Measurement and understanding of methane emission from sewers

Yiwen Liu

A thesis submitted for the degree of Doctor of Philosophy at The University of Queensland in 2015

School of Chemical Engineering
Advanced Water Management Centre
Abstract

Sewer emissions are a notorious problem that water utilities have to deal with. The production and emission of hydrogen sulfide is a well-known problem for decades, which is the primary cause of sewer odors and corrosion. However, hydrogen sulfide is not the only harmful emission from sewer networks. Methane can also be generated in sewers through methanogenesis. Methane is a highly potent greenhouse gas, which is significantly contributing to climate change. Over a 100-year horizon, 1 ton of CH$_4$ will induce a warming effect equivalent to 34 tons of CO$_2$. It is also explosive with a lower explosive limit (LEL) of approximately 5% by volume, and thus poses a serious safety issue. Currently, very little attention has been paid to methane formation in sewer networks. Therefore, the overall aim of this thesis is to measure and understand methane emission from sewers.

The limited studies conducted so far on methane measurement in both gas and liquid phases in sewers have relied on manual sampling followed by off-line laboratory-based chromatography analysis. These methods are labor-intensive when measuring methane emissions from a large number of sewers, and do not capture the dynamic variations in methane production.

Therefore, the suitability of infrared (IR) spectroscopy-based online methane gas sensors for measuring methane in humid sewer air was investigated in both laboratory and field conditions. Under certain circumstances, humidity could become an issue, however, this can be solved by removing the humidity on the sensor probe surface. Also, IR sensors exhibit excellent linearity and can be applied with factory calibration. Furthermore, the detection limit of sensors is suitable for measuring methane gas in sewers. Field application of the sensors revealed that methane concentrations in sewer air are 3 – 4 orders of magnitude higher than in the atmosphere, confirming that sewers are a source of methane. The continuous measurement also revealed that methane concentrations in sewer are highly dynamic.

Complementary to the gas phase sensors, a new dissolved methane sensor was developed in this thesis. This device uses an online IR gas-phase methane sensor to measure methane under equilibrium conditions in a stripping chamber. The measured gaseous methane levels were then
converted to liquid-phase methane concentrations according to Henry's Law. The detection limit and range was noted to be suitable for sewer applications. Good linearity was also obtained during field application. The newly developed online dissolved methane sensor was demonstrated through monitoring dissolved methane concentrations at the end of a rising main sewer network. This was done over two periods of three weeks each, in summer and early winter, respectively. Wide variations in dissolved methane concentrations were measured at 5 - 15 mg/L in summer and 3.5 - 12 mg/L in winter. This corresponded to significant average daily summer and winter methane productions of 24.6 and 19.0 kg-CH₄/d, respectively, from a network with a daily average sewage flow of 2,840 m³/day. The dissolved methane concentrations demonstrated a clear diurnal pattern coinciding with flow and sulfide fluctuations and implying a relationship with the wastewater hydraulic retention time (HRT).

Contributions of sediments in gravity sewers to overall sewer emissions are poorly understood at present. Sediments collected from a gravity sewer were cultivated in a laboratory reactor fed with real wastewater for more than one year to obtain intact sediments for the study. Batch test results clearly showed significant sulfide and methane production from sewer sediments. Microsensor and pore water measurements of sulfide, sulfate and methane in the sediments, microbial community profiling along the depth of the sediments and mathematical modelling revealed that sulfide production takes place near the sediment surface due to the limited penetration of sulfate. In comparison, methane production occurred in a much deeper zone below the surface likely due to the better penetration of soluble organic carbon. Modelling demonstrated the dependency of sulfide and methane production on the bulk sulfate and soluble organic carbon concentrations, and these relationships were described well by half-order kinetics.

In order to control sewer emissions from sediments, the effect of nitrate dosing on sulfide and methane production in sewer sediments was investigated through laboratory studies. It was found that nitrate addition does not suppress sulfide production in sewer sediment, but it reduces sulfide accumulation through anoxic sulfide oxidation in the sediment and hence, also reduces sulfide accumulation in the bulk water. Microsensor measurement of sediment sulfide revealed the presence of sulfide oxidation and sulfide production zones with the interface dynamically regulated.
by the depth of nitrate penetration. In contrast, with nitrate dosing the methane production activity of sewer sediment was substantially reduced. This was likely due to the long-term inhibitory effects of nitrate on methanogens. Pore water measurements showed that methane production activity in the sediment zone was completely suppressed with frequent nitrate exposure, and consequently, the methane production zone re-established deeper in the sediment where nitrate penetration was infrequent.
**Declaration by author**

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

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<td>Author Liu, Y. (Candidate)</td>
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<td>Data analysis, processing and modelling (80%)</td>
</tr>
<tr>
<td></td>
<td>Wrote and edited paper (70%)</td>
</tr>
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<td>Author Ni, B.</td>
<td>Designed research methodology and experiments (15%)</td>
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| Author Liu, Y. (Candidate) | Designed research methodology and experiments (65%)  
Conduct Experiments (100%)  
Data analysis, processing and modelling (70%)  
Wrote and edited paper (70%) |
| Author Sharma, K. R. | Designed research methodology and experiments (15%)  
Data analysis, processing and modelling (10%)  
Wrote and edited paper (10%) |
| Author Fluggen, M.  | Designed research methodology and experiments (5%)  
Helped with sensor development and field studies |
| Author O’Halloran, K.| Data analysis, processing and modelling (5%)  
Helped with field studies |
| Author Murthy, S.    | Data analysis, processing and modelling (5%) |
| Author Yuan, Z.      | Designed research methodology and experiments (15%)  
Data analysis, processing and modelling (10%)  
Wrote and edited paper (20%) |


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Conduct Experiments (95%)  
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| Author Ni, B.      | Designed research methodology and experiments (5%)  
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| Author Ganigue, R. | Designed research methodology and experiments (5%)  
Conduct Experiments (5%)  
Helped with reactor operation |
| Author Werner, U.  | Data analysis, processing and modelling (5%)  
Helped with microsensor experiments |
| Author Sharma, K. R.| Designed research methodology and experiments (5%) |

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<tr>
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</tr>
<tr>
<td>Author Fan, L.</td>
<td>Designed research methodology and experiments (5%)&lt;br&gt;Helped with microbial sampling</td>
</tr>
<tr>
<td>Author Murthy, S.</td>
<td>Data analysis, processing and modelling (5%)</td>
</tr>
<tr>
<td>Author Tyson, G.</td>
<td>Designed research methodology and experiments (5%)</td>
</tr>
<tr>
<td>Author Yuan, Z.</td>
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**Contributions by others to the thesis**

This thesis includes contributions made by others, particularly in the chemical analysis of wastewater and reactor samples. These contributions are acknowledged as follows:

Dr. Beatrice Keller-Lehmann, Jianguang Li and Nathan Clayton operated ion chromatography (IC), gas chromatography (GC) and flow injection analyzer (FIA) to analyse dissolved sulfur species, volatile fatty acids, dissolved methane and dissolved nitrogen species.

**Statement of parts of the thesis submitted to qualify for the award of another degree**

None.
Acknowledgements

First and foremost, I owe my heartfelt gratitude to my principal supervisor, Professor Zhiguo Yuan, for his excellent guidance and generous help during my PhD study. He has been supervising my research with not only his broad and profound knowledge but also his passion and enthusiasm. This thesis would have been impossible without his continual guidance, encouragement and support. I feel very lucky to have worked with him and have learned a lot from him, such as his rigorous attitude to research and endless passion to his beloved work, which is very important and helpful in my future career.

I would like to extend my gratitude to my co-supervisor, Dr. Keshab, R Sharma, who supported me in a number of ways. He provided a lot of valuable advice and discussion with his expertise and insight. His encouragement helped me get through lots of difficulties. I also would like to thank Dr. Bing-jie Ni, who educated me with modeling skills and smart ways to do research, and has been an important support of my later research.

My sincere thanks also go to Markus Fluggen, who helped me with methane sensor development and application, which has been very important in my entire research. To Dr. Ursula Werner, who helped me with the microsensor study. To Richard Gilbert, who helped me with reactor maintenance and field study. Thanks to all the people who used to work in or is still working in the sewer research team, especially Dr. Guangming Jiang, Dr. Ramon Ganigue, Dr. Jing Sun, Xiaoyan Sun, Hui-wen Lin, Dr. Gatut Sudarjanto et al. Special thanks also to Dr. Stephan Tait, Dr. Ying Shi, Dr. Fan Lu, for helping me somehow during my PhD.

I am grateful to the AWMC academics, researchers, laboratory staff, administrative staff, students who gave so generously their support and kindness. Thanks to them for making the centre an enjoyable and fun place to work. I thank all my friends in Australia and China. Their continued friendship and love have made my life full of happiness.

I am grateful to the generous financial support from the Australian government and The University of Queensland, through two scholarships: Endeavour International Postgraduate Research
Scholarship (IPRS) and University of Queensland Centennial Scholarship (UQ Cent). I also thank Advanced Water Management Centre for topping up the scholarship. My research was supported by the Australian Research Council, Gold Coast City Council, Melbourne Water Corporation, South East Water Limited, Water Corporation Western Australia, and District of Columbia Water and Sewer Authority through ARC Project LP110201095.

Last but not least, I would to deeply thank my dear parents and my lovely girlfriend. Your continuous faith and moral support is a great contribution to this thesis.
Keywords
wastewater, sewer, greenhouse gas, methane, sensor, online, sediment, nitrate, sulfide, mathematical modelling

Australian and New Zealand standard research classifications (ANZSRC)
ANZSRC code: 090703, Environmental Technologies, 90%
ANZSRC code: 090702, Environmental Engineering Modelling, 10%

Fields of research (FoR) classification
FoR code: 0907, Environmental Engineering, 100%
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A/V            Biofilm area to water volume ratio  
COD            Chemical oxygen demand  
DNA            Deoxyribonucleic acid  
DO             Dissolved oxygen  
FIA            Flow-injection analyzer  
FISH           Fluorescence in situ hybridization  
FNA            Free nitrous acid  
GC             Gas chromatograph  
GHG            Greenhouse gas  
GWRC           Global Water Research Coalition  
HRT            Hydraulic retention time  
IPCC           Intergovernmental Panel on Climate Change  
IC             Ion chromatography  
IR             Infrared  
LEL            Lower Explosive Limit  
MA             Methanogenic archaea  
MIMS           Membrane inlet mass spectrometer  
PLC            Programmable logic controller  
ppm            Parts per million  
ppmv           Parts per million volume  
SCOD           Soluble COD  
soNRB          Sulfide-oxidizing nitrate-reducing bacteria  
SRB            Sulfate reducing bacteria  
TS             Total solids  
VFA            Volatile fatty acids  
vol            Volume  
VS             Volatile solids  
WERF           Water Environment Research Foundation
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Chapter 1 Introduction

1.1 Background

Sewer systems are an important and integral component of urban water infrastructure, which collect and transport wastewater from households or industry to wastewater treatment plants (WWTPs) for pollutant removal prior to discharge. Sewer systems protect our urban society against sewage-born diseases, unhygienic conditions and obnoxious odours, allowing us to live in ever larger and more densely populated cities (Pikaar et al., 2014).

Sewer emissions are a notorious problem that water utilities have to deal with (Ganigue et al., 2011). The production and emission of hydrogen sulfide has since long been identified as a major cause of odor and corrosion in sewer systems (Boon, 1995), which incurs large costs to the water industry due to assets depreciation and mitigation measures (WERF, 2007b). However, hydrogen sulfide is not the only harmful emission from sewer networks. Recent studies also demonstrate that methane (CH$_4$), a highly potent greenhouse gas (GHG) that greatly contributes to climate change, is also generated in anaerobic sewers through methanogenesis (Foley et al., 2009, Guisasola et al., 2008, Shah et al., 2011). CH$_4$ has a Lower Explosive Limit (LEL) of approximately 5% by volume (vol), and thus poses a serious safety concern (Spencer et al., 2006). In addition, methane generation in sewers may consume a significant amount of soluble chemical oxygen demand (COD), which may limit nutrient removal capabilities in downstream WWTPs (Guisasola et al., 2008).

Currently, there is a major effort aimed at understanding and quantifying methane production in WWTPs (Bani Shahabadi et al., 2009, Daelman et al., 2012, Wang et al., 2011). Significant progress has enabled better management of methane emissions in treatment plants. In contrast, very little attention has been paid to methane formation in sewer networks (IPCC, 2013). The limited studies conducted so far on methane measurement in both gas and liquid phases in sewers have relied on manual sampling followed by off-line laboratory-based chromatography analysis. For example, Guisasola et al. (2008) detected dissolved methane
with concentrations of 5 - 25 mg/L at two rising mains over a 6 h measurement campaign with half-hourly manual sampling of sewage and estimated methane production in sewers would potentially contribute 9–26% of the total GHG emission during wastewater handling and treatment. Corroborating the liquid phase data, the gas phase methane concentrations of up to 50,000 ppmv, i.e. 5% vol, were detected in the air of a gravity sewer by one-point sampling in several manholes (GWRC, 2011). In contrast, the current atmospheric methane concentration is 1.8 ppmv (GWRC, 2011).

However, because sewers are dynamic systems, manual sampling campaigns may not capture dynamic methane variation in both the liquid and gas phases (Sharma et al., 2008), imposing a serious limitation on accurate quantification. In addition, manual sampling is not practical for long-term, intensive quantification of methane concentration in complicated sewer networks with a large number of sampling sites. Therefore, online methane sensors suitable for sewer gas and liquid-phase measurement are required.

There are several potential gas detectors with data logging capabilities available for online gas-phase CH₄ measurement (Lawrence, 2006), however, sensor performance in humid sewers is unknown and requires evaluation before wide application to the sewer environment. Furthermore, although a limited number of commercial sensors for online detection of dissolved CH₄ are available (Boulart et al., 2010), these are mainly designed for measuring methane in clean water bodies by using gas-permeable membranes to extract methane gas from water. This method cannot be used for measuring domestic sewage containing a large amount of impurities as well as sulfide at high concentrations. Therefore, it is necessary to develop a new online dissolved methane measurement technology for sewer methane monitoring.

According to the operational nature, sewer systems can be divided into fully-filled rising main sewers (anaerobic), and partially-filled gravity sewers, where re-aeration takes place. Over the years, most of the studies on sulfide and methane production in sewers have focused
on sewer biofilms, particularly those in rising mains (Jiang et al., 2010, Sharma et al., 2008, Sun et al., 2014). These studies demonstrated that both sulfide and methane are generated in significant amounts from biofilms in anaerobic rising main sewers due to the biological sulfate reduction process mediated by sulfate reducing bacteria (SRB) and methanogenesis mediated by methanogenic archaea (MA) within the sewer biofilms that are attached to the walls of rising mains.

In fact, sediments settled in gravity sewers are also believed to be biologically active (Schmitt and Seyfried, 1992), and would also contribute to sulfide and methane production. However, research in gravity sewers to date has mainly focussed on physical processes such as the sewer sediment deposition, erosion and transport (Banasiak et al., 2005, Gasperi et al., 2010, Rodríguez et al., 2012). In comparison, little effort has been dedicated to the biological reactions in the sediment despite several studies recognizing their significance (Ashley et al., 2003). Schmitt and Seyfried (1992) showed that the sulfate reduction rates in sewer sediment could be ca. 80% higher than that in sewer biofilms. In fact, with plentiful supply of biodegradable organic carbon, sewer sediment can have great potential to produce sulfide and methane biologically. The significant knowledge gaps related to the biological transformations within the sewer sediment are currently limiting our ability to understand sulfide and methane production in gravity sewers.

Various chemical dosing strategies for sulfide control have been practiced by the water industry (Ganigue et al., 2011). The most commonly used chemicals include oxygen and nitrate for sulfide oxidation, iron salts for sulfide precipitation, and alkali for pH elevation to minimize liquid to gas mass transfer of hydrogen sulfide (Ganigue et al., 2011, Zhang et al., 2008). In addition to sulfide control, these chemicals can simultaneously induce inhibitory effects on methanogens in sewers, thus leading to possible methane elimination (Ganigué and Yuan, 2014, Gutierrez et al., 2014, Jiang et al., 2013b, Zhang et al., 2009). For example, a recent study conducted by Mohanakrishnan et al. (2009a) demonstrated that the long-term addition of 30 mg N/L of nitrate in a laboratory rising main sewer reactor reduced the sulfide
and methane concentrations in the effluent by 66% and 94%, respectively. In comparison, little effort has been dedicated to studying the effect of chemical dosing such as nitrate on gravity sewer sediments. In contrast to rising main sewer biofilms, which are measured in terms of micrometers, sewer sediments contain a thicker, biologically active layer of several centimeters or more. It is expected that penetration of nitrate into the sediment would be very limited. Additionally, nitrate addition to gravity sewers could potentially lead to N₂O emission due to denitrification and the known inhibitory effects of hydrogen sulfide on N₂O reduction (Pan et al., 2013).

1.2 Objectives of the thesis

The aim of this PhD thesis is to measure and understand methane emission from sewers. In particular, online sensors suitable for sewer gas and dissolved methane measurement were evaluated/developed, and then further applied in actual sewers to capture dynamic methane data, in order to better understand and quantify methane production and emission from sewers. Also, the nature, extent and control of methane and sulfide production in sewer sediments were investigated.
The literature review below summarizes findings of previous studies that are highly related to the thesis topic. Section 2.1 gives brief overviews of sewer systems and in-sewer microbial processes. In section 2.2, aspects of sources and sinks of methane in sewers are reviewed in detail. Section 2.3 reviews methane measurement in sewers. Following a summary on sewer methane production modelling in section 2.4, section 2.5 reviews effects of chemical dosing on methane formation in sewers. Section 2.6 introduces sewer sediments in terms of physicochemical and biological properties.

2.1 Overview of sewer systems and in-sewer microbial processes

2.1.1 Development of sewer systems

Sewer systems have existed during very early times in many ancient civilizations including the ancient Roman, Chinese, Greek and Egyptian (Gray, 1940). These sewers were mainly utilized to deliver the storm water in case of flooding. Since the middle of the 19th century, sewer systems were also designed as hygienic and sanitary installations with the aim of reducing the spread of epidemic diseases. Nowadays, sewers have become an indispensable component of urban wastewater systems, which collect and transport wastewater from residential houses or industry to WWTPs and for disposal. Sewers have also been recognized as chemical and biological reactors (Hvitved-Jacobsen, 2002), well beyond the original concept that sewers are simple vessels for collecting and transporting wastewater.

2.1.2 Design and operation of sewers

Operationally, sewer systems can be divided into fully-filled pressure sewers (or rising main sewers) which are anaerobic, and partially-filled gravity sewers that are mostly aerobic. In the latter re-aeration takes place (Fig. 2.1). The key difference between gravity and pressure sewers is the oxygen concentration in the sewage.

† This chapter is part of the paper “Liu et al., Methane emission from sewers. Science of The Total Environment, 2015, 524-525, 40-51.”
In rising main sewers, pumping stations receive wastewater and then transport it along the pressure sewer, which is usually fully-filled with wastewater. Intense gas-liquid transfer can occur when the wastewater is discharged into the wet well, the connection between pressure and gravity sewers. Wastewater will move to gravity sewers when reaching the overflow level in the wet well. In gravity sewers, the wastewater flow is driven by gravity and the sewers are not fully filled. Aerobic conditions can prevail in the wastewater phase due to the transfer of oxygen across the air-water interface. Generally, gas emission from sewers can take place in at the locations of the headspace of the pumping station, the wet well, the manholes of gravity sewers and influent works of WWTPs.

**Figure 2.1.** The main components of a sewer comprise of pressure and gravity sections. The reactions of the sewer biofilms and sediments developed in sewers are represented, modified from Jiang (2010).

**2.1.3 Overview of in-sewer microbial processes**

In addition to transporting wastewater, sewers also act as biological reactors for various microbial processes. Generally, there are four major phases in a sewer pipe: namely the
suspended wastewater phase, the sewer biofilms, the sediments, and the sewer air phase (in gravity sewers) (Fig. 2.1). In-sewer microbial processes mainly take place in biofilms and sediments, with little contribution from the suspended biomass in the water phase (Mohanakrishnan et al., 2009a).

The wastewater in sewers is rich in organic substances, which can serve as electron donors for different heterotrophic processes. The types of heterotrophic process depend on the potential electron acceptors available in sewer systems. Aerobic transformations of organic matter with oxygen as an electron acceptor take place in gravity sewers due to the re-aeration. Similar heterotrophic processes also occur when utilizing nitrate or nitrite which may be present or added to the wastewater as electron acceptors in the absence of oxygen. In contrast, anaerobic conditions appear after oxygen is depleted, when sulfate becomes an electron acceptor and this leads to the generation of sulfide through a biological process mediated by sulfate reducing bacteria (SRB). Meanwhile, anaerobic fermentation and methane formation by utilization of organic matter as electron acceptors can also occur (Hvitved-Jacobsen, 2002). Previous studies have been mainly focused on the aerobic transformations of organic matter by heterotrophic microorganisms when oxygen is present (Hvitved-Jacobsen, 2002), or they have focused on the activities of sulfate reducing bacteria (SRB) when sulfate serves as the electron acceptor to produce hydrogen sulfide (Zhang et al., 2008).

Compared with the sewer sediment, previous studies believed that microbial reactions that take place in the biofilm developed on the pipe wall (Fig. 2.1) play the most important roles in the sewer transformations (Hvitved-Jacobsen, 2002, Mohanakrishnan et al., 2009b). Anaerobic biofilms with thickness of a few hundred µm prevail in pressure sewers. This is where microbial transformation such as fermentation, methane production and sulfate reduction take place. The interaction between anaerobic carbon and sulfur transformations are important in sewers. In contrast, in gravity sewers two main kinds of biofilms may exist (Hvitved-Jacobsen, 2002). The biofilms existing below the water surface will experience
partially or fully anaerobic conditions even when oxygen is in the bulk wastewater, due to the limited penetration of oxygen (Gutierrez et al., 2008). These would be performing similar functions to those of the biofilms in the pressure mains as mentioned above. Sulfide and methane generation are detected in the deeper biofilm layers of these biofilms even when oxygen is in the bulk wastewater (Guisasola et al., 2008, Gutierrez et al., 2008). The second main biofilm type in gravity sewers is those that develop on the sewer walls above the water line. These are largely aerobic biofilms that produce sulfuric acid through sulfide oxidation, resulting in sewer corrosion of the concrete sewer wall (Joseph et al., 2012).

2.2 Sources and potential sinks of methane in sewers

2.2.1 Methane formation in sewers

Overview

CH$_4$ can be microbially produced from organic matter under anaerobic conditions via a series of reactions including hydrolysis, fermentation and methanogenesis (Speece, 1983). Organic matter, such as protein, carbohydrates and lipids, firstly undergo hydrolysis processes, which degrades hydrolysable organic matter into fermentable substrate. Then during fermentation, the organic matter is converted to hydrogen, carbon dioxide, acetic acid and volatile fatty acids (VFAs). Among them, acetic acid and hydrogen (with carbon dioxide) can then be directly converted to CH$_4$ by acetogenotrophic and hydrogenotrophic methanogens, respectively. The former pathway accounts for about two-thirds of the methane emitted in nature (Ferry, 1992).

Since anaerobic fermentation processes, by using organic matter as electron acceptors, occur in sewer biofilms, CH$_4$ can be subsequently produced from acetate or hydrogen within sewer biofilms under anaerobic conditions through microbial methanogenesis (Hvitved-Jacobsen et al., 1998). CH$_4$ is a highly potent GHG and contributes significantly to climate change (IPCC, 2013). Also, it is a highly explosive gas and displays a LEL of approximately 5% vol. Uncontrolled release of methane could cause a potential explosion when mixed with air in confined spaces, consequently its formation in sewers poses a serious safety risk (Spencer et
al., 2006). In addition, methane generation in sewers may consume a significant amount (i.e., constituting 72% of total loss) of soluble chemical oxygen demand (COD), which is detrimental to biological nutrient removal in downstream WWTPs (Guisasola et al., 2008). However, limited work has been done regarding the understanding of methane formation and emission from sewer systems as compared with sulfide-related problems.

**Physiology and ecology of methanogens**

All known methane producing microorganisms belong to the Archaea domain and are obligate anaerobes (Whitman et al., 1999). Different from other Archaea, the methanogenic archaea (MA) are very sensitive to pH and temperature. MA grow optimally at temperatures > 28 °C and in pH ranges of 5.5-9.0 (Whitman et al., 1999). MA are slow growers with typical doubling times between 1 and 9 days, depending on the species and growth conditions.

Most MA belong to the phylum of Euryarchaeota and can be divided into five orders: *Methanobacteria*, *Methanococcales*, *Methanomicrobiales*, *Methanosarcinales* and *Methanophyrales* according to the phylogenetic analysis of 16S rRNA gene (Liu and Whitman, 2008, St-Pierre and Wright, 2013). The five orders can be further classified into 10 families and 31 genera (Liu and Whitman, 2008). Theoretically, the genera such as *Methanothermobacter*, *Methanothermus*, *methanotorris*, *methanocaldococcus*, and *methanopyrus* will not exist in sewer biofilms since they grow under extreme thermophilic conditions. MA of the *Methanosataceae*, *Methanomicrobiales*, *Methanosarcinaeae*, *Methanococcales* and *Methanocaldococcaceae* are detected in rising main sewer biofilms while *Methanobacteriales* is absent (Mohanakrishnan et al., 2009b). In a recent study of a sewer rising main biofilm it was found that 90% of the MA population belonged to the genus *Methanoseta*, and these are obligate acetoclastic methanogens (Sun et al., 2014). MA that use other substrates such as hydrogen only accounted for less than 10% of the total MA population in the sewer biofilm. A possible explanation for that is that hydrogenotrophic MA were out-competed by the hydrogen-utilizing SRB (Kristjansson et al., 1982).
Competition between MA and SRB
Both SRB and MA can use a wide range of organic carbon generated by hydrolysis and fermentation processes, e.g., hydrogen, acetate and propionate. They will compete for hydrogen and acetate and this has been intensively investigated (Chou et al., 2008, O’Reilly and Colleran, 2006, Omil et al., 1998, Yoda et al., 1987). SRB can outcompete methanogens for substrates in sulfate-rich and carbon-limiting conditions (Robinson and Tiedje, 1984, Schonheit et al., 1982, Uberoi and Bhattacharya, 1997). Sewers usually have limited sulfate (ca. 10–30 mg/L) and sufficient carbon substrates (ca. 200–500 mg COD/L) for both SRB and MA to co-exist in sewer biofilms, thereby allowing simultaneous methane and sulfide production despite their competition for substrates (Conrad et al., 1987, Raskin et al., 1996, Robinson and Tiedje, 1984). This co-existence is due to stratification of these anaerobic microorganisms in the biofilm (Guisasola et al., 2008, Sun et al., 2014). SRB are found to dominate the microbial community in the top layers of the biofilms where the sulfate concentration is relatively high (Fig. 2.2). However, MA require low-sulfate conditions, and absence of sulfate in the deeper layers of biofilms due to the diffusional limitation of sulfate combined with an adequate supply of methanogenesis precursors promotes its growth (Guisasola et al., 2008, Sun et al., 2014).

Figure 2.2. A: Relative abundance of SRB and MA; B: Depth profiles of sulfate and soluble biodegradable COD in a sewer biofilm, adapted from Sun et al. (2014). The surface of the biofilm was defined as depth 0 µm.
2.2.2 Potential sinks of methane in sewers

It is reported that CH$_4$ could be oxidized by methane oxidizers under anaerobic, anoxic and aerobic conditions in biofilms and sediments (Islas-Lima et al., 2004, Schreiber et al., 2010, Waki et al., 2005). These processes play an important part in regulating methane release in nature, e.g., in seas and lakes.

Biofilms in gravity sewers typically have a shallow aerobic zone at the surface followed by an anaerobic zone deep in the profile (Gutierrez et al., 2008). The depth of the shallow aerobic zone depends upon the DO level in the bulk phase. Therefore, the CH$_4$ produced in the anaerobic zone could be oxidized by methanotrophs under both anaerobic and aerobic conditions, with sulfate and oxygen being the respective terminal electron acceptors (Bastviken et al., 2002, Iversen and Jørgensen, 1985). However, the limited evidence indicates that the growth rates of methane oxidizers are very slow (Valentine and Reeburgh, 2000). For example, a reported areal rate of ca. 0.02 g CH$_4$/m$^2$-d for aerobic or anaerobic methane oxidation by lake or ocean sediments (Bastviken et al., 2002, Iversen and Jørgensen, 1985), is substantially lower than that of methane production rate by sewer biofilms, i.e., 1.26±0.14 g CH$_4$/m$^2$-d (Foley et al., 2009). Damgaard et al. (2001) measured the methane profile in a biofilm grown at a sewage outfall, and found that a portion of the methane produced in the deep anaerobic layer was oxidized in the superficial aerobic layer. However, no additional research has been conducted since, and there is no direct evidence for the presence of methane oxidizers in sewer biofilms or sediments submerged in the water. Therefore, consumption of dissolved methane via methane oxidation in the sewer liquid phase is likely to represent a weak sink.

Also, biofilm grown on the crown and the sides of a sewer pipe above the sewage level is exposed to the sewer air in gravity sewers and could be another sink of methane. However, a recent study reports the total absence of aerobic methanotrophs in such biofilms due to the unfavorable acidic environment (Cayford et al., 2012), Thus, the biofilms on the crown and non-submerged portions of the sewer pipe are unlikely major sinks for methane.
Another possibility is that methane could be removed by various types of sewage odor treatment units (Burgess et al., 2001, Daelman et al., 2013) employed to remove odour producing hydrogen sulfide from extracted sewer air. However, there is currently very little knowledge on this. In addition, methane can be effectively oxidized (50%) by activated sludge in aeration units at WWTPs (Daelman et al., 2014).

2.3 Methane measurement in sewers

2.3.1 Offline methane measurement in sewers

To date, the primary method for CH₄ measurement in sewers has comprised manual sampling at regular intervals over several hours followed by off-line gas chromatography (GC) analysis (Guisasola et al., 2008; Foley et al. 2009; Shah et al., 2011).

Particular sampling arrangements are required for measuring gas phase methane concentrations. The gas can be sampled from a ventilation point (Shah et al., 2011) using gas bags or evacuated Exetainer® tubes. The collected gas samples are then analyzed for methane using a GC equipped with a flame ionization detector (FID).

Dissolved methane sampling in rising main sewers is generally done using a small but flexible pipe connecting a sampling tap at ground level to the tapping arrangement of the underground pipe. Samples are collected from the pipe using a hypodermic needle and plastic syringe (Fig. 2.3). This procedure prevents exposure of sampled wastewater to the atmosphere and avoids any oxygen contamination (Foley et al., 2009). For sampling dissolved methane in gravity sewers, manholes, wet-wells and pumping stations, wastewater samples are usually collected with a sampling device consisting of an open-head cylindrical container. The container is lowered and filled below the water level, and then gently retrieved. Within the container, sample aliquots are extracted with a plastic syringe from ca. 5 cm below the water surface to avoid contact with air (GWRC, 2011). Alternatively, a submersible pump can be used to collect sample from below-ground at low speed in order to
avoid turbulence. Sub-samples are subsequently extracted into an evacuated Exetainer® tube (Labco, Wycombe, UK) or a pre-treated serum bottle (Daelman et al., 2012). The contents of the tube or bottle are kept mixed overnight to allow gas-liquid equilibrium to occur, and then gas samples are taken and methane is measured by GC. Concentrations of dissolved methane in the liquid sample are calculated using Henry’s Law and mass balance. These methods are continuing to develop and a more accurate method using evacuated Exetainer® tubes for both gas and liquid phase methane sampling and measurement has been proposed recently.

![Collection of dissolved methane sample directly from the rising main into an airtight syringe, adapted from Foley et al. (2009).](image)

Sewer systems are highly dynamic (Sharma et al., 2008) as sewage flows fluctuate substantially over time, leading to varied wastewater HRT in sewers. In addition, in rising main sewers, pumps are frequently turned on and off resulting in intermittent flow, which further adds to the sewer dynamics. Similar to the dynamics already observed for hydrogen sulfide production in sewers (Sharma et al., 2008), CH₄ concentrations in both the liquid and gas phases are also expected to fluctuate. Therefore, continuous monitoring of CH₄ concentrations in both the gas and liquid phases over long periods is important for the accurate quantification and overall understanding of CH₄ production and emission from sewers. However, these dynamics in sewer CH₄ concentrations are very difficult to capture with current manual sampling methods. This therefore imposes a serious limitation to accurate quantification of methane emission. In addition, methane production and emission
data are expected to vary from site to site (Foley et al., 2009), and manual sampling is not feasible for long-term quantification of methane concentrations over a large number of sampling sites in extensive sewer networks. Therefore, online sensors for continuous CH\textsubscript{4} measurement are highly needed. In the development of such online sensors, calibration of these using the manual methods would be appropriate.

**2.3.2 Online methane measurement**

*Online gas-phase CH\textsubscript{4} measurement technologies*

Online gas sensors for continuous CH\textsubscript{4} measurement potentially provide a solution to the aforementioned problems. Instruments that are able to measure CH\textsubscript{4} gas online are available and have been widely used in combination with detecting systems such as infrared (IR) spectroscopy, photoacoustic and Raman spectrometry, and pellistors or metal-oxide semiconductors (Lawrence, 2006, Rothfuss et al., 1996).

**Photoacoustic detection**: Photoacoustic detection is based on the photoacoustic effect in which energy from a radiation source is first converted to a sound and then to an electrical signal; this is a developing technology used for methane measurement and there are few products on the market (Rothfuss et al., 1996).

**Raman spectroscopy**: Raman spectroscopy is based on the principle that when a molecule exhibits rotation or vibration, a part of light will be scattered thereby encountering a frequency Raman shift. The characteristic shift for rotation and vibration state makes Raman spectroscopy a method with high specificity. It also can be performed rapidly. But the equipment is much larger in size and not suitable as a portable device (Prien, 2007).

**Pellistors**: Pellistors are calorimetric flammable gas sensors, which detect a temperature variation when a heated catalytic element is exposed to a mixture of combustible gases. Pellistors are not expected to be applicable in sewer conditions due to the known toxic effect of hydrogen sulfide on electrodes (Lawrence, 2006).
**Metal-oxide semiconductors**: Metal-oxide semiconductors will vary in conductance or resistance in response to the presence of different gases. The major limitation is that a semiconductor can respond to any gas that can be oxidized and hence is not specific to a particular gas (Lawrence, 2006).

**IR spectroscopy**: IR spectroscopy is a mature technology that has been applied in methane detection for years. It is based on the principle of measuring an absorption line unique to the detected gas, with significant sensitivity and selectivity (Lawrence, 2006). Although alkanes such as propane, pentane, butane and hexane can interfere with CH$_4$ measurement via IR spectroscopy, these hydrocarbons are not expected to exist in sewers in significant amounts unless directly discharged (GWRC, 2011). Therefore, of the methods described here, IR spectroscopy is likely the most promising for online CH$_4$ measurement in sewer conditions.

Gas sensors with IR spectroscopy technology are currently used as safety devices for detecting flammable gases such as CH$_4$ in underground mining and petrochemical industries (Taylor et al., 2008). Almost all commercial IR sensors are of the non-dispersive type, which use discrete optical band-pass filters. It is claimed that these sensors are applicable to methane detection in wastewater treatment facilities, however, sensor performance has not been fully studied and there are no reports in the scientific literature evaluating the suitability of these sensors for online methane measurement in sewers.

Both temperature and humidity can affect IR sensor performance. An IR detector is essentially a temperature sensor and is, therefore, potentially sensitive to changes in the temperature. The temperature in sewers varies between day and night as well as with seasons, which may influence the sensor performance. Humidity can often cause major interference with infrared systems (Sun et al., 2011). Water vapour has a significant absorption spectrum that has peaks similar to CH$_4$ and this could cause false readings. Water vapour can also condense on the optics or in the light path and cause the beam to be deflected or diffracted so
that an erroneous reading or instrument failure can occur. The relative humidity in sewers is usually above 90% and sometimes it can be fully condensing (Joseph et al., 2012), and this could have an adverse effect on IR detection of CH₄. The performance of IR sensors in humid sewers is unknown and requires evaluation before its application to the sewer environment.

**Online dissolved CH₄ measurement technologies**

The above gas-phase methane measurement technologies cannot be directly applied for measurement of dissolved methane gas. Thus, a system that can extract dissolved methane into the gas phase is required. The most commonly used gas extraction systems mainly include a gas-permeable membrane and an equilibrator. After that, the methane gas can be measured by the technologies detailed above.

**Gas-permeable membrane:** The gas-permeable membranes applied in the construction of dissolved methane sensors are generally made of a solid substrate with open porosity and a continuous polymeric layer (Boulart et al., 2010). The common materials used for membranes are silicon rubbers. Currently, there are a limited number of commercial sensors using membrane extraction for online detection of dissolved CH₄ as listed in Table 2.1. It should be noted that these sensors are mainly designed for measuring methane in clean water bodies.

Of the available sensors, the METS CH₄ sensor has been applied for methane monitoring in reservoirs, rivers and lakes. It is claimed that the sensor has high sensitivity and long-term stability. The detecting range and resolution are 7-1000 ppm and 1ppm for methane, respectively. The major limitation of this sensor is the use of a metal-oxide semiconductor for methane gas detection, which can respond to any gas that can be oxidized, such as H₂S in sewers (Boulart et al., 2010, Lawrence, 2006). Another sensor, the HydroC/CH₄ is similar to the METS sensor except that the detection principle is based upon IR absorption spectroscopy (Boulart et al., 2010). The system can detect methane concentrations between 30 nM and 500 µM with a resolution of 3–30 nM. Additionally, the Membrane Inlet Mass
Spectrometer Gas Analyser (MIMS) is also available for dissolved methane measurement. It is a fully automated Quantitative Gas Analysis system with a temperature controlled membrane inlet for fast and repeatable analysis of gases and dissolved gases (i.e., methane) in liquids at the parts-per-trillion level (Camilli and Hemond, 2004). However, due to its large volume and high price, it is difficult to be applied for online dissolved methane measurement in the field for water industries.

The main drawback of the sensors using gas-extraction membranes is that the membrane is sensitive to environmental conditions; thus any changes in membrane diffusivity induce recalibration of the sensor. In addition, continuous exposure to high sulfide concentrations in sewage could also affect membrane integrity. Furthermore, domestic sewage contains a great amount of impurities, likely to cause problems such as membrane fouling and blocking, deeming these sensors less applicable to sewers.

Table 2.1: Summary of some currently available commercial dissolved methane sensors

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Gas extraction method</th>
<th>Detection Technology</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>METS</td>
<td>Silicon rubber</td>
<td>SnO$_2$ semiconductors</td>
<td>(Lamontagne et al., 2001)</td>
</tr>
<tr>
<td>HydroC/CH$_4$</td>
<td>Modified silicon rubber</td>
<td>IR spectroscopy</td>
<td><a href="http://www.contros.eu">www.contros.eu</a></td>
</tr>
<tr>
<td>MIMS</td>
<td>Semi-permeable membrane inlet</td>
<td>In situ mass spectrometer</td>
<td>(Camilli and Hemond, 2004)</td>
</tr>
</tbody>
</table>

**Equilibrator**: Equilibrators, usually designed for CO$_2$ analyses in air-sea exchange studies (Frankignoulle et al., 2001), comprise tubes filled with gas-partitioning material (increasing the gas-liquid exchange surface) where water and gas flow, in opposite directions, in an air circuit. Abril et al. (2006) utilized a modified equilibrator connected to a gas analyzer for measuring dissolved methane concentrations in a tropical reservoir. However, the modified equilibrator system was only tested in a water reservoir for one day, rather than in polluted
water such as sewage, and equilibrators are notoriously difficult to construct, operate and calibrate in situ (Boulart et al., 2010).

Later, Yu et al. (2006) developed a method for online estimation of dissolved methane concentration in a laboratory anaerobic fermenter based on the equilibrator method. The liquid-phase methane concentration was calculated based on the gas-phase methane measurement and an estimated \(kLa\) for methane. The \(kLa\) for methane was estimated using an empirical equation from \(kLa\) for oxygen, which is a challenge for wastewater systems due to the interference of on-going biological activities consuming oxygen (Pratt et al., 2004). In addition, no long-term measurement performance was presented.

In summary, both gas-permeable membrane and equilibrator methods are not suitable for dissolved methane extraction from sewage. Therefore, a new method is required. In fact, a simple principle to strip the dissolved gas in the liquid into gas phase, and then convert this gas phase concentration under equilibrium back to liquid phase concentration using Henry's Law has been used for dissolved nitrous oxide measurement in the wastewater (von Schulthess and Gujer, 1996). This method could be potentially feasible for dissolved methane measurement in sewers as methane is more easily to strip out of water in comparison to nitrous oxide.

### 2.3.3 In-sewer dissolved and gaseous methane data

**Dissolved methane concentrations**

The significant contribution of sewers to methane production and emission was not recognized until recently (Table 2.2). Over a 4-h measurement campaign in the afternoon with half-hourly manual sampling of sewage, dissolved methane with concentrations of 4.4 – 6.1 mg/L was detected at the end of a 828-m long rising main (UC9, Gold Coast, Australia). This system had a HRT of 3.1 – 4.6 h, yielding an average methane production of 1.1 kg CH\(_4\)/d given an average flow of 200 m\(^3\)/d (GWRC, 2011). However, due to diurnal variations of the wastewater flow, the actual HRT of this sewer varied between 1.5 and 6 h. Therefore,
the current estimation may misrepresent the actual methane production without considering the entire range of HRT.

Dissolved methane concentrations of 11 – 33 mg/L (case I, GWRC, 2011) and 3.4 – 6.6 mg/L (case II, Foley et al., 2009) were measured at the end of a 1100-m long rising main (CO16, Gold Coast, Australia), during respective 4- and 6-h sampling campaigns in the early morning with hourly, manual sampling. The average daily flow in this pipe was 707 m$^3$/d, resulting in an average daily methane production of 9.8 and 2.6 kg CH$_4$/d, respectively. This substantial difference in the results could not be fully explained by the differences in HRT (3.9 – 11.0 h for 4-h sampling and 1.5 – 7.3 h for 6-h sampling) and by the slight temperature differences (22.5 °C and 23.5 °C, respectively). A longer-term continuous monitoring campaign is required to provide more insight into the methane production at this site.

Chaosakul et al. (2014) measured dissolved methane levels in a 1-km long gravity sewer in Thailand (Table 2.2). The concentrations varied from 8.0 to 13.7 mg/L in dry weather (HRT of 22 – 31.4 h) and 0.1 – 11.4 mg/L in wet weather (HRT of 0 – 12 h). This observation demonstrates that, after methane emission in the gravity sewer following sewage discharge from an upstream rising main, a significant proportion of methane still remains in the liquid phase, and eventually this is emitted at the downstream gravity section or at the inlet head works of the downstream WWTP.

Pumping station (PS) methane concentrations have also been reported (Table 2.2). In our experience, the dissolved methane concentrations are close to 0 if the station receives ‘fresh’ sewage from nearby households. If the PS receives aged sewage from other upstream pumping stations, then dissolved methane concentrations usually vary from 1 to 2 mg/L (see data for CO16 in Table 2.2).
Table 2.2: Dissolved methane concentrations and methane emission in sewer systems

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>Length (m)</th>
<th>Diameter (mm)</th>
<th>A/V (m$^{-1}$)</th>
<th>HRT (h) Average (min-max)</th>
<th>Average wastewater temperature (°C)</th>
<th>Dissolved CH$_4$ (mg/L) Average (min-max)</th>
<th>Daily flow (m$^3$/d)</th>
<th>Production (kg CH$_4$/d)</th>
<th>Overall emission: kg CO$_2$-e/m$^3$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>UC9</td>
<td>Rising main</td>
<td>828</td>
<td>150</td>
<td>26.7</td>
<td>2.5 (3.1–4.6)</td>
<td>27.7</td>
<td>5.3 (4.4–6.1)</td>
<td>200</td>
<td>1.1</td>
<td>0.18</td>
<td>(GWRC, 2011)</td>
</tr>
<tr>
<td>CO16</td>
<td>Rising main</td>
<td>1,100</td>
<td>300</td>
<td>13.3</td>
<td>2.6 (3.9–11.0)</td>
<td>22.5</td>
<td>15.3 (11.0–33.0)</td>
<td>707</td>
<td>9.8</td>
<td>0.52</td>
<td>(GWRC, 2011)</td>
</tr>
<tr>
<td>CO16</td>
<td>Rising main</td>
<td>1,100</td>
<td>300</td>
<td>13.3</td>
<td>2.6 (1.5–7.3)</td>
<td>23.5</td>
<td>5.2 (3.4–6.6)</td>
<td>707</td>
<td>2.6</td>
<td>0.18</td>
<td>(Foley et al., 2009)</td>
</tr>
<tr>
<td>RV</td>
<td>Gravity</td>
<td>1,000</td>
<td>1,000</td>
<td>—</td>
<td>—</td>
<td>27.9 (22–31.4)</td>
<td>10.1 (8.0–13.7)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>(Chaosakul et al., 2014)</td>
</tr>
<tr>
<td>RV</td>
<td>Gravity</td>
<td>1,000</td>
<td>1,000</td>
<td>—</td>
<td>7.8 (0–12)</td>
<td>30.2</td>
<td>4.6 (0.1–11.4)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>(Chaosakul et al., 2014)</td>
</tr>
<tr>
<td>CO16</td>
<td>Pumping station</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>23.5</td>
<td>1.5 (1.0–1.92)</td>
<td>707</td>
<td>—</td>
<td>—</td>
<td>(Foley et al., 2009)</td>
</tr>
</tbody>
</table>
Gas phase methane concentrations

Methane can be produced and accumulated beyond saturated concentrations in pressure sewers (Table 2.2) due to the sewer pressure exceeding atmospheric pressure (Guisasola et al., 2008). When sewage flow from an enclosed anaerobic sewer pipe is discharged into a ventilated space, i.e., at a pumping station, a wet-well, a gravity sewer or at the influent works of WWTPs, a large proportion of dissolved methane is stripped off to the atmosphere under the turbulent conditions, resulting in significant methane emissions (Table 2.3).

Chaosakul et al. (2014) detected gas phase methane concentrations between 7,164 and 17,183 ppmv at the end of a 1-km long gravity sewer (Thailand). Furthermore, in a study in Melbourne, Australia, almost half of the 14 manholes along a gravity sewer line (GWRC, 2011) contained methane concentrations of up to 50,000 ppmv or 5%, i.e., equivalent to the methane Lower Explosive Limit (LEL) (Table 2.3). Another field study in the US also found a large number of locations where methane concentrations in manholes exceeded the LEL (Phillips et al., 2013). Besides the issue of direct GHG emission, methane at high concentration poses a serious safety issue in sewers.

By conducting gas phase methane measurements at discharge manholes, other studies attempted to illustrate direct methane emission rates after rising mains during sewage transport (Table 2.3). In a US study, gas phase methane concentrations of 500–900 ppmv were detected by off-line measurement of samples from a discharge location of a 5.3 km rising main (HCPS). This had a daily wastewater flow of 1855 m³/d and yielded a direct CH₄ emission of 7.44 kg/d (Shah et al., 2011). Grab sampling at 65 different pumping stations across the US revealed methane emission rates between 1.13 and 11.68 kg CH₄/d (GWRC, 2011). For example, gas phase CH₄ at SMPLS pumping station (Table 2.3) receiving daily sewage discharge of 378.5 m³/d varied between 65 and 275 ppmv, resulting in an emission rate of 1.18 kg CH₄/d. This illustrates that the pumping stations should also be considered as hot spots for direct GHG emission.
### Table 2.3: Gas phase methane concentrations in sewer air

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>Length (m)</th>
<th>Diameter (m)</th>
<th>A/V (m³)</th>
<th>Daily flow (m³/d)</th>
<th>CH₄ (ppmv) Average (min-max)</th>
<th>Direct emission (kg CH₄/d)</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>RV</td>
<td>Gravity</td>
<td>1,000</td>
<td>1,000</td>
<td>—</td>
<td>—</td>
<td>17,183 (13,500–23,000)</td>
<td>—</td>
<td>Dry weather</td>
<td>(Chaosakul et al., 2014)</td>
</tr>
<tr>
<td>RV</td>
<td>Gravity</td>
<td>1,000</td>
<td>1,000</td>
<td>—</td>
<td>—</td>
<td>7,164 (65–19,000)</td>
<td>—</td>
<td>Wet weather</td>
<td>(Chaosakul et al., 2014)</td>
</tr>
<tr>
<td>SEW</td>
<td>Gravity</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1,500–50,000</td>
<td>—</td>
<td>Data from several manholes receiving industrial wastewaters</td>
<td>(GWRC, 2011)</td>
</tr>
<tr>
<td>HCPS</td>
<td>Rising</td>
<td>5,310</td>
<td>406</td>
<td>9.9</td>
<td>1,855</td>
<td>600 (500–900)</td>
<td>7.44</td>
<td>Measured at discharge manhole</td>
<td>(Shah et al., 2011)</td>
</tr>
<tr>
<td>CO16</td>
<td>Rising</td>
<td>1,300</td>
<td>300</td>
<td>13.3</td>
<td>707</td>
<td>10,000 (2,500–45,000)</td>
<td>—</td>
<td>Measured at discharge manhole</td>
<td>(GWRC, 2011)</td>
</tr>
<tr>
<td>SMPLS</td>
<td>Pumping</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>378.5</td>
<td>116 (65–275)</td>
<td>1.18</td>
<td>—</td>
<td>(Shah et al., 2011)</td>
</tr>
<tr>
<td>PS</td>
<td>Pumping</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.13–11.68</td>
<td>Data from 65 pumping stations across the US</td>
<td>(GWRC, 2011)</td>
</tr>
</tbody>
</table>
2.3.4 Factors affecting methane production in sewers

Some key factors regulating methane production and emission in sewers have been identified in recent studies (Foley et al., 2009, Guisasola et al., 2008). These include the sewage hydraulic retention time (HRT), the area-to-volume (A/V) ratio of the pipe, COD, and the sewer temperature.

**HRT:** Guisasola et al. (2009) found that dissolved methane concentration was positively correlated with the HRT in sewers. Foley et al. (2009) also confirmed that long retention times caused high methane production in the field studies. The concentrations increased along the length of the sewer, which indicated the influence of increasing HRT. In addition, Chaoskul et al. (2014) found higher methane concentrations in both the liquid and gas phases in a gravity sewer during a period of longer HRT.

**A/V ratio:** It is also documented that the dissolved methane concentration is related to the A/V ratio of the sewer pipe. Higher A/V ratio indicates more biofilm per unit volume of the wastewater and thus could result in a higher methane production rate. Both Guisasola et al. (2009) and Foley et al. (2009) revealed that higher A/V ratios resulted in higher methane production.

**Temperature:** Temperature also plays an important role in methane production. Higher methane production rate is usually observed at higher sewer temperatures (GWRC, 2011). The results from the pumping stations in the US show that the concentration of CH₄ in the gas phase was, in 80% of the cases, higher in summer than in winter (GWRC, 2011).

**COD:** Organic carbon measured as COD will be transformed to substrates for methanogenesis. It has been found that trade waste containing high COD discharged into domestic sewers was found to significantly increase the methane production (Sudarjanto et al., 2011).

Dissolved sulfide concentrations also have a positive relationship with the above factors (Hvitved-Jacobsen, 2002). Thus dissolved sulfide and methane concentrations are likely to be correlated in sewage (Guisasola et al., 2008), so that high methane concentrations are expected at sulfide ‘hot spots’ (severe odor or corrosion), and this could provide a convenient way of locating likely areas with high methane levels in a sewer network.

2.3.5 Overall estimation of methane emission

With respect to quantifying methane production in a rising main sewer, the dissolved methane concentrations at the upstream pumping station and at the end of the pipe, and the sewage flow data
are required (Fig. 2.4). Since gravity sewers are partially-filled, both liquid and gas phase methane levels in the upstream manhole and at the end of the sewer, and both water and gas flow rates are required for the evaluation of methane production. Considering that methane oxidation in sewers is expected to be a slow process (Valentine and Reeburgh, 2000), it is reasonable to assume that the majority of the methane formed would be eventually stripped to the atmosphere in gravity sewers or at the WWTPs. Therefore, these data can also be used to calculate potential overall emission rates from sewer systems. On one occasion the quantification of overall CH$_4$ emissions was determined by direct measurement of methane gas flux from a discharge manhole (Shah et al., 2011). However, this is expected to underestimate emissions as CH$_4$ could also be emitted at other locations in the network.

To date, the overall methane emission data have been available only for single-pipe rising main sewers (e.g. UC09 and CO16). The overall methane emission potential of these rising main sewers varies substantially, ranging from 0.18 to 0.52 kg CO$_2$-e/m$^3$ of wastewater transported (Table 2.2, Table 2.2, Table 2.2).
assuming that 1 kg CH₄ is equivalent to 34 kg CO₂ in terms of global warming potential). Previous studies performed on methane formation and emission have identified WWTPs as an important source of methane emission (Bousquet et al., 2006), with several reported direct methane emission factors ranging from 0.14 to 3.44 g CH₄/ influent m⁻³, i.e., 0.005–0.117 kg e-CO₂/ influent m⁻³ (Daelman et al., 2012). Therefore, methane production from sewers could play an important role in contributing to overall methane emissions of the entire wastewater system.

2.4 Modelling of methane production/emission in sewers

2.4.1 Development of sewer models

The first in-sewer biochemical process model was established by (Pomeroy, 1959), which is an empirical model for evaluating H₂S production in a sewer pipe. Following that, other empirical models were developed in the 1970s (Boon and Lister, 1975, Pomeroy and Parkhurst, 1977, Thistlethwayte, 1972) for the same purpose. The models predict sewer sulfide production using a single rate expression depending on organic matter concentrations, pipe characteristics and flow conditions. These empirical models have been used in sewer engineering for nearly 40 years.

In 2002, Hvitved-Jacobsen (2002) developed the Wastewater Aerobic/Anaerobic Transformations in Sewers (WATS) model. This was an important step in sewer process modeling as it included in-sewer aerobic, anoxic and anaerobic processes and incorporated in-sewer sulfur and carbon transformations. The parameters were calibrated using both lab data, and field data in Japan and Denmark. Field data were used to validate the model simulation. However, the application of WATS model has been limited to sewer systems under steady state conditions (Guisasola et al., 2009), and temporal sulfide concentration variations are completely ignored.

On the other hand, Huisman and Gujer (2002) developed a model for describing aerobic conversions in a sewer system based on Activated Sludge Model No. 3 (ASM3). This model was shown to successfully describe the aerobic conversions occurring in sewers. Parameters were calibrated by lab-scale experiment data and validated by field data.

Freudenthal et al. (2005) predicted sulfide formation in pressure mains by adding the sulfide formation process to the IWA Anaerobic Digestion Model No.1 (ADM1). This was the first time that ADM1 was used in sewer modeling. However, parameters were calibrated by lab-scale experiment data and the simulation result was validated by lab-scale experiment data on different days. Also, the microorganisms used in the experiment were in suspended form and the result might not be able to represent the situation in real sewers.
Recently, Jiang et al. (2009) established a biofilm model for the prediction of pollutant transformation in sewers. The model describes dynamic biofilm growth, multiple biomass evolution and competition among organic oxidation, denitrification, nitrification, sulfate reduction and sulfide oxidation in heterogenic biofilm in sewers. Parameters was calibrated and validated by data from a pilot scale sewer with aspects of biofilm thickness, biofilm density, vertical SRB distribution and spatial profiles of soluble substances.

Overall, the detailed models mentioned above all ignored methane production processes in sewers.

2.4.2 Sewer methane models
SeweX: a mechanistic model predicting methane production by anaerobic sewer biofilm
Sharma et al. (2008) developed the SeweX model to present the dynamics of sulfide and VFA production in sewers. The SeweX model is a dynamic sewer model, describing the in-sewer biological, chemical and physical processes. It predicts both the temporal and spatial variations of wastewater composition, including sulfate and sulfide, in sewers, using sewer network configuration, pipe geometry, sewage characteristics and hydraulic data as inputs. The most recent version of the SeweX model is now expanded to include methane generation by incorporating the model developed by Guisasola et al. (2009). The model is now able to predict, in addition to others, the spatial and temporal variation of methane in sewers. SeweX is the first model to predict the spatial and temporal variation in sewer methane concentration. The following processes underpinning methane production in sewers are included in the model:

1. Acidogenesis
2. Acetogenesis
3. Acetoclastic methanogenesis
4. Hydrogenotrophic methanogenesis
5. Hydrogenotrophic sulfidogenesis
6. Acetate-based sulfidogenesis
7. Propionate-based sulfidogenesis

Fermentation has been modelled as the two separate processes, acetogenesis and acidogenesis. Three fermentation products are considered, namely H₂, acetate and propionate. The biofilm-catalyzed processes were modelled using Monod kinetics, and higher values for saturation constants
were used to account for diffusion limitations in biofilms. This model can be utilized to study the effect of key sewer operational parameters on methane formation.

The key parameters of the SeweX model were calibrated by using data collected from lab-scale experiments. Also, the model was validated using manually sampled off-line methane data, without consideration of the actual dynamics of methane formation in sewers. Therefore, more online field measurement data are needed for better calibration and validation of the model. Furthermore, the in-sediment biological reactions in gravity sewers are modelled as biofilm processes, due to the knowledge gaps related to the biological transformations in sewer sediment.

**Empirical models predicting methane production in sewers**

Foley et al. (2009) proposed a simple empirical model (Eq. 1) for estimating methane production in a rising main sewer. This is based upon the observation that methane formation in a rising main sewer is related to the HRT of wastewater and the A/V ratio of the pipe. This simple equation offers a tool for water authorities to predict the methane emissions from a rising main sewer.

\[
C_{CH4}=5.24\times10^{-5}\times[A/V\times HRT]+0.0015 \quad \text{Eq. 1}
\]

where \(C_{CH4}\) is the concentration of dissolved methane (kg/m\(^3\)); \(5.24\times10^{-5}\) kg/m\(^2\)/h is the rate of methanogenic activity of the pipeline biofilm; and 0.0015 kg/m\(^3\) equals the average residual concentration of dissolved methane.

However, it should be noted that the value of methane production rate (5.24\(\times\)10\(^{-5}\)) is expected to be affected by other factors such as wastewater composition (specifically COD) and temperature, and thus would vary from system to system. Therefore, more field data are required in order to develop and calibrate this empirical model for its application.

Chaosakul et al. (2014) proposed a similar empirical model to predict methane formation in gravity sewers based on the A/V ratio, HRT and the wastewater temperature (Eq. 2). The model has been calibrated with field methane data and partially validated using rising main sewer data.

\[
C_{CH4}=6\times10^{-5}\times[A/V\times HRT]\times1.05^{(T-20)}+0.0015 \quad \text{Eq. 2}
\]
where $C_{\text{CH}_4}$ is the concentration of dissolved methane (kg/m$^3$); $6 \times 10^{-5}$ kg/m$^2$/h is the rate of methanogenic activity of the pipeline biofilm; 0.0015 kg/m$^3$ equals the average residual concentration of dissolved methane; and $1.05^{(T-20)}$ is a function of temperature.

2.5 Effects of chemical dosing on methane formation in sewers

Sulfide build-up in sewers is a major problem and commonly found in sewers with small pipe radius, large pipe length, slow flow rates and insufficient re-aeration, at high temperature (Nielsen et al., 1998, Zhang et al., 2008). Recent studies have used different chemical dosing approaches to mitigate sulfide emission from sewers (Zhang et al., 2008). Methane formation can also be suppressed by these chemicals, such as oxygen, nitrate, oxygen, ferric irons, hydroxide (pH elevation) and free nitrous acid (FNA), that are typically used for treating sulfide-related problems (Table 2.4) (Ganigue et al., 2011). The reason for the suppression of methane formation is that methanogens are slow growers and are very sensitive to environmental conditions, particularly in comparison to SRB (Whitman et al., 1999). However, as methanogens typically inhabit the deeper layer of sewer biofilms, this may offer some projection from the dosed chemical due to its limited penetration. Thus, for effective suppression of methanogenesis, higher dosage of chemicals may be needed to achieve full penetration during the initial dosing period, when the bacterial activity is high.

**Oxygen**

Ganigué and Yuan (2014) found that long-term oxygen injection (i.e., 15–25 mg/L) reduced methane formation by 47% in laboratory-scale sewer reactors. Also, the methane production rate dropped to 15% during a short-term oxygen injection over an exposure time of 6 h and following that the production fully recovered after ca. 20 d. Full control of CH$_4$ production was not achieved, as likely only partial oxygen penetration into sewer biofilm occurred. Additionally, oxygen injection would potentially lead to N$_2$O production in sewers due to the development of a nitrifying microbial community.

It should be noted that the presence of oxygen also promotes heterotrophic activity, resulting in oxidation of a significant amount of organic matter in the sewage, which will in turn, impact nutrient removal processes at the WWTP. Also, it has been suggested that oxygen should be dosed at a downstream sewer location for maximum effectiveness in sulfide control (Gutierrez et al., 2008, Mohanakrishnan et al., 2009a). In contrast, since the biological or chemical oxidation of methane by oxygen is very slow as compared with that of sulfide, oxygen should be dosed at multiple locations within the sewer system to achieve network-wide control on methanogenic
activity. This approach is likely to incur significant costs for chemical usage and further impact on COD removal.

Nitrate

Sulfide can be oxidized under anoxic conditions where nitrate is dosed. Generally, nitrate is considered to promote biological sulfide oxidation along with negligible chemical oxidation (Jiang et al., 2009, Mohanakrishnan et al., 2009a). Jiang et al. (2009) demonstrated anoxic sulfide oxidation in rising main sewers firstly occurred through the oxidation of sulfide to elemental sulfur and then through the oxidation of elemental sulfur to sulfate. Mohanakrishnan et al. (2009a) revealed that nitrate dosing neither inhibited the SRB activity nor did it reduce the SRB abundance in rising main sewer biofilms. The reason for sulfide elimination was attributed to the development of sulfide-oxidizing nitrate-reducing bacteria (soNRB), which oxidize sulfide coupled with the reduction of nitrate (Garcia-de-Lomas et al., 2007).

A recent study by Jiang et al. (2013b) demonstrated that the long-term addition of 30 mg N/L of nitrate resulted in a 90% reduction in methanogenic activity in a rising main sewer reactor due to an inhibitory effect (Mohanakrishnan et al., 2009a). The long-term dosing reduced the methane concentrations in the effluent by 42%, while negligible nitrous oxide was produced. It was suggested that methanogenesis may persist in the deeper sections of the biofilms due to the availability of soluble organic substrates, and the limited penetration of nitrate and sulfate. Field trials were conducted to demonstrate the effect of intermittent nitrate addition in sewers, i.e., methane production was reduced by 27% after one nitrate shock dose of 50 mg-N/L and full recovery of methanogenesis occurred after 2 days (Table 2.4). Similar to oxygen, nitrate dosing also promotes sewer heterotrophic activity, thereby affecting the downstream nutrient removal in WWTPs.

Ferric irons

Zhang et al. (2009) investigated the impact of long-term ferric chloride dosing (ca. 21 mg/L) on methanogenic activity of sewer biofilms, and reported that effluent methane concentrations of a sewer reactor were reduced by 43%, together with almost complete removal of sulfide (i.e., 99%). It is reported that, despite limited application in Australia, iron salts contribute most to sulfide control in sewers in terms of sewage flow treated, accounting for about 66% of the total sewage treated with chemicals (Ganigue et al., 2011). Further field trials are required to confirm the effectiveness of Fe³⁺ in mitigation of methane production.
Elevated pH

Gutierrez et al. (2009) reported that long-term elevated pH to 8.6–9.0 suppressed the growth of methanogens in sewer reactors. The model simulation of long-term hydroxide dosing at the upstream section of the network indicated that full control of both methane and sulfide production was achievable. Further field trials (Gutierrez et al., 2014) demonstrated that effective methane control could be also achieved with short-term, moderately-elevated pH. The exposure of the entire sewer line to pH=11.5 for 6 h was adequate for complete suppression of methane production for more than 2 weeks. Additionally, 67% of sulfide reduction occurred 2 days following the shock alkali dose. Following the dose, the SRB activity recovered gradually over a period of 7 days, while the methanogenic activity took much longer to recover. Recently, an electrochemical caustic generation system (Pikaar et al., 2013, Pikaar et al., 2011) has been able to continuously produce, in-situ, ca. 3% hydroxide w/w from sewage at a lower cost than the scenario of caustic dosing, once a week at pH 11. This electrochemical method is a promising technology for methane control in small sewers, but field trials are needed to confirm effectiveness.

FNA

Recent laboratory studies reported the inhibitory effect of FNA on SRB and methanogenic activities in sewer biofilms (Jiang et al., 2010, Jiang et al., 2011b). Jiang et al. (2011a) showed a strong biocidal effect of FNA on methanogens in sewer biofilms through its intermittent dosing. FNA dosing at 0.26 mg-N/L for 12 h was adequate to completely suppress methanogenesis in the sewer reactor, with only 20% recovery of methane production occurring in the following two weeks. This cost-effective dosing method has also been verified in an actual sewer (Jiang et al., 2013a). Sulfide production was also reduced by more than 80% over a period of 10 days after FNA was once dosed at a pumping station for a period of 8 h. MA are more sensitive than SRB to FNA, and the laboratory dosing study demonstrated complete methane control, giving good evidence that FNA is effective for both methane mitigation and sulfide control in sewer systems.
Table 2.4: Comparison of the effects of chemical addition on methane production in sewers

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Dosing levels</th>
<th>Condition</th>
<th>Dosing plan</th>
<th>CH₄ reduction level (%)</th>
<th>H₂S reduction level (%)</th>
<th>Methane production recovery</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>15–25 kg O₂/ML</td>
<td>Lab</td>
<td>Continuous</td>
<td>47</td>
<td>—</td>
<td>—</td>
<td>(Ganigué and Yuan, 2014)</td>
</tr>
<tr>
<td>Oxygen</td>
<td>15–25 kg O₂/ML</td>
<td>Lab</td>
<td>Continuous</td>
<td>—</td>
<td>35</td>
<td>—</td>
<td>(Gutierrez et al., 2008)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>30 kg N-NO₃⁻/ML</td>
<td>Lab</td>
<td>Continuous</td>
<td>42</td>
<td>—</td>
<td>—</td>
<td>(Jiang et al., 2013b)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>30 kg N-NO₃⁻/ML</td>
<td>Lab</td>
<td>Continuous</td>
<td>94</td>
<td>66</td>
<td>—</td>
<td>(Mohanakrishnan et al., 2009a)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>17 kg N-NO₃⁻/ML</td>
<td>Field</td>
<td>One shock</td>
<td>13</td>
<td>—</td>
<td>100% in 2 d</td>
<td>(Shah et al., 2011)</td>
</tr>
<tr>
<td>Nitrate</td>
<td>50 kg N-NO₃⁻/ML</td>
<td>Field</td>
<td>One shock</td>
<td>27</td>
<td>—</td>
<td>100% in 2 d</td>
<td>(Shah et al., 2011)</td>
</tr>
<tr>
<td>Hydroxide</td>
<td>pH=9</td>
<td>Simulation</td>
<td>Continuous</td>
<td>98</td>
<td>99</td>
<td>—</td>
<td>(Gutierrez et al., 2009)</td>
</tr>
<tr>
<td>Hydroxide</td>
<td>pH=11.5</td>
<td>Field</td>
<td>Shock for 6 h</td>
<td>97</td>
<td>67ᵃ</td>
<td>3% in 15 d</td>
<td>(Gutierrez et al., 2014)</td>
</tr>
<tr>
<td>Iron salts</td>
<td>21 kg Fe/ML</td>
<td>Lab</td>
<td>Continuous</td>
<td>43</td>
<td>99</td>
<td>—</td>
<td>(Zhang et al., 2009)</td>
</tr>
<tr>
<td>FNA</td>
<td>0.26 kg N-FNA/ML</td>
<td>Field</td>
<td>Shock for 8 h</td>
<td>—</td>
<td>&gt;80ᵇ</td>
<td>—</td>
<td>(Jiang et al., 2013a)</td>
</tr>
<tr>
<td>FNA</td>
<td>0.26 kg N-FNA/ML</td>
<td>Lab</td>
<td>Shock for 12 h</td>
<td>99</td>
<td>—</td>
<td>20% in 14 d</td>
<td>(Jiang et al., 2011a)</td>
</tr>
</tbody>
</table>

ᵃ 67% sulfide reduction in next 2 days following shock dosing. The SRB activity recovered gradually over a period of 7 days.

ᵇ over 80% decrease in sulfide production for 10 days.
2.6 Sewer sediments

2.6.1 Characteristics of sewer sediments

Sewer sediments are mainly generated from the participation of solids in sewage and wash-off from land surfaces during rain events (USEPA, 2004). Different from biofilms on sewer walls that may be at most a few mm thick, sediments settled in gravity sewers can be up to 5–7.5 cm thick (Schmitt and Seyfried, 1992). Sewer sediments are believed to be biologically active, and would also contribute to sulfide and methane production (Nielsen and Hvitved-Jacobsen, 1988). They have a complex structure, as these are composed of inert inorganic substrates, organic matters and active biomass, which could lead to organic bonding and thus create a cohesive-like bed (Williams et al., 1989). The bonding may loosen when sediments are entrained and in movement. It is difficult to obtain intact sediment samples from real systems or establish lab-scale set-ups that could be representative. According to Crabtree (1989), sewer sediments can be classified into five primary classes:

A: coarse, granular bed material – widespread;
B: as Type A but concreted by the addition of fat, bitumen, cement, etc.;
C: mobile, fine grained deposits found in slack zones, in isolation or overlying Type A;
D: organic pipe wall slimes;
E: fine-grained mineral and organic deposits found in combined sewer overflow storage tanks.

2.6.2 Current findings and knowledge gaps on sewer sediments

Research in gravity sewer sediments to date has mainly focused on physical processes such as the sewer sediment deposition, erosion and transport (Banasiak et al., 2005, Gasperi et al., 2010, Rodríguez et al., 2012). The hydraulic and structural conditions in sewers, as well as the nature of sewage inputs, will determine the solid deposition (Ashley et al., 2003). It has been reported that the sediment deposition rate ranges from 30 to 500 g per meter length of sewer per day (Ashley et al., 2003). Ashley and Verbanck (1996) also revealed that sediment transport in sewers was influenced by the sewer cross-sectional shape, sediment supply and hydraulic conditions, as well as the relationship between sediment erosion and shear stresses. Mathematical models are proposed to predict these physical processes (Ashley et al., 2003, Bertrand-Krajewski et al., 1993, Mouri and Oki, 2010, Skipworth et al., 1999).

In comparison, little effort has been dedicated to the biological reactions in the sediments despite several studies recognizing their significance (Ashley et al., 2003). In fact, sewer sediments are bacteria accumulators. Schmitt and Seyfried (1992) demonstrated that the sulfate reduction rates in
sewer sediment could be ca. 80% higher than that in sewer biofilms. In fact, considering the high sediment deposition rates (Ashley et al., 2003), with plentiful supply of biodegradable organic carbon in the sewage, sewer sediment could have great potential for biological sulfide and methane production.

The bio-transformations occurring in sediments are controlled by the mass transfer processes, namely advection in the bulk liquid and diffusion in the sediments, which effectively regulate the availability of substrates between the sediments and water. A hydrodynamic boundary layer is present between the sediment matrix and surrounding water, and this creates mass transfer resistance (Mohanakrishnan, 2008). Concentration gradients can develop in the sediments and the boundary layer, and these reflect the varying rates of microbial conversions through the sediments. High vertical gradients of COD and volatile solids (VS) are detected in sewer sediments (Ashley et al., 2003), and these could impact the locations that sulfide and methane production take place. However, limited previous studies only investigated biological reactions in the bulk liquid phase by using suspended sewer sediments (Schmitt and Seyfried, 1992, Vollertsen and Hvitved-Jacobsen, 1998), and these would not represent well the real mass transfer and microbial conversion processes in the sediments.

In addition, the significant knowledge gaps of the biological transformations within the sewer sediment are currently limiting our ability to model sulfide and methane production in gravity sewers. To our knowledge, the in-sediment biological reactions are being modelled as biofilm processes in most of the sewer models such as the WATS and the SeweX models (Sharma et al., 2008). The validity of such an assumption is currently unknown.

2.7 Summary

Based on the past findings noted in the literature review above, it is apparent that methane can also be significantly produced in sewers and further emitted to the atmosphere at ventilated spaces. However, the limited studies conducted so far on methane measurement in both gas and liquid phases in sewers have relied on manual sampling followed by off-line laboratory-based chromatography analysis. These methods are labor-intensive for a large number of sewers, and do not capture the dynamic variations in methane production. Therefore, online methane sensors suitable for sewer measurement are highly required. Also, over the years, most of the studies on methane and sulfide production in sewers have focused on sewer biofilms, particularly those in rising mains. Sediments settled in gravity sewers are also believed to be biologically active, and
could also significantly contribute to sulfide and methane production. There are significant knowledge gaps related to the biological transformations within the sewer sediment which are currently limiting our ability to understand methane and sulfide production in gravity sewers. In addition, to date, little effort has been dedicated to studying the effect of chemical dosing on sulfide and methane production by gravity sewer sediments.
Chapter 3 Research Objectives

3.1 Research Objective I
Evaluating and developing online sensors for gaseous and dissolved methane quantification in sewers

3.1.1 Evaluating the feasibility of IR methane gas sensor for in-sewer application
Sewers are highly dynamic systems (Sharma et al., 2008) and CH₄ concentrations in sewers are also expected to fluctuate. Therefore, continuous monitoring of CH₄ concentrations in both the gas and liquid phases is important for the accurate quantification and overall understanding of CH₄ production and emission from sewers.

Part of the first objective in this thesis is to provide a comprehensive evaluation of IR methane sensors for in-sewer application. In the laboratory study, measurement linearity, detection limit, reproducibility, and effects of environmental conditions such as humidity and temperature on two types of IR methane sensors were evaluated. After that, field validation was performed to examine sensor long-term performance and accuracy when applied to actual sewer conditions.

3.1.2 Developing and applying a simple and robust method for long-term dissolved methane measurement to better understand and quantify methane production/emission from sewers
Although a limited number of commercial sensors for online detection of dissolved CH₄ are available, these are mainly designed for measuring methane in clean water samples, and cannot be used for sewage which contains a great amount of impurities and high sulfide concentrations.

The aim of this part of study is to develop a measuring device for dissolved methane measurement in sewer systems, which can then be effectively applied to understand and quantify dynamic methane production and emission from sewers. The device comprises a stripping vessel, where dissolved methane is stripped to the gas phase, and a measuring chamber, where an online gas-phase methane sensor is used to quantify the methane. This measurement is then converted to liquid-phase dissolved methane concentration according to Henry's Law. The sensor performance was verified through both laboratory experiments and field applications. The sensor was then applied to long-term monitoring of dissolved methane concentrations at the end of a rising main sewer network for a period of three weeks each in both summer and winter.
3.2 Research Objective II

Understanding and controlling methane and sulfide production in sewer sediments

3.2.1 Understanding and modelling methane and sulfide production in sewer sediments

Sewer sediments have a complex structure, being mainly composed of inert inorganic materials, organic substrates and biomass. In gravity sewers, sediments are in partially or fully anaerobic conditions even when oxygen is present in the bulk wastewater, due to limited penetration of the oxygen (Gutierrez et al., 2008). Therefore, with plentiful supply of organic matter in the sewage, anaerobic methane production and sulfate reduction can occur in deep layers of sediments (Hvitved-Jacobsen, 2002). However, little effort has been dedicated to initiating to study the biological reactions in the sediments.

The aim of this study is to understand the methane and sulfide production processes in gravity sewer sediment, and to propose models to describe these processes. Sediments collected from a real gravity sewer were cultivated in a laboratory sediment reactor mimicking gravity sewer conditions over a period of one year to achieve steady-state performance. A comprehensive evaluation of the in-sediment sulfide and methane production processes was then carried out through integrating batch production tests, microsensor and pore water measurements of sulfide, sulfate and methane in the sediment, microbial community profiling along the depth of the sediment and detailed mathematical modelling. Empirical models were then proposed and calibrated for the prediction of sulfide and methane production in sewer sediment.

3.2.2 Evaluating the feasibility of chemical dosing on methane and sulfide control in sewer sediments

Various chemical dosing strategies for sulfide control have been practiced by the water industry (Ganigue et al., 2011). The most commonly used chemicals include oxygen, nitrate, iron salts and alkali. In addition to sulfide control, these chemicals can simultaneously induce inhibitory effects on methanogens in sewers, thus leading to possible methane elimination (Ganigué and Yuan, 2014, Gutierrez et al., 2014, Jiang et al., 2013b, Zhang et al., 2009).

To date, research on chemical dosing for sulfide and methane control has mainly focused on rising mains. Little effort has been dedicated to studying the effect of chemical dosing on gravity sewer sediments. In contrast to rising main sewer biofilms, which are measured in terms of micrometers, sewer sediments contain a thicker, biologically active layer of several centimeters or more. It is
expected that the penetration of chemicals into the sediment would be limited, thus affecting the dosing performance on methane control.

The aim of this study is to determine the effect of chemical addition on methane and sulfide production in gravity sewer sediment. Here, we used nitrate as an example. Sediment collected from an actual gravity sewer was cultivated in laboratory sediment reactors mimicking gravity sewer conditions over a period of one year to achieve steady-state performance. Following that nitrate was continuously dosed for 3 months at a rate of 15 mg NO$_3^-$-N per liter of wastewater, which is typical of actual sewer applications. A comprehensive evaluation of in-sediment sulfide and methane production processes was then carried out through integrating batch production tests, and microsensor and pore water measurements of sulfide, sulfate and methane in the sediment.

3.3 Organization of the thesis

To address the Research Objectives stated above, this thesis is organized into four chapters and five appendices as follows:

- Chapter 1 gives a general introduction to the background and objectives.
- Chapter 2 presents a comprehensive literature review directly relevant to the thesis topic.
- Chapter 3 describes two main research objectives of this thesis, and organization of this thesis.
- Chapter 4-7 presents the detailed background, methods and results addressing each research objective in the form of peer reviewed research articles.
- Chapter 8 summarizes the significant conclusions and implications of this thesis work, and recommends directions for future research.
Chapter 4 Online monitoring of methane in sewer air†

Abstract
Methane is a highly potent greenhouse gas and contributes significantly to climate change. Recent studies have shown significant methane production in sewers. The studies conducted so far have relied on manual sampling followed by off-line laboratory-based chromatography analysis. These methods are labor-intensive when measuring methane emissions from a large number of sewers, and do not capture the dynamic variations in methane production. In this study, we investigated the suitability of infrared spectroscopy-based online methane sensors for measuring methane in humid and condensing sewer air. Two such sensors were comprehensively tested in the laboratory. Both sensors displayed high linearity ($R^2 > 0.999$), with a detection limit of 0.023% and 0.110% by volume, respectively. Both sensors were robust against ambient temperature variations in the range of 5 to 35 °C. While one sensor was robust against humidity variations, the other was found to be significantly affected by humidity. However, the problem was solved by equipping the sensor with a heating unit to increase the sensor surface temperature to 35 °C. Field studies at three sites confirmed the performance and accuracy of the sensors when applied to actual sewer conditions, and revealed substantial and highly dynamic methane concentrations in sewer air.

4.1 Introduction
Methane (CH$_4$) is a highly potent greenhouse gas and contributes significantly to climate change (IPCC, 2006, Wang et al., 2014, Xiao et al., 2013). It displays a Lower Explosive Limit (LEL) of approximately 5% by volume (vol), and thus poses a serious safety concern (Spencer et al., 2006). Thus, water utilities are committed to reducing methane emission from wastewater systems, namely sewer networks and wastewater treatment plants (WWTPs). Recently, significant progress has been made in quantifying and mitigating methane emission from WWTPs (Daelman et al., 2012, Wang et al., 2011). In comparison, little work has been done regarding the understanding of methane emission from sewer systems. The knowledge gap has led the Intergovernmental Panel on Climate Change (IPCC) to conclude that, “…wastewater in closed underground sewers is not believed to be a significant source of methane” (IPCC, 2006). However, this has been proven to be untrue by several recent studies. Dissolved methane concentrations of 5–25 mg/L were measured at several rising main sewers (Foley et al., 2009, Guisasola et al., 2008). Corroborating the liquid phase data, the gas phase methane concentrations of up to 50,000 ppmv, i.e. 5% vol, were detected in the air of a gravity sewer (GWRC, 2011). In contrast, the current atmospheric methane concentration is 1.8

† This chapter has been published as “Liu et al., On-line monitoring of methane in sewer air. Scientific reports, 2014, 4, 6637.”
ppmv (GWRC, 2011). In a US study, gas phase methane concentrations of 500-900 ppmv, i.e. 0.05-
0.09 % vol, were detected at the discharge of a 5.3 km rising main with a diameter of 406 mm,
yielding a CH$_4$ emission of 7.44 kg/d (Shah et al., 2011). These data confirmed significant methane
production and emission from sewers, which is currently not accounted for.

Sewer systems are highly dynamic (Sharma et al., 2008). Sewage flows vary substantially over time,
leading to fluctuating wastewater hydraulic retention time (HRT) in sewers. In addition, in rising
main sewers, pumps are frequently turned on and off resulting in intermittent flow, which further
adds to sewer dynamics. Similar to the dynamics already observed for hydrogen sulfide production
in sewers (Sharma et al., 2008), CH$_4$ concentrations in both the liquid and gas phases are also
expected to fluctuate. Therefore, continuous monitoring of CH$_4$ concentration is important for the
accurate quantification and overall understanding of CH$_4$ production and emission from sewers.
However, manual sampling for off-line chromatographic (GC) analysis has been the primary
method for CH$_4$ measurement from sewers (Foley et al., 2009, Guisasola et al., 2008, Shah et al.,
2011). It is difficult to capture the expected fluctuation in CH$_4$ concentration with this method;
therefore it imposes a serious limitation on accurate quantification. In addition, methane emission
data are expected to vary from site to site (Foley et al., 2009), and manual sampling is not feasible
for long-term quantification of methane concentrations over a large number of sampling sites along
extensive sewer networks.

Online sensors for continuous CH$_4$ measurement potentially provide a solution to the
aforementioned problems. Instruments that are able to measure CH$_4$ online are available and have
been widely used in combination with detecting systems such as infrared spectroscopy,
photoacoustic spectrometry, and pellistors or metal-oxide semiconductors (Lawrence, 2006).
Photoacoustic detection is based on the photoacoustic effect in which energy from a radiation
source is first converted to a sound and then to an electrical signal; this is a developing technology
used for methane measurement and there are few products on the market. Pellistors are calorimetric
flammable gas sensors, which detect a temperature variation when a heated catalytic element is
exposed to a mixture of combustible gases. Pellistors are not expected to be applicable in sewer
conditions due to the known toxic effect of hydrogen sulfide on electrodes (Deng et al., 1993).
Metal-oxide semiconductors will vary in conductance or resistance in response to the presence of
different gases. The major limitation is that a semiconductor can respond to any gas that can be
oxidized and hence is not specific to a particular gas (Schierbaum et al., 1992). Infrared (IR)
spectroscopy is based on the principle of measuring an absorption line unique to the detected gas,
with significant sensitivity and selectivity. Although alkane such as propane, pentane, butane and
hexane can interfere with CH₄ measurement via IR spectroscopy, these hydrocarbons are not expected to exist in sewers in significant amounts unless directly discharged (GWRC, 2011). Therefore, out of the methods described, IR spectroscopy is likely the most promising method for online CH₄ measurement in sewer conditions (GWRC, 2011).

Gas sensors with IR spectroscopy technology are mainly used as safety devices for detecting flammable gases such as CH₄ in underground mining and petrochemical industries (Taylor et al., 2008). Almost all commercial IR sensors are of the non-dispersive type, which uses discrete optical band-pass filters. Even though it is claimed that these sensors are applicable to methane detection in wastewater treatment facilities, sensor performance has not been fully studied and there have been no reports in the scientific literature evaluating the suitability of these sensors for online methane measurement in sewers.

Both temperature and humidity can affect IR sensor performance. An IR detector is essentially a temperature sensor and is, therefore, potentially sensitive to changes in the temperature. The temperature in sewers varies between day and night as well as with seasons, which may influence the sensor performance. Humidity is often a major interference with infrared systems (Sun et al., 2011). Water vapour has a significant absorption spectrum that has peaks similar to CH₄. Therefore, water vapour could interfere with CH₄ signals and cause false readings due to potential overlap in spectrum. Water vapour can also condense on the optics or in the light path and cause the beam to be deflected or diffracted so that an erroneous reading or instrument failure can occur. The relative humidity in sewers is usually above 90% and sometimes it can be fully condensing (Joseph et al., 2012), and this may have an adverse effect on IR detection of CH₄. The performance of IR sensors in humid sewers is unknown and requires evaluation before wide application to the sewer environment.

This study provides a comprehensive evaluation of IR methane sensors for in-sewer application. In the laboratory study, linearity, detection limit, reproducibility, and effects of environmental conditions such as humidity and temperature on two types of IR methane sensors were evaluated. After that, field validation was performed to examine sensor long-term performance and accuracy when applied to actual sewer conditions. This study provides scientific evidence to support the wide application of IR methane sensors for methane measurement in sewers.

4.2 Materials and Methods

4.2.1 Sensors
Two IR CH\textsubscript{4} sensors, i.e. one portable gas detector (OdaLog 7000 IR, operated with battery, named as Sensor I) and one fixed gas detector (GasTech S-Guard IR, operated with external power supply, named as Sensor II), were selected for both the laboratory testing and in-situ evaluation. The key specifications of the two sensors are summarized in Table 4.1.

**Table 4.1: Specifications of two IR methane sensors**

<table>
<thead>
<tr>
<th></th>
<th>Sensor I</th>
<th>Sensor II</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Name</strong></td>
<td>OdaLog 7000 IR</td>
<td>GasTech S-Guard IR</td>
</tr>
<tr>
<td><strong>Detection range</strong></td>
<td>0-5.00 % vol</td>
<td>0-5.00 % vol</td>
</tr>
<tr>
<td><strong>Resolution</strong></td>
<td>0.01% vol</td>
<td>0.05% vol</td>
</tr>
<tr>
<td><strong>Temperature range</strong></td>
<td>-20 to 40 ºC</td>
<td>-20 to 50 ºC</td>
</tr>
<tr>
<td><strong>Relative humidity range</strong></td>
<td>0 to 95% non-condensing</td>
<td>5 to 99% non-condensing</td>
</tr>
<tr>
<td><strong>Operation power</strong></td>
<td>Battery</td>
<td>24V DC</td>
</tr>
</tbody>
</table>

Sensor I is designed as a personal safety device for petrochemical industry and underground mining, but is also claimed to be applicable in the wastewater industry for CH\textsubscript{4} measurement at sewerage pumping stations, sewer manholes, inside of sewer collection lines, drains and pits. The sensor is claimed to be corrosion-resistant. According to the sensor manual, temperature and relative humidity can affect the sensor performance. As it is battery-operated, it can only be applied for about 24 hours in each application. It is able to log data for this period at a frequency of up to 1 s\textsuperscript{-1}.

Sensor II has similar specifications except that it has a resolution of 0.05% vol, which is five times that of Sensor I. It requires an external power supply and hence can be operated for a longer period of time.

**4.2.2 A laboratory setup for sensor testing**

The two gas phase methane sensors were evaluated in the laboratory for linearity, detection limit, reproducibility and effects of environmental conditions such as humidity and temperature.

Fig. 4.1 shows the experimental setup for the laboratory testing of the sensors’ performance. The gas-phase methane sensor was placed at the top of an airtight chamber (700 mL). Relative humidity (RH) in the chamber was controlled at an intended level by adding supersaturated aqueous salt solutions (30 mL) of MgCl\textsubscript{2}, Mg(NO\textsubscript{3})\textsubscript{2}, NaCl, KCl, KNO\textsubscript{3}, K\textsubscript{2}SO\textsubscript{4} into a container inside the chamber, which are estimated to yield approximately 33, 54, 75, 85, 93 and 97% RH at room temperature (20 ºC), respectively (Li et al., 2008). Also, the RH levels thus generated are quite
stable in the temperature range of 5-35 °C (Greenspan, 1977). 100 % RH was acquired by adding water only. Three different temperatures were created during the testings by placing the chamber in 3 different temperature-controlled rooms, namely the cold room (5±1 °C), an air-conditioned laboratory (23±1 °C), and an anaerobic incubator (35±1 °C). An air recirculation pump (Xinweicheng, FML201.5, flow rate 1.5 L/min) was used to ensure complete mixing in the gas chamber during the tests. Also, a humidity/temperature sensor (KIMO, HST-D) was placed inside the chamber to monitor the humidity and temperature continuously. The sampling port on the top of the chamber was used to inject known amounts of the methane gas into the chamber, and to take gas samples for GC analysis. The chamber was fully sealed during the tests.

Figure 4.1. Schematic diagram of the experimental setup.

4.2.3 Experimental design

Experiments to determine linearity, detection limits and reproducibility

The sensors’ linearity of response, limits of detection and reproducibility were tested. According to the data reported in a study conducted on 14 manholes in a sewer line in Melbourne (GWRC, 2011), gas phase methane concentrations usually vary from 1000 to 50000 ppm (or 0.10 – 5.00% vol), which was chosen as the basis for the calibration range. During the tests, different volumes of 90% methane gas (also containing CO₂ and N₂ at 5% each) were injected to the measurement chamber to achieve selected methane concentrations in the gas, giving rise to theoretical concentrations in the range of 0.1 – 5% vol. The tests allowed the evaluation of linearity and limits of detection. All these tests were done under a room temperature of 23±1 °C and a humidity level of 54% RH, under which factory calibration of both sensors was carried out. In order to check whether the sensor gave credible readings, gas samples were taken from the reactor in each test after well-mixed conditions were established and transferred to pre-evacuated Exetainers (Labco, Wycombe, UK). The gas samples were subsequently analyzed with Gas Chromatograph (GC) for their CH₄ concentrations.
The GC results thus obtained were compared with the sensor readings to evaluate the sensor’s performance in terms of the linearity ($R^2$ value of the fitting curve) and limit of detection (defined as the lowest concentration of a substrate that can be determined by a certain method with 99% confidence that the concentration is higher than zero). In this study, the limit of detection was calculated by using the formula as $3.3 \sigma/S$ (Kamboj et al., 2011), where $\sigma$ is the standard deviation of the response relatively to the GC-measured values, and $S$ is the slope of the fitting curve. In addition, the reproducibility of measurement using the two sensors was assessed by repetitive measurement of 20 individual methane samples with the theoretical methane concentration of 1.35% vol under the same operating conditions as described above.

Short-term tests on the effects of humidity and temperature
Before each short-term test, the intended RH and temperature levels were maintained in the chamber for 2-4 hours to achieve stable conditions in the chamber. Then the cap of the chamber was opened for a very short time (approximately 10 s) so that the sensor could be quickly put into the chamber and the sensor was left for 0.5 – 1 h, which ensured stable RH reading. 10 mL of a gas containing CH$_4$ at 90% was then injected to the chamber. When the sensor reading became stable (~3 mins), a gas sample was taken from the reactor and transferred to a Labco Exetainer for further GC analysis. For the study of the effect of humidity on the sensor performance, the temperature was at 23±1 ºC. For the study of effect of temperature on the sensor performance, the RH levels were 85, 97 and 100% for each of the 3 different temperature conditions, namely 5±1 ºC, 23±1 ºC, and 35±1 ºC.

The tests above revealed that Sensor II was robust against short-term humidity change. Therefore, two 4-point calibrations of Sensor II were further performed at 85% and 97% RH (23±1 ºC), respectively.

Long-term performance tests
Continuous measurement of methane in the field under humid conditions was expected to have some interference due to accumulation of water vapor near the sensor optical path or condensation of water vapor. The long-term stability tests were therefore conducted in laboratory prior to field tests to examine their long-term performance by continuously placing the sensor in a specific humid condition for several days, and injecting methane gas at regular interval (every 1–2 days). The sensor performance was monitored by comparing sensor readings with GC data after the gas injection. The experiments allowed to obtain two different observations: (1) apparent sensor reading under zero methane concentration - before methane gas is injected; and (2) sensor reading for a
known gas phase methane concentration - after methane gas is injected. Since Sensor II was robust against long-term humidity exposure, a further test after being exposed for 40 days at a condensing condition was conducted. Details of the testing procedures are summarised below.

**Sensor II**

The following experimental procedure was applied every 24 hours:
1. The sensor was continuously placed under given humidity and temperature conditions.
2. 10mL of 90% CH₄ gas was injected to the chamber. When the sensor reading became stable (~3 mins), a gas sample was taken from the chamber for further GC analysis.
3. The valve on the chamber was opened and the chamber was flushed with air for 5-10 mins at a flow rate of 1.5 L/min to strip CH₄ from the chamber (the CH₄ readings by the IR sensor became zero). During this period, the humidity also changed towards that in the ambient condition.
4. The valve was closed. The desired humidity and temperature conditions were reestablished after 1 – 2 hours.
5. After about 24 hours, Steps 2 - 4 were repeated for additional tests.

**Sensor I**

This sensor is powered with a battery with a normal measurement cycle of ~24 hr. To be able to examine the sensor performance over several days under a constant condition, different from the procedure applied to Sensor II, Sensor I was switched off manually between measurements to prolong the battery life. During each measurement, the sensor was turned on. Then Steps 2 – 5 were followed except that the sensor was turned off after Step 4.

### 4.2.4 Increasing the surface temperature on Sensor I

The tests above revealed that Sensor I was sensitive to humidity while Sensor II was robust against humidity. To understand the mechanism involved and also to improve the robustness of Sensor I towards humidity variation, we modified Sensor I by adhering a heating chip (1cm×1cm) at the sensor probe surface to increase the probe surface temperature from 25 to 35 ºC, a temperature measured at the surface of Sensor II probe (the Sensor II surface temperature was at this level despite the variation of ambient temperatures, due to its higher power consumption). The Sensor I surface temperature was controlled by changing the voltage on the heating chip. The experiment was conducted at 93% RH condition with a procedure as described for the short-term tests. It should be noted that the heating chip was only used in this laboratory test aimed at studying Sensor I performance against humidity at increased sensor surface temperature.
4.2.5 Field application

To verify performance of the sensors under in-situ conditions, Sensor II was installed at the headspace of two discharge manholes in two sewer lines. Manhole A receives discharge from a large gravity sewer with a pipe diameter of 1800 mm. The daily flow is about 17,000 m$^3$/d. Manhole B receives discharge from a 15-km long pressure sewer with a pipe diameter of 900 mm. The daily flow is about 11,000 m$^3$/d. A temperature sensor (SL-H$_2$S-200, Odalog), a humidity sensor (HMP60, Vaisala) and a hydrogen sulfide sensor (SL-H$_2$S-200, Odalog) were installed along with Sensor II. The measurement campaign at each site lasted for 12 days, with data logged by all sensors collected at the end.

Due to the short lifetime of the battery (~24 hrs), Sensor I was tested for 8 hrs (daytime) at a local Pumping Station (Site C). As the laboratory evaluation revealed that high humidity affected its performance, Sensor I was installed at the headspace of the pumping station with a device similar to that shown in Fig. 4.1. A gas pump continuously transported the gas from the sewer headspace to the chamber and then back to the sewer. A chiller (Resun CL85 Nano Chiller) was set in the gas line feeding the chamber to maintain the humidity in the chamber at the desired level of 50–60% RH. This pumping station receives wastewater at a daily flow of 2000 m$^3$/d from three upstream gravity sewers, with lengths ranging from 1.0 to 3.0 km and diameters from 225 to 375 mm. Gas samples were manually taken from the chamber, at an interval of about 30 mins during the 8–hr measurement period, using the protocol described in the next section. The samples were analyzed for CH$_4$ concentrations with GC, to verify the data measured by the sensor.

4.2.6 Off-line chemical analysis

For the analysis of gas methane concentration, 25 mL of gas sample was collected using a syringe through the sampling port installed on the chamber and then immediately injected into a 12 mL pre-vacuumed Labco Exetainer (Emery and Fulweiler, 2014). The methane gas in the Exetainer was measured by GC (Agilent 7890A) equipped with a flame ionization detector (FID) within 1-2 weeks after sample collection.

4.3 Results

4.3.1 Linearity, limit of detection and reproducibility

Fig. 4.2 presents laboratory results from the linearity tests, by showing sensor measurements against the off-line GC measurements. The response of both sensors to the change in methane concentration was linear up to 5% vol (the highest concentration tested in this study) with the R$^2$ values above
0.999 for both sensors. The ratio between the sensor and the GC readings was 0.995 for Sensor I and 0.985 for Sensor II. Both ratios are close to 1, indicating that the factory calibration can be used for CH₄ measurement under conditions applied in these tests, and no further calibration is required. Also, the observed intercept on the y-axis for both sensors was about -0.05, which is close to zero. These results indicate both sensors are able to measure methane concentration accurately without the need for further calibration within the range expected in a sewer.

![Graphs showing sensor vs GC readings with regression lines and R² values](image)

**Figure 4.2.** Calibration of Sensor I (A) and Sensor II (B) at 54% RH and 23±1 °C.

The limit of detection was calculated to be 0.023% vol (i.e. 230 ppm) and 0.110% vol (i.e. 1,100 ppm) for Sensor I and Sensor II, respectively. The calculated relative standard deviations (RSD) in the 20 tests at a methane concentration of 1.35% vol were 2.24% and 1.44% for Sensor I and Sensor II, respectively. Both are smaller than 2.50%, implying good reproducibility.

### 4.3.2 Short-term effects of humidity and temperature on sensor performance

The sensor and GC readings for samples under different laboratory humidity levels are presented in Fig. 4.3A and Fig. 4.3B for Sensor I and Sensor II, respectively. Sensor I is significantly affected by humidity. As the sensor was factory calibrated at 40 – 60% RH, the readings below this level of RH were lower than the actual level measured with GC. On the other hand, the relative error ((Sensor reading – GC reading) / GC reading) increased significantly from 2.1% to 58.1% with the increase in humidity beyond 70% RH. Also, it should be noted that the zero reading (sensor readings in the absence of methane) increased with increased humidity.
Figure 4.3. Short-term effect of humidity on Sensor I (A) and Sensor II (B) readings. Zero readings are sensor readings in the absence of methane.

On the other hand, the Sensor II readings were relatively stable within the RH range of 33-100% (Fig. 4.3B). There is no systematic trend in the relative errors, with a mean value of -3.82% and a standard deviation of 2.42%. Also, there was no zero reading drift during the tests (data not shown). Two 4-point calibrations of the sensor were further performed at 85% and 97% RH, respectively. Fig. S4.1 shows excellent linearity in both cases ($R^2 > 0.99$), with slopes and intercept values close to those at 54% RH (Fig. 4.2). These results clearly indicate that the Sensor II performance is not affected by humidity and the device can provide credible methane readings under a wide range of humidity.

Temperature in the range of 5 – 35 °C had negligible impact on the Sensor II readings in the RH range of 85 – 100% (Fig. 4.4B). No zero reading drift was observed even under extreme temperature and humidity conditions (i.e. under 100% RH and 5 or 35 °C) (data not shown). In comparison, Sensor I showed some variation in its readings when the temperature was varied (Fig. 4.4A). The variation was relatively small (< 12%) but without an obvious pattern.

Figure 4.4. Short-term effect of temperature on Sensor I (A) and Sensor II (B) readings.
4.3.3 Long-term stability under various humidity conditions

In this test, Sensor II showed no zero reading drift when used to measure methane concentration of normal air (without methane gas injection) regardless of the humidity level and time. The sensor readings were found to be close to the GC readings at all the RH levels tested (85%, 97% and 100%, selected according to Section 4.3.2) (Fig. 4.5B, D and F). Even after being exposed for 40 days at a condensing condition, the sensor’s reading was still stable and close to the GC reading.

Figure 4.5. Performance of Sensor I (A, C and E) and Sensor II (B, D and F) during long-term exposure to various levels of RH. Zero readings are sensor readings in the absence of methane.

For Sensor I, the relative error was small and consistent during a 6-day test at 54% RH (Fig. 4.5A). In this case, there was no zero reading drift. However, at higher RH levels of 97% and 100%, the sensor reading increased significantly after 1 day, and then remained at a relatively constant level, which was 47% and 88% higher than the GC readings (Fig. 4.5C and 4E), resulting in large relative
errors in measurement. The sensor showed a substantial zero reading drift of 0.28 % vol and 0.51% vol, respectively.

4.3.4 Sensor I performance at increased surface temperature
We hypothesized that the different sensitivity of the two sensors to humidity could be related to the different surface temperatures of the sensors during their operation. With an external power supply, Sensor II consumes a large amount of power (3.6 – 6.25W, 150 – 250mA at 24VDC), and the heat produced led to a surface temperature around 35 ºC. This likely eliminates the impact of water vapor. In comparison, operated with a Ni-MH integrated battery pack, portable Sensor I was designed to have a lower power consumption and has a surface temperature close to the environment (about 25 ºC on the sensor surface as room temperature). Further laboratory experiments (Fig. 4.6) showed with the surface temperature increased from 25ºC to 30ºC and 35ºC (using a heating chip), the relative error of Sensor I at 93% RH reduced from about 15% to -1.4% and 0.4%, respectively, comparable to those obtained with Sensor II. Similarly, the zero reading decreased from 0.08% vol at 25ºC to 0.02% vol and zero at 30ºC and 35ºC, respectively. The relative error of Sensor I stayed at a negligible level (< 0.6%) in a further test, during which the sensor was exposed to 93% RH for two days (Fig. S4.2), contrasting the results shown in Fig. 4.5. These results clearly indicate that increasing surface temperature of the sensor is effective to eliminate the effect of humidity on Sensor I readings.

![Figure 4.6](image_url)

**Figure 4.6.** Effect of surface temperature of Sensor I on the relatively measurement error and zero drifting at 93% RH.

4.3.5 Field application and evaluation of sensors
Fig. 4.7A and 4.7B presents the field study results acquired with Sensor II. Temperature and humidity levels were relatively stable and these averaged to 28.3±0.3 ºC and 97.9±0.4% RH for
Manhole A in October, and 24.2±0.3 °C and 87.3±3.6 % RH for Manhole B in November during the entire measurement campaign (Fig. S4.3). The CH₄ concentrations varied between 0.7% to 1.2% vol with an average concentration of 0.9% vol in Manhole A. In comparison, it fluctuated from 1.5% to 2.9% with an average concentration of 2.0% vol in Manhole B. In both cases, the CH₄ profile displayed a clear diurnal pattern. Manhole B had higher concentrations than Manhole A, possibly because it receives discharge from a pressure sewer dominated by anaerobic conditions. In comparison, Manhole A receives discharge from a gravity sewer, in which the transfer of CH₄ from liquid to gas is presumably an on-going process due to the presence of liquid and gas interface throughout the sewer line. The CH₄ profile in Manhole B also displayed more frequent spikes, possibly related to the intermittent pump operation feeding the pressure main. In both cases, the CH₄ diurnal pattern is very similar to that displayed by the H₂S profiles, which varied between 50 to 200 ppm for Manhole A and 100 to 800 ppm for Manhole B, respectively. Our previous research has shown that CH₄ and H₂S are simultaneously produced in sewers (Guisasola et al., 2008). The almost identical pattern in the two profiles suggests that both the CH₄ and H₂S sensors are capturing the dynamics correctly.

Fig. 4.7C shows the field data obtained by Sensor I with humidity control device (see 4.3.5 Field application) from the pumping station C. Several gas samples were also manually taken and measured with GC to validate the sensor results. The average temperature and humidity during the measurement campaign at this site were 28.3°C and 90.3% RH in January, respectively. The sensor readings (with humidity control) have an excellent fit with the GC data. Also, it should be noted that the CH₄ profile displayed a similar trend to that of the H₂S data. The methane concentration was not as high as that measured at the other two sites (Fig. 4.7A and 4.7B). Similarly, the H₂S concentration at this site was also substantially lower than that at the other two sites (Fig. 4.7A and 4.7B). The reason could be that this pumping station receives sewage from three small upstream gravity sewers, and methane and H₂S emissions should have been an on-going process in the upstream sewer pipes.
4.4 Discussion

While many sensors are available for online monitoring of CH$_4$ concentrations, their application in sewer environment has not been investigated to date. A key feature of sewer air is its high humidity with RH typically in the range of 80 – 100%, which could potentially interfere with CH$_4$ measurement. One of the two sensors displayed excellent robustness towards high humidity and its variation. While the other was found to be sensitive to humidity, solutions were developed and demonstrated in this work to resolve issue. The robustness against humidity could be achieved either by elevating the surface temperature of the sensor or by developing a device that reduces...
humidity to RH levels in the range of 40–60%. The sensors are insensitive to temperature variations. Excellent performance was obtained with both sensors in the short- and long-term tests in both laboratory and field.

Both sensors exhibited excellent linearity in the calibration studies with $R^2$ values above 0.999, slopes close to 1 and intercepts close to 0. These results imply that the sensors can be applied with factory calibration.

The two sensors had a detection limit of 0.023% vol (Sensor I) and 0.110% vol (Sensor II), respectively. The three field measurement campaigns showed that these limits are much lower than the values measured. However, it should be noted that the CH$_4$ concentration data reported in the US study (Shah et al., 2011) are below the detection limit of Sensor II. In this case, the sensors will not be able to provide accurate measurement. However, the CH$_4$ emission in this case is expected to be low, and its accurate quantification would not be critical.

After comprehensive laboratory evaluation, both sensors were applied to actual sewer conditions. This is to our knowledge the first time that performances of different online methane gas sensors for measuring sewer gas were rigorously and systematically evaluated in sewer air. The results revealed a substantial presence of CH$_4$ in sewer air (3–4 orders of magnitude higher that in atmosphere), supporting the conclusions drawn in several recent studies that sewers are a source of methane and CH$_4$ is produced from sewers in significant quantities (Foley et al., 2009, Guisasola et al., 2008). The CH$_4$ profile displayed a clear diurnal pattern, which is likely caused by the diurnal variation of HRT in sewer networks (Sharma et al., 2013). In addition, the intermittent pump operation brings further variations to the CH$_4$ profile. These results further confirmed that the CH$_4$ concentration in sewer air is highly dynamic and cannot be accurately quantified through infrequent (i.e. hourly) manual sampling. The IR-based CH$_4$ sensors, in conjunction with gas flow meters, provide powerful tools for quantifying CH$_4$ emissions from sewers. The continuous measurement also provides information-rich data to the calibration of mathematical models for the prediction of CH$_4$ emissions from sewers (Foley et al., 2009, Guisasola et al., 2009).

In summary, this study revealed that IR sensors are suitable for measuring gas phase CH$_4$ concentrations in sewers with concentrations above the detection limits, which may not be the case for all sewers as stated earlier. Sensor I, operated with battery, is suitable for short-term preliminary quantification of methane concentration before intensive measurement. In contrast, Sensor II,
operated with an external power supply, is more suitable for long-term quantification to identify the weekly, monthly and seasonally variations in methane emissions.

4.5 Supporting information

**Figure S4.1.** Calibration of Sensor II at (A) 85% RH and (B) 97% RH, both at room temperature (23±1 ºC)

**Figure S4.2.** Performance of Sensor I at a surface temperature of 35 ºC during long-term exposure to 93% RH

**Figure S4.3.** RH and temperature profiles at Manhole A (A) and Manhole B (B).
Chapter 5 Online dissolved methane measurement in sewers†

Abstract
Recent studies using short-term manual sampling of sewage followed by off-line laboratory gas chromatography (GC) measurement have shown that a substantial amount of dissolved methane is produced in sewer systems. However, only limited data has been acquired to date due to the low frequency and short span of this method, which cannot capture the dynamic variations of in-sewer dissolved methane concentrations. In this study, a newly developed online measuring device was used to monitor dissolved methane concentrations at the end of a rising main sewer network, over two periods of three weeks each, in summer and early winter, respectively. This device uses an online gas-phase methane sensor to measure methane under equilibrium conditions after being stripped from the sewage. The data are then converted to liquid-phase methane concentrations according to Henry’s Law. The detection limit and range are suitable for sewer application and can be adjusted by varying the ratio of liquid-to-gas phase volume settings. The measurement presented good linearity ($R^2 > 0.95$) during field application, when compared to off-line measurements. The overall data set showed a wide variation in dissolved methane concentration of 5–15 mg/L in summer and 3.5–12 mg/L in winter, resulting in a significant average daily production of 24.6 and 19.0 kg-CH$_4$/d, respectively, from the network with a daily average sewage flow of 2840 m$^3$/day. The dissolved methane concentration demonstrated a clear diurnal pattern coinciding with flow and sulfide fluctuation, implying a relationship with the wastewater hydraulic retention time (HRT). The total dissolved sulfide (TDS) concentration in sewers can be determined simultaneously with the same principle.

5.1 Introduction
Sewer systems are an important and integrated component of the urban water infrastructure. Sewer networks collect and transport wastewater through underground pipelines to wastewater treatment plants for pollutant removal prior to environmental discharge. They protect our urban society against sewage-born diseases, unhygienic conditions and obnoxious odours, allowing us to live in ever larger and more densely populated cities (Pikaar et al., 2014). However, sewer emissions are a notorious problem that water utilities have to deal with (Ganigue et al., 2011, USEPA, 1974). The production and emission of hydrogen sulfide is a well-known problem for decades. Under anaerobic conditions...
conditions, sulfate is reduced to sulfide through a biological process mediated by sulfate-reducing bacteria (SRB). Dissolved hydrogen sulfide thus produced can be released from wastewater as the hydrogen sulfide gas, which is the primary cause of sewer odors and corrosion (Joseph et al., 2012, Santry Jr, 1966). However, hydrogen sulfide is not the only harmful emission from sewer networks. Methane can also be generated in anaerobic sewers through methanogenesis (Foley et al., 2009, Guisasola et al., 2008, Jiang et al., 2013b). Methane is a highly potent greenhouse gas which is significantly contributing to climate change (IPCC, 2013). It is also explosive with a lower explosive limit (LEL) of approximately 5% by volume (vol), and thus poses a serious safety issue (Spencer et al., 2006). In addition, methane generation in sewers may consume a significant amount of soluble chemical oxygen demand (COD), which is detrimental to nutrient removal in downstream wastewater treatment plants (WWTPs).

There is currently a major effort aimed at understanding and quantifying methane production in WWTPs (Bani Shahabadi et al., 2009, Daelman et al., 2012, Wang et al., 2011). Significant progress is enabling better management of methane emissions in treatment plants. In contrast, very little attention has been paid to methane formation in sewer networks.

Recent studies have shown substantial methane production and emission from sewers by manual sampling followed by off-line laboratory analysis of CH$_4$ content in wastewater samples using gas chromatography (GC). Over a 6 h measurement campaign with half-hourly manual sampling of sewage, Guisasola et al. (2008) detected dissolved methane with concentrations of 5–25 mg/L at two rising mains. Foley et al. (2009) also measured dissolved methane concentrations of 1.5–9 mg/L during a 4 h manual sampling campaign with a sampling interval of one hour. However, because sewers are dynamic systems, manual sampling campaigns may not capture dynamic variation in methane production (Sharma et al., 2008), imposing a serious limitation on accurate quantification. In addition, manual sampling is not practical for long-term, intensive quantification of methane concentration in complicated sewer networks with a large number of sampling sites.

The overall aim of this study is to capture online dynamic methane data from sewer networks, to better understand and quantify methane production and emission from sewers. To achieve this goal, an online dissolved methane sensor suitable for sewer measurement is required. Although a limited number of commercial sensors for online detection of dissolved CH$_4$ are available (Camilli and Hemond, 2004, Lamontagne et al., 2001, Tsunogai et al., 2007) (Table S5.1), these are mainly designed for measuring methane in clean water bodies by using gas-permeable membranes to extract methane gas from water. This method cannot be used for measuring domestic sewage
containing a large amount of impurities as well as sulfide at high concentrations (Boulart et al., 2010).

In this study, a measuring device was specifically designed and developed for dissolved methane measurement in sewer systems. The device comprises a stripping vessel, where dissolved methane is stripped to gas phase, and a measuring chamber, where an online gas-phase methane sensor is used to acquire the methane data, which is then converted to liquid-phase dissolved methane concentration according to Henry’s Law. The measurement performance was verified through both laboratory experiments and field applications. The sensor was then applied to long-term monitoring of dissolved methane concentrations at the end of a rising main sewer network for a period of three weeks in both summer and winter. To the best of our knowledge, this is the first reported study of in-situ continuous quantification of dissolved methane concentration in sewers. In addition, simultaneous dissolved methane and total dissolved sulfide (TDS) were achieved by the same principle, and validated under field sewer conditions.

5.2 Materials and Methods

5.2.1 Method development

Fig. 5.1 shows the laboratory experimental set-up for in-situ dissolved methane and TDS measurement. The principle is to strip the dissolved gas in the liquid into the gas phase, and then convert this gas phase concentration under equilibrium back to liquid phase concentration using Henry’s Law (von Schulthess and Gujer, 1996). In order to carry out the measurement, a wastewater sample (500 mL) was pumped into the stripping chamber using a feed pump (Masterflex L/S, 77800-50, flow rate 1 L/min). For CH₄ measurement, once the feed pump was stopped, the air recirculation pump (Xinweicheng, FML201.5, flow rate 1.5 L/min) and stirrer (Heidolph, MR Hei-Standard, 1400 rpm) were started, enhancing the transfer of dissolved methane from liquid to the headspace with a total gas volume of 1070 mL including 370 mL headspace in the stripping vessel and 700 mL of the gas measurement chamber. A chilling unit was incorporated between the stripping and measurement chambers to eliminate the effect of moisture on the gas sensor by maintaining the relative humidity to a level below 70%. The recirculation continued until equilibrium was attained (about 4–5 min from stripping, as confirmed by the sensor reading curve as well as GC analysis). Based upon the equilibrated gas phase measurement using a GasTech S-Guard methane detector (range, 0–5.00% vol, and resolution, 0.05% vol), the liquid phase methane concentration under equilibrium was calculated using Henry’s Law (Eq. 3). The total amount of methane in the original sewage sample is calculated as the sum of the measured amount of methane
in the headspace and the calculated amount of methane in the sewage sample after stripping using mass balance (Eq. 4).

\[ C_{w,eq} = H \cdot R \cdot T \cdot C_{g,eq} \] \hspace{1cm} Eq. 3

\[ C_s = \frac{(V_r - V_s) \cdot C_{g,eq} + V_s \cdot C_{w,eq}}{V_s} \] \hspace{1cm} Eq. 4

Where,

- \( V_s \): Volume of liquid sample (L)
- \( V_r \): Volume of both reactors (L)
- \( C_s \): Dissolved methane concentration in the sewage sample (mol/L)
- \( C_{g,eq} \): Methane concentration in gas under equilibrium (mol/L)
- \( C_{w,eq} \): Methane concentration in water under equilibrium (mol/L)
- \( H \): Henry’s Law constant (mol/L \cdot atm)
- \( R \): Ideal gas constant (0.0821 L \cdot atm/mol \cdot K)
- \( T \): Temperature (K)

**Figure 5.1.** Schematic diagram of the laboratory experimental set-up.

The sensor was further augmented for the TDS measurement. The basic principle is the same as described for methane measurement, but with an additional acid-dosing system. Once the feeding was stopped, 1 mL 1 M HCl was dosed to the stripping chamber to acidify the wastewater to pH <3, and thus converting >99.99% of the dissolved sulfides to the H\(_2\)S form. Lowering the pH can significantly accelerate the H\(_2\)S stripping process (Wang et al., 2009), as examined in Fig. S1.
Secondly, under acidic conditions, TDS is mainly present as H$_2$S ($\text{H}_2\text{S} = \text{TDS}/(1+10^{\text{pH}-6.99})$, 25°C), lowering the likelihood of oxidation by oxygen because HS$^-$ is the main chemical oxidizing reactant (Chen and Morris, 1972). In our tests, no more sulfur species such as sulfite, sulfate and thiosulfate were generated during the stripping process (Table S5.2), confirming that the air stripping method is feasible. An ODASL-H$_2$S-2000 sensor (0–2000 ppm, with a resolution of 1 ppm) was chosen for gas-phase hydrogen sulfide measurement. The TDS concentration in the original sewage sample is calculated with Eq. 3 and Eq. 4, with methane concentrations replaced with hydrogen sulfide concentrations.

5.2.2 Measurement method verification

Dissolved methane measurement
The dissolved methane stock solution (ca. 23 mg/L) was prepared by sparging 2 L tap water for 30 min with 90% methane gas (also containing CO$_2$ and N$_2$ at 5% each). The stock solution was diluted by 1.33, 2, 4, 8 and 16 times with tap water to acquire solutions with theoretical methane concentrations of 17.3, 11.5, 5.8, 2.9 and 1.5 mg/L, respectively. 500 mL of the stock and diluted stock solutions were then pumped into the measuring set-up (Fig. 5.1) according to the procedure described in 5.2.1 for dissolved methane measurement. Prior to the commencement of the pumping, a 6 mL sample of solution was collected for GC analysis of the dissolved methane. The dissolved methane concentration thus measured was used for comparison with the sensor measurement, to evaluate the sensor’s performance in terms of linearity ($R^2$ value) and limit of detection (defined as the lowest concentration of a substrate that can be determined by a certain method with 99% confidence that the concentration is higher than zero). In this study, the limit of detection was calculated as $3.3 \sigma/S$, where $\sigma$ is the standard deviation of the response relative to the GC-measured values, and $S$ is the slope of the fitting curve (Kamboj et al., 2011).

Dissolved sulfide measurement and simultaneous dissolved methane and TDS measurement
Anhydrous sodium sulfide (Na$_2$S·9H$_2$O) (Sigma-Aldrich) was used for the preparation of the sulfide stock solutions. Milli-Q water (>18 MΩ), purged with helium for 5 min, was used for preparation of the solutions. A stock solution of 300 mg S/L in 0.02 M NaOH, freshly prepared each day, was diluted with tap water to acquire the solutions with theoretical sulfide concentrations of 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0 and 9.0 mg S/L for TDS measurement. Prior to commencement of the pumping, a 2 mL sample of solution was taken for offline chemical analysis and sensor measurement verification. After feeding, 1 mL 1 M HCl was dosed to the stripping chamber to acidify the solution to pH <3 as described in 5.2.1. When the equilibrium condition was established as indicated by the constant reading of the H$_2$S sensor during stripping, another 2 mL sample was
taken from the liquid in the stripping chamber to verify whether sulfide was oxidized during the stripping process.

Simultaneous measurement of dissolved methane and TDS was carried out by preparing a solution with dissolved methane and sulfide. The dissolved methane solution was diluted using the same method as indicated above. Meantime, similarly, a certain amount of the sulfide stock solution was added during the dilution of the methane solution. The theoretical concentration ranges for dissolved methane and sulfide in the test were 5.0–20.0 mg/L and 0.2–5.0 mg-S/L, respectively. An 8 ml sample solution was taken for offline dissolved methane and sulfide analysis prior to the pumping.

5.2.3 Field application
The prototype sensor
After laboratory verification of the sensor principle (Fig. 5.1), a prototype was built (Fig. 5.2, 0.66 m×0.46 m×0.72 m). As the laboratory set-up, the stripping and measurement chambers have a volume of 970 mL and 250 mL, respectively. Details of the equipment used are summarized in Table S5.3. Further, a programmable logic controller (PLC) was included to automatically control the sensor operation. The system was run in batch mode. A wastewater sample was injected every 12 min, and discharged once the measurement was completed. Following each discharge, the whole system was flushed with air until methane and hydrogen sulfide readings of the sensors reached zero, before the injection of the next wastewater sample.

Figure 5.2. The prototype and its field installation.

The measurement site
The field measurement site was at the end of a rising main sewer network (Fig. 5.3), located at the Gold Coast, Australia. The network comprises six pumping stations (A, B, C, D, E and F) feeding sewage into a 4.4 km rising main. The pumping stations were operated in an ON/OFF manner with
The pump turned on when the sewage level in the wet well reaching pre-defined upper limits, and turned off when pre-defined lower limits were reached. The total pipe volume in this network is 1071 m$^3$. The network collects domestic wastewater with an average daily flow of 2840 m$^3$/d, resulting in an average hydraulic retention time (HRT) in this network of 9.1 h.

**Figure 5.3.** Details of the sewer network and the sensor location.

**Prototype installation**

The prototype sensor was connected to the end of the rising main through a fully-sealed buffer tank (2 L). The sewage in the rising main continuously flowed (at ca. 2 L/min) through the buffer tank and overflowed from the top of tank to a drainage pit, leaving no headspace. The buffer tank also allowed large particles to settle to avoid blockage of the tubing. We periodically (weekly) cleaned the buffer tank to avoid excessive solids buildup. The sensor was fed with ca. 750 mL wastewater from the buffer tank for dissolved methane and/or sulfide measurement every 12 min (120 measurements per day), with 720 mL retained in the stripping vessel and the excess amount discharged to the drainage pit. After measurement, the wastewater was disposed into the drainage pit.

**Short-term simultaneous dissolved methane and sulfide measurements**

At the beginning of the field trial, measurements were taken continuously over an 8 h period to determine the dissolved methane and TDS concentrations in the sewage. Liquid samples were manually taken from the buffer tank before each feed (prior to pumping) for offline dissolved methane and TDS analysis, to verify the accuracy of the prototype sensor under field conditions.
Long-term dissolved methane measurement

After successful verification of the prototype sensor in the field, dissolved methane concentrations were continuously measured over 3-weeks in both summer (January 2014) and early winter (May 2014). Dissolved methane samples were also manually taken on day 14 in summer and day 16 in winter, respectively, to validate the prototype performance.

To determine the sewage flow rates in these periods, the pump station operation data (time when each of the pumping stations was switched on or off) recorded by supervisory control and data acquisition (SCADA) systems installed at these pumping stations was collected. These data, along with the geometry of the pumping station wet wells were used to calculate the sewage flow rates using the method previously described in Chen et al. (2014).

5.2.4 Chemical analysis

To determine the dissolved methane concentrations in different solutions and sewage, 5 mL sample was filtered (0.22 μm) and injected into vacuumed Exetainer® tubes (Labco, Wycombe, UK) made of borosilicate glass, using a hypodermic needle attached to a plastic syringe. The tubes were allowed to reach gas-liquid equilibrium overnight. The gas phase was measured with gas chromatography (GC, Agilent 7890A) equipped with a flame ionization detector (FID) for methane. Concentrations of dissolved methane in the sample were calculated using mass balance and Henry’s law (Guisasola et al., 2008).

The concentrations of dissolved inorganic sulfur species (sulfide, sulfite, thiosulfate, and sulfate) in different solutions and sewage were determined with ion chromatograph (IC). A 1.5 mL sample was filtered (0.22 μm) into a 2 mL vial containing 0.5 mL preserving solution of sulfide anti-oxidant buffer (SAOB) (Keller-Lehmann et al., 2006). Samples were then analyzed within 24 h using an ion chromatograph (IC) with a UV and conductivity detector (Dionex ICS-2000).

5.3 Results

5.3.1 Laboratory dissolved methane and TDS measurement

A series of tests was carried out with varying methane concentrations in the water samples using the laboratory set-up (Fig. 5.1). The time for reaching gas-liquid equilibrium was shorter than 4 min (Fig. 5.4a) for all tests.
It has been established that the methane sensor gives credible gas-phase methane readings (Chapter 4). Based on sensor readings, the dissolved methane concentration was calculated according to Eq. 3 and 4. The sensor response to the change in dissolved methane concentration was linear up to ca. 24 mg/L of dissolved methane (the highest concentration used in this study) with $R^2 > 0.999$ (Fig. 5.4b). The slope of the best line of fit was $1.04 \pm 0.01$, and the y-axis intercept was $-0.84 \pm 0.13$. The limit of detection for dissolved CH$_4$ measurement is calculated to be 0.75 mg/L, which can be further enhanced by adjusting the ratio between liquid phase and headspace volumes, as will be further discussed in the Discussion section. These results indicate this method is able to measure the dissolved methane concentration accurately within the range (1.0–25 mg/L) expected in a rising main sewer (Foley et al., 2009, Guisasola et al., 2008).

**Figure 5.4.** (a) Sensor reading profiles acquired during dissolved CH$_4$ measurement; (b) Correlation between dissolved methane measured by sensor and by GC.

After confirming that the stripping method for measuring TDS was efficient and accurate at pH<3 without the need for further calibration (Fig. S5.1 and S5.2), a process for simultaneous dissolved methane and TDS measurements was developed. The results show that the sensor response to the change in methane and sulfide concentration was linear, with both $R^2 > 0.997$ (Fig. 5.5). The slope and y-axis intercept of the line of fit were $1.02 \pm 0.03$ and $-0.50 \pm 0.37$, respectively, for methane measurement, and $1.03 \pm 0.01$ and $-0.02 \pm 0.03$, respectively, for sulfide measurement, which is close to those obtained from individual dissolved methane (Fig. 5.4) and TDS (Fig. S5.2) measurement, thus confirming that simultaneous dissolved methane and TDS measurement is accurate. Similar to methane measurement alone, the range and resolution of the combined methane and sulfide measurements can be adjusted according to different detection purposes in sewers.
**Figure 5.5.** Simultaneous dissolved CH$_4$ (a) and TDS (b) measurement.

### 5.3.2 Field verification

Initially, dissolved methane and TDS concentrations in the sewage were simultaneously measured by the prototype sensor during an 8 h trial. The results (Fig. 5.6a and c) show that the dissolved methane and TDS concentrations measured by the prototype have an excellent agreement with the GC and IC data obtained with manual sampling and offline chemical analysis, respectively. Furthermore, the measured results correlate well with manual sampling data (Fig. 5.6b and d). The slopes of the line of fit are 0.95 ± 0.04 and 0.93±0.05 for methane and sulfide, respectively, with the respective R$^2$ values of 0.95 and 0.94. Also, it can be noted that the dissolved CH$_4$ and TDS profiles have a strong positive correlation with an R$^2$ value of 0.47 (Fig. S5.3).
Figure 5.6. Simultaneous measurement of dissolved methane and TDS at the end of a rising main sewer network in Gold Coast (a) Dissolved methane measured by the prototype sensor and GC; (b) Correlation between the sensor and GC measurements; (c) TDS measured by the prototype sensor and IC; (d) Correlation between the sensor and IC measurements.

5.3.3 Long-term field monitoring

Fig. 5.7a and b present results from 3 weeks’ continuous field measurements at the field site, during summer and winter, respectively. The dissolved CH₄ concentrations varied from 5 to 15 mg/L with an average concentration of 9.1 mg/L during the summer period (average atmosphere temperature was 24.6°C), and from 3.5 to 12 mg/L with an average concentration of 7.1 mg/L during the early winter period (average atmosphere temperature was 20.3°C). It can be concluded that temperature plays an important role in methane production from sewers. Two manual sampling campaigns (Fig. 5.7c and d) showed consensus between the sensor and GC data, confirming the reliability of the online data. The profile also displayed a clear diurnal pattern, with higher dissolved CH₄ concentrations during nighttime and lower concentrations during daytime (Fig. 5.7). The variation was likely caused by the diurnal variation of HRT in the network (Sharma et al., 2013), corroborating studies undertaken by Guisasola et al. (2008) and Foley et al. (2009). The short-term (e.g. within an hour) variation was likely caused by the intermittent pump stations operations. It is worthwhile to note that each pumping event delivered a slug of sewage into the rising main, resulting in highly dynamic wastewater compositions at the end of the network.
Figure 5.7. Three-week field methane measurement with the prototype sensor at the end of a rising main sewer network at Gold Coast: (a) summer; (b) winter. The agreement between the sensor measured results and those obtained through manual sampling and offline GC measured results is shown in (c) and (d).

5.4 Discussion

5.4.1 Online dissolved methane and TDS measurement in sewers

The laboratory test results (Fig. 5.4 and Fig. 5.5) showed that the designed system accurately measures dissolved methane as well as TDS concentrations. Field measurement results further verified the performance of the method, and demonstrated that the prototype sensor is suitable for sewer applications (Fig. 5.6).

The range and resolution of gas-phase methane sensor used in this study are 0 – 5.00% vol and 0.05% vol, respectively. The volume ratio between the liquid phase and the headspace in the prototype sensor is approximately 7:5, therefore the theoretical measurement range and resolution of the prototype dissolved methane sensor are estimated to be 0 – 24.2 mg/L and 0.24 mg/L, respectively (Given a conversion factor of 4.95). This range covers the methane concentration range reported to date (Guisasola et al., 2008; Foley et al., 2009, and also this study). A resolution of 0.24 mg/L of
the sensor is also deemed adequate for sewer applications given the known ranges of methane concentrations, i.e., 0 – 24 mg/L (Guisasola et al., 2008).

It should be noted that the liquid phase to gas phase volume ratio can be adjusted according to specific applications. By increasing the ratio, the resolution can be significantly improved as shown in Fig. 5.8. For example a resolution of 0.09 mg/L can be achieved if a liquid to gas phase ratio of 4 is used, however with a reduced measurement range of 0 – 9.3 mg/L. This is suitable for measuring relatively fresh wastewater, where the methane concentration is relatively low (Foley et al., 2009). Similarly, a higher management range can be achieved if the liquid to gas phase volume ratio is decreased, at the expense of measurement resolution. It is worth noting that the measured dissolved methane resolution can be improved with the use of a gas-phase methane sensor with a better resolution. Gas-phase methane sensors with a resolution of, 0.01% vol (in comparison to 0.05% of the GasTech sensor used in this study) are available (Chapter 4). For TDS measurement, a theoretical resolution of 0.003–0.008 mg S/L can be achieved with the H2S sensor used in this study (with a resolution of 1 ppmv), by varying the liquid to gas phase volume ratio between 4 to 0.25. The corresponding measurement range would be 6.3 and 16.3 mg S/L, respectively (Fig. S5.4). Thus, it is suitable for sewer applications.

**Figure 5.8.** Theoretical calculation of the dissolved methane measurement range and resolution, varying with the liquid to gas phase volume ratio.

In contrast to the stripping method used in this study, Abril et al. (2006) utilized a modified equilibrator connected to a gas analyzer for measuring dissolved methane concentrations in a tropical reservoir. Equilibrators, usually designed for CO2 in air-sea exchange studies (Frankignoule et al., 2001), comprise tubes filled with gas-partitioning material (increasing the gas-liquid exchange area) with water flowing in the opposite direction to gas pumped in an air circuit.
However, the modified equilibrator system was only tested in a water reservoir for one day, rather than in polluted water such as sewage, and equilibrators are notoriously difficult to construct, operate and calibrate in situ (Boulart et al., 2010). Later, Yu et al. (2006) developed a method for online estimation of dissolved methane concentration in a laboratory anaerobic fermenter based on the equilibrator method. The liquid-phase methane concentration was calculated based on gas-phase methane measurement and an estimated $k_l a$ for methane. $k_l a$ for methane was estimated using an empirical equation from $k_l a$ for oxygen, which is a challenge for wastewater systems due to the interference of on-going biological activities consuming oxygen (Pratt et al., 2004). In addition, no long-term measurement performance was presented. Our method provides a simple alternative for in-situ dissolved methane measurement in a range of water bodies and environments. The method can be easily expanded to simultaneously measure dissolved sulfide, as demonstrated in this study.

5.4.2 Methane production in sewers

We reported, for the first time, semi-continuous measurement of dissolved methane concentrations in sewers. The rapid variation of the methane concentration clearly demonstrates that it may not be practically possible to adequately capture the dynamics with manual sampling.

Based on the methane and flow data, the average daily methane production in the measured network was 24.6 kg-$\text{CH}_4$/d in summer and 19.0 kg-$\text{CH}_4$/d in winter, respectively. Therefore, this site is estimated to produce about 8 ton CH$_4$ or 168 ton CO$_2$-e annually. It should be noted that the present analysis assumes that one ton CH$_4$ is equivalent to 21 ton CO$_2$ in terms of global warming potential (IPCC, 2006), in order to estimate the relative contribution of sewer methane production to overall methane emission over the entire wastewater systems according to de Haas et al. (2014). Considering that methane oxidation in sewers is expected to be a slow process (Valentine and Reeburgh, 2000), it is reasonable to assume that the majority of the methane formed would be eventually stripped to the atmosphere in gravity sewers or at the wastewater treatment plants (Daelman et al., 2012). The direct greenhouse gas emission from this site is thus estimated to be 0.16 kg CO$_2$-e/m$^3$ of wastewater transported. Considering both direct and indirect emissions, de Haas et al. (2014) estimated that the total GHG emissions from WWTPs in Australia is 0.5–2.0 kg CO$_2$-e/m$^3$ with a mean value of 1.0 kg CO$_2$-e/m$^3$ of wastewater treated. Thus, methane production in part of this sewer network will potentially contribute ca. 14% of the total GHG emission during wastewater handling and treatment, comparable to the estimate of 9–26% made in Guisasola et al. (2008). It should be noted that this network is only a small part of a much larger network, and hence more methane production is expected when the wastewater discharged from this network is transported through the remaining part of the network before reaching the WWTP as Guo et al.
revealed, using a modeling approach, that methane production in sewers could contribute more than 38% of the total GHG emission during wastewater handling and treatment.

In addition, it should be noted that the method developed in this thesis consists of a semi-continuous measurement, i.e., it takes 12 mins to acquire one data point. It may not capture some short-term rapid sewer methane variations during frequent pumping station operations (i.e., early morning and late night), according to Shannon sampling theorem, which states “If a function x(t) contains no frequencies higher than B Hertz, it is completely determined by giving its ordinates at a series of points spaced 1/(2B) seconds apart. A sufficient sample-rate is therefore 2B samples/second, or anything larger”. Recently, a continuous dissolved gas measurement method based on continuous stripping has been proposed (Mampaey et al., 2015), which might be an alternative to our semi-continuous method. However, the method of Mampaey et al. may require verification under dynamic conditions such as sewers over a longer term period. Also, a continuous method would consume a large amount of power and may not be suitable for application in remote sewer sites with limited power supply.

Overall, it is impractical to quantify methane concentrations either by online (semi or continuous) or manual methods over a large number of sampling sites along extensive sewer networks, particularly on a long-term basis. However, mathematical modeling is a viable option for predicting and estimating methane production and emission in sewer networks, and therefore can be a powerful tool for supporting industry in operational optimization and the development of mitigation strategies. The semi-continuous methane data can be used to calibrate and validate the SeweX model for better prediction of methane production (Guisasola et al., 2009). The current methane prediction component of this model has so far only been calibrated with very limited laboratory and field data measured through grab sampling and off-line chemical analysis. The online measurement of dissolved methane made possible by this sensor will enable more accurate determination of the model parameters.
5.5 Supporting information

Table S5.1: Summary of currently available in-situ dissolved methane sensors

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Measurement conditions</th>
<th>Detection Technology</th>
<th>Gas extraction method</th>
</tr>
</thead>
<tbody>
<tr>
<td>METS (Lamontagne et al., 2001)</td>
<td>Gas phase/water column</td>
<td>SnO$_2$ semiconductors</td>
<td>Silicon rubber</td>
</tr>
<tr>
<td>HydroC/CH$_4$</td>
<td>Gas phase/water column</td>
<td>IR spectroscopy</td>
<td>Modified silicon rubber</td>
</tr>
<tr>
<td>Deep-sea methane sensor (Tsunogai et al., 2007)</td>
<td>Gas phase/water column</td>
<td>Laser absorption spectroscopy</td>
<td>Silicon-membrane tubes</td>
</tr>
<tr>
<td>In situ mass spectrometer (Camilli and Hemond, 2004)</td>
<td>Gas phase/water column</td>
<td>In situ mass spectrometer</td>
<td>Semi-permeable membrane inlet</td>
</tr>
</tbody>
</table>

Table S5.2: Concentrations of various inorganic sulfur species in a water sample prior to stripping and after equilibrium was reached

<table>
<thead>
<tr>
<th></th>
<th>Sulfide-S mg/L</th>
<th>Sulfite-S mg/L</th>
<th>Sulfate-S mg/L</th>
<th>Thiosulfate-S mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial sample</td>
<td>0.74</td>
<td>0.02</td>
<td>0.04</td>
<td>Not detected</td>
</tr>
<tr>
<td>After equilibrium</td>
<td>0.38</td>
<td>Not detected</td>
<td>0.04</td>
<td>Not detected</td>
</tr>
</tbody>
</table>

Table S5.3: Details of the equipment used in the prototype

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Brand</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed pump</td>
<td>Masterflex L/S</td>
<td>77800-50</td>
</tr>
<tr>
<td>Syringe pump</td>
<td>New Era</td>
<td>NE-1000</td>
</tr>
<tr>
<td>Gas pump</td>
<td>Xinweicheng</td>
<td>FML201.5</td>
</tr>
<tr>
<td>Liquid solenoid valve</td>
<td>Tianfei high-tech</td>
<td>CWX15Q</td>
</tr>
<tr>
<td>Gas 3-way solenoid valve</td>
<td>Mac</td>
<td>35A-ACA-DDBA-1ba</td>
</tr>
<tr>
<td>PLC controller</td>
<td>Arduino</td>
<td>Uno</td>
</tr>
<tr>
<td>Overhead stirrer</td>
<td>IKA</td>
<td>26000001</td>
</tr>
<tr>
<td>Chilling unit</td>
<td>Resun</td>
<td>CL85 Nano</td>
</tr>
</tbody>
</table>
Figure S5.1. Effect of pH on H$_2$S stripping. Measurements were conducted at four different pH levels (2.85, 3.31, 3.80 and 5.77) to examine the time required to achieve a steady-state sensor reading. Equilibrium conditions with respect to H$_2$S stripping were achieved in ca. 5–6 min in the first three cases. In the case of pH 5.77, 9 min was needed to achieve equilibrium.

Figure S5.2. (a) Variation of gas-phase H$_2$S concentrations during dissolved sulfide stripping; (b) Correlation between TDS measured with the TDS sensor and with IC. For TDS measurement, a series of samples containing a range of initial sulfide concentrations (0.5–9.0 mg S/L) were injected into the system. The equilibrium time was less than 5 min in all tests. The results show that the total dissolved sulfide concentrations calculated from the gas-phase H$_2$S sensor reading using Henry’s Law agree well with the IC results for dissolved sulfide concentrations of 9.0 mg S/L (the highest concentration used in this study) with $R^2$ above 0.999. The slope of the regression line was 1.09±0.01, and the y axis intercept was -0.07±0.03. These results indicate this method is able to measure the TDS concentration accurately.
Figure S5.3. Correlation of dissolved methane and TDS during field simultaneous measurement.

\[ y = 0.88x + 0.47 \]
\[ R^2 = 0.47 \]

Figure S5.4. Theoretical calculation of the TDS measurement range and resolution, varying with the liquid to gas phase volume ratio.
Chapter 6 Methane and sulfide production in sewer sediment†

Abstract
Recent studies have demonstrated significant methane and sulfide production by sewer biofilms, particularly in rising mains. Sewer sediments in gravity sewers are also biologically active; however, their contribution to biological transformations in sewers is poorly understood at present. In this study, sediments collected from a gravity sewer were cultivated in a laboratory reactor fed with real wastewater for more than one year to obtain intact sediments. Batch test results show significant sulfide production with an average rate of 9.20±0.39 g S/m²·d from the sediments, which is significantly higher than the areal rate of sewer biofilms. In contrast, the average methane production rate is 1.56±0.14 g CH₄/m²·d at 20°C, which is comparable to the areal rate of sewer biofilms. These results clearly show that the contributions of sewer sediments to methane and sulfide production cannot be ignored when evaluating sewer emissions. Microsensor and pore water measurements of sulfide, sulfate and methane in the sediments, microbial profiling along the depth of the sediments and mathematical modelling reveal that sulfide production takes place near the sediment surface due to the limited penetration of sulfate. In comparison, methane production occurs in a much deeper zone below the surface likely due to the better penetration of soluble organic carbon. Modelling results illustrate the dependency of methane and sulfide productions on the bulk soluble organic carbon and sulfate concentrations can be well described with half-order kinetics.

6.1 Introduction
Sewer systems are an important and integral component of urban water infrastructure, which collects and transports wastewater from residential houses or industry to treatment and disposal. According to the operational nature, sewer systems can be divided into fully-filled pressure sewers (anaerobic), and partially-filled gravity sewers, where re-aeration takes place.

The production and emission of hydrogen sulfide has since long been identified as a major cause of odor and corrosion in sewer systems (Boon, 1995), which incurs large costs to the water industry due to assets depreciation and mitigation measures (WERF, 2007). Sulfide build-up in sewers is commonly found in pressure sewers as well as in gravity sewers with low slope and deposits (Nielsen et al., 1998). Recent studies also demonstrated that methane, a highly potent greenhouse

† This chapter has been published as “Liu et al., Sulfide and methane production in sewer sediments. Water research, 2015, 70: 350-359.”
gas that greatly contributes to climate change, is also significantly produced in pressure mains by methanogenic archaea (MA) within the sewer biofilm (Foley et al., 2009, Guisasola et al., 2008, Shah et al., 2011).

Over the years, most of the studies on sulfide and methane production in sewers have focused on sewer biofilms, particularly those in rising mains. These studies demonstrated that sulfide is generated in significant amounts from biofilms in anaerobic pressure sewers (Pomeroy, 1959, Sharma et al., 2008) primarily due to the biological sulfate reduction process mediated by sulfate reducing bacteria (SRB), which grow in the biofilm attached to the walls of rising mains. MA have also been reported with a high activity in sewer biofilms of rising mains, which would consume significant amounts of soluble organic carbon (Guisasola et al., 2008). SRB and MA have been previously hypothesized to co-exist in anaerobic sewer biofilms but reside in different zones of sewer biofilm (Guisasola et al., 2008).

Sediments settled in gravity sewers are also believed to be biologically active (Schmitt and Seyfried, 1992), and would also contribute to sulfide and methane production. However, research in gravity sewers to date has mainly focussed on physical processes such as the sewer sediment deposition, erosion and transport (Banasiak et al., 2005, Gasperi et al., 2010, Rodriguez et al., 2012). It has been reported that the sediment deposition rate ranges from 30 to 500 g per meter length of sewer per day (Ashley et al., 2003). Ashley and Verbanck (1996) also revealed that sediment transport in sewers was influenced by the sewer cross-sectional shape, sediment supply and hydraulic conditions, as well as the relationship between sediment erosion and shear stresses. Mathematical models have been proposed to predict these physical processes (Ashley et al., 2003, Bertrand-Krajewski et al., 1993, Mouri and Oki, 2010, Skipworth et al., 1999). In comparison, little effort has been dedicated to the biological reactions in the sediment despite several studies recognizing their significance (Ashley et al., 2003). Schmitt and Seyfried (1992) demonstrated that the sulfate reduction rates in sewer sediment could be ca. 80% higher than that in sewer biofilms. In fact, with plentiful supply of biodegradable organic carbon, sewer sediment could have great potentials to produce sulfide and methane biologically.

The significant knowledge gaps related to the biological transformations within the sewer sediment are currently limiting our ability to model sulfide and methane production in gravity sewers. To our knowledge, the in-sediment biological reactions are being modelled as biofilm processes in most of the sewer models such as the WATS (Hvitved-Jacobsen et al., 1998) and the SeweX (Sharma et al., 2008) models. The validity of such an assumption is currently unknown.
The aim of this study is to understand the sulfide and methane production processes in gravity sewer sediment, and to propose models to describe these processes. Sediments collected from a real gravity sewer were cultivated in a laboratory sediment reactor mimicking gravity sewer conditions over a period of one year to achieve steady-state performance. A comprehensive evaluation of the in-sediment sulfide and methane production processes was then carried out through integrating batch production tests, microsensor and pore water measurements of sulfide, sulfate and methane in the sediment, microbial community profiling along the depth of the sediment and detailed mathematical modelling. Empirical models were then proposed and calibrated for the prediction of sulfide and methane production in sewer sediment.

6.2 Materials and methods

6.2.1 Reactor set-up, sediment collection and system operation

A laboratory reactor system was specifically designed to mimic gravity sewer conditions and to cultivate sediment (Fig. 6.1). The reactor had a working volume of 3.2 L (2.7 L and 0.5 L for the liquid and gas phase, respectively), with a diameter of 140 mm and a height of 210 mm. The bottom part contained an additional cylinder vessel (120 mm diameter and 60 mm depth) as the sediment carrier aimed at keeping the sediment intact, especially for microsensor study. A mechanical overhead stirrer was set at the water surface (ca. 12 cm above the sediment). A mixing speed of 40 rpm was applied on the stirrer to achieve aeration in the reactor, leading to an estimated oxygen transfer coefficient of ca. 0.5 h⁻¹. The DO concentrations in the bulk water were in the range of 0.1–0.4 mg/L, within the reported DO concentration range in gravity sewers (Hvitved-Jacobsen, 2002).

![Figure 6.1. Schematic diagram of the sediment reactor.](image)

Sediment samples were collected from a mature gravity sanitary sewer receiving domestic wastewater in Sydney. Sediment collection was conducted using a shovel, and the sample was
transported to the laboratory and stored at 4°C before usage. The bulk density of the sediment was 1.37 g/cm³ and the porosity was 96.7%. This coarse sediment can be classified as Type A sediment according to Crabtree (1989). The total solids (TS) and volatile solids (VS) contents were 74.0% and 3.4% of the wet weight, respectively. 600 mL sediment was inoculated in the sediment carrier of the reactor, resulting in an initial sediment depth of ca. 4 cm.

The reactor was intermittently fed with domestic sewage dripping in at the top through a peristaltic pump and the effluent drained through the outlet on the sidewall. The feed pattern consisted of 18 pump events per day, with 300 mL of wastewater fed during each event, resulting in an average wastewater retention time of 12 h, i.e., 2.7 L / (18 times/d × 0.3 L/times) = 0.5 d. Raw sewage was collected weekly from a nearby pumping station and stored at 4°C. It was warmed up to 20°C through a heat exchanger and a water bath before being pumped into the reactor. The fresh sewage typically contained 15–25 mg SO₄²⁻-S/L, <1 mg H₂S-S/L, 50–100 mg VFA-COD/L and <1 mg CH₄/L. The total suspended solids (TSS) and volatile suspended solids (VSS) concentrations averaged 103.7±31.8 mg/L and 91.7±27.7 mg/L, respectively, in the influent sewage, and averaged 71.7±16.5 mg/L and 63.9±12.7 mg/L, respectively, in the effluent of the sediment reactor. The reactor was completely covered with aluminum foil to avoid exposure to light.

To monitor the sulfide and methane production rates from the sediment, batch tests were carried out every 2-3 weeks after 300-day operation. During the batch tests, the wastewater in the reactor was drained first and the reactor was then fully refilled with fresh sewage, without any headspace to prevent methane and hydrogen sulfide loss through liquid to gas phase transfer. Liquid samples were drawn at 0, 40, 90 and 120 min. The collected samples were analyzed for dissolved sulfide and methane concentrations. Linear regression was used to calculate the methane and sulfide production rates.

The reactor was operated for more than one year to cultivate mature intact sewer sediment (the sediment was not disturbed in terms of stratification of microbial community in the sediments) and to establish pseudo steady-state conditions as indicated by stable sulfide and methane concentrations in the effluent, as well as the stable sulfide and methane production rates.

### 6.2.2 Chemical and microbial profiling along the depths of the sediment

To gain insights into the in-sediment biotransformation, chemical and microbial profiling along the sewer sediment depths was carried out, after pseudo steady-state conditions were established. pH,
dissolved oxygen (DO) and sulfide profiles along the sediment depth were measured using microsensors (described in section 6.2.3) on day 384 and day 396. During these measurements, the sediment carrier part was taken out from the sediment reactor and mounted in a flow cell (a diameter of 140 mm, 1.2 L) containing 1 L of 0.22 μm filtered wastewater for microsensor measurements. Mixing of wastewater in the cell was achieved by recirculating the water at 2-3 cm above the sediment surface using a peristaltic pump. Steady-state profiles were obtained by incubating the sediment at least 4 hours in the fresh sewage prior to measurements. The pH (7.6–7.8) in the bulk liquid was not controlled during the test, while two DO concentrations (ca. 0.5 mg/L and 4 mg/L) were chosen for testing.

The concentration gradients of DO, pH and H₂S through the sediment depth were recorded by moving the microsensors with an automatic micromanipulator in increments of 100–200 μm and recording the sensor signals at each depth using the software SensorTrace Pro (Unisense A/S, Denmark). 15–20 profiles were measured at different locations of the sediment each day. The total dissolved sulfide profiles were calculated from the H₂S and pH profiles as described in Kuhl et al. (1998). The sulfide production activity within the sediment was calculated using the diffusion reaction model developed by Kuhl and Jørgensen (1992). The diffusion coefficient in the sediment was assumed to be identical to molecular diffusion, as the porosity of the entire sediment depths averaged ca. 96%, and was adjusted according to the temperature. At 20 °C, the diffusion coefficients used for total sulfide in the sediment was 1.39×10⁵ cm²/s (Kuhl and Jørgensen, 1992).

On day 397, pore water samples were taken in triplicate at depths of 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 cm below the sediment surface using the method described by Hoehler et al. (1994). Samples were collected with 3 mL cut-off plastic syringes from sediment cores for dissolved sulfur species measurements (mainly sulfate and sulfide) and dissolved methane analysis.

On day 397, biomass samples at the depths of 0, 1.0, 2.0 and 3.0 cm were also taken for fluorescence in situ hybridization (FISH) analysis.

6.2.3 Analytical methods

The concentrations of dissolved inorganic sulfur species (sulfide, sulfite, thiosulfate, and sulfate) in the samples was determined with ion chromatograph (IC). 1.5 mL sample was filtered (0.22 μm membrane) into a 2 mL vial containing 0.5 mL of sulfide anti-oxidant buffer (SAOB), a solution preserving the sample against sulfide oxidation (Keller-Lehmann et al., 2006). Samples were then
analyzed within 24 hours using an ion chromatograph (IC) with a UV and conductivity detector (Dionex ICS-2000).

For dissolved methane measurement, 5 mL sample was filtered (0.22 µm membrane) and injected into a pre-evacuated Exetainer® tube (Labco, Wycombe, UK) made of borosilicate glass, using a hypodermic needle attached to a plastic syringe. The tube was allowed to reach gas-liquid equilibrium overnight. For detecting dissolved methane concentrations from pore water samples, the nitrogen-flushed Exetainer® tube containing 3 mL of 5% NaOH (Riedinger et al., 2010) was immediately capped after extruding sediment cores and subsequently shaken to reach equilibrium. The gas phase was measured with a gas chromatograph (GC, Agilent 7890A) equipped with a flame ionization detector (FID) for methane. Concentrations of dissolved methane in the sample were calculated using mass balance and Henry’s law (Guisasola et al., 2008).

All microsensors (pH, DO and H₂S) used were purchased from Unisense A/S (Denmark). The sensors had tip diameters between 50 and 100 µm. Calibration of the oxygen, H₂S and pH sensors was done as described previously (Mohanakrishnan et al., 2008).

Biomass samples for FISH analysis were fixed in 2% paraformaldehyde in phosphate-buffered saline (PBS) for 30 min, washed in 50% ethanol–PBS, and stored in 96% ethanol at –20°C. Then they were transferred to microscope slides, and dehydrated in an ethanol dilution series of 50%, 80%, and 96%. FISH was performed as described in Mohanakrishnan et al. (2009a). Samples were then tested for the presence of SRB using the Cy5-labeled probes SRB385 and SRB385Db (Dar et al., 2007), for the presence of methanogenic populations using the FITC-labeled probe ARC915 and for the presence of bacteria using the Cy3-labeled probe EUBMIX (Liu et al., 2011). Samples were visualized using a confocal laser scanning microscope (Zeiss LSM 510), equipped with krypton–argon (488 nm) and helium–neon lasers (543 and 633 nm). 20 images were acquired in each sample. All images were processed using the DAIME Version 1.3 and split into individual colour channels before image segmentation (Daims et al., 2006). Cells were identified using the automatic segmentation in the DAIME and artefacts (irregular shapes and bright autofluorescence) were rejected manually. Segmentation was performed for all images using the ‘batch processing’ option. The quantification data were calculated based on the average results of images from each sample. The relative fraction of SRB to overall SRB and MA was calculated as the abundance of SRB divided by total abundance of SRB and MA. The relative fraction of MA to overall SRB and MA was determined in a similar way.
6.2.4 Mathematical modelling

To better understand in-sediment processes, mathematical modelling was performed to describe the methane and sulfide concentration profiles, as well as the microbial distribution within the sediment. The biological reactions in this model were adapted from (Guisasola et al., 2009) with modifications summarized in Table S6.1–S6.3 in Supporting Information. Four biological processes were considered, namely hydrolysis, fermentation, sulfidogenesis and methanogenesis. Fermentation is in this study modelled as two separate processes: acetogenesis (converting the fermentable COD to acetate and hydrogen) and acidogenesis (converting the fermentable COD to acetate and propionate), with acetate and propionate being the main volatile fatty acid (VFA) species existing in sewers (Guisasola et al., 2009). MA utilize acetate and hydrogen as electron donors to produce methane (Yoda et al., 1987). SRB consume H$_2$, acetate and propionate to reduce sulfate for sulfide production (Nielsen and Hvitved-Jacobsen, 1988). Given the fact that SRB tend to outcompete acetogenic bacteria for propionate utilization and that propionate concentrations in real sewage are typically lower than 10 mg COD/L, propionate was considered as an electron donor for sulfate reduction only (Guisasola et al., 2009). The sulfate reduction using fermentable COD is not considered in the model due to its extremely low consumption rate. In addition, the hydrolysis of slowly degradable substrate (Xs), which is either from the raw sewage or generated through biomass decay, can produce fermentable COD.

Some sulfide consumption in the sediment was clearly observed experimentally (see Results section). As there was neither oxygen nor nitrate in the sediment or bulk liquid, this consumption was likely caused by sulfide metal precipitation. Sulfide sink is introduced into the model to simulate the decrease in sulfide concentration in the sediment.

A one-dimensional model was utilized to simulate the sewer sediment. For the soluble components involved in the biological reactions, the first step is their diffusion into the sediment where the reactions take place. Only vertical diffusion in the sediment is considered, which is described by Fick’s law with multiple layers. The whole sediment is modelled with 50 layers, each with a depth of 0.8 mm.

All model parameter values were obtained from literature, as presented in Table S6.4. No model calibration was performed as the main aim of the one-dimensional modelling was to verify if the measured profiles of SRB, MA and the chemical species (methane, sulfide and sulfate) could be qualitatively predicted by the known kinetics of SRB and MA.
6.3 Results and Discussion

6.3.1 Sulfide and methane production by sewer sediment

Fig. 6.2 shows the areal sulfide and methane production rates by the sediment determined through batch tests. At the beginning of the cultivation, both the sulfidogenic and methanogenic activities were relatively low, with sulfide and methane production rates of 3.34 g S/m²·sediment·d and 0.29 g CH₄/m²·sediment·d, respectively. These could be related, at least partially, to the disturbance of the sediment during the collection and transport. In fact, they were not intact sediments but slurries. Therefore, the activities could have been decreased due to the microbial community (SRB and MA) re-distribution or/and exposure to oxygen. Both rates increased gradually with time, and became relatively stable after one year of incubation. While the stratification of microbial community in the sediments was re-established, the overall sulfide and methane production activity of our laboratory sediments may not necessarily represent that in real sewers. Similarly, Okabe et al. (2002) found that the sulfide production activity increased by ca. 4 times after 5-week inoculation in an activated sludge immobilized agar gel film, which is due to an upward movement of SRB towards the surface for more available sulfate there. During day 330–400, the average sulfide and methane production rates were 9.20±0.39 g S/m²·sediment·d and 1.56±0.14 g CH₄/m²·sediment·d, respectively. The sulfide production rate was close to the measured value of 12.8 g S/m²·d in a pilot-scale sediment reactor (Schmitt and Seyfried, 1992).

![Figure 6.2.](image)

**Figure 6.2.** The variation of sulfide and methane production rates by the laboratory sewer sediment during the cultivation phase, determined through batch tests.

In our laboratory rising main biofilm reactors operated with the same wastewater and temperature, Guisasola et al. (2008) reported an areal sulfide production rate of 1.27±0.13 g S/m²·d. Hvitved-Jacobsen (2002) summarized several empirical equations to describe sulfide production by sewer biofilms and these equations predict sulfide production rates between 0.48 and 2.4 g S/m²·d at a soluble COD concentration of 200 mg/L. The sulfide production activity measured for the sediment
is approximately one order of magnitude higher than that of the sewer biofilms. This comparison indicates that sulfide production by sewer sediment is significant, and may not be adequately described by the predictive models previously proposed for sewer biofilms.

In a laboratory sewer reactor study, Guisasola et al. (2008) reported an areal methane production rate of 3.25±0.63 g CH₄/m²·d. Foley et al. (2009) estimated a methanogenic activity of 1.26 g CH₄/m²·d for a real rising main sewer pipe. The values are close to the methane production rate by the laboratory sewer sediment measured in this study. The results indicate that methane production by sewer sediment is also significant, and should be considered when evaluating methane production in sewers.

### 6.3.2 In-sediment microbial conversions

The dissolved sulfide and DO profiles measured with microsensors at pseudo steady-state on day 396 are shown in Fig. 6.3. A diffusive boundary layer (DBL) of approximately 1 mm thick was consistently present above the sediment as deduced from DO profiles (Fig. 6.3b). The sulfide concentrations increased quickly from the sediment surface to the depth of 1–2 mm in the sediment, indicating sulfide production in this zone. This is supported by the activity data calculated using the diffusion reaction model, where the highest activity was found between ca. 0–2 mm. De Beer et al. (2006) observed similar sulfide profiles with a narrow sulfide production zone (less than 5 mm thick) in a 10–cm mud volcano sediment. The DO was completely consumed above the sediment surface (Fig. 6.3b) and thus anaerobic conditions prevailed along the whole depth of sediment. Deeper than 2 mm, the sulfide production activity started to drop and became negative, which indicated that there was sulfide consumption in the deep part of the sediment. In addition, there was no obvious DO penetration in the sediments even in the presence of ca. 4 mg/L DO in the bulk liquid (Fig. S6.1), and similar sulfide production profiles were observed.
Figure 6.3. (a): Total dissolved sulfide and sulfide production profiles in the sediment at pseudo steady-state; (b): DO profile near the sediment surface. The surface of the sediment was defined as depth 0 cm. The profiles shown are average of 6 profiles measured on day 396, with error bars showing standard deviations.

The sulfate profile obtained from the pore water measurement corroborated the sulfide data. The sulfate concentration was 13.0 mg S/L near the sediment surface and then dropped significantly to 2.3 mg S/L at 0.5 cm (Fig. 6.4a). Afterwards, it showed a much slower decreasing trend and the sulfate concentrations in the deeper sediment were close to zero. The main sulfate consumption zone was between 0–1 cm. This supports that only the first cm of sediment is the main activity zone in terms of sulfate reduction. Similar decreasing trends of sulfate from the surface to the deeper layer were also observed in other sediment systems such as marine and lakes (Jørgensen and Parkes, 2010, Leloup et al., 2009, Werner et al., 2006).

Fig. 6.4b shows the dissolved methane profile in the sediment. The methane concentration increased gradually along the depth and became stable at 2.5–3.5 cm. The slope of methane concentration increase was higher near the surface (0–2 cm) and became much lower at the deeper depth (2–3.5 cm), indicating that the main methane production zone was also located near the surface but deeper than that of sulfide. In contrast to sulfate reduction, there was still some production in the deeper layer of the sediment. Coincidently, several studies also reported methane production rates decreased significantly from the near surface to the deep layers in lake sediment (Chan et al., 2005, Varjo et al., 2003).

Fig. 6.4d presents the relative fractions of FISH-determined SRB and MA to the overall MA and SRB populations. The highest SRB fraction (SRB / SRB+MA) of 35% was observed near the surface. Then it gradually decreased to 4% after 1 cm, reaching negligible levels at 2 cm and 3 cm. The MA fractions (MA / SRB+MA) appeared to increase along the depth. This is due to the lower
amount of bacteria in the deeper layers than the top layers. FISH analysis results clearly revealed the significantly high abundance of microorganisms near the surface and very low abundance of microorganisms in the deeper layers (Fig. S6.2), which confirmed that more microorganisms (both SRB and MA) inhabited near the surface of sediment but MA located deeper than SRB. These data coincided with chemical measurement data and further supported the sulfide and methane production zones located near the sediment surface, although the methane production zone was deeper. Thus, the stratification of SRB and MA induced vertical distribution of sulfate, sulfide and dissolved methane in the sediment.

**Figure 6.4.** Experimental and modelled depth profiles of (a) sulfate, (b) methane, (c) sulfide, (d) relative fractions of SRB and MA; Simulation results of fermentable COD penetration profile (e) in the sediment. The surface of the sediment was defined as depth 0 cm.

It is well-known that both SRB and MA can use a wide range of organic carbon generated by hydrolysis and fermentation processes, e.g., hydrogen, acetate and propionate. The competition
between SRB and MA has been intensively investigated (Chou et al., 2008, O'Reilly and Colleran, 2006, Omil et al., 1998, Yoda et al., 1987). SRB can outcompete methanogens for substrates in sulfate-rich and carbon-limiting conditions (Robinson and Tiedje, 1984, Schonheit et al., 1982). Sewers usually have limited sulfate and sufficient carbon substrates for both SRB and MA, thereby allowing simultaneous methane and sulfide production (Fig 6.4b and c) despite their competition for carbon substrates (Conrad et al., 1987, Raskin et al., 1996, Robinson and Tiedje, 1984). The relatively high abundance of SRB is found in the top layer of sediment where sulfate is relatively high. MA require low sulfate conditions, and the lower presence and even absence of sulfate in the deeper layer of sediment due to diffusional limitation of sulfate promoted its growth (Guisasola et al., 2008).

### 6.3.3 Model-predicted in-sediment sulfide and methane production

A one-dimensional mathematical model with the whole sediment divided into 50 layers was used to predict the methane and sulfide production and microbial distribution in the sediment by employing model parameter values previously reported in literature (see Table S6.4). Figure 6.4 compares the model predicted results with the experimental data. The model predicted sulfate reduction and methane production profiles within the sediment matched very well with the experimental data from pore water measurements (Fig. 6.4a and b). The model predicted sulfide production data (Fig. 6.4c) also generally fit with the microsensor measurements of sulfide along the sediment depth. Similarly, the model predicted relative abundance of SRB and MA also captured the experimental results well (Fig. 6.4d). The modeled abundance of SRB and MA was not sensitive to the initial SRB and MA concentrations since we have used several different combinations of initial SRB and MA concentrations in our simulations and similar steady-state bacterial stratification structure were obtained in terms of depth profiles of SRB and MA. The relative fraction of SRB was 35% at the surface and decreased gradually to below 4% at the depth of 1 cm. The relative fraction of MA was lower than 65% at the surface and increased to 96% at depth of 1 cm. The good agreement between the experimental data and the model simulated results, even without parameter calibration, indicates that the experimentally observed stratification of SRB and MA populations and their activities within sewer sediments can be well explained by the known kinetics of SRB and MA.

Simulations with the one-dimensional model reveals that the penetration depths of sulfate and fermentable COD in the sediment are likely the determining factors for the active sulfide and methane production zones. As shown in Fig. 6.4e, sulfate was at ca. 15 mg S/L near the sediment surface and then decreased to ca. 1 mg S/L at 1 cm depth, suggesting that sulfate reduction mainly
occurs near the surface area. As a result, SRB growth and activity was restricted to this zone. In contrast, fermentable COD was at ca. 180 mg/L near the surface and was still at ca. 40 mg/L at 1 cm depth, allowing MA to develop in deeper layers. It has been reported that, in freshwater or marine sediment, sulfate reduction dominated over methanogenesis with sulfate concentration above 6 mg/L and methanogenesis is not limited when sulfate concentration was below 3–4 mg/L (Kuivila et al., 1989, Lovley and Klug, 1983). As in our case (Fig. 6.4d), SRB dominated at ca. 0–0.5 cm and coexisted with MA between ca. 0.5–1.0 cm. After that, MA dominated the microbial populations. The simulations further revealed that fermentable COD would be limiting at 2 cm depth at ca. 13 mg/L, resulting in much lowered methane production rate compared to the upper layers, i.e., 0–2 cm, indicating that methane production is driven by fermentable COD and will be limited in the deeper sections of sediments where the fermentable COD does not penetrate. Modelled acetate profiles (Fig. S6.3) showed a similar tendency. This also explains the low microbial content in the deeper layers due to substrate limitation rather than sulfide toxicities to SRB or MA as the sulfide concentration after 2 cm (ca. 10 mg/L) was far below its toxic threshold levels (e.g., 300 mg/L to induce 50% inhibition) to either SRB or methanogens (O'Flaherty et al., 1998). These modelling results further indicate that the stratification of the microbial community and microbial activities along the sediment depth is in accordance to the substrate transfer limitation and the kinetic differences between SRB and MA (Guisasola et al., 2008).

6.3.4 An empirical model for predicting sulfide and methane production in sewer sediment

With the one-dimensional sediment model, we also conducted simulation runs by varying the sewage sulfate (Scenario I) and fermentable COD (Scenario II) concentrations to evaluate the effects of these factors on the in-sediment sulfide and methane production rates. In Scenario I, the bulk sulfate concentrations were increased from 5 to 30 mg S/L (Pikaar et al., 2014) at a constant fermentable COD concentration of 150 mg/L. In Scenario II, bulk fermentable COD concentrations were raised from 150 to 400 mg/L with a fixed sulfate concentration of 20 mg S/L. Figure 6.5a and b show that the areal sulfide production rate increases with the increase of bulk sulfate concentration (Fig. 6.5a), due to the deeper penetration of sulfate (Kuhl and Jørgensen, 1992). However, the variation of sulfate concentrations does not have a significant effect on the methane production rate (data not shown). In contrast, the variation of fermentable COD concentrations has a negligible limited effect on the sulfide production rate (data not shown), while the methane production rate increases with the increase in fermentable COD concentration (Fig. 6.5b), attributing to the enhanced penetration and consumption of fermentable COD by MA (Guisasola et al., 2008, Jiang et al., 2013b). However, it should be noted that fermentable COD to sulfate ratio in the sewage could also play a crucial role in regulating sulfide and methane production. In some
cases where the ratio is relatively low in the sewage, sulfate concentration could affect methane production and fermentable COD concentration could also affect sulfide production.

**Figure 6.5.** (a) Effect of bulk sulfate concentration on the areal sulfide production rate of the laboratory sewer sediment; (b) Effect fermentable COD concentration on the areal methane production rate of the laboratory sewer sediment.

While the one-dimensional multi-layer sediment model well describes the in-sediment reactions (Fig. 6.4), it is difficult to be implemented in a model for network-wide sulfide and methane formation (e.g. Sharma et al., 2008) due to the computational demand caused by the large number of layers. With these new insights generated by the detailed mechanistic model, simplified empirical models could then be proposed and applied to describe sulfide and methane emissions from sewer sediment with different wastewater conditions (e.g., different sulfate or COD concentrations) for practical applications. Based on the observations above (Fig. 6.5), it can be concluded that the dependency of the areal sulfide production is only related to sulfate concentrations and the areal methane production is only related to fermentable COD concentrations. Half-order reaction kinetics has previously been established to describe biological reactions in biofilms in the presence of substrate diffusion limitation (Harremoes, 1978). Given the partial penetration of sulfate and fermentable COD and their effects on sulfide and methane production, respectively, we attempted to use the following half-order kinetics to describe sulfide and methane production in sewer sediment:

\[
\begin{align*}
    r_{H2S} &= k_1 \times (S_{SO4})^{0.5} \quad \ldots \quad \text{Eq.5} \\
    r_{CH4} &= k_2 \times (S_F)^{0.5} \quad \ldots \quad \text{Eq.6}
\end{align*}
\]

where,

- \( r_{H2S} \) = areal sulfide production rate (g S/m\(^2\)·d);
- \( k_1 \) = rate constant for sulfide production ((g S/m\(^{0.5}\))/d);
- \( r_{CH4} \) = areal methane production rate (g CH\(_4\)/m\(^2\)·d);
- \( k_2 \) = rate constant for methane production ((g CH\(_4\)/m\(^{0.5}\))/d).
$S_{SO4}$ = bulk sulfate concentration (mg S/L);
$r_{CH4}$ = areal methane production rate (g CH$_4$/m$^2$·d);
k$_2$ = rate constant for methane production ((g CH$_4$/m)$^{0.5}$/d);
$S_F$ = bulk fermentable COD concentration (mg/L).

Thus, parameter $k_1$ and parameter $k_2$ were calibrated through reproducing the one-dimensional model predicted dependencies of the sulfide production rate on sulfate concentrations and the methane production rate on fermentable COD concentrations (Fig. 6.5), respectively (see Supporting information for the calibration procedure). As shown in Fig. 6.5, the half-order kinetic models ($k_1$=1.898±0.014, $k_2$=0.224±0.002) could well reproduce the one-dimensional model results, with the $R^2$ values of 0.99 in both cases.

These proposed half-order kinetic models could be useful in practical applications to determine the contribution of sewer sediments to the overall sewer network emissions. For example, they could be incorporated into the dynamic SeweX model, a sewer model predicting in-sewer physical, chemical and biological processes (Sharma et al., 2008). These models are simple as they each involve only one parameter to be calibrated. While the $k_1$ and $k_2$ values estimated above could well describe the laboratory sediment used in this study, these parameters may require further calibration when applied to real sewers.

### 6.4 Supporting information

**Estimation of $k_1$ and $k_2$**

The two parameter values ($k_1$ and $k_2$) were estimated by minimizing the sum of squares of the deviations between the generated data by the one-dimensional model (dependencies of the areal sulfide production rate on sulfate concentrations and the areal methane production rate on fermentable COD concentrations) and the half-order kinetic model predictions with the objective function:

$$F(p) = \left( \sum_{i=1}^{n} (y_{1-Ddata,i} - y(p)_i)^2 \right)^{1/2}$$

where $y_{1-Ddata}$ and $y(p)$ are vectors of n one-dimensional model predicted values and half-order kinetic model predictions at sulfate or fermentable COD concentration levels $S_i$ ($i$ from 1 to $n$), and $p$ is the vector of the half-order kinetic model parameters.
Figure S6.1. (a): Total dissolved sulfide and sulfide production profiles in the sediment at pseudo steady-state; (b): DO profile near the sediment surface with high DO in the bulk. The surface of the sediment was defined as depth 0 cm. The profiles shown are average of 6 profiles measured on day 384, with error bars showing standard deviations.

Figure S6.2. Typical FISH images of sediment samples from (a) 0 cm; (b) 1 cm; (c) 2 cm and (d) 3 cm. Green represents bacteria, indigo represents SRB (overlap between the Cy5-labeled probes SRB and Cy3-labeled EUBMIX) and red represents MA.
Figure S6.3. Modelled depth profiles of (a) VFA and (b) fermenters in the sediment. The surface of the sediment was defined as depth 0 cm.

Table S6.1. Definition and Units of Model Components

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<thead>
<tr>
<th>Variable</th>
<th>Definition</th>
<th>Unit</th>
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<tr>
<td>$S_F$</td>
<td>Fermentable COD$^a$</td>
<td>g COD/m$^3$</td>
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<tr>
<td>$S_{pro}$</td>
<td>Propionate</td>
<td>g COD/m$^3$</td>
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<td>$S_{ac}$</td>
<td>Acetate</td>
<td>g COD/m$^3$</td>
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<tr>
<td>$S_h$</td>
<td>Hydrogen</td>
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<td>$S_{CH4}$</td>
<td>Methane</td>
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<td>$S_{H2S}$</td>
<td>Total dissolved sulfide</td>
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<td>$S_e$</td>
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<td>$X_{SRB,h}$</td>
<td>SRB grown on hydrogen</td>
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$^a$ The fermentable COD was determined as the soluble COD minus the VFA COD and poorly fermentable fractions. It was usually degraded during the first 3 - 4 h in the batch test. The poorly fermentable fraction was assumed as the amount of soluble COD remaining after a batch test (i.e., 7 h)
Table S6.2. Stoichiometric matrix for the biological reaction model

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<tr>
<th>( S_F )</th>
<th>( S_{pro} )</th>
<th>( S_{ac} )</th>
<th>( S_h )</th>
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<th>( S_e )</th>
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<th>( X_{ace} )</th>
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<th>( X_{MA,h} )</th>
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### Table S6.3. Process kinetic rate equations for the biological reaction model

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<th>Kinetics rates expressions</th>
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<td>1. Hydrolysis</td>
<td>( k_{\text{hydro}} X_i )</td>
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<tr>
<td>2. Acidogenesis</td>
<td>( k_{\text{a}} \frac{S_F}{K_F + S_F} X_{ac} )</td>
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<tr>
<td>3. Acetogenesis</td>
<td>( k_{\text{ac}} \frac{S_F}{K_F + S_F} X_{ace} )</td>
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<td>4. Acetoclastic methanogenesis</td>
<td>( k_{\text{MA,ac}} \frac{S_{ac}}{K_{\text{MA,ac}} + S_{ac}} X_{\text{MA,ac}} )</td>
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<td>5. Hydrogenotrophic methanogenesis</td>
<td>( k_{\text{MA,h}} \frac{S_h}{K_{\text{MA,h}} + S_h} X_{\text{MA,h}} )</td>
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<td>6. Propionate-based sulfidogenesis</td>
<td>( k_{\text{SRB,pro}} \frac{S_{pro}}{K_{\text{SRB,pro}} + S_{pro}} \frac{S_{SO4}}{K_{\text{SO4}} + S_{SO4}} X_{\text{SRB,pro}} )</td>
</tr>
<tr>
<td>7. Acetate-based sulfidogenesis</td>
<td>( k_{\text{SRB,ac}} \frac{S_{ac}}{K_{\text{SRB,ac}} + S_{ac}} \frac{S_{SO4}}{K_{\text{SO4}} + S_{SO4}} X_{\text{SRB,ac}} )</td>
</tr>
<tr>
<td>8. Hydrogenotrophic sulfidogenesis</td>
<td>( k_{\text{SRB,h}} \frac{S_h}{K_{\text{SRB,h}} + S_h} \frac{S_{SO4}}{K_{\text{SO4}} + S_{SO4}} X_{\text{SRB,h}} )</td>
</tr>
<tr>
<td>9. Sulfide sink</td>
<td>( k_{\text{H}<em>2S} \frac{S</em>{\text{H}<em>2S}}{K</em>{\text{H}_2S}} S_e )</td>
</tr>
<tr>
<td>10. Decay of ( X_{ac} )</td>
<td>( k_{\text{dec,ac}} X_{ac} )</td>
</tr>
<tr>
<td>11. Decay of ( X_{ace} )</td>
<td>( k_{\text{dec,ace}} X_{ace} )</td>
</tr>
<tr>
<td>12. Decay of ( X_{\text{MA,ac}} )</td>
<td>( k_{\text{dec,MA,ac}} X_{\text{MA,ac}} )</td>
</tr>
<tr>
<td>13. Decay of ( X_{\text{MA,h}} )</td>
<td>( k_{\text{dec,MA,h}} X_{\text{MA,h}} )</td>
</tr>
<tr>
<td>14. Decay of ( X_{\text{SRB,pr}} )</td>
<td>( k_{\text{dec,SRB,pr}} X_{\text{SRB,pr}} )</td>
</tr>
<tr>
<td>15. Decay of ( X_{\text{SRB,ac}} )</td>
<td>( k_{\text{dec,SRB,ac}} X_{\text{SRB,ac}} )</td>
</tr>
<tr>
<td>16. Decay of ( X_{\text{SRB,h}} )</td>
<td>( k_{\text{dec,SRB,h}} X_{\text{SRB,h}} )</td>
</tr>
</tbody>
</table>
Table S6.4. Kinetic and stoichiometric parameters of the model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>Values</th>
<th>Unit</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{hydro}}$</td>
<td>Hydrolysis rate of $X_s$</td>
<td>3</td>
<td>d$^{-1}$</td>
<td>(1)</td>
</tr>
<tr>
<td>$k_{\text{aci}}$</td>
<td>Maximum uptake rate of $S_F$ by $X_{aci}$</td>
<td>6</td>
<td>g COD m$^{-3}$ _S/  g COD m$^{-3}$ _X d$^{-1}$</td>
<td>(2)</td>
</tr>
<tr>
<td>$k_{\text{ace}}$</td>
<td>Maximum uptake rate of $S_F$ by $X_{ace}$</td>
<td>6</td>
<td>g COD m$^{-3}$ _S/  g COD m$^{-3}$ _X d$^{-1}$</td>
<td>(2)</td>
</tr>
<tr>
<td>$K_F$</td>
<td>Half saturation constant for $S_F$</td>
<td>10</td>
<td>g COD m$^{-3}$</td>
<td>(3)</td>
</tr>
<tr>
<td>$k_{\text{MA,ac}}$</td>
<td>Maximum uptake rate of $S_{ac}$ by $X_{MA,ac}$</td>
<td>9.62</td>
<td>g COD m$^{-3}$ _S/  g COD m$^{-3}$ _X d$^{-1}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$K_{\text{MA,ac}}$</td>
<td>Half saturation constant of $X_{MA,ac}$ for $S_{ac}$</td>
<td>210</td>
<td>g COD m$^{-3}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$k_{\text{MA,h}}$</td>
<td>Maximum uptake rate of $S_h$ by $X_{MA,h}$</td>
<td>24.24</td>
<td>g COD m$^{-3}$ _S/  g COD m$^{-3}$ _X d$^{-1}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$K_{\text{MA,h}}$</td>
<td>Half saturation constant of $X_{MA,h}$ for $S_h$</td>
<td>0.1</td>
<td>g COD m$^{-3}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$k_{\text{SRB,pro}}$</td>
<td>Maximum uptake rate of $S_{pro}$ by $X_{SRB,pro}$</td>
<td>12.6</td>
<td>g COD m$^{-3}$ _S/  g COD m$^{-3}$ _X d$^{-1}$</td>
<td>(4)</td>
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<tr>
<td>$K_{\text{SRB,pro}}$</td>
<td>Half saturation constant of $X_{SRB,pro}$ for $S_{pro}$</td>
<td>110</td>
<td>g COD m$^{-3}$</td>
<td>(4)</td>
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<tr>
<td>$k_{\text{SRB,ac}}$</td>
<td>Maximum uptake rate of $S_{ac}$ by $X_{SRB,ac}$</td>
<td>7.1</td>
<td>g COD m$^{-3}$ _S/  g COD m$^{-3}$ _X d$^{-1}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$K_{\text{SRB,ac}}$</td>
<td>Half saturation constant of $X_{SRB,ac}$ for $S_{ac}$</td>
<td>220</td>
<td>g COD m$^{-3}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$k_{\text{SRB,h}}$</td>
<td>Maximum uptake rate of $S_h$ by $X_{SRB,h}$</td>
<td>26.7</td>
<td>g COD m$^{-3}$ _S/  g COD m$^{-3}$ _X d$^{-1}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$K_{\text{SRB,h}}$</td>
<td>Half saturation constant of $X_{SRB,h}$ for $S_h$</td>
<td>0.1</td>
<td>g COD m$^{-3}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$K_{\text{SO4}}$</td>
<td>Half saturation constant for $S_{SO4}$</td>
<td>1.8</td>
<td>g S m$^{-3}$</td>
<td>(3)</td>
</tr>
<tr>
<td>$k_{\text{H2S}}$</td>
<td>Sink rate</td>
<td>1</td>
<td>m$^3$ g$^{-1}$ d$^{-1}$</td>
<td>(1)</td>
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<tr>
<td>$k_{\text{dec,aci}}$</td>
<td>Decay rate coefficient of $X_{aci}$</td>
<td>0.02</td>
<td>d$^{-1}$</td>
<td>(2)</td>
</tr>
<tr>
<td>$k_{\text{dec,ace}}$</td>
<td>Decay rate coefficient of $X_{ace}$</td>
<td>0.02</td>
<td>d$^{-1}$</td>
<td>(2)</td>
</tr>
<tr>
<td>$k_{\text{dec,MA,ac}}$</td>
<td>Decay rate coefficient of $X_{MA,ac}$</td>
<td>0.015</td>
<td>d$^{-1}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$k_{\text{dec,MA,h}}$</td>
<td>Decay rate coefficient of $X_{MA,h}$</td>
<td>0.01</td>
<td>d$^{-1}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$k_{\text{dec,SRB,pro}}$</td>
<td>Decay rate coefficient of $X_{SRB,pro}$</td>
<td>0.01</td>
<td>d$^{-1}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$k_{\text{dec,SRB,ac}}$</td>
<td>Decay rate coefficient of $X_{SRB,ac}$</td>
<td>0.015</td>
<td>d$^{-1}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$k_{\text{dec,SRB,h}}$</td>
<td>Decay rate coefficient of $X_{SRB,h}$</td>
<td>0.01</td>
<td>d$^{-1}$</td>
<td>(4)</td>
</tr>
<tr>
<td>$f_1$</td>
<td>Stoichiometric parameters</td>
<td>0.78</td>
<td>—</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td>Description</td>
<td>Value 1</td>
<td>Value 2</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>----------------------------------</td>
<td>---------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>$f_2$</td>
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<td>—</td>
<td></td>
</tr>
<tr>
<td>$f_3$</td>
<td>stoichiometric parameters</td>
<td>0.67</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>$f_4$</td>
<td>stoichiometric parameters</td>
<td>0.33</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>$\eta$</td>
<td>stoichiometric parameters</td>
<td>1.65</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>$Y_{aci}$</td>
<td>Microorganism yield coefficient</td>
<td>0.1</td>
<td>g COD / g COD</td>
<td></td>
</tr>
<tr>
<td>$Y_{ace}$</td>
<td>Microorganism yield coefficient</td>
<td>0.06</td>
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<tr>
<td>$Y_{MA,ac}$</td>
<td>Microorganism yield coefficient</td>
<td>0.0317</td>
<td>g COD / g COD</td>
<td></td>
</tr>
<tr>
<td>$Y_{MA,h}$</td>
<td>Microorganism yield coefficient</td>
<td>0.0403</td>
<td>g COD / g COD</td>
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</tr>
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<td>$Y_{SRB,ac}$</td>
<td>Microorganism yield coefficient</td>
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<td>g COD / g COD</td>
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</tr>
<tr>
<td>$Y_{SRB,pro}$</td>
<td>Microorganism yield coefficient</td>
<td>0.0342</td>
<td>g COD / g COD</td>
<td></td>
</tr>
<tr>
<td>$Y_{SRB,h}$</td>
<td>Microorganism yield coefficient</td>
<td>0.0366</td>
<td>g COD / g COD</td>
<td></td>
</tr>
</tbody>
</table>

Source: (1) ASM 3; (2) Bastone et al., 2002; (3) Guisasola et al., 2009; and (4) Fedorovich et al., 2003.

Reference:


Chapter 7 Effect of nitrate dosing on methanogenic and sulfidogenic activities in sewer sediment

Abstract
Nitrate dosing is widely used to control sulfide and methane formation in sewers. The impact of nitrate on sulfide and methane production by sewer biofilms in rising mains has been elucidated recently. However, little is known about the effect of nitrate on biologically active sewer sediment, which is substantially thicker than rising main biofilms (centimeters vs. hundreds of micrometers, respectively). In this study, we investigated the effect of nitrate addition to sewer sediment cultivated in lab-scale sewer sediment reactors. Batch test results showed that nitrate addition does not suppress sulfide production in sewer sediment, but it reduces sulfide accumulation through anoxic sulfide oxidation in the sediment and hence, also reduces sulfide accumulation in the bulk water. Microsensor measurement of sediment sulfide revealed the presence of sulfide oxidation and sulfide production zones with the interface dynamically regulated by the depth of nitrate penetration. In contrast, the methane production activity of sewer sediment was substantially reduced, likely due to the long-term inhibitory effects of nitrate on methanogens. Pore water measurements showed that methane production activity in the sediment zone with frequent nitrate exposure was completely suppressed, and consequently, the methane production zone re-established deeper in the sediment where nitrate penetration was infrequent.

7.1 Introduction
Sewers are an important component of urban water infrastructure. Through collecting and transporting domestic and industrial wastewaters to treatment plants for pollutant removal before environmental discharge, sewers protect our society against sewage-borne diseases, unhygienic conditions, and noxious odors (Pikaar et al., 2014). However, sewers are biologically active systems. It is well known that in-sewer biological processes lead to the production and emission of hydrogen sulfide, methane and other hazardous compounds (Guisasola et al., 2008, Hvitved-Jacobsen, 2002, Wang et al., 2014). Sulfide build-up in sewers causes serious odor and corrosion problems, and incurs a large cost on the water industry due to mitigation measures and the depreciation of assets (WERF, 2007a). Meanwhile, methane is a potent greenhouse gas which contributes significantly to the carbon footprint of wastewater management (Daelman et al., 2012). Methane is also flammable,

† This chapter has been published as “Liu et al., Effect of nitrate dosing on methanogenic and sulfidogenic activities in sewer sediment. Water Research, 2015, 74, 155-165.”
with a lower explosive limit (LEL) of approximately 5% by volume, and thus poses a serious safety issue in confined spaces (Spencer et al., 2006).

Operationally, sewer systems can be divided into two categories, i.e. fully-filled rising main (or pressurized) sewers and partially-filled gravity sewers, where re-aeration takes place. Previous studies have identified rising main sewers as a source of hydrogen sulfide and methane (Boon, 1995, Guisasola et al., 2008). Sulfate-reducing bacteria (SRB) and methanogenic archaea (MA) that grow in the biofilm attached to the inner surfaces of sewer walls are primarily responsible for sulfide and methane production in rising main sewers (Foley et al., 2009, Guisasola et al., 2008, Sun et al., 2014). Sediment in gravity sewers is also believed to be biologically active (Schmitt and Seyfried, 1992), and thus could contribute to sulfide and methane production. In Chapter 6, it has been confirmed that sewer sediment produces significant amounts of sulfide and methane, with a real rate higher than, or comparable to, those of rising main sewer biofilms. SRB and MA were found to co-exist in sewer sediment. These results, along with the widespread presence of sewer sediment (Ashley et al., 2003) clearly show that the contribution of sewer sediment to sulfide and methane production cannot be ignored when evaluating sewer emissions.

Various chemical dosing strategies for sulfide control have been practiced by the water industry (Ganigue et al., 2011). The most commonly used chemicals include oxygen and nitrate for sulfide oxidation, iron salts for sulfide precipitation, and alkali for pH elevation to minimize liquid to gas mass transfer of hydrogen sulfide (Ganigue et al., 2011, Zhang et al., 2008). In addition to sulfide control, these chemicals can simultaneously induce inhibitory effects on methanogens in sewers, thus leading to possible methane elimination (Ganigué and Yuan, 2014, Gutierrez et al., 2014, Jiang et al., 2013, Zhang et al., 2009). For example, a recent study conducted by Mohanakrishnan et al. (2009a) demonstrated that the long-term addition of 30 mg N/L of nitrate in a laboratory rising main sewer reactor reduced the sulfide and methane concentrations in the effluent by 66% and 94%, respectively. Nitrate dosing does not inhibit SRB activity, but stimulates the development of sulfide-oxidizing, nitrate-reducing bacteria (soNRB), which oxidize sulfide coupled to the reduction of nitrate, thus achieving sulfide control (Garcia-de-Lomas et al., 2007). Methanogenic rates were maintained below 10% of baseline level after nitrate dosing due to the inhibitory effect on MA (Jiang et al., 2013b).

To date, research on chemical dosing for sulfide and methane control has mainly focused on rising mains. Little effort has been dedicated to studying the effect of chemical dosing such as nitrate on gravity sewer sediments. In contrast to rising main sewer biofilms, which are measured in terms of
micrometers, sewer sediments contain a thicker, biologically active layer of several centimeters or more. It is expected that penetration of nitrate into the sediment would be very limited. Additionally, nitrate addition to gravity sewers could potentially lead to N₂O emission due to denitrification and the known inhibitory effects of hydrogen sulfide on N₂O reduction (Pan et al., 2013).

The aim of this study is to determine the effect of nitrate addition on sulfide and methane production in gravity sewer sediment. Sediment collected from an actual gravity sewer was incubated in laboratory sediment reactors mimicking gravity sewer conditions over a period of one year to achieve steady-state performance. Nitrate was then continuously dosed for 3 months at a rate of 15 mg NO₃⁻-N per liter of wastewater, typical of actual sewer applications (Ganigue et al., 2011). A comprehensive evaluation of in-sediment sulfide and methane production processes was carried out through integrating batch production tests, and microsensor and pore water measurements of sulfide, sulfate and methane in the sediment. The N₂O production in the system was also evaluated.

7.2 Materials and methods
7.2.1 Reactor set-up, sediment collection and system operation

Three laboratory-scale reactors, specifically designed to mimic gravity sewer conditions and to cultivate sediments, were operated in parallel (Fig. 7.1). Each reactor had a working volume of 3.2 L (2.7 L and 0.5 L for the liquid and gas phase, respectively), with a diameter of 140 mm and height of 210 mm. An additional cylinder in the base of the reactor (120 mm diameter and 60 mm depth) acted as the sediment carrier. A mechanical overhead stirrer was positioned at the water surface (ca. 12 cm above the sediment surface). A mixing speed of 40 rpm was applied to achieve aeration in the reactor, leading to an estimated oxygen transfer coefficient of ca. 0.5 h⁻¹. The DO concentration in the bulk water was 0.1–0.4 mg/L, within the reported DO concentration range in gravity sewers (Hvitved-Jacobsen, 2002).

Sediment samples were collected from a mature gravity sanitary sewer receiving domestic wastewater in Sydney. Sediment collection was conducted using a shovel, and the sample was transported to the laboratory and stored at 4°C before use. The bulk density of the sediment was 1.37 g/cm³ and the porosity was 96.7%. The total solids (TS) and volatile solids (VS) contents were 74.0% and 3.4% of the wet weight, respectively. Sediment (600 mL) was added to the sediment carrier of each reactor, resulting in an initial sediment depth of ca. 4 cm.

The reactors were intermittently fed with domestic sewage via the inlet using a peristaltic pump, and the effluent was drained through the outlet on the sidewall. The feed pattern consisted of 18
pump events per day, with 300 mL of wastewater fed during each event, resulting in an average wastewater retention time of 12 h, i.e., 2.7 L / (18 times/d × 0.3 L/times) = 0.5 d. Raw sewage was collected weekly from a nearby pumping station and stored at 4°C. It was warmed up to 20°C through a heat exchanger and water bath before being pumped into the reactor. The fresh sewage typically contained 15–25 mg SO$_4^{2-}$/L, <1 mg H$_2$S/L, 50–100 mg volatile fatty acid (VFA)-COD/L, and <1 mg CH$_4$/L. The reactor was completely covered with aluminum foil to avoid exposure to light.

![Schematic diagram of the sewer sediment reactors](image)

**Figure 7.1.** Schematic diagram of the sewer sediment reactors.

The reactors were operated for more than one year (Phase I, Chapter 6) before nitrate dosing commenced, in order to cultivate mature intact sewer sediment and to establish pseudo steady-state conditions, as indicated by stable sulfide and methane concentrations in the effluent, and stable sulfide and methane production rates.

Nitrate was dosed in one of the three reactors (R1) for a period of 110 days (Phase II). Day 0 represents the start of nitrate dosing in the experimental reactor, R1. A nitrate solution of 1 g-N/L was prepared weekly as the dosing stock. Following each pumping event (300 mL sewage), another peristaltic pump was turned on for 20 s, adding 4.5 mL of the nitrate stock solution to the reactor, the equivalent of 15 mg NO$_3^-$-N/L influent sewage, a dosing rate that is in the typical range in practical applications (Ganigue et al., 2011). In contrast, no changes were made to the operation of the second reactor (R2) in Phase II, which served as a control for R1. Additionally, the third reactor (R3) was exposed to 40 mg NO$_3^-$-N/L for 24 hrs on day 0, and was then operated under the same
conditions as R2. This test was performed to verify the hypothesis that a short dose of nitrate could control methane production over a long period, due to the long-lasting inhibitory effect on MA in the sewer sediment.

A UV-VIS spectrometer (Messtechnik GmbH, Austria) was used for regular online measurement (for 24 hours, every 14 days) of dissolved sulfide and nitrate in R1 (Gutierrez et al., 2010, Sutherland-Stacey et al., 2008). A bypass system was used to connect the spectrometer with the reactor allowing sample to be diverted to the spectrometer optics through a peristaltic pump. A TPS miniChem-pH controller was used to measure pH (Version 2.1.1). The recorded online data for HS⁻ and pH were used to calculate the total dissolved sulfide concentration (Sutherland-Stacey et al., 2008). In addition, dissolved methane samples were taken from R1 before and after pumping events during one of three identical 8-hour periods in a day, i.e., from 8:00 to 16:00. Dissolved sulfide and methane concentrations in the effluent of R2 and R3 were similarly tested.

7.2.2 Sediment reactor batch tests
To monitor the dynamics of sulfide and methane production rates during long-term sediment reactor operation, batch tests were carried out every 1 to 2 weeks in R1, R2 and R3 in the absence of nitrate during both Phases I and II. During batch tests, the wastewater in the reactor was drained first and the reactor was fully refilled with fresh sewage, without headspace in order to prevent methane and hydrogen sulfide loss through liquid to gas phase transfer. Liquid samples were drawn at 0, 40, 90 and 120 min for wastewater composition analysis.

Additional batch tests were done to determine methane and sulfide production, and nitrate reduction rates in R1 in the presence of nitrate. These tests were performed similarly to the batch tests described, except that 15 mg-N/L nitrate was added after replacing the sewage in the reactor. Liquid samples were drawn at 0, 30, 60, 120, 180 and 240 min for wastewater composition analysis. The samples were analyzed for dissolved sulfide, methane, nitrate, nitrite, N₂O, SCOD and VFA concentrations. Linear regression was used to calculate methane and sulfide production, and nitrate reduction rates.

7.2.3 Sediment depth chemical profiling
To gain insight into the in-sediment biotransformations, chemical profiling along the sewer sediment depths was carried out in R1, after pseudo steady-state conditions in both Phases I and II were established. Sediment depth profiles for pH, dissolved oxygen (DO) and sulfide were established using microsensors (described in section 7.2.4) on day -10 (before nitrate dosing), and
between days 100 to 102 (after dosing). During these measurements, the sediment carrier was taken out of R1 and mounted in a flow cell (a diameter of 140 mm, 1.2 L) containing 1 L of 0.22 μm filtered wastewater for microsensor measurements. Mixing of wastewater in the cell was achieved by recirculating the water at 2–3 cm above the sediment surface using a peristaltic pump. Steady-state profiles were obtained by incubating the sediment for at least 4 hours in fresh sewage prior to measurements. The pH (7.6–7.8) and DO (0.4–0.6 mg/L) in the bulk liquid were not controlled during the test.

The concentration gradients of DO, pH and H₂S through the sediment were recorded by moving the microsensors with an automatic micromanipulator in increments of 100–200 μm and recording the sensor signals at each depth using the software SensorTrace Pro (Unisense A/S, Denmark). Approximately 20–30 profiles were recorded at different locations within the sediment each day. The total dissolved sulfide profiles were calculated from the H₂S and pH profiles as described in Kuhl et al. (1998). The sulfide production activity within the sediment was calculated using the diffusion reaction model developed by Kuhl and Jørgensen (1992). The diffusion coefficient in the sediment was assumed to be identical to molecular diffusion (as the porosity of the entire sediment depths averaged ca. 96%), and was adjusted according to temperature. At 20 °C, the diffusion coefficients used for total sulfide in the sediment was 1.39×10⁵ cm²/s (Kuhl and Jørgensen, 1992).

Table 7.1 summarizes the objectives and conditions of the microsensor experiments.

<table>
<thead>
<tr>
<th>Set</th>
<th>Objective of the microsensor measurement</th>
<th>Time</th>
<th>Wastewater conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. I</td>
<td>To investigate long-term effects of nitrate on the sulfide production capabilities of the sediment</td>
<td>Day -10 and 100</td>
<td>Fresh wastewater</td>
</tr>
<tr>
<td>No. II</td>
<td>To investigate short-term effects of nitrate on the sulfide production capabilities of the sediment</td>
<td>Day 101</td>
<td>Fresh wastewater + nitrate added (15 mg-N/L)</td>
</tr>
<tr>
<td>No. III</td>
<td>To investigate the location of sulfide-oxidizing, nitrate-reducing zone in the sediment</td>
<td>Day 102</td>
<td>Fresh wastewater + sulfide added (10 mg-S/L) + nitrate added (15 mg-N/L)</td>
</tr>
</tbody>
</table>

On day 109, pore water samples were taken in triplicate from R1 in the absence of nitrate at depths of 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 3.5 cm below the sediment surface using the method described
by Hoehler et al. (1994). Samples were collected with 3 mL cut-off plastic syringes from sediment cores for dissolved methane analysis.

7.2.4 Analytical methods
The concentration of dissolved inorganic sulfur species (sulfide, sulfite, thiosulfate, and sulfate) in the samples was determined with ion chromatography (IC). A 1.5 mL sample was filtered (0.22 µm membrane) into a 2 mL vial containing 0.5 mL of sulfide anti-oxidant buffer (SAOB), a solution which prevents sulfide oxidation (Keller-Lehmann et al., 2006). Samples were then analyzed within 24 hours using an ion chromatograph (IC) with a UV and conductivity detector (Dionex ICS-2000). For the analysis of nitrogen species (nitrate, nitrite and ammonia), 1 mL sewage was filtered similarly, diluted 10 times and analyzed using a Lachat QuikChem 8000 (Milwaukee) flow-injection analyzer (FIA). VFA was measured by gas chromatography (PerkinElmer, Inc.) (Jiang et al., 2013b).

For dissolved methane and nitrous oxide measurement, 5 mL sample was filtered (0.22 µm membrane) and injected using a hypodermic needle attached to a plastic syringe, into a pre-evacuated Exetainer® tube (Labco, Wycombe, UK) made of borosilicate glass. The tube was allowed to reach gas-liquid equilibrium overnight. For detecting dissolved methane concentrations from pore water samples, a nitrogen-flushed Exetainer® tube containing 3 mL of 5% NaOH (Riedinger et al., 2010) was immediately capped after extruding sediment cores, and subsequently shaken to reach equilibrium. The gas phase was measured with a gas chromatograph (GC, Agilent 7890A) equipped with a flame ionization detector (FID) for methane and a micro-electron capture detector (ECD) for nitrous oxide. Concentrations of dissolved methane and nitrous oxide in the sample were calculated using mass balance and Henry’s law (Guisasola et al., 2008).

All microsensors (pH, DO and H2S) were purchased from Unisense A/S (Denmark). The sensors had tip diameters between 50 and 100 µm. Calibration of the oxygen, H2S and pH sensors was done as described previously (Mohanakrishnan et al., 2008).

7.3 Results
7.3.1 Sulfide, methane and nitrate profiles in the sewer sediment reactor with continuous nitrate dosing
Steady-state dissolved sulfide, methane and nitrate profiles were generated from the nitrate-dosed sediment reactor, R1, during a 24-hour operation cycle, before (Phase I) and after (Phase II) nitrate dosing (Fig. 7.2). Each day could be divided into three identical 8-hour periods, namely 0:00 to
Before dosing, the sulfide concentration increased quickly from 0 to ca. 2.0 mg/L after three sequential pumping events (0.25-h interval) between 8:00 and 8:30 (Fig. 7.2A). Sulfide concentration continued to rise to ca. 3.4 mg/L before 10:00 and kept relatively stable during the next three pumping events (1.5-h interval) from 10:00 to 14:00. Following, the sulfide concentration began to decrease before the longest pumping event (3-h interval) at 16:00 due to the depletion of sulfate and sulfide re-oxidation in the presence of oxygen. The average sulfide concentration during this 8-h cycle was 2.5±1.2 mg/L. In comparison, the dissolved methane concentration was steady for the whole cycle, averaging 2.3±0.3 mg/L. In addition, there was no obvious change in sediment depth in both R1 and R2 during the study period, likely due that both reactors achieved steady-state condition where growth equals to detachment.

**Figure 7.2.** Typical steady-state cycle profiles of dissolved sulfide, methane and nitrate in the sewer sediment reactor, R1, before (A) and after (B) nitrate dosing.

Sulfide production was completely suppressed in the presence of nitrate (Fig. 7.2B). However, sulfide concentration increased immediately after nitrate depletion, implying nitrate did not cause irreversible inhibitory effects on SRB. The average sulfide concentration was 0.2±0.2 mg/L during an 8-h cycle, significantly lower (92%) than that (2.5±1.2 mg/L) during the baseline period.
Methane generation also decreased significantly (87%), from an average value from 2.3±0.3 mg/L (Phase I) to 0.3±0.1 mg/L (Phase II).

7.3.2 Microbial activities in the sewer sediment reactor with continuous nitrate dosing
Fig. 7.3 shows the microbial activities in R1, measured as the sulfide and methane production rates, and nitrate reduction rate determined through batch tests.

**Figure 7.3.** A: Sulfide production rates in R1 during batch tests in the presence and absence of nitrate at 15 mg N/L in sewage; B: Methane production rates in the presence and absence of nitrate in R1; C: Nitrate reduction rates in the presence of nitrate in R1. Nitrate dosing was initiated on day 0.
After nitrate dosing commenced on day 0, the sulfide production rate in batch tests in the absence of nitrate slightly decreased from the baseline level of 13.9±2.2 g S/m²·d to approximately 7.3 g S/m²·d over the initial 10 days in Phase II. Sulfide then fluctuated between 8 and 14 g S/m²·d, with an average rate of 11.1±1.9 g S/m²·d, which was slightly lower than the baseline level (p<0.05). In comparison, sulfide production in the presence of nitrate was completely suppressed (Fig. 7.3A).

The methane production rate was 4.4±1.0 g CH₄/m²·d before nitrate dosing commenced (Fig. 7.3B, Phase I), but markedly decreased (by ca. 80%) to 0.6±0.2 g CH₄/m²·d in the presence of 15 mg N/L nitrate during batch testing (Phase II). Methane production in Phase II was also suppressed in the absence of nitrate during batch testing, declining to 1.1±0.5 g CH₄/m²·d. However, the methane production rate in the absence of nitrate was higher than the rate in the presence of nitrate (p<0.05).

It should be noted that both sulfide and methane production in control reactor, R2, increased slightly during Phase II as compared to Phase I (Fig. S7.1). The trend, which was likely caused by continued development of the sediment microbial community, was opposite to that observed in R1.

The nitrate reduction rate in R1 increased gradually in the initial 10 days of Phase II, and then remained relatively constant at 45.2±6.7 g N/m²·d in the remaining period (Fig. 7.3C). In addition, dissolved N₂O concentrations were generally below 0.15 mg/L during the 4-h batch tests (Fig. S7.2). The relatively high N₂O level at 0.5 h suggests that N₂O was formed during nitrate reduction. During the next 3.5 h, N₂O concentrations slowly decreased, likely due to reduction to N₂ by denitrifiers. The negligible N₂O accumulation indicates that nitrate dosing for sulfide and methane control in gravity sewer sediment will unlikely lead to N₂O emission.

7.3.3 Sulfide and methane depth profiles in the sewer sediment reactor with continuous nitrate dosing

The dissolved sulfide and DO profiles measured with microsensors at pseudo steady-state conditions before and after nitrate dosing are shown in Fig. 7.4. DO was completely consumed above the sediment surface and thus anaerobic conditions prevailed throughout the sediment in all cases.

Ten days prior to nitrate dosing, sulfide concentration increased quickly from the sediment surface to the depth of 1–2 mm in the sediment (Fig. 7.4A), indicating sulfide production in this zone. Deeper than 2 mm, the sulfide production activity declined, becoming slightly negative, indicating that there was minor sulfide consumption in the deeper part of the sediment.

Fig. 7.4B shows the sediment sulfide profile in the absence of nitrate 100 days after commencement...
of dosing. The main sulfide production zone was still near the surface (0–2 mm), similar to the profile in Fig. 7.4A, indicating that long-term nitrate dosing did not alter the sulfide production zone.

The sulfide profile in the presence of 15 mg-N/L nitrate on day 101 is shown in Fig. 7.4C. The sulfide concentration was negligible in both the bulk water and the 0–5 mm surface sediment. Then it gradually increased with depth, reaching 6 mg S/L at 1 cm. Beyond this depth, the sulfide concentration was relatively stable. The main sulfide consumption and production zones were at 4–6 mm and 6–10 mm, respectively. The sulfide production zone migrated to the deeper layer (6–10 mm) in the presence of nitrate in the water phase. It should be noted that consumption and production were nearly equal, explaining why no sulfide accumulated in the bulk water.

Fig. 7.4D shows the sulfide profile in the presence of sulfide and nitrate at initial concentrations of 10 mg-S/L and 15 mg-N/L, respectively. There was a significant sulfide consumption zone near the sediment surface (0–2 mm), indicating nitrate-induced sulfide oxidation near the surface.

**Figure 7.4.** Total dissolved sulfide concentration and sulfide production rate profiles in the sediment at pseudo steady-state (A) On day -10, prior to nitrate dosing; (B) 100 days after commencing nitrate dosing and in the absence of nitrate during microsensor profiling; (C) 101 days after commencing nitrate dosing and in the presence of 15 mg-N/L nitrate during microsensor profiling; (D) 102 days after commencing nitrate dosing and microsensor profiling experiment using sewage with a sulfide concentration of 10 mg-S/L and the addition of 15 mg-N/L nitrate. The surface of the sediment was defined as depth 0 cm. The profiles shown are an average of 5 profiles, with error bars showing standard deviation.
Fig. 7.5 shows the dissolved methane profile in the sediment in the absence of nitrate prior to- and 109 days after the commencement of nitrate dosing. Prior to nitrate dosing, the methane concentration increased rapidly from the surface to a depth of 2 cm, and plateaued deeper in the sediment at 2–3.5 cm. This indicated that the main methane production zone was also located near the surface but deeper than that of sulfide, which could be explained by kinetic differences between SRB and MA (Guisasola et al., 2009). In contrast, in the nitrate-adapted sediment (109 days after the commencement of nitrate dosing), the methane concentration was relatively constant within the first 1 cm of the sediment, but increased gradually from 1–3.5 cm, even though nitrate was not dosed during the test. The major methane production zone moved downward to 1–2.5 cm possibly due to the inhibitory effect of nitrate on MA in the 0–1 cm zone.

Figure 7.5. Methane profiles along sediment depth before- and 109 days after commencement of nitrate dosing. Test was carried out in the absence of nitrate. The surface of the sediment was defined as depth 0 cm. The profiles shown are an average of three samples per depth, with error bars showing standard deviation.

7.3.4 Effect of nitrate shock dosing on the performance of the sewer sediment

The methane production rate was ca. 3.6 g CH₄/m²·d before the nitrate shock dosing was carried out in sediment reactor, R3. After a 24-h exposure to 40 mg-N/L nitrate on day 0, the methane production rate in R3 dropped to 0 on day 4 and then gradually recovered to the initial level in the following four months (Fig. 7.6). This has significant implications for the use of nitrate for methane emission management, as it reveals that a nitrate shock at a moderate concentration, i.e., 40 mg-N/L is effective. In contrast, the sulfide production activity was not affected by shock dosing with nitrate.
Figure 7.6. Sulfide and methane production rates in the absence of nitrate in the sewer sediment reactor R3 before and after shock dosing with 40 mg-N/L nitrate for 24 h, determined through batch tests. Nitrate shock dosing was carried out on day 0.

7.4 Discussion

7.4.1 Nitrate does not inhibit SRB activity but reduces sulfide accumulation in the sewer sediment

Continuous nitrate addition did not affect the sulfide production capability of the sewer sediment (R1, Fig. 7.3A). Microsensor profiling further confirmed there was no substantial change in location of the sulfide zone (0–2 mm) in R1 sediment before and after the commencement of nitrate addition (Fig. 7.4A and B), when nitrate was absent during batch tests. Therefore, nitrate addition does not have a long-lasting inhibitory effect on sulfide production in sewer sediment. In the presence of nitrate, however, the sulfide production zones migrated deeper into the sediment (Fig. 7.4C). It appears that the lack of nitrate penetration in such deeper layers permitted sulfide production, while the shallow layers become a sulfide oxidation zone (Fig. 7.4C).

When present, nitrate suppressed sulfide accumulation in the sediment reactor (Fig. 7.2B and Fig. S7.3). After depletion of the nitrate, sulfide production continued in the sediment reactor. There is clear sulfide consumption in the sediment reactor in the presence of nitrate (Fig. 7.4C and D), which could be attributed to sulfide-oxidizing nitrate-reducing process (Garcia-de-Lomas et al., 2007, Hubert et al., 2009). A similar observation was made by Jiang et al. (2013b) when anaerobic sewer
biofilms were dosed with nitrate. It has been reported that there is a syntrophic association between SRB and sulfide-oxidizing, nitrate-reducing bacteria (soNRB) in wastewater treatment reactors (Garcia-de-Lomas et al., 2007). Mohanakrishnan et al. (2009a) demonstrated that the indigenous soNRB community in anaerobic sewer biofilms responded very quickly to nitrate addition to develop anoxic sulfide oxidation abilities. In this study, the soNRB activity in the sediment increased with repeated exposure to nitrate (Fig. 7.3C), and eventually led to zero net sulfide accumulation in the sediment in the presence of nitrate (Fig. 7.4C). The main anoxic biological sulfide oxidation activity was found near the surface of the sediment (i.e., 0–2 mm, Fig. 7.4D). Such spatial positioning would allow soNRB to better utilize both nitrate from the bulk sewage and sulfide produced from SRB in deeper zones of the sediment (Mohanakrishnan et al., 2009a).

### 7.4.2 Nitrate suppresses MA activity and reduces methane production in sewer sediment

Here, the addition of nitrate substantially reduced methane production in the sediment (Figs. 7.2B and 7.3B). Nitrate has been shown to be inhibitory to MA in previous studies in mixed methanogenic communities (Klüber and Conrad, 1998, Tugtas and Pavlostathis, 2007), ruminal cultures (Zhou et al., 2011), soil slurries (Chidthaisong and Conrad, 2000, Roy and Conrad, 1999), freshwater sediment (Okutman Tas and Pavlostathis, 2008, Van Kessel, 1978), and sewer biofilms (Damgaard et al., 2001, Jiang et al., 2013b, Mohanakrishnan et al., 2009a). For example, Jiang et al. (2013b) revealed that methanogenic rates were maintained at 10% below baseline level after addition of 30 mg-N/L nitrate to a rising main sewer reactor. Hence, the presence of nitrate in the upper part of the sediment was likely responsible for the suppression of MA in this study (Fig. 7.5). The nitrate shock dose experiment further confirmed this hypothesis. Methanogenic activity was completely suppressed with 24-hour exposure to 40 mg-N/L nitrate (Fig. 7.6), most likely due to deeper penetration of nitrate into the sediment. The recovery of methanogenic activity is slow even after a single dose of nitrate (Fig. 7.6).

After nitrate addition, major methane production zones moved from the upper 0 to 2 cm to deeper within the sediment (Fig. 7.5, 1.0–2.5 cm). Due to a comparatively lower nitrate concentration, MA inhabiting the deeper layer of sediment could potentially utilize SCOD for methane production. However, it should be noted that both acetate and propionate were relatively limited in the presence of nitrate (Fig. S7.3), as compared with prior to nitrate addition (Fig. S7.4). This was likely due to community succession and consumption by denitrifiers. Therefore, the limited SCOD supply in the deeper layer of sediment was also likely responsible for the low MA activity (around 25% of the baseline level) after nitrate dosing commenced.
7.4.3 Practical implications

In this study, nitrate dosing is shown to reduce sulfide and methane production by sewer sediment. Since nitrate does not inhibit SRB activity but induces consumption of sulfide by soNRB, nitrate should be added at a level that maintains anoxic conditions throughout the sewer to prevent resumption of sulfide production once nitrate is depleted. In contrast, nitrate addition has a long-lasting, inhibitory effect on methanogens in the upper zone of sewer sediment, but there was no evidence that methane oxidation coupled to nitrate reduction (Haroon et al., 2013) occurred in the sewer sediment. This implies that nitrate addition can substantially reduce methane production but cannot completely suppress it. This study further showed that one-time, nitrate shock dosing effectively reduced methanogenic activity by more than 50% in the following weeks (Fig. 7.6). Hence, intermittent application of nitrate shock dosing could be an effective approach to reduce methane emission from sewers. Additionally, our study showed that nitrate addition to gravity sewers would not induce significant N₂O emission.

7.5 Supporting information

Figure S7.1. Sulfide (A) and methane (B) production rates in the control sediment reactor (R2).
Figure S7.2. Box plot of dissolved nitrous oxide concentrations in reactor, R1, at time 0, 0.5, 1, 2, 3 and 4 h after the addition of nitrate at 15 mg-N/L during the batch tests.

Figure S7.3. (A) Sulfide, methane, nitrate and nitrite, and (B) SCOD, acetate and propionate concentrations during a 4-h batch test in the presence of nitrate after the commencement of nitrate dosing (Phase II); (C) Sulfide and methane concentrations, and (D) SCOD, acetate and propionate concentrations during a 4-h batch test in the absence of nitrate during Phase II.
**Figure S7.4.** (A) Sulfide and methane, and (B) SCOD, acetate and propionate concentrations during a 4-h batch test prior to the commencement of nitrate dosing (Phase I).
Chapter 8 Research outcomes, conclusions and future work

8.1 Research Objective I - Evaluating and developing online sensors for gaseous and dissolved methane quantification in sewers

8.1.1 Conclusions on sensor development/evaluation

In this study, IR-based methane gas sensors were comprehensively evaluated and shown to be suitable for sewer applications. IR sensors exhibit excellent linearity and can be applied with factory calibration. The detection limit of the sensors was found to be suitable for measuring methane gas in sewers. Also, IR sensors are robust to ambient temperature variations. Under certain circumstances (i.e., RH>80%), humidity could become an issue for the portable sensor (Sensor I), however, this can be solved by removing the humidity on the sensor probe surface. The other fixed sensor (Sensor II) was robust against humidity variations. Field application of the sensors confirmed the suitability of both sensors when applied to the actual sewers. IR-based methane sensors provide a powerful tool for accurate quantification of methane emissions from sewers, when used in conjunction with gas flow meters.

Also, a simple and robust method for in-situ dissolved methane measurement in sewage was developed and applied to a real sewer for understanding and quantifying dynamic methane production and emission from sewers. Dissolved methane concentrations in sewage can be reliably measured through its stripping to the gas phase followed by gas-phase measurement. This method possesses good linearity in both laboratory and field studies, and has detection limits and measurement ranges suitable for sewer applications.

8.1.2 Conclusions on online methane quantification in actual sewers

Methane is a highly potent fugitive GHG that contributes significantly to climate change. The plentiful carbon flow into wastewater systems creates potential for GHG emission, and consequently, concern has grown significantly in recent decades. Wastewater systems comprise WWTPs and sewer networks. There is currently a major effort aimed at understanding and quantifying methane production in WWTPs. Studies to date have considered methane emission from WWTPs to be the major contributor, with direct methane emission factors ranging from 0.14 to 3.44 g CH₄/ influent m³ (Daelman et al., 2012). In contrast, very little attention has been paid to methane formation in sewer networks. Despite some recent studies have attempted to detect methane
concentrations in sewers, these manual sampling campaigns may not capture dynamic methane variation, imposing a serious limitation on accurate quantification.

In this research objective, we measured, for the first time, significant dissolved and gaseous methane concentrations in sewers by using online sensors, enabling better understanding and management of methane emissions in sewer networks. The measured data showed a wide variation in dissolved methane concentration i.e., 5 – 15 mg/L in summer and 3.5 – 12 mg/L in winter at the end of a 4.4-km long rising main sewer carrying a flow of 2840 m$^3$/d (Chapter 5). Based on these measurements, the average daily production of methane was estimated as 24.6 and 19.0 kg-CH$_4$/d, respectively. When sewage flow from an enclosed anaerobic sewer pipe is discharged into a ventilated space, i.e., pumping station, wet-well or gravity sewer, a large proportion of dissolved methane is stripped off to the atmosphere under turbulence, resulting in significant emissions, i.e., 1400 – 29000 ppm, 3 – 4 orders of magnitude higher than that of 1.8 ppm in atmosphere (Chapter 4). These data clearly demonstrated that sewers are a significant source of methane and CH$_4$ is produced from sewers in significant quantities. Also, sewer methane production and emission display significant temporal and spatial variation, indicating that online measurement will be the most suitable method for quantification.

Furthermore, the direct GHG emission from this rising main site is thus estimated to be 0.16 kg CO$_2$-e/m$^3$ of wastewater transported, assuming that 1 kg CH$_4$ is equivalent to 21 kg CO$_2$ in terms of global warming potential (IPCC, 2006), in order to estimate the relative contribution of sewer methane production to overall methane emission over the entire wastewater systems, as de Haas et al. (2014) estimated that the total GHG emissions from WWTPs in Australia is 0.5–2.0 kg CO$_2$-e/m$^3$ with a mean value of 1.0 kg CO$_2$-e/m$^3$ of wastewater treated, considering both direct and indirect emissions. Using this data, methane production in this rising main site, contributes ca. 14% of the total GHG emission during wastewater handling and treatment. Higher contribution is expected if using a recent higher global warming potential of methane (1 kg CH$_4$ is equivalent to 34 kg CO$_2$ in terms of global warming potential (IPCC, 2013)). It should be noted that this particular sewer is only a small part of a much larger network, and hence more methane production is expected when the wastewater is transported through the remaining parts of the network before reaching the WWTP (Pikaar et al., 2014). Therefore, methane production from sewers plays an important role in contributing to overall methane emissions over the entire wastewater systems.

8.1.3 Recommendation for future research
Some research challenges have been identified that entail further research and are summarized below:

- In this study, we have developed/verified both gas and liquid phase methane sensors for sewer application. These sensors should be employed continuously on a short-term basis (i.e., daily or weekly) in a wide range of representative sewer networks to collect more comprehensive methane data for development of reliable sewer accounting guidelines. With respect to quantifying methane production and emission in a rising main sewer, the dissolved methane concentrations at the upstream pumping station and at the end of the pipe, and the sewage flow data are needed. In contrast, for quantifying methane production and emission in a gravity sewer, additional gas phase methane levels in the upstream manhole and at the end of the sewer, and gas flow rates are required. Therefore, these field measurement campaigns should be carried out in the future.

- In fact, it is impractical to quantify methane concentrations either by online or manual methods over a large number of sampling sites along extensive sewer networks, particularly on a long-term basis. However, mathematical modeling is a viable option for predicting and estimating methane production and emission in sewer networks. Currently, the methane prediction component of the state-of-the-art SeweX model has so far only been calibrated with very limited laboratory and field data measured through grab sampling and off-line chemical analysis, without consideration of the actual dynamics of methane formation in sewers. Therefore, the comprehensive and detailed online methane measurement data collected above will enable better calibration and validation of parameter values in this model, which can be used to assess methane emissions from large-scale and complicated sewer networks (e.g., city).

**8.2 Research Objective II - Understanding and controlling methane and sulfide production in sewer sediments**

**8.2.1 Conclusions on understanding methane and sulfide production in sewer sediments**

Previous studies suggested that activities which take place in the biofilm are the most important microbial transformations in sewers (Hvitved-Jacobsen, 2002). In this study, a comprehensive investigation on the sediment contribution to biological transformations in sewers was initiated for the first time using a laboratory sewer sediment reactor. Our study has revealed substantial methane
and sulfide production from gravity sewer sediment, with areal production rates of methane and sulfide that were comparable to or larger than those of sewer biofilms (Chapter 6). Considering that the sediment deposition rates are ranging from 30 to 500 g per meter length of sewer every day (Ashley et al., 2003), sewer sediment will be a significant source of methane and sulfide.

Our study also demonstrated sulfide production takes place near the sediment surface, and methane production also occurs closer to sediment surface but in a much thicker zone in comparison to sulfide production. These findings can be explained by the deep penetration of soluble organic carbon and that sulfate is utilized near the sediment surface. The stratification of the microbial community and microbial activities along the sediment depth is governed by kinetic differences between sulfate reducing bacteria and methanogenic archaea.

In addition, a detailed, one-dimensional sediment model was built to predict methane and sulfide production and microbial distribution in sewer sediment. The model-predicted methane production profiles within the sediment matched very well with the experimental data. A simple half-order kinetic equation was derived from the detailed sediment model to predict methane and sulfide production in sewer sediment. The model is simple as it involves only one parameter to be calibrated, and could potentially be incorporated into the dynamic SeweX model. Therefore, this proposed model may be useful in practical applications to determine the contribution of sewer sediments to the overall sewer network emissions in the future.

8.2.2 Conclusions on controlling methane and sulfide production in sewer sediments

Methanogens are likely to be protected from being exposed to chemicals added for in-sewer sulfide and methane mitigation. Therefore, further study by dosing nitrate as an example on methane mitigation was carried out in sewer sediment reactors (Chapter 7). The methane production activity of sewer sediment was substantially reduced but not completely suppressed. Its activity in the sediment zone with frequent nitrate exposure was completely suppressed, and consequently, the methane production zone re-established deeper in the sediment where nitrate penetration was infrequent.

Meantime, nitrate addition reduces sulfide accumulation in gravity sewers. This is achieved through anoxic sulfide oxidation rather than suppression of sulfide production. In the presence of nitrate, the sewer sediment is stratified, with sulfide being produced in deeper zones and biological sulfide oxidation occurring nearer the sediment surface where nitrate is present. Therefore, the persistent presence of nitrate is required for sulfide control in gravity sewers.
8.2.3 Recommendations for future research

Some of research challenges have been identified that entail further research and are summarized below:

- Research in gravity sewer sediment to date has mainly focused on sediment formation processes such as the sediment deposition, erosion and transport. Our study demonstrated a significant role of sewer sediment in terms of methane and sulfide production. It should be noted that the overall methane and sulfide production potential of sewer sediment also depends on the total surface area of sewer sediment, which varies to a great extent depending on several parameters in a gravity sewer including the slope, water depth, and flow. Therefore, continued study should be carried out in more representative pilot-scale sewer pipes, leading to better understanding of contribution of sewer sediment to methane and sulfide emissions along the sewer networks.

- The sewer sediment model built in this thesis was only calibrated and validated using data from one laboratory reactor. More laboratory as well as field data are required to examine the accuracy of this sediment model. In addition, this simple model could be incorporated into the dynamic SeweX model in the future.

- Methane and sulfide control from sewer sediments using nitrate was only carried out in the laboratory reactor. Further field demonstration of the mitigation methods will be essential for trialing other cost-effective chemicals (i.e., FNA), and for the development of better control options such as online dynamic control of dosing rates. Furthermore, from a network-wide view, the side effect of chemical dosing in sewers on the downstream WWTP should be investigated.

- Sediments in gravity sewers typically have a shallow aerobic zone at the surface followed by an anaerobic zone deep in the profile. Therefore, the CH₄ produced in the anaerobic zone could be oxidized by methanotrophs near the surface. However, it is currently unknown how quickly these processes proceed, how much they contribute to methane removal, and how they are affected by operational and hydraulic conditions.
Despite the basic knowledge of microbials along the sediment in this study, the detailed microbial structure of sewer sediment remains unknown. Understanding the microbial structures in sewer sediment could provide further fundamental knowledge of ecosystems in sewers, which would help for better understanding the in-sewer processes.
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