SP6: Field and laboratory testing of biomaterials and chemical additives for H2S and odorous compound control

Summary

(1) Background

The project *Optimal management of corrosion and odour problems in sewer systems* included evaluation of the effectiveness of the following substances for management of sulphide and, to a lesser extent, methane generation is rising mains:

- Biomaterials: Biosol, Biokat and Probac
- Chemical additives: ferric salts, free nitrous acid added as nitrite ion and caustic addition.

(2) Biomaterials

The effectiveness of the biomaterials was evaluated in a laboratory test based on two well mixed reactors operated in series. The reactors were provided with a packing to ensure a higher ratio of film surface area to sewage volume than is typical of a rising main. The reactors were operated on domestic sewage and the throughput was varied diurnally so that the detention time varied over the range 2 to 6 hours.

There were two sets of reactors. One set was dosed with the test material and the other was operated as a control.

The experimental design excluded air from the reactors. Thus the design was intended to simulate sewage behaviour in a rising main rather than in a gravity system.

(2.1) Biosol

The supplier claimed that Biosol acts by destabilising the biofilm on the sewer wall and argued that a reduction in the extent of the biofilm would lead to a decrease in the rate of sulphide generation.

The extent of destabilisation of the biofilm following dosing with Biosol was evaluated by comparing the mass of biofilm in the dosed reactors with that in the control. The results indicated that both were similar. Likewise, suspended solids levels in the effluent from the dosed reactor train were similar to those in the effluent from the control. Thus, there was no evidence that Biosol destabilised the biofilm as claimed by the supplier.

The general conclusion that Biosol did not affect the biofilm was supported by further testing which indicated that both sulphide and methane concentrations were similar in the effluent from the dosed and control reactor trains.

Thus the experimental program failed to find evidence that Biosol was an effective agent for managing sulphide generation in a rising main.

(2.2) Biokat

Both sulphide and dissolved methane concentrations were measured in the effluent from the two reactor trains (ie the dosed and the control) following dosing with Biokat. There was no systematic difference between the two sets of results. Thus the experimental program did not find any evidence that Biokat would affect sulphide or methane generation in a rising main.

(2.3) Probac

The results for Probac were similar to those for Biokat. Thus there was no systematic change in either sulphide or dissolved methane concentrations due to dosing with Probac. There is therefore no evidence that use of Probac would affect either sulphide or methane generation in a rising main.

(3) Chemical additives

(3.1) Ferric salt

Addition of ferric salts to a sewage system is known to decrease the rate of sulphate reduction (ie decrease the rate of sulphide generation) and to also reduce sulphide concentrations by precipitation of FeS. The experimental program focussed on evaluating the first of these effects.

Inhibition of sulphate reduction under steady state conditions

The effect of ferric salt addition on the rate of sulphate reduction was investigated using the laboratory reactors described in Section 2. Trials based on continuous dosing demonstrated that the rate of sulphate reduction in the reactor trains decreased by about 50% for ferric ion dose rates over the range 5 to 35 mg Fe/L, with no systematic trend due to ferric ion concentration. This result occurred in a reactor train with a diurnal variation in detention time of 2 to 6 hours.

Inhibition of sulphate reduction has implications for the preferred location of ferric ion dosing. Thus upstream dosing can be expected to require less ferric ion because inhibition of sulphate reduction will reduce the amount of sulphide to be removed by precipitation.

Inhibition of sulphate reduction under transient conditions

Investigation of the rate of recovery of the sulphate reduction rate following the cessation of iron dosing at 15 mg Fe/L indicated that the rate increased from 50% of its original value during chemical dosing to 75% of its original value with about 2 days following cessation of dosing.

This result indicates that the inhibitory affect of ferric dosing persists for some period. This raises the possibility that intermittent dosing of ferric ion would be a tenable alternative to continuous dosing in cases where the extent of inhibition achieved reduced sulphide levels to values low enough so that ferric ion dosing was not required to achieve further reductions by precipitation.

Effect on anaerobic digestion
Laboratory testing indicated that ferric ion added to sewage in the stoichiometric ratio required to precipitate sulphide reduced H2S concentrations in sludge gas by a factor in the range 2 to 3. The reason for this effect is unclear.

(3.2) Free nitrous acid

Chemistry

Free nitrous acid (FNA) exists in equilibrium with nitrite ion. The position of the equilibrium is pH dependent. Thus the molar ratio of the 2 species (FNA/nitrite ion) at pH 7 is 0.02%. This ratio increases by a factor of 10 for every unit increase in pH. Thus the ratio is 2% when pH = 5.

FNA is toxic to the organisms in biofilms responsible for sulphide and methane production. However, due to the equilibrium with nitrite ion, FNA will not be present unless the sewer pH is below 7.

Effect on biofilm viability under steady state conditions

The effect of FNA on biofilm viability was investigating using the laboratory test reactors described in Section 2 and a staining technique to identify the proportion of live cells in samples of biofilm.

The results indicated that exposure to FNA under steady state conditions was able to reduce the proportion of viable material in the biofilm from the normal value of about 70% to values as low as 10 to 20%. The extent of reduction was greater at higher FNA concentrations but the increment was small at FNA concentrations beyond about 0.2 mg N/L.

The extent of reduction in biofilm viability was also dependent of the exposure time. An increase in exposure time from 6 to 24 hours typically reduced the fraction of viable cells in the biofilm by a factor of 0.65.

Effect on sulphide and methane generation under transient conditions

The effect of a single dose of FNA on sulphide and methane generation in the test reactor trains was assessed by monitoring effluent quality. The results at an FNA dose of 0.18 mg N/L were similar to those obtained at a dose of 0.36 mg N/L. This result is consistent with the observation that there was limited further reduction in biofilm activity at dose rates beyond 0.2 mg N/L.

The general trend of both sets of results was that sulphide production was reduced to about 5% of the pre dose value during the dosing period. There was a subsequent recovery in the sulphide production rate after the dosing event and a value equal to 50% of the pre dose value was obtained after about 8 days.

The trend for methane production was similar except that recovery to 50% of the pre dose value took about 55 days.

The long recovery time following a single dose of FNA implies that intermittent dosing is a realistic option for simultaneously controlling sulphide and methane levels and also minimising chemical costs.

Effect of simultaneous hydrogen peroxide addition under transient conditions

The effect of simultaneous dosing with FNA and hydrogen peroxide (H2O2) was investigated by operating the laboratory reactor trains without dosing until a steady state was achieved. At this point the packing was removed and dosed with mixtures of FNA and H2O2 in a batch test for 6 hours. The impact on cell viability was determined using the staining technique described above.

The results were expressed as the ratio of the proportion of live cells in the dosed reactor train to that in the control. A value of this 'killing efficiency' less than 1 indicates a biocidal effect due to the chemical dose.

The results of these tests are summarised in Table S1.

Table S1. Combination of FNA and H2O2 dosing to achieve target killing efficiency of microbes in sewer biofilm based on an exposure time of 6 hours

FNA	*Approximate H2O2 concentration required to achieve the target killing efficiency (mg/L)*		
(mg N/L)	*50%*	*80%*	*90%*
0	*25*	*>90*	*>90*
0.05	*10*	*50*	*75*
0.10	*0*	*25*	*55*
0.20	*0*	*5*	*20*
0.30	*0*	*0*	*15*
0.40	*0*	*0*	*0*

The results in Table S1 indicate that dose rates of H2O2 in the range 5 to 20 mg/L are required to achieve a significant improvement in biofilm inactivation at an FNA dose rate of 0.2 mg N/L for a period of 6 hours.

Effect of FNA dosing on sulphide and methane generation in a full scale rising main under transient conditions

The effect of FNA dosing in a full scale system was investigated in a 150 mm rising main of the Gold Coast. The diurnal variation in detention time to the sample point was about 1 to 4 hours.

The FNA dosing rate was 0.25 mg N/L.

The sulphide results were generally consistent with those obtained in the laboratory. Thus sulphide levels at the sample point decreased to zero during the dosing period and increased to 50% of the pre dose value within about 5 days. The results based on measurement of dissolved methane concentrations were similar. Thus, levels at the sample point were similar to those at the inlet to the rising main during the dosing period. However, unlike sulphide levels, there was no significant increase in downstream methane levels over a period of up to 5 weeks after the dosing event.

(3.3) Caustic shock

Mechanism

Exposure of biofilms to elevated pH levels has a biocidal effect.

Effect on sulphide and methane generation under transient conditions

The effect of transient increases in pH on sulphide and methane generation was investigated in the laboratory reactors described above.

The results indicated that sulphide generation rates decreased to very low values at the time of dosing. The time taken for sulphide generation rates to recover to 50% of the pre dose value is listed in Table S2. This data indicates that pH levels beyond 10.5 achieve little further increase in the time taken for sulphide generation rates to recover. Furthermore, the increase in recovery time as the dose period increase beyond 1 hour also appears marginal. Thus the results suggest that pH levels around 10.5 for a period of 1 hour are probably appropriate.

Table S2: Time taken for sulphide generation rates to recover to 50% of the rate prior to a transient caustic dosing.

Dose pH	Exposure time (hr)	Time for sulphide generation to reach 50%
10.5	0.5	3.5
	1	2.8
	2	4.0
	6	4.5
11.5	1	3.0
	6	4.5
12.5	6	4.5

The trend in the results for methane generation is similar to that for sulphide. Thus methane production rates are very low during dosing and the influence of exposure time is also marginal and an exposure time of 1 hour at pH = 10.5 appears appropriate. However, the rate of recovery in methane production flowing the dosing period is very low and methane concentrations were only about 25% of the pre dose levels after 17 days.

Effect on biofilm viability under transient conditions

The effect of a caustic dose on biofilm viability was investigated using the laboratory reactors and the staining technique described above. The results indicated that dosing at pH = 10.5 for 1 hr decreased the proportion of viable biomass from a pre dose value of around 80% to a value below 40%. The rate of increase in viable biomass following the transient dose of caustic was consistent with the observed rate of recovery in sulphide production.

Effect of caustic dosing on sulphide generation in a full scale rising main under transient conditions

The effect of a transient caustic dose was investigated by dosing into the wet well at the start of the UC09 rising main described above.

The results for a pH = 10.5 in the wet well indicate that the pH at the sampling location 1 to 4 hours downstream only increased to about 8.5. There was a corresponding decrease in sulphide concentrations to about 10% of the normal values. These values increased to 100% of normal levels within about 24 hours.

A subsequent test was based on a pH of 11.5 in the wet well for a period of 6 hours. In this case, the pH at the sampling location increased to about 10.5 during the dosing period and 50% recovery of sulphide levels occurred after about 4 to 5 days.

The general conclusion arising from the field tests is consistent with observations arising from the laboratory tests. Thus exposure to a pH of around 10.5 for a period of several hours will achieve a significant reduction in sulphide levels. This reduction will persist after the dosing event and recover to say 50% of the pre dose value after about 3 to 5 days. However, a pH higher than 10.5 is required at the dosing point in a full scale sewer to ensure that the biofilm is exposed to pH's above 10.5 over the whole sewer length.

SP6: Field and laboratory testing of biomaterials and chemical additives for H2S and odorous compound control

Draft

(1) Introduction

This section of the *Optimal management of corrosion and odour problems in sewer systems* manual describes the results of laboratory and field testing of a number of commonly available biomaterials and chemical additives used to control both odour and corrosion in sewerage systems.

The biomaterials included in the test program were:

- Biosol
  The supplier claims that Biosol utilizes trace amount of "cell signaling chemicals" that can slow down the reproduction and metabolic rates of bacteria in sewers. If such a phenomenon occurs, the "down-regulation" of the bacteria would weaken the biofilm, which will then be detached from the pipe wall by shear due to flowing sewage.
  The expectation is that H2S production would be reduced because of the absence of a biofilm on the sewer walls.

- Biokat
  Biokat is claimed to be an innovative cellular bio-activation liquid that stimulates indigenous bacteria to accelerate biological activity. It functions by providing many intracellular micro enzymes that are lacking in the wastewater, which further accelerates the metabolism of microorganisms. By accelerating the metabolic rate of the indigenous organisms, the availability of a carbon source to sulfate reducing bacteria is reduced, thereby decreasing the rate of sulfide production.

- Probac
  Probac is claimed to stimulate both the metabolic and reproductive rate of the naturally occurring desirable bacteria that may be functioning improperly because of the inhibition by oxidants, poisons, or extremes conditions such as high temperature or very long age. This will cause the desired bacteria to become dominant, thereby out-competing the odorous compounds producing bacteria as these utilize the same food sources.

The chemical additives evaluated as part of the research program were:

- Ferric salts
  Ferric salts are widely used to limit sulphide levels in sewage by precipitating ferric sulphide.

- Free nitrous acid
  Free nitrous acid (FNA) exists in solution when nitrite ion is added to sewage. The

equilibrium between the two species depends on pH and increased concentrations of FNA are favoured by low pH.

FNA is toxic to the organisms in the sewer biofilm and this biocidal action reduces sulphide production.

- Caustic solutions
  Addition of alkaline materials to increase the sewage pH provides a toxic shock which inactivates the organisms responsible for sulphide production.

(2) Testing of biomaterials

(2.1) Experimental arrangement

The experimental arrangement used to evaluate biomaterials was laboratory based and designed to simulate sulphide production in a rising main. This alternative was adopted in preference to simulation of a gravity sewer since the sulphide production rates were expected to be higher. Thus adoption of an experimental arrangement based on a rising main was expected to provide a more stringent test of the effectiveness of the test chemicals.

The experimental arrangement is illustrated in Figure 1. This figure indicates that the laboratory tests were undertaken in sets of 2 sealed reactors operated in series. Other principal features of the experimental program were:

Control
There were two reactor trains, one of which was dosed with the test chemical and the other was operated as a control.

Area to volume ratio
The reactors were each 0.75 L in volume and each was provided with a packing material.

The objective of the packing material was to provide a film surface area to sewage volume ratio typical of a full scale rising main to ensure geometric similarity. The ratio for a rising main has the value 4/D, where D is the pipe diameter. The actual value of the ratio in the laboratory test cells was 56 m^{-1}, corresponding to a rising main diameter of about 75 mm. The diameter of rising mains is generally larger than 75 mm so the test cells tended to have a higher film surface area to sewage volume ratio than a typical rising main.

Reactor mixing
Each of the reactors was well mixed.

Reactor feed
The reactor feed was domestic sewage collected from a sewer in Brisbane. Typical characteristics of the feed sewage were:

- COD: 270 to 485 mg/L.

- Sulphate concentration 10 to 25 mg S/L, sulphide concentration <3 mg S/L. Other species of sulphur (eg sulphite and thiosulfate) were at concentrations <1 mg S/L.

These values are typical of domestic sewage in Australia. The feed temperature was 20 C, which is also typical of Australian conditions.

Detention time

The system detention time varied between 2 and 6 hours during each cycle of the feed pumps and there were 3 cycles of the feed pumps each day.

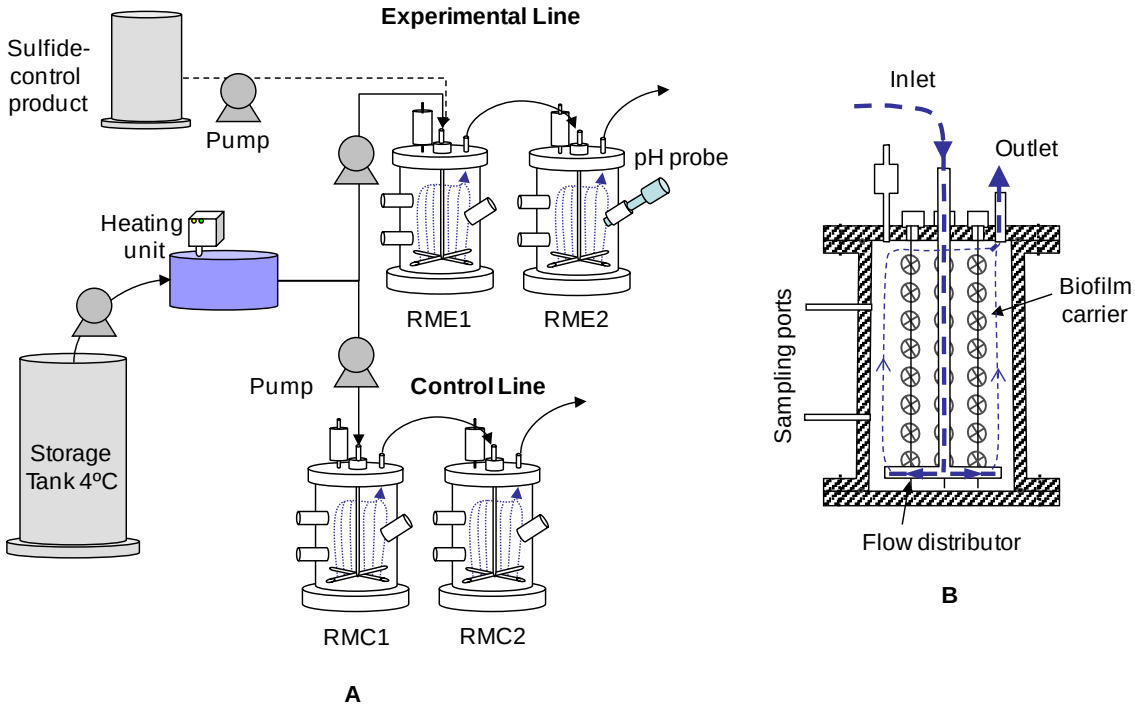

Figure 1. Reactor-based lab-scale sewer systems. A: Rising main reactors; B: Sectional view of a lab reactor. Biofilms carriers (appearing in white strings inside reactors) are placed in the reactors for biofilm growth. The carriers can be removed for micro-scale studies on biofilm structure and

(2.2) Test results

(2.2.1) Biosol

The results of suspended solids testing following dosing of the laboratory reactor train with Biosol are shown in Figures 2A and 2B. These tests span 4 periods:

- The baseline period where the biofilms in all 4 reactors were stabilised in the absence of Biosol dosing.

- Periods 1, 2 where the Biosol dose rate was 10 mg of Biosol solution /L of sewage. The mixing intensity was 0.29 Pa in period 1 and 2.97 Pa in period 2. This range is typical of rising main operation The low value is typical of normal rising main operation and the higher value would not normally be achieved in a rising main. However the high value was trialled to determine if increased shear would strip biofilm off the packing as the Biosol supplier claimed.

- Period 3 where a high mixing intensity was adopted and a second Biosol formulation was used.

The data in Figure 2A indicates that the mass of biofilm on the packing is similar in the first reactor in both the dosed and the control process trains. This situation persisted over a period of 100 days. Likewise, the data in Figure 5B indicates that the concentration of solids in the effluent from both reactors was similar. Thus, the data in these figures provides no evidence that Biosol acts to reduce biofilm accumulation or acts to destabilise existing biofilms.

The general conclusion that Biosol dosing has no effect on biofilm activity was supported by additional testing. Thus:

- Figure 3 indicates that the concentration of sulphide ion and methane is similar in the final effluent from both the dosed and the control process train.

- Figure 4 demonstrates that Biosol did not affect sulphide production rates in any of the test reactors.

- Figure 5 demonstrates that Biosol did not affect methane production rates in any of the test reactors.

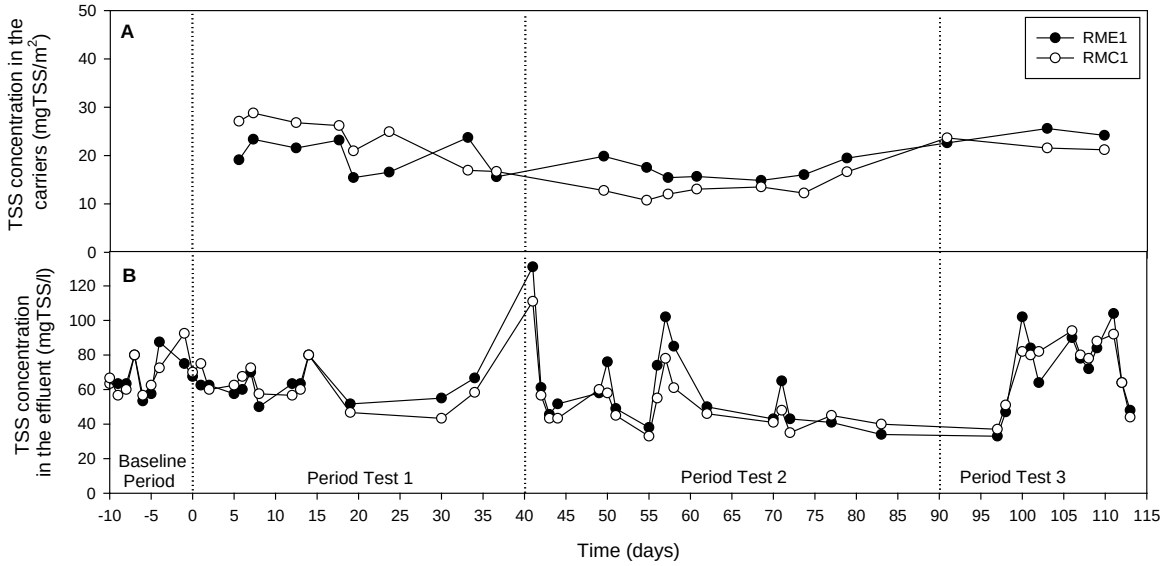

Figure 2. Solids concentration (A): Total suspended solids (TSS) concentration measured in the biofilm. (B): TSS concentration in effluent

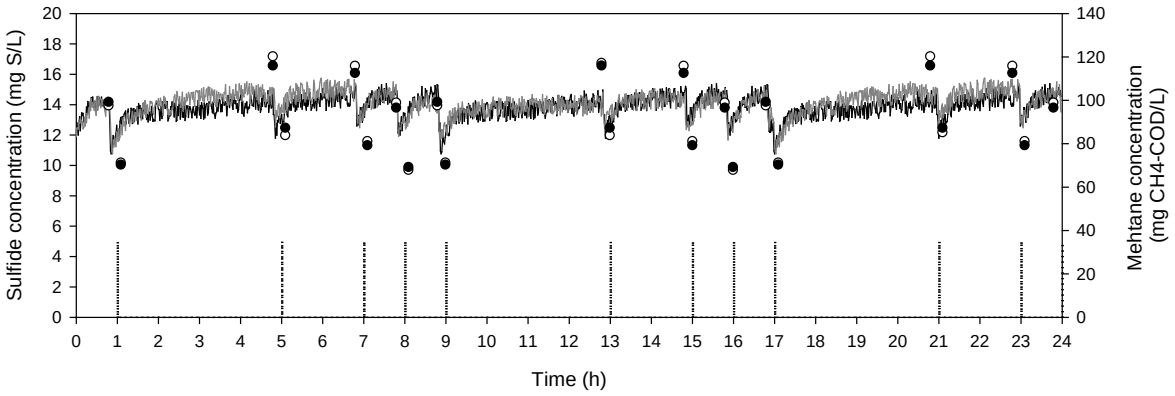

Figure 3. 24 hour methane and online sulfide data from RME2 and RMC2 corresponding to Days 109-110 after Biosol was initiated. (—): Sulfide online in RME2; (—): Sulfide online in RMC2; (o): Methane in RMC2; (•): Methane in RME2

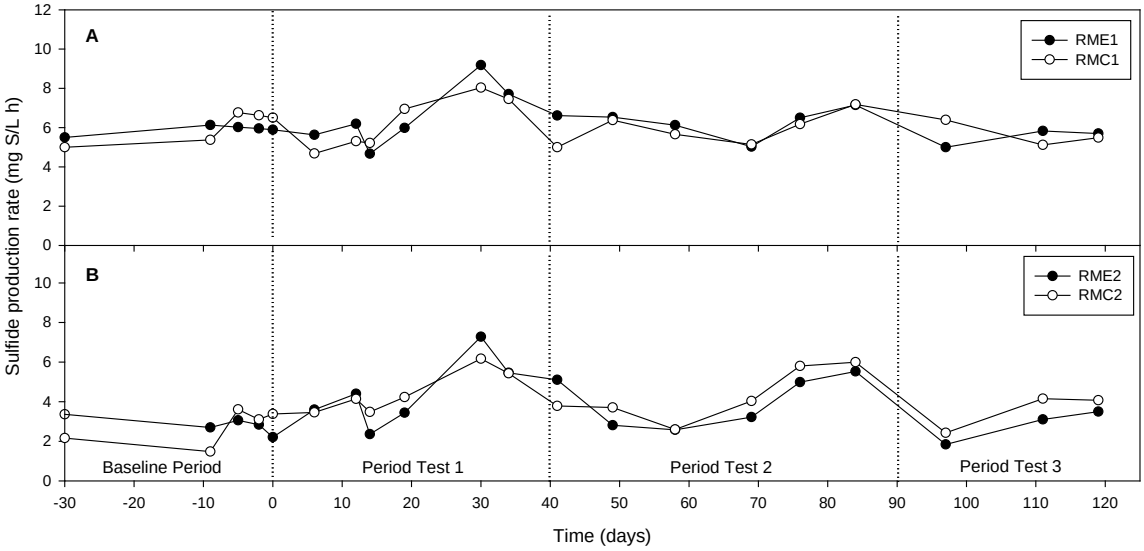

Figure 4. Sulfide production rates obtained in the activity tests from Biosol. (A): Upstream reactors (B): Downstream reactors. The rate is expresses as mg S per L reactor volume per hour.

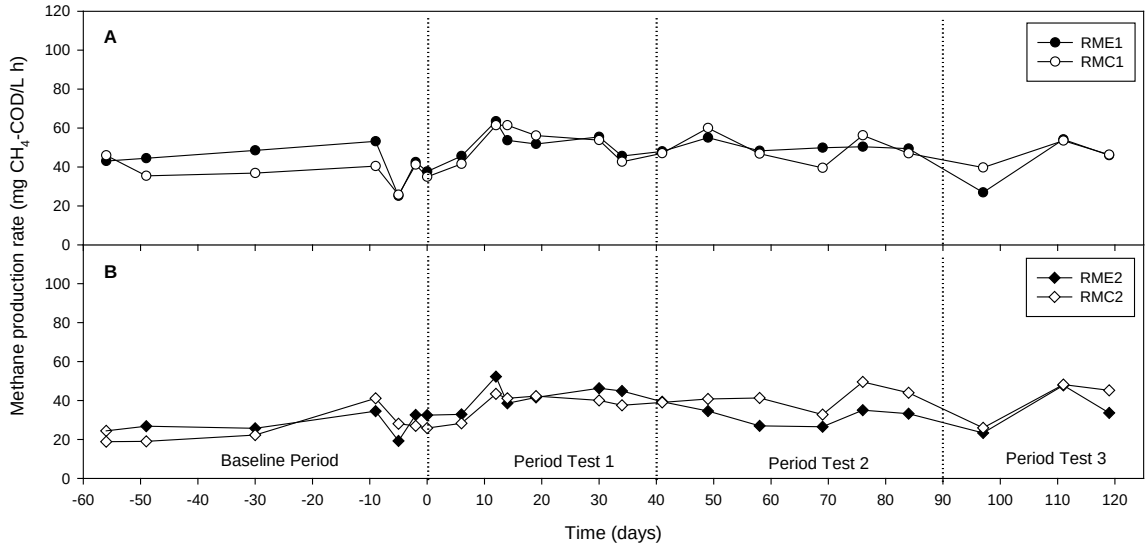

Figure 5. Methane production rates obtained in the activity tests from Biosol. (A): Upstream reactors (B): Downstream reactors. The rate is expresses as mg CH_4 as COD per L reactor volume per hour.

(2.2.2) Biokat

The effectiveness of Biokat was also evaluated in the laboratory reactors. The measured sulphide production rate in all 4 test reactors following dosing with Biokat is summarised in Figure 6. The data spans a period of about 100 days and includes data obtained during 4 test periods:

- A baseline period to stabilise the test reactors.

- Test periods 1, 2 and 3 where the dose rate was 1, 2 and 3 mg Biokat solution/L of sewage. The test reactors were operated at a low mixing intensity during these tests.

The results in Figure 6 indicate that Biokat did not affect the rate of sulphide generation in any of the test reactors. Likewise the data in Figure 7 indicates that Biokat did not affect methane production rates.

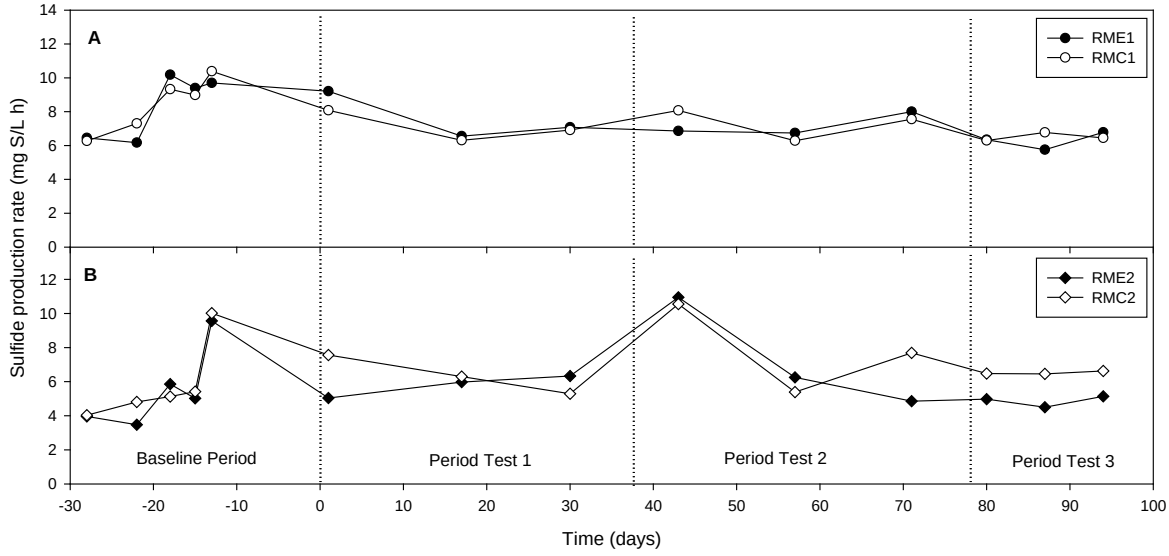

Figure 6. Sulfide production rates obtained in the activity tests from Biokat. (A): Upstream reactors (B): Downstream reactors. The rate is expresses as mg S per L reactor volume per hour.

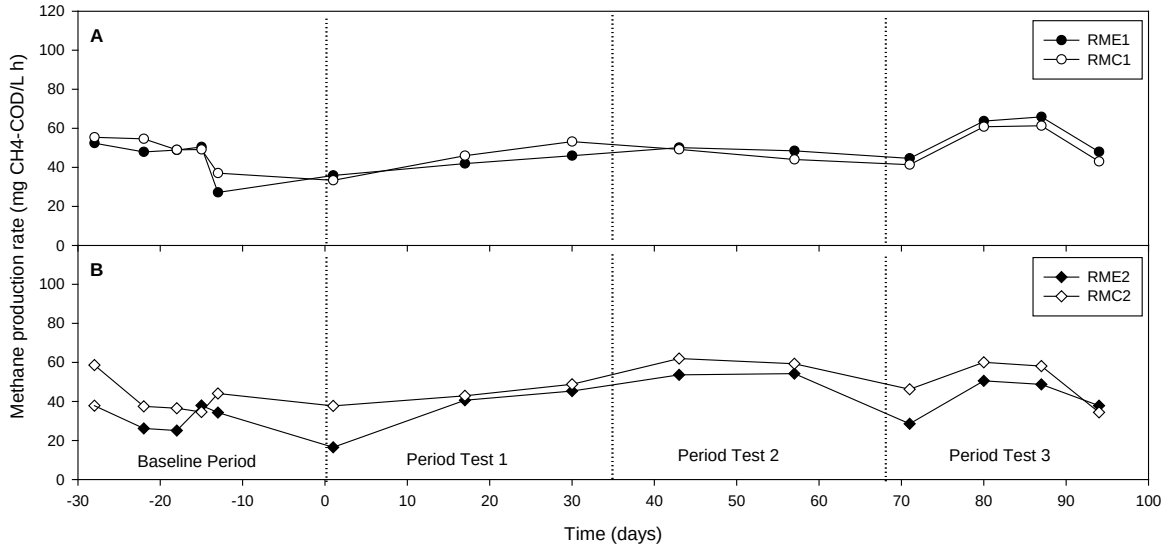

Figure 7. Methane production rates obtained in the activity tests from Biokat. (A): Upstream reactors (B): Downstream reactors The rate is expresses as mg CH_4 as COD per L reactor volume per hour.

(2.2.3) Probac

The results following dosing of the laboratory reactors with Probac are compared with those from the control process stream in Figure 8. The results span two test periods:

- A 'Baseline' period where the reactor biofilms were stabilised and

- A test period where the dose rate was varied between 5 and 15 mg Probac solution/L of sewage. The 'Steady State' data presented in Figure 8 is the average steady state result for all dose rates.

Figure 8 also includes values of the standard deviation for each test variable. These deviations are typically less than 5% of the average value, indicating that any systematic differences due to variations in the dose rate are very small.

The data in Figure 8 indicates that the sulphide generation rate was similar in both of the primary test reactors (ie the first reactor in both the dosed process train and the control process train) and also in both of the secondary reactors. Likewise, the data shows that the observed methane production rates were similar in both primary reactors and in both secondary reactors.

Thus, the data provides no evidence that Probac has any effect on biofilm activity in the test reactors.

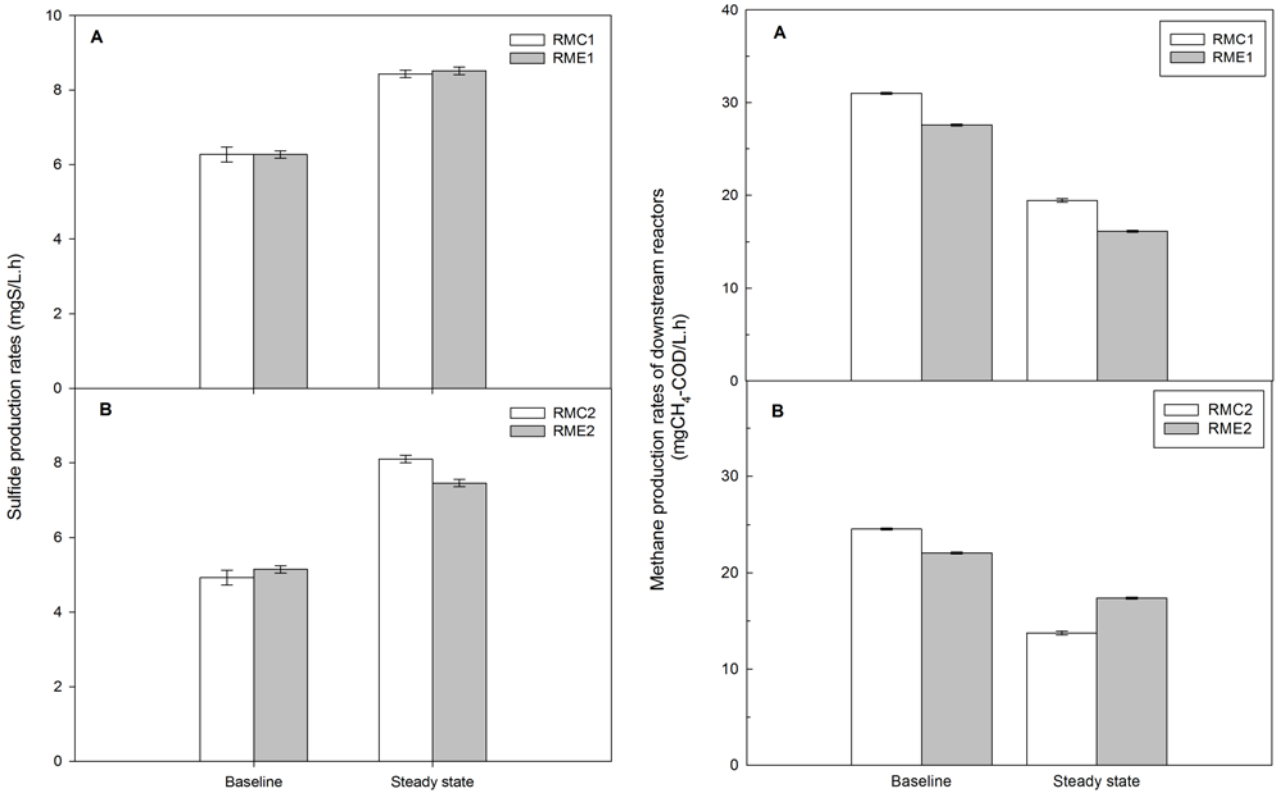

Figure 8. Average sulfide and methane production rates obtained from the activity tests with reactors dosed with Probac. (A): Upstream reactors (B): Downstream reactors. Bars on the data plot represent standard errors.

(3) Testing of chemical additives

(3.1) Ferric Salt

(3.1.1) Mechanism

Possible precipitation reactions involving ferric ion are listed below:

$$Fe^{3+} + 3HS^- \rightarrow 2FeS + S^0 + 3H^+$$

$$FeS \rightleftharpoons Fe^{2+} + S^{2-} \quad (Ksp = 6 \times 10^{-19})$$

$$Fe^{3+} + PO_4^{3-} \rightleftharpoons FePO_4 \quad (Ksp = 1.3 \times 10^{-22})$$

$$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_3 \quad (Ksp = 4 \times 10^{-38})$$

Addition of ferric salt to sewer precipitates the sulfide that is already present or is produced after its addition. When the ferric salt is added to a sewer in excess of demand for sulfide precipitation, it will bind with phosphate and hydroxide. However, the bound ferric ions will become available for sulfide precipitation when sulfide is generated again since the solubility product of the FeS precipitate is higher than that for other two precipitation products. In addition to this, addition of ferric salt inhibits the production of sulfide by sewer biofilm, which has been demonstrated by previous laboratory tests on sewer biofilm.

(3.1.2) Test results

Inhibition of sulphate reduction

The effect of ferric ion addition was evaluated using the laboratory reactor train described in Section 2.1. The results following dosing with ferric ion concentrations in the range 5 to 35 mg of ferric ion/L of sewage are shown in Figure 9.

The *Remaining relative sulphate reducing activity* presented in Figure 9A is the ratio of the rate of sulphate reduction in the dosed reactor train to the rate in the control reactor train once steady state conditions were reached. Values less than 1 indicate an inhibiting effect on sulphate reduction. Thus the data in Figure 9A shows that ferric ion concentrations in the range 5 to 35 mg/L all achieved a similar decrease in sulphate reduction rate of about 55%. This occurred in reactors with a high ratio of biofilm area to sewage volume operated with a detention time in the range 2 to 6 hours.

The data in Figure 9B is the volatile solids fraction in the final effluent from the dosed and control reactor trains under steady state conditions. The data indicates that suspended solids from the control reactor had a volatile solids fraction of around 80% whereas the ratio for the dosed reactor train was around 55%. This difference is attributed to the presence of inert iron sulphide in the biofilm.

The observation that ferric salt dosing inhibits sulphate reduction has implications for the preferred dosing point. Thus, in principle there are two possible dosing locations:

a) At the start of the sewerage system or

b) At a point slightly upstream of the point where sulphide control is required.

In both cases, all sulphide will be precipitated provided the dose rate is adequate. However if dosing occurs at the upstream location then the rate of sulphide production is expected to be reduced and a lower dose rate of ferric ion will be required.

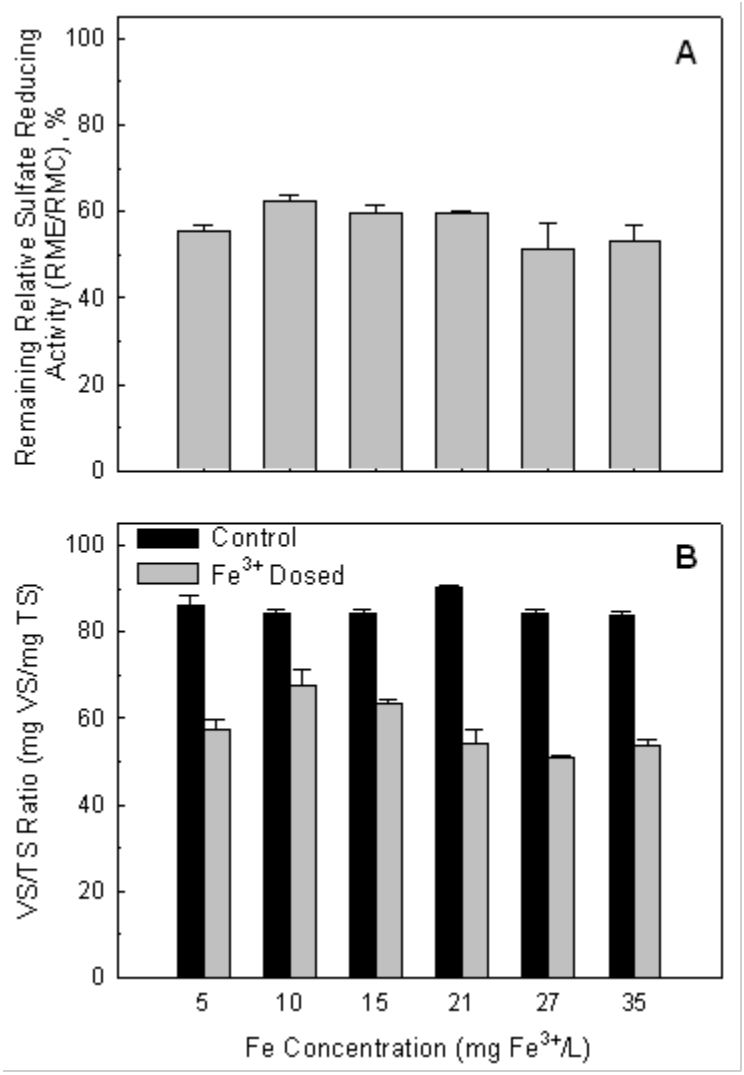

Figure 9. Steady state response of anaerobic sewer biofilm to ferric dosing (A): Remaining relative sulfate reducing activity of cultures exposed to different iron concentrations over long periods of time. (B): Steady state VS/TS ratio of control and ferric dosed biofilm reactors.

The rate at which sulphate reduction recovers following cessation of ferric ion dosing is summarized in Figure 10. This figure is based on data obtained with a dose rate of 15 mg ferric ion/L of sewage. The principal features are:

- Figure 10A shows that sulphate reducing activity in the dosed reactor train increased to about 90 to 95% of that in the control reactor within 7 days following cessation of dosing.

- Figure 10B indicates that the volatile solids fraction of the biofilm in the dosed reactor train increased only marginally to about 70% over the 30 days after dosing ceased.

The conclusion drawn from these results is that ferric ion dosing does have a residual effect and intermittent dosing may be a practicable approach to managing sulphate reduction and minimizing the total dose amount. The residual effect following cessation of dosing may persist for up to 7 days but an interval between dosing of less than 1 day appears necessary if biofilm activity is to remain suppressed at very low levels.

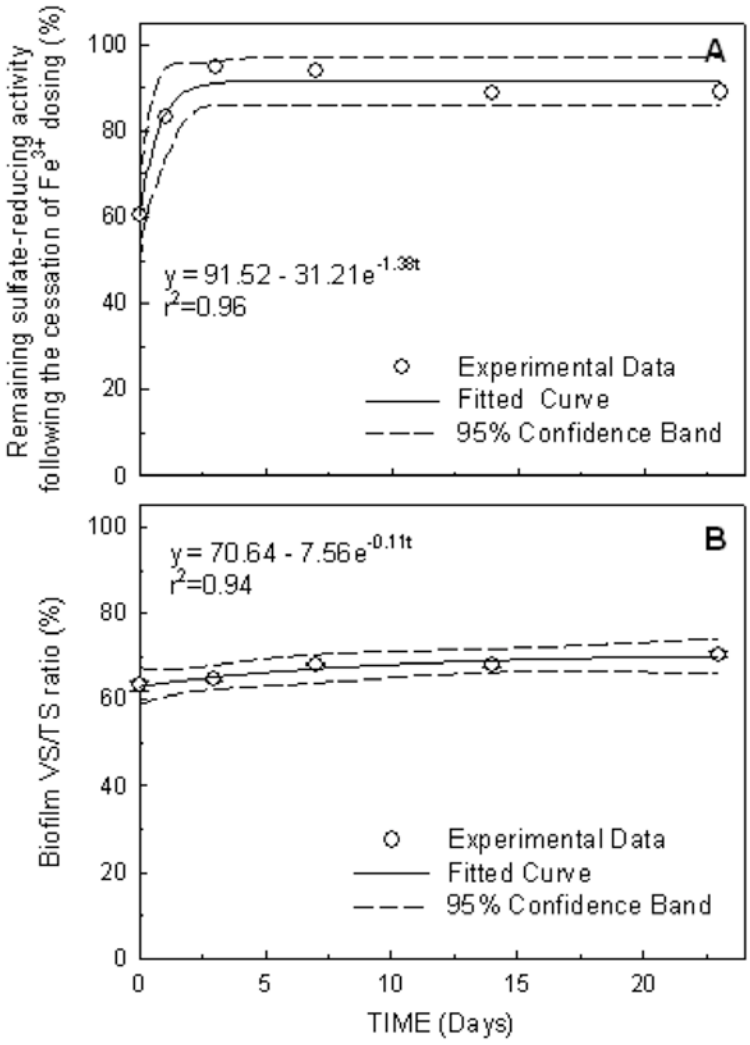

Figure 10. Response of the 15 mg Fe3+/L dosed culture subsequent to cessation of iron dosing. (A): Remaining relative sulfate reducing activity. (B): VS/TS ratio of the culture previously exposed to iron.

Effect on anaerobic digestion

The experimental program also included an evaluation of the effect of ferric ion dosing in a sewer on H2S levels in sludge gas from an anaerobic digester. The experiments were based on laboratory tests using a batch digester. The feed to the batch digester was prepared by:

a) Dosing sewage with a mixture of ferric and sulphide ion added in a stoichiometric ratio.

b) Adding the dosed sewage to an equal volume of waste activated sludge thickened by settling.

c) Aerating the mixture of sewage and thickened waste activated sludge for about 30 hours. This mixture was regarded as a laboratory analog of thickened mixed liquor in a sewage treatment plant.

The aerated mixture was then blended with waste activated sludge and primary sludge, both thickened to 3% dry solids, in the volumetric ratio 2:3:3. The waste activated sludge and primary sludge was obtained from a full scale plant operating on a predominantly domestic sewage.

The consequent mixture was then inoculated with sludge from an operating anaerobic digester and digestion was allowed to proceed to completion at 35 C over a period of about 20 days, at which time sludge gas production ceased.

Two sets of tests were undertaken. In one case the sewage samples were dosed with an additional 13 mg S/L (added as sulphate) and in the second set of tests the dose rate was 40 mg S/L. The consequent increased sulphur concentration in the batch digester is about 10% of this value because of the way the digester feed was prepared.

The concentration of hydrogen sulphide in sludge gas from the two sets of tests is shown in Figure 11. The results for the 13 mg S/L reactors include data for ferric ion dose rates in sewage over the range zero to 400 mg/L. The actual concentration of iron salt in the batch digester was 10% of these values. The data indicates that a high ferric ion dose rate of 400 mg/L reduced the peak concentration of H2S in sludge gas by a factor of 3. Lesser reductions were observed at lower dose rates.

Likewise, the data in Figure 11 for a sulphur dose rate in sewage of 40 mg S/L indicates that the peak H2S concentration in sludge gas was reduced by a factor of 2 at the highest sewage dose rate of 400 mg of ferric ion/L.

The conclusion reached following this investigation is that ferric ion dosed to a sewer at a rate equal to the stoichiometric rate required to precipitate sulphide ion is still able to suppress H2S emissions in an anaerobic digester.

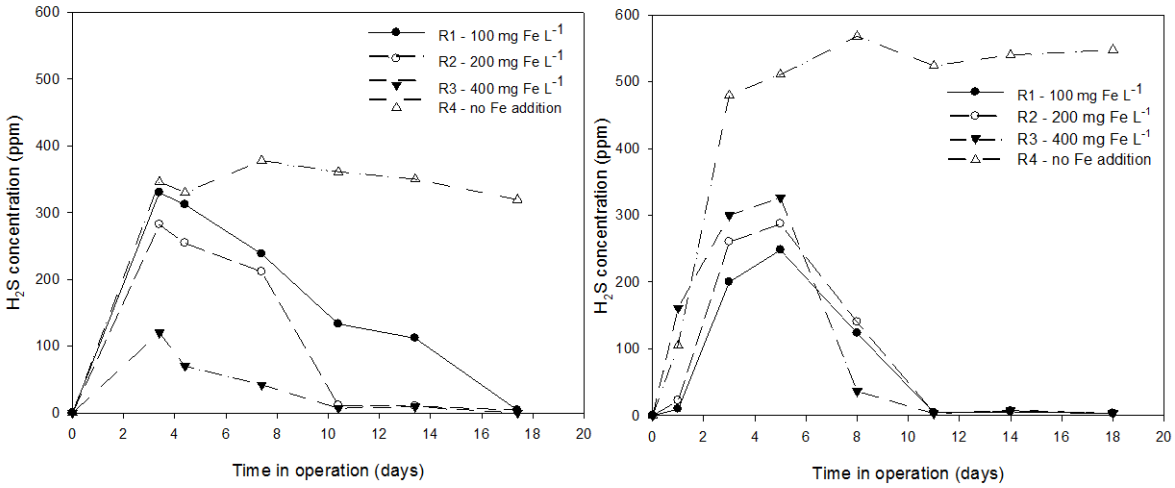

Figure 11. H_2S removal in anaerobic digestion batch tests with low-sulfur (13 mg/L, left) and high-sulfur (40 mg/L, right)

(3.2) Free Nitrous Acid (FNA)

(3.2.1) Mechanism

Dosing of nitrite solution to sewer at a pH below 7 produces FNA. FNA is toxic to the organisms in sewer biofilms thereby reducing sulfide and methane production.

The equilibrium between the concentrations of FNA and nitrite ion in water is given by:

$$FNA = \mathrm{NO_2^-}\text{-N} / (K_a \times 10^{pH})$$

where K_a is the ionization constant of the nitrous acid given by the following expression:

$$K_a = e^{-2300/(T+273)}$$

and T is temperature (°C).

The expressions above indicate that the equilibrium between FNA and nitrite ion is pH dependent. The molar ratio of the two species at pH 7 is 0.02%. This ratio increase by a factor of 10 for every unit decrease in pH. Thus the ratio is 2% when pH = 5.

(3.2.2) Laboratory testing

Biofilm viability

The effect of exposure to FNA on biofilm viability was evaluated using the reactors described in Section 2.1. The biofilm was established by operating the reactors in continuous mode for some time prior to stopping the feed and dosing the reactor with FNA. Two sets of trials were conducted. In one case the exposure persisted for 6 hours and in the other case the exposure was for 24 hours. At the end of the exposure time, the biofilm viability was determined using a staining process capable of differentiating between cells with a damaged outer membrane (ie dead cells) and those with an intact membrane (ie live cells).

The results of the cell viability tests are presented in Figure 12. Two sets of data are included. The data for 'intact' biofilms is based on analysis of biofilm attached to the packing within the test reactors. The data for 'disrupted' biofilm refers to testing of cellular material removed from the packing by sonication.

The results in Figure 12 indicate:

- Exposure to FNA reduced the biofilm viability. In general, exposure for 24 hrs achieved a viability about 65% of that achieved after a 6 hr exposure.

- The extent of reduction in biofilm viability is dependent on the FNA concentration. However there is limited additional decrease in biofilm viability at FNA concentrations beyond about 0.2 mg N/L.

- The proportion of viable cells in material removed by sonication is typically about 50% of the proportion in the intact biofilm.

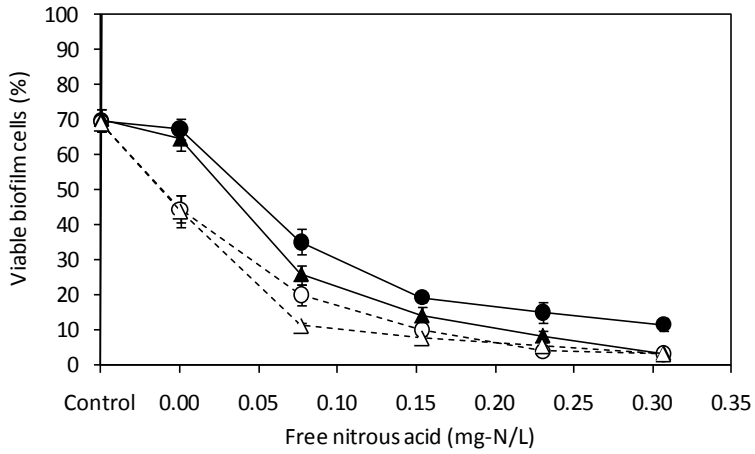

Figure 12. The viable biofilm cells (%) in intact (filled symbols) and disrupted (empty symbols) biofilms after being exposed to FNA at pH 6 for 6 (● and ○) and 24 (▲ and Δ) hours. The first data points for each series are the control biofilm samples (pH = 7.6). X-axis is the initial free nitrous acid concentration during a batch test, and Y-axis is the percentage viable cells in the biofilm sample collected from the experimental reactor.

Effect on sulphide and methane production

The effect of FNA addition on sulphide and methane production was evaluated by operating the test reactors described in Section 2.1 in continuous mode. The test reactors received a single slug dose of FNA once steady state operation had been established. The effect of this single dose on sulphide and methane production rates in presented in Figure 13. The data in this figure is the ratio of observed production rates in the test reactors to that observed in a control reactor.

The data in Figure 13 indicates:

- There is limited difference between the results obtained at an FNA dose rate of 0.18 mg N/L and 0.36 mg N/L.

- Slug dosing with FNA has a residual impact on biofilm activity. Thus the rate of sulphide production recovered to about 50% of the control value about 8 days after the dosing event. The corresponding interval for methane production is around 55 days.

These results suggest that intermittent dosing of FNA would be an effective approach to reducing biofilm activity and simultaneously minimizing chemical costs.

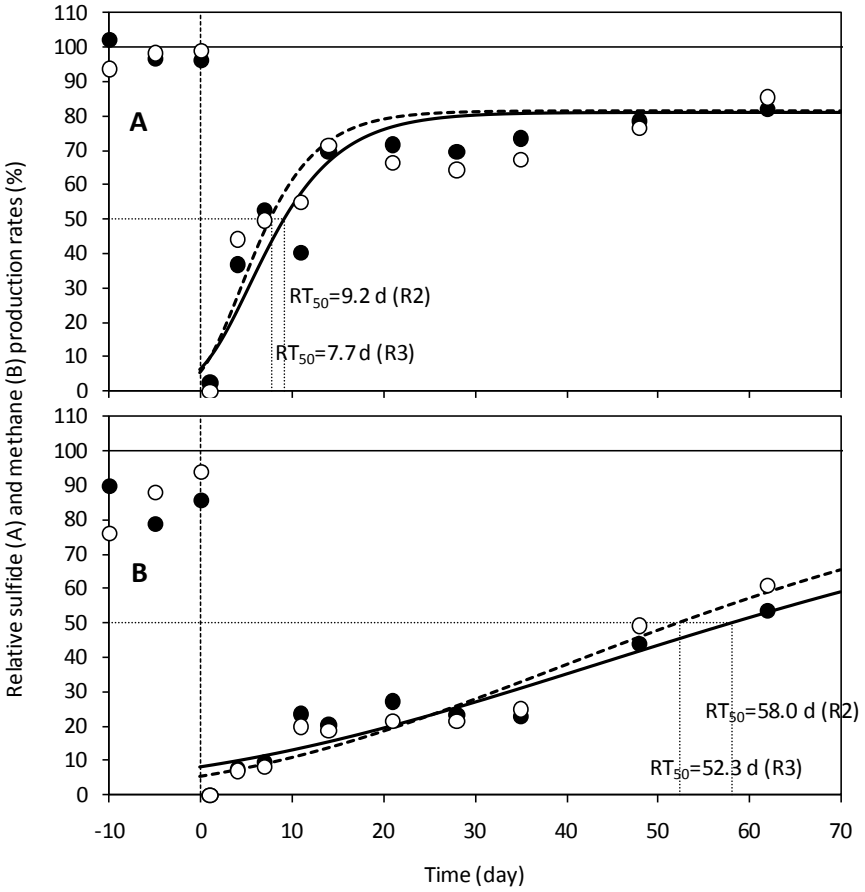

Figure 13. Relative hydrogen sulfide (A) and methane (B) production rates during the stabilization and recovery periods after being exposed to free nitrous acid at 0.18 (●) or 0.36 (○) mg-N/L, in reactor R2 and R3 respectively, on day 0. The solid (——) and dashed (- - -) lines are regression lines.

Effect of simultaneous hydrogen peroxide addition

The effect of simultaneous addition of both FNA and hydrogen peroxide (H2O2) on cell viability was tested by operating the reactors described in Section 2.1 for some time until steady state

conditions were achieved. At this time the packing was removed from the test reactors and placed in a separate capped container filled with sewage. A solution of FNA and H2O2 was added at this time and the biofilm was homogenized using sonication 6 hours later and stained to determine the proportion of viable cells. This proportion was compared with that in a control reactor to determine the 'killing efficiency' of the chemical dose.

The results of the simultaneous dosing tests are presented in Figure 14. These results indicate that H2O2 dosing increase the extent of biofil degradation achieved by FNA alone. The extent of this reduction is summarized in Table 1 and this data can be used to evaluate the cost benefit of supplementary dosing with H2O2.

Table 1. Combination of FNA and H2O2 dosing to achieve target killing efficiency of microbes in sewer biofilm

FNA	*Approximate H2O2 concentration required to achieve the target killing efficiency (mg/L)*		
(mg – N/L)	*50%*	*80%*	*90%*
0	*25*	*>90*	*>90*
0.05	*10*	*50*	*75*
0.10	*0*	*25*	*55*
0.20	*0*	*5*	*20*
0.30	*0*	*0*	*15*
0.40	*0*	*0*	*0*

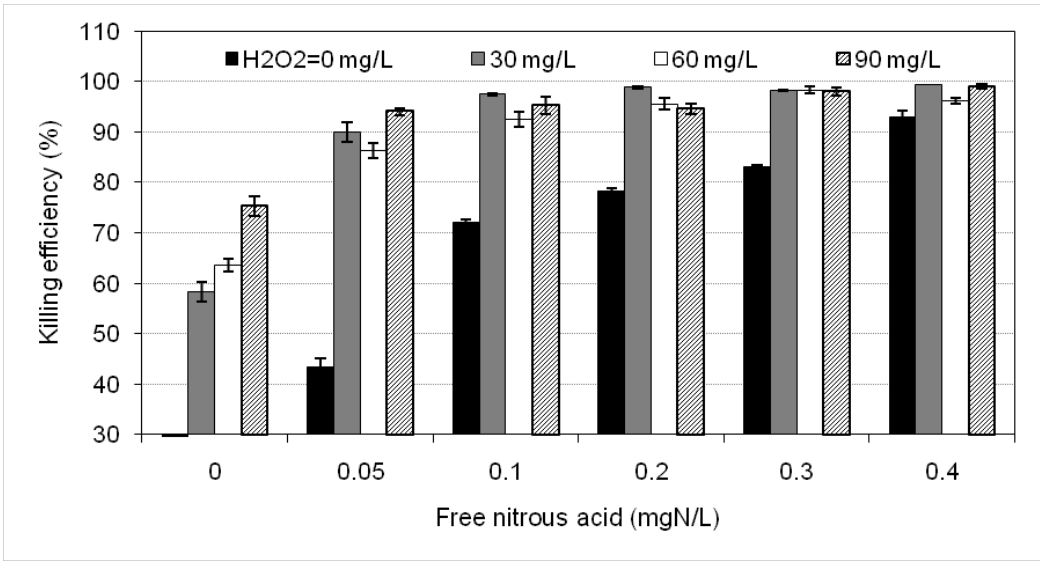

Figure 14. Killing efficiency of free nitrous acid (0, 0.05, 0.1, 0.2, 0.3, 0.4 mgN/L), hydrogen peroxide (0, 30, 60, 90 mg/L) and their combination

(3.2.3) Field tests

(3.2.3.1) Test arrangement

The field test program was based on testing in the UC09 rising main located on the Gold Coast. The principal features of the main include:

- The diameter is 150 mm and the length is 1080 m.
- The main receives domestic sewage and the hydraulic detention time typically varies between 1.7 and 5.7 hours. This estimate has been determined by considering the travel time of sewage slugs in the main. The variability arises because of the diurnal variability in the frequency of operation of the wet well pumps at the inlet to the rising main.
- Typical water velocities in the main during pump operation are 1 m/sec.
- The sampling location is a manhole, 828 m downstream of the inlet. The hydraulic detention time to this point is 75% of the values listed above.

(3.2.3.2) Test results for sulphide and methane generation

Average sulphide concentrations in sewage measured at the sampling location for a flow paced FNA dose rate of 0.25 mg N/L are shown in Figures 15 and 16.

Figure 15 applies to a dosing regime that extended over 2 days from 2000 to 0800 the next day. This corresponds to the period when the detention time in the main was a maximum of about 4 hrs to the sampling point. By contrast the data in Figure 16 is based on a trial where the dosing regime involved two dosing periods separated by 4 days. The first dosing period was protracted, about 20 hours and the second was 8 hours at a time of peak flow in the main.

The data in Figure 15 indicates that the sulphide concentration in sewage at the sample point decreased to zero during the dosing period. It subsequently recovered to about 50% of the original value within about 5 days. This result is consistent with the outcomes of the laboratory trails described in Section 3.2.2. A similar outcome is indicated in Figure 16 although the second 8 hour dose at a period of peak flow in the main did not reduce sulphide levels to zero at the sample point.

Methane concentrations in sewage at the sample point are shown in Figure 17. This figure includes data obtained at 3 different times:

- Before FNA addition
- 33 days after the 2 separate dosing events applicable to Figure 15.
- 36 days after the 2 separate dosing events applicable to Figure 16.

The principal conclusion arising from the data in Figure 17 is that there has been no recovery of the organisms responsible for methane production in the period up to 5 weeks after the cessation of FNA dosing.

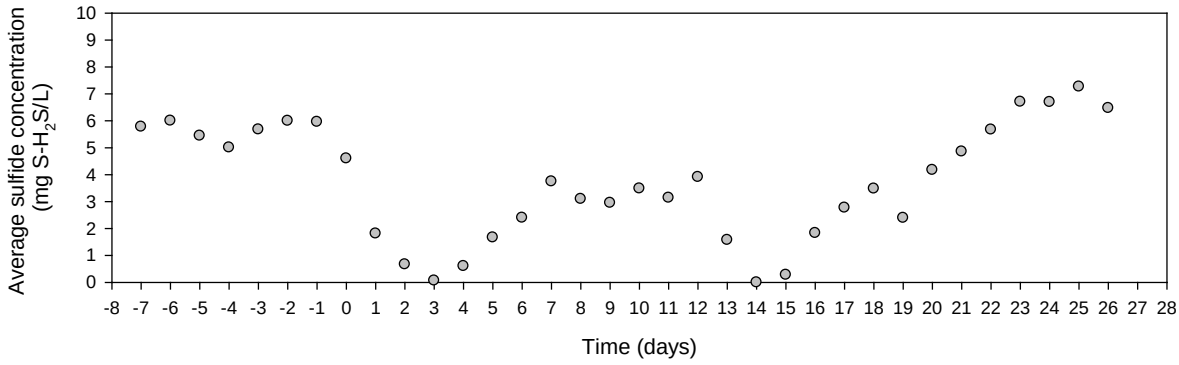

Figure 15. Daily average sulfide concentrations in sewage at the UC09 sample point.. Days -8 to 0: baseline period; Days 0 to 2: FNA dosing period; Days 3 to 26: recovery after stoppage of FNA dosing.

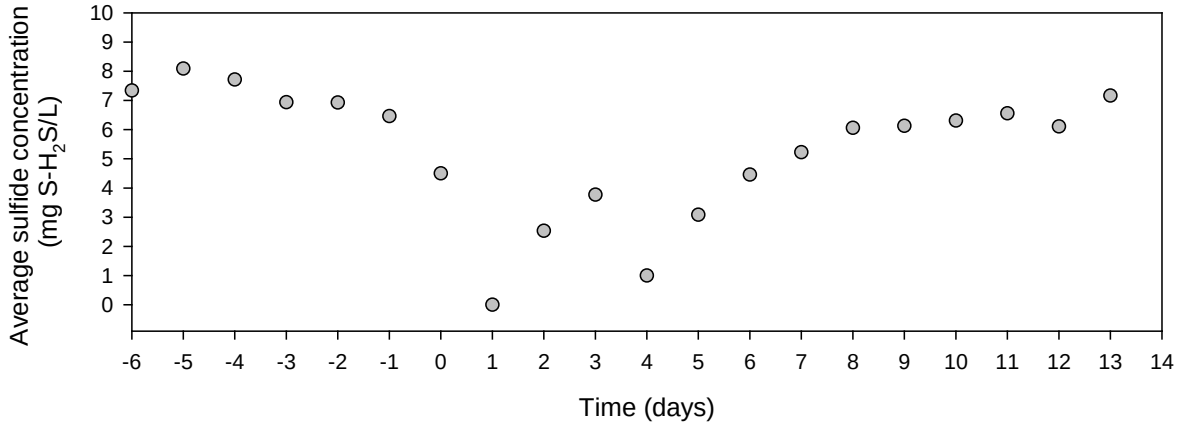

Figure 16. Daily average sulfide concentrations in sewage at the UC09 sample point. Dosing occurred in the interval day 0 to 1 and at day 4.

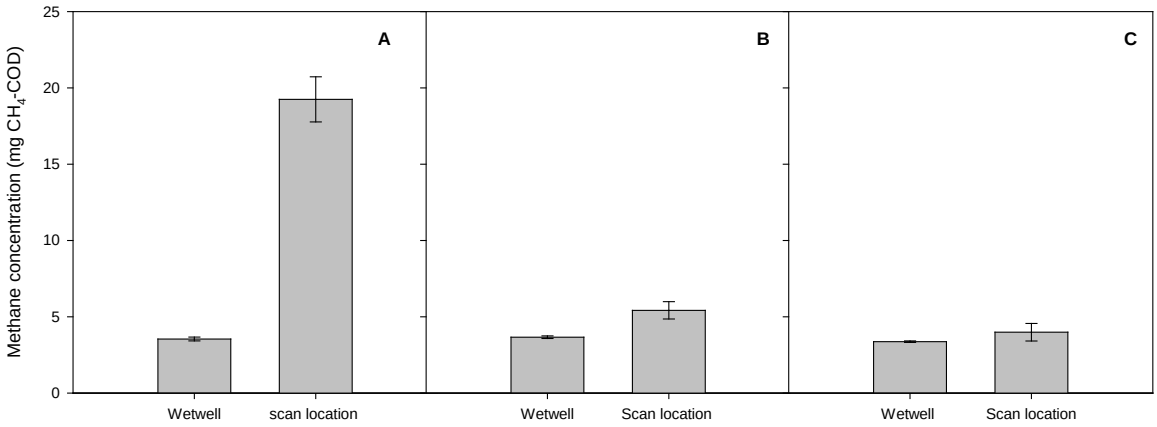

Figure 17. Daily average methane concentrations in sewage at the UC09 wet-well and at the UC09 sample point. A: Baseline period, before FNA addition; B: 33 days after 2 consecutive days of dosing; C: 36 days after two separate dosing events 4 days apart

(3.3) Caustic shock

(3.3.1) Mechanism

Exposure of biofilm to an elevated pH level (beyond 10.5) has a biocidal effect on the microorganisms responsible for both sulfate reduction and methane production.

(3.3.2) Laboratory studies

Sulphide and methane generation

The effect of caustic dosing on sulphide and methane generation was investigated using the test reactors described in Section 2.1.

The results following a short term exposure of 6 hours at a series of pH's in the range 10.5 to 12.5 are presented in Figure 18A. These results indicate that pH has little effect on the rate of recovery of sulphide production subsequent to the dosing event at this long exposure time. Furthermore, sulphide levels did not reach 50% of the pre dosing value until about 4 days after the dosing event.

The data in Figure 18B does show a systematic trend towards lower recovery rates as pH increases at the lower exposure time of 1 hour. Finally Figure 18C shows a systematic decrease in the rate at which sulphide generation recovers as exposure time is increased at a pH of 10.5.

The data in Figure 18 has been summarised in Table 2 to indicate the effect of variations in pH and exposure time. Table 2 indicates that recovery times at pH 11.5 and 12.5 are similar to those at 10.5 and dosing at the higher pH's is unlikely to be justifiable. Likewise the data suggests that, when dosing occurs at pH 10.5, the decrease in recovery time as exposure time increases is marginal and it is therefore quite likely that low exposures around 1 hour are suitable. Under these conditions, the data suggests that sulphide generation rates will recover to 50% of the pre dose levels within about 3 days.

Table 2: Time taken for sulphide generation rates to recover to 50% of the rate prior to caustic dosing.

Dose pH	Exposure time (hr)	Time for sulphide generation to reach 50%
10.5	0.5	3.5
	1	2.8
	2	4.0
	6	4.5
11.5	1	3.0
	6	4.5
12.5	6	4.5

Similar results for the rate of recovery of methane generation following dosing at pH 10.5 are shown in Figure 19. The influence of increased exposure time is marginal in this case also and an exposure time of 1 hour appears appropriate. However the rate of recovery of methane generation is much lower than that for sulphide generation and 50% recovery did not occur within 17 days of the dosing event.

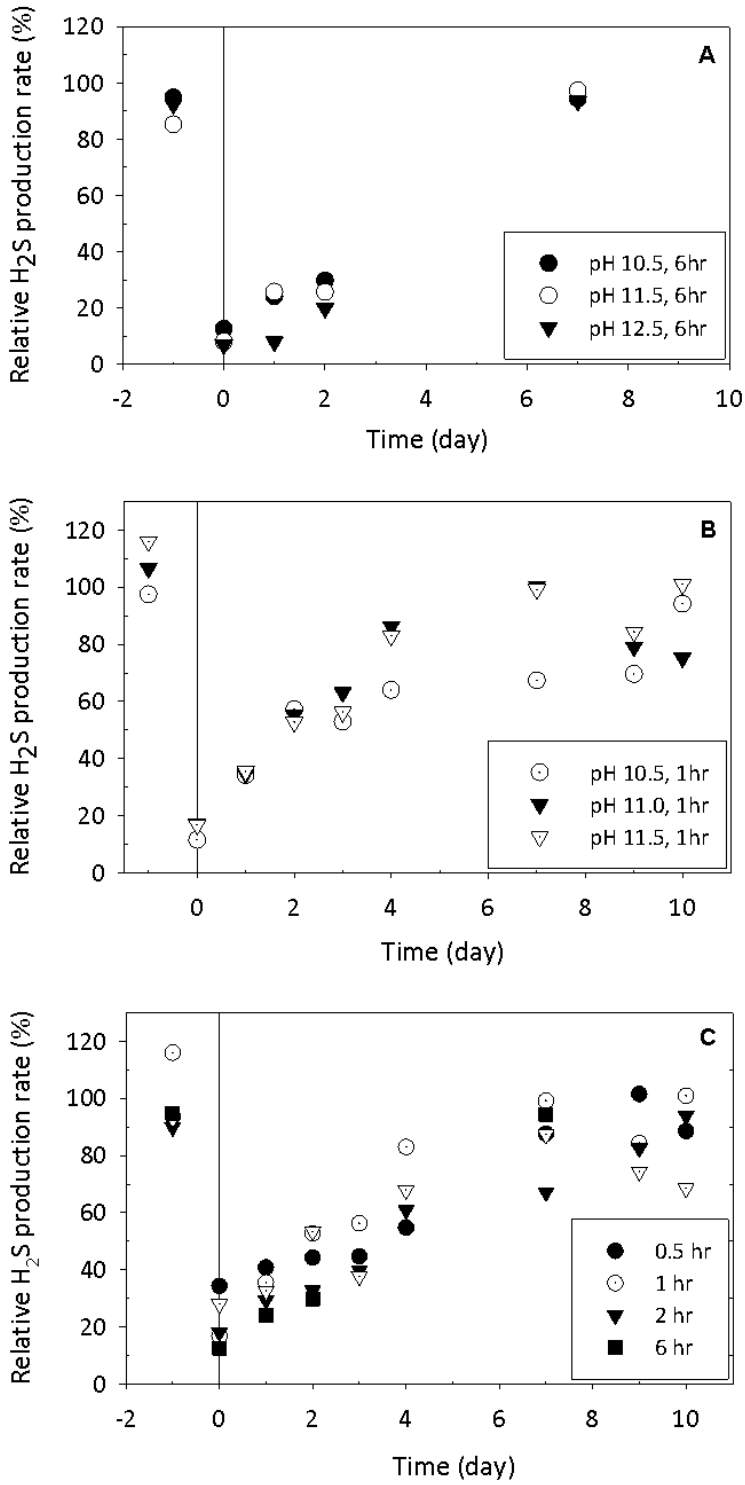

Figure 18. Relative sulfide production rates. (A): 6 h exposure time of different pH. (B): 1h exposure time of different pH, and (C) different exposure time at pH 10.5.

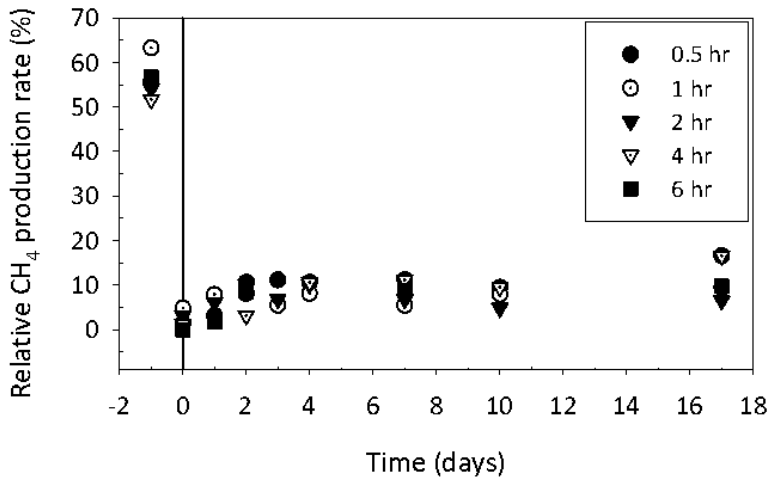

Figure 19. Relative methane production rates at pH 10.5 with different exposure times

Biofilm viability

The effect of caustic dosing on the viability of the biofilm in the laboratory reactors was evaluated using the staining technique described in Section 3.2.2. The results are presented in Figure 20.

The data in Figure 20B indicates that the proportion of viable biomass dropped to below 50% following exposure to a caustic shock at pH = 10.5 for periods greater than 0.5 hour. The subsequent increase in the proportion of viable biomass over a period of days is consistent with the observed rate of recovery in suphide generation summarized in Table 2.

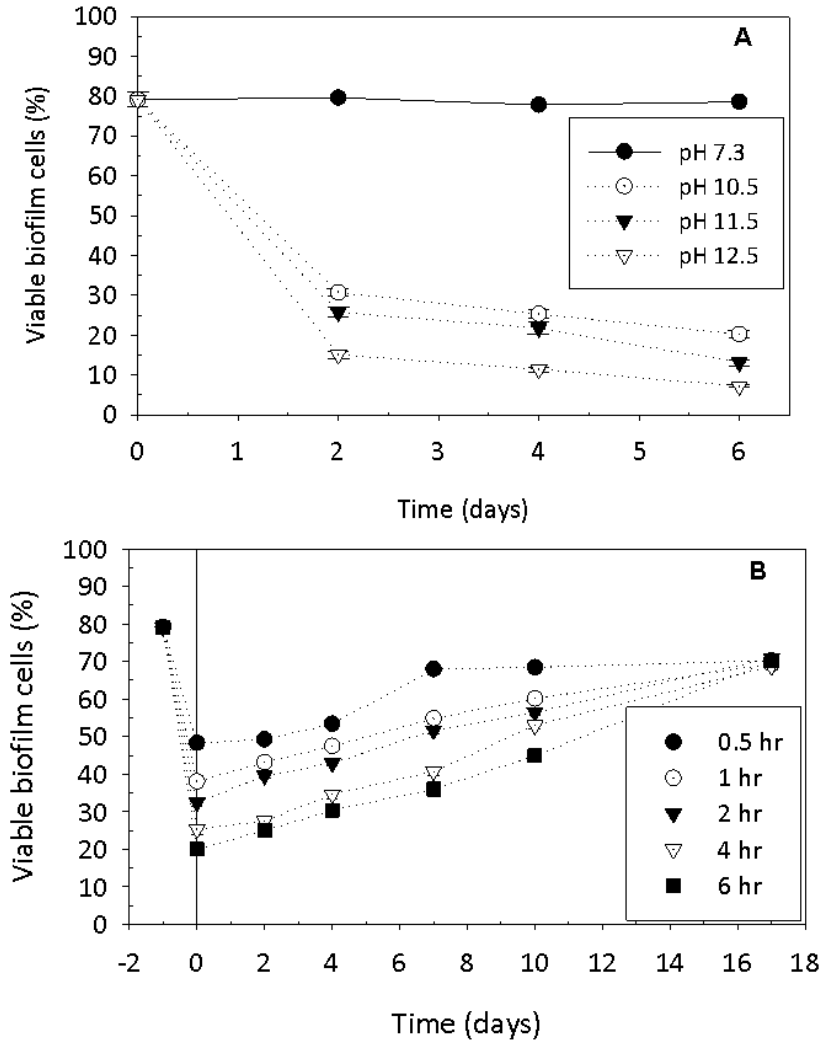

Figure 20. The viable biofilm cells (%) at (A) Different pH level ***(exposure time?)****, (B) Different exposure times at pH 10.5*

(3.3.3) Field tests

(3.3.3.1) Test arrangement

The effect of caustic shock on sulphide generation was evaluated by dosing into the wet well at the start of the UC09 rising main described in Section 3.2.3.1.

(3.3.3.2) Test results for sulphide generation

The concentration of total dissolved sulphide at a location 829 m downstream of the dosing point in the UC09 main is shown in Figure 21 following a caustic dose to pH = 10.5 for 2 hours. The travel time to the sampling point typically varies between about 1.3 and 4.3 hours due to the normal diurnal variability in sewage flow rate.

The data in Figure 21 shows a small increase of about 1.5 in the pH at the sampling point following the dosing event midway through Tuesday 23. This increase in pH is much less than at the dosing point. The data also shows a decrease in sulphide levels at the sampling point after

the dosing event. This decrease was very marked during the dosing period when downstream sulphide levels were say 10% of the normal values. However full recovery of sulphide levels appears to have occurred within 24 hours of the dosing event.

Figure 22 includes similar data following a 6 hour exposure to pH = 11.5. In this case the pH at the sampling point increased to about 10.5 during the dosing period and 50% recovery of sulphide generation rates took 4 to 5 days.

The general conclusion arising from these field tests is similar to that arising from the laboratory tests discussed in Section 3.3.2. That is, a short term exposure to a pH around 10.5 reduces sulphide production to below 50% of the normal value for a period of about some days, in the range 3 to 5. However dosing to a pH above 10.5 is required to ensure all of the biofilm is exposed to the requisite pH increase. A nominal target value is pH = 11.5 at the inlet of a rising main with a detention time in the range 1 to 4 hours.

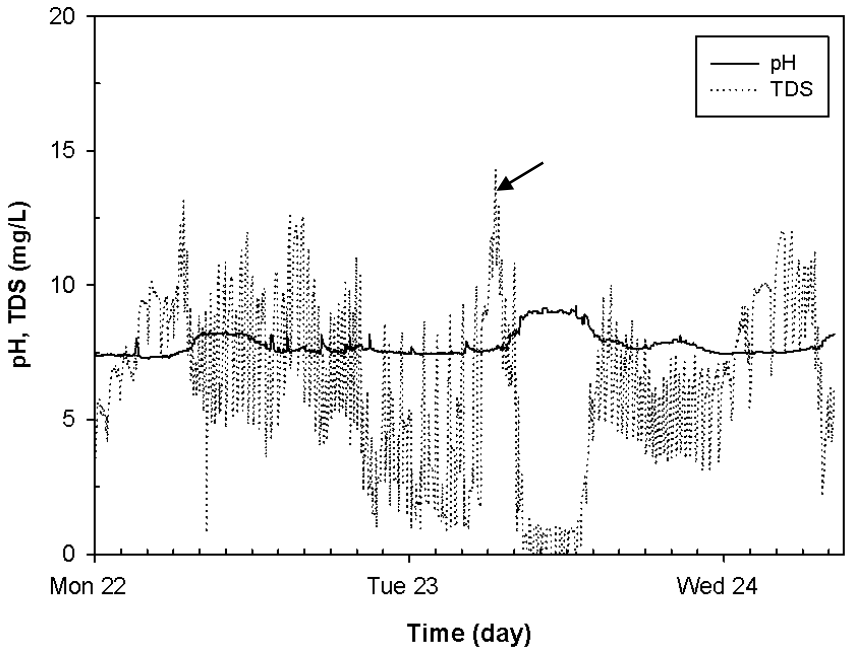

Figure 21. Online sulfide profiles in the UC09 main (828m downstream location) following a 2 hour exposure to pH = 10.5. (TDS is the concentration of total dissolved sulphide).

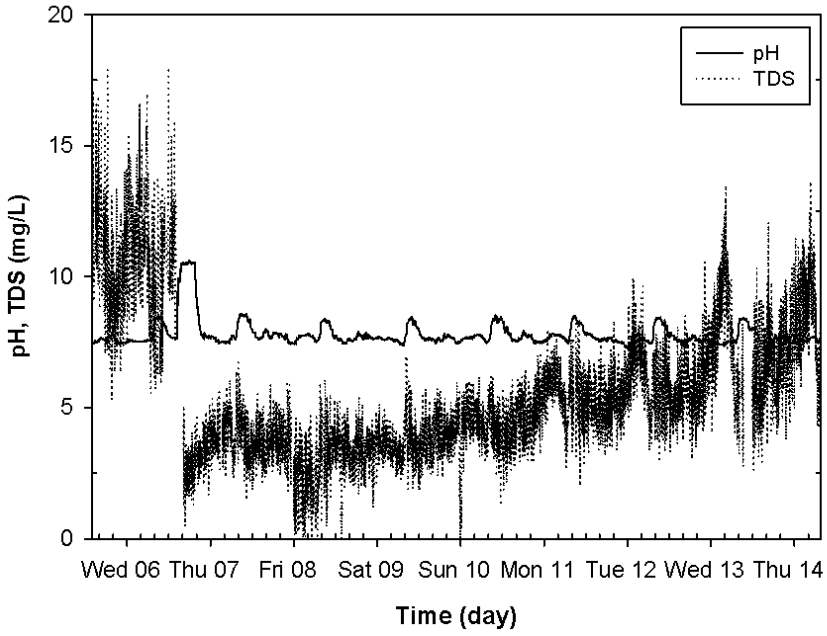

Figure 22. Online sulfide profiles in the UC09 main (828m downstream location) following a 6 hour exposure to pH = 11.5. (TDS is the concentration of total dissolved sulphide).