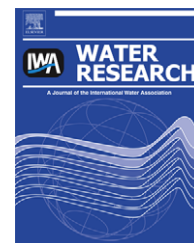


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Effects of long-term pH elevation on the sulfate-reducing and methanogenic activities of anaerobic sewer biofilms

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ABSTRACT

The dosage of alkali is often applied by the wastewater industry to reduce the transfer of hydrogen sulfide from wastewater to the sewer atmosphere. In this paper the activities of Sulfate Reducing Bacteria (SRB) and Methanogenic Archaea (MA) under elevated pH conditions (8.6 and 9.0) were evaluated in a laboratory scale anaerobic sewer reactor. Compared to those in a control reactor without pH control ($\text{pH } 7.6 \pm 0.1$), the SRB activity was reduced by 30% and 50%, respectively, at pH 8.6 and pH 9.0. When normal pH was resumed, it took approximately 1 month for the SRB activity to fully recover. Methanogenic activities developed in the control reactor in 3 months after the reactor start-up, while no significant methanogenic activities were detected in the experimental reactor until normal pH was resumed. The results suggest that elevated pH at 8.6–9.0 suppressed the growth of methanogens. These experimental results clearly showed that, in addition to its well-known effect of reducing H_2S transfer from the liquid to the gas phase, pH elevation considerably reduces sulfide and methane production by anaerobic sewer biofilms. These findings are significant for the optimal use of alkali addition to sewers for the control of H_2S and CH_4 emissions. A model-based study showed that, by adding the alkali at the beginning rather than towards the end of a rising main, substantial savings in chemicals can be achieved while achieving the same level of sulfide emission control, and complete methane emission control.

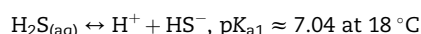
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1. Introduction

Anaerobic conditions in sewer systems result in the production of sulfide by sulfate reducing bacteria (SRB). The build-up of hydrogen sulfide in sewer atmosphere causes detrimental effects such as odour nuisance, corrosion of pipes and health hazards (Thistlethwayte, 1972; Hvitved-Jacobsen, 2002; US EPA, 1974). The dose of chemicals in sewer networks to control the production or emission of H_2S has been widely employed by the wastewater industry. These included the addition of oxygen, nitrate, iron salts, alkali and molybdate ion, among others (Boon, 1995; Boon et al., 1998; Gutierrez et al., 2008;

Hobson and Yang, 2000; Hvitved-Jacobsen, 2002; Mohanakrishnan et al., 2008; Nemati et al., 2001; Zhang et al., 2008).

The dose of alkali to sewers is a widespread operational strategy for sulfide control. Hydrogen sulfide in sewage is primarily present as two sulfide species, H_2S and HS^- , depending on the pH (Yongsiri et al., 2003):



The rise of pH can drastically reduce the concentration of dissolved molecular hydrogen sulfide for a given total

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dissolved sulfide concentration. At pH 8.0, only around 8% of the sulfide is present as dissolved hydrogen sulfide, while at pH 9.0, the hydrogen sulfide level drops to less than 1%. Given the fact that only the molecular H_2S can be transferred across the air–water interface to the sewer atmosphere, the elevation of pH reduces the release of hydrogen sulfide gas to atmosphere, where it can be harmful.

Elevation of pH to levels around 9.0 is a sulfide control strategy commonly used by the wastewater industry due to both practical and safety reasons. The commercial alkali products for sulfide control are generally based on Magnesium Hydroxide, $\text{Mg}(\text{OH})_2$ (e.g. Sulfalock™). Magnesium Hydroxide is a non-hazardous chemical classified as a weak base, easier and safer to handle and store, when compared to other alkalis based on caustic soda (NaOH) or lime (CaO) (Material Safety Data Sheets, Australia). The self buffering feature of $\text{Mg}(\text{OH})_2$ could allow a sewer to be loaded with residual or unreacted alkalinity, extending the length of effectiveness in sulfide control, as this residual component would be available in the event that re-acidification occurs. The maximum pH achievable by $\text{Mg}(\text{OH})_2$ dosing is approximately 9.0 due to its limited solubility in water, a level that would not endanger the performance of the downstream biological wastewater treatment plants. Notably, pH 9.0 is the upper limit specified in many trade waste discharge agreements in Queensland (Queensland, 1997) as it is close to the maximum tolerance of aerobic and anaerobic digester bacteria.

An alternative sulfide control strategy also involving manipulating pH is the pH shock strategy. In the field trials reported in *Hydrogen Sulfide Control Manual* (1989), it was observed that a drastic pH increase to 12 or above through the use of caustic soda for a short period of time (h) caused complete suppression of sulfide production. However, in most cases sulfide production completely recovered within 1–2 weeks. To maintain low production of sulfide, pH shock has to be applied regularly (e.g. weekly). Compared to pH elevation using $\text{Mg}(\text{OH})_2$, the pH shock strategy has several disadvantages. The high pH potentially disturbs the operation of the downstream treatment facilities (Parsons et al., 2003; Portch and Van Merkesteyn, 2003). A buffer tank would therefore be needed to temporarily store the wastewater. In addition, the high pH can also cause other problems like carbonate

precipitation, sludge generation and ammonia gas release (Hvitved-Jacobsen, 2002).

pH is an important factor affecting bacterial growth. We hypothesize that pH elevation in sewers would have a significant impact on SRB activities. Indeed, the pH shock strategy relies on the biocidal effect of high pH. However, the effects of a pH elevation to 8.5–9.0 achievable with $\text{Mg}(\text{OH})_2$ on the activities of SRB in sewer biofilms are not known. If the hypothesis is proven true, the addition of $\text{Mg}(\text{OH})_2$ would reduce not only the transfer of H_2S , but also its production. The main aim of the present work is to assess the effect of long-term pH elevation on the sulfide producing capability of sewer biofilms. Anaerobic sewer biofilms were grown in laboratory reactors fed with domestic wastewater. The sulfate reduction activities were assessed at elevated pH levels of 8.6 and 9.0, and compared to that of the control reactor without pH adjustment (pH = 7.6).

The coexistence of methanogenic Archaea (MA) with SRB in sewer environments has been confirmed in recent studies. Guisasola et al. (2008) demonstrated the high-level presence of methane (5–35 mg/L) in rising main sewers, and highlighted the negative effects of MA activities. These included significant greenhouse gas emissions, consumption of the valuable COD required for the downstream biological nutrient removal facilities, and built-up of potentially explosive gas mixtures in sewer atmosphere. This study also evaluated the effects of pH elevation on methane production by sewer biofilms.

2. Material and methods

2.1. Biofilm reactor setup, operation and monitoring

Two cylindrical reactors of 1 L each were used in this study (Fig. 1). One, named R1, was used as the Experimental System, while the other, named R2, used as Control. The reactors were made of Perspex™, an acrylic polyvinyl chloride sheet, completely sealed, and covered with aluminium foil to avoid exposing the sewage and biofilm to light. Each reactor has an inner surface area of 0.06 m² for biofilm development. Each reactor lid was equipped with a small container with a volume of 70 mL (Fig. 1) filled with the same wastewater as in the

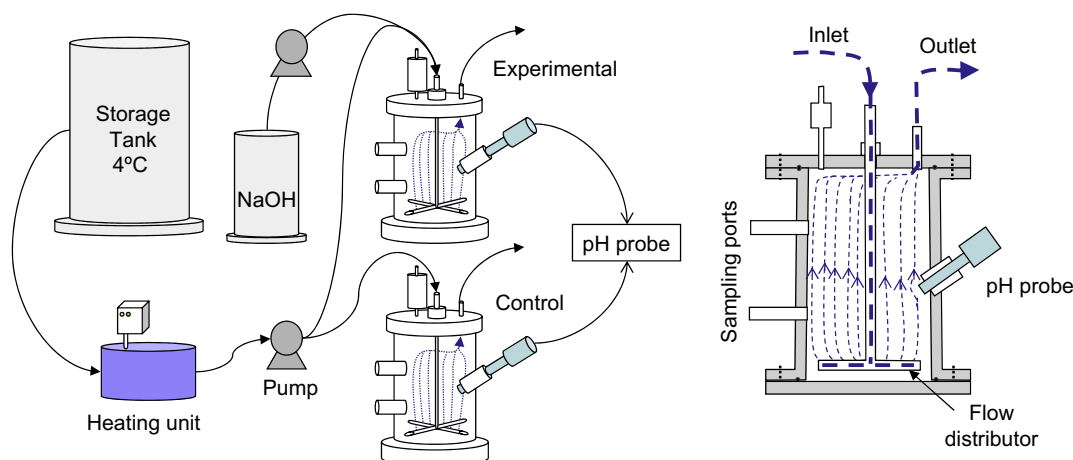


Fig. 1 – Layout of the experimental setup and a sectional view of the reactor.

reactors, so as to prevent any vacuum and oxygen entry during wastewater displacement due to sampling. Both reactors were fed with domestic sewage, collected weekly from the Robertson Park Pumping Station (Indooroopilly, Brisbane), by means of a Masterflex peristaltic pump (model 7520-47). The sewage, stored at 4 °C to minimize biological transformations, typically contained sulfide at concentrations of <3 mg S/L, sulfate between 10 and 25 mg S/L, approximately 50 mg N/L of ammonia and 50–100 mg COD/L of volatile fatty acids (VFAs). Negligible amounts (<1 mg/L) of sulfite and thiosulfate were present. The sewage was heated to 20 °C before it was pumped into the reactors. The pump was turned on for 2 min every 6 h, delivering 1 L of wastewater to each reactor. This resulted in a Hydraulic Retention Time (HRT) of 6 h, corresponding to the average HRT in a real rising main at the Gold Coast (Hutchinson and Hamilton, 2005) used as a reference in this study. As shown in Fig. 1, wastewater was introduced from the bottom of the reactors through a cross-shaped distributor to ensure uniform distribution. The wastewater left the system from an overflowing outlet on the top lid of the reactor. Gentle mixing was continuously provided to the reactors through a magnetic stirrer (Heindolph Model MR 3000R) operated at 240 rpm. pH adjustment in Reactor R1 was done by injecting a 0.05 M NaOH solution using a Masterflex pump (model 7553-79) during a feeding event to keep the pH at the required set points (see below). $Mg(OH)_2$ was not used due to concerns of tube blockage. However, the pH levels used in this study are easily achievable with $Mg(OH)_2$ in practice.

The sulfide concentrations in the two reactors were monitored online using a S::CAN UV–VIS spectro::lyzer (Sutherland-Stacey et al., 2008). Liquid phase samples were also taken from the reactors regularly for the analysis of sulfide, sulfate, sulfite, thiosulfate, VFAs, ammonium and methane. These online and offline methods are to be further described in the next section.

The operation of the reactor systems was divided into 4 periods depending on the pH conditions applied to the experimental reactor. The experimental details are summarised in Table 1. The effect of the pH increase on biofilm activities was determined by means of batch tests. A total of 46 tests were conducted in a temperature-controlled lab (20 ± 1 °C) (see Table 1). At the start of each test, fresh sewage was pumped into the system. Gentle mixing conditions were provided with the magnetic stirrer (240 rpm). Liquid samples were drawn from the reactors at an interval of 30 min for 3 h. Dissolved sulfur species (sulfide, sulfate, sulfite and thiosulfate), VFA species (acetic, propionic, butyric, isobutyric, valeric, isovaleric and hexanoic acids) and methane were analysed using methods

further described below. The production or consumption rate of a compound was calculated by linear regression.

2.2. Analytical methods

Liquid samples for analyses of dissolved sulfur species (SO_4^{2-} , HS^- , $S_2O_3^{2-}$ and SO_3^{2-}) were immediately preserved with a special sulfide anti-oxidant buffer (SAOB) as described by Keller-Lehmann et al. (2006). The method allows samples to be stored at 4 °C for 5 days without deterioration of any sulfur species. The soluble sulfur species were measured on an ion chromatograph with an UV and conductivity detector (Dionex ICS-2000). A S::CAN UV–VIS spectro::lyzer sensor (Messtechnik GmbH, Austria) was used for online measurements of dissolved sulfide as described in Sutherland-Stacey et al. (2008). A bypass system was used to connect spectrometer with the sewer reactor allowing sample to be diverted to the spectrometer optics. Cleaning of the s::can lens was carried out before each batch test and every second day during normal functioning periods. The sensor was calibrated at the beginning of the study using methods described in Sutherland-Stacey et al. (2008), and no further calibration was required. pH was measured with a TPS minichem-pH controller (Version 2.1.1). Ammonia concentrations were analysed using a Lachat QuikChem8000 Flow Injection Analyser (Lachat Instrument, Milwaukee, WI). VFAs were measured by Perkin-Elmer gas chromatography with column DB-FFAP 15 m \times 0.53 mm \times 1.0 μ m (length \times ID \times film) at 140 °C, while the injector and flame ionisation detector were operated at 220 and 250 °C, respectively. High purity helium was used as carrier gas at a flow rate of 17 mL/min. Filtered sample (0.9 mL) was transferred into a GC vial to which 0.1 mL of formic acid was added. For the analysis, a volume of 1 mL of sample was injected in splitless mode. The VFA species analysed included acetic, propionic, butyric, isobutyric, valeric, isovaleric and hexanoic acids. The measured values were converted to COD using the theoretical chemical oxygen demands of these chemicals. Dissolved methane was analysed using a method described in Guisasola et al. (2008), modified from Alberto et al. (2000).

2.3. Simulation studies

Simulation studies were carried out to demonstrate the importance of the $Mg(OH)_2$ dosage location for sulfide control, based on the experimental findings. A dynamic rising main model describing in-sewer carbon and sulfur transformations (Sharma et al., 2008; Guisasola et al., 2009) was implemented in MATLAB®/Simulink®. The model was also able to predict

Table 1 – Experimental conditions applied during the entire course of the experimental study.

Operational periods	Length (days)	Control reactor	Experimental reactor	Number of batch tests
Period 1	0–40	No pH control 7.6 ± 0.1	No pH control 7.6 ± 0.1	7
Period 2	51–110	No pH control 7.6 ± 0.1	pH adjusted to 8.6 ± 0.1 with 88 mL 0.05 M NaOH in each pumping event	12
Period 3	111–170	No pH control 7.6 ± 0.1	pH adjusted to 9.0 ± 0.1 with 120 mL 0.05 M NaOH in each pumping event	12
Period 4	171–332	No pH control 7.6 ± 0.1	No pH control 7.6 ± 0.1	15

dynamic changes in pH as a result of the biological and physiochemical processes in sewers and $\text{Mg}(\text{OH})_2$ addition. The effects of pH on biofilm activities were also incorporated in the model based upon the results of this study.

3. Results and discussion

3.1. Effect of pH elevation on the SRB activity

During the first 40-day start-up period (Period 1), feeding of fresh wastewater to the reactors promoted the development of anaerobic biofilms on the inner walls of the Control and Experimental reactors. The sulfide production capacity of both systems increased steadily to $2.3 \text{ g S/m}^2 \text{ d}$ (approximately 5.8 mg S/L h). Batch tests using wastewater without biofilms showed that the planktonic microorganisms had a negligible contribution to the overall sulfide production (approximately 0.1 mg S/L h , or 2% of the overall rate). This rate is comparable to that determined for a real rising main (approximately $2.0 \text{ g S/m}^2 \text{ d}$) (Sharma et al., 2008). It also falls in the range summarised by Hvitved-Jacobsen (2002) for sulfide production in rising mains (0.48 and $2.4 \text{ g S/m}^2 \text{ d}$). Thickness of mature biofilms was estimated to be 1–2 mm based on visual examination. Fig. 2 shows typical sulfide and sulfate concentration profiles obtained in R2 at the end of Period 1 (R1 displayed very similar performance). After each pumping event, the incoming sulfate was progressively reduced to sulfide by SRB. Sulfide remained at a constant concentration after complete sulfate reduction. Intermediate sulfur compounds (thiosulfate and sulfite) were negligible at all times ($<0.5 \text{ mg S/L}$). The sum of all measured dissolved inorganic sulfur species (sulfate, sulfide, sulfite and thiosulfate) remained stable during the entire cycle indicating no additional sulfur sinks.

The pH in the raw sewage used was stable and was around 7.6. This is within the optimal range for anaerobic bacteria development (Hvitved-Jacobsen, 2002). As shown in Fig. 3, without pH control the sewage pH decreased slightly in the sewer reactor, reaching 7.5 at the end of the cycle. The average pH in the cycle was $7.6 (\pm 0.1)$. The slight pH drop was likely caused by fermentation. In Periods 2 and 3, the NaOH dose was carefully adjusted to maintain the pH at the intended set

points, 8.6 and 9.0, respectively (Fig. 3). Indeed, the average pH in R1 in Period 2 and Period 3 was calculated as $8.6 (\pm 0.1)$ and $9.0 (\pm 0.1)$, respectively.

Effects of elevated pH on the SRB activity were assessed by means of batch tests where sulfide production was measured after fresh sewage was fed to the reactors. As an example, Fig. 4 shows the sulfide, sulfate, total dissolved inorganic sulfur, VFA and methane concentrations measured in a batch test. Concomitant sulfate reduction and sulfide production were observed without sulfur losses. The sulfate reduction rate and sulfide, VFA and methane production rates were determined using the linear parts of the profiles (first hour data points). The sulfide production rates measured on the two reactors in the first three periods are compared in Fig. 5. Towards the end of Period 1, the biofilms in the two reactors consistently showed comparable sulfidogenic activity. From day 30 to 45, sulfide production rates of 5.7 ± 0.5 and $5.8 \pm 0.4 \text{ mg S/L h}$ were recorded in the control and experimental reactors, respectively. From day 45, the NaOH solution was injected to the experimental reactor. Under pH 8.6 conditions, a gradual decrease of sulfide production in R1 was observed in the first two weeks, which was followed by an “inhibited steady state” where lower and stable sulfidogenic capacity was detected. The sulfide production rate was only $4.4 \pm 0.3 \text{ mg S/L h}$, representing $70 \pm 4\%$ of that measured on the control line, $6.4 \pm 0.4 \text{ mg S/L h}$. The further increase of pH to 9.0 resulted in a further decrease of SRB activity, reaching a steady rate of $3.3 \pm 0.2 \text{ mg S/L h}$ after an initial transient period. This corresponded to $48 \pm 2\%$ of the sulfide production rate measured in the control reactor in the same period, $6.7 \pm 0.4 \text{ mg S/L h}$.

A number of factors could have contributed to the decrease in SBR activity at elevated pH. Although sulfidogenic activity can occur in a wide range of pH (5.0–9.0), the optimal pH has previously been reported to be in the range of pH 7.0–8.0 (Postgate, 1979; Visser et al., 1996). Also, the increased free ammonia (NH_3) concentration under elevated pH conditions could also have had an inhibitory effect on the SRB activity. The inhibitory effects of free ammonia on anaerobic processes had been widely described (Calli et al., 2005; Chen et al., 2008; Kadam and Boone, 1996; Wittmann et al., 1995). The non-ionic NH_3 can pass through the cellular membrane producing

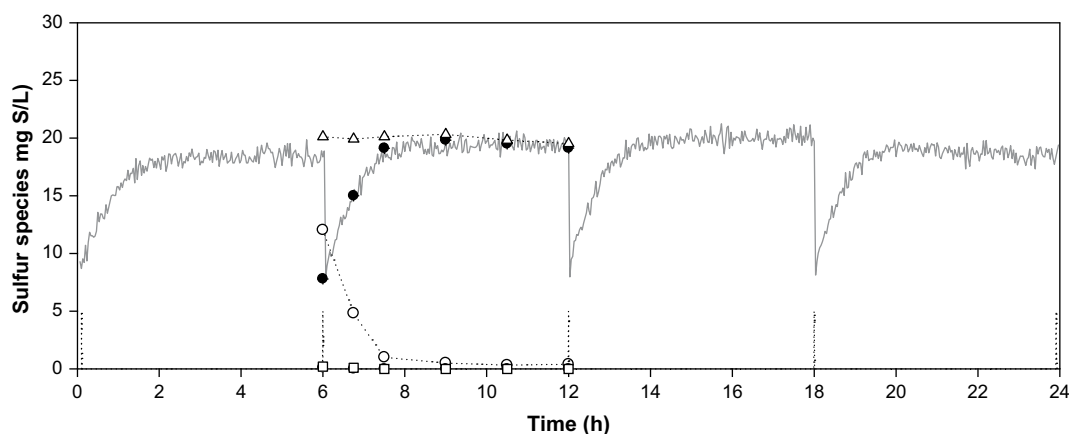


Fig. 2 – 24-h sulfide profile in R2 (Control line) on Day 35. Online sulfide (—), offline sulfide (●), sulfate (○), thiosulfate (+), sulfite (□) and total dissolved inorganic sulfur (Δ). Dashed vertical lines corresponded to pumping events.

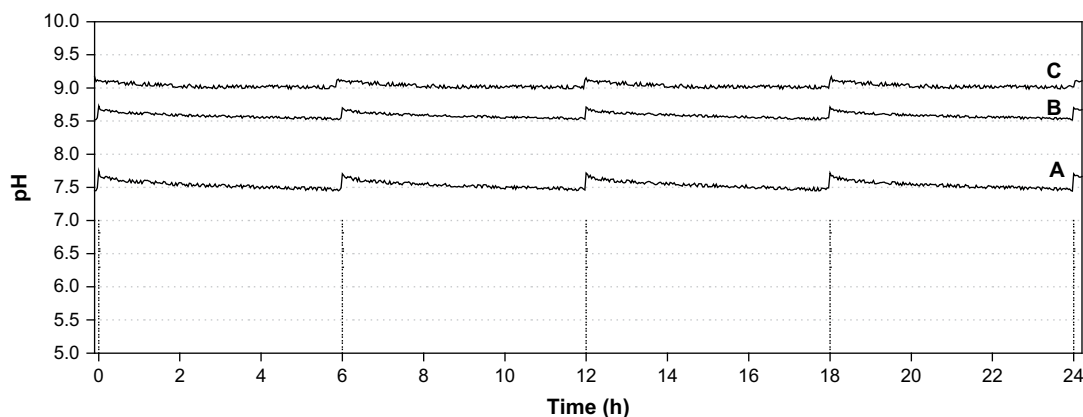


Fig. 3 – Typical 24-h pH profiles in the experimental system: (A), Period 1, no pH control; (B) Period 2, elevation to pH 8.6 (C) Period 3, elevation to pH 9.0. Dashed vertical lines corresponded to pumping events.

changes in the intracellular pH, which increases the maintenance energy, inhibits specific enzymatic reactions, and disrupts cell homeostasis (Henderson, 1971). Complete inhibition of anaerobic bioprocesses was observed at 34 mg NH₃/L (Calli et al., 2005). The total ammonium + ammonia concentration in the sewage used in this study was around 50 mg N/L. This would result in free ammonia concentrations of 0.9, 7.7 and 15.3 mg NH₃/L at pH 7.6, 8.6 and 9.0, respectively, assuming a pK_a value of 9.25 for NH₄⁺ ↔ NH₃ + H⁺. The incomplete inhibition of the SRB activity in the experimental reactor would be explained by the relatively low free ammonia concentrations. In addition, microniches with pH levels lower than that in the bulk liquid phase are expected to be present in deep layers of sewer biofilms. This would protect SRB at those locations against high pH and high free ammonia concentrations (Matthias, 2008; Guisasola et al., 2008).

In Period 4, the resumption of normal pH in the experimental system produced a subsequent increase of the SRB activity. As presented in Fig. 6, the ratio of the sulfide production rates in the experimental (R1) and in the control (R2) reactors did not recover immediately. It took approximately one month for the R1 activity to reach 90% to that of R2.

Fitting the data with the equation $Y = Y_0 + (1 - Y_0)(1 - e^{-\alpha t})$, where Y_0 is the activity ratio at the end of the pH elevation, t is time and α is the recovery constant, a recovery constant of 0.024 d⁻¹ with a 95% confidence interval of 0.019–0.030 d⁻¹ was obtained. This clearly indicates that pH elevation has a long-lasting effect on the SRB activity of sewer biofilms.

More research is required in order to gain a more detailed understanding of the mechanisms responsible for the reduction in SRB activity of the anaerobic sewer biofilm under elevated pH conditions. Molecular analysis of the microbial community during the transitional period would provide some insights into the adaptation of the community to pH variations.

3.2. Effect of pH elevation on development of methanogenic activity

In contrast to sulfide production, the development of the methanogenic activity was much slower in both reactors. In the control reactor, the methanogenic activity started after three months, reaching steady state after six months, with an average methane production rate of 21.4 ± 0.3 mg CH₄-COD/

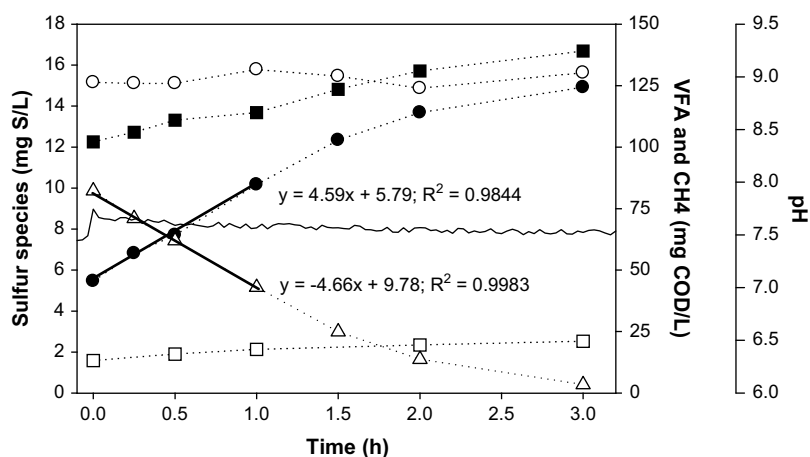


Fig. 4 – Sulfide (●), sulfate (Δ), total sulfur (○), VFA (■), methane (□) and pH (—) profiles measured in a typical batch test on the control reactor.

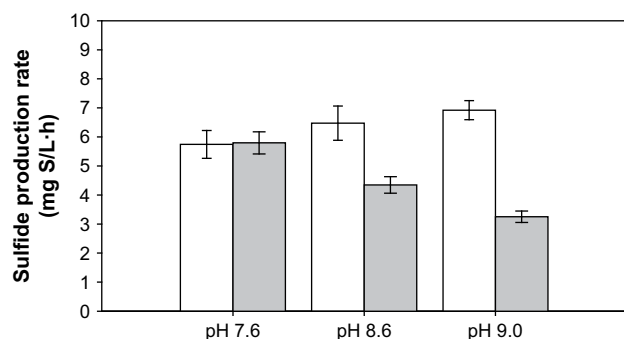


Fig. 5 – Average sulfide production rates of the control (white columns) and experimental (grey columns) reactors over Periods 1–3.

L h (Fig. 7A). The slow MA development in the control reactor was likely caused by the lower growth kinetics of MA compared to SRB. O'Flaherty et al. (1998) reported the maximal growth rates of key SRB and MA species in anaerobic sludge based on their ability to utilize key anaerobic digestion intermediates, such as acetate, H_2/CO_2 , propionate, butyrate and ethanol. At optimal pH (7.0–7.5), the maximum MA growth rate varied between 0.07 and 0.10 d^{-1} while the SRB growth rate varied between 0.13 and 3.17 d^{-1} , which was substantially higher. The MA–SRB competition for substrate was generally reported as the most likely mechanism determining the dominating population in anaerobic environments (Kristjansson et al., 1982; Omil et al., 1998; Visser et al., 1996; Raskin et al., 1996). However, this should have not played a major role in the slow development of the methanogenic activity in our reactors, as VFAs, the primary substrates for SRB and MA, were always present in excess during the start-up period. Recent studies also indicated that the spatial arrangement of various populations in sewer biofilms could enhance SRB–MA coexistence (Guisasola et al., 2008). Microniches with different COD to sulfate ratios exist in sewer biofilms, which have a thickness of several hundred micrometers (Mohana-krishnan et al., in press) thus permitting the co-development of SRB and MA populations.

The increased methane production in the control reactor caused a significant increase in the VFA consumption rate

(Fig. 7A). The methanogenic activity reached the maximum level of 21.0 mg CH_4 -COD/L h on day 153, which resulted in a net VFA consumption rate of 14.1 ± 0.6 mg VFA-COD/L h. In contrast, there was a net production of VFAs in the period prior to the development of methanogenic activity, with an average production rate of 12.9 ± 2.8 mg VFA-COD/L h. The data clearly show that a considerable amount of the wastewater COD was converted to methane in the presence of methanogens. This reduces the availability of COD for the downstream biological nutrient removal on the one hand and causes greenhouse gas emissions on the other (Guisasola et al., 2008). Mass balance analysis shows that in the control reactor methanogens consumed COD as a rate twice that of SRB.

MA didn't develop significantly in the experimental reactor while it was subjected to high pH in Periods 2 and 3 (Fig. 7B), as evidenced by the very low methane production rates measured (<0.7 mg CH_4 -COD/L h). This is in agreement with literature reports that MA seemed to be completely inhibited at pH above 8.0 in pure cultures, in anaerobic sludge and in anaerobic granules systems (O'Flaherty et al., 1998). At pH levels away from the optimum (7.0–7.5), MA must expend energy to maintain homeostasis rather than perform anabolism. Aceticlastic methanogens, the most probable dominant MA group in high acetate receiving reactors, are more inhibited by the free base when compared to other methanogens (Batstone et al., 2002). Inhibition of MA growth could have also been caused by the increased free ammonia (NH_3) concentrations under elevated pH, which disrupt the proton motive force and MA homeostasis (Henderson, 1971; Chen et al., 2008).

Elevated pH conditions also reduced the activity of fermentative bacteria (FB) in the reactors. Prior to the development of the methanogenic activity, a stable VFA production rate of 11.5 ± 1.2 mg VFA-COD/L h was observed in the control and experimental reactors. FB activity decreased to 5.1 ± 0.4 mg VFA-COD/L h in the experimental reactor under pH 9.0 (with negligible methane formation). This indicates that the fermentation activity was reduced by 54% at pH 9.0 in comparison to pH 7.6.

The resumption of normal pH on Day 191 in the experimental reactor resulted in significant changes in terms of the activities of both the fermentative bacteria and the MA. The activity of the fermentative bacteria accelerated reaching a VFA production rate of up to 16.2 mg VFA-COD/L h on Day 233. After this point, MA developed with the methane production rate increasing progressively to a stable level of 16.5 ± 0.5 mg CH_4 -COD/L h. As previously observed in the control reactor, the methanogenic activity was accompanied by a net consumption of VFAs.

The above results showed that the long-term pH elevation to 8.6–9.0 is effective in preventing MA activity from developing anaerobic sewer biofilms. Methane formation in sewers was previously demonstrated to potentially contribute very significantly to the greenhouse gas emissions from wastewater systems (Guisasola et al., 2008). It would also minimize the consumption of easily biodegradable carbon sources required for biological nutrient removal. However, the present study has been conducted under a completely controlled lab setup, and in-situ field studies are necessary to confirm these benefits.

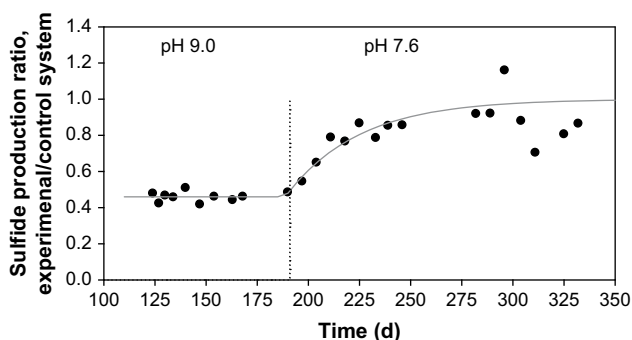


Fig. 6 – Sulfide production rate ratio corresponding to the end of Period 3 (pH 9.0) and Period 4 (pH 7.6). (●) Rate ratio: experimental/control; solid line: model fitting; dashed line indicates the end of pH control.

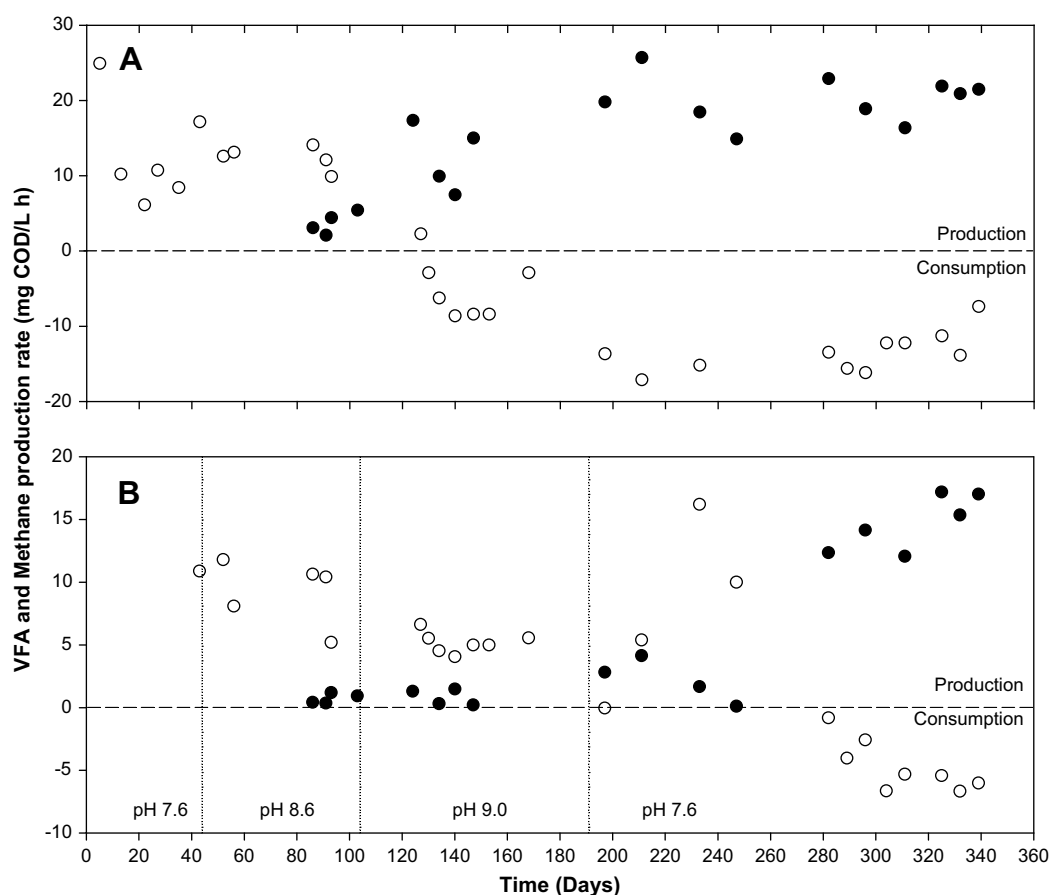


Fig. 7 – Evolution of the VFA (○) and methane production rates (●) in the control (A) and experimental (B) reactors. All data were measured during batch tests.

3.3. Practical implications of the findings

Magnesium hydroxide is generally used in sewer systems to raise the sewage pH thereby limiting the presence of $\text{H}_2\text{S}(\text{aq})$ and hence its transfer to the atmosphere. This study showed that the pH increase also affects the rates of several biological reactions such as fermentation, sulfate reduction and methane formation. These factors should therefore be taken into consideration when designing $\text{Mg}(\text{OH})_2$ dosing. Findings in this paper can help to identify the optimal dosing locations and dosage rates, when applied in conjunction with a sewer model reported previously (Sharma et al., 2008), which is able to predict the carbon and sulfur transformations in sewers as well as pH variations.

Simulation studies were performed to compare the performance of two different dosing strategies. UC09, a rising main of Gold Coast Water with a diameter of 150 mm and a length of 1086 m was used as the object. The model established for this sewer line is as described in Sharma et al. (2008), with the biological component of the model extended to also include methane production (Guisasola et al., 2009). The model parameters reported in Sharma et al. (2008) and Guisasola et al. (2009) were used for biofilms exposed to normal pH (no pH control). For biofilms exposed to pH 9.0, the sulfate reduction and fermentation rates were reduced by 50% and 54%,

respectively, according to the findings of this work. Methanogens were assumed to have negligible activities at pH 8.6 and above.

With the first strategy, $\text{Mg}(\text{OH})_2$ was assumed to be dosed at the beginning of the pipe. The dosing regime followed the pumping pattern, with $\text{Mg}(\text{OH})_2$ being dosed only when the pump was running. A $\text{Mg}(\text{OH})_2$ concentration in the wastewater of 54 mg/L was required to achieve a pH of 9.0 at the end of the pipe. However, the pH in the entire pipe varied between 9.1 and 9.3. The model-predicted average concentrations of total dissolved sulfide, dissolved molecular H_2S , total COD, VFA and methane and their discharge loads are compared with the respective baseline values (without magnesium hydroxide dosing, pH in the pipe was approximately 7.2) in Table 2. The dynamic sulfide and methane profiles at the end of the pipe are compared in Fig. 8. A higher pH in the entire sewer pipe resulted in significantly lower level of total dissolved sulfide and almost no production of methane. Furthermore, there was an increase in both total COD and VFA concentrations. The higher COD concentration was because that almost no COD was used for methane production and also that a lowered rate of sulfide production required a smaller amount of COD. Despite of a lowered fermentation rate at elevated pH, the VFA concentration also increased due to the absence of methane production and also reduced consumption of VFAs for sulfate reduction.

Table 2 – Summary of simulation results in the three simulated cases (Baseline – no pH elevation, Case I – $\text{Mg}(\text{OH})_2$ addition at the beginning of the pipe, and Case II – $\text{Mg}(\text{OH})_2$ addition 100 m before the end of the pipe). In Case I and Case II, the amount of $\text{Mg}(\text{OH})_2$ added was adjusted so that the dissolved molecular H_2S concentration at the end of the pipe was identical at 0.05 mg S/L.

Parameter	Unit	Baseline	$\text{Mg}(\text{OH})_2$ dosing	
			Case I	Case II
$\text{Mg}(\text{OH})_2$ dosing location	m	–	0	986
$\text{Mg}(\text{OH})_2$ dosing rate	-Rate	–	4.32	5.88
	-Concentration in wastewater	–	54.0	73.4
pH at outlet	-Median	7.2	9.0	9.2
	-Average conc.	8.76	5.21	8.1
Total dissolved sulfide	-Discharge load	734	437	712
	-Average conc.	3.43	0.05	0.05
Dissolved H_2S	-Discharge load	288	4.31	4.76
	-Average conc.	373.7	402.6	378.2
Total COD	-Discharge load	31.14	33.07	31.29
	-Average conc.	15.7	19.3	16.2
Volatile fatty acids	-Discharge load	1.35	1.63	1.36
	-Average conc.	21.5	0.5	17.2
Methane (CH_4)	-Discharge load	1.77	0.05	1.63
	-Average conc.			

In the second case, $\text{Mg}(\text{OH})_2$ was assumed to be dosed at 100 m upstream of the end of the pipe. The results of model simulation are also presented in Table 2 and Fig. 8. With this strategy, pH elevation only affected the biofilm activity in the last 100 m of the sewer pipe, and hence the sulfide and methane formation in this case was similar to that in the baseline case. Because of the higher dissolved sulfide level in this case (8.1 mg S/L) in comparison to Case I (5.2 mg S/L), a higher pH (median of 9.2 vs. 9.0) was required to achieve the same $\text{H}_2\text{S}(\text{aq})$ level as in the previous case. This resulted in an increased $\text{Mg}(\text{OH})_2$ dose (36.1%), from 4.32 kg/day in the previous case to 5.88 kg/day in this case.

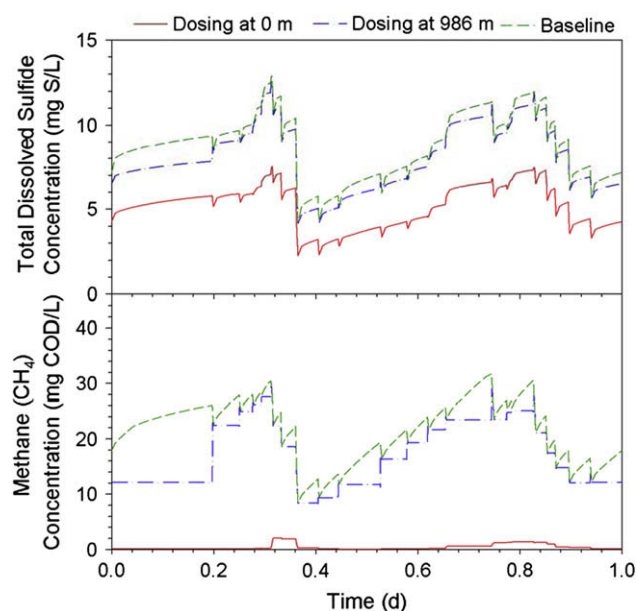


Fig. 8 – Comparison of total dissolved sulfide and methane concentrations at the end of the pipe in the three simulated cases.

The above example illustrates that it is beneficial to have the $\text{Mg}(\text{OH})_2$ dosing at an upstream location. A significantly less amount of dosage is required to achieve the same level of sulfide control. The downstream wastewater treatment plant would receive higher levels of COD and VFA for biological nutrient removal. Further, a higher pH throughout the length of the pipe would minimize odour and corrosion problems in the entire sewer pipe rather than just the end of pipe.

4. Conclusions

The effects of long-term alkaline dosing on the sulfide and methane production by anaerobic sewer biofilms were investigated. The following conclusions are drawn:

- Long-term pH elevation to 8.6–9.0 significantly reduces SRB activities of sewer biofilms. The sulfide production rate of the biofilm was reduced by 30% at pH 8.6 and 50% at pH 9.0, in comparison to biofilms operated at pH 7.6 (without pH control).
- Long-term pH elevation to levels of 8.6–9.0 prevents the development of methanogenic activity in sewer biofilms.
- It is beneficial to dose $\text{Mg}(\text{OH})_2$ at an upstream location. This controls sulfide and methane emissions in the entire sewer pipe, with reduced chemical consumption. It also increases the availability of organic carbon for the downstream biological nutrient removal due to reduced consumption of organic carbon for methane formation.

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