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UNDERSTANDING THE BIOTRANSFORMATION PROCESSES IN A SEWER SYSTEM TO ACHIEVE OPTIMAL MANAGEMENT (ARC LP0454182)

Final Report

This is the draft version of the final report summarizing the key findings of the project. The project was funded by Australian Research Council (ARC) through a ARC Linkage Project (ARC LP0454182). Gold Coast Water and Sydney Water Corporation were the research partners in this project and contributed to the funding of the project.

**Advanced Water Management Centre
The University of Queensland**

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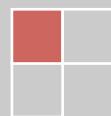


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EXECUTIVE SUMMARY

This research work on “Understanding the Biotransformation Processes in a Sewer System to Achieve Optimal Management” was jointly undertaken by the Advanced Water Management Centre at The University of Queensland (AWMC-UQ), Gold Coast Water (GCW) and Sydney Water Corporation (SWC) during June 2004 and August 2007. The project was jointly funded by the Australian Research Council (ARC), Gold Coast Water and Sydney Water Corporation. The cash budget was approximately \$1.2m including \$708k cash contribution from the ARC. Additionally, all partners involved including the University also made substantial in-kind contributions to the project.

The project aimed to gain a fundamental understanding of the biochemical as well as physico-chemical processes in sewer systems, and on this basis to provide the wastewater industry with knowledge and tool support for its management of hydrogen sulfide production and emission in sewer systems.

The project delivered strong outcomes with most milestones achieved. The knowledge and model generated are being applied by both GCW and SWC for the management of their sewer systems, both rising and gravity mains.

The main outcomes of the project are summarised below.

- An advanced model for predicting sulfide production and emission in sewers was developed based on the results of extensive laboratory and field studies. The UQ Sewer Model, which is by far the most advanced sewer model in the world, is capable of predicting: (1) Biological carbon transformations under aerobic, anoxic and anaerobic conditions; (2) Biological sulfur transformations consisting of anaerobic sulfate reduction and aerobic and anoxic oxidation of sulfide; (3) Chemical oxidation of sulfide by oxygen; (4) Chemical precipitation of sulfide and several other competing anions by metal ions; (5) Mass transfer of sulfide and several other volatile compounds between liquid and gas phases; (6) pH variation in wastewater caused by in-sewer physical, chemical and biological processes. All reaction stoichiometry and kinetics were developed with most parameters calibrated through laboratory and field studies. Major inventions included new kinetic expressions for biological reactions in intermittently operated sewers. These were developed by taking into consideration the impact of boundary layer formation on reaction rates. The model has been successfully applied to optimising sulfide control strategies in two sewer networks.
- Effect of oxygen injection on sulfide control was fully assessed though both laboratory and full-scale investigations. Oxygen injection could be a cost-effective approach to sulfide control in rising main sewer networks. However, both its effectiveness and efficiency are highly sensitive to the injection locations. In general, the point of injection (POI) should be “reasonably” close to the points where sulfide control is required (Point of Control - POC). An injection site should be selected such that (1) there would be an adequate hydraulic retention time (HRT) between a POI and the POC to enable full oxidation of any sulfide present at the POI before it reaches the POC, and that (2) aerobic conditions are maintained between the two points with minimum requirement of oxygen. The selection of the injection sites and the determination of the dosage profiles could be a difficult task, particularly for



large, complex networks. The UQ Sewer Model provides a powerful tool for these tasks, as already demonstrated through the case study carried out for the Tugun-Elanora network. A further lesson directly learnt from field studies was that there should be no high points between a POI and a POC, as otherwise air pockets rich in oxygen and hydrogen sulfide would form at such locations causing corrosion of pipes. Other findings related to oxygen injection include (1) Oxygen suppresses sulfide production as long as it is present in the bulk liquid phase. However, oxygen has no long-lasting inhibitory/toxic effect on sulfate reducing bacteria (SRB). Sulfide production resumes within minutes after the depletion of oxygen; (2) sulfide oxidation with oxygen occurs both biologically (primarily sewer biofilms) and chemically (in bulk liquid); (3) Oxygen injection enhances SRB activities in the downstream sections of sewers. This is due to the re-generation of sulfate (from sulfide) at sites where oxygen is injected so that more downstream sewer biofilms are exposed to sulfate, which enhances the growth of SRB.

- Effect of nitrate addition on sulfide control was fully assessed through laboratory investigations. Like oxygen, nitrate was also found effective in controlling sulfide in sewage when properly added. The injection site should be selected such that (1) there would be an adequate hydraulic retention time between the POI and the POC to enable the full oxidation of any sulfide present at the POI before it reaches the POC; and that (2) anoxic conditions are maintained between the two points with minimum requirement of nitrate. In a single main, the temporal dosage profile should be kept proportional to the HRT between the POI and POC with a proportionality coefficient dependent on the diameter of the pipe as well as the strength of the wastewater. This coefficient could be found through the use of the UQ Sewer Model or through trial and error. For a large network, the optimal dosage locations and profiles could both be found through the use of the UQ Sewer Model. Compared to oxygen, nitrate is more expensive for the same amount of electron-accepting capacity. However, nitrate can be added to any desired levels in wastewater, while the amount of oxygen that can be injected is limited by its solubility in water. Other findings related to the use of nitrate for sulfide control include (1) Nitrate does not seem to be inhibitory to the SRB activity, and therefore sulfate reduction is likely to continue in the presence of nitrate; (2) Nitrate addition stimulates the growth of indigenous nitrate-reducing, sulfide-oxidising bacteria, which rapidly oxidises the sulfide formed by SRB thereby preventing sulfide accumulation in the presence of nitrate; (3) Sulfide production/accumulation occurs within minutes after nitrate depletes from the liquid phase (4) Nitrate addition enhances SRB activities in the down stream sections of sewers. This is due to the re-generation of sulfate (from sulfide) at sites where nitrate is injected so that more downstream sewer biofilms are exposed to sulfate, which enhances the growth of SRB); (5) Chemical oxidation of sulfide by nitrate does not occur in the bulk liquid phase.
- Effect of ferrous ion addition under anaerobic conditions on sulfide control was investigated through thorough investigations on a lab-scale sewer system. The main findings are: (1) the stoichiometric ratio between ferrous ion and sulfide ($\text{Fe}^{2+}:\text{S}$) is 0.6-0.7:1, which is substantially lower than the ratio commonly used by the industry and is also considerably lower than the theoretically minimum ratio of 1:1. While the fundamental reasons for this low ratio are yet to be fully revealed (the research is being continued as a PhD project), it is believed that pyrite (FeS_2) was formed as a precipitation product, along with FeS , through



sophisticated biochemical reactions mediated by sewer biofilms. A mixture of FeS₂ and FeS would give an Fe²⁺:S ratio of 0.5-1:1. This finding has major implications to the use of ferrous ions for sulfide control in sewers; (2) The Fe²⁺:S ratio reported above is independent of the dosage locations. It is therefore more desirable to add ferrous ions in the upstream rather than downstream sections of sewers. In this way, the dissolved sulfide level in the entire sewer network may be controlled at acceptable levels with the same consumption of ferrous ions. (3) Phosphate does not precipitate with ferrous ions under anaerobic conditions in sewers.

- Effect of pH elevation on SRB activities was assessed through investigations using a lab-scale sewer system. pH elevation through the addition of magnesium hydroxide has been previously demonstrated to shift the balance between H₂S and HS⁻ so that the transfer of H₂S to the gas phase is reduced. In this project, we demonstrated that pH elevation to a level of approximately 8.5 reduces the SRB activities and hence the sulfide production rate in -sewers.
- A method for on-line measurement of dissolved sulfide in sewage has been developed in collaboration with DCM Process Control. The method involves mathematically analysing the spectra measured with a UV-VIS spectrometer to extract the absorbance of HS⁻ using an algorithm developed by the DCM, leading to the quantification of the HS⁻ concentration. With the pH signal measured in parallel, the H₂S concentration can be calculated, which along with the HS⁻ concentration gives the total dissolved sulfide concentration in wastewater. The sensor has been successfully applied to measuring sulfide as well as nitrate/nitrite concentrations in wastewater in both field and laboratory conditions with excellent accuracy and reliability in most cases. The sensor is being used by industry partners as an on-line tool for sulfide measurement.
- An ion chromatography (IC) based method has been developed to simultaneously and reliably measure sulfide, sulfate, thiosulfate and sulfide species in wastewater. This was developed based on the discovery in the project that the Australian Standard Methods for sulfide and sulfate measurement often do not yield reliable results. A preservation solution (Sulfide Anti-Oxidation Buffer, or SOAB) has also been developed, which allows wastewater samples to be preserved for up to four days (or possibly longer) prior to being analysed without significant sulfide loss and transformation between different sulfur species. Furthermore, a new protocol for wastewater sample collection and preparation has been developed.
- Other significant findings included (1) the biofilm structure and activities vary significantly along the length of a sewer pipe resulting in different sulfide production potentials; (2) methane may be formed in sewers in significant quantities. Up to 20 mg methane was found in the two rising main sewers investigated.
- Further, the research outcomes from this project provided strong support to the development of a new ARC Industry Linkage project on corrosion and odour management in sewers, of which UQ is a leading research partner and SWC and GCW are two important industry partners. The University of New South Wales, The University of Sydney and The University of Newcastle, Brisbane Water, CH2MHILL, SA Water, South East Water, United Water and WA



Water Corporation are other partners of the project. The new project with a combined ARC and industry cash budget of approximately \$8m has a much broader scope compared to the completed project, and is expected to continually enhance the capability of the Australian Water industry in managing the corrosion and odour problems in sewers.



1. INTRODUCTION

1.1. BACKGROUND

Sewer systems are an integrated and very important component of the urban wastewater and stormwater management system. By design, their primary function is the conveyance of wastewater and/or stormwater to wastewater treatment plants or directly to the receiving waters. The nature of the wastewater, however, leads to a range of complex chemical and biochemical transformations in sewer systems, resulting in profound impacts on the structural integrity of the sewer system, the environment and the performance of the downstream wastewater treatment plants (WWTPs).

The production and emission of hydrogen sulfide in sewer systems has since long been a well-known problem (USEPA, 1974). When anaerobic conditions prevail in a sewer system, the sulfate present in the wastewater is reduced to sulfide by microorganisms such as *Desulfovibrio* and *Desulfotamaculum* (collectively called sulfate reducing bacteria-SRB) through sulfate respiration, resulting in significant emissions of H₂S, particularly in sewer sections without full flow. The build-up of H₂S in the sewer atmosphere causes major detrimental effects:

- CORROSION OF THE SEWER SYSTEM. The concrete and metal corrosion problems are caused commonly by the absorption of hydrogen sulfide and its subsequent oxidation to sulfuric acid by microorganisms, in the liquid film that exists on moist surfaces in the sewer system. The highly corrosive sulfuric acid causes damage to the sewer wall and other installations in the sewer. Similar damage is also caused in the inlet zones to treatment plants.
- HEALTH HAZARD. H₂S is a toxic compound, a high level presence of which in the sewer atmosphere is a threat to the health and life of anyone working in the sewer or close to the inlet structure of treatment plants;
- MALODOUR IN THE NEIGHBOURHOOD OF THE SEWER SYSTEM particularly in areas with high turbulence causing increased stripping of H₂S. It is not uncommon that wastewater authorities receive complaints and even fines for the odour nuisance originating from sewers (information from Industry Partners). The malodour is also caused by other volatile organic compounds such as indoles, skatoles, mercaptans, volatile fatty acids, which may also be generated anaerobically in sewer systems.

A large number of strategies have been employed by the wastewater industry to minimise the production or emission of H₂S (Thistlethwayte, 1972; Boon, 1995). The commonly used strategies included oxygen injection to rising mains (e.g. employed by GCW), and the addition of nitrate (employed by SWC), Fe²⁺/Fe³⁺ (employed by both GCW and SWC) or Mg(OH)₂ (being considered by both GCW and SWC) to wastewater.

While these strategies have found applications with various degrees of success (USEPA, 1974), the selection and optimal use of these strategies have proven to be extremely difficult. *There is in general a lack of adequate understanding of the in-sewer biotransformation processes to support the wastewater authorities in achieving optimal sewer management.*



The sophisticated in-sewer sulfur and carbon transformation cycles coupled with the highly dynamic and complex hydraulic, solids sedimentation/erosion and biofilm formation processes make the management of sewer systems very difficult. Modelling and simulation has been playing important roles in the design and management of sewer systems. Indeed, hydrological and hydraulic modelling has since long been used to assist the design of sewers (Bertrand-Krajewski *et al.*, 1993). The modelling of solids sedimentation/erosion has also attracted considerable attention in the last 10 to 20 years, primarily in the context of predicting and minimising the suspended solids concentration in the combined sewer overflows (CSO) (e.g. Mark *et al.*, 1995; Schlütter, 1999). In contrast, detailed studies on in-sewer biotransformation processes started more recently (Hvitved-Jacobsen *et al.*, 1995; Hvitved-Jacobsen, 2002). Large knowledge gaps exist, which limited the capability of the water industry to manage the corrosion and odour problems cost-effectively. In particular, there is a lack of good quality models enabling the prediction of "hot spots" in sewers and the optimisation of the sulfide control strategies discussion above.

1.2. OBJECTIVES OF THE PROJECT

The project aimed to gain a better fundamental understanding of the biochemical transformation processes occurring in a sewer system to provide scientific and engineering support for the optimal management of urban wastewater systems. Specifically, this project will:

- Generate scientific insight into the biochemical transformation processes in a sewer system by integrating controlled laboratory experiments, field measurements/experiments and advanced computer modelling;
- Develop detailed models characterising the biochemical reaction and mass transfer processes in the biofilms, the sediments and the suspended phase;
- Develop a protocol as well as experimental and numerical procedures for the calibration of the above models, and their effective integration with the existing hydraulic, solids sedimentation and gas/liquid mass transfer models, to provide an adequate description of a sewer system for the evaluation of different management options;
- Apply the knowledge and models to the management of two sewers, generating direct operational knowledge on optimal sewer management.

The production and control of hydrogen sulfide was chosen to be the primary focus of the project as H_2S is the cause of corrosion and is potentially also a surrogate for other odorous compounds.

1.3. ABOUT THIS REPORT

This report is written to summarise the main conclusions of the research, rather than to provide a complete description of all the tasks/activities undertaken during the project. It is structured in such a way that each section is dedicated to a particular conclusion/outcome. Whenever necessary, key experimental evidence is presented to support the conclusions. The summary of the project outcomes is preceded with sections documenting the project methodology/research plan and the key materials and methods, and followed by key issues to be addressed by future research.



During the course of the project (June 2004 and August 2007), 12 Quarterly Project Reports were produced which contained all the technical details of the project. Readers are referred to these reports for detailed scientific and technical information arising from the project.

2. PROJECT METHODOLOGY AND PLAN

Figure 1 summarises the project methodology and plan, which was developed based on the ARC project proposal, and agreed upon by the Project Management and Steering Committee at the beginning of the project. Five inter-linked tasks were defined to deliver knowledge and tool support to the wastewater industry to achieve optimal management of corrosion and odour problems in sewers.

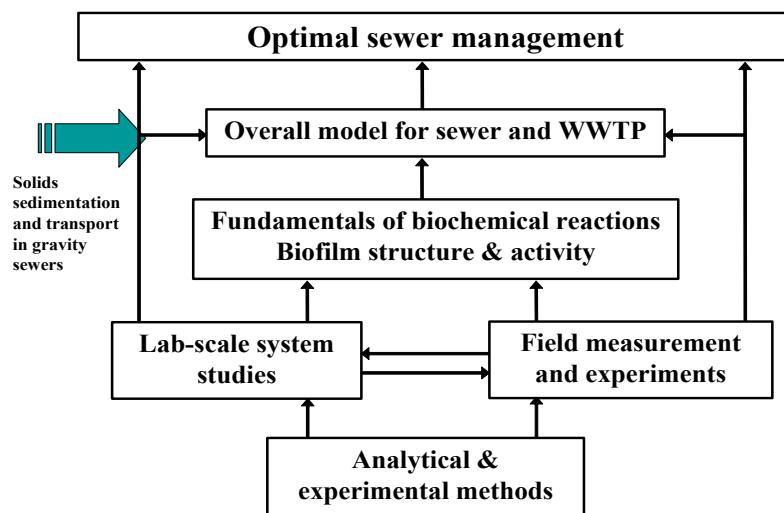


Figure 1: The project plan (the block arrow from the left indicates that the information on the aspect specified will be primarily from literature)

1. Method development: This task aimed to develop some 'basic' methods for the study of sewer systems. It was defined as an important component of the project based on the recognition that there was a serious lack of tools for the study of sewer systems. One such example is the fact that *the Australian Standard Method for sulfide measurement was found in this project not to give accurate and reliable measurement of the sulfide content in wastewater samples*. In addition, no method was available for on-line measurement of dissolved sulfide in wastewater. This made data collection from sewer systems a tedious, labour-intensive and time-consuming process, which formed one of the bottleneck problems in sewer research.

2. Lab-reactor studies: This task aimed to produce fundamental knowledge on in-sewer biotransformation processes, and to comprehensively assess, using controlled lab-scale experiments, the effectiveness of various strategies that are commonly used by the wastewater industry for H₂S control. This task also aimed to generate comprehensive data to support model development.

3. Field investigations: This task aimed to generate field data to support model development and validation, and subsequently, to transform the knowledge outcomes into practical benefits to industry partners through direct application of knowledge and models.

4. Biofilm structure and activity studies: This task aimed to examine, at a micro-scale, the microbial structure and function of in-sewer biofilms and their responses to different H₂S management strategies. This was proposed as a separate task based on the fact that



biofilms are the main contributors to the in-sewer biotransformation processes and also the fact that the sewer biofilms have rarely been studied at a micro-scale in previous research.

5. Model development and application: This task aimed to encapsulate the knowledge generated in the project in the form of a mathematical model, which would provide the two industry partners with strong support for the management of their sewer systems. The model was also expected to be made available to other wastewater authorities through commercialisation.

The integration of laboratory studies, field investigations and mathematical modelling is a unique feature of the project, which distinguish it from many other previous projects.

3. KEY MATERIALS AND METHODS

The key materials and methods used by the project are summarised in this section to provide readers with background information support. These materials and methods were extensively used in this project to collect the data/information to support model formulation and calibration.

3.1. NOVEL LABORATORY SEWER SYSTEMS

The systems widely used to simulate sewer systems in laboratory environment are typically a short (up to 10-20 meters) section of a pipe with wastewater circulated through the section continuously or intermittently. This design does not allow the development of biofilms with different structures and functions as a function of the wastewater composition they are exposed to; biofilms at different locations of a sewer pipe are exposed to wastewaters with different compositions due to the biotransformations occurring upstream. Such spatial variations, which have been confirmed in this project (to be reported below), should be investigated in order to understand and accurately predict H₂S production in sewer systems.

The reactor-based laboratory-scale system designed in this project (Figure 2) is a flexible setup for sewer research. Four completely-sealed reactors (750 ml in volume) are connected to simulate rising mains. Similarly, four non-sealed reactors are connected to mimic a gravity sewer, which receives the effluent from the rising main system. The system was fed with domestic wastewater collected from a local wet well on a weekly basis and stored in a cold room (4°C). The feeding pump was operated intermittently mimicking the pattern observed for the UC09 pumping station (see below).

Carriers were inserted into all reactors to support biofilm growth. No wastewater recirculation was employed so that different reactors were exposed to wastewaters with different compositions (due to biotransformation in upstream reactors) potentially leading to growth of biofilms with different characteristics (as confirmed in this project). Two such systems were established at the beginning of the project; one was used as the experimental and the other as a reference system.

The design allows the spatial and temporal variations of sewer biofilms to be examined at both macro- and micro-scales. Each reactor can be isolated for batch tests and the carriers in all reactors can be removed for micro-scale measurement (see below).





Figure 2: Reactor-based lab-scale sewer systems. Left – Rising main reactors; Right: Gravity reactors. Biofilms carriers (appearing in photos as white strings inside reactors) are placed in the reactors for biofilm growth. The carriers can be removed for micro-scale studies on biofilm structure and function (to be detailed below). Two sewer systems involving 16 reactors were operated during the course of the project. Photos were taken before operation commenced.

The laboratory systems were used for the following purposes:

- To provide data for the development and calibration of the sewer model;
- To test the effectiveness of various H₂S control strategies and to optimise these strategies.
- To provide biofilms for fundamental studies of the structure and activity of the microbial communities in the biofilms and the impact of various H₂S control strategies on these properties.

3.2. REAL SEWER SYSTEMS

A number of real rising main and gravity sewers were used for field investigations. These included the UC09, C016, D6 rising mains and the Tugun-Elanora C27 rising main network of the GCW, and the Bellambi-Wollongong rising main and the Malabar gravity system of the SWC. Field studies typically involved sampling the wastewater for an extended period of time (6–28 hours) at the beginning and the end of the pipes and in many cases also at the sampling ports installed along the length of the pipes. These wastewater samples were then analysed in analytical labs for its composition including the sulfur species. On-line sensors for sulfide, dissolved oxygen, pH, ORP as well as flow were also installed at some of these sites to provide detailed information of these sites.

The UC09 rising main was used extensively in the project. In addition to the sampling points, two types of biofilm samplers were installed at UC09 to obtain in-situ biofilms (Figure 3 and Figure 4) for advanced biofilm studies. One involved the use of Robbins Devices (Figure 3). The other type was made of removable pipe sections (35 cm long each), which can be transferred to the laboratory environment for biofilm characterization.



Figure 3: In-situ biofilm samplers using the Robbins Devices (RDs). Three Robbins devices (arrow) were installed at a pumping station. The three RDs, each with an inner diameter of 25 mm, are connected with tubes of a diameter of 13mm and are approximately 200 m apart. Each time when the wet well pump is turned on, wastewater is pumped into the tube (and the RDs) at a velocity that is similar to that in the real rising main. Each RD has several coupons where biofilms grow. The coupons and the RDs are removed regularly (see the photo inserted) for microbial and activity measurement in the laboratory.



Figure 4: Photos showing (left) manhole on the UC 9 rising main with 2 removable sections of 150 mm PVC sewer pipe held in place with gibbolts; (right) the same section of sewer pipe (after removal) being tested in the laboratory.

3.3. THE S::CAN UV/VIS-BASED SPECTROMETER

The s::can spectro::lyzer (Figure 5) measures the attenuation of light in the UV-VIS spectrum between 200 and 730nm across a measurement gap of between 0.5 and 2mm. Different components of wastewater absorb light in different regions of the UV-VIS spectrum, and the spectrometer can detect the total absorption from all the compounds present. Each measurement takes about 15 seconds. The probe is kept clean automatically

with a compressed air system and data is logged on a control computer and hence can operate independently for long periods of time.



Figure 5: The s:can spectro:lyzer used in the project

At the beginning of the project, the sensor had not been used for the on-line measurement of dissolved sulfide in wastewaters. However, DCM Process Control observed an absorbance peak at 230 nm (Figure 6), which was hypothesised to be caused by HS⁻ absorption.

Collaboration was set up between the project and DCM Control, which resulted in the development of the above sensor into one capable of measuring dissolved sulfide on-line in wastewater (see Section 4.2). The sensor has since been applied extensively in both laboratory and field studies with highly satisfactory results in most cases.

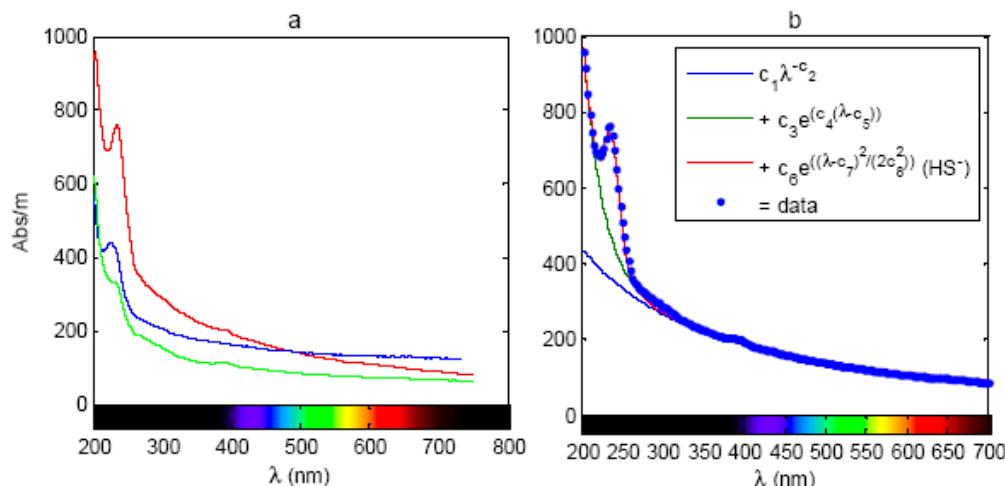


Figure 6: Characteristic UV/VIS spectra from three different sites. The bisulfide signal is clearly visible around 230 nm. Right: Curve fitting to isolate the amplitude of the bisulfide signal.

3.4. MICRO-SENSOR FACILITIES

While it is generally recognised that sewer biofilms play a central role in in-sewer biotransformation, advanced techniques for biofilm study have rarely been employed for sewer biofilm studies. A microsensor laboratory previously established at AWMC-UQ was used for the micro-scale measurement of the biofilm structure and activities. Understanding and controlling the microbial activities in biofilms is crucial for H₂S control. Micro-electrodes, typically with a tip diameter of several micro-meters can be penetrated into biofilms to measure the substrate and/or products of microbial activities. Oxygen, sulfide, ORP and pH micro-sensors have been extensively used in the study of biofilms taken from both the lab reactors and the in-situ biofilm samplers.

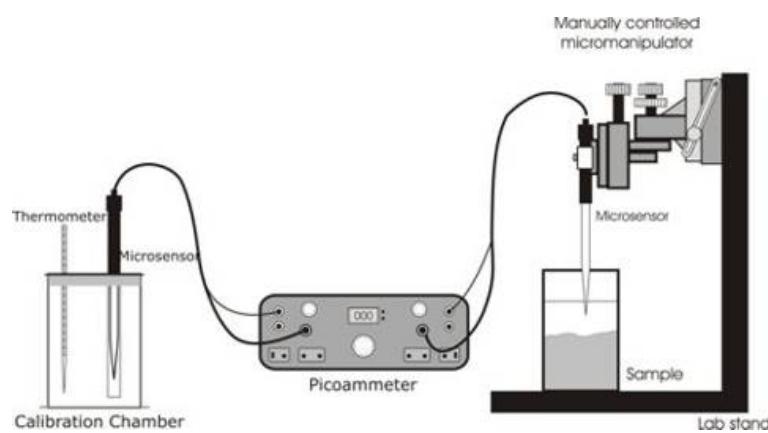


Figure 7: Schematic of the micro-sensor setup. The position of the head of the micro-sensor can be progressively lowered with a resolution of 100 μ m in each step so that the concentrations can be measured at different locations.

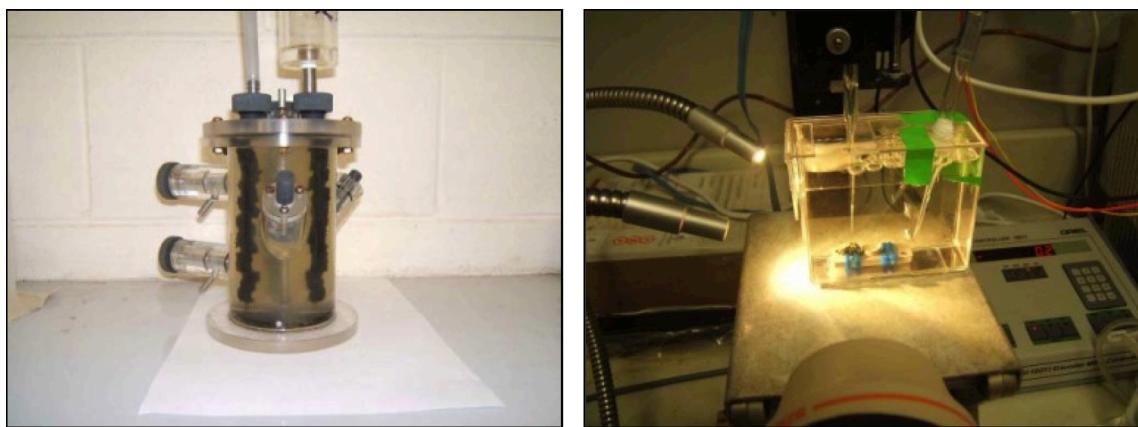


Figure 8: A flow cell (right) where the biofilm carriers from the lab-reactor (left) or the Robbins Devices can be placed into controlled environment where the micro-scale biofilm activities can be measured.

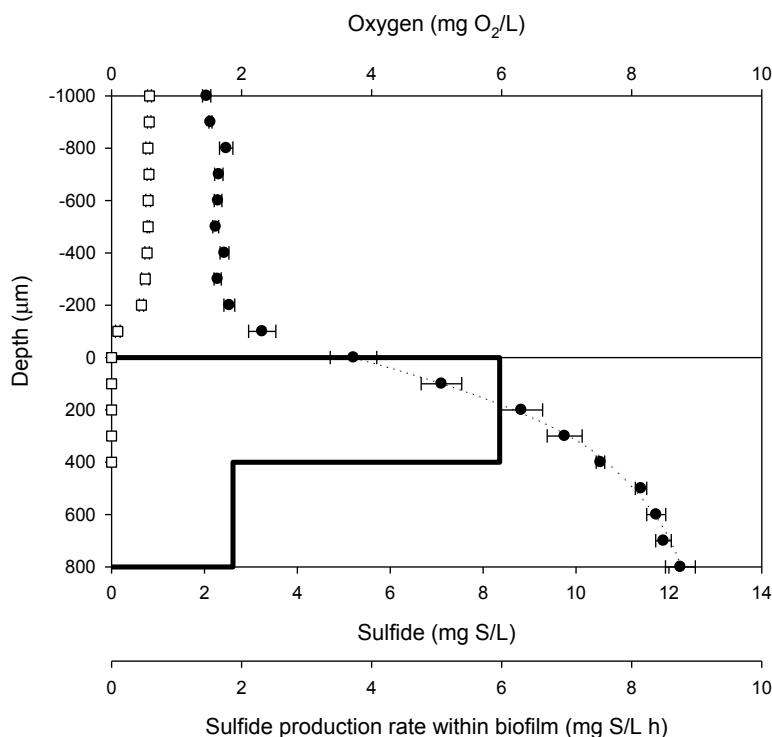


Figure 9: The DO and sulfide micro-profiles measured during a micro-sensor experiment. Depth 0 is the surface of the biofilm. The micro-profiles shows the sulfide production within the biofilms.

4. SUMMARY OF OUTCOMES

4.1. DEVELOPMENT OF METHODS FOR PRESERVATION AND MEASUREMENT OF SOLUBLE SULFUR SPECIES

An ion-chromatography based method was developed for the measurement of various dissolved sulfur species including sulfide, sulfate, thiosulfate and sulfite in wastewater samples. This was delivered along with a novel sample preservation method, which allowed a wastewater sample to be stored for at least 5 days before being analysed without significant conversion of sulfide to other sulfur species (Figure 10).

These developments have major practical implications to the wastewater industry. With the sample preservation method and a high throughput (80 samples a day) measurement method now available, reliable results can now be expected with considerably reduced costs. In addition, large measurement campaigns can now be organised as analysis of samples is no longer a bottleneck. These methods are being heavily used by the project, and are also used by both GCW and SWC.

Various methods were used in Australia for sulfide and sulfate measurement at the time when the project was started. For sulfide, the GCW analytical lab used the DMP-copper method, while SWC used the APHA 4500 S2 D Methylene Blue method. Both labs used the APHA 4500 SO₄ E Turbidimetric method to measure sulfate. The DMP-copper method was and still is the Australian Standard Method for sulfide measurement.



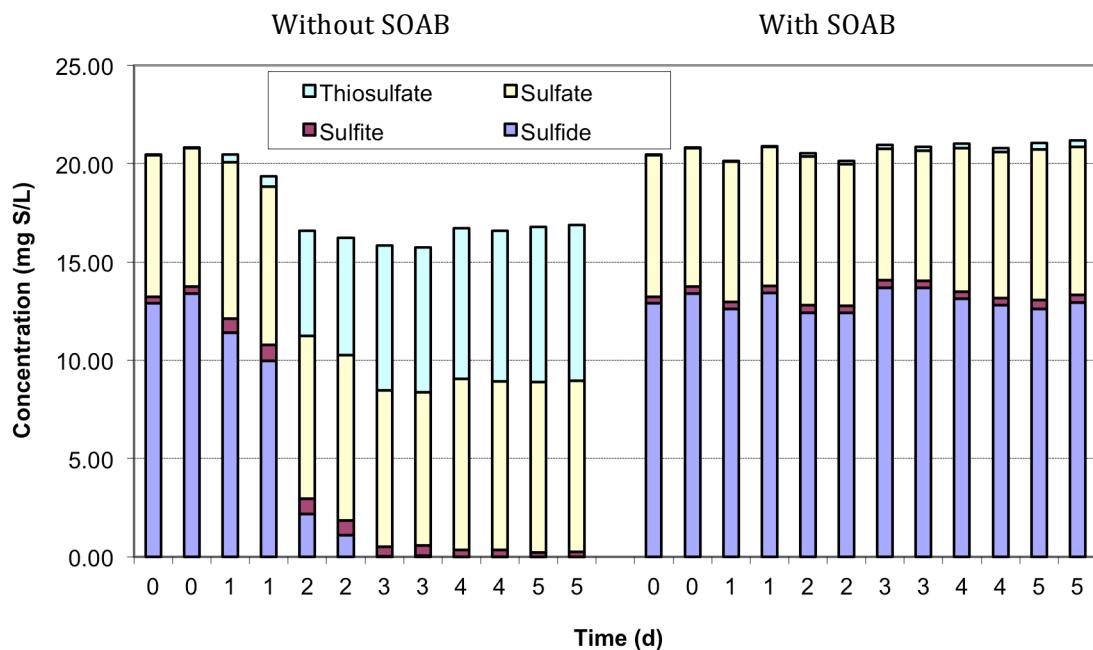


Figure 10: Effect of the preservative reagent (SOAB) on the preservation of soluble sulfur species. Results shown on the left (without SOAB) shows that, without preservation, sulfide is completely oxidized within 2-3 days, with a concomitant production of thiosulfate and sulfate and also a significant loss of soluble sulfur (possibly due to the oxidation to elemental sulfur). This is not the case when the samples were preserved using the SOAB solution developed in this project.

However, serious problems were found with these methods.

- The APHA 4500 SO₄ E Turbidimetric method was found not to give reliable measurement of sulfate. The sulfate results obtained in two measurement campaigns (over 100 samples) were found to be completely out of scale.
- The DMP-copper method (Australian Standard Method for sulfide measurement) was found to give unreliable results when measuring sulfide in wastewater samples. The results are strongly influenced by the presence of thiosulfate, among other problems. This suggests that data currently used by many wastewater authorities for decision making could be erroneous.
- Further, the preservation methods used for both the DMP and the Methylene Blue methods (using DMP-copper and zinc acetate, respectively) did not allow the wastewater samples to be preserved for more than 24 hours, without significant loss of sulfide to other sulfur species. With the DMP method, the recommendation is for samples to be stored for a maximum of 12 hours with no accurate figure for sulfide loss provided. For the Merck based Methylene Blue Method, sulfide loss of 4.5% occurs after 16 hours, and losses increase exponentially with further storage. Therefore, samples should be transported to analytical labs and analysed quickly. For precisely this reason, GCW had to set up an on-site analytical laboratory for timely measurement of sulfide during the implementation of an intensive measurement program before the IC-based method was developed by the project.

4.2. DEVELOPMENT OF A METHOD FOR ON-LINE MEASUREMENT OF DISSOLVED SULFIDE

An on-line sensor for measuring dissolved sulfide in wastewater was developed in collaboration with DCM Process Control. The method has been demonstrated to be accurate and reliable for measuring sulfide in domestic wastewater, and likely applicable to many types of industrial wastewaters as well (subject to verification of the method with each type of industrial method). The sensor has become a tool routinely used for both laboratory studies and field investigations. Several types of installations are shown in Figure 11 and 12.

Figure 13 shows the calibration results when the sensor was used in both laboratory and field conditions. Figure 14 compares the total dissolved sulfide concentration measured by the sensor at two sites with the values measured through manual sampling and off-line laboratory analysis. The two types of measurement matched very well; however, the on-line signals displayed dynamics that would be practically impossible to be captured using sampling.



Figure 11: Deployment of the spectrometer (left to right) Site 1: in a bypass fitting; Site 2: suspended from a float in a wet well; and Site 3: installed in a sealed box channel. The location of the spectrometer is indicated with an arrow except in the lower picture where the spectrometer is hidden from view 2 m under the metal plate and the mounting bracket is indicated with a white arrow.

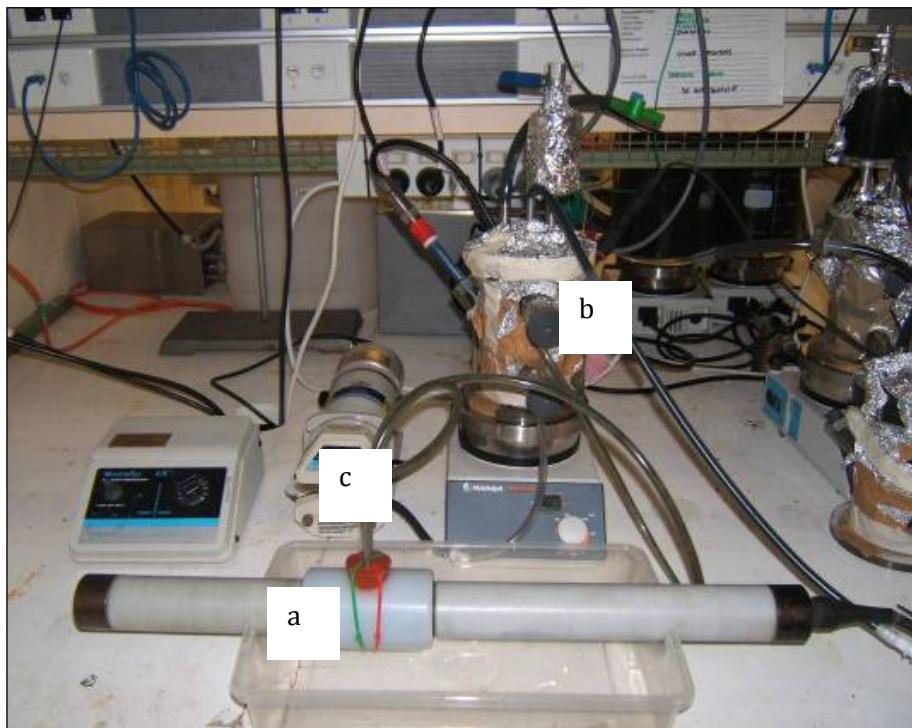


Figure 12: Laboratory scale sewer system and associated equipment, with the s::can spectrolyzer in the foreground. (a) s::can spectrolyzer and bypass fitting; (b) one section of the pilot scale sewer system; and (c) circulation pump.

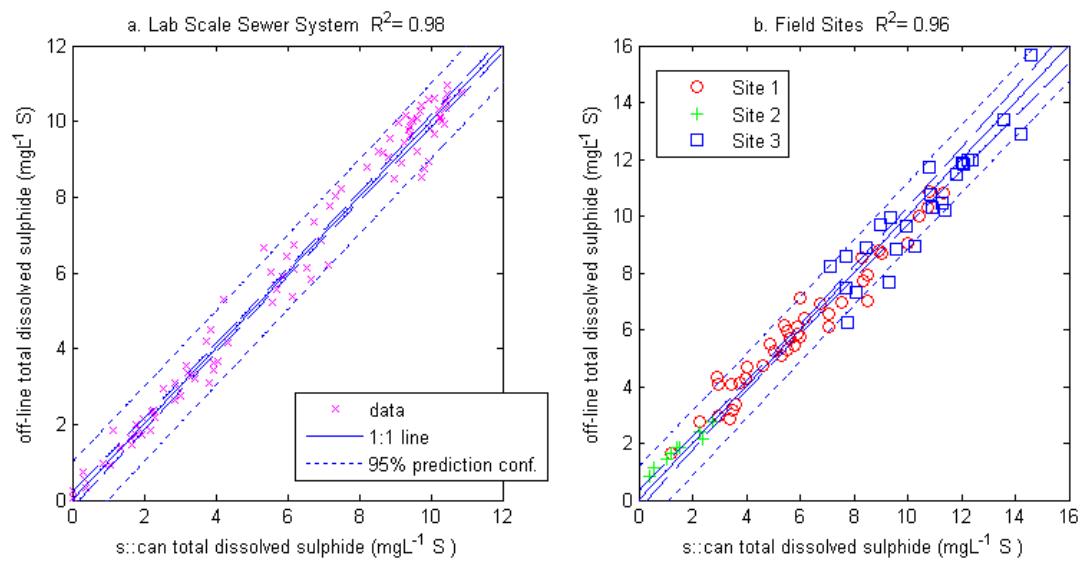


Figure 13: Total dissolved sulfide measured off-line vs. total dissolved sulfide measured using an s::can and a pH probe. (a) lab-sewer samples; (b) field samples.



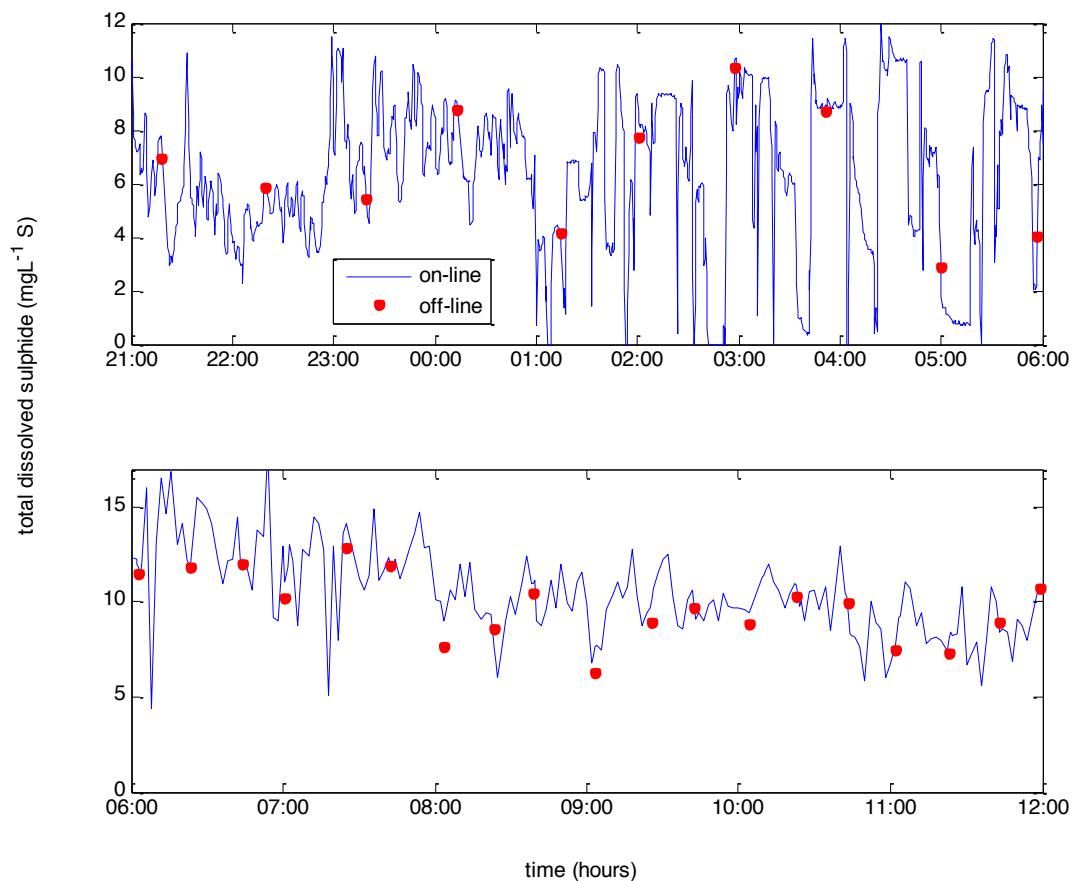


Figure 14: Total dissolved sulphide measurement at the inlets of two different WWTPs
(top: Site 1 in Figure 11 and bottom: Site 3 in Figure 11)



4.3. IMPACT OF OXYGEN INJECTION ON H₂S CONTROL

The lab-scale sewer systems with the configuration shown in Figure 15 were used to investigate the effectiveness of pure oxygen injection on sulfide control.

The results of the study showed that:

- The oxygen injection is effective in controlling sulfide production during periods when oxygen is present. In addition to preventing sulfide from formation, any sulfide present would be oxidized (Figure 16).
- However, oxygen injection has no long-lasting inhibitory or effect on the SRB activities. Figure 16 shows that sulfide production by the biofilms that have received oxygen injection for 86 days resumed as soon as oxygen depleted. This has been further confirmed by the results presented in Figure 17, which shows that the sulfide production capability of the oxygen receiving biofilms, measured as the maximum sulfide production in the absence of oxygen and substrate limitation, was no lower than that of the reference biofilms.
- Figure 17 further shows that oxygen injection enhances SRB activities in the downstream sections of sewers. This is due to the re-generation of sulfate (from sulfide) at sites where oxygen is injected so that more downstream sewer biofilms are exposed to sulfate, which enhances the growth of SRB.

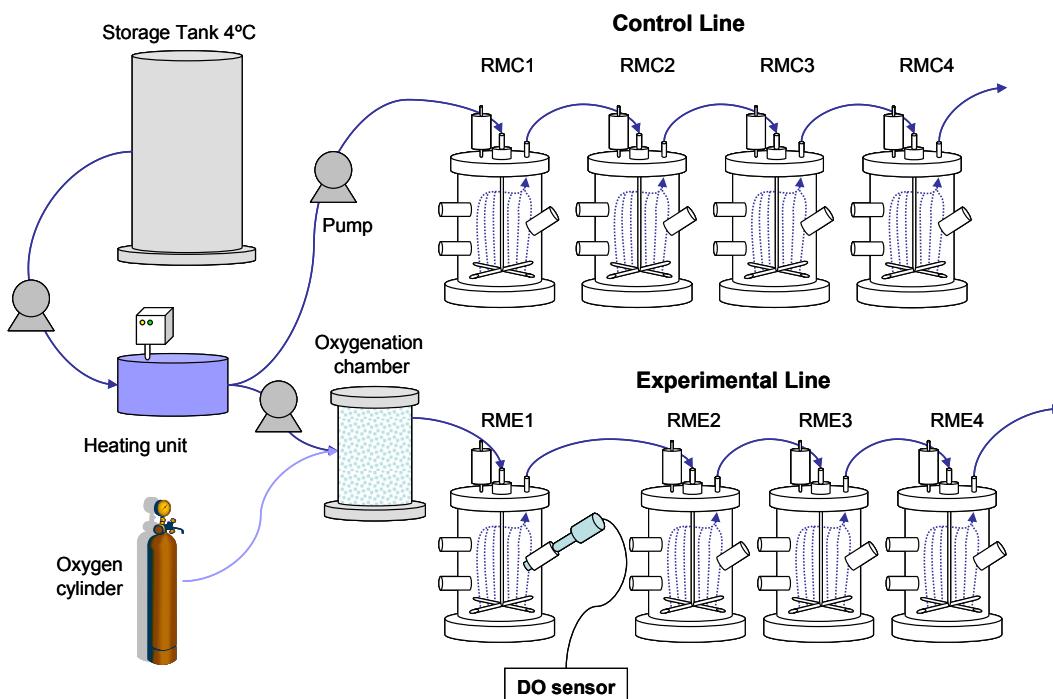


Figure 15: Reactor setup showing the series of rising main control reactors (RMC1-4) and the parallel experimental reactors (RME 1-4) with the oxygenation chamber prior to the first reactor.



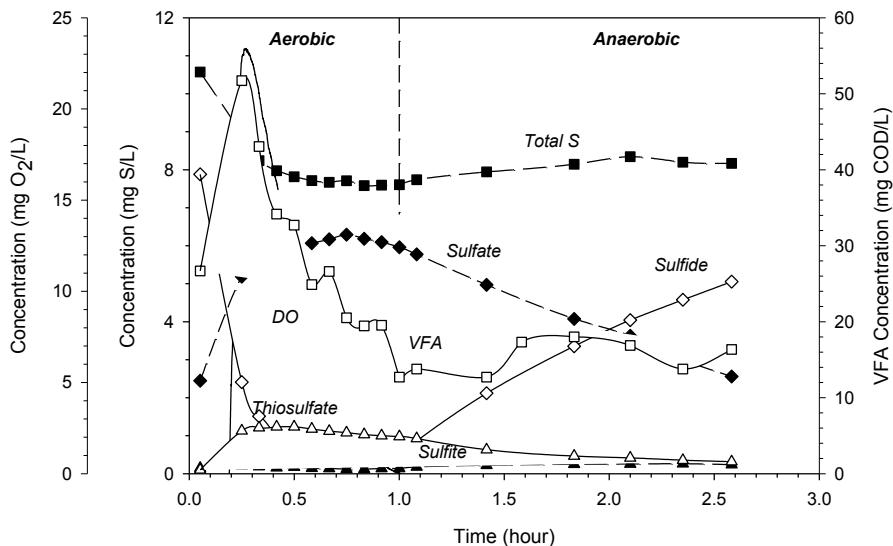


Figure 16: Profiles for oxygen, VFA and various sulfur species during both aerobic and anaerobic conditions following oxygen injection (Batch tests conducted on Day 86 of continuous oxygen injection).

- Figure 18 shows that oxygen uptake rate and VFA consumption rate of the oxygen-receiving biofilms increased dramatically after oxygen injection. This means available oxygen would be quickly consumed and during long quiescent periods, the anaerobic conditions favourable for sulfide production would be quickly established in the system, thereby negating any positive effect achieved by oxygen injection. High VFA consumption is another main concern as this would create a limitation of carbon source for downstream nutrient removal plant.

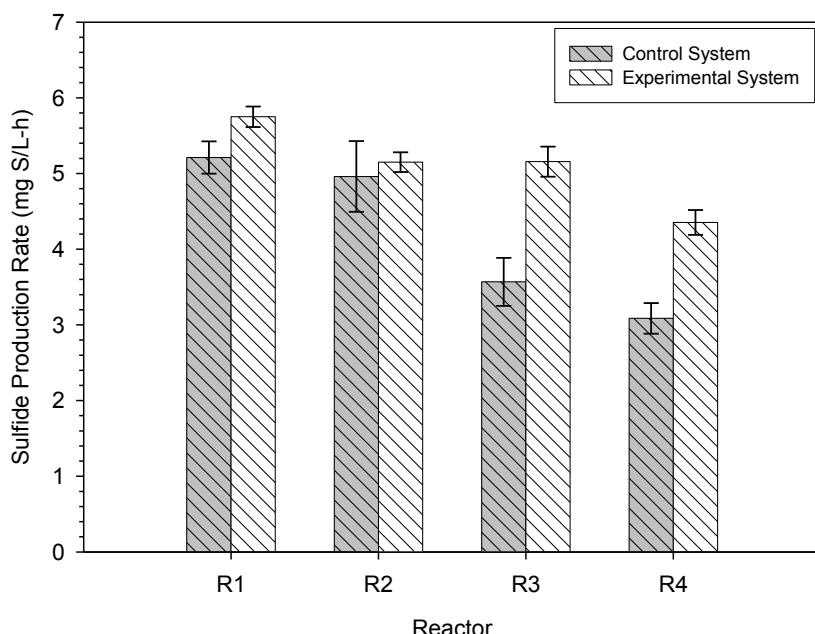


Figure 17: A comparison of the sulfide generation rate in the experimental and the control system



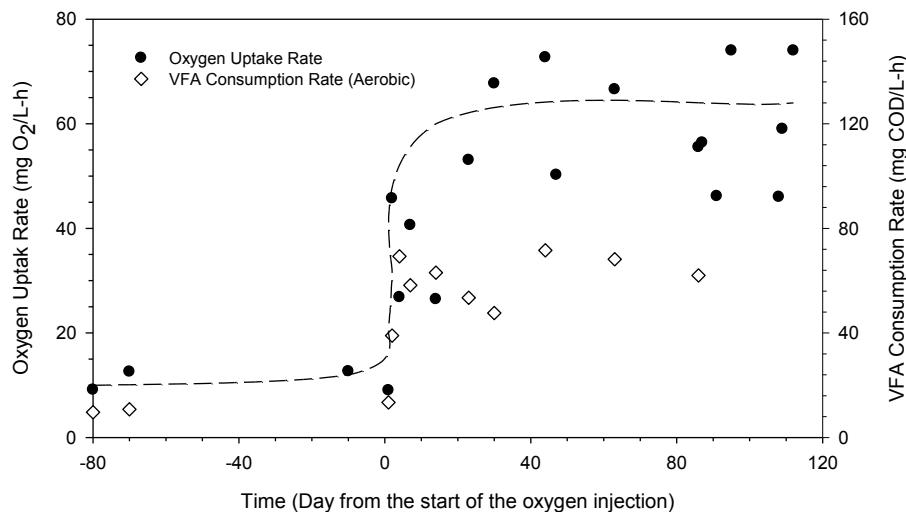


Figure 18: Change in oxygen uptake and VFA consumption rates before and after continuous oxygen injection in laboratory-scale rising main reactors.

The above results lead to the conclusions that, while oxygen is effective in controlling sulfide production; however, its effectiveness and efficiency are highly sensitive to the injection locations. In general, the point of injection (POI) should be “reasonably” close to the points where sulfide control is required (Point of Control - POC). An injection site should be selected such that (1) there would be an adequate hydraulic retention time (HRT) between POI and the POC to enable the full oxidation of any sulfide present at the POI before it reaches the POC, and that (2) aerobic conditions are maintained between the two points with minimum requirement of oxygen.

The selection of the injection sites and the determination of the dosage profiles could be a difficult task, particularly for large, complex networks. As will be shown later in the report, the sewer model developed in this project provides a powerful tool for these tasks (Section 4.9).

A further lesson directly learnt from field studies was that there should be no high points between POI and POC, as otherwise air pockets rich in oxygen and hydrogen sulfide would form at such locations causing corrosion of pipes. This has been observed in several GCW's rising mains.

4.4. IMPACT OF NITRATE ADDITION ON H₂S CONTROL

Nitrate injection is also commonly used as a measure for H₂S control. For example, SWC uses this strategy for H₂S control in their sewer systems. It is hypothesized that the presence of nitrate creates anoxic environment in sewers and thus prevents sulfide formation. In recent years, the microbial oxidation of sulfide using nitrate as the electron acceptor has been observed, which might have an effective role on sulfide control. To explore further these different possibilities, and evaluate the long term effectiveness of nitrate injection, a comprehensive study on the impact of nitrate on sulfide control was carried out.

The configurations of the laboratory systems for nitrate testing are as shown in Figure 15 with however oxygen replace by nitrate. At a later stage of the study, the injection point was moved from RME1 to RME4 to test the impact of injection location on the effectiveness.

Key results of this study are:

1. Nitrate did not have any inhibitory effects on sulfide production. This is confirmed when the sewer biofilm was exposed nitrate for the first time, there was continuous sulfide production in a batch reactor despite nitrate being consumed (Figure 19a).
2. The addition of nitrate showed a complete control of sulfide production only after four exposures to nitrate (Figure 19b). This leads to some important conclusions: (i) the adaptation to nitrate is necessary for the control of sulfide; and (ii) the controlling mechanism could be oxidation of produced sulfide by nitrate rather than the production of sulfide being prevented by nitrate uptake.
3. Microsensor measurements within the biofilms confirmed findings of the batch tests. Significant differences were observed in the net sulfide production profiles of biofilm exposed to nitrate for the first time, biofilm in the process of adapting to nitrate, and biofilm adapted to nitrate (Figure 20).
4. Nitrate addition was effective in controlling sulfide production as long as it was available in bulk liquid. Sulfide was not detected in the experimental line under anoxic conditions. However, once anaerobic conditions are established after nitrate is completely taken up, sulfide build-up resumed (Figure 21). It is evident from the figure that a nitrate-acclimated sewer system would require anoxic conditions to be maintained at all times to prevent sulfide build-up.
5. Biological sulfide oxidation with nitrate resulted in a rapid consumption of sulfide (Figure 22a). However, the sulfide was only partially oxidized to sulfate. There was a loss in total dissolved sulfur (sum of measured sulfate, sulfide, sulfite and thiosulfate), indicating accumulation of some intermediate compounds that were not measured, e.g. polysulfide or elemental sulfur. Rapid nitrate consumption with partial nitrite accumulation was observed in the system. Chemical sulfide oxidation with nitrate (Figure 22b) was insignificant when compared with biological sulfide oxidation.
6. The way nitrate was dosed to the system very much influenced the effectiveness of sulfide control. Figure 23 presents a comparison of sulfide concentration at the end of the system under different dosing arrangements when nitrate was dosed in the first reactor. As the results show, anoxic conditions could not be maintained throughout the system all the time with this strategy.



7. It is possible to control the sulfide production effectively by choosing a right location and employing an appropriate dosing strategy. A 24 hour sulfide profile in a case where nitrate was dosed to the last reactor and its dosing followed the dynamics of pumping pattern in Figure 24. The sulfide concentration was controlled to a very low level using this strategy.

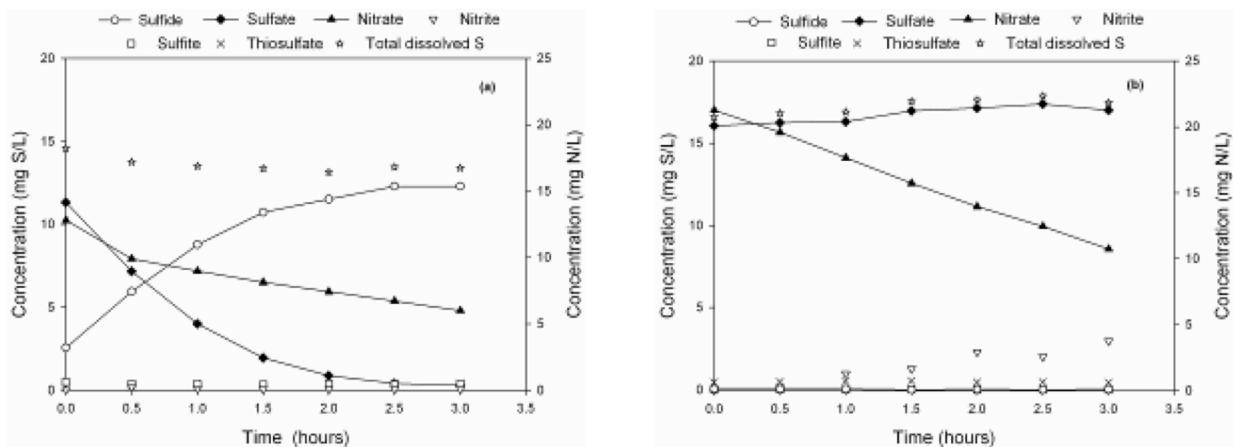


Figure 19. Changes in sulfur and nitrogen species in RM exposed to nitrate (a) twice and (b) four times.

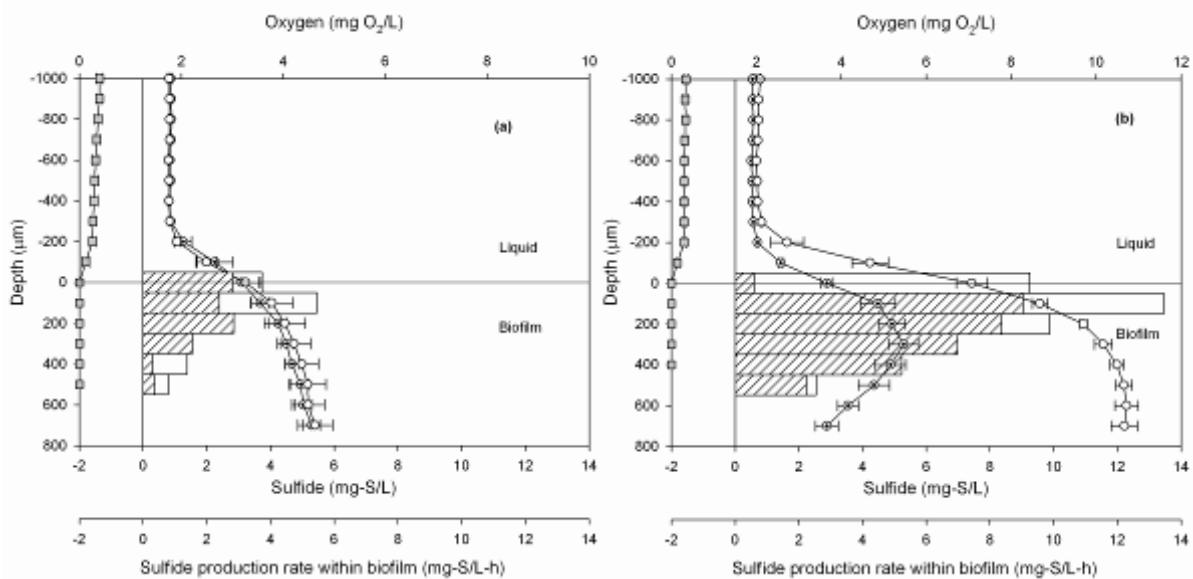


Figure 20. Steady-state profiles of total sulfide (mg-S/L) in the absence (○) and presence (◎) of nitrate (20 mg N/L) in (a) biofilm exposed for the first time to nitrate, and (b) biofilm exposed to three doses of nitrate. Sulfide production within the biofilms in the absence (□) and presence (▨) of nitrate are also shown. Oxygen profiles (□) obtained at the start of the experiment illustrate oxygen in the bulk was minimal and completely depleted before the surface of the biofilm was reached.



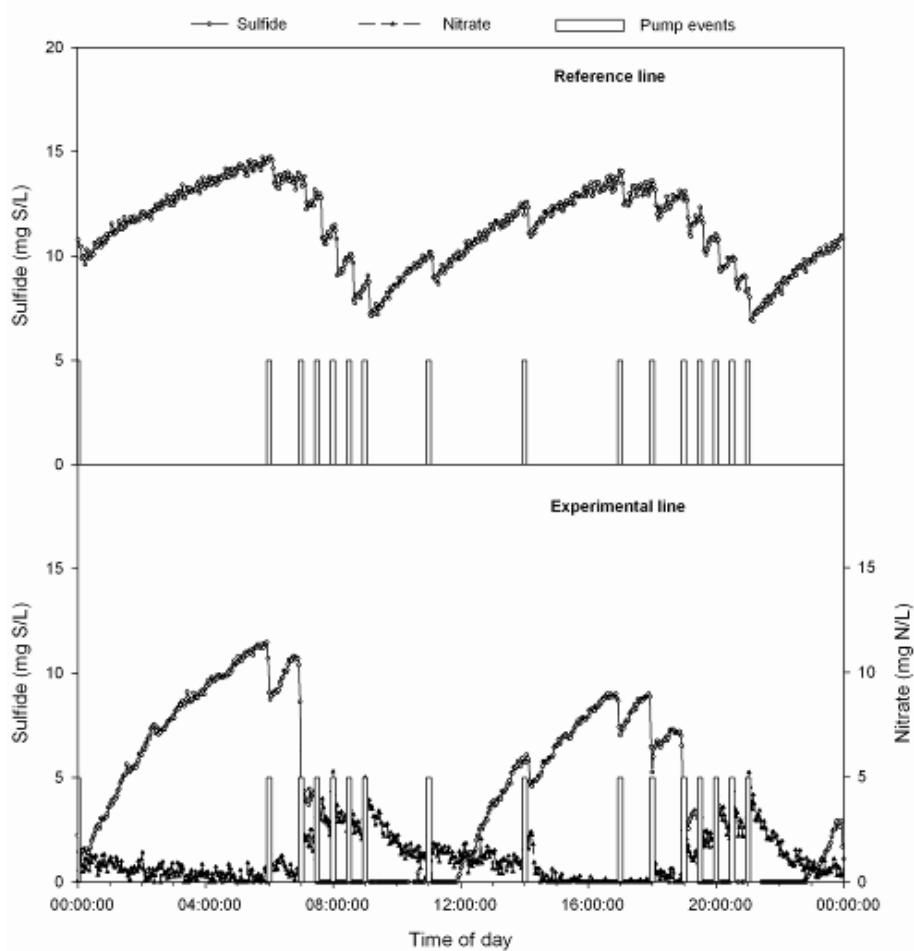


Figure 21. Online measurements of sulfide in the outlets of the reference and experimental lines. The start of the experimental line was exposed to a nitrate concentration of 30 mg N/L per pump event. The vertical bars in the graphs represent pump events.

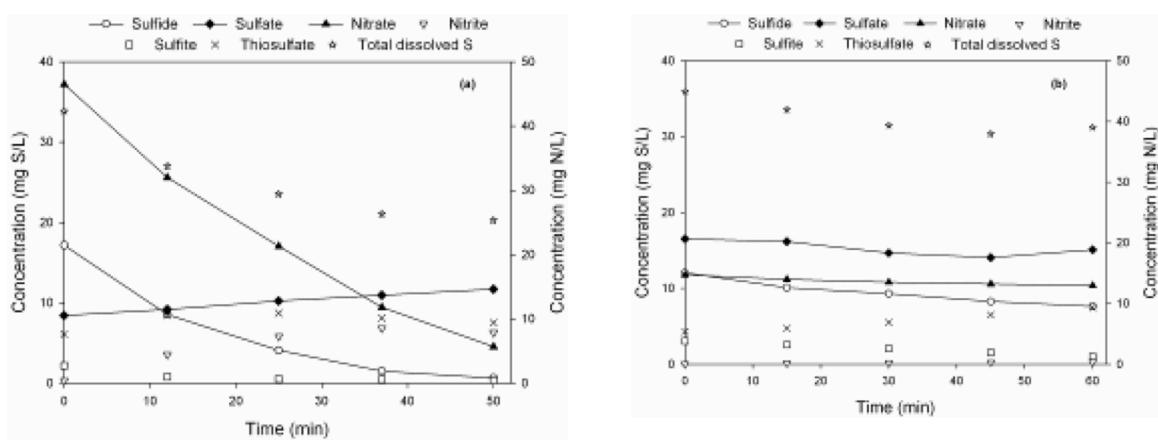


Figure 22. Changes in dissolved sulfur and nitrogen species observed in (a) biological sulfide oxidation with nitrate, and, (b) chemical sulfide oxidation with nitrate



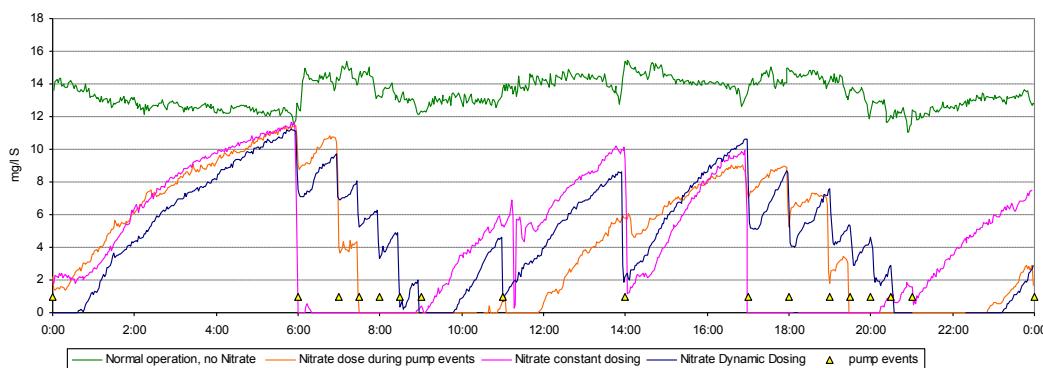


Figure 23. 24 hour sulfide concentrations profiles in Reactor 4 depending of the nitrate dosing strategy

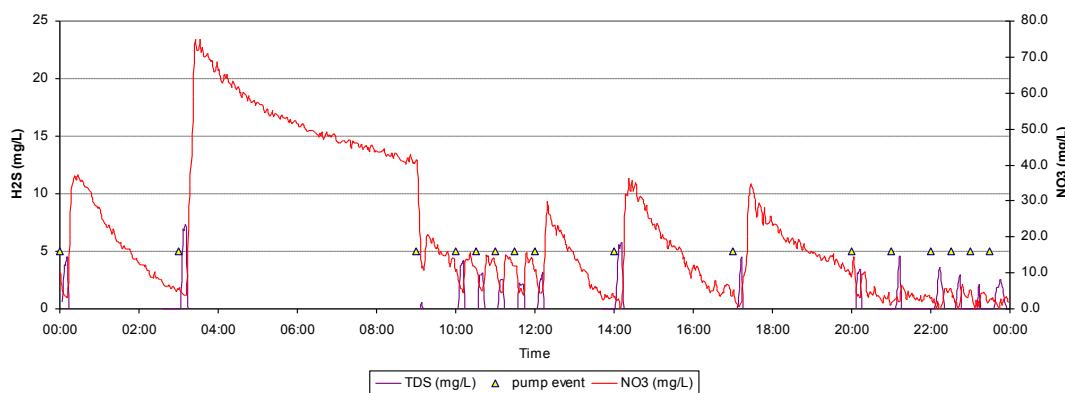


Figure 24. 24 hour profile of Sulfide and Nitrate concentrations under the dynamic nitrate dosing towards the end of the rising main (RM4 in laboratory system)

4.5. EFFECT OF pH ADJUSTMENT ON H₂S PRODUCTION

Mg(OH)₂ is normally dosed to sewer to elevate the pH to a higher level (about 9.0). This may effectively control the release of H₂S gas to atmosphere as at this pH, H₂S(aq) is present in the solution at a insignificant quantity. However, the impact of this pH rise on the activity of sewer biofilm is a matter of speculations. It has been postulated that there could be less sulfide production under high pH, but this has not been substantiated by experimental evidences. The effects of long term exposure of sewer biofilm to increased pH conditions were therefore investigated using the laboratory reactor system.

Batch tests were carried out at three different pH levels: (i) 7.5 – without pH control; (ii) 8.6; and (iii) 9.0. The rates of sulfide and methane production were measured using the data obtained in batch experiments. The results show that both the sulfide and the methane production decreased significantly with the increase in pH (Figure 25 and Figure 26). However, the effect on methane production was much more pronounced than that in sulfide generation. The results are summarized in Table 1.



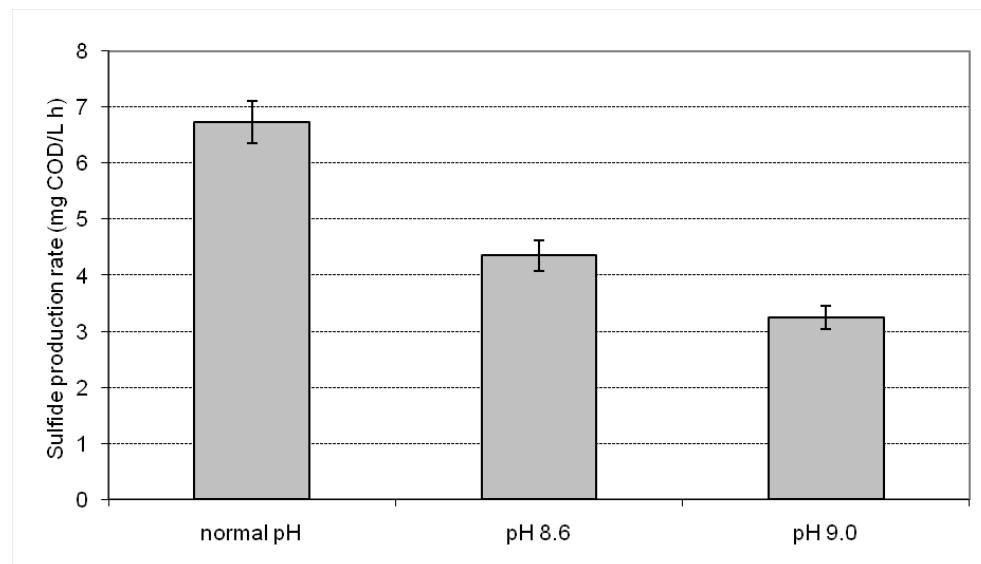


Figure 25. Average sulfide production rates at different reactor pH levels

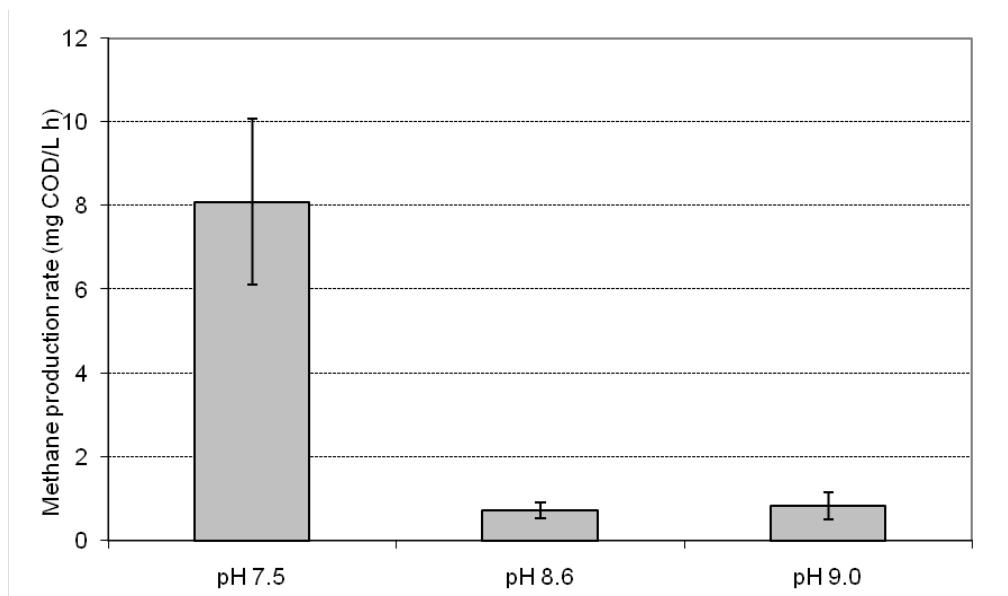


Figure 26. Average methane production rates at different reactor pH levels

Table 1. Comparison of results at different pH

pH	Sulfide production		Methane production	
	Rate (mg S/L-h)	Change as compared to the control reactor	Rate (mg COD/L-h)	Change as compared to the control reactor
7.5	6.74	-	8.09	-
8.6	4.35	-35.5%	0.72	-91.1%
9.0	3.25	-51.8%	0.82	-89.8%



4.6. EFFECT OF $\text{Fe}^{2+}/\text{Fe}^{3+}$ ADDITION ON H_2S CONTROL

4.6.1. BACKGROUND

The addition of iron salts to wastewater leads to the precipitation of sulfide as iron sulfide and therefore minimises the transfer of H_2S from the liquid to the gas phase. SWC, like many other wastewater authorities, uses this strategy in some of its H_2S control programs.

Iron ions can be added in the form of either Fe^{3+} or Fe^{2+} , to either rising or gravity mains and at different locations. Fe^{3+} and Fe^{2+} may precipitate not only with sulfide, but also other anions such as phosphate and hydroxide. Fe^{2+} may be oxidised to Fe^{3+} in the presence of O_2 at a suitable pH, while Fe^{3+} may be reduced to Fe^{2+} in the presence of suitable reductants such as sulfide. The complex precipitation and redox reactions involving Fe^{3+} , Fe^{2+} , HS^- , and other anions as well as oxygen makes it difficult to decide on which form of iron salt to use, how much to add and where to add. Over-dosage of iron is common practice today.

Several batch and continuous experiments were conducted to investigate these aspects.

4.6.2. RESULTS OF BATCH EXPERIMENTS

The key results of these experiments are discussed below:

- As expected, iron salts (e.g. ferrous chloride FeCl_2 , ferric chloride FeCl_3) are very effective in precipitating dissolved sulfide. There is evidence that a mixture of FeCl_2 - FeCl_3 is more efficient for sulfide precipitation. The attributable reason is that iron pyrite (FeS_2) is formed, which has a more favourable stoichiometry in terms of Fe:S ratio than FeS (amorphous FeS or mackinawite $\text{FeS}_{(1-x)}$).
- Iron pyrite (FeS_2 or FeS.S^0) is an iron (II) polysulfide and occurs commonly in the Earth's crust under anaerobic or marginally aerobic conditions. It is the most likely form of iron sulfide precipitate in the pH and redox range of raw sewage. Its formation depends on the formation of polysulfide anions (S_2^{2-}) from sulfide ions, which involves oxidation of sulfide ions to elemental sulphur (S^0) and then further reaction with S^{2-} ions to form of the S_2^{2-} -dimers or other polysulfides. (The oxidation of sulfide ions to elemental sulphur or polysulfides in the presence of oxygen is strongly catalysed by metal ions, including iron). The S_2^{2-} -dimers precipitate with Fe^{2+} as FeS_2 in a cubic structure similar to NaCl , with the exact mechanism of its formation still being the subject of some debate.
- The partial oxidation and precipitation of sulfide ions to form pyrite may occur in the presence of oxygen and ferrous (Fe^{2+}) ions. Alternatively, if ferric (Fe^{3+}) ions are present, these may act as the oxidant for sulfide ions (themselves reduced to Fe^{2+}), leading to pyrite precipitation. This explains the above-mentioned greater efficiency of sulfide precipitation using a blend of ferrous-ferric salts. However, other precipitates may also form (e.g. $\text{Fe(II)}\text{Fe(III)}_2\text{S}_4$ (greigite) or a mixture between FeS and FeS_2 , which would account for a range of Fe:S precipitation stoichiometry).
- For sewage in the absence of sulfide, addition of dissolved iron (Fe^{2+} or Fe^{3+}) will lead to competing chemical reactions for precipitation of iron hydroxides (e.g. Fe(OH)_2 , Fe(OH)_3 or amorphous FeOOH) as well as iron phosphate (e.g.



$\text{Fe}_3(\text{PO}_4)_2$, FePO_4 or $\text{Fe}_r\text{PO}_4\text{OH}_{(3r-3)}$). Alternatively, phosphate ions (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}) may be adsorbed to colloidal or solid forms of iron hydroxides. However, it appears that the iron precipitates of sulfide (e.g. FeS or FeS_2) are more stable and insoluble than the hydroxide, phosphate or hydroxy-phosphate precipitates. For example, batch tests show that phosphate precipitated in the absence of sulfide is released back into solution when dissolved sulfide is added, while the sulfide disappears from solution. This occurs in the absence of dissolved iron species.

- The available data indicates that iron salts can be dosed ahead of sulfide formation and will react to form hydroxyl-phosphate complexes and/or precipitates. These will act as “carriers”, suppressing the appearance of dissolved sulfide (and hence dissolved or gaseous H_2S) where sulfate reduction occurs downstream.
- Bacterially-mediated formation of iron sulfides (e.g. FeS or FeS_2) appears to be the same in composition and structure to those formed by purely inorganic (or abiogenic) processes. The iron sulfides may be precipitated on the cell wall, with a capsule or slime layer surrounding the cell itself.
- Exposure of pyrite (or other iron sulfide precipitates) to oxygen will likely result in the formation of iron oxides, such as Fe_3O_4 (magnetite) or Fe_2O_3 (hematite), and elemental sulphur (S^0). The sulphur may then be further oxidised, eventually to sulfate (e.g. by acid-producing sulphur oxidising bacteria).

A diagram showing some of the likely interactions between iron, phosphate and hydroxide ions is shown in

Figure 27. Currently, laboratory work is being carried to test the reactions presented and to determine the stoichiometry. From this, model precipitation reactions can be developed with greater confidence.

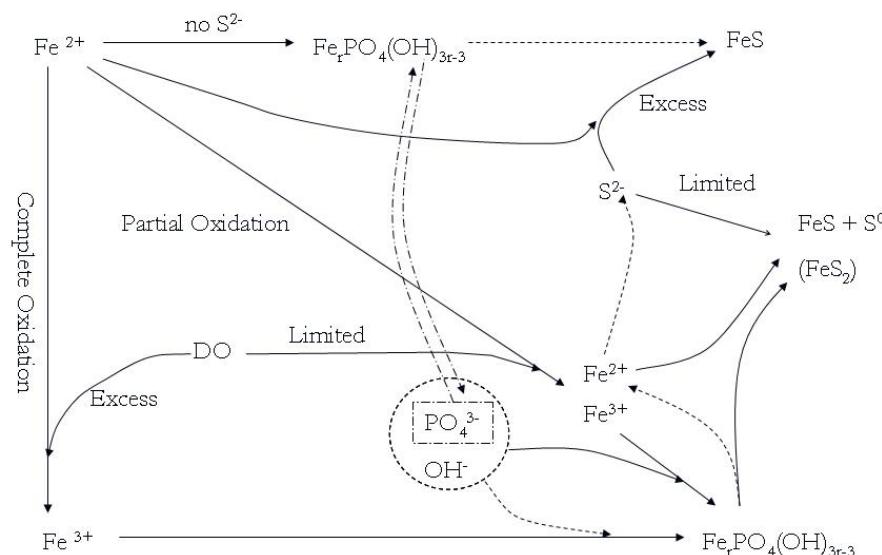


Figure 27. Hypothetical chemical precipitation interactions between phosphate, hydroxide and sulfide and iron species.



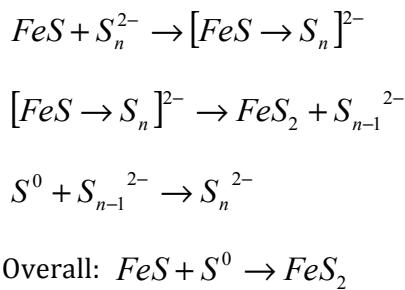
4.6.3. RESULTS OF CONTINUOUS EXPERIMENTS

Fe^{2+} was dosed to the laboratory experimental setup of the rising main described previously, and measurements were done to investigate the fate of added Fe^{2+} , and its effect on sulfide production and phosphate precipitation. The results of Fe^{2+} dosing to the first reactor are shown in Figure 28.

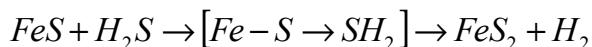
The results show that the Fe^{2+} dosing at 21 mg/l could completely prevent sulfide accumulation (concentration <1.0 mg S/L) in all reactors. Based on sulfate balance, the dosing ratio of Fe(II) to dissolved sulfide was found to be 0.76:1 (molar ratio). It is interesting to note that this strategy could keep dissolved sulfide concentrations below 1 mg/L in the four rising main reactors. In addition, ferrous phosphate precipitation was not significant in rising main reactors. Although the stoichiometric ratio of Fe(II) to S(-II) seems to be lower than the theoretical ratio based on the assumption that FeS is the product of precipitation, the value of about of 0.7 was consistently obtained with repeated experiments. With a lower amount of Fe(II) dosing, this ratio further decreased to 0.5-0.6.

Based upon these results, it can be postulated that pyrite (FeS_2) may be formed during the precipitation and iron precipitates may consist of FeS and FeS_2 . The process of pyrite formation at ambient temperature is determined by two alternative mechanisms.

a. The polysulfide mechanism



b. The H_2S mechanism



Since there was no significant accumulation of elemental sulfur in the reactor, the second mechanism is thought to be prevalent in the system. The hydrogen generated in this reaction could be further used in other anaerobic reactions such as sulfate reduction or methane production.



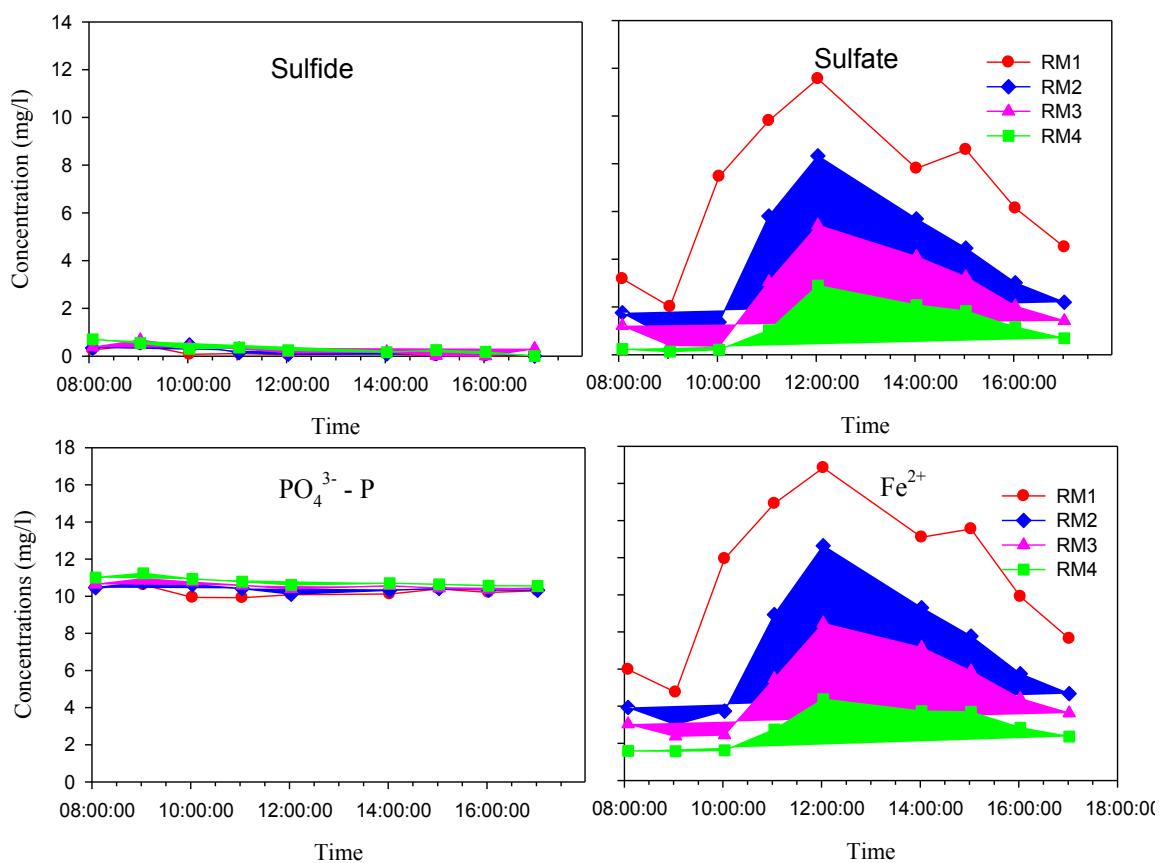


Figure 28: Sulfide control by ferrous addition – 1 week after ferrous dosing

4.7. SPATIAL VARIATIONS OF BIOFILM ACTIVITIES ALONG A SEWER LINE

In all existing sewer models, the biofilm activities are assumed identical along a sewer pipe. This is questionable as the biofilm at different locations of a sewer pipe is expected to be exposed to depleting substrate levels leading to reduced bacterial activity. If proven untrue, this could significantly compromise the quality of sewer models.

Both the lab-reactor and the in-situ Robbin's Device systems clearly show that both the actual and maximum H₂S production rates of sewer biofilms at different locations are considerably different. As an example, Table 2 shows that the sulfate reducing capacity of the sewer biofilm (represented as the maximum sulfate reduction rate) decreases with increase in biofilm location. The lab-reactor as well as field data (not given here) show that the biofilm further downstream has less opportunities to be exposed to sulfate so that less sulfate reducing bacteria will develop at these locations. The results presented in Table 2 also show that mixing has a major impact on the activity of biofilms. This aspect is also being incorporated into the sewer model.



Table 2: Comparison of sulfate reduction rates among the 4 rising main reactors in the lab-system. Fresh wastewater was added to each reactor at the beginning of each test. Samples were taken hourly for sulfur measurement. Sulfate reduction rates were determined from the slope of the sulfate profiles with time. In Experiment #1, the reactors were stirred continuously. In Experiment #2, reactors were mixed prior to sampling. RM denotes rising main.

Experimental Conditions	Sulfate reduction rate (mg S/L-h)			
	RM#1	RM#2	RM#3	RM#4
Experiment #1: Continuous stirring	4.20	3.46	2.61	2.29
Experiment #2: Stirred while sampling	3.15	2.51	2.39	2.10

4.8. METHANE FORMATION IN RISING MAIN SEWERS

4.8.1. BACKGROUND

The interaction between sulfate reducing bacteria (SRB) and methanogenic bacteria (MB) in sewer systems is a recent focus of interest. Sewer systems are sulfate-fed anaerobic environments where, according to the previous works, SRB should easily outcompete MB. However, the fact that the biomass is clustered in biofilms and that sulfate may become limiting enables MB to grow, probably in the inner part of the biofilm near the wall. MB would grow on the excess VFA and hydrogen produced by fermentation that is not taken up by SRB.

Methane formation in sewer systems is very important not only from the point of view of modelling sulfide production, but also for correctly predicting soluble COD transformations. The methane itself is likely to be supersaturated in the sewage as it is pumped through a rising main at pressures exceeding atmospheric pressure. Gaseous methane may come out of solution at points in the system where there is a pressure drop (e.g. high points in the rising main hydraulic profile) and is then likely to be vented to atmosphere where air vents are located at such points. Similarly, the dissolved methane will most likely be stripped from the sewage when it is discharged to the wastewater treatment plant. This may occur partly at the inlet works as the raw sewage passes through the screens and grit removal system, or in downstream processes such as the weirs of primary sedimentation tanks (if present) or via aeration devices (e.g. in an activated sludge treatment process).

Methane released to the atmosphere contributes is a significant greenhouse gas with a lifespan of about 12 years and a global warming potential of roughly 21-23 times higher than carbon dioxide. In practical terms, the release of 1 kg of CH₄ is roughly equivalent to the CO₂ emissions associated with the generation of roughly 20kWh of electricity. For a system such as the Tugun-Elanora rising main network, assuming the sewage enters the WWTP with an average dissolved methane concentration of 10 mg/L, the release of that methane to the atmosphere will be equivalent to the global warming potential arising from power generation emissions equivalent to about 30% of the Elanora WWTP power consumption on the SE QLD power generation grid.

Methane concentrations were measured during several batch experiments as well as the continuous operation of laboratory reactor system.



4.8.2. KEY RESULTS

The followings were the findings of the study:

1. Methanogens and SRB can coexist in a sewer biofilm. This is demonstrated by the fact that both methane production and sulfide generation occurred concurrently (Figure 29). The fact that substrate (VFA, hydrogen) is never limiting causes that the lower affinity for substrate of MB is not a handicap for this population to survive. Moreover, in many areas sulfate is probably only partially penetrating the biofilm. Hence, two different zones could be distinguished in the biofilm, a sulfate-reducing anaerobic zone dominated by SRB and an anaerobic zone dominated by MB.
2. A large amount of the soluble COD is lost due to methanogenic activity. The amount of methane formed is around 70 mg COD/L in eight hours of batch test. This high methane production is very important not only from the point of view of modelling sulfide production and correctly predicting soluble COD transformations, but from an environmental point of view (methane is a green house gas).
3. No significant spatial variation in methane production was observed (Figure 30).
4. Two fractions of fermentable substrate can be distinguished (Figure 30). Fermentable substrate is calculated by subtracting the total COD due to VFA to the total measured soluble COD. Each fraction of the fermentable substrate represents approximately 50% of the total value. A first fraction is quickly degraded in 3 hours and the rest of soluble COD remains constant until the end of the experiment (see Figure 30e). The existence of this inert soluble fraction non degradable under anaerobic conditions is not strange. Several authors have described similar profiles. We decided to consider glucose to model this quickly degradable fermentable substrate analogously to Batstone et al. (2002) in the widespread Anaerobic Digestion Model. The modelling of the evolution of this compound is very important since its degradation produces high amount of hydrogen. The expected profile of hydrogen will be similar to the measured acetate profile (Figure 30c). Acetate increases the first three hours because biological acetate consumption rate is lower than the acetate production from the glucose degradation. Once, glucose is degraded, acetate consumption is observed.
5. There was a significant production of methane during normal operation of laboratory rising main system (Figure 31). Methane production of 80-120 mg/L was measured in the last reactor of the system. Moreover, the pumping pattern has a great influence in both methane and sulfide generation.
6. In real systems, the SO_4^2- -S/COD ratio downstream is lower than at the start and, hence, SRB will outcompete MB upstream whereas MB will be more favoured in the last section of the pipe.
7. The hydrogen produced in the fermentation process is quickly scavenged (Figure 31). The period from 12 to 17 hours shows it very clear. After the pumping event of 2pm (14 hours), methane and sulfide are produced in the first reactor at a higher rate, while VFA is taken up at the same rate in the four reactors. When fresh swage is pumped, the hydrogen produced from fermentation is consumed very fast. This only happens in reactor 1. According to batch experiments done in this study, the fast fermentable substrate is consumed in two hours. Hence, the reactors 2, 3, 4 receive sewage without fermentable substrate or hydrogen and thus, methane and sulfide production rates are similar.



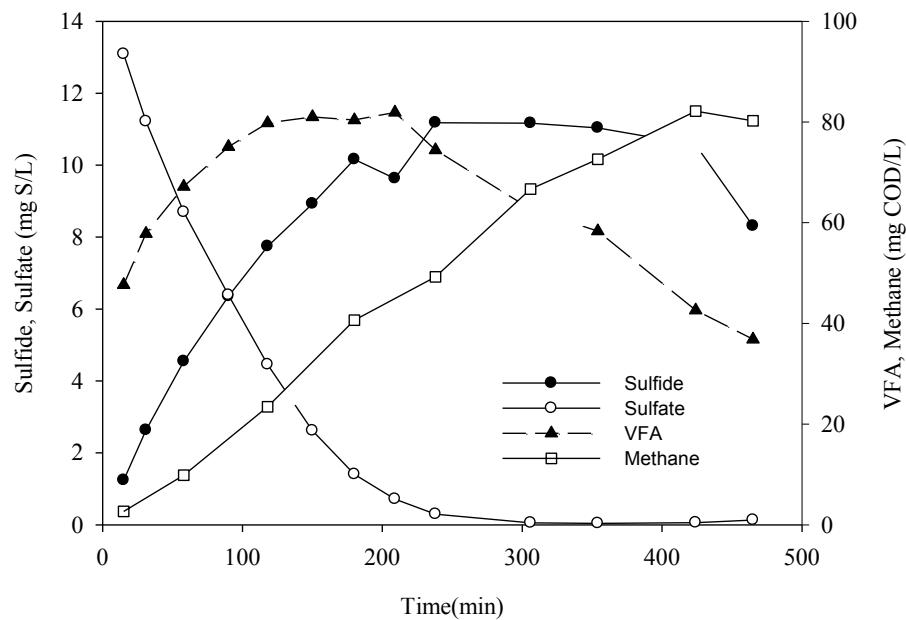


Figure 29. Experimental profiles obtained in the batch test with Reactor 2 of the reference line of the rising main experimental set-up.

8. The results collected from UC09 system of GCW and presented in Figure 32 also show methane formation at a significant amount (around 25 mg COD/L). This methane level should not be directly compared with the values obtained in the lab-scale reactor since the A/V ratio is very different.

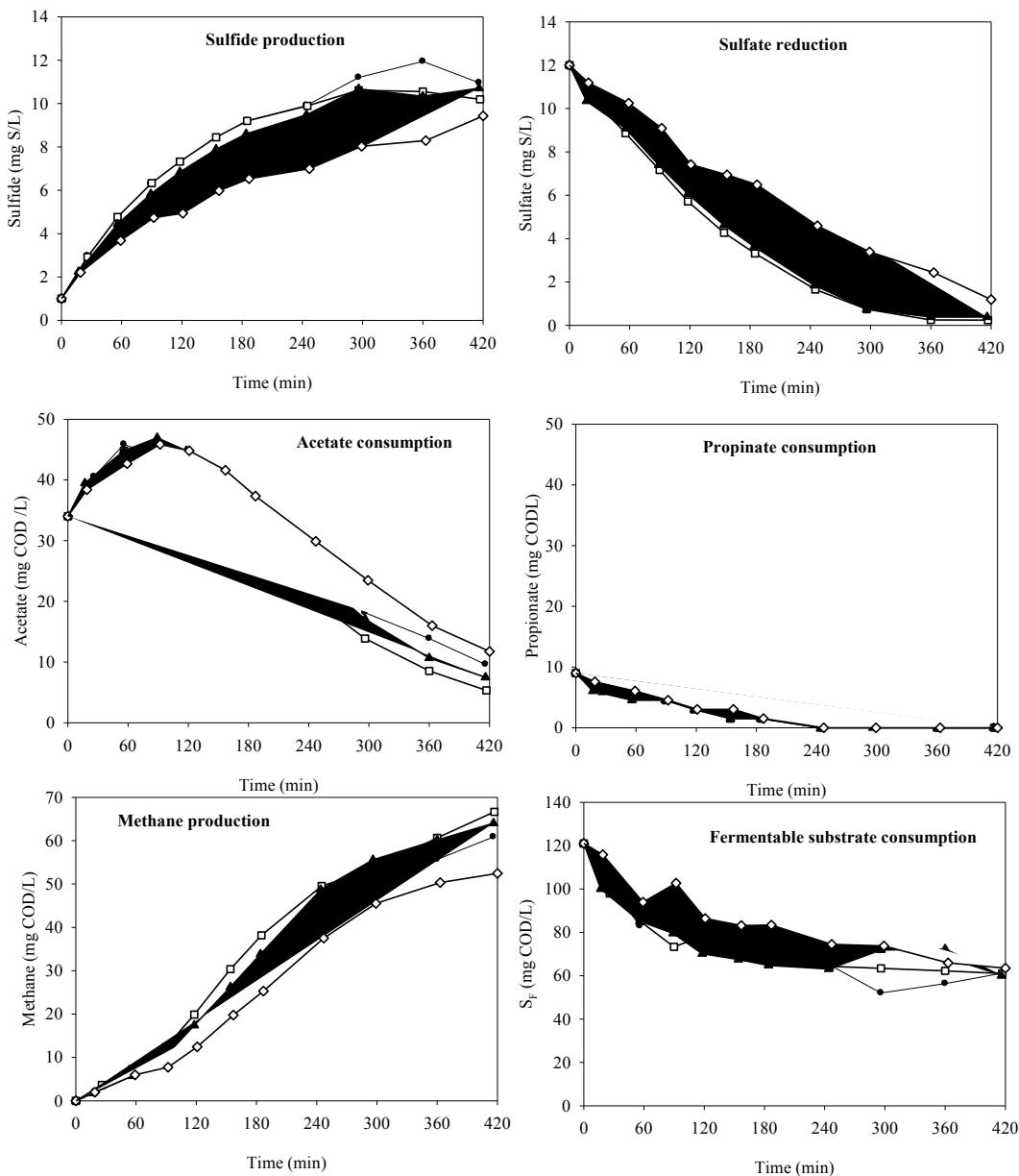


Figure 30. Comparison of the experimental profiles obtained in each of the four reactors of the rising main experimental set-up. RM1 (\bullet), RM2 (\square), RM3 (\blacktriangle) and RM4 (\diamond).



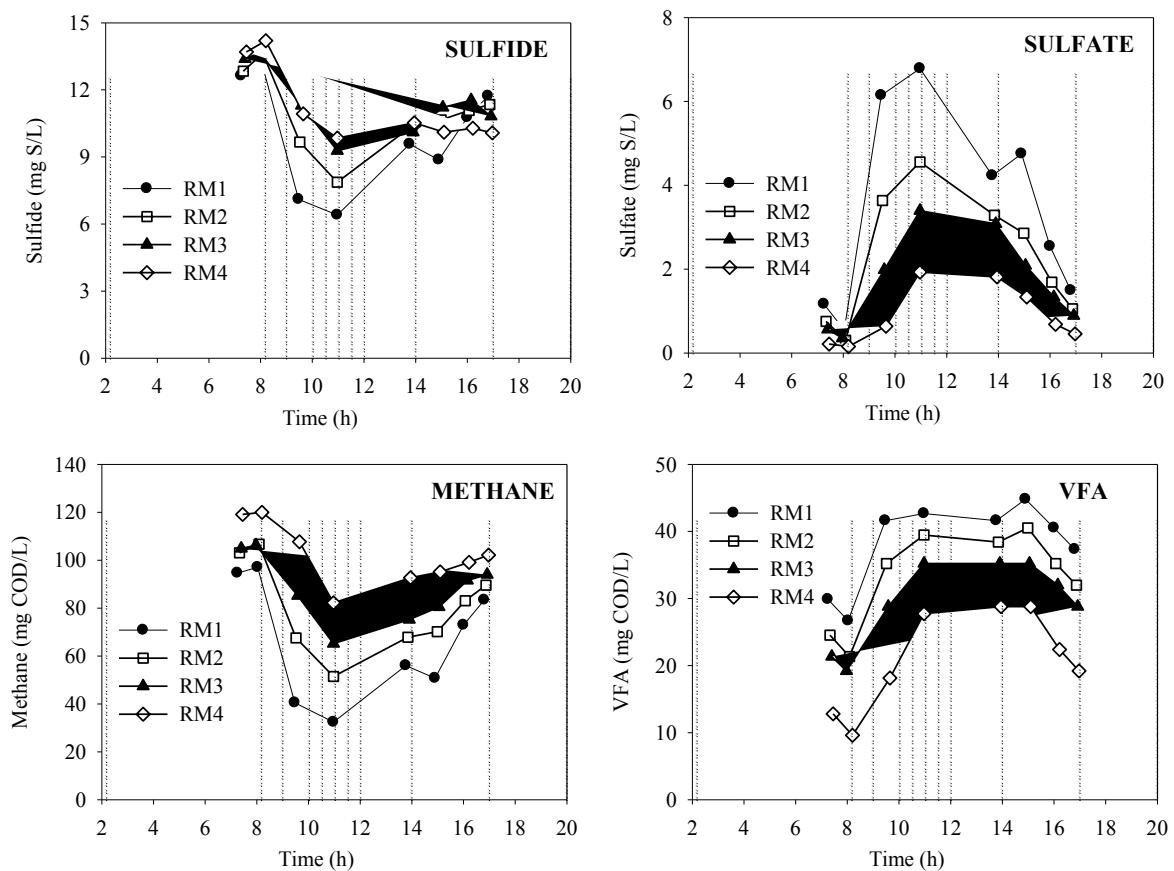


Figure 31. Experimental sulfide (a), sulfate (b), methane (c) and VFA (d) profiles obtained in the rising main experimental set up during half day. The dashed lines indicate the pumping events

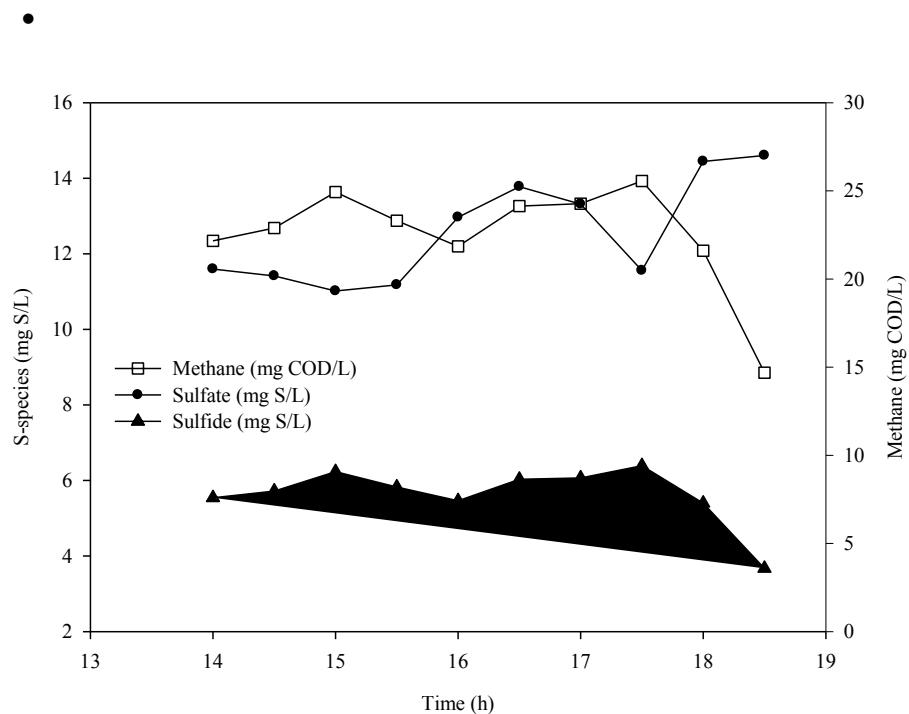


Figure 32. Field data measurements (UC09) to confirm the significance of methane production in sewer systems



4.9. MODEL DEVELOPMENT, CALIBRATION AND VALIDATION

4.9.1. BACKGROUND

Accurate and reliable prediction of sulfide generation in sewer systems is important for effective sewer management. The models commonly used by the consulting companies are still the empirical expressions proposed some twenty to thirty years ago summarised from data observed in some isolated case studies then. These expressions neither take into account the effect of biofilms nor the effect of sewer hydraulics. The predictions are therefore crude and of limited value to sewer management particularly considering the dynamics in sewer systems.

In recent years, Prof. Hvítved-Jacobsen, a collaborator on this project, and his colleagues from Aalborg University developed the WATS (Wastewater Aerobic/ Anaerobic Transformations in Sewers) model. The model describes both the COD and sulfur transformations in sewers, and was regarded as the state-of-the-art model at the time when this project was started.

Currently several strategies are being employed by the wastewater industry to control sulfide production in sewer systems. The chemical dosing strategy is generally based on the steady state predictions, which is not an ideal approach from both the cost and effectiveness point of view. A better control strategy can be formulated if exact variation in H₂S production could be known. One of the options for this would be long term monitoring of sewer system to have enough data to represent the dynamics. Collection of wastewater samples from an underground rising main has a lot of challenges as the site is not easily accessible, and tools to sample, analyse, monitor and evaluate H₂S production are not well established. Tremendous efforts and investments would be needed to conduct such field studies, and consequently it is almost impossible to perform such studies on all sewer systems of concern. Modelling is clearly a much more economical means for obtaining information of the dynamic change in sulfide production. A dynamic sewer model able to predict the impact of temporal changes in hydraulic conditions and wastewater composition would serve as a valuable tool for optimal sewer management.

4.9.2. THE UQ MODEL – A NEW SEWER MODEL

Starting from the basic concepts described by the WATS model, we have developed a new model characterising the in-sewer physical, chemical and biological processes. The model has been demonstrated to predict sulfide production in sewers much more accurately than the WATS model and indeed any other model available in literature. The better performance was achieved by the use of new kinetic expressions for sulfide production and COD conversion, which properly account for the impact of mass transfer limitations on the reaction rates. The mass transfer limitations occur between bulk liquid and biofilms, and also within the bulk liquid phase during quiescent period.

The UQ model is also capable of predicting pH variations in sewer systems by accounting for the pH effect of the in-sewer physical, chemical and biological processes. pH prediction is essential for correctly predicting the transfer of H₂S as well as CO₂ and Volatile Fatty Acids (also odorous) between liquid and gas phases. The UQ model achieves pH prediction, which is typically computationally demanding, without losing simulation speed through the use of an innovative numerical algorithm.



The UQ Sewer Model consists of the following components:

1. Biological transformation reactions including both carbon and sulfur transformations
2. Chemical sulfide oxidation
3. Weak acid-base equilibrium reactions
4. Chemical precipitation reactions involving Fe^{2+} , Fe^{3+} , Ca^{2+} , Mg^{2+} and S^{2-} , PO_4^{3-} , OH^- and CO_3^{2-} .
5. Exchange of gaseous constituents between the gas and the liquid phase (for gravity sewers only)
6. Convective transport of water
7. Convective transport of gas in gas phase (for gravity sewer only)

The model was based upon the following considerations:

- No respirometric experiment was conducted for the fractionation of COD. Instead, the COD fractions were obtained from the measured VFA, soluble, flocculated soluble and total COD concentrations.
- Sulfide generation by the suspended biomass was ignored, while that by the biofilm was modelled using double Monod kinetics using VFA and sulfate as substrates. The volumetric sulfide generation rate ($\text{g S/m}^3\text{d}$), was calculated by multiplying the aerial sulfide generation rate ($\text{g S/m}^2\text{d}$) with the biofilm area to water volume (A/V) ratio.
- Chemical oxidation of sulfide with oxygen was modelled using the data collected from the laboratory experiments. The kinetic parameters of the model were determined by fitting the model predictions with the measured data.
- Most of the available sewer models assume sulfate as a non-limiting substrate for sulfide production. However, in sewers having long HRT, sulfate could be a limiting substrate. Sulfate limitation was therefore included in the kinetic expression for sulfide production. To highlight the diffusion limitation of substrate transfer to biofilm, a higher value of saturation constant was used.
- The reduction in the volumetric sulfide generation and VFA production rates described in Hydrogen Sulfide Control Manual (Melbourne and Metropolitan Board of Works, 1989) during non-mixing (no flow) periods was considered.
- The rising main was modelled as tanks-in-series to mimic plug flow in a real sewer pipe.

The model was greatly enhanced with the new experimental data and knowledge generated in the project.



4.9.3. MODEL CALIBRATION AND VALIDATION

The sewer model includes several biochemical processes and hence several kinetic parameters are involved. To calibrate these parameters, intensive sampling and monitoring program was conducted in sewer systems of Gold Coast Water. Based on the field data collected, the UQ model has been calibrated for several GCW rising mains. As an example, the fit between the measured and model predicted sulfide concentrations at four different locations along the rising main UC09 is shown in Figure 33. While there are some mismatches at several places (which we are addressing currently), the overall fit is very good, considerably better than any existing models could have achieved.

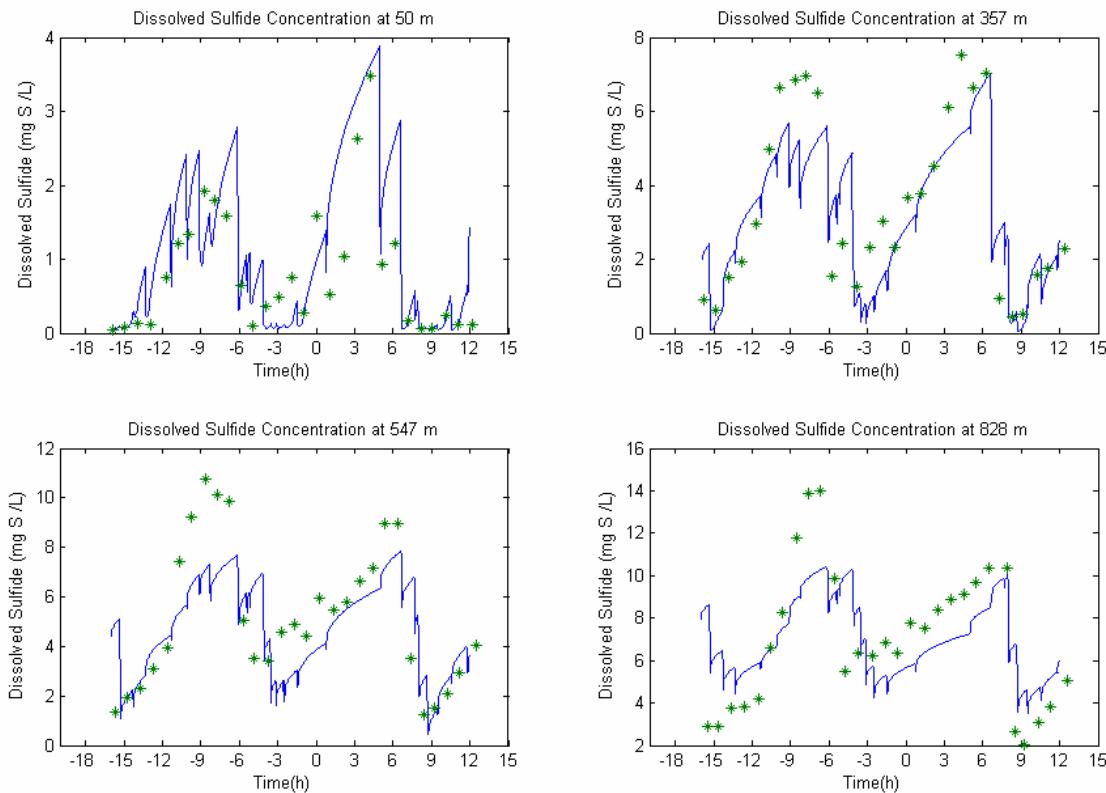


Figure 33. Model predictions vs. measured data for sulfide in UC09 (Nov. 2005 data) using the UQ Sewer Model. UC09 is a rising main with a length of 1.1 km and a diameter of 150 mm. During this particular measurement campaign, sulfate and sulfide were measured in the wet well (which was used as the model input) as well as four other locations (50 m, 357 m, 547 m and 828 m from the wet well) using the tapping points specifically installed for sampling purpose. Time 0 in the plots is mid-night.

As another example for a case with oxygen injection, the results of model calibration for D6 sewer system of GCW are presented in Figure 34 and Figure 35. The results show that the model was able to predict accurately the changes in both DO and H₂S concentrations. A very good fit is observed between the measured and simulated DO levels and same is true for H₂S concentration. This validates both the sulfide oxidation model (biological and chemical) and the parameters related to the oxidation model (biofilm oxygen consumption rate etc.).



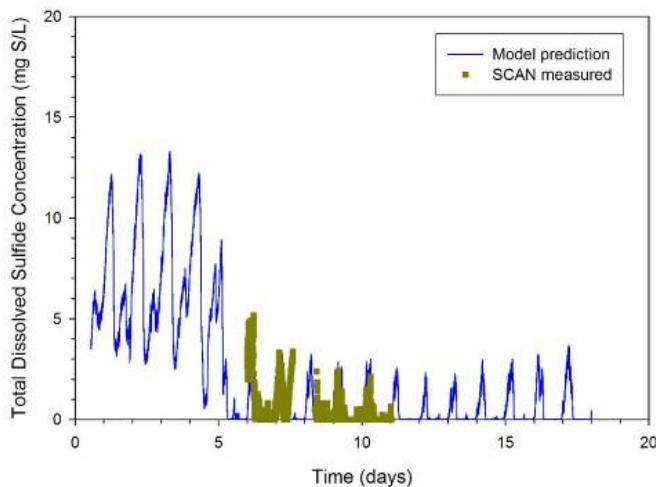


Figure 34. Measured versus model predicted sulfide concentration at 735 m (measured data available only from Day 6 to Day 11)

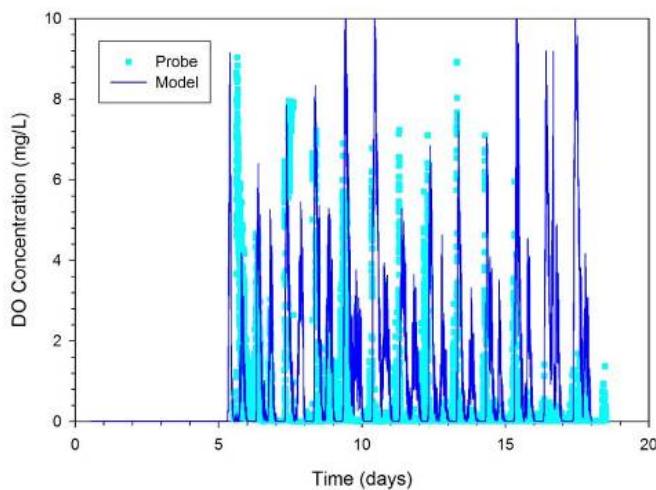


Figure 35. Measured versus model predicted DO concentration at 735 m

4.10. CASE STUDY 1: THE TUGUN-ELANORA SEWER NETWORK

4.10.1. BACKGROUND

The Tugun Elanora sewer system consists of 17 pump stations, 1 flow balancing tank, 1 flow splitter, 28.9 km pipe length, and average daily flow of 14.3 ML/day. A layout of the system is presented in Figure 36. Elanora Wastewater Treatment Plant is consistently experiencing odor problem at the inlet structure and one of the causes of this problem is high sulfide level in sewage arriving from three sewer trunks. The system being investigated here is one of them, and carries a significant portion of the flow. The UQ sewer model was therefore implemented for Tugun Elanora sewer system: (1) to investigate various options for sulfide control at Elanora Treatment Plant; (2) to identify optimal chemical dosing locations and optimize the chemical dosage; and (3) to make cost comparison of different options based on the modeling results.



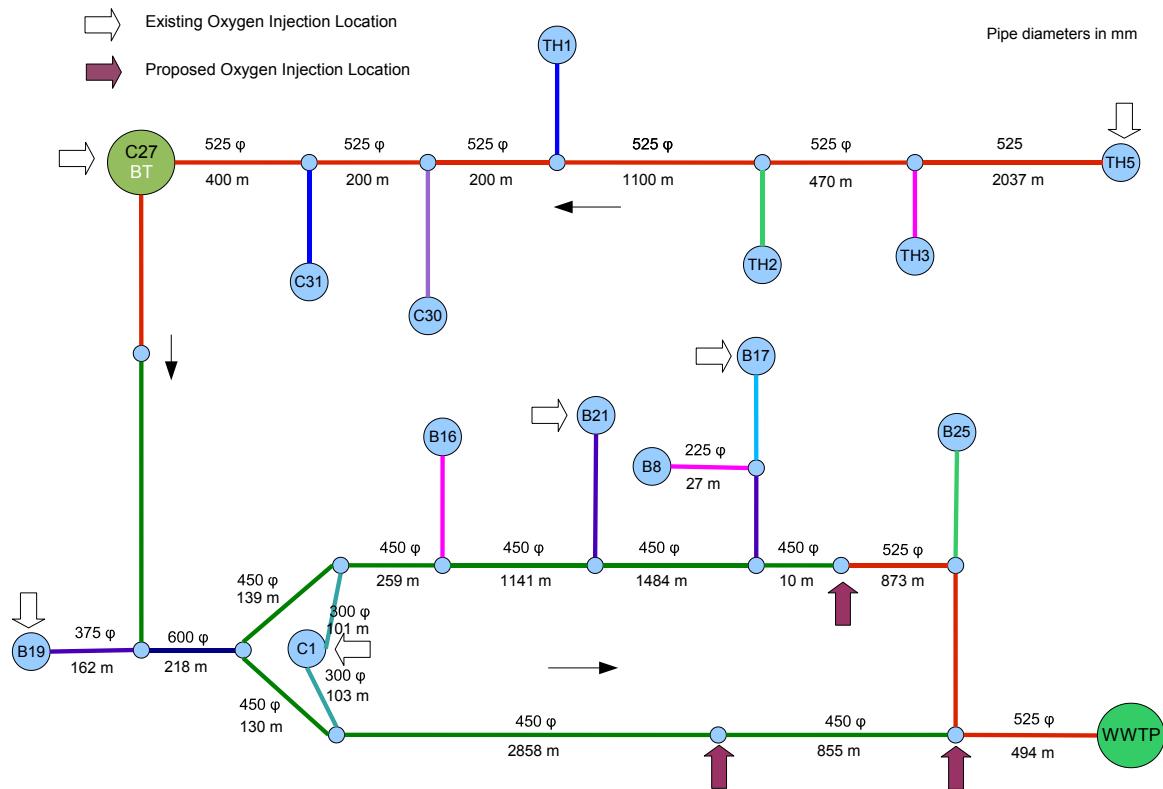


Figure 36. Schematic of the Tugun Elanora Sewer Network showing existing and proposed oxygen injection locations

The following options were considered for the control of sulfide:

1. Oxygen
2. Calcium Nitrate
3. Ferric Chloride
4. Ferrous Chloride
5. Magnesium Hydroxide for pH Control

4.10.2. METHODOLOGY

Target sulfide level at Elanora Treatment Plant was set at 1 mg S/L average with 95 percentile value of less than 3 mg S/L. The location of the injection stations for all the chemicals were chosen by trial (through a series of simulation studies) to achieve the target sulfide level with a minimum chemical consumption. The dosing rates of chemical followed a diurnal pattern based on the HRT. The effects of changes in dosing rate and also the location of injection points on sulfide accumulation were also investigated to shed some lights on the sensitivity of the choice of injection location. For simplicity only one injection point was moved up or down at a time in the latter case (all the cases involved multi point injections).

The key model parameters such as biofilm oxygen consumption rate ($\text{g O}_2/\text{m}^2\text{-day}$), nitrate consumption rate ($\text{g NO}_3^-\text{-N}/\text{m}^2\text{-day}$), and relevant parameters for precipitation reactions were taken based on the information available from laboratory experiments.

The model was first run for a case without the addition of chemicals (normal operation) to establish a base line sulfide level at the inlet of the treatment plant. The simulation results



are compared with IC measured sulfide levels in Figure 37. The calibrated model showed a good match with the measured data and this validated the parameters used in the model. Once the base line sulfide production was established, other cases with chemical injection were investigated.

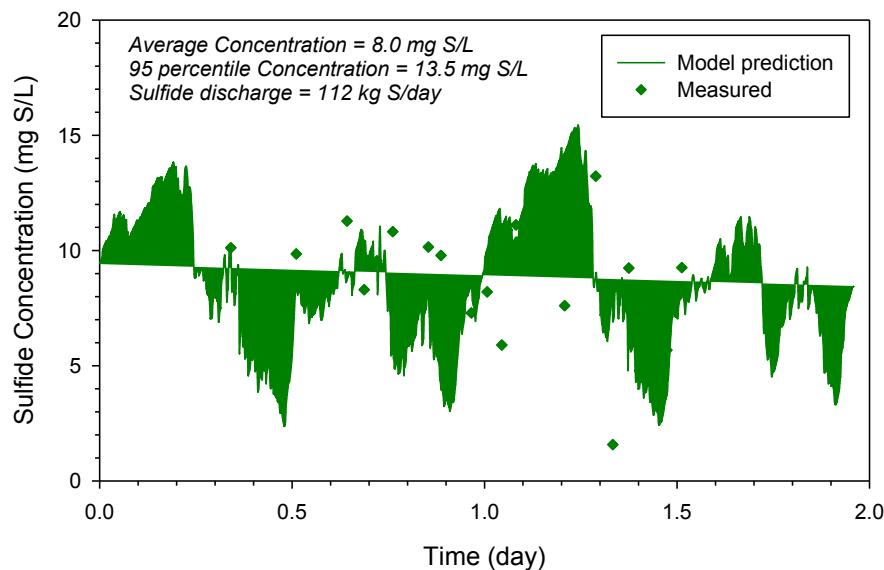


Figure 37. Comparison of model predicted sulfide levels with measured values

4.10.3. OXYGEN INJECTION

Two simulations were done, one with current oxygen injection arrangement and another with alternative arrangements. Several trials were conducted for the latter case and injection of oxygen at three locations located close to the treatment plant gave best results in terms of the control of sulfide discharge to Elanora WWTP. The optimal locations of oxygen injection determined by this simulation study are shown in Figure 36. The variation in sulfide concentration at the discharge point with oxygen supply rate of 176 kg O₂/day (oxygen actually dissolved in water, not what is supplied) is presented in Figure 38. The figure also compares the sulfide discharges without any control measures and with current oxygen injection. This rate of oxygen supply was required to bring the average sulfide concentration to a level of 1 mg S/L. The results suggest that, with injection at three locations, oxygen injection was effective in controlling the sulfide generation/accumulation in the sewer line, and hence its discharge at Elanora WWTP. It is interesting to note that, with a proper selection of injection sites, the sulfide discharge can be controlled to a much lower level than what is being currently achieved with current oxygen injection system and that also at a lower oxygen supply rate.

Simulations were done for a series of oxygen supply rate ranging from 0 - 176 kg O₂/day to investigate the effect of variation in oxygen supply rate on overall sulfide control. The results of these simulations are summarized in Figure 39. A decrease in average and 95 percentile sulfide concentrations is observed with the increase in oxygen supply rate and vice versa. Much more additional oxygen is required to achieve a small decrease in the sulfide level once the sulfide reaches a level of about 2 mg S/L. The same applies to sulfide discharge load. As a consequence of oxygen injection, VFA discharge to the WWTP decreases with increase in oxygen supply rate. This will have significant impact on nutrient removal in downstream treatment plant. Sulfide level can be brought down to a lower level at the expense of higher oxygen supply incurring higher VFA consumption. Considering the

negative impact it would have, a very careful consideration should be given in establishing a target sulfide level.

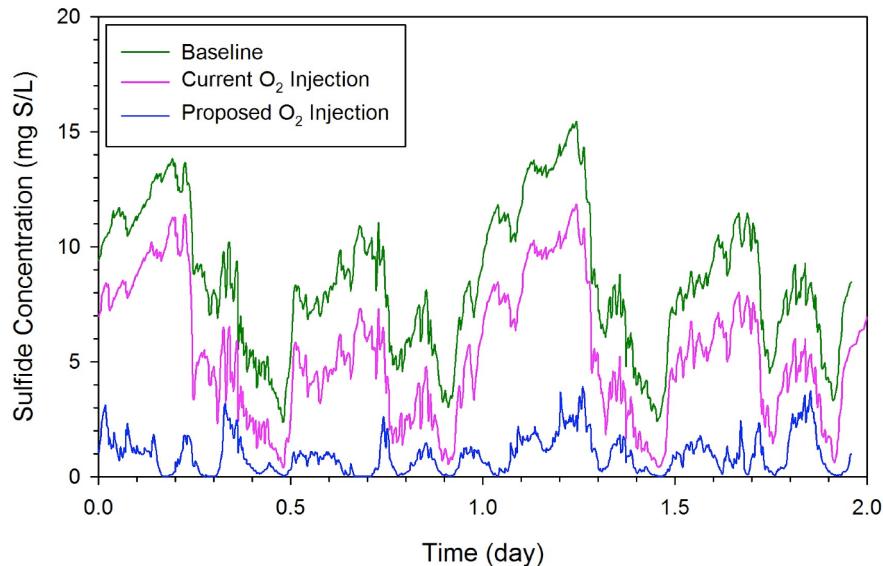


Figure 38. Sulfide concentration with oxygen injection at proposed 3 locations and its comparison with current oxygen injection

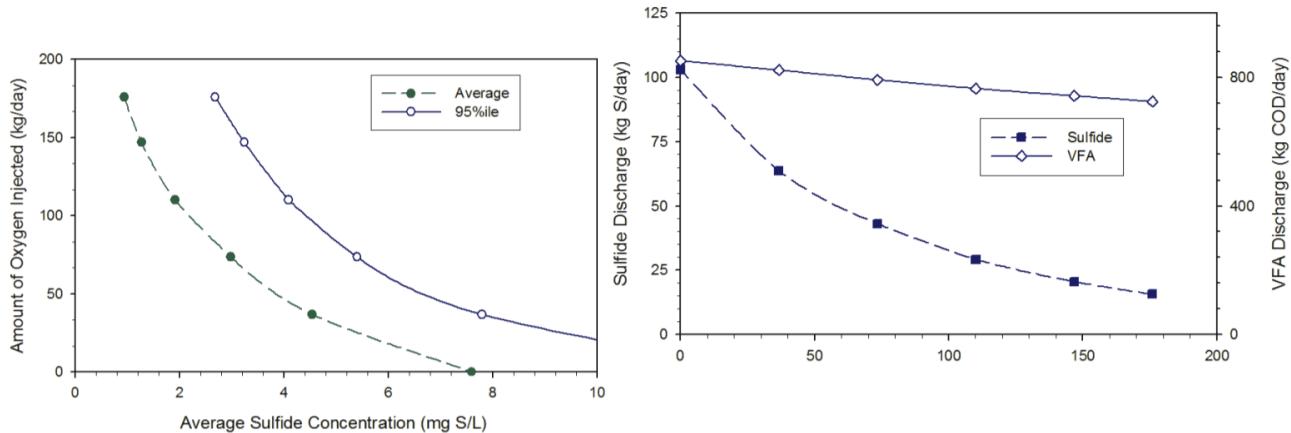


Figure 39. Effect of the amount of oxygen injection on sulfide levels (left) and sulfide and VFA discharge (right)

To examine the sensitivity of shifting the location of oxygen injection on overall control of sulfide accumulation, further simulations were done making changes in the injection locations. For this, one location was shifted upstream or downstream at one time, and the results were compared. The effects of changing location for Injection Point 1 (873 m upstream of the point where feeder from B25 enters the trunk) are shown in Figure 40. The same for Injection Point 2 (855 m upstream of the point where two parallel sewer lines meet, on second sewer line) are shown in Figure 41.



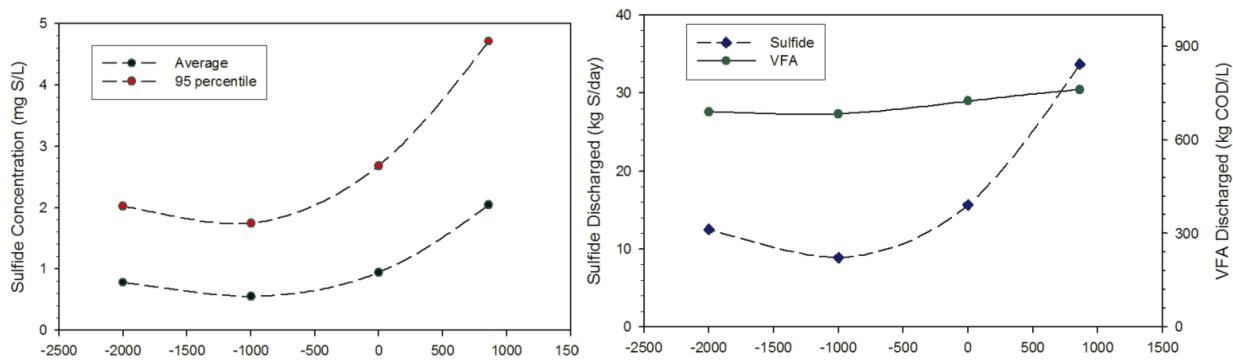


Figure 40. Effect of changing injection location for Location 1

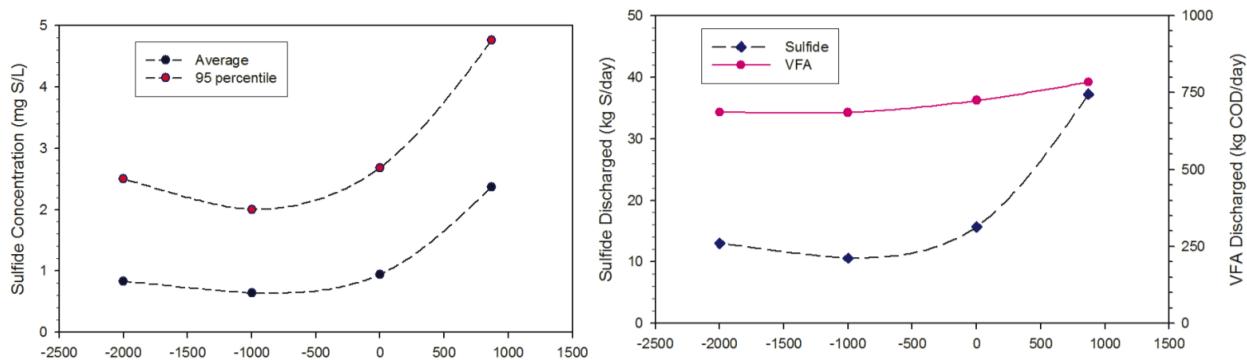


Figure 41. Effect of changing injection location for Location 2

Shifting the injection location upstream by 2 km didn't show any significant impact on the overall sulfide control. On the other hand, moving the location downstream showed negative impact as both the sulfide level and the load increased rapidly. The VFA discharge load decreased in the former case, and increased in the latter. The results indicated a window of about 2 km in the upstream side of the proposed injection locations along which actual injection sites could be located without affecting the effectiveness of controlling sulfide discharge. This provides a greater flexibility in implementation of the strategy.

4.10.4. NITRATE INJECTION

Similar to the case with oxygen, several simulations were carried out to arrive at the optimal injection points for nitrate. Injection at two locations as shown in Figure 42 was found to be optimal. The difference in these locations and those in case of oxygen is that, the points are located slightly upstream in this case. Nitrate is only utilized in biofilm for sulfide oxidation, while chemical oxidation of sulfide in bulk phase is possible with oxygen. As a result of this, the oxidation of sulfide with nitrate requires a longer time for complete oxidation of sulfide than with oxygen. This is reflected in the selection of injection points here.



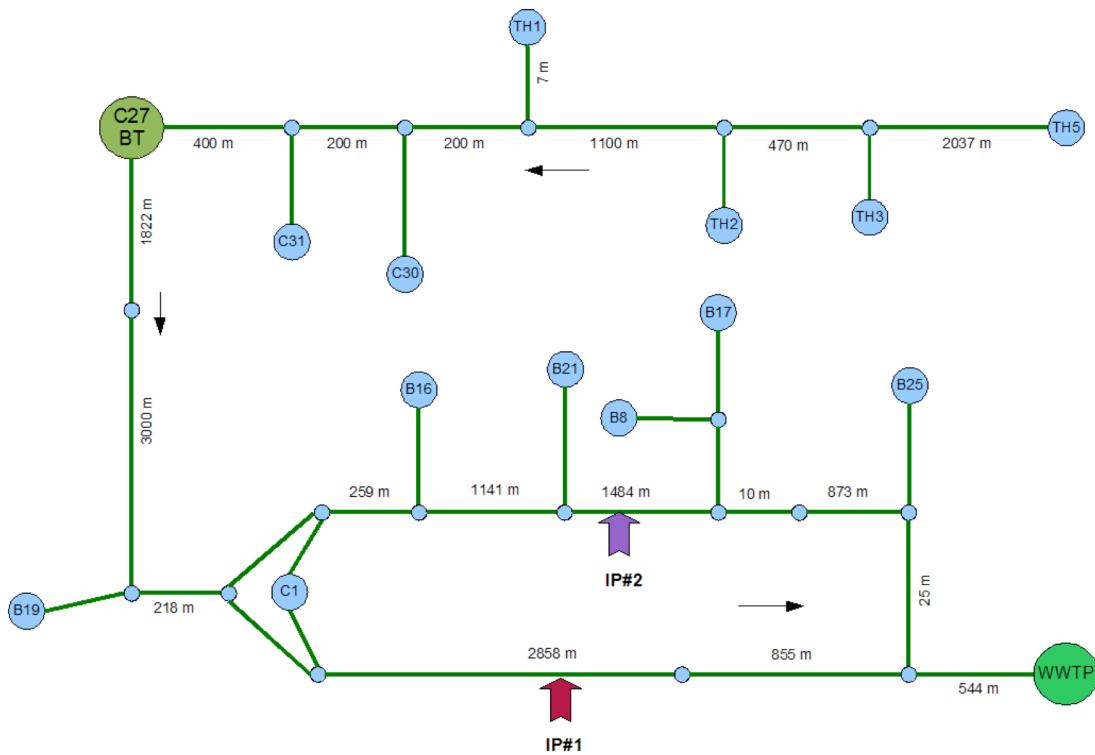


Figure 42. Location of injection points for nitrate

The variation in sulfide concentration at the discharge point at nitrate supply rate of 113 kg N/day is presented in Figure 43. This rate of nitrate supply was required to bring the average sulfide concentration to a level of 1 mg S/L. The results suggest that, with injection at two locations as indicated in Figure 42, nitrate addition was effective in controlling the sulfide generation/accumulation in the sewer line, and hence its discharge at Elanora WWTP. The nitrate level in the sewage at the end of the pipe varied from 0 to about 4 mg N/L, depending upon the dosing rate and the HRT. Since high levels of nitrate would add nitrate load and also impact the performance of anaerobic stages of the downstream treatment plant, it is critically important that the dosing rates be manipulated to minimize the nitrate discharge.

Results of the investigation of the effect of variation in nitrate supply rate (0-113 kg N/day) on overall sulfide control are summarized in Figure 44. A decrease in average and 95 percentile sulfide concentrations is observed with the increase in nitrate supply rate and vice versa. As it was with oxygen, the incremental benefit of dosing additional nitrate diminished considerably once the sulfide reaches a level of about 2 mg S/L. Same applies to sulfide discharge load. VFA discharge to the WWTP decreased with increase in nitrate supply rate, and the effect was more pronounced in this case as compared to oxygen. This is expected to have significant impacts on nutrient removal in downstream treatment plant. Although, sulfide level can be brought down to a lower level at the expense of higher nitrate supply, the trade off between the degree of sulfide control achieved and the extent of VFA consumption should be taken into consideration.



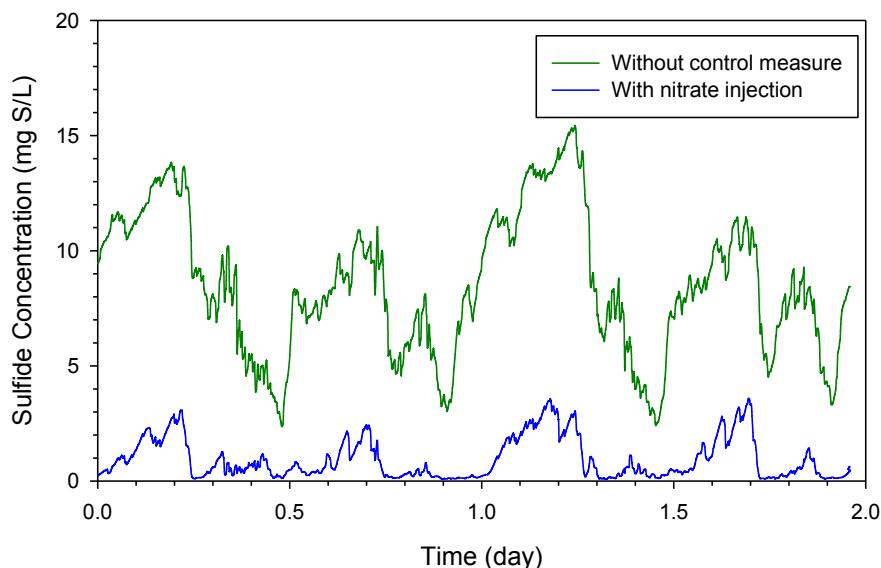


Figure 43. Effect of nitrate dosing on sulfide accumulation

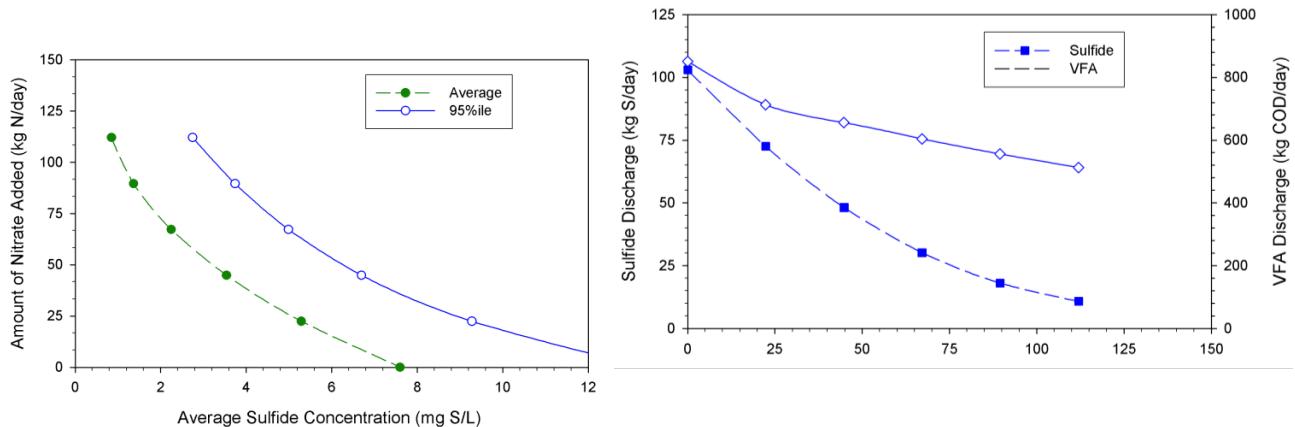


Figure 44. Effect of the amount of nitrate dosed on sulfide levels (left) and sulfide and VFA discharge (right)

The results of the sensitivity analysis with respect the choice of location for nitrate addition for Location 1 (500 m downstream of B21) and Location 2 (1100 m downstream of C1 on the second sewer line) are presented in Figure 45 and Figure 46 respectively. For Location 1, moving the injection point up or down by 1 km did affect but only marginally. Shifting the Injection Point 2 downstream showed better sulfide control. On the other hand, moving the same injection point upstream slightly increased the average sulfide level. The results further suggest that, although the overall control of sulfide accumulation is affected by the location of injection, shifting the locations by 1 km upstream or downstream does not produce any significant effects. This gives greater flexibility to the selection of injection points when this strategy is implemented.

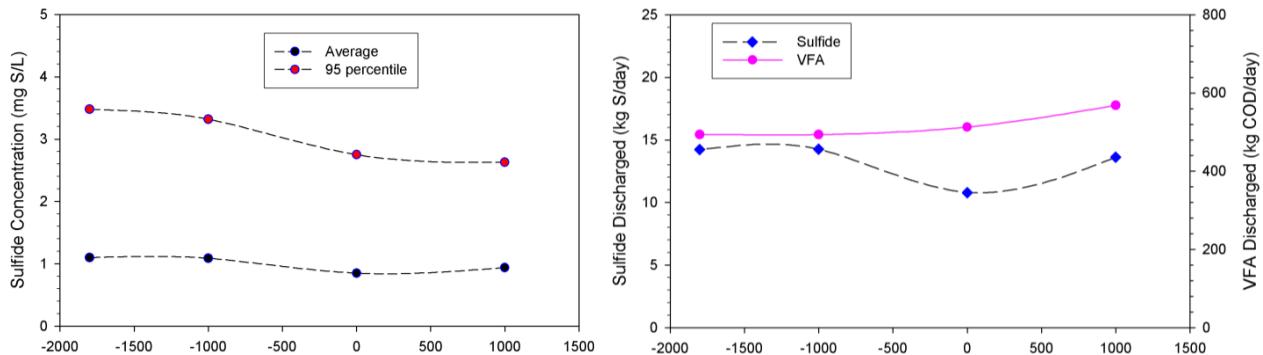


Figure 45. Effect of changing injection location for Location 1

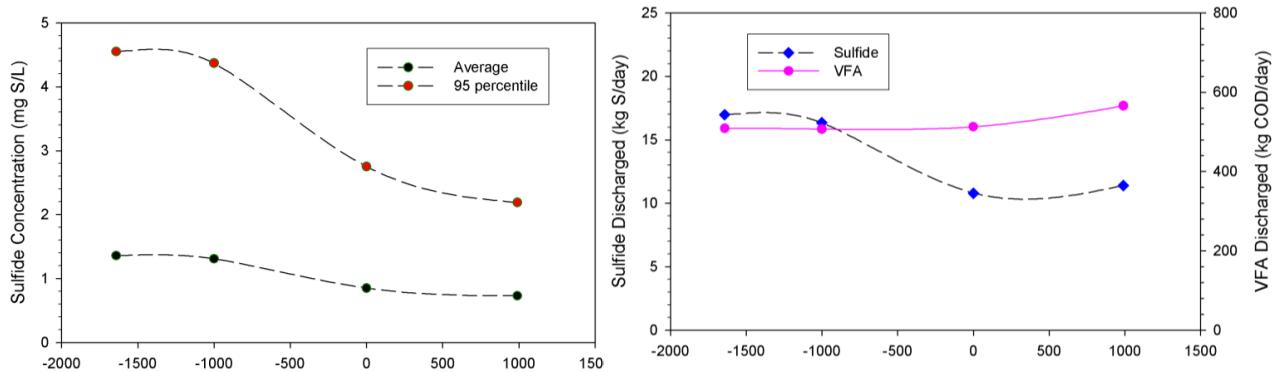


Figure 46. Effect of changing injection location for Location 2

4.10.5. OTHER CHEMICAL ADDITION

Chemicals for sulfide precipitation and also for pH control were studied. Since the chemical reactions involved in precipitation and acid-base equilibrium are much faster than those involving oxygen and nitrate, the hydraulic retention time does not play a major role in such a case. Although dosing the chemicals far upstream is desirable for keeping the entire sewer network free from H₂S related problems, the effectiveness cannot be guaranteed because of considerable side stream flow entering the sewer network. It was attempted to keep a considerable portion of network with a low H₂S /high pH with a minimum numbers the injection points. The injection points shown in Figure 47 were therefore used.

FeCl₂ ADDITION

The variation in sulfide concentration at the discharge point with FeCl₂ dosing rate of 172 kg Fe²⁺/day is presented in Figure 48. This rate of FeCl₂ dosing was required to bring the average sulfide concentration to a level of below 1 mg S/L. As the results suggest, with the injection at two locations, FeCl₂ dosing was effective in controlling the sulfide accumulation in the sewer line by precipitating the generated sulfide. Simulations were done for a series of Fe²⁺ dosing rate ranging from 0 - 215 kg Fe²⁺/day to investigate the effect of variation in Fe²⁺ dosing rate on overall sulfide control. The results of these simulations are summarized Figure 49.



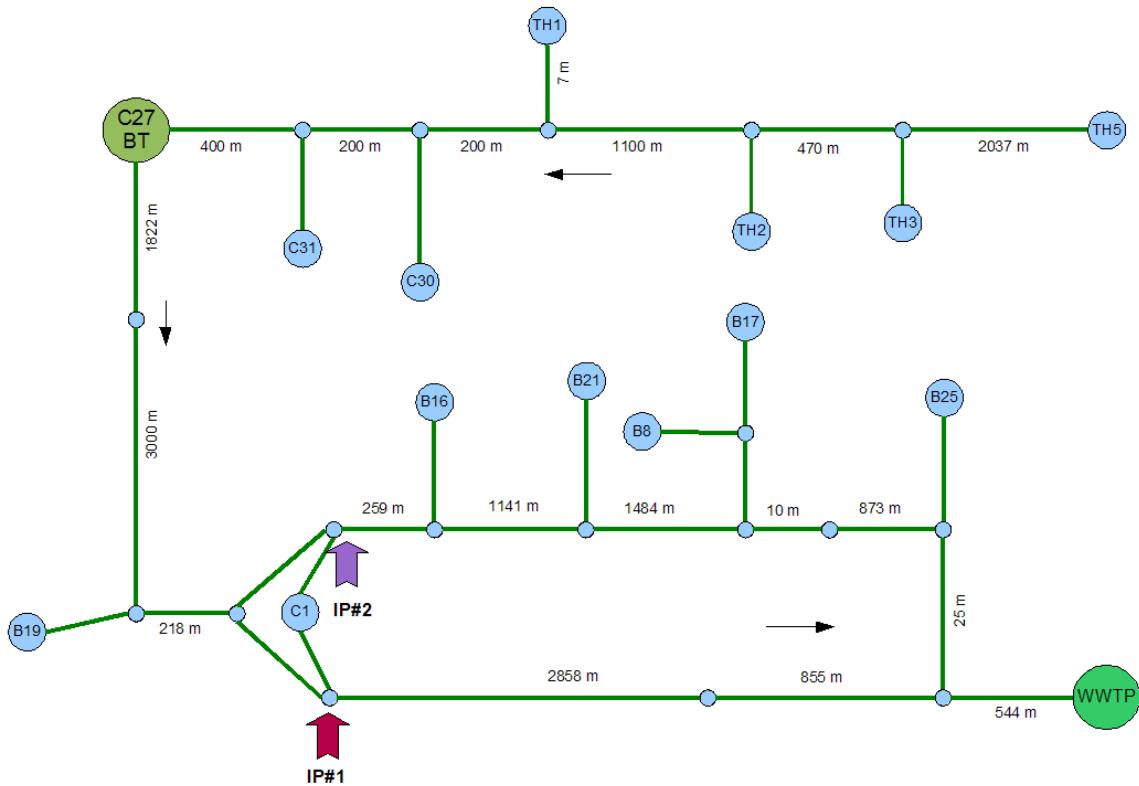


Figure 47. Locations of injection for FeCl_2 , FeCl_3 , and $\text{Mg}(\text{OH})_2$

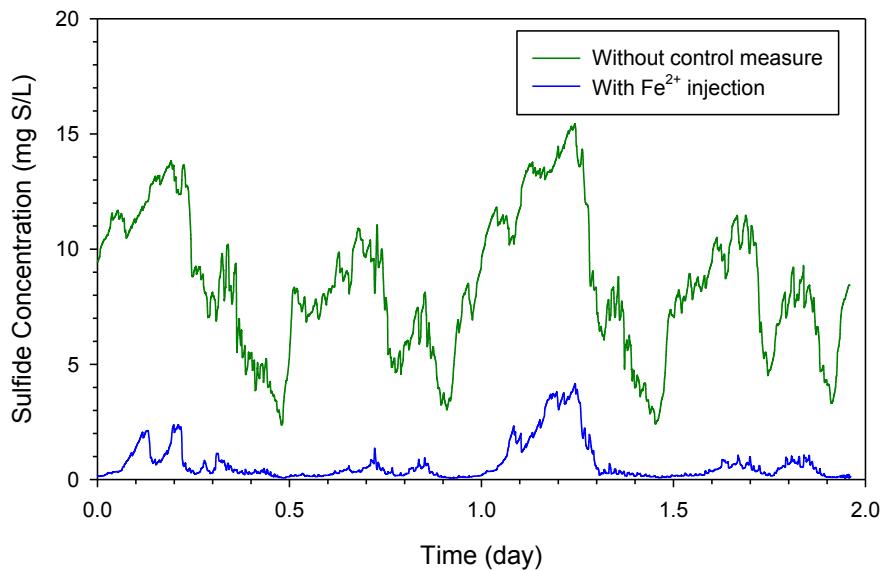


Figure 48. Effect of FeCl_2 addition on H_2S discharge

A decrease in average and 95 percentile sulfide concentrations is observed with the increase in Fe^{2+} dosing rate and vice versa. Dosing Fe^{2+} beyond the dose of 150 kg/day seems to provide only a marginal improvement on sulfide control, which obviously will not be a cost effective option.



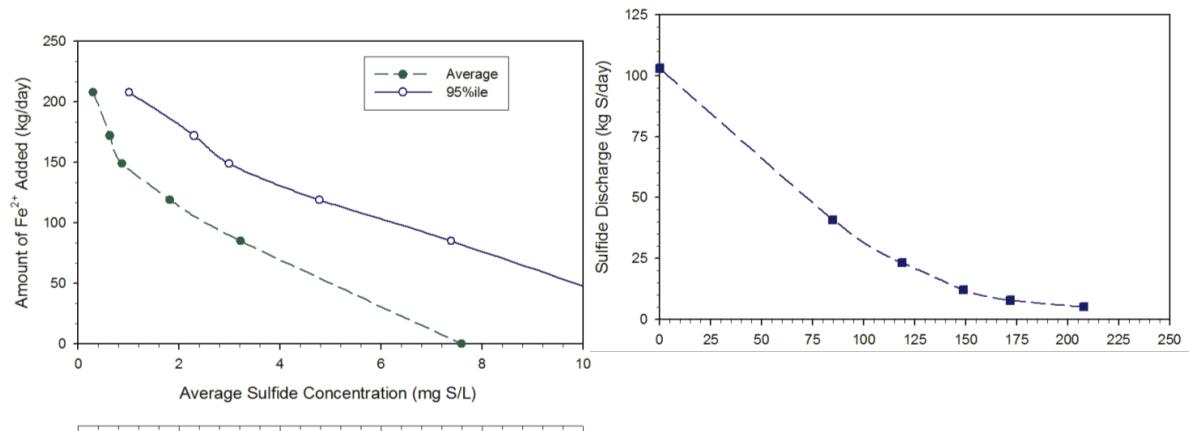


Figure 49. Effect of the amount of Fe^{2+} dosed on sulfide levels (left) and sulfide and VFA discharge (right)

FeCl_3 ADDITION

As an alternative to FeCl_2 , dosing of FeCl_3 dosing was investigated and the results are presented in Figure 50. The results show that FeCl_3 was equally effective in controlling sulfide accumulation in the system. No effort was made to optimize the dosing in this case as the model used in simulation was based on the theory rather than the experimental work. Experimental work on the effects of FeCl_3 addition is in progress.

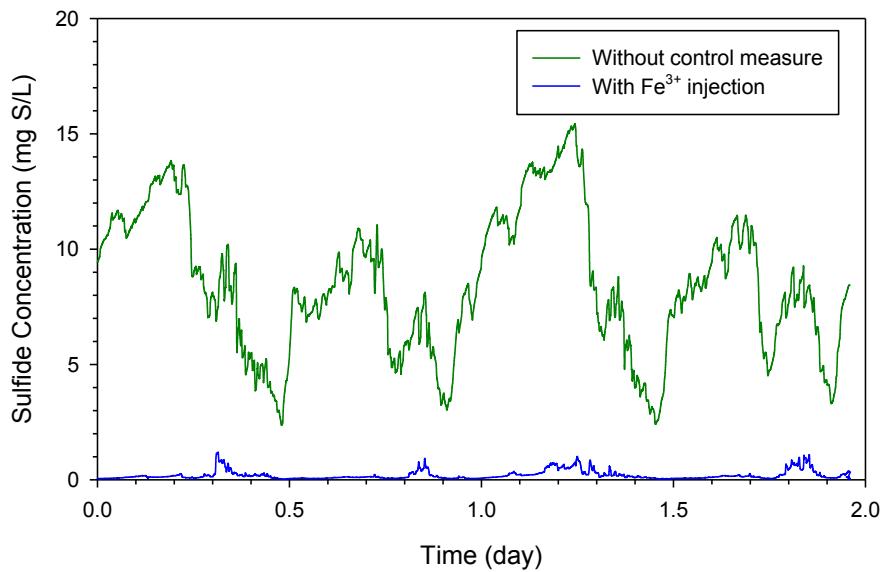


Figure 50. Effect of FeCl_3 addition on H_2S discharge

Mg(OH)_2 ADDITION

Magnesium hydroxide addition and subsequent increase in pH was studied as a means of controlling H_2S release. A pH of 8.5 is thought to reduce the H_2S emission by 90-95%, and hence was chosen as the target pH level. The effect of pH change in biological activity was also considered. Through several trials, Mg(OH)_2 dosing at two locations (because of two parallel sewer lines) with the dosing rate of 858 kg/day was found to raise the average pH to about 8.8. The variation in pH is presented in Figure 51 and that in H_2S concentration is presented in Figure 52.



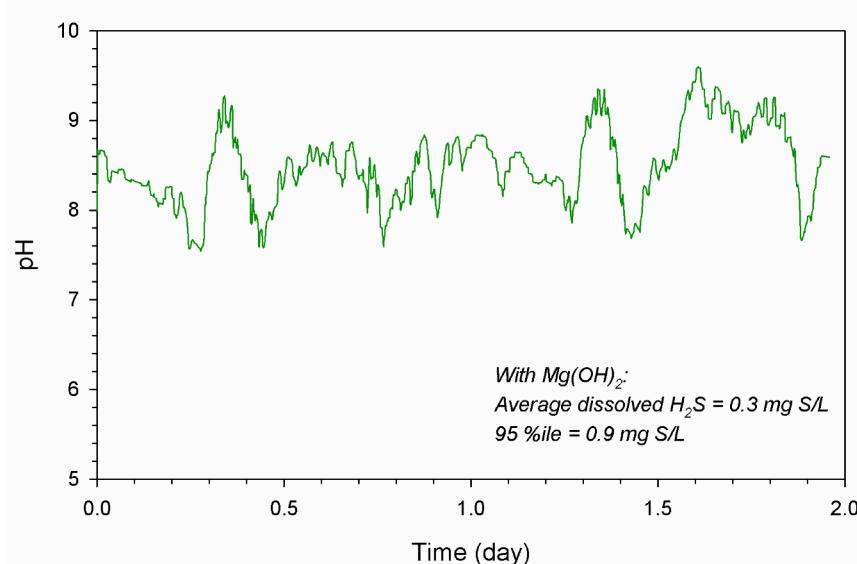


Figure 51. Effect of $Mg(OH)_2$ addition on pH

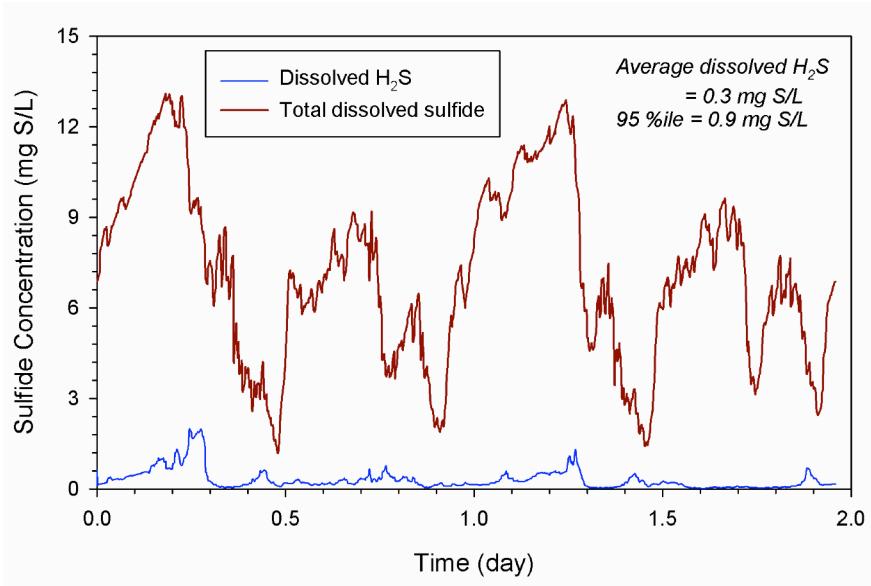


Figure 52. Effect of $Mg(OH)_2$ addition on H_2S

4.10.6. SUMMARY

The results of the simulation study are summarized in the following table.



Chemical	Dosage	Injection Locations	Average H ₂ S (mg S/L)	95 percentile H ₂ S (mg S/L)	Median pH
Oxygen	176 kg O ₂ /day*	3	0.9	2.7	-
Nitrate	113 kg N/day	2	0.7	2.0	-
FeCl ₂	172 kg Fe ²⁺ /day	2	0.6	2.3	-
FeCl ₃	191 kg Fe ³⁺ /day ⁺	2	0.2	0.7	-
Mg(OH) ₂	858 kg/day	2	-	-	8.8

*without considering the efficiency factor

+ dosing not optimized

The economical analysis presented in the following section of the report is based on the chemical doses presented in the table.

4.10.7. FINANCIAL ANALYSIS

A financial analysis of chemical dosing options for the Tugun-Elanora rising main sewer system was performed taking into account the predictions from the kinetic model. The objective was to enable Gold Coast Water (GCW) to pre-select the option(s) most likely to be cost-effective. The intention was for this research to serve as a guide to GCW management in implementing an appropriate chemical dosing strategy through more detailed engineering for this and similar rising main systems.

The kinetic model described in previous sections was set up for the Tugun-Elanora (T-E) network on the Gold Coast. As described in earlier sections, this model includes biological, chemical and some of the physical processes that occur in the sewer system, based on current understanding. The model was used to predict the chemical doses required to minimise odour at Elanora WWTP when the sewage is discharged for treatment.

CHEMICAL DOSE

The model data was compared to “rules of thumb” for expected chemical doses, based on experience of suppliers and literature sources. The four alternative chemicals compared were:

- Dissolved oxygen (injected in pure gas form into the pipeline);
- Magnesium hydroxide;
- Ferrous chloride; and
- Calcium Nitrate

Note that oxygen injection has been used in the past in the T-E network, whereas the other chemicals could be considered possible alternatives to oxygen. For equivalent cost comparison purposes between the alternatives, it was assumed that new oxygen injectors would be installed at optimal locations, based on model predictions.



The model dynamic flow inputs (based on real operating data collected from the various pump stations in the Tugun-Elanora system) resulted in totalised daily flow from this system of 14.32 ML/d. In the absence of any chemical dosing, the model predicted an average total dissolved sulfide (H_2S / HS^- / S^{2-}) concentration of 8.8 mgS/L at the discharge to Elanora WWTP. The model predictions in respect of key parameters (e.g. VFA, total dissolved sulphide and sulfate) had been previously calibrated to real measurements taken at several sampling points in the Tugun-Elanora system.

The chemical dose required to minimise odour was based on a benchmark target of an average total dissolved sulfide concentration at the discharge to Elanora WWTP of < 1 mgS/L from model predictions or experience. In the case of magnesium hydroxide (which does not remove dissolved sulphide but shifts its species equilibrium distribution with pH), the adopted target was <1 mg dissolved H_2S . The model predicted an average dissolved sulphide concentration of 0.3 mgS/L, at a median pH of 8.6, for a dose of just over 100 mg/L as delivered magnesium hydroxide product.

As a “sanity check”, the model predictions were compared with either actual (historical) oxygen doses for this network, or, in the case of ferrous chloride, magnesium hydroxide and calcium nitrate, with literature and experience-based estimates of the likely chemical doses. Due to the many different formats of dose units in the “rules of thumb” found from the literature or industry experience, several units have been listed for comparative purposes, where possible. A summary of the adopted doses (Model vs. Actual in the case of oxygen or Model vs. Experience in the case of the other chemicals) is presented in

Table 3-Table 6.

A comparison was made between the various options in two scenarios for chemical dosing, as listed in Table 7. The reason that model data was used for oxygen dose assumptions in both scenarios is that the actual Gold Coast Water data (from 2005, refer to

Table 3) came from a period when the average sulphide concentration at Elanora WWTP was not reduced to the benchmark level applied in this study, namely an average dissolved sulphide concentration of <1 mg S/L. To keep the cost comparison valid in all scenarios, the chemical dose applied was expected to produce this benchmark. The model suggested that the main reason for oxygen injection being non-ideal and failing to meet the chosen benchmark for controlling odour at the WWTP is that the pump stations fitted with oxygen injectors are located too far up the catchment. Oxygen is rapidly consumed and can only be injected when the pump stations are running. With sufficient retention time in the rising pipelines downstream of the points of oxygen injection, sulphide reforms and produces odour at the WWTP inlet.

It is worth noting that both oxygen and nitrate control sulfide through oxidation. In the case of oxygen, both biological and chemical oxidation mechanisms take place, whereas for nitrate only the biological mechanism occurs. The biological mechanism is slower and located mainly in the biofilm, to the extent that dissolved oxygen (or nitrate) from the bulk liquid penetrates the biofilm and sulfide-oxidisers are present, with oxygen or nitrate serving as electron acceptor. The chemical oxidation mechanism for oxygen is faster and takes place mainly in the bulk phase and to a limited extent in the biofilm. Hence, research has shown that longer retention times are required to achieve the equivalent degree of sulfide oxidation with nitrate than with oxygen. For this reason the ideal dosing point(s) for



nitrate needs to be further back in a rising main system than for oxygen, relative to the odour-sensitive discharge point.

Table 3. Oxygen dosing assumptions based on Model (base case comparison for Scenarios 1 and 2) vs. Actual (2005 Gold Coast Water) data

Parameter	Actual (2005)	Model	Units
Average concentration	Unknown	12	mg/L as dissolved O ₂
	22 (Notes 2 & 3)	42	mg/L O ₂ injected
	Unknown	40%	Dosing efficiency (%) (Note 1)
	Unknown	1.40	mol dissolved O ₂ / mol S (initial)
Daily mass dosed	Unknown	176	kg/d as dissolved O ₂
	369	440	kg/d as O ₂ injected
No. of dosing points	up to 6	3	No.
Delivered product active ingredient (% w/w)	>99.5%		as pure compressed O ₂ gas
Delivered product specific gravity	1.429		kg/m ³ (Note 4)

Note 1: Dosing efficiency assumed (40%), based on model estimates from model calibration against full-scale data, where available. Significant loss of undissolved oxygen as gas is suspected to occur via air/gas release valves downstream of injection points.

Note 2: Based on oxygen injector orifice settings (information supplied by Gold Coast Water, Nov. 2005) for 6 no. pump station injection points, assuming all were operational (only five were operational in Nov. 2005). Oxygen can only be injected when the pumps are operating. Actual pump run times for the period modelled (9-10 May 2006) were applied. At the actual doses applied, oxygen dosing was only partially effective in practice in lowering sewage sulfide concentrations at the Elanora WWTP discharge point during the 2005-6 study periods. Refer also to Note 1.

Note 3: Average actual dose range (5 to 60 mg/L) varied significantly between pump stations, depending on the settings for oxygen gas injection rate and flow rates through respective pump stations. The tabulated value is the flow-weighted average.

Note 4: Gas phase density of compressed oxygen = 1.429 kg/m³ at STP (0°C, 1 atm). Sm3 refers to "standard cubic metre" at 0°C, 1 atm.

An unfortunate consequence of the longer retention time required for sulfide oxidation with nitrate (compared to oxygen) is that greater consumption of nitrate occurs by competing growth from heterotrophic bacteria (non-sulfide oxidisers). Not only does this necessitate a higher nitrate dose than oxygen (when compared on an electron-equivalent basis) but it may result in thicker biofilm growth. Ironically this may lead to accelerated sulfide production due to sulfate reduction in the event that the nitrate is depleted and anaerobic conditions resume.



Table 4. Magnesium hydroxide dosing assumptions based on Experience (Scenario 1) vs. Model (Scenario 2) data

Chemical and Dose	Experience	Model	Units
Average concentration	100	69	L/ML as delivered product
	150	103	mg/L as delivered product (Note 5)
	87	60	mg/L as Mg(OH) ₂
	150	103	mg/L as CaCO ₃
Daily mass dosed	1432	986	L/d as delivered product
No. of dosing points	2	2	No.
Typical delivered product active ingredient (% w/w)	58%		as Mg(OH) ₂
Delivered product specific gravity	1.5		kg/L

Note 5: Range from industry experience: approximately 50 to 150 mg/L magnesium hydroxide as delivered product to achieve 80 to 90% H₂S reduction respectively.

Table 5. Magnesium hydroxide dosing assumptions based on Experience (Scenario 1) vs. Model (Scenario 2) data.

Chemical & Dose	Experience	Model	Units
Average concentration	203	79	L/ML as delivered product
	250	97	mg/L as delivered product
	70	27	mg/L as FeCl ₂
	31	12	mg/L as Fe
	28	11	Kg FeCl ₂ delivered product/ kg S (initial) (Note 6)
	3.5	1.36	kgFe/ kgS (initial) (Note 7)
	2.0	0.78	mol Fe/mol S (initial) (Note 8)
Daily mass dosed	2908	1134	L/d as delivered product
No. of dosing points	2	2	No.
Typical delivered product active ingredient (% w/w)	28%		as Fe(Cl) ₂
Delivered product specific gravity	1.23		kg/L



Note 6: Indicative range from industry experience: ~30 to 50 mg FeCl₂ as delivered product per mg S (initial).

Note 7: Optimal value suggested by WEF (2004).

Note 8: Laboratory data used for model suggests range 0.5 to 1.0 (average ~0.7) mol Fe (dosed)/ mol S (removed). Literature and industry experience suggests that around 2 mol Fe/mol S (initial) is required in practice.

Table 6. Calcium Nitrate dosing assumptions based on Experience (Scenario 1) vs. Model (Scenario 2) data.

Chemical and Dose	Experience	Model	Units
Average concentration	39	60	L/ML as delivered product
	57	89	mg/L as delivered product
	29	46	mgCa(NO ₃) ₂ /L
	5.0	7.8	mgNO ₃ -N/L
	0.57	0.89	kg NO ₃ -N/kg H ₂ S-S
	4.4	6.9	L Ca(NO ₃) ₂ solution/ kg S (Note 9)
	1.30	2.0	mol NO ₃ -N/mol S initial (Note 10)
Daily mass dosed	554	865	L/d as delivered product
No. of dosing points	2	2	No.
Typical delivered product active ingredient (% w/w)	8.75%		as NO ₃ -N (Note 11)
Delivered product specific gravity	1.48		kg/L (Note 11)

Note 9: Range ~5 to 7.5 L CaNO₃ solution/ kg S (WEF, 2004)

Note 10: Laboratory data used for model suggests range ~0.6 to 1.6 mol NO₃-N/ mol S (removed) for oxidation of sulfide alone, with partial oxidation at the lower doses to some intermediate with a lower oxidation state than sulfate (e.g. polysulfide or molecular sulphur). Increasing sewer retention times tends to promote anoxic growth of heterotrophic biofilms with sustained nitrate dosing, which tends to increase nitrate consumption with little added benefit of greater sulfide oxidation. For practical purposes, the molar ratio of nitrate dose to sulfide oxidised is likely to be limited to a maximum of approximately 2 mol NO₃-N/mg S. For example, WEF (2004) suggest doses in the range ~5 to 7.5 L Ca(NO₃)₂ solution/ kg S (initial), which corresponds to a molar ratio of ~0.9 to 1.3 mol NO₃-N/mg S for the stated concentration of solution (42% as calcium nitrate).

Note 11: Calcium nitrate delivered product typically ranges 8.4 to 9.1 (adopt 8.75) w/w active NO₃-N. SG = 1.45 to 1.55 (adopt 1.48) kg/L. The adopted values are equivalent to 51% w/w as Ca(NO₃)₂.

Table 7. Chemical doses applied in scenarios for cost comparison

SCENARIO	CHEMICAL	
	Oxygen	Magnesium Hydroxide, Ferrous Chloride, Calcium Nitrate



Scenario 1	Model dose (Table 1)	Experience (Tables 2,3,4)
Scenario 2	Model dose (Table 1)	Model (Tables 2,3,4)

ASSUMPTIONS FOR COST COMPARISON

The following assumptions were made in the financial analysis:

1. Average daily flow (14.32 ML/d) and chemical doses as defined above for the Tugun-Elanora case study.
2. Capital cost estimates for each dosing station (3 no. for oxygen; 2 no. for each the other chemicals) included road easement to allow access for tanker delivery, concrete slab, security, lighting and other services (power, water, drainage etc.) for the dosing facility. In the case of ferrous chloride, due to the higher chemical use and delivery requirements, a larger bulk storage tank (30 kL) in a bunded area was allowed this chemical. For the other liquid chemicals (i.e. except oxygen, a smaller storage tank size (13 kL) with bund provisions to prevent spillage to the environment was allowed. Oxygen was assumed to be injected in gaseous form and delivered from a pressurised tank storing pure liquid oxygen, which is typically supplied and maintained by the supplier.
3. Operating cost estimates included delivered costs of bulk chemicals, hire of dosing equipment, as well as preventative and breakdown maintenance plus spares. Routine maintenance of the dosing systems was assumed to occur at a frequency of every six months for all the chemicals.
4. Gold Coast Water staff costs were assumed to allow for one operator attending each dosing facility for 2 hours per week (plus 0.5 h travel time). One operator was assumed to have a base salary cost of \$55,000 pa, with allowance of an additional 25% made for overtime, annual leave and 40% of the base operator salary cost to cover staff overheads and laboratory services.
5. Estimated power costs were relatively insignificant but were taken into account for completeness (approximately \$1000 to \$2000 pa).
6. The analysis was carried out over a 30-year time period (2007-2037), with civil structures assumed to have a life of 30 years and mechanical and electrical equipment a life of 15 years. Replacement of the dosing equipment was not separately included since these are typically costed on a "hire" basis from the chemical suppliers. Maintenance and replacement costs of the dosing facilities were therefore covered in the hire and maintenance component of the operating cost for these units.
7. Chemical dosing costs were escalated annually in proportion to flow rate. The flow rate through the sewer network was assumed to increase at a rate of 1% pa, which is very close to the weighted average projected by Gold Coast Water planners for the Tugun-Elanora catchment in the period adopted for the analysis here (2007-2037).
8. Inflation was excluded from the financial analysis.
9. The discount rate in the Net Present Value (NPV) analysis was assumed to be 7%.





RESULTS

The results of Net Present Value (NPV) analysis are summarised in Table 8 and Figure 53 for the following dosing assumptions, named SCENARIO 1 (refer to Table 7 for definition):

1. Oxygen injection at 12 mg/L dissolved O₂ (1.4 mol O₂/ mol initial H₂S), or 440 kg/d injected at 40% efficiency
2. Magnesium hydroxide at 100 L delivered product/ML (87 mg/L as Mg(OH)₂, equivalent to 150 mg/L as CaCO₃)
3. Ferrous chloride at 203 L delivered product/ML (2.0 mol Fe/ mol S as initial H₂S)
4. Calcium nitrate at 39 L delivered product/ML (1.3 mol NO₃-N/ mol S as initial H₂S)

It is apparent from Table 8 that the whole of life cost (or NPV) for chemical dosing to control odour is heavily dominated by the operating cost, which, in turn is dominated by cost of the delivered chemical consumed. In fact, for all the options in Scenario 1, approximately 90% to 98% of the NPV is contributed by operating and maintenance (O&M) costs. The cost of the chemicals contributed approximately 70% to 80% of the O&M cost, depending on the chemical and projected year.

The results of the financial analysis for Scenario 1 suggest that oxygen dosing is the most cost-effective option for odour control, assuming the dosing regime can be optimized in practice to produce the target outcome defined (<1 mg/L dissolved H₂S). For the dosing assumptions based on "Experience" (Scenario 1), calcium nitrate dosing was the next most cost-effective option after oxygen, followed by ferrous chloride and magnesium hydroxide (the most expensive option).

Table 8. Results of financial analysis for SCENARIO 1

Chemical Dosed	Capital Cost	Operating Costs (per year)	Net Present Value (at 7% discount rate)
Oxygen injection	\$293,000	\$161,700	\$2,440,000
Magnesium hydroxide dosing	\$196,000	\$563,000	\$7,838,000
Ferrous chloride dosing	\$357,000	\$478,900	\$6,834,000
Calcium nitrate	\$196,000	\$351,200	\$4,905,000

Figure 53 shows that for the assumed dose rates in Scenario 1, oxygen is the most cost-effective chemical for the whole range of likely current costs of delivered bulk chemical. The cost range examined was the approximate (indicative) delivered price of chemical in South East Queensland ±20%, based on Gold Coast Water information and industry experience. It is obvious that if the cost of chemical is heavily discounted (dotted trend line on the extreme left in Figure 53), then the NPV for all options cluster around a rough common point, reflecting the similarity in capital and operating costs (other than chemical) between options.



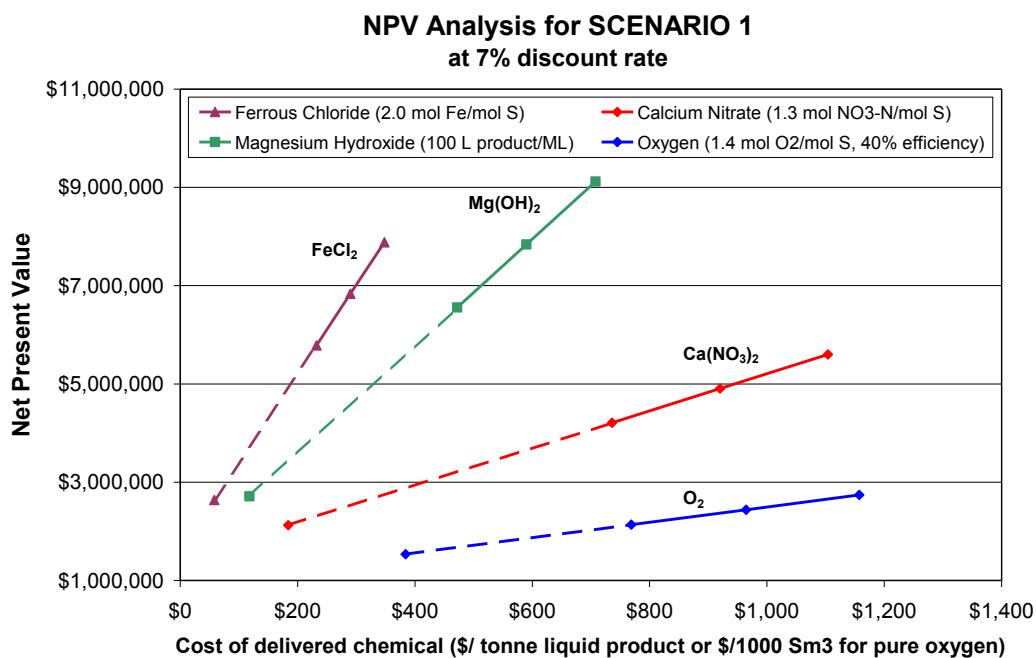


Figure 53. Chart showing Net Present Value and sensitivity to delivered cost of bulk chemicals for the four options of chemical dosing in the Tugun-Elanora rising main case study defined as Scenario 1.

In order to further test the financial model sensitivity to chemical dose, SCENARIO 2 was examined, based on the following dosing assumptions (refer to Table 7):

- Oxygen injection at 12 mg/L dissolved O₂ (1.4 mol O₂/ mol initial H₂S), or 440 kg/d injected at 40% efficiency (same as Scenario 1)
- Magnesium hydroxide at 69 L delivered product/ML (60 mg/L as Mg(OH)₂, equivalent to 103 mg/L as CaCO₃)
- Ferrous chloride at 79 L delivered product/ML (0.78 mol Fe/ mol S as initial H₂S)
- Calcium nitrate at 60 L delivered product/ML (2.0 mol NO₃-N/ mol S as initial H₂S)

The financial results for Scenario 2 are presented in Table 9 and Figure 54.

Table 9. Results of financial analysis for SCENARIO 2

Chemical Dosed	Capital Cost	Operating Costs (per year)	Net Present Value (at 7% discount rate)
Oxygen injection	\$293,000	\$161,700	\$2,440,000
Magnesium hydroxide dosing	\$196,000	\$418,800	\$5,841,000
Ferrous chloride dosing	\$357,000	\$247,900	\$3,634,000
Calcium nitrate	\$196,000	\$492,300	\$6,859,000



From the results in Table 9, oxygen remains the most cost-effective chemical in Scenario 2, but calcium nitrate becomes the most expensive (similar to magnesium hydroxide). Ferrous chloride is the next most cost-effective after oxygen, assuming the lower dose (based on laboratory/ model observations) works in practice at full-scale. Similar conclusions may be drawn from Figure 54 for the range of bulk chemical costs considered.

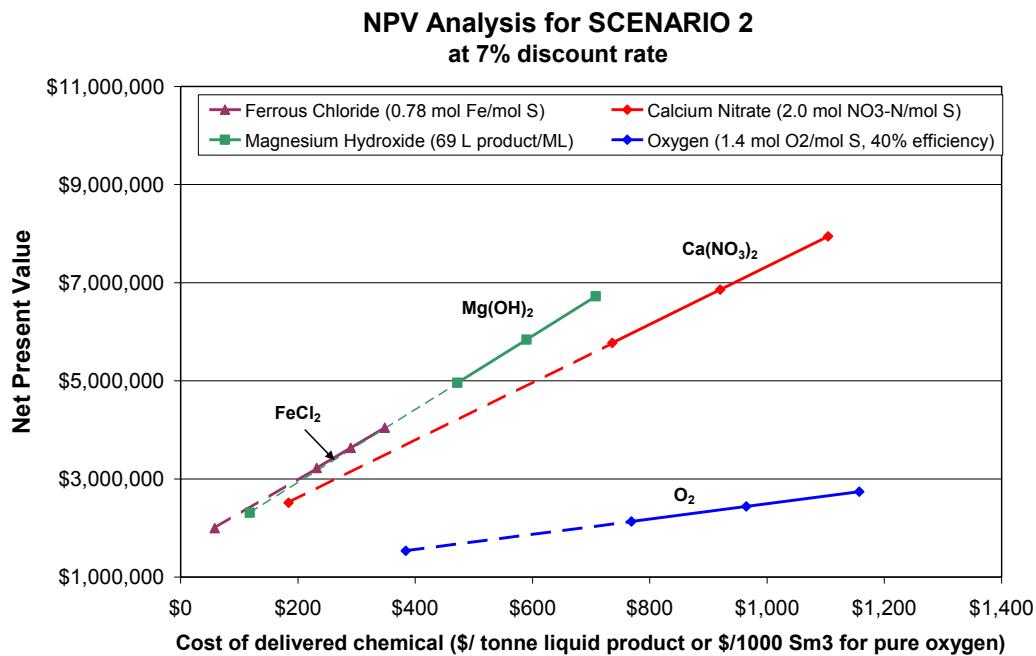


Figure 54. Chart showing Net Present Value and sensitivity to delivered cost of bulk chemicals for the four options of chemical dosing in the Tugun-Elanora rising main case study defined as Scenario 2.

DISCUSSION

The results of the financial analysis are surprising since conventional “wisdom” at the start of the research project was that one or more of the alternative liquid chemicals for odour control would be more cost-competitive than injecting gaseous oxygen. Moreover, oxygen injection was generally perceived by Gold Coast Water to be of dubious cost-effectiveness and presented certain occupational health and safety challenges. However, the model developed as part of the research project suggested that the positioning of the oxygen injectors relative to the system retention time and odour sensitive discharge location is critical to the effectiveness of oxygen. The same is true of nitrate dosing.

The financial analysis shows that actual (or assumed) chemical consumption will be critical in choosing the most cost-effective chemical. Although oxygen and nitrate may have lower costs (in Scenario 1), both have the disadvantage that they are rapidly consumed by heterotrophic bacterial activity in the sewage and/or biofilms on the sewer pipe inner walls. For example the oxygen (or nitrate) uptake rates per unit biofilm area (pipe wall) determined from laboratory studies and used in the model are approximately 16 g O₂/m².d (12 g N/m².d for nitrate) at temperatures of approximately 23 (± 1)°C. Therefore, under quiescent conditions (when rising main pump station pumps not running) when oxygen (or nitrate) cannot be injected, the rapid consumption of oxygen or nitrate results in growth of heterotrophic bacteria and loss of biodegradable COD in the sewage. In the long term this



can have negative consequences, which to some extent reduces the effectiveness of dosing oxygen (or nitrate), namely:

- Sulfide generation (due to SRB activity) recommences in any case under anaerobic conditions when oxygen (or nitrate) is depleted.
- More growth of heterotrophic biofilm can accelerate oxygen (or nitrate) uptake rates, resulting in more rapid return to anaerobic conditions and sulfide generation. Therefore oxygen dosed too far back in the catchment is largely ineffectual in controlling sulfide concentrations at the end of the pipeline (e.g. at the WWTP) and ironically may even be counter-productive.
- Loss of biodegradable COD may result in loss of nitrogen (and/or phosphorus) removal potential at the WWTP if the process relies on biological nutrient removal.

The advantage of dosing iron salts or magnesium hydroxide is that they give a “storage” effect for controlling sulfide. In the case of iron salts, a precipitate is formed when added to water (or wastewater). In the absence of sulfide, the precipitate will be some form of iron-hydroxy-phosphate ($\text{Fe}\sim\text{P}\sim\text{OH}$). Research as part of this project has shown that when sulfide is subsequently formed (or added), sulfide displaces phosphate (or hydroxide) from the $\text{Fe}\sim\text{P}\sim\text{OH}$ precipitate since the iron-sulfide precipitates are thermodynamically more stable. Effectively, the $\text{Fe}\sim\text{P}\sim\text{OH}$ precipitate acts as “reservoir” of iron that can be transported up the sewer and remains present to control dissolved sulfide if anaerobic conditions develop. If the $\text{Fe}\sim\text{P}\sim\text{OH}$ precipitate is not completely used up, it will serve a useful function in providing supplementary chemical P removal in the WWTP.

Similarly, magnesium hydroxide “locks” dissolved sulfide in the non-volatile ionic forms (mainly HS^- with traces of S^{2-}) at a pH in the range ~8.0 to 9.0 irrespective of whether conditions are aerobic, anoxic or anaerobic. Moreover, the chemical dosed will deliver useful alkalinity to the WWTP. Many WWTPs require alkalinity supplementation in any case to achieve stable biological nitrogen removal, especially where supplementary chemical P removal (typically with alum or iron salts) is practiced. Magnesium hydroxide dosing in the catchment will therefore at least partially offset supplementary alkali dosing at the WWTP,

One of the key uncertainties in the cost-effectiveness of oxygen is the efficiency of its injection. Inefficient (coarse bubble) injection directly into the rising main pipeline can result in significant loss of undissolved gas from air release valves downstream (or manholes and vent pipes where the system incorporates gravity sections). In this study we were unable to directly measure the efficiency of oxygen injection but the models suggested that it lies in the range approximately 20 to 50%.

For the cost comparisons presented in above (Scenarios 1 & 2), an injection efficiency of 40% was adopted, based on modelling a full-scale rising main pipeline where residual dissolved oxygen was measured *in situ*. If the efficiency is lowered to 20%, the outcome of the financial analysis is not changed. However, the margin in whole of life cost (NPV) difference between oxygen injection and the next cheapest option (nitrate dosing in Scenario 1) is reduced from \$1.8 million (about 40% cheaper) to approximately \$0.3 million (6% cheaper). In Scenario 2, ferrous chloride dosing might be cost-comparable to oxygen (or marginally cheaper on an NPV basis) if oxygen injection efficiency is as low as 22%. More careful investigation of the efficiency of oxygen injection (e.g. using updated and better diffuser systems) seems warranted. The position of oxygen (or nitrate) injection relative to the target point for odour control (e.g. WWTP) is critical and needs to be based on dynamic model simulation.



CONCLUSIONS

Depending on the emphasis on cost minimization by Gold Coast Water, a full-scale trial of one or more of the alternative chemicals to oxygen is warranted. The financial analysis shows that oxygen is likely to be the most cost-effective if the dosing efficiency and location are optimised. On balance, ferrous chloride may be the next best alternative to oxygen, given that it may have indirect cost offsets against savings on chemicals for supplementary P removal in the WWTP and is not as labile as oxygen. Laboratory data from this research project suggest that the iron dose required may be lower than suggested by suppliers or manuals of practice ("industry experience"). To test this premise and truly minimize cost at full-scale, it will be important to optimise not only dosing location but also iron dosing control based on dynamic model predictions. The objective will be to ensure a sufficiently high dose of chemical for diurnal periods (or "slugs of wastewater pumped into the rising main) when retention times and sulphide production are expected to be high. To this extent, simulation using dynamic models is an invaluable tool.

Finally it should be noted that this case study was focussed on a rising main sewer system. Sulphide production rates in gravity sewers follow the same mechanism but the net production rates will differ for partially filled pipes, particularly if significant gas transfer (including oxygen) occurs. Oxygen dosing is not appropriate for gravity sewers, since these are not pressurised but vented to the atmosphere. Oxygen solubility limitations as well as losses of oxygen and stripping of gases to atmosphere are therefore likely to be problematic. Nevertheless, with the exception of oxygen, on a relative basis the findings made in this paper regarding chemical dosing for hydrogen sulfide control are expected to be similar for gravity mains.

Main conclusions of the study are:

1. H₂S discharge can be effectively controlled using any of the chemicals by choosing a right dose and adding to sewer at proper locations. The model served as a very good tool to optimize both the dose and the location.
2. Chemical dosing can be manipulated to achieve a set target H₂S level.
3. The selection of location is critical for both oxygen and nitrate. Targeting oxidation of produced sulfide rather than attempting prevention of its formation gives better results in terms of chemical use. Also oxidation of VFA can be minimized using this approach.
4. A greater flexibility in relation to the location of injection point has been demonstrated. A window of about 2 km is available for the selection of a proper injection site without affecting the effectiveness of sulfide control.
5. Location is not important for Fe²⁺, Fe³⁺ or Mg(OH)₂. Also, additional benefit of using these chemicals is that a low H₂S levels (total sulfide in case of Fe and dissolved H₂S in case of Magnesium Hydroxide) can be maintained over a longer length of sewer.



4.11. CASE STUDY 2: THE BELLAMBI-WOLLONGONG RISING MAIN

4.11.1. BACKGROUND

The Bellambi-Wollongong Rising Main pumps sewage from Bellambi catchment to Wollongong STP. The average DWF is 21 ML/d with variable speed pump capacity of 240-800 L/s. The rising main system is 10 km long and 600-750mm in diameter. The hydraulic retention time in the pressure main is 2.5-8.5 hours. Severe odour and corrosion problem exist at Wollongong STP. SWC is investigating different options for solving this problem. The Sewer Model described in this report has been used for this purpose.

The following sections describe the validation of the model that is to be used for optimizing the chemical dosage of the current ferric dosing and also for investigating the alternative options for sulfide control.

4.11.2. BASELINE STUDY WITHOUT Fe³⁺ DOSING

Simulation of the Bellambi-Wollongong Rising Main for the case without Fe³⁺ dosing was done with the available flow profile, SCAN measure sulfide and COD data, pH data for wet-well and the rising main, and the IC measured sulfate and sulfide concentrations. Feed wastewater characteristics were derived from the monitoring data for wet-well (April, 2007). Typical concentrations have been assumed for parameters that were not monitored. A comparison of simulation results and the measured data for various parameters is presented in Figure 55.

The SCAN measured dissolved sulfide concentrations were significantly higher than those predicted by the model. The variation in measured sulfide was also large, which evidently was related to the variability of pH. It is worth mentioning here that the SCAN measures only the dissolved H₂S concentration and the total dissolved sulfide concentration is calculated based on the pH.

Looking at all the measured SO₄ and sulfide data available, the total sulphur (sulfate+sulfide) never exceeded 15 mg S/L. It is therefore reasonable to assume SO₄ concentration in the feed as 15 mg S/L, which has been confirmed from the data obtained on 17th April. With this sulfate concentration, the dissolved sulfide concentration would never exceed 15 mg S/L. However, the SCAN results have shown the sulfide concentrations of as high as 25 mg S/L. It is likely that there were problems with either pH measurement or the SCAN measurement, which needs further investigations. For this exercise, the SCAN measured sulfide data is not considered and the results are compared with available IC data instead. It should be borne in mind that only limited IC data was available, which did not allow for a comprehensive comparison of the results to be made.

The model was able to predict the trend in COD and pH changes reasonably well, though there were some discrepancies in the values. The model predicted values were generally higher than the measured values.



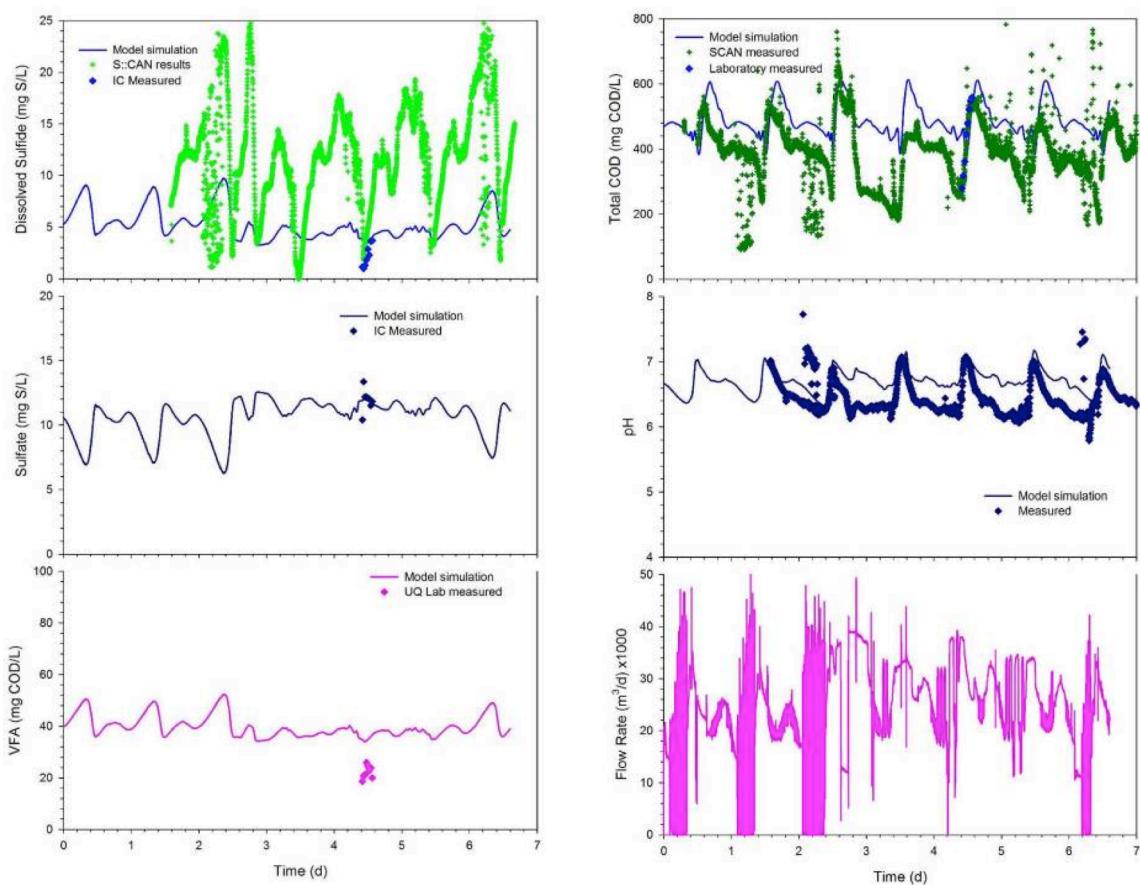


Figure 55. Model Simulation Results for the case without Fe^{3+} dosing

4.11.3. FLOW PACED Fe^{3+} DOSING

Simulation of the Bellambi-Wollongong Rising Main for the case with flow paced Fe^{3+} dosing was done with the available flow profile, SCAN measure sulfide and COD data, pH data for wet-well and the rising main, and the IC measured sulfate and sulfide concentrations. Feed wastewater characteristics were the same as those used in previous simulation. It was assumed that no phosphate precipitation occurs as long as sulfide is present in the wastewater and all the available iron is used up by sulfide before phosphate could be precipitated. This is based on the results of an ongoing laboratory study. A comparison of simulation results and the measured data for various parameters is presented in Figure 56 to Figure 57.

For the first case (25th -27th of March) the SCAN measured data was from the one provided by Sydney Water. For the second case (29th -31st of March), however, SCAN measured H_2S data was available only for a short period of time. Without any pH data available, the dissolved sulfide concentrations shown in the figure were estimated assuming wastewater pH of 7.0.

The model underestimated the H_2S concentrations in the first case, while the predictions were reasonably good in the second case. The model was also able to predict the trend in COD and pH changes reasonably well, though there were some discrepancies in the values. The model predicted values were generally lower than the measured values. The measured VFA concentrations were much lower than the model predictions. This is most likely due to VFA consumption in processes not included in the model (such as CH_4 production).



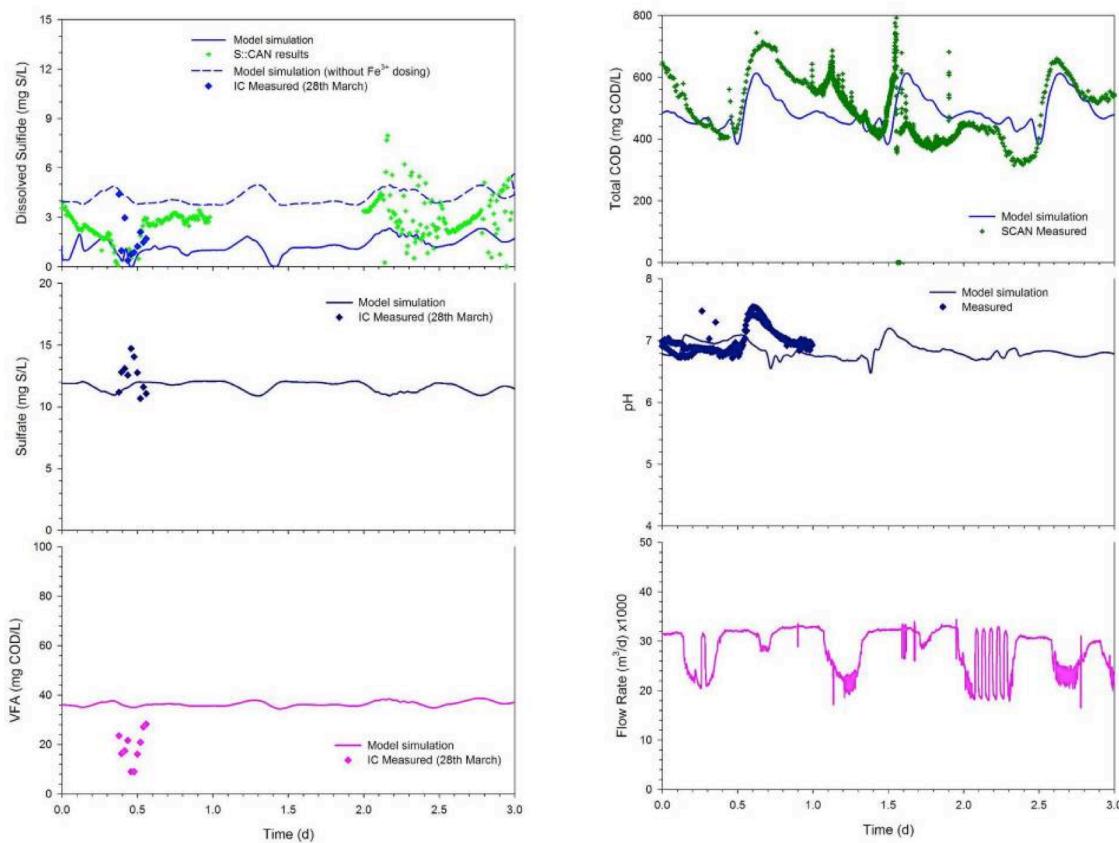


Figure 56. Model Simulation for flow paced Fe^{3+} dosing: Period I (25th -27th March)



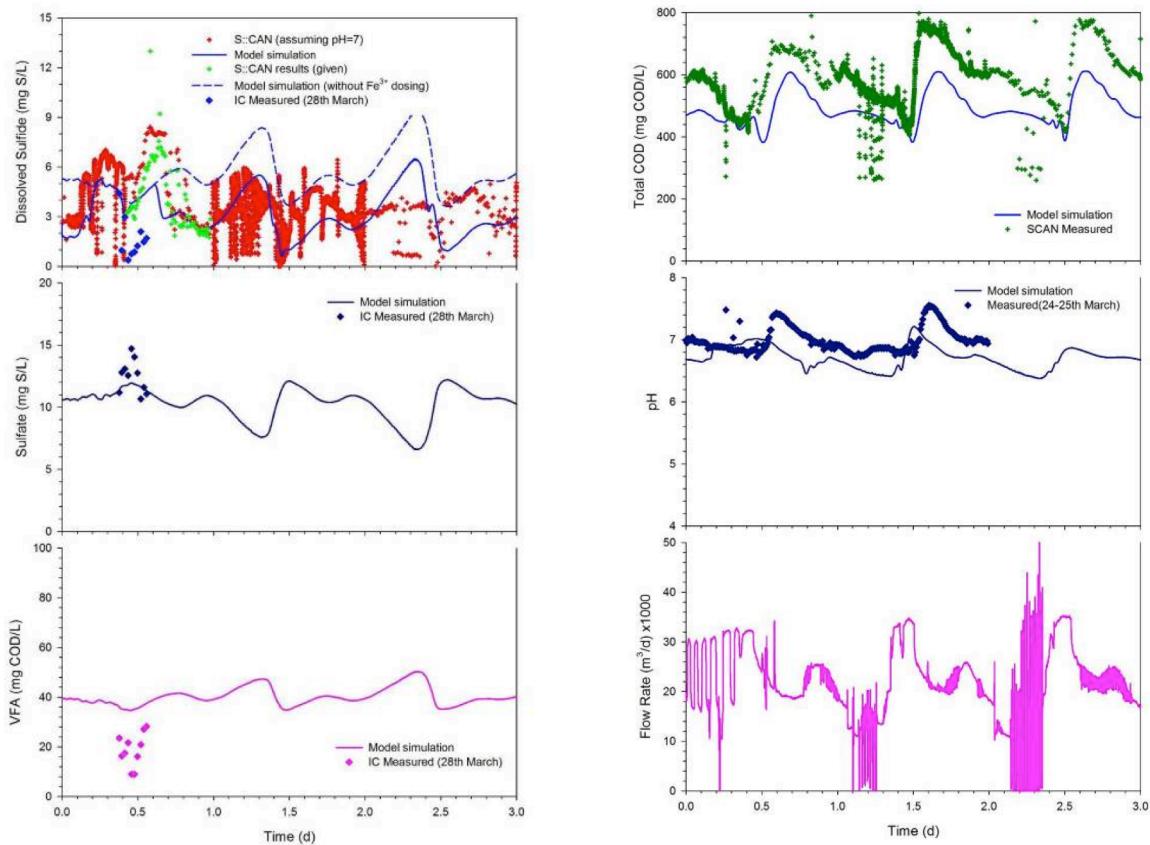


Figure 57. Model Simulation for flow paced Fe^{3+} dosing: Period II (29th-31st March)

4.11.4. HRT BASED Fe^{3+} DOSING

Simulation was done for the case with HRT based Fe^{3+} dosing using the data that was available. Feed wastewater characteristics were same as those used in previous simulation. A comparison of simulation results and the measured data for various parameters is presented in Figure 58.

The model was able to predict the levels of H_2S reasonably well in this case. The model was also able to predict the trend in COD and pH changes reasonably well, though there were some discrepancies in the values. The model predicted values were generally higher than the measured values. The measured VFA concentrations were much lower than the model predictions. As in the previous case, this is most likely due to VFA consumption in processes not included in the model.



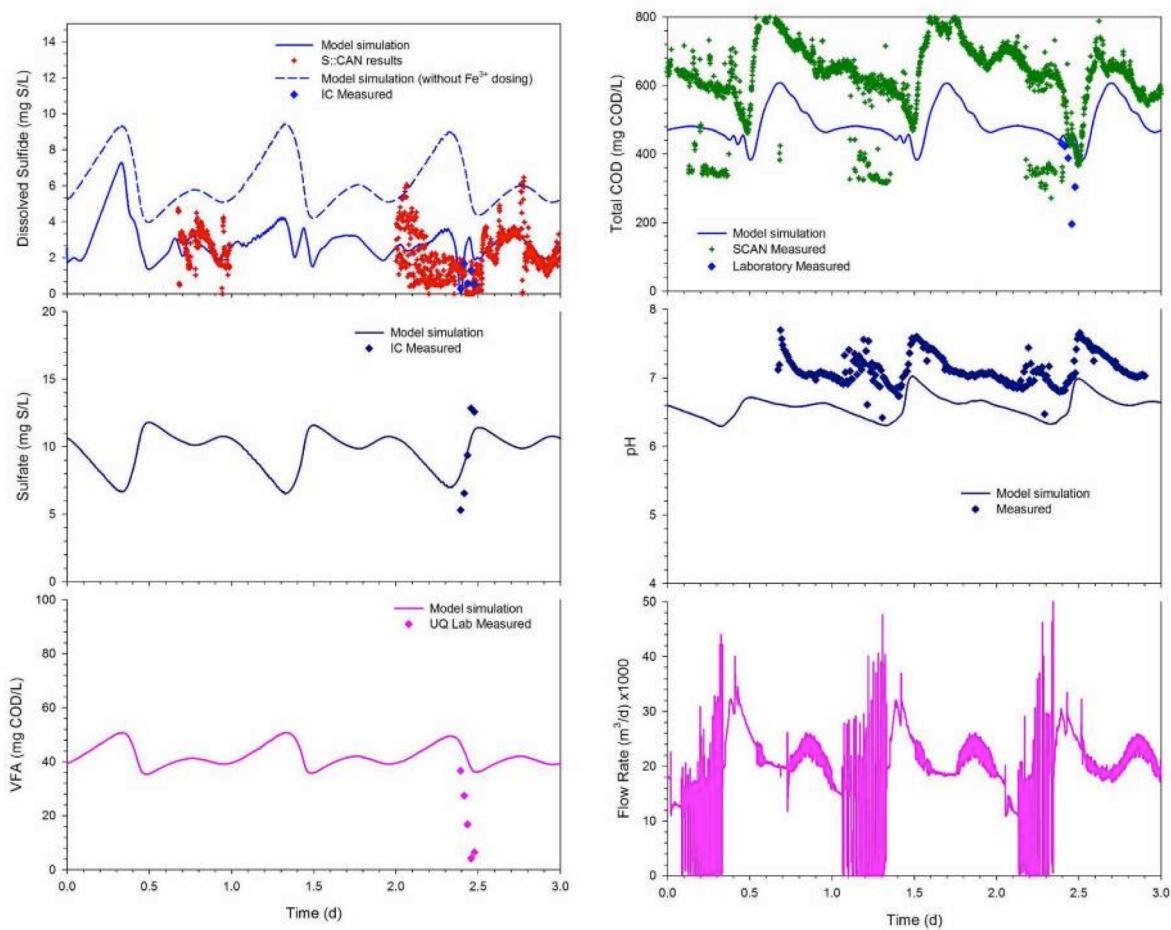


Figure 58. Model Simulation Results: HRT Based Fe^{3+} Dosing (2nd - 4th April)

5. FUTURE RESEARCH

- SEWER MONITORING. Few on-line sensors are now available for the monitoring of sewer systems. Sensors that are regularly used by the wastewater industry are even fewer, often limited to flow meters and in some cases the gas phase H₂S meters. In the current project, data were collected using intensive measurement campaigns. Each of these typically required multiple staff members working at different sites in a sewer network and in shifts for 24 – 30 hours (to cover diurnal variations). This can clearly not be accepted as an industry standard for routine sewer monitoring. *To measure is to know.* Reliable sensors and sensor networks should be developed for optimal sewer management.
- DYNAMIC CONTROL OF CHEMICAL DOSAGE. Due to the lack of on-line sensors, the on-line dynamic control of chemical dosage to sewer systems for H₂S control is not investigated in the current project. However, sewer systems are highly dynamic and optimal sewer management require on-line control. This will be possible when on-line sensors for sewer monitoring are made available.
- NETWORK-WIDE MANAGEMENT AND OPTIMISATION. The current project is limited to the H₂S control of an isolated sewer section. Optimal sewer management requires decisions to be made towards an overall goal of H₂S management for the entire network possibly including the downstream wastewater treatment plant(s), instead of (or in addition to) the localised management objectives. The choices of proper sites for chemical addition, appropriate target sulfide levels at these locations and suitable H₂S control strategies are interrelated and should be optimised for the entire network.
- UNDERSTANDING OF THE CORROSION PROCESSES. The current project focuses on minimising the production of H₂S and its emission to the gas phase. The actual corrosion processes are out of the scope of the project. Understanding the corrosion processes, in particular the knowledge on the factors controlling the rate of corosions, is critically important for setting proper limits for H₂S emission.
- NOVEL H₂S CONTROL STRATEGIES. The current project is limited to understanding and assessing existing H₂S control strategies. There is a need for innovative strategies which could revolutionise H₂S management.



6. REFERENCES

- Batstone, D.J., Keller, J., Angelidaki, I., Kalyuzhnyi, S., Pavlostathis, S.G., Rozzi, A., Sanders, W.T.M., Siegrist, H., and Vavilin, V.A. (2002) Anaerobic Digestion Model 1. Scientific and Technical Report 13. IWA Publishing.
- Boon, A.G. (1995) Septicity in sewers: Causes, consequences and containment. *Water Sci. Technol.* 31(7), 237-253.
- Hvitved-Jacobsen, T. (2002) *Sewer processes: Microbial and chemical process engineering of sewer networks*, CRC PRESS, Washington D. C.
- Hvitved-Jacobsen, T., Raunkjaer, K., Nielsen, P.H. (1995) Volatile fatty acids and sulfide in pressure mains. *Wat. Sci. Technol.* 31(7), 169-179.
- Mark, O., Appelgren, C. and Larsen, T. (1995) Principles and Approaches for Numerical Modelling of Sediment Transport in Sewers. *Wat. Sci. Tech.* 31(7), 107-115.
- Schlüter, F. (1999) A Conceptual Model for Sediment Transport in Combined Sewer Systems. *Wat. Sci. Tech.* 39(9), 39-46.
- Thistlethwayte, D. T. (1971) *The control of sulfides in sewerage systems*, Butterworth, Sydney.
- USEPA (1974) Process design manual for sulfide control in sanitary sewerage systems. 625/1-74-005, USEPA, Washington, D.C.

