorants with significant characteristics of sewer emissions

Chapter 7 Geographic Comparative Analysis on Chemical Emissions

7.1 Introduction

The nature and magnitude of sewage-driven odour emissions can depend on several factors such as the wastewater influents characteristics (upstream discharge types, stream flow rate, temperature of wastewater), metrological conditions (rainfall, ambient temperature, humidity) and the design of collection system (drain, manholes, lift station, mixing chamber). Therefore, the profile of individual VOCs and odorants emitted from sewer networks may vary substantially from one urban area to another or from one country/region to another (Atasoy et al. 2004, Muñoz et al. 2010). Some studies on the emission of odours from sewerage systems and/or wastewater treatment plants have been undertaken (Atasoy et al. 2004, Dincer and Muezzinoglu 2008, Ras et al. 2008a), however this information neither may not represent conditions in Australia.

A one-year intensive monitoring program (consisting of multiple sampling sites and geographical locations) from June 2011 to May 2012 was performed at 18 sewer sites located in three large cities (Sydney, Melbourne and Perth) in Australia. In this chapter, VOCs/VSCs emissions from these networks will be assessed to (1) identify the range of VOCs present and typical concentrations in different distinct climatic regions and (2) identify the urban-scale concentration variations for VOCs and odorants from different geographically located sewer systems. The additional sampling during the monitoring program at different geographical scale allows for the data and conclusions present in the previous chapters 4 and 5 to be more fully appreciated in the Australian context.

7.2 Experiment Approach

Sampling Scheme

Sewer headspace air samples were collected periodically over a one year monitoring period for each of the sites. This monitoring period captures the summer period (January to March) in which peak odour emissions are commonly observed. Samples were collected on a weekly basis from each of the sites during the summer period, and then on a biweekly basis thereafter, with between 10 and 19 sampling events at each of the monitoring sites over the 1 year period (Table 7-1).

	Sydney	Melbourne	Perth	
Number of Sites	12	7	2	
Total Sampling Events	134	134	20	
Average Sampling Events Per Site	11	19	10	
Total Samples Collected	263	233	38	
Average Samples Collected Per Site	22	33	19	

Data Analysis Approach

Data reduction in terms of the number VOCs studied was a necessary first step towards identifying the broad trends in VOC emissions from the headspace air in different distinct geographical regions. The goal of this data reduction step was to prioritise VOCs that were present in higher concentrations (greater probability of being odorous) and ones that appeared more frequently in the dataset (eliminate highly site and episode specific compounds and ones that appear rarely). The prioritisation was performed using combined concentration. Data was pooled for each of the three cities, and the mean abundance per litre of gas sampled (MALGS) for each VOC was calculated (Equation7-1).

$$MALGS = \frac{\sum_{i} A_{c,i}}{\sum_{i} V}$$
Equation 7-1

Where A = Abundance; V = Sample volume (litres); i = sample number; c = VOC ID

Individual VOCs were then ranked for each city based on the MALGS. As the calibration factors on the GC-MS system do not typically vary by a factor of more than 2 to 4, VOCs with a relative MALGS of 20 to 100% of the top VOC were compiled into a list of priority VOCs for the city.

7.3 Results and Discussion

7.3.1 Variation in Meteorological Parameters

The study was based on data collected during a field monitoring program conducted at three cities (Sydney, Melbourne, and Perth) that represent three climatically distinct regions of Australia (Figure 7-1).

Sydney, with a population of 4.61 million (Australian Bureau of Statistics 2012), has a humid subtropical climate (Köppen climate classification Cfa) with an mean maximum daily temperature of 22.5°C and a mean minimum daily temperature of 14.5°C (Bureau of Meteorology 2013c). Typically, Sydney has a wetter summer than winter receiving a mean annual rainfall of 1222.7 mm over an average of 134.7 rain days per year (Bureau of Meteorology 2013c).

Melbourne, population 4.17 million (Australian Bureau of Statistics 2012), has a maritime climate (Köppen climate classification Cfb) with an average maximum daily temperature of 20.4°C and an average minimum daily temperature of 11.4°C (Bureau of Meteorology 2013a). Melbourne receives lower, less intense rainfalls than Sydney (mean annual rainfall of 602.6 mm over an average of 139 days of rain per year) although it is generally overcast with a mean of 45.8 clear days per year (Bureau of Meteorology 2013a).

Perth, with a population of 1.83 million (Australian Bureau of Statistics 2012), has a climate that is significantly distinct from that of Sydney and Melbourne. Perth is a dry summer subtropical climate (Köppen climate classification Csa) with an average maximum daily temperature of 24.8°C and an average minimum daily temperature of 12.4°C (Bureau of Meteorology 2013b). While Peth has an average annual rainfall that is similar to Melbourne (725 mm over 106.7 mean days of rain), it is a much drier city over most of the year with the majority of the rainfall occurring during the winter

months and an average of less than 3 rainy days per month during the summer (Bureau of Meteorology 2013b).



Figure 7-1 Temperature and rainfall profiles - based on data from Bureau of Meteorology (2013 a, b, c)

7.3.2 Geographic Specific Prioritised Sewer Headspace Air VOCs and Odorants *Results of VOCs*

A total of 534 samples were analysed using gas chromatography and mass spectrometry (GC-MS) to identify and quantify VOCs. Most samples had between 100 and 140 individual VOC peaks. The priority VOCs (as selected in a list of MALGS) that ranked top 20 in concentration for Sydney, Melbourne, and Perth were picked to stress out the significant components in the sewer air in different climatic conditions. An overview of the top 20 VOCs list over the whole year measurements at three cities is present in Table 7-2. A total of 30 compounds in different chemical groups appeared as the most abundant compounds in the three cities.

In general, the Melbourne sample set was dominated by alkanes followed by a small number of other compounds including acetone and propylene carbonate. Whilst, both Sydney and Perth had a wider range of VOCs and are dominative of aromatics group, although the Sydney samples generally had a higher content of halogenated compounds than their Perth counterparts. The presence of propylene carbonate is either associated with its application as an industrial organic solvent (Nie et al. 2013) as Melbourne sites we sampled had a higher content of industrial trade wastes (~37%- 38% trade wastes) within mixed sewers as indicated in **Chapter 3**. However, due to the reported lack of

industrial sewage dominated sewers, further research should be adjusted to include sewers with industrial trade wastes, in order to verify the presence of specific odorants and VOCs at an emission sample.

Family	Тор 2	0 Compounds in abundar	nce
гашну	Sydney	Melbourne	Perth
Alkane	Undecane; Dodecane; Decane; Hexane; Nonane	Heptane; Hexane; Undecane; Pentane; Decane; Pentane, 2- methyl-; Nonane; Dodecane; Butane; Cyclohexane, methyl	Decane; Undecane; Nonane; Dodecane; Hexane
Aromatics	Toluene; m,p-Xylene; Benzene, 1,2,3-trimethyl; Benzene, 1-ethyl-2- methyl-; Benzene, 1,3,5- trimethyl-; o-Xylene; Ethylbenzene; p-Cymene	Toluene; Benzene, 1,2,3-trimethyl-; m,p- Xylene; Benzene, 1- etyl-2-methyl-	Styrene; Toluene; Benzene, 1,2,3- trimethyl-; o-Xylene; Ethylbenzene; Benzene, 1,3,5- trimethyl-; Benzene, 1- ethyl-2-methyl-; m,p- Xylene; m-Cymene; p- Cymene
Halogenated Hydrocarbon	Tetrachloroethylene; Trichloromethane; Trichloroethylene; Benzene, 1,4-dichloro-;	Trichloromethane	Benzene, 1,4-dichloro-; Trichloromethane
Terpinene	Limonene; Eucalyptol; Camphene	Limonene; alpha-Pinene	Limonene; Camphene; alpha-Pinene
Others		Propylene carbonate; Acetone	

Table 7-2 City specific compounds with significant concentration throughout the year

Results of VSCs

Sulfur compound concentrations in the samples (collected simultaneous to the VOC samples discussed previously) were analysed via GC-SCD analysis. Throughout this sampling campaigns on different climatic distinctly regions, 11 VSCs of interest were identified in the collected samples, including H₂S, MeSH, EtSH, DMS, DMDS, DMDS, EMS, CS₂, DES, DEDS and DETS.

The VSCs measured from the sewer sites across all three cities were dominated by H_2S , followed by methyl mercaptan (Table 7-3). A similar range of VSCs were identified in the Sydney and Melbourne samples. Variations in the types and number of VSCs could

be observed at Perth sites. More species, i.e. ethyl mercaptan and its associated decay products (diethyl sulfide, diethyl disulfide, and diethyl trisulfide) were consistently detected at the Perth sites, but not at the Sydney or Melbourne sites. The atmospheric VSCs compositions in sewer networks in this study (Australia) is consistent with the previous reports that the VSCs is one of the most frequently produced volatile organic compounds in sewage-derived water-air samples (Escalas et al. 2003, Wu et al. 2006, Sun et al. 2014).

Prioritised VOCs were quantified for all samples and aggregated into city specific data pools for each VOC evaluated. Table 7-3 presents the statistic summaries of each of the selected compounds along with their associated OTVs. The lists for Sydney, Melbourne, and Perth were combined to form a list of 20 VOCs and 11 VSCs for subsequent quantification and evaluation.

Table /-	- Concentrations (p	<u>10 (111/8</u>	I VUUS AIIU Svdne		annic		Melhor				Part		
Family	Compounds	Ave	95th	Max	Freq	Ave	95th	Max	Freq	Ave	95th	Max	Freg (%)
	2		Percentile		(%)		Percentile		(%)		Percentile		(ar) har
	H_2S	7682	39381	130339	100	2370	9061	23698	100	141441	286885	313650	100
	MeSH	680	2330	9796	93.7	1390	4964	8462	96.6	5638	14699	18279	97.9
	EtSH	8.66	3.81	740	7.9	4.73	8.86	39.6	18.9	362	1760	3212	70.2
	DMS	87.6	248	894	93.3	194	660	1207	97.3	384	913	1032	97.9
	DMDS	15.0	47.6	195	91.3	111	530	853	95.3	39.6	79.3	137	97.9
VSCS	DMTS	10.6	33.8	75.3	88.5	44.1	169	255	85.8	35.1	98.9	373	100
	EMS	4.83	13.4	165	30.6	8.72	39.5	89.5	50.0	29.7	<i>L</i> .06	194	53.2
	CS_2	11.0	35.2	185	91.7	14.2	39.2	67.2	84.5	69.7	295	424	66.0
	DES	4.85	6.70	397	7.1	1.38	1.12	20.6	1.4	7.11	23.5	107	31.9
	DEDS	0.41	0.15	54.2	2.4	0.32	0.15	11.7	2.0	1.81	5.10	6.31	53.2
	DETS	0.52	1.72	19.1	9.1	0.00	0.00	0.00	0	6.51	23.5	107	55.3
	Decan	73.1	230	3623	55.5	13.9	0.52	1381	4.3	88.3	280	410	89.5
	Dodecane	45.4	185	955	62.7	8.89	25.7	510	29.6	37.5	140	151	86.8
A11-	3-Methylpentane	90.1	169	5052	27.4	9.96	46.2	111	46.8	0.56	0.52	2.35	2.6
VIV	Hexane	92.9	193	4478	43.0	18.3	77.8	361	33.9	4.97	16.8	51.2	42.1
	Nonane	55.4	194	2533	59.7	13.5	2.54	1255	6.4	55.5	164	301	89.5
	Undecane	74.0	311	2429	68.1	17.5	5.63	1852	6.4	73.8	213	333	89.5
	Cymene	31.9	175	732	37.6	3.22	0.31	347	2.6	531	1440	4889	76.3
	2-Ethyltoluene	63.0	189	3683	57.4	4.47	0.31	531	2.6	87.1	271	807	71.1
	Ethylbenzene	38.7	118	1650	79.9	1.56	5.10	44.2	45.9	10.9	50.2	80.3	79.0
Aro	Trimethylbenzene	155	461	9162	74.5	9.85	2.56	879	8.6	262	591	1396	86.8
	Toluene	151	527	10468	91.3	577	2790	12617	96.1	123	281	1750	89.5
	m,p-Xylene	170	368	8668	75.7	5.92	10.3	430	42.9	11.6	48.7	99.5	52.6
	o-Xylene	44.7	123	7146	33.8	1.01	2.58	65.1	25.8	15.0	40.4	336	50.0
	1,4-Dichlorobenzene	44.8	228	834	40.3	7.31	1.05	469	4.3	87.3	246	568	65.8
Hal	Tetrachloroethylene	352	1226	24799	72.6	4.51	36.5	72.6	10.7	13.7	21.6	357	34.2
	Trichloromethane	106	387	950	82.9	71.9	234	432	76.8	25.9	55.2	286	86.8
Tarn	α-Pinene	16.1	81.5	319	6.99	4.96	7.06	251	20.6	22.5	127	264	26.3
ıcıp	Limonene	130	712	1217	83.3	11.9	7.89	655	42.5	61.9	268	541	29.0

and Parth centrations (11a/m³) of VOCs and VSCs in Sydney Melha Tahla 7.3 Con

7.3.3 Geographical Variations in Concentrations of Key Compounds

Geographical Variations of VOCs Concentration

Concentration distributions for each of the VOCs are presented in Figures 7-2 (a, b, c) according to their different chemical families. A similar distribution of alkanes and aromatics were observed in the Sydney and Perth samples, with generally higher concentrations and detection frequencies in the samples collected in Perth. The Melbourne sites were characterised by lower concentrations of alkanes and aromatics that were infrequently detected. The sole exception for Melbourne was toluene, which was by far the highest concentration VOC measured in the samples and was detected with a high frequency (present in 96% of all samples analysed). Alkane and aromatic concentrations were generally less than 200 μ g/m³, with the exception of toluene and trimethylbenzene in Sydney, cymene and trimethylbenzene in Perth, and toluene in Melbourne.

Trichloromethane was the sole halogenated hydrocarbon (Figure 7-2 b) that was regularly observed in the Melbourne samples, while 1,4-dichlorobenzene and trichloromethane were consistently observed in Perth. All three halogenated hydrocarbons (1,4-dichlorobenzene, tetrachloroethylene, and trichloromethane) were consistently detected at the Sydney sites, with tetrachloroethylene being observed at the greatest concentrations. The terpenes (α -pinene and limonene) were consistently identified in the samples collected from Sydney (Figure 7-2 c), but were less frequently detected in Melbourne and Perth. Propylene carbonate was only detected in the Melbourne samples and appeared consistently across the sites.

Measured concentrations of halogenated hydrocarbons, terpenes and propylene carbonate were typically less than 250 μ g/m³, although the concentrations of tetrachloroethylene in Sydney were highly variable with some episodes of higher concentrations observed.

Considering the 95th percentile values, nearly all of the VOC concentrations were well below their associated OTV range. The exceptions were trimethylbenzene and limonene in Perth, and m-, p-xylene and limonene in Sydney. These concentrations were, however, at the low end of large OTV ranges, for examples a 95th percentile concentration of 368 $\mu g/m^3$ of m,p-xylene in Sydney compared to an OTV range of 52 - 86,000 $\mu g/m^3.$



Figure 7-2 Concentrations of alkanes (a); Aromatics (b); Halogenated (c) and Terpenes in sewer headspace air at three cities; Error bar represent the Standard Error (\pm SE)

Geographical variations of VSCs concentration

Observed VSC concentration ranges for each of these compounds over the entire dataset on a city by city basis are provided as Figure 7-3. In general, the sulfur concentrations were of similar order of magnitude between the sites, with the Melbourne sites having higher sulfur compound concentrations than the Sydney sites and markedly high concentration of sulfur were emitted from sewers in Perth (3-4 times greater than Sydney and Melbourne sites). H_2S was the only compound that was detected in a greater concentration in the Sydney sites (annual mean: 7682 μ g/m³) compared to the Melbourne sites (annual mean: $2370 \ \mu g/m^3$). If we consider that equivalent wastewater discharge occur into these two large cities and that similar upstream conditions (in terms of industrial containing domestic sewage), the observed increase in the annual non- H_2S VSCs concentration for Melbourne could be explained with the difference in prevailing rainfall profiles for the two cities. During the studied period, relatively dry weather was recorded in Melbourne (range: 34 ~113 mm, mean: 59.5, totally: 713 mm) whereas Sydney had significantly wetter conditions with a total rainfall about 1507 mm (range: 37~269 mm, mean: 125.6 mm) as present at Figure 7-1. The higher concentrations observed in Perth maybe the result of samples (to date) only been conducted during the summer period (November 2012 to February 2013) such representing the peak sewer emission period.

Most measured VSC concentrations were above the reported odour threshold value ranges (Table 7-3) and are expected to be significant contributors to odour emissions from sewers. The implication of these results is that mercaptan and sulfides should be considered in addition to H_2S in odour abatement process design and performance assessment.



Figure 7-3 Concentrations of individual VSCs in sewer headspace air at three cities; Error bar represent the Standard Error (±SE)

The difference in VSCs concentrations between the three geographic points (Sydney vs Melbourne, Sydney VS Perth, and Melbourne VS Perth) was evaluated by t-test (Table 7-4). The dataset for the t-test was log-transformed to fit with Gaussian distribution and the value of the halved MDL was used in the dataset for non-detected VSCs due to statistics requirements. The results indicate that the variation in most of the cases were statistically significant with the most significance been observed for the more abundant compounds (i.e. H_2S , MeSH and DMS), with the exception being CS_2 . The geographical distribution patterns observed for CS_2 is most likely to be influenced by meteorological factors but further analysis is needed. The analysis showed that a simple comparison of the VSCs data (in terms of geographic difference) could be employed as an efficient analysis criterion to distinguish their spatial patterns.

 Table 7-4 Statistical summary of concentration of VSCs in the sewer emissions at

 three Australian cities

VSC	Sydney V	S Melbourne	Sydney V	VS Perth	Melbourr	ne VS Perth
VSCS	P value	t value	P value	t value	P value	t value
MeSH	0.0023	3.108	< 0.001	7.957	0.0011	3.346
DMS	0.0001	3.969	0.0008	4.135	0.0055	3.165
CS_2	0.6292	0.483	0.0012	3.911	0.0014	3.848
DMDS	< 0.01	4.912	0.0039	3.362	0.3489	0.9454
DMTS	0.0002	3.816	0.0885	1.814	0.2387	1.222

7.4 Summary

Monitoring of VOCs in sewer headspace air across three Australian cities identified a list of 30 dominant VOCs, which consisted of alkanes, aromatics, halogenated hydrocarbons, terpenes, and a carbonate ester. Generally, most measured VOC concentrations were less than 250 μ g/m³, although some VOCs (toluene, trimethylbenzene and cymene) were present at higher concentrations for some of the cities studied. Significantly greater VOC concentrations (in the order of 1,000 to 25,000 μ g/m³) were observed at a low frequency, and could be related to specific trade waste discharges and/or sewer catchment characteristics however further analysis is needed to confirm these correlations. Given that a similar range of VOCs (and in many cases similar dominant VOCs) have been identified in sewer headspace air and sewage across diverse countries and climatic regions, the data and conclusions presented in this chapter are not restricted to the Australian context and is useful for identifying the odour

Measured VSCs compounds from sewer sites across all three cities were dominated by H_2S and MeSH. The yearly measurement data, generally fell into a wide range of concentrations across the sampled sewer sites located in three geographical cities. Statistical analysis of the VSCs emissions in the different urban locations showed that variations in the emitted VSCs were significantly differed due to the geographical locations. Generally, the emission patterns observed between the three cities was in most cases distinguishable, confirming the possibly important role of geographic conditions played for most of targeted VSCs. Therefore, according to the difference, it is recommended that the characterisation of odour emissions, as well exposure risk aroused by VSC components, at the sewer atmospheres should be assessed on different climatic scales.

Chapter 8 Conclusions and Recommendations

8.1 Introduction

As a high rate chemical and biological reactor with aerobic, anoxic, and anaerobic environments, sewage collection networks are suggested as the major contributor to the offensive emissions that result in odour complaints for water utilities in Australia. Recent expansion in the urban population in Australian cities has resulted in an increased pressure upon the effectively management of these emissions. This project commenced with the principle objective to develop a detailed understanding of the gas phase emissions from different sewer networks in Australia. This was implemented with three primary components: (i) the development and optimisation of analytical methodology to reliably determine and quantify the compounds of interests that would be present at the sewer networks; (ii) leading to the chemical speciation of VSCs and VOCs to procedure accurate and precise datasets that are representative of the emissions from sewer sties being sampled from across different Australia climates; and (iii) the identification and subsequently prioritisation the odorant species within the VOCs using simultaneous mass spectrometry and olfactory stimulus detection (ODP).

A summary of the key results obtained in this work is presented as Section 8.2. Recommendations and prospective directions are provided in Section 8.3 for future work to address identified knowledge gaps and limitations in the chemical assessment of emissions from sewage collection networks.

8.2 Conclusions

8.2.1 Conclusions from Methodology Development

Analytical methods were developed to optimise for the determination of a wide range of VSCs and VOCs from sewer emissions by TD-GC-SCD and TD-GC-MS as demonstrated in **section 4.2** and **section 5.2**, respectively. Various factors affecting these techniques have been studied in order to achieve high recoveries for most of the analytes. Table 8-1 summarise the optimised operating parameters for the thermal desorption stage of the analysis for VOCs and VSCs.

Table 8-1 Instrument controlling parameters for the thermal desorption of bag(for VSCs) and sorbent tube (for VOCs)

Parameters	VSCs	VOCs
Adsorption Temperature/Tube Desorption	-20 °C	275°C
Sampling Flow	10 ml/min	50 mL/min
Desorption Temperature	270 °C	290 °C
Desorption Flow (split + column flow)	~ 6 ml/min	22.5 mL/min
Trap hold	5.0	5 mins
Flow Path Temperature	80 °C	150 °C
Split Mode (Y/N)	Y	Y (trap)

The most appropriate sorbent material was selected as Tenax TA to acquire optimum capture capacity for VOCs from sewer emissions. Breakthrough tests showed that there is no significant breakthrough when 5000 ppmv stock solution was spiked into the Tenax sorbent tubes (breakthrough volume <1%). To fully resolve all targeted VSCs and enable good TD recoveries, particularly for good separation of the less volatile compounds (e.g. H₂S, MeSH), the optimum GC configuration was determined as an initial temperature of 37 °C, ramping at 15 °C/min with a flow of 1 ml/min.

The developed methods presented high precision (RSD < 10%) and good linearity ($R^2 > 0.99$) for all the compounds being tested, which showe them as suitable and promising methods to measure VSCs and VOCs at trace level (sub-pptv). The method

8.2.2 Conclusions from Chemical Speciation

The chemical speciation provided an extensive list of volatile components. The dominant chemical species within the captured analytes consisted of alkanes, aromatics, halogenated hydrocarbons, terpenes, and sulfur compounds as characterised in **section 4.3 and section 5.3.** The further sampling of emissions at different geographical scales of this project are presented at **Chapter 7**, which allowed for the conclusions to be more fully appreciated in the Australian context, an indicated a similar range of VOCs and VSCs have been identified in sewer headspace air across diverse countries and climatic regions. However, measured VSC concentrations from the Perth sampling sites (representing a tropical climate) were significantly higher than those at more temperate climate cities (Sydney and Melbourne). This indicated the important role that climatic conditions played in the emission of VSCs at sewer networks.

Conclusions from VSCs Speciation

Monitoring of VSCs in sewer headspace air across 12 sewer sites identified that the dominant species were hydrogen sulfide, methyl mercaptan and dimethyl sulfide, and that these were measured in relatively significant amounts, in the order of tens to hundreds of μ g/m³, whereas other sulfur species were present at trace levels, roughly ~ 10 μ g/m³ (section 4.3.1).

The assessment of seasonal-temporal variability of VSCs concentrations indicated that seasonal variations of VSC concentrations were observed to generally follow the trends of cold season (winter) low and warm seasons (summer, autumn) high. Significant seasonal differences (p < 0.05) were observed between winter and either of other three seasons, having mean seasonal concentrations differences by a factor of two. The observed seasonal patterns can be explained by climatic conditions (for Sydney) where significant lower average temperature and relatively lower rainfall were measured during winter sampling sessions according to the long-term (20 years) meteorological records. Inter-site comparisons also showed spatial variability across the 12 sampled

sewer sites, with peak concentrations for the different VSCs, up to 7-24 times greater than the other measured concentrations.

Overall, strong correlations between VSC species were generally observed as discussed in **section 4.3.4**, supporting previous conclusions that the production of VSCs was more likely due to anaerobic processes in the sewer network rather than wastewater discharge characteristics. Three VSCs pairs (H_2S -MeSH, DMS-CS₂ and DMDS-DMTS) were moderate to highly correlated, suggests the volatilisation processes, in addition to biodegradations, may also play a major role as a source for the origin of sewer headspace VSCs.

Conclusions from VOCs Speciation

Non-target screening analyse observed 585 VOCs during the 24 months sampling program. 25 compounds were selected (in terms of frequency and abundance of detection, potential malodour and healthy impacts) and were further quantified. Aromatics, monocyclics, alkanes and halogenates were found to be a significant percentage of the total VOC concentrations measured in the sewer headspace air. Generally, most measured VOC concentrations were less than 130 μ g/m³ (section 5.4.3).

The random-effects model, with the assist of principle component analyses (PCA) confirmed that the temporal component of the variation were more dominant, with temporal variances general larger than the spatial ones for most of investigated VOC species. However, the spatial variations of VOC concentration are also significant for some VOC analysts, ascertained by one-way ANNOVA analysis. These results suggest the necessity of undertaking multiple monitoring sites over a significant period of time (e.g. more than one year) for understanding the headspace VOCs at sewer air. Temporal variations of concentration were observed to follow the trends of cold season low (winter) and warm seasons (summer, autumn) in most of the chemical classes.

To provide a greater understanding of the influence of short-term sewer conditions on emission variability in addition to the knowledge we obtained from long-term emissions monitoring, a diurnal study was undertaken at the pump station (S2) to represent a typical diurnal hydraulic cycle of a sewer networks using 2-hour composition samples. The concentrations of aromatics, terpenes and alkanes varied significantly during the day while halogenated compounds were observed to fluctuate at relatively narrow range of concentrations. The maximum concentration of all the species was constantly measured after the mid-day. The diurnal distribution of the VOCs is more likely explained by the hydraulic characteristics (e.g. temperature, gas flow, and discharges amount in sewage) and their volatility (i.e. temperature driven) potentials between aqueous-gaseous interfaces.

Conclusions from Geographic comparative analysis on Chemical Emissions

Monitoring of VOCs in sewer headspace air across three Australian cities confirmed the dominant chemical group compositions of alkanes, aromatics, halogenated hydrocarbons, terpenes as illustrated in **Chapter 4**. Given that a similar range of VOCs (and in many cases similar dominant VOCs) have been identified in sewer headspace air and sewage across diverse countries and climatic regions, the data and conclusions presented of this study are not restricted to the Australian context and is useful for identifying the odour implications of sewer headspace VOCs for the wider industry.

Whilst, measured VSCs compounds from sewer sites across all three cities were dominated by H₂S and MeSH. The yearly measurement data, generally fell into a wide range of concentrations across the sampled sewer sites located in the three geographical cities. Statistical analysis of the VSCs emissions in the different urban locations showed that variations in the emitted VSCs were significantly differed due to the geographical locations. The emission pattern observed between the three cities was in most cases distinguishable according to ANNOVA results (section 7.7.3), confirming the possibly important role that geographic conditions played for most of targeted VSCs. Therefore, according to the observed difference, it is recommended that for the characterisation of odour pollution, as well exposure risk at sewer atmospheres, VSCs should be assessed at different climatic scales.

8.2.3 Conclusions from Odorants Identification and Prioritisation

The identification and characterisation of the odorants within the VOC suite provides an understanding of the chemicals that potentially cause annoyance to local receptors. In total, approximately 20 odour active VOCs were identified in the sewer headspace emissions. These were predominantly characterised by odour descriptor categories of rancid/putrid (scents of pyridine and heptanal), solventy/plastics (aromatics), rotten cabbage/garlic (sulfur compounds) and green/fruity/woody (terpenes). Concentrations of the odorous compounds correlated well with the measured intensity. These odorants are known nuisance odorants and would most likely contribute to an overall unpleasant odour from sewer networks. Field samples from sewers confirmed that target compounds quantified included those contributing to the overall characteristic odour.

8.2.4 Implication related to Future Monitoring Campaign Design

The findings from the field emission data provided for implications in the context of future monitoring campaign designs. As discussed in Section 4.4.6, strong and consistent correlations between seasonal and annual values among the measured VSCs indicates that autumn and spring sampling campaigns were more representative of the annual concentrations, whereas comparisons between annual CV with seasonal CV suggested that the spatial variability in the summer season provided the best representation for annual variability. In this study, there is no single sampling site that represented the annual means. This conclusion supports the importance of extensive spatial samplings to better characterise VSCs temporal variability in sewer environments. However, when resources are limited (i.e. costs, labour) a single season sampling (spring and autumn) at particular sewer sites (S4 and S10) will provide an estimation of long-terms VSCs trends with the Sydney sewer network. Based on the inter-species results obtained for the three correlated pairs, volatility of VSCs could be used as a factor to approximate the changing trends of compounds exhibiting similar volatile properties. This will further benefit monitoring, due to the probability of reducing the targeted analysts (VSCs).

Similarly in **Chapter 5**, the results from the VOC emission dynamics, highlighted the importance of sample timing and understanding the short-term variability in terms of sample representation from sewer networks. As the maximum odour and specific odorants concentrations was peaking at early evening, where typical sample collection (during working hours) may underestimate the emission loading for odour monitoring and odour abatement process design.

8.3 Recommendations and Future Direction

As this investigative study progressed towards the principle outcome of establishing a reputable list of VOCs and odorants emitted from sewage collection networks in Australia. Understanding and insight was gained into the primary source of the nuisance odours. A number of research questions remain to be addressed. A summary of residual research questions based on this research program, along with recommendations for future work is provided:

Monitoring Techniques

- 1) The sampling component of the analysis chain remains a source of weakness due to the continued existence of significant knowledge gaps. There exists a lack of stability studies with regards to the fate and transformation of odorants in sample containers, as well as odorant transformation during analysis. Further research and development is required to address these issues, particularly dedicated to sulfur sampling and analysis methodologies due to highly reactive nature of those compounds and the transportation challenges in Australia.
- 2) The monitoring techniques employed in this study, the quality control and quality assurance for sampling and analysing VO(S)Cs and odorants still has areas for improvement in terms of the quality and representativeness of the quantified data. Further investigation should focus on the introduction of surrogate standards into a gas sample matrix to correct the loss during the sampling and analysis procedures. Research is needed to improve the quantifications of a broad range of VOCs when limited or no standards are available, it is recommended to develop a strategy in terms of the determination of a relative response factor being representative for a group of analytes with similar functionalities and electron impact fragmentation patterns.
- 3) Due to limitations in analysing these nitrogen or and sulfur containing compounds using sorbent tubes and GC-MS analysis, further GC-olfactory assessment via dedicated nitrogen/sulfur analysis would be required to resolve those odour peaks.
- 4) Real-time measurements techniques (e.g. proton transfer-reaction mass spectrometry (PTR-MS) and selected ion flow tube mass spectrometry (SIFT-MS) provide a direct method without sample collection and preparation and have

previously been used for measuring odorous compounds from different operations. Investigation of the applicability of on-line techniques for monitoring the sewer odorous emissions will be of interest for the further work to (i) directly characterisation of emission sources; (ii) compare/validate/supplement the emission data we obtained from GC measurements.

Chemical and Odorants Speciation and Characterisation

- Sewer headspace VOCs are generally unlikely to be a significant contributor to sewer odours and VOC monitoring is not recommended for characterising these odours. VOC monitoring is, however, recommended for sites with a history of significant trade waste discharges or where the odour character descriptors are typical of VOCs.
- 2) In order to accurately determine sources of nuisance emissions with the aim of abatement and mitigation, further studies are need to determine which VOCs may have an impact on the effectiveness of odour abatement processes. Additionally, evaluation is also needed to determine the fate of nuisance chemicals in odour abatement technologies and any impacts on their removal performance (particularly with regards to adsorption based systems).
- 3) Due to the reported lack of industrial sewage dominated sewers (as indicated in Chapter 3), further research should be adjusted to include sewers with industrial trade wastes, in order to identify the significant odorants and VOCs present at an emission sample.

Liquid Phase Monitoring and Analysis

Further research is required to evaluate the potential for linkages between liquid phase conditions and sewer odorants in order to identify a swift and cheaper predictor of key odorants emitted from sewers.
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APPENDICES

VOCs compounds	S1		S2		S3		S4		S5		S	6
	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre
Alcohols												
Ethanol												
Benzyl Alcohol									+	5.6		
Halogenates												
Trichloromethane	+	82.9	+	94.3	+	95	+	81.1	+	94.4	+	93.5
Ethane, 1,1,1-trichloro-									0	27.8		
Methane, dichloro-	0	39	0	28.6	0	35	0	24.3	0	36.1	0	38.7
Methane, bromodichloro-	0	36.6	0	91.4	0	52.5	0	86.5	+	97.2	0	71
Trichloroethylene	+	78	0	97.1	0	80	+	5.4	+	91.7	+	83.9
Benzene, 1,2-dichloro-	0	9.8	0	14.3	0	25	+	13.5	+	8.3	0	19.4
Benzene, 1,4-dichloro-	+	31.7	+	40	0	35	0	45.9	+	69.4	+	51.6
Methane, dibromochloro-	0	9.8	0	11.4			+	13.5	0	33.3	0	22.6
Tetrachloroethylene	++	78	++	37.1	+	97.5	++	67.6	+++	94.4	++	90.3
Ethene, 1,2-dichloro-, (Z)-	0	19.5	0	22.9	0	17.5			0	38.9	0	29
Ethene, 1,2-dichloro-, (E)-	0	29.3	0	17.1	0	17.5			0	19.4	0	38.7
Benzene, 1,3-dichloro-	0	26.8	0	8.6	0	12.5	0	21.6	+	8.3	0	16.1
Aromatics												
Benzene	0	36.6	0	42.9	0	17.5	0	27	0	44.4	0	25.8
Naphthalene	0	17.1	0	8.6	0	12.5	0	13.5	+	38.9	+	12.9
o-Xylene	+	24.4	++	31.4	0	32.5	+	40.5	+	52.8	+	32.3
Benzene, 1,2,4,5-tetramethyl-	+	39	+	28.6	0	30	0	24.3	+	47.2	+	45.2
Cumene	0	29.3	0	20	0	10	0	10.8	0	5.6		
p-cymene	0	36.6	+	31.4	+	30	++	24.3	+	38.9	+	25.8
Ethylbenzene	+	80.5	++	62.9	0	60	0	78.4	+	94.4	0	83.9
m,p-Xylene	+++	61	+++	65.7	+	62.5	+	73	++	80.6	+	74.2
Benzene, 1,3,5-trimethyl-	+	43.9	++	25.7	+	45	+	45.9	+	66.7	+	64.5
Toluene	++	80.5	+	88.6	+	82.5	+	91.9	++	97.2	+	90.3
Benzene, 1,2,3,4-tetramethyl-	0	51.2	+	28.6	0	30	0	18.9	+	41.7	+	35.5
Benzene, 1,2,3-trimethyl-	++	68.3	++	45.7	+	55	++	45.9	+	75	++	51.6
Benzene, 1,2,3,5-tetramethyl-	0	31.7	+	28.6	0	22.5			0	11.1	0	22.6
Benzene, 1-methyl-2-(1-methylethyl)-	+	36.6	+	37.1	+	27.5	++	24.3	+	38.9	+	45.2
Benzene, 1-methyl-3-(1-methylethyl)-	0	17.1	+	20	0	15	+	21.6	+	22.2	+	16.1
Benzene, 1-ethyl-2-methyl-	+	65.9	++	34.3	+	27.5	+	51.4	+	66.7	+	67.7
Benzene, 1-ethyl-3-methyl-	0	41.5	+	34.3	+	35	0	54.1	+	50	+	48.4
Benzene, 1-ethyl-2,3-dimethyl-	0	26.8	+	14.3	0	15	0	16.2	+	33.3	0	19.4
Benzene, 4-ethyl-1,2-dimethyl-	0	19.5	0	17.1	0	12.5	0	5.4	0	16.7	+	12.9
Benzene, 2-ethyl-1,4-dimethyl-	0	26.8	0	8.6	0	20	0	16.2	0	11.1	+	19.4
Benzene, 1,2,4-TRIMETHYL	0	17.1	+	14.3	+	20	0	18.9	0	16.7	0	12.9
Benzene, propyl-	+	7.3	0	5.7	+	7.5						
Benzene, 1-ethyl-2,4-dimethyl-	0	12.2	++	8.6					+	8.3	+	6.5
Benzene, 1-methyl-2-propyl-	0	14.6	0	11.4			0	10.8	+		+	6.5
Benzene, 1-methyl-3-propyl-	+		+	8.6	+		0	5.4				
Styrene	+	34.1	0	11.4	+	15	0	29.7	0	13.9	0	19.4

Table A-1 VOCs identified by non-target screening in the atmosphere of sewer networks (complete list)

VOG someounds	S	7	S8		S9		S10		\$11		S	12
VOCs compounds	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre
Alcohols												
Ethanol	0	7.7									0	27
Benzyl Alcohol					0						+++	18.9
Halogenates												
Trichloromethane	+	61.5	+	80	0	64.9	0	78.1	0	59.3	++	81.1
Ethane, 1,1,1-trichloro-												
Methane, dichloro-	0	30.8	0	36	0	16.2	0	15.6	0	7.4	0	21.6
Methane, bromodichloro-	0	53.8	0	16	0	52.7	0	68.8	0	25.9	0	70.3
Trichloroethylene	0	46.2		0	0	9.5	0	0	0	37	0	81.1
Benzene, 1,2-dichloro-	+	15.4	0	8	0	10.8	0	18.8	0	14.8	0	16.2
Benzene, 1,4-dichloro-	++	34.6	+	8	0	36.5	0	34.4	0	25.9	+	35.1
Methane, dibromochloro-					0	25.7					+	13.5
Tetrachloroethylene	+++	88.5	0	32	0	39.2	0	40.6	+	74.1	++	89.2
Ethene, 1,2-dichloro-, (Z)-									0	11.1	0	13.5
Ethene, 1,2-dichloro-, (E)-	0	7.7									0	21.6
Benzene, 1,3-dichloro-	++	15.4	0	12	0	23	0	12.5			+	21.6
Armoatics												
Benzene	0	19.2	0	12	0	9.5	0	12.5	0	11.1	0	10.8
Naphthalene	+	42.3	0	12	0	10.8	0	9.4	0	11.1	0	8.1
o-Xylene	++	30.8	0	20	0	21.6	++	34.4	+	22.2	++	43.2
Benzene, 1,2,4,5-tetramethyl-	+	57.7	0	12	0	8.1	0		+	7.4	+	51.4
Cumene	++	15.4	0	12			0	9.4				0
p-cymene	+	11.5	0	16	0	17.6	0	6.3	0	11.1	+	37.8
Ethylbenzene	++	92.3	0	36	0	45.9	0	68.8	0	55.6	+	73
m,p-Xylene	+++	84.6	+	52	0	47.3	+	71.9	0	48.1	++	62.2
Benzene, 1,3,5-trimethyl-	+++	38.5	+	12	+	32.4	+	31.3	+	37	+	43.2
Toluene	++	96.2	+	68	+	77	+++	87.5	+	88.9	++	75.7
Benzene, 1,2,3,4-tetramethyl-	+	23.1			0	5.4			0	18.5	+	29.7
Benzene, 1,2,3-trimethyl-	+++	61.5	+	28	0	23	+	50	++	37	++	54.1
Benzene, 1,2,3,5-tetramethyl-	++	30.8			0	2.7					0	8.1
Benzene, 1-methyl-2-(1-methylethyl)-	++	34.6	+	40	0	17.6	+	25			++	35.1
Benzene, 1-methyl-3-(1-methylethyl)-	++	26.9	+	8	0	6.8	0	12.5	0	11.1	+	13.5
Benzene, 1-ethyl-2-methyl-	+++	50	+	24	0	27	+	43.8	+	33.3	+	40.5
Benzene, 1-ethyl-3-methyl-	+++	34.6	0	12	0	25.7	0	43.8	0	33.3	0	24.3
Benzene, 1-ethyl-2,3-dimethyl-	++	19.2	0	16	0	8.1	0	9.4			+	18.9
Benzene, 4-ethyl-1,2-dimethyl-	+	26.9		0	0	4.1			0	7.4	+	13.5
Benzene, 2-ethyl-1,4-dimethyl-	++	15.4			0	2.7					+	10.8
BENZENE, 1,2,4-TRIMETHYL	+++	15.4	0	12	0	14.9	+	12.5	0		+	10.8
Benzene, propyl-	++	7.7	0									
Benzene, 1-ethyl-2,4-dimethyl-	+++	19.2	0		0	2.7	+				0	10.8
Benzene, 1-methyl-2-propyl-	++	11.5	0	12	0	2.7					+	
Benzene, 1-methyl-3-propyl-	+++	15.4	0						+			
Styrene	+	19.2	0	8	0	20.3	0	6.3	0	11.1	0	24.3

	S1		S2		S3		S4		S5		S	6
	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre
Sulfides												
DMS	0	43.9	0	31.4	0	40	0	35.1	0	41.7	0	45.2
DMDS	0	78	0	80	0	82.5	0	91.9	0	91.7	0	74.2
DMTS	+	17.1	0	22.9	0	47.5	0	18.9	+	27.8	0	35.5
Alkanes												
Butane, 2,2-dimethyl-												
Butane, 2-methyl-	0	24.4	0	28.6	0	17.5	+	5.4	0	25	0	19.4
Pentane, 3-methyl-	0	19.5	0	28.6	0	17.5	0	5.4	0	22.2	0	12.9
Pentane, 2-methyl-	0	22	+	25.7	0	27.5	0	10.8	0	27.8	0	22.6
Pentane	0	4.9	0	37.1	0	12.5		0	+	8.3	0	9.7
Hexane	0	51.2	+	42.9	0	45	0	29.7	0	44.4	0	32.3
Octane	0	19.5	+	22.9			0	21.6	+	5.6	+	25.8
Nonane	0	41.5	+	40	0	20	+	67.6	0	63.9	+	61.3
Dodecane	+	51.2	++	57.1	0	35	0	56.8	++	58.3	+	54.8
Decane	0	46.3	+	45.7	0	7.5	+	67.6	+	50	+	61.3
Heptane	0	51.2	+	42.9	0	15	0	54.1	0	38.9	0	35.5
Pentane, 2,3-dimethyl-												
Pentane, 2,3,4-trimethyl-			+	11.4					+	8.3	0	9.7
Hexane, 3-methyl-	0	26.8	+	25.7	0	17.5	+	10.8	0	19.4	0	25.8
Hexane, 2,4-dimethyl-	0	4.9	0	28.6	0	5	0	10.8	0	8.3	0	12.9
Heptane, 4-methyl-	0	4.9	+	17.1					0	5.6	0	6.5
Heptane, 3-methyl-	0	12.2	+	22.9			+	8.1	+	13.9	0	29
Heptane, 2-methyl-	0	12.2	+	22.9			0	5.4	0	13.9	0	29
Tridecane	0	12.2	+	20	0	7.5	0	13.5	+	36.1	0	12.9
Tetradecane	+	4.9	0	8.6					+	13.9	0	6.5
Undecane	+	61	+	48.6	0	35	+	64.9	+	72.2	+	67.7
Heptane, 2,5-dimethyl-			0	17.1							0	9.7
Octane, 3-methyl-	0	12.2	0	31.4			0	21.6	0	13.9	0	32.3
Heptane, 2,3-dimethyl-	0	9.8	0	20			0	32.4	0	16.7	0	32.3
Heptane, 3-ethyl-2-methyl-	0	4.9	+	17.1			0	10.8	+	25	+	22.6
Hexane, 2,3-dimethyl-			0									
Nonadecane	0								++	5.6	0	
Heneicosane	++	4.9	++				0		++	11.1		
Octane, 2,6-dimethyl-			+	11.4	+		+	8.1	+		+	9.7
Decane, 2-methyl-			++	8.6			+	5.4	++	13.9	+	12.9
Terpenes		-			-				1	-	1	
Camphene	+	31.7	+	45.7	0	22.5	0	54.1	+	30.6	+	45.2
alpha-Pinene	0	41.5	0	54.3	0	30	0	54.1	0	72.2	0	48.4
gamma-Terpinene	+	12.2	0	8.6	0	5	0	35.1	+	41.7	0	9.7
alpha-Terpinene	+	26.8	+	17.1	0	17.5	+	35.1	+	52.8	0	22.6
Limonene	++	63.4	++	62.9	+	30	+++	59.5	++	66.7	++	58.1
Eucalyptol	+	48.8	+	11.4	0	25	+	37.8	+	36.1	+	51.6

VOCs compounds	S7		S8		S9		S10		S11		S	12
	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre
Sulfides												
DMS	0	30.8	0	52	0	14.9	0	50	0	3.7	0	37.8
DMDS	+	57.7	+	76	0	66.2	0	87.5	0	48.1	+	75.7
DMTS	+	23.1	+	72	0	21.6	0	40.6	0	25.9	+	40.5
Alkanes												
Butane, 2,2-dimethyl-	0	30.8										
Butane, 2-methyl-	++	34.6					0	12.5			0	29.7
Pentane, 3-methyl-	+++	46.2					0	9.4			0	24.3
Pentane, 2-methyl-	+++	61.5					0	18.8			+	29.7
Pentane	++	42.3									+	10.8
Hexane	+++	76.9	0	8	0	9.5	0	12.5	0	7.4	+	51.4
Octane	++	30.8	0	32	0	5.4	0	40.6	+	11.1	++	13.5
Nonane	+++	38.5	0	48	0	40.5	+	75	+	25.9	+	54.1
Dodecane	+	53.8	0	24	+	58.1	+	65.6	0	55.6	++	59.5
Decane	+++	46.2	0	36	+	44.6	+	65.6	++	25.9	++	48.6
Heptane	++	57.7			0	12.2	0	34.4	0	18.5	+	21.6
Pentane, 2,3-dimethyl-	++	42.3									0	5.4
Pentane, 2,3,4-trimethyl-	++	30.8										
Hexane, 3-methyl-	+++	65.4			0	2.7	0	9.4			0	40.5
Hexane, 2,4-dimethyl-	+	61.5					0	12.5			0	21.6
Heptane, 4-methyl-	++	46.2					0	6.3			0	16.2
Heptane, 3-methyl-	++	30.8					0	9.4			0	24.3
Heptane, 2-methyl-	0	19.2					0	9.4			0	27
Tridecane	+	30.8	0	12	0	23	0	25			+	35.1
Tetradecane	0	26.9	0	8	0	18.9	0	18.8	0	22.2	+	16.2
Undecane	++	50	0	40	+	56.8	+	75	+	44.4	++	64.9
Heptane, 2,5-dimethyl-	+	26.9				0	0	6.3				
Octane, 3-methyl-	+	19.2	0	8	0	13.5	0	25		3.7	0	32.4
Heptane, 2,3-dimethyl-	+	34.6					0	21.9			0	32.4
Heptane, 3-ethyl-2-methyl-	++	65.4			0	2.7	0	9.4	0	14.8	+	24.3
Hexane, 2,3-dimethyl-	++	11.5										
Nonadecane	+		0				0	6.3			0	5.4
Heneicosane	+		0		0	2.7	0				+	
Octane, 2,6-dimethyl-	++	15.4	0		0	5.4	+	15.6	++		++	5.4
Decane, 2-methyl-	+	7.7			+	8.1	+	12.5	++		+	10.8
Terpenes					-							_
Camphene	+	34.6	+	36	+	36.5	0	46.9	0	63	0	24.3
alpha-Pinene	+	73.1	0	36	0	29.7	0	56.3	0	11.1	+	45.9
gamma-Terpinene		0	+	20	0	10.8	+	15.6			+	16.2
alpha-Terpinene	+	11.5	++	24	0	18.9	++	25			++	21.6
Limonene	++	80.8	+	32	+	52.7	+	65.6	0	63	++	27
Eucalyptol	+	34.6	+	32	0	43.2	+	53.1	0	37	+	40.5

		S1		S2		S3		S4		S5		6
vocs compounds	Ab	Fre										
Cyclics												
Naphthalene, decahydro-	0	24.4	+	17.1	0	25	+	21.6	+	38.9	+	25.8
Cyclopentane, methyl-	0	19.5	0	28.6	0	17.5	0	5.4	0	22.2	0	9.7
Cyclohexane, methyl-	0	53.7	+	37.1	0	32.5	0	24.3	0	55.6	0	54.8
Cyclohexane	0	19.5	0	17.1	0	30	0	5.4	+	36.1	0	16.1
Naphthalene, decahydro-, trans	0	17.1		0	0	10	0	16.2	0	25	0	41.9
Cyclohexene, 1-methyl-4-(1-methylethy	0	9.8	0	20	0	12.5	+	37.8	+	27.8	0	16.1
Cyclohexane, 1,3-dimethyl-	0	4.9	+	8.6							0	6.5
Cyclohexane, 1,3-dimethyl-, cis-	0	9.8	+	14.3	0	7.5	+	5.4	0	19.4	0	29
Cyclopentene, 1-methyl-			0	8.6					0	5.6		
Cyclopropane, 1,2-dimethyl-, cis-												
Cyclopentane, 1,2-dimethyl-, cis-			0	8.6								
Cyclohexane, ethyl-	0	39	0	45.7	0	20	0	40.5	0	63.9	0	48.4
Naphthalene, decahydro-1,6-dimethyl-	0	4.9	+	14.3	0	5			0	13.9	+	22.6
Cyclopentane, 1,3-dimethyl-, cis-	0	7.3	+	11.4					0	5.6		
Methyldecahydronaphthane	0	9.8	+	11.4	0	12.5	+	13.5	+	13.9	+	9.7
Naphthalene, decahydro-2-methyl-	0	39	+	22.9	0	25	+	13.5	+	44.4	+	48.4
Cyclohexane, 1,1,3-Trimethyl-	0	4.9	0	22.9	0	5	0	16.2	0	25	0	19.4
1-Ethyl-4-methylcyclohexane	0	4.9							0	5.6	0	9.7
Cyclohexane, 1,2-dimethyl-, trans-	0	9.8	0	14.3					0	19.4	0	16.1
trans-Decalin, 2-methyl-	0	22.9	+	15	0	16.2	+	38.9	0	38.7	+	34.6
Cyclopentane, ethyl-	0		+	14.3			+		+			
Cyclopentane, 1,3-dimethyl-, trans	0	7.3	0				+		+			
Cyclopentane, 1,3-dimethyl-	0		0	14.3			0				0	9.7
Cyclopropane, 1,1,2-trimethyl-												
Cyclopentene, 4-methyl-	0		0	5.7					0			
Alkenes												
1-Pentene, 2-methyl-			0	14.3					0	13.9		
2-Pentene, 3-methyl-			0	11.4					0	5.6		
2-Hexene, 2-methyl-									0	5.6		
1-Pentene, 2,3-dimethyl-												
2-Hexene, 2,3-dimethyl-			0	5.7								
(E)-3-Methyl-2-hexene			0	5.7								
2-Butene, 2,3-dimethyl-			0				+					
3-Hexene												
2-Pentene, 3-methyl-, (E)-			0	14.3					0	5.6		
2-Pentene, 3-methyl-			0									
2-Hexene, (E)-												
Aldehyde												
Benzaldehyde			0	14.3	0	30	0	18.9	+	52.8	0	22.6
2-Hexenal, (E)-												

VOCs compounds	S7		S8		S 9		S10		S11		S	12
	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre	Ab	Fre
Cyclics												
Naphthalene, decahydro-	+	57.7	0	12	0	9.5	0	9.4	+		+	35.1
Cyclopentane, methyl-	+++	53.8					0	15.6			0	29.7
Cyclohexane, methyl-	++	69.2	0	8	0	8.1	0	9.4			+	48.6
Cyclohexane	+	26.9									+	10.8
Naphthalene, decahydro-, trans	+	7.7	0	8	0	5.4			0	7.4	+	21.6
Cyclohexene, 1-methyl-4-(1-methyleth	+		+	16	0	2.7	0	6.3			+	10.8
Cyclohexane, 1,3-dimethyl-	+	30.8									+	16.2
Cyclohexane, 1,3-dimethyl-, cis-	+	38.5									+	27
Cyclopentene, 1-methyl-	++	30.8									0	
Cyclopropane, 1,2-dimethyl-, cis-	+	30.8									+	5.4
Cyclopentane, 1,2-dimethyl-, cis-	++	38.5									0	8.1
Cyclohexane, ethyl-	+	73.1	0	16	0	9.5	0	25	0	14.8	0	59.5
Naphthalene, decahydro-1,6-dimethyl-	+	23.1			0	2.7					+	32.4
Cyclopentane, 1,3-dimethyl-, cis-	++	30.8									0	8.1
Methyldecahydronaphthane	+	26.9									+	21.6
Naphthalene, decahydro-2-methyl-	+	26.9	0	8	0	4.1	0	6.3	0	11.1	+	45.9
Cyclohexane, 1,1,3-Trimethyl-	+	34.6					0	18.8			0	40.5
1-Ethyl-4-methylcyclohexane	+	46.2									+	10.8
Cyclohexane, 1,2-dimethyl-, trans-	+	26.9									0	24.3
trans-Decalin, 2-methyl-	+			12.2	0					37.8	+	24
Cyclopentane, ethyl-	++	23.1									0	
Cyclopentane, 1,3-dimethyl-, trans	++	19.2									0	
Cyclopentane, 1,3-dimethyl-	++	19.2									0	18.9
Cyclopropane, 1,1,2-trimethyl-	++	11.5										
Cyclopentene, 4-methyl-	++	11.5									0	
Alkenes												
1-Pentene, 2-methyl-	++	46.2									0	8.1
2-Pentene, 3-methyl-	++	38.5									+	5.4
2-Hexene, 2-methyl-	+++	26.9					0					
1-Pentene, 2,3-dimethyl-	0	26.9										
2-Hexene, 2,3-dimethyl-	+	46.2										
(E)-3-Methyl-2-hexene	+	34.6										
2-Butene, 2,3-dimethyl-	++	23.1									+	5.4
3-Hexene	++	15.4										
2-Pentene, 3-methyl-, (E)-	++	19.2									0	
2-Pentene, 3-methyl-	++	15.4										
2-Hexene, (E)-	++	11.5										
Aldehyde												
Benzaldehyde	0	7.7	0	20	0	33.8	0	21.9	0	44.4	+	51.4
2-Hexenal, (E)-	++	11.5										

Ab: Abundance of a compound: peak area/sampled volume (abundance/ml)

Fre: Frequency of detections (%)

+++ Extremely high content in a sample (abundance/ml >12446)

++ High content in a sample (abundance/ml: 12466~3111.5)

+ Low content in a sample (abundance/ml: 3115.5~777.9)

0 traces in a sample (abundance/ml<777.9)



Figure A-1 Calibration factors for TD-GC-SCD analysis of VSCs



Figure A-2 Calibration factors for TD-GC-MS analysis of VOCs