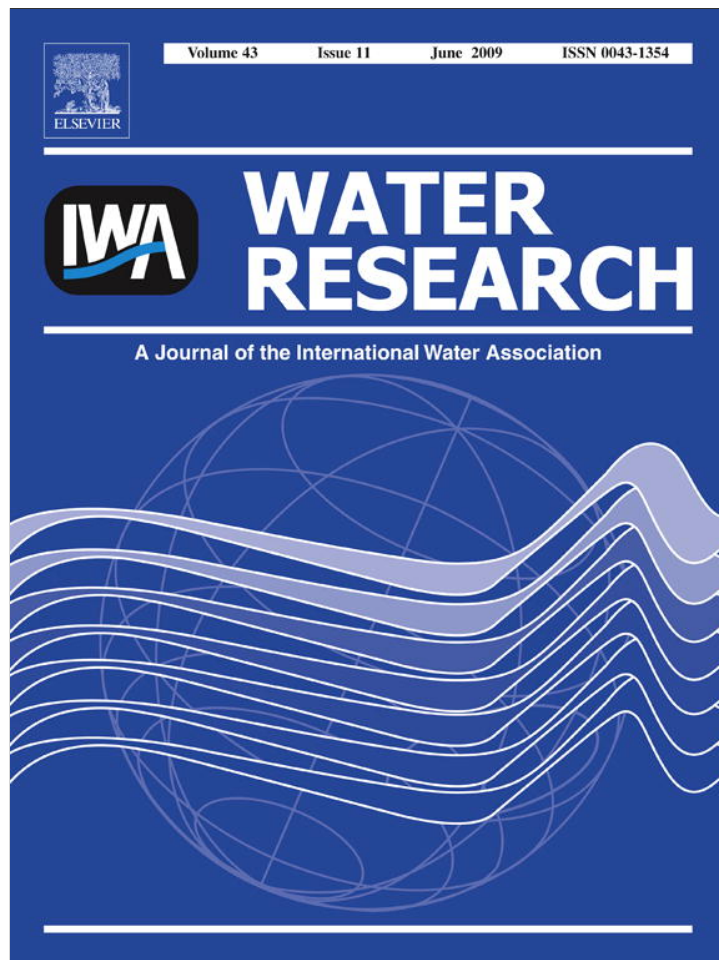


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Development of a model for assessing methane formation in rising main sewers

Albert Guisasola^{a,b,1}, Keshab R. Sharma^{a,2}, Jurg Keller^{a,3}, Zhiguo Yuan^{a,*}

^aAdvanced Water Management Centre, The University of Queensland, St. Lucia, 4067 Queensland, Australia

^bDepartament d'Enginyeria Química, ETSE, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

ARTICLE INFO

Article history:

Received 18 November 2008

Received in revised form

24 March 2009

Accepted 24 March 2009

Published online 5 April 2009

Keywords:

Sewers

Greenhouse gas emissions

Methane

Methanogens

Sulfate-reducing bacteria

Sulfide

Modelling

ABSTRACT

Significant methane formation in sewers has been reported recently, which may contribute significantly to the overall greenhouse gas emission from wastewater systems. The understanding of the biological conversions occurring in sewers, particularly the competition between methanogenic and sulfate-reducing populations for electron donors, is an essential step for minimising methane emissions from sewers. This work proposes an extension to the current state-of-the-art models characterising biological and physicochemical processes in sewers. This extended model includes the competitive interactions of sulfate-reducing bacteria and methanogenic archaea in sewers for various substrates available. The most relevant parameters of the model were calibrated with lab-scale experimental data. The calibrated model described field data reasonably well. The model was then used to investigate the effect of several key sewer design and operational parameters on methane formation. The simulation results showed that methane production was highly correlated with the hydraulic residence time (HRT) and pipe area to volume (A/V) ratio showing higher methane concentrations at a long HRT or a larger A/V ratio.

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1. Introduction

The build-up of hydrogen sulfide in sewer systems is a well-known problem resulting in sewer wall corrosion, serious health hazards and odour nuisance (Pomeroy, 1959; U.S. EPA, 1974; Boon, 1995; Hvitved-Jacobsen, 2002). Hydrogen sulfide is formed when the organic matter present in sewage is oxidised under sulfate-reducing anaerobic conditions. However, hydrogen sulfide is not the only detrimental emission from sewer systems. In a recent study, Guisasola et al. (2008) demonstrated that a significant amount of methane (20–100 mg/L as Chemical

Oxygen Demand or COD) was formed in the sewers studied. Methane is a potent greenhouse gas with a global warming potential of 21–23 times higher than carbon dioxide (Minami and Takata, 1991; IPCC, 2006). Its emission therefore would have a significant impact on the overall greenhouse gas emissions of urban wastewater systems (Guisasola et al., 2008), also called carbon footprint, and therefore has to be minimised.

The understanding and modelling of methanogenic and sulfidogenic processes in sewers is highly valuable for its optimal operation. In anaerobic environments, both sulfidogenesis (i.e. sulfate reduction) and methanogenesis (i.e. CO₂

* Corresponding author. Tel.: +61 7 3365 4374; fax: +61 7 3365 4726.

E-mail addresses: albert.guisasola@uab.cat (A. Guisasola), keshab@awmc.uq.edu.au (K.R. Sharma), j.keller@awmc.uq.edu.au (J. Keller), zhiguo@awmc.uq.edu.au (Z. Yuan).

¹ Tel.: 34 9 3581 2695; fax: 34 9 3581 2013.

² Tel.: 61 7 3365 7204; fax: 61 7 3365 4726.

³ Tel.: 61 7 3365 4727; fax: 61 7 3365 4726.

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doi:10.1016/j.watres.2009.03.040

reduction, acetate utilisation) are similarly favoured from an energetic point of view. The two processes are expected to occur simultaneously using organic materials in wastewaters as electron donors. The synergistic or competitive interactions between methanogenic archaea (MA), sulfate-reducing bacteria (SRB) and fermentative bacteria (FB) are important.

Previous research on the modelling of in-sewer biological processes primarily focused on predicting sulfide formation and emission. Pomeroy (1959), Thistlethwayte (1972), and Boon and Lister (1975) proposed empirical equations to predict sulfide formation depending on organic strength (COD or BOD – Biochemical Oxygen Demand), pipe characteristics and flow conditions. More recently, the WATS (Wastewater Aerobic/Anaerobic Transformations in Sewers) model was developed, which describes in considerably more detail the carbon and sulfur transformations in sewers (Hvitved-Jacobsen et al., 2000). The WATS model has been extended several times to account for oxygen addition (Gudjonsson et al., 2002), anoxic conditions (Abdul-Talib et al., 2005), emission of sulfide to the gas phase (Yongsiri et al., 2003; Nielsen et al., 2005a) and chemical sulfide oxidation (Nielsen et al., 2005b, 2006). Despite all these developments, the application of the WATS model has so far been limited to sewer systems under steady state conditions (Nielsen et al., 2005a; Mourato et al., 2003). On the other hand, Huisman et al. (2003) aimed to unify the traditional transport and conversion models for sewers with the Activated Sludge Model No. 3 (ASM3) (Henze et al., 2000) in a new sewer system model. This model was shown to describe successfully the aerobic conversions occurring from the households through the sewer to the outlet of the wastewater treatment plant (WWTP). Sharma et al. (2008) have recently developed a sewer model to describe the dynamics of sulfide production in sewer systems. In addition to components characterising the aerobic, anoxic and anaerobic carbon, sulfur and nitrogen conversions, the model also describes several chemical reactions including the most important acid/base systems in typical wastewaters so that pH can be predicted. The model was successfully used to predict both temporal and spatial variations of sulfide (and other sulfur and carbon species) concentrations as a function of wastewater composition, pipe diameter and hydraulic flow. However, none of these models considered methane formation in sewers. This not only results in the inability of these models to predict methane emission from sewers, but also leads to inaccurate predictions of the COD concentration in the wastewater.

This work aims to enhance the current sewer models with the capability to predict methane formation in rising main sewers. First of all, the model presented in Sharma et al. (2008) was extended to account for the competition between SRB and MA for the common electron donors. This was done based on similar work previously reported for several other anaerobic environments such as wetlands, rice paddies, landfills or anaerobic sludge and wastewater treatment systems (*inter alia* Sørensen et al., 1981; Oremland and Polcin, 1982; Gupta et al., 1994; Bhattacharya et al., 1996; Kalyuzhnyi and Ferdorovich, 1998; Sahrawat, 2004; Khanal and Huang, 2005). The model was then calibrated using experimental data obtained from a lab-scale sewer system, and compared with field data. Finally, the significance of methanogenesis in sewers was investigated through simulation studies. The impact of several key

parameters, including the hydraulic retention time and the geometric dimensions of the sewer pipes, was assessed.

2. Model formulation

The sewer model presented in Sharma et al. (2008) was extended to account for methanogenic activity with the processes displayed in Table 1 and schematically summarised in Fig. 1. The temperature factor was modelled as in the WATS model (Hvitved-Jacobsen, 2002). The biofilm-catalysed processes were modelled using the Monod kinetics, and higher values of saturation constants were used to account for diffusion limitations in biofilms. MA are known to be good scavengers of acetate or hydrogen as electron donors (Robinson and Tiedje, 1984; Isa et al., 1986; Yoda et al., 1987; Raskin et al., 1996). Both of these two processes are considered in the model. The acetoclastic methanogenesis is known to be the predominant mechanism when Methanosaetaceae are present in the biomass (Karashev et al., 2006). Fermentation consists of the transformation of the fermentable COD to VFA (Volatile Fatty Acids) and molecular hydrogen. The prediction of the type and amount of VFA produced in this process is a current focus of interest for many researchers aiming to model anaerobic digestion (Rodriguez et al., 2006). In Sharma et al. (2008), acetate was assumed to be the only fermentation product, in line with the IWA activated sludge model (Henze et al., 2000). As H₂, which is produced by fermentation, is an electron donor for methanogens, fermentation is in this study modelled as two separate processes: acetogenesis and acidogenesis. Consequently three fermentation products are considered, namely H₂, acetate and propionate. Glucose is used in the reaction to represent fermentable substrates (e.g. sugars or other carbohydrates), in the same way as the widely used Anaerobic Digestion Model Nr. 1 (ADM1, Batstone et al., 2002). SRB tend to outcompete acetogenic bacteria for propionate utilisation due to their strong affinity for the carbon substrate (Rinzema and Lettinga, 1988; Uberoi and Bhattacharya, 1997). Given the fact that direct propionate utilisation by methanogens is not possible (i.e. propionate is converted to acetate and hydrogen) (Öztürk, 1991) and that propionate concentrations in real sewage were always lower than 10 mgCOD/L (see the Results section), propionate was considered as an electron donor only for sulfate reduction.

SRB are known to be able to use a variety of substrates as electron donors including H₂, acetate and propionate (Nielsen and Hvitved-Jacobsen, 1988). While sulfate reduction using fermentable substrates (e.g. sugars or other carbohydrates) is also possible, it is not considered in our model. Fermentative bacteria are likely able to outcompete SRB for these compounds (Kalyuzhnyi and Ferdorovich, 1998). Also, the use of these substrates by SRB is accounted for by the use of the fermentation products from these substrates.

3. Materials and methods

3.1. Lab-scale experimental set-up

The laboratory experimental set-up, simulating a rising main sewer (Fig. 2), consisted of four completely mixed air-tight

Table 1 – Stoichiometry and kinetics of the model describing the interactions among MA, FB and SRB.

	CH ₄ (Methane)	C ₂ H ₄ O ₂ (Acetate)	C ₆ H ₁₂ O ₆ (Glucose)	C ₃ H ₆ O ₂ (Propionate)	CO ₂	H ₂	H ₂ O	H ₂ SO ₄	H ₂ S	Kinetics
Hydrogenotrophic methanogenesis	1					-1	-4	2		$k_{CH_4,H_2} \cdot \frac{S_{H_2}}{K_{H_2,MA} + S_{H_2}} \cdot \frac{A}{V} \cdot \alpha^{T-20}$
Acetoclastic methanogenesis	1	-1			1					$k_{CH_4,SAC} \cdot \frac{S_{AC}}{K_{S_{AC},MA} + S_{AC}} \cdot \frac{A}{V} \cdot \alpha^{T-20}$
Acetogenesis		2	-1		2	4	-2			$q_{ACETO} \cdot \frac{S_F}{K_F + S_F} \cdot \frac{A}{V} \cdot \alpha^{T-20}$
Acidogenesis		2	-3	4	2	2				$q_{ACIDOG} \cdot \frac{S_F}{K_F + S_F} \cdot \frac{A}{V} \cdot \alpha^{T-20}$
Hydrogenotrophic sulfidogenesis						-4	4	-1	1	$k_{H_2,S,H_2} \cdot \frac{S_{H_2}}{K_{H_2,SRB} + S_{H_2}} \cdot \frac{S_{SO_4}}{K_{SO_4} + S_{SO_4}} \cdot \frac{A}{V} \cdot \alpha^{T-20}$
Acetate-based sulfidogenesis		-1			2	2	-1	1		$k_{H_2,S,SAC} \cdot \frac{S_{AC}}{K_{AC,SRB} + S_{AC}} \cdot \frac{S_{SO_4}}{K_{SO_4} + S_{SO_4}} \cdot \frac{A}{V} \cdot \alpha^{T-20}$
Propionate-based sulfidogenesis		1		-1	1	2	-3/4	3/4		$k_{H_2,S,SPROP} \cdot \frac{S_{PROP}}{K_{PROP} + S_{PROP}} \cdot \frac{S_{SO_4}}{K_{SO_4} + S_{SO_4}} \cdot \frac{A}{V} \cdot \alpha^{T-20}$

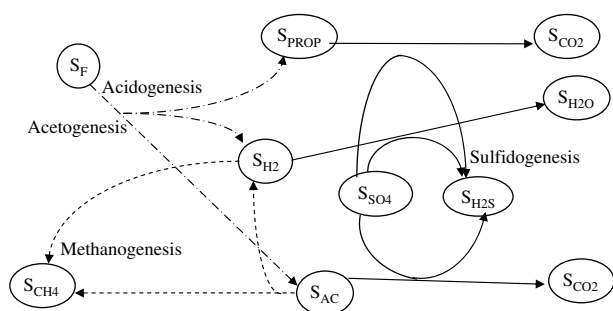


Fig. 1 – Schematic representation of the presented biological model. SRB processes (solid line), FB processes (dash-dotted line) and MA processes (dashed line).

reactors in series (named RM1–RM4), each with a volume of 0.75 L. The diameter of the reactors was 80 mm, resulting in an A/V ratio of 56.7 m²/m³ by considering the biofilm areas both on the wall and on the top of the reactor. There was no visible biofilm growth on the bottom of the reactor due to the use of a magnetic stirrer, see below. The system was intermittently fed with real sewage that had been screened and settled, using a peristaltic pump following a typical operating pattern observed at a rising main at the Gold Coast, Australia. The feed pattern consisted of sixteen pumping events per day, each lasting for 2 min, which resulted in an average HRT in the system of 6 h with minimum and maximum HRTs of 2 and 10 h respectively. The system was maintained under quiescent conditions except during pumping events, when the reactors were stirred via magnetic stirrers. All the experiments were conducted at a temperature of 22 ± 1 °C. Fresh sewage was collected weekly from the Robertson Park pumping station, Indooroopilly (Brisbane), which primarily collects domestic wastewater from the local area, and thus contains a low amount of sulfide (<1 mg S/L) and methane (<5 mg COD/L). The average composition of the fresh sewage was 15 mg SO₄-S/L and 200 mg/L of soluble COD, of which the VFA content was approximately 50 mg COD/L as acetate and 15 mg COD/L as propionate. Sewage was stored at 4 °C to minimise biological transformations and warmed to 20 °C through a heat exchanger and water bath before entering the reactor system.

After several months of operation, an anaerobic biofilm was fully developed in the laboratory system, leading to pseudo-steady state conditions. Baseline monitoring of the system showed that the trend of sulfide production in the

laboratory sewer system was similar to that in a real rising main in the Gold Coast (Hutchinson and Hamilton, 2005). In addition to the batch tests (described below), the experimental system was monitored with periodic sampling of methane, VFA and soluble sulfur species.

Batch tests were performed on RM2 and RM3 to assess the methanogenic and sulfate-reducing activity of the biofilms. During a batch test, the selected reactor was temporarily isolated from the system. At the start of each batch test, the reactor was carefully emptied and drained before being filled with fresh sewage. Each batch test lasted for 7 h. Methane, VFA, COD and soluble sulfur species (sulfate, sulfite, thiosulfate and sulfide) were periodically measured using methods to be further described. A sampling frequency of 30 min was maintained for the first 3 h, while the last 5 h were sampled hourly.

Several batch tests were also conducted to assess the methanogenic and sulfidogenic activity in the reactors with acetate as the sole electron donor. For this purpose, a synthetic sewage consisting of macronutrient solution (NH₄Cl: 0.204 g/L, MgCl₂·6H₂O: 0.039 g/L, CaCl₂: 0.074 g/L, MnSO₄·H₂O: 0.001 g/L, FeSO₄·7H₂O: 0.053 g/L, KH₂PO₄: 0.058 g/L, K₂HPO₄: 0.098 g/L, NaHCO₃: 0.090 g/L, Na₂SO₄: 0.089 g/L) was used. Acetate was added as sodium acetate resulting in an initial concentration of 50 mg COD/L in the reactor. Sulfate concentration was maintained at an intended level through manual addition of sodium sulfate. Two different sulfate concentrations were tested (15 and 50 mg S/L), resulting in a variable COD/S ratio (from 0.7 to 3.3).

3.2. Field data

Field measurements of methane and sulfide were obtained in a rising main (UC09) operated by Gold Coast Water (Australia). The UC09 is a 1084 m long rising main with a pipe diameter of 150 mm and an average flow rate of 123 m³/d. The sites and times of sampling were chosen to cover a wide range of hydraulic retention times (HRT). A measurement campaign was conducted, during which hourly samples were collected for 10 h at the end of the rising main and analysed for sulfide and methane. A detailed description of the sampling procedure can be found in Sharma et al. (2008). The wastewater typically contained 440 mg/L of total COD, 230 mg/L of soluble COD, 14 mg COD/L of VFA and 17 mg S/L of sulfate on average. The wastewater temperature ranged from 24 to 27 °C during the measurement campaign.

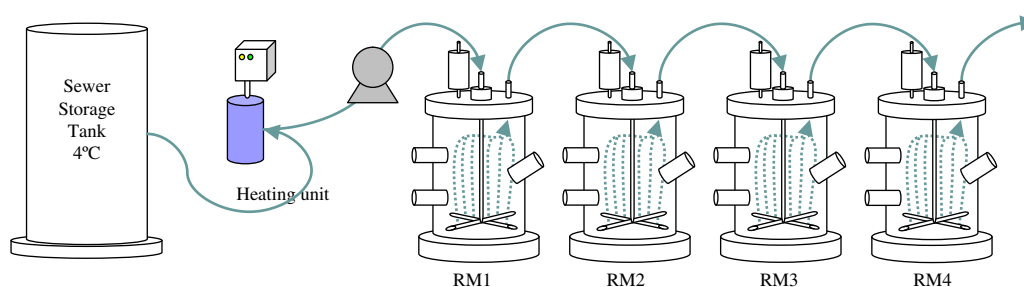


Fig. 2 – Schematic representation of the lab sewer experimental set-up.

3.3. Chemical analysis

Samples for analysis of soluble sulfur species were immediately preserved with a special sulfide anti-oxidant buffer that allows storing the samples at 4 °C for at least four days without deterioration of any of the sulfur species, as described by Keller-Lehmann et al. (2006). The soluble sulfur species were measured using an ion chromatograph with a UV and conductivity detector (Dionex ICS-2000). VFA were measured by gas chromatography using a Perkin Elmer Autosystem equipped with a polar capillary column DB-FFAP and a flame ionisation detector (FID). Soluble COD was measured using the colorimetric method described in APHA (1995) using commercial Lovibond tubes in a range of 0–150 mg COD/L. The soluble COD was assumed to contain three different fractions: Volatile Fatty Acids (acetic, propionic, butyric, isobutyric, valeric, isovaleric and hexanoic), a readily fermentable fraction (S_F) and a poorly fermentable or inert fraction. The latter fraction was assumed as the amount of soluble COD remaining after a batch test (7 h). In fact, the readily biodegradable fraction of the soluble COD was usually degraded during the first 3–4 h (see Fig. 3 below). Thus, the readily fermentable COD was determined as the soluble COD minus the poorly fermentable and VFA COD fractions.

Dissolved methane was measured using a modification of the methodology described by Alberto et al. (2000). Methane was sampled into freshly vacuumed BD vacutainer tubes using a hypodermic needle attached to a filter and a 5 ml plastic syringe that contained the sewage sample. The tubes were mixed overnight in a shaker to allow equilibration of gas and liquid phases. Most of the methane (~97% at 25 °C) was transferred to the gas phase in this process. Then, methane concentration in the gas phase of the tubes was measured using a Shimadzu GC-9A Gas Chromatograph equipped with an FID. The concentration of methane in the initial liquid phase (reactor) was calculated using a mass balance and Henry's law.

3.4. Model implementation and parameter estimation

The model presented in Fig. 1 and Table 1 was implemented in MATLAB® 7.0.4 (The MathWorks, Natick, MA). Several batch

tests with off-line sulfide, sulfate, VFA, methane and non-VFA soluble COD measurements were used for model calibration. The model involves a great number of parameters and due to identifiability issues not all of them could be reliably estimated with these experimental batch tests. The substrate affinity constants of FB, MA and SRB for VFA and hydrogen were assumed from literature values and only the rates of the new processes added (Table 1) were estimated. Parameter estimation was carried out to estimate the seven maximum rates by using the Nelder-Mead Simplex minimization algorithm. The confidence intervals of parameter estimates were determined as described in Dochain and Vanrolleghem (2001) using the Fisher Information Matrix (FIM), equation (1). A detailed example of the utilisation of this technique is available in Guisasola et al. (2006).

$$\text{FIM} = \sum_{k=1}^N Y_{\theta}^T(t_k) Q_k Y_{\theta}(t_k) \quad (1)$$

where Y_{θ} is the so-called output sensitivity function and Q_k is the inverse of the covariance matrix of the measurement noise. Assuming no model mismatch, no data autocorrelation, white measurement noise (i.e. independent and normally distributed with zero mean) and uncorrelated errors (i.e. Q_k is a diagonal matrix), the inverse of the FIM (namely, the covariance matrix, COV, equation (2)) provides the lower bound of the parameter estimation error covariance matrix, which can be used for assessing the uncertainty of the parameter estimates.

$$\text{COV}(\theta_0) = \text{FIM}^{-1} \quad (2)$$

Then, approximate standard errors for the estimated parameters can be calculated as the square root of the diagonal elements of COV (equation (3)) and the confidence intervals of the parameters can be calculated as equation (4) for a certain confidence level (α) and t values obtained from the Student- t distribution.

$$\sigma(\theta_i) = \sqrt{\text{COV}(i, i)} \quad (3)$$

$$\theta \pm t_{\alpha, N-P} \cdot \sigma(\theta_i) \quad (4)$$

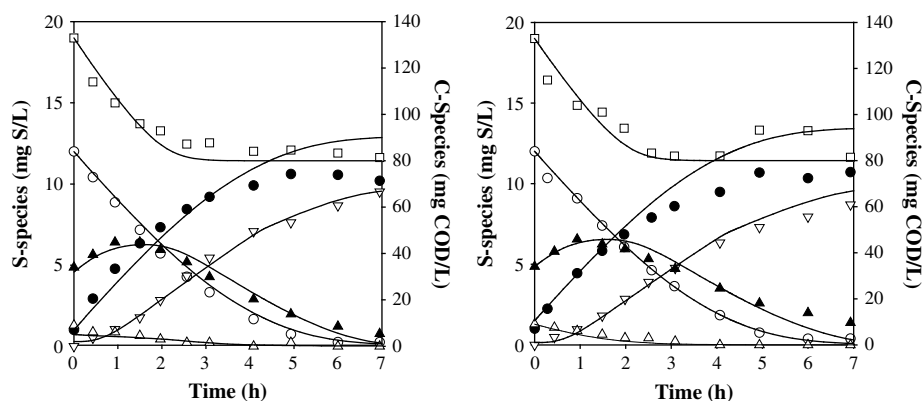


Fig. 3 – Model calibration: experimental and modelled profiles of various carbon and sulfur compounds during two batch experiments carried out on RM2 (left) and RM3 (right), respectively. Both reactors were fed fresh sewage at the start of the experiments. Experimental data: acetate (▲), propionate (△), methane (▽), non-VFA soluble COD (□), sulfate (○) and sulfide (●). Model predictions: solid lines.

To assess the correlations between the model parameters, the Correlation Matrix (CM) was calculated based on the COV matrix as described in equation (5):

$$CM(i,j) = \frac{COV(i,j)}{\sqrt{COV(i,i) \cdot COV(j,j)}} \quad (5)$$

The calibrated model was further integrated into the sewer model presented in Sharma et al. (2008) for the simulation of real rising main sewers.

4. Results and discussion

4.1. Calibration and validation of the conceptual model

The parameter estimates are presented in Table 2, along with the 95% confidence intervals of these estimates (Student-t = 1.782). The Correlation Matrix is shown in equation (6):

$$CM = \begin{matrix} & q_{ACETOG} & k_{CH_4,AC} & k_{H_2S,AC} & k_{CH_4,H_2} & k_{H_2S,PROP} & q_{ACIDOG} \\ q_{ACETOG} & 1.000 & -0.429 & 0.541 & 0.719 & -0.542 & -0.596 \\ k_{CH_4,AC} & -0.429 & 1.000 & -0.714 & -0.620 & 0.632 & 0.655 \\ k_{H_2S,AC} & 0.541 & -0.714 & 1.000 & 0.689 & -0.577 & -0.707 \\ k_{CH_4,H_2} & 0.719 & -0.620 & 0.689 & 1.000 & -0.654 & -0.930 \\ k_{H_2S,PROP} & -0.542 & 0.632 & -0.577 & -0.654 & 1.000 & 0.663 \\ q_{ACIDOG} & -0.596 & 0.655 & -0.707 & -0.930 & 0.663 & 1.000 \end{matrix} \quad (6)$$

The correlations between the parameters are acceptable. The highest correlation coefficient in CM is found between parameters q_{ACIDOG} and k_{CH_4,H_2} . The contour plot developed for these two variables around the optimum values (not presented in the paper) shows that, while the correlation between these two variables are fairly strong, it is sufficiently low to allow reasonable estimation of the parameter values.

It should be noted here that these parameters are derived from the experiments conducted at 22 ± 1 °C using domestic sewage. Two data sets obtained from two different reactors, namely RM2 and RM3 (Fig. 3), were used in the parameter estimation. An excellent fit could be achieved between the experimental and simulated profiles for methane, sulfur species and various COD fractions. The model accurately describes the experimental profiles obtained, particularly methane formation which is simultaneous to sulfate reduction. The model slightly over predicted sulfide production, indicating that sulfate was not completely stoichiometrically converted to sulfide, and the non-sulfide product(s) were not among those measured using the IC method (sulfite and thiosulfate). The inert or poorly fermentable fraction of the COD (S_I) was approximately 80 mg COD/L.

This model was validated with experimental data obtained in RM1 and RM4, which were not used for model calibration. Fig. 4 shows that the model predictions are in agreement with the experimental data sets of RM1 and RM4, which indicate that the model describes well the biological activities in RM1 and RM4. Figs 3 and 4 jointly indicate that both methanogenesis and sulfidogenesis can be reasonably well predicted with the simple conceptual model presented in Fig. 1.

4.2. Competition of MA and SRB in sewers

According to the parameter estimates (Table 2), it could be concluded that MA utilise both acetate and hydrogen in a more effective way than SRB. In fact, the hydrogen utilisation of SRB was found to be negligible when compared to hydrogenotrophic methanogenesis. The coexistence and even the out competition of SRB by MA in sulfate-reducing anaerobic environments are widely reported in the literature although it may seem to be in disagreement with the kinetics and thermodynamics of MA and SRB. This observation has been attributed to COD to sulfate ratios, mass transfer limitations, differences in microbial adhesion properties and sulfide toxicity (Isa et al., 1986; Nielsen, 1987; Yoda et al., 1987; Raskin et al., 1996).

Previous studies have shown that the COD/SO₄-S (mg COD/mg S) ratio is a key parameter in determining the competition between sulfate reducers and methanogens (Omil et al., 1998). A COD/S ratio of 6.08 was proposed as the threshold value, below which all the COD should be oxidised by SRB and thus methanogenesis could be prevented (Rinzema and Lettinga, 1988). The average COD/S ratio in the real sewage used was 13.3, resulting in sulfate limiting conditions. The relatively high COD to sulfate ratio would generally support the occurrence of methanogenesis in sewers.

Biofilms are the primary contributors to biological reactions in sewer systems. In a separate anaerobic batch study conducted using the effluent from a rising main sewer in the absence of sewer biofilms, the sulfide production rate was approximately 0.1 mg S/L, in comparison to a sulfate reduction rate of 4–6 mg S/L/h that is typically measured in our sewer reactors (in the presence of sewer biofilms). This suggests that the contribution of microorganisms in the planktonic phase has a negligible contribution to sulfide production and the same can be expected for methane production. The sewer biofilm being the main contributor to sulfide and methane production, mass transfer is likely to play an important role in the competition between SRB and MA in sewers. Sulfidogenesis requires sulfate as the electron

Table 2 – Parameter estimation values for the model presented in Fig. 3.

	Value	Units		Value	Units
q_{ACETOG}	12.2 ± 0.96	g COD _{GLUC} /m ² d	K_F	10	g COD/m ³
q_{ACIDOG}	2.14 ± 1.08	g COD _{GLUC} /m ² d	$K_{H_2,SRB}$	0.01	g COD/m ³
k_{H_2S,H_2}	<0.001	g S _{H_2S} /m ² d	$K_{AC,SRB}$	5	g COD/m ³
$k_{H_2S,AC}$	1.36 ± 0.16	g S _{H_2S} /m ² d	K_{PROP}	5	g COD/m ³
$k_{H_2S,PROP}$	0.90 ± 0.41	g S _{H_2S} /m ² d	K_{SO_4}	1.8	g S/m ³
k_{CH_4,H_2}	1.92 ± 0.52	g COD _{CH_4} /m ² d	$K_{AC,MA}$	1	g COD/m ³
$k_{CH_4,AC}$	4.44 ± 0.30	g COD _{CH_4} /m ² d	$K_{H_2,MA}$	0.002	g COD/m ³

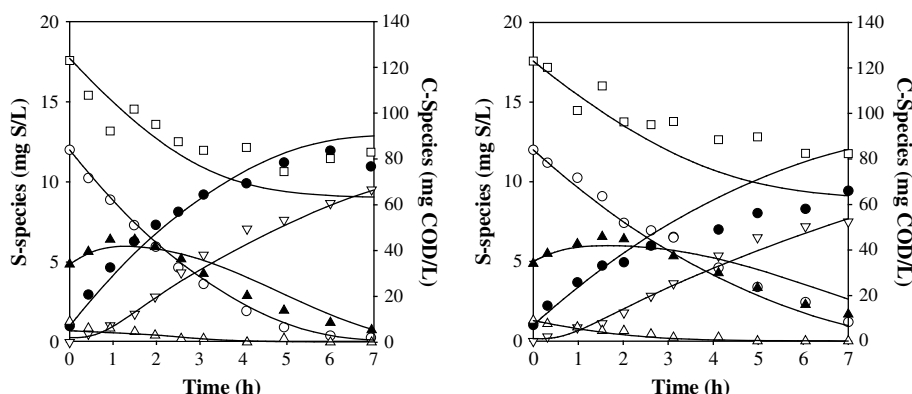


Fig. 4 – Model validation: experimental and modelled profiles of various carbon and sulfur compounds during two batch experiments carried out on RM1 (left) and RM4 (right), respectively. Both reactors were fed fresh sewage at the start of the experiments. Experimental data: acetate (▲), propionate (△), methane (▽), non-VFA soluble COD (□), sulfate (○) and Sulfide (●). Model predictions: solid lines.

acceptor and acetate, propionate or H₂ as the electron donors. While acetate, propionate or H₂ are produced in situ by FB, sulfate is transferred into biofilms through diffusion, which could be the limiting factor for the reactions in situations where sulfate concentration is low. In comparison, MA require acetate or H₂ and CO₂, all of which are produced in situ by FB. This implies that mass transfer limitations could favour MA over SRB. Fig. 5 shows the sulfate, VFA, methane and sulfide levels in RM2 and RM3 during the monitoring of the lab-scale sewer system over a 14 h period. As can be observed, VFA were present in both reactors at elevated levels (>20 mg COD/L). Considering the fact that VFA are produced in biofilms, an even higher concentration is expected in the biofilms. This implies that the methanogenesis process should not be limited by the substrate concentrations and high methane concentrations (>60 mg COD/L) were measured. In contrast, relatively low sulfate concentrations (lower than 5 mg SO₄-S/L) were observed in both reactors. Sulfate at such concentration would only partially penetrate into biofilms, limiting the development of SRB and thus their capability to compete with MA for the electron donors.

With respect to the use of acetate, the results indicate that acetate utilisation for methanogenesis is higher than for sulfidogenesis (Table 3). Neglecting the SRB and MA growth yields, the Ac-COD to S ratio for sulfate reduction (or sulfide production) is 2 g COD/gS and the Ac-COD to CH₄-COD ratio for methanogenesis is 1. The acetate uptake rate (AUR) to form sulfide would be $1.36 \times 2 = 2.72$ mg Ac-COD/m²/d, whereas the AUR due to methane formation would be 4.44 mg Ac-COD/m²/d. Thus, 38% of the acetate is utilised for sulfide production. This value was corroborated with several batch tests performed with acetate as the sole carbon source. In these experiments, sulfate was maintained constant with manual sulfate addition and both sulfide production and acetate consumption rates were calculated through a linear regression (Table 3). As can be observed, the percentage of acetate used for SRB is in agreement with the observation with real sewage that approximately one third of the metabolised acetate was used by SRB. Note that the ratio is specific for the particular sewer biofilm under study. For sewer biofilms developed under a different condition to that used in this study (e.g. with a different wastewater composition), this ratio

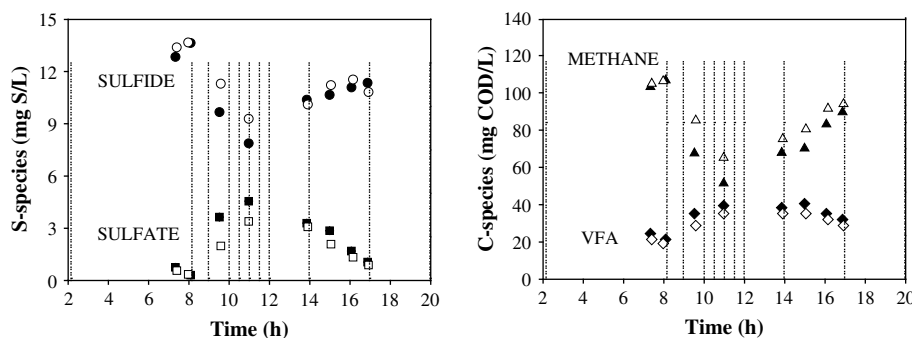


Fig. 5 – Sulfide (circles), sulfate (squares), VFA (diamonds) and methane (triangles) measurements in RM2 (black) and RM3 (white) during a normal operation of the lab-scale sewer system. Each vertical line represents a pumping event, during which 0.75 L of wastewater was delivered into the system. Methane and sulfide display similar and positive correlation with HRT. Frequent pumping events in the early morning resulted in shorter HRTs and lower methane and sulfide production.

Table 3 – Comparison of the experimental acetate uptake rate (AUR) and sulfide production rates (SPR) with the theoretical AUR due to sulfidogenesis (AUR_{TH}) in batch experiments with acetate as the sole carbon source.

Run	COD/S	AUR_{EXP} (g COD/m ³ /d)	PR (g S/m ³ /d)	$AUR_{TH} = SPR \times 2$ g COD/g S (g COD/m ³ /d)	% Of acetate consumed by SRB ($AUR_{TH}/AUR_{EXP} \times 100$)
A	1.07	206.9	34.3	68.6	33%
B	2.5	220.1	39.1	78.2	36%
C	2.9	141.4	24.7	49.4	35%

may be different, as a result of a different microbial structure and activity of the biofilm.

Finally, the estimated acetogenesis rate was more than six times higher than the estimated acidogenesis rate (Table 2). Experimentally, Fig. 3 shows that acetate rather than propionate was formed during the first 2 h of the batch tests, when fermentation occurred (evidenced by the decrease in the non-VFA soluble COD concentration). This is not surprising as FB gain considerably more energy from acetogenesis (4 mole ATP per mole of glucose) than from acidogenesis (4/3 mole ATP per mole glucose, Batstone et al., 2002). The rapid consumption of hydrogen produced during acetogenesis by MA ensures a low H₂ partial pressure in the reactor, further favouring the acetogenesis process.

4.3. Preliminary assessment of methane production in rising main sewers

The model was used to predict sulfide and methane formation in the UC09 sewer system of Gold Coast Water (Australia). The simulation results are compared to the field data in Fig. 6. The flow rate in the UC09 rising main is illustrated in Fig. 6(A). The intermittent flow pattern was due to the pump being turned on and off, depending up on the volume of wastewater entering the wet well. The model is able to reproduce the sulfide and methane concentrations reasonably well demonstrating the predictive capability of the model. The predicted methane concentration varied from a low of 4 mg COD/L to a high of 26 mg COD/L with an average concentration of 8.7 mg COD/L. The large variation in the concentration is related to the HRT of the wastewater slug exiting the sewer pipe at a given time. Infrequent pumping in early morning and late afternoon resulted in longer HRTs and hence higher methane levels. In contrast, frequent pumping from 6:00 am to 9:00 am, and also from 8:00 pm to 9:30 pm caused short HRTs resulting in lower methane levels. The same trend was observed with sulfide production.

Preliminary assessment of methane formation in rising main sewers is performed using the model (Fig. 7). For a given wastewater composition, two key factors that affect the extent of biological activity and hence methane production in sewers are biofilm area to liquid volume (A/V) ratio and the hydraulic retention time (HRT). The A/V ratio, which is dictated by the pipe diameter, gives a measure of the biofilm activity per unit volume of the wastewater. A higher A/V ratio would give higher methane production rate and vice versa. On the other hand, a longer HRT means longer time for biological transformations, and thus results in higher methane levels. The HRT in a rising main is determined by the pumping rate and the frequency of pumping. It should be noted at this point that, for a given flow

rate and pumping pattern, changing the diameter of the pipe would result in changes in both the A/V ratio and the HRT. A change in pipe length, however, only affects the HRT.

In order to make an assessment of methanogenesis under different sewer conditions with respect to the A/V ratio and

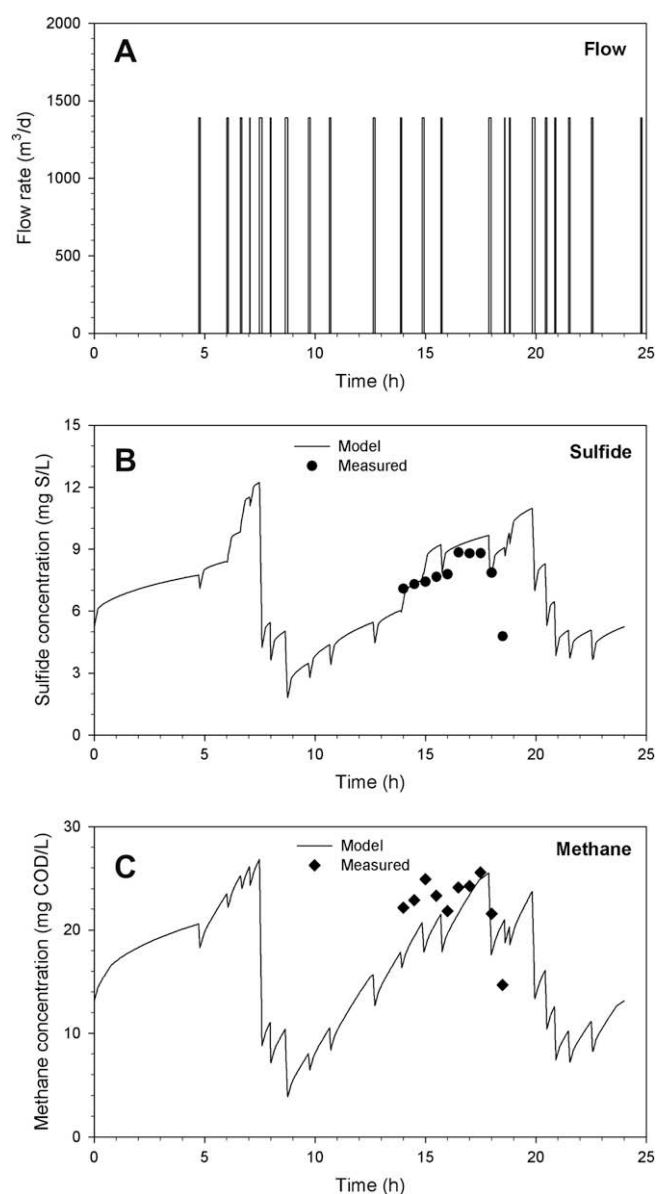


Fig. 6 – Model validation: comparison of modelling predictions for the UC09 rising main with field data obtained from this site (A) pumping events; (B) sulfide; and (C) methane.

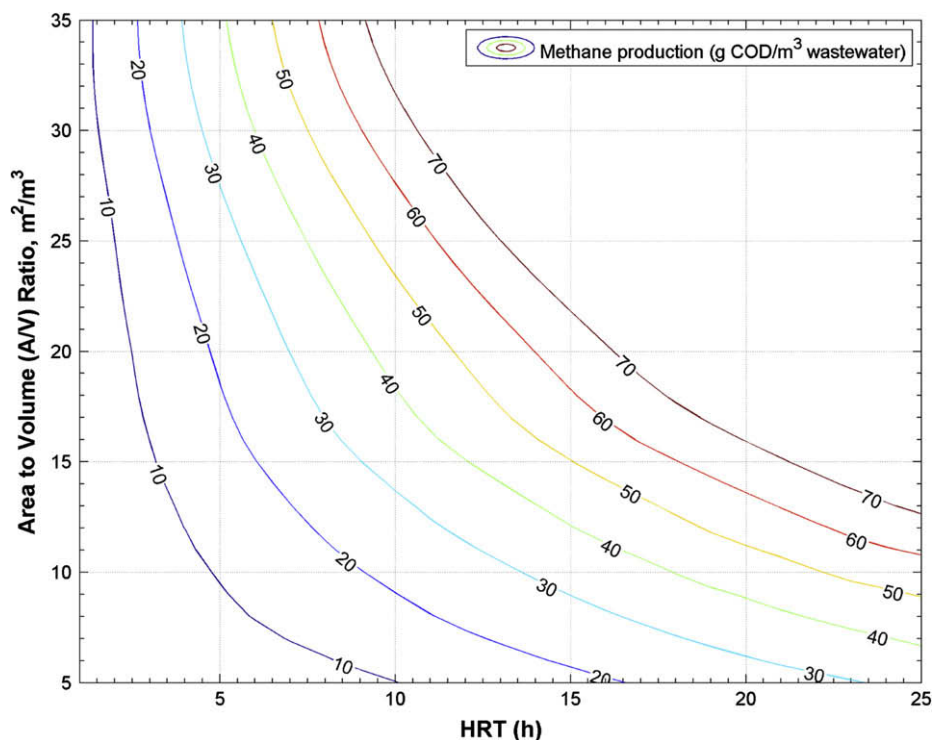


Fig. 7 – Contour graph of methane production as a function of HRT and A/V ratio.

HRT, the sewer model was employed to simulate hypothetical rising mains with different pipe diameters (ranging from 100 mm to 500 mm) and lengths, but receiving the same sewage flow (1230 m³/d). The average HRT of wastewater in a given sewer line was calculated as equation (7):

$$\text{Average HRT (h)} = \frac{\text{Pipe length (m)}}{(\text{Daily flow (m}^3/\text{d)}/\text{Cross sectional area of pipe (m}^2))} \quad (7)$$

The length of the rising main for each pipe size was varied so that the average HRT was between 1 and 25 h. The methane production rate (g COD/m³ wastewater) was calculated as the daily methane discharge (g COD/d) at the end of the rising main divided by the daily flow rate (m³/d). The simulation results are presented as a contour graph for methane production rate as a function of A/V ratio and HRT in Fig. 7. Using this plot, the methane production rate can be calculated for a given A/V ratio and HRT. Since the plot was developed for a given flow rate and pumping pattern, any changes in these parameters are expected to produce different results. However, the contour plot presented here can be used to make a preliminary estimate of the methane production potential of a given rising main.

From the modelling results presented above, a methane concentration of about 30 g COD/m³ is expected for a pipe of diameter 300 mm (A/V ratio of 13.3 m²/m³) and an average HRT of 10 h. This is equivalent to 158 g CO₂-e/m³, assuming a Global Warming Potential of 21 for methane.

The estimated wastewater production is about 23 ML/d for a catchment with 100 000 population equivalents (PE). A typical BNR WWTP operation for such a flow may be expected to produce 5300–7400 t CO₂-eq per annum of GHG emissions (de Haas and Hartley, 2004). This is equivalent to a GHG production

of 630–880 g CO₂-eq/m³ wastewater. On the basis of the above estimates, if a WWTP plant receives all its flow from a sewer network with an average retention time in rising main sections of 10 h, the GHG emissions from methanogenesis in the sewer would be equivalent to approximately 20% of the GHG emissions due to the energy consumption by the WWTP. It should be noted that despite the value of 20% is an upper limit (obtained by neglecting methane oxidation in subsequent gravity sewer sections), GHG emissions in sewers may be very significant.

The methane concentration values estimated in this work are lower than some of the values reported in our previous work (Guisasola et al., 2008) based on field measurements. In a real sewer studied, 20–100 g CH₄-COD/m³ was measured. The emission of these amounts of methane would be equivalent to 15–65% of the CO₂ emission due to energy consumption for the treatment of the same amount of wastewater. Unfortunately, methane production in the sewer system reported in Guisasola et al. (2008) could not be modelled due to the lack of sufficient information including the flow data.

Since the results presented here are based upon limited field data, the absolute values predicted should be taken with caution. However, this study clearly demonstrates that the sewer model presented would serve as a valuable tool in achieving this goal, although more intensive field measurements are still needed to obtain more accurate model parameters.

The model proposed deals with the rising main sections of sewer networks. Predicting the extent of methanogenesis in gravity sewers is more complex due to the transfer of oxygen into wastewater through surface aeration. Oxygen can inhibit methanogenesis. However, oxygen can only penetrate into sewer biofilms for a limited depth (Gutierrez et al., 2008), leaving the deeper layers of sewer biofilms/sediments

anaerobic. Methane may still form at such locations, but may get oxidised when diffused into aerobic layers. Aerobic methane oxidation has been widely reported (Costa et al., 2000).

5. Conclusions

The simple conceptual model proposed for methane formation in rising main sewers can successfully describe the methane and sulfide data observed at a lab-scale sewer system and also a real rising main sewer. However, more field data are needed to more accurately calibrate the model parameters.

Model simulations show that methane production in rising main sewers is highly dependent on the hydraulic residence time (HRT) and the A/V (biofilm surface area to volume) ratio, showing higher methane concentrations at longer HRT or larger A/V ratios.

Kinetic calibration shows that methanogens are more competitive than sulfate-reducing bacteria (SRB) for common electron donors (H_2 and acetate) in the sewer biofilm investigated. Several factors likely contributed to this observation. Sewage has a relatively high COD to sulfate ratio (13 mg COD/mg S in this study), which stimulates the growth of methanogens. Secondly, both sulfate reduction and methanogenesis primarily occur in biofilms rather than in the planktonic phase. The substrates required by methanogens (e.g. H_2 , CO_2 and acetate) are produced in situ by fermentation bacteria, while sulfate, a key substrate for SRB needs to be transferred from the bulk liquid phase to the biofilms, limiting the development of SRB in the inner locations of sewer biofilms.

The modelling results clearly illustrate that methane production in sewers may add significantly to the overall GHG emissions from wastewater systems which include significant rising mains. The results presented here are based upon the preliminary assessment of methane production. For a more reliable and accurate prediction, the model needs to be calibrated for different field conditions. Further studies should include the processes of biological methane degradation and methane stripping from gravity sewers.

Acknowledgements

The research was supported by the Australian Research Council through Project LP0454182, with Gold Coast Water and Sydney Water Corporation as industry partners. The authors also want to acknowledge Dr. Beatrice Keller-Lehmann and Dr. David de Haas for their helpful collaboration during this work, particularly with setting up the sulfide and methane measurement procedures.

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