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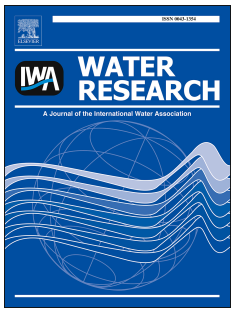

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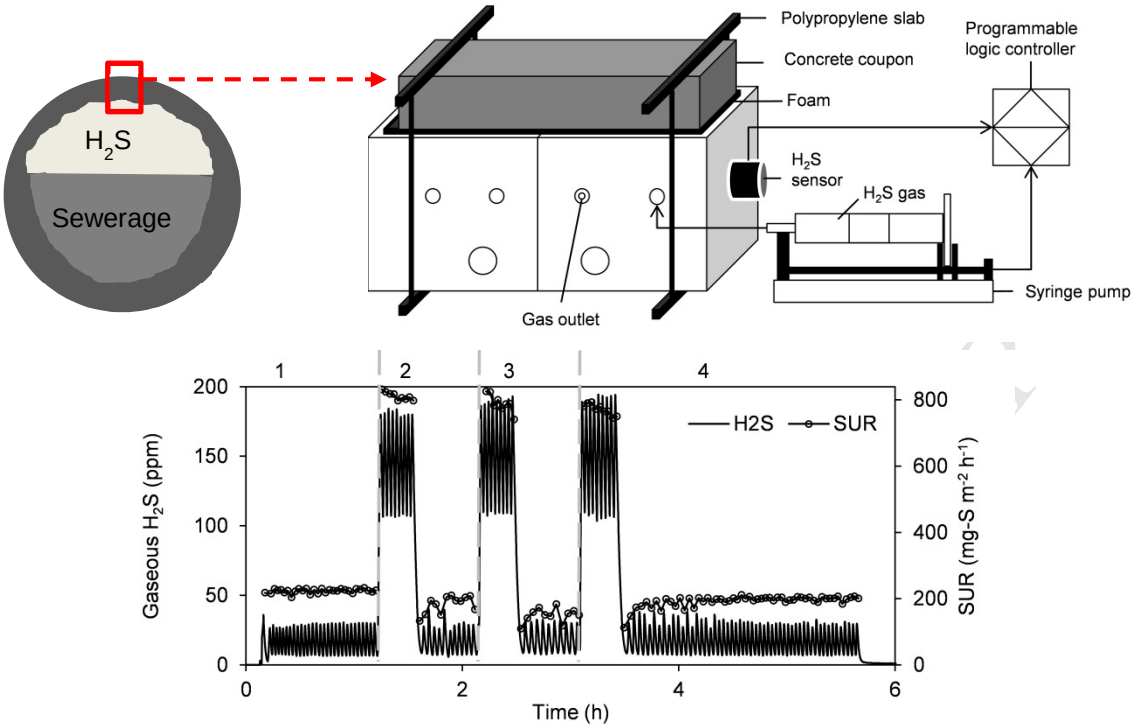

Impact of fluctuations in gaseous H_2S concentrations on sulfide uptake by sewer concrete: the effect of high H_2S loads

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Abstract

The acid production from the oxidation of hydrogen sulfide (H_2S) in sewer air results in serious corrosion of exposed concrete surfaces in sewers. Large fluctuations of gaseous H_2S concentrations occur in sewers due to the diurnal profiles of sewage flow and retention times and the necessity of intermittent pumping of sewage from pressure pipes into gravity pipes. How the high concentrations of H_2S due to these events may affect H_2S uptake and subsequent corrosion by concrete sewers is largely unknown. This study determined the effect of short- and long-term increases in H_2S levels on the sulfide uptake rate (SUR) of concrete surfaces with an active corrosion layer. The results showed that during the high load situation the SUR increased significantly but then decreased (compared to the baseline SUR) by about 7 – 14% and 41 – 50% immediately after short- and long-term H_2S high-load periods, respectively. For both exposure conditions, the SUR gradually (over several hours) recovered to approximately 90% of the baseline SUR. Further tests suggest multiple factors may contribute to the observed decrease of SUR directly after the high H_2S load. This includes the temporary storage of elemental sulfur in the corrosion layer and inhibition of sulfide oxidizing bacteria (SOB) due to high H_2S level and temporary acid surge. Additionally, the delay of the corrosion layer to fully recover the SUR after the high H_2S load suggests that there is a longer-term inhibitive effect of the high H_2S levels on the activity of the SOB in the corrosion layer. Due to the observed activity reductions, concrete exposed to occasional short-term high H_2S load periods had an overall lower H_2S uptake compared to concrete exposed to constant H_2S levels at the same average concentration. To accurately predict H_2S uptake by sewer concrete and hence the likely maximum corrosion rates, a correction factor should be adopted for the H_2S fluctuations when average H_2S levels are used in the prediction.

Key words: hydrogen sulfide; fluctuation; high load; sewer; concrete; corrosion

1. Introduction

Sulfide induced concrete corrosion in sewers is present worldwide, causing severe structural deterioration and ultimate structural damage to wastewater catchment networks, requiring very difficult and costly rehabilitation efforts (Sydney et al., 1996; US Environmental Protection Agency 2010). According to ASCE's 2013 Report Card for America's Infrastructure and the report from United States Environmental Protection Agency (US Environmental Protection Agency 2010), many of the approximately 1.2 million km of sewer mains in the United States were installed after World War II and are in need to be repaired or replaced now. The sewer rehabilitation costs in US were estimated to be about $3.2 billion for 2009 alone and the national capital investment for repair of the wastewater and stormwater system is evaluated to be approximately $298 billion in the next twenty years (US Environmental Protection Agency 2010). Hence protecting sewers from deterioration has a major beneficial impact globally through increased service life and reduced repair/replacement costs.

In sewers, sulfide is produced by a diverse group of bacteria (e.g. *Desulfovibrio desulfuricans*) using sulfate or organic sulfur as the electron acceptor in strict anaerobic conditions, mostly in sediments and biofilms occurring in fully filled (pumped) pressure pipes (Hvitved-Jacobsen et al., 2013; Sharma et al., 2008). The sulfide is mainly produced in the biofilm and diffuses outwards into the bulk sewage (Gutierrez et al., 2008; Parker 1951; Pomeroy and Boon 1976; Satoh et al., 2009; US Environmental Protection Agency 1974). Once a gas phase is present in sewers, for example in partially filled gravity pipes, at manholes or pumping station wet wells, H_2S can transfer from the liquid to the gas phase. The gaseous H_2S can be absorbed by the exposed, wet concrete surfaces and chemically and/or biologically oxidized to sulfuric acid. Sulfide oxidizing bacteria (SOB) are detected in the biofilms in aerobic (gas-phase exposed) sections of sewer pipes and their sulfuric acid

production is directly associated with concrete corrosion (Cayford et al., 2012; Ling et al., 2014; Okabe et al., 2007; Pagaling et al., 2014). The reactions between sulfuric acid and concrete components (e.g. calcium silicate hydrates) will form expansive products, e.g. ettringite and gypsum, causing cracks and loss of mechanical strength of the concrete pipe (Müllauer et al., 2013; O'Connell et al., 2010; Zivica and Bajza 2001). However, recent findings indicate that the iron dissolution in the corrosion layer and rust precipitation near the corrosion front was the actual cause for the formation of cracks, which accelerated the overall corrosion process (Jiang et al., 2014b).

To facilitate the prediction and extension of the service-life of concrete sewers, it is very important to identify the relationship between environmental factors and the concrete corrosion rate. It has been recognized for decades that environmental factors, such as relative humidity, temperature and H_2S levels, can affect the concrete corrosion rate (Apgar and Witherspoon 2007; Islander et al., 1991; Parker 1951; Rootsey et al., 2012; Wiener et al., 2006). However, research on identifying the effects of key environmental factors on concrete corrosion is still limited due to the very slow progression of concrete corrosion and the difficulties of measuring directly relevant factors under realistic conditions (Romanova et al., 2014). In fact, many studies related to concrete corrosion were conducted through accelerated experiments under conditions that are very different from those in real sewers (De Belie et al., 2002; Herisson et al., 2013; Yousefi et al., 2014). Recently, laboratory studies were performed over several years under controlled conditions to simulate the corrosion processes in the sewer environment (Jiang et al., 2014a; Joseph et al., 2012). The results clearly confirmed that H_2S is the key influencing factor determining concrete corrosion rates. Additionally it was found that relative humidity was important only for the sewer crown areas while temperatures between 15-30°C showed no obvious difference.

Well-designed laboratory investigations of sewer corrosion can mimic sewer conditions (Jiang et al., 2014a; Joseph et al., 2010). However, in these laboratory-based investigations the concrete is typically exposed to a constant level of H_2S, which is quite different to the conditions observed in real sewers. In pressure pipes of real sewers, significant amounts of sulfide can be built up during the hydraulic retention time (HRT) that typically reaches several hours in such rising mains (Pomeroy and Boon 1976; Sharma et al., 2008). Sewage containing high concentrations of sulfide is then periodically pumped from pressure pipes into gravity pipes. The pumping events create turbulent flow conditions near the outlet of the pressure pipe and in the gravity pipe downstream and thus increase the H_2S transfer from the liquid phase (sewage) into the gaseous head space of the gravity pipes. This leads to sudden increases of H_2S levels in the gravity pipe gas phase, creating so called 'spikes' or H_2S peak concentrations. During the pump off period, the H_2S concentration in the headspace is reduced due to the uptake of H_2S by concrete exposed to the gas phase and possible dissolution in the continuously flowing sewage, as well as ventilation of the sewer air. These effects are significantly exacerbated due to the diurnal flow variation and the corresponding change in retention time in the pumped rising mains (Sharma et al., 2008). As a consequence, the periodical pumping events and the temporal variation of sulfide concentrations can intermittently create gaseous H_2S levels up to 100 times as high as the average concentrations, most typically in the first pump cycles in the morning (Gutierrez et al., 2012; Jiang et al., 2013). How this temporal variation of gaseous H_2S levels affects the sulfide uptake activity of concrete with an active sulfide-induced corrosion layer is largely unknown.

This study investigated the effects of such H_2S peak concentrations on the sulfide uptake activity of corroding concrete. The concrete utilised in this study was incubated in laboratory chambers under conditions similar to those in real sewers. The influence of short- and long-term high H_2S load scenarios on the sulfide (H_2S) uptake rate (SUR) was determined. Further

tests were carried out to examine the cumulative effect of high H_2S loads on the SUR of corroding concrete and the impact of historical H_2S exposure levels on the SUR during and after high H_2S loads.

2. Materials and methods

2.1. H_2S profiles in real sewers

Gaseous concentrations of H_2S were monitored at five minute intervals in a manhole at Melbourne's Western Trunk Sewer (WTS) from 5th April 2011 to 11th April 2011 (Figure S1A in Supplementary Information (SI)) and at one minute intervals in a manhole at Queensland's Sunshine Coast region (Morgans discharge manhole, Unity Water, Queensland, Australia) from 25th June 2014 to 1st July 2014 (Figure S1B in SI). The measured H_2S concentration profiles were analysed to identify the characteristics of H_2S peak concentrations, particularly the frequency and the scale of the high H_2S load events. These H_2S high load events occurring in real sewers were used to design high H_2S load experiments in the lab-scale system and to investigate their effect on H_2S uptake by concrete. In this study, the level and duration of H_2S peak events was designed to be between five and ten times the average H_2S level for a duration of 8 to 25 mins. In addition, the temperature in this study was also controlled to a level similar to those observed in the real sewers, which was relatively constant over the testing period with an average of 22.6 °C and 22.9 °C for Melbourne and Unity Water sewers, respectively.

2.2.Concrete coupons and corrosion chambers

Several corrosion chambers were designed and set up to incubate concrete coupons over several years under corrosive conditions. Each chamber was made of glass panels (thickness 4 mm) and had a length of 550 mm, width of 450 mm and height of 250 mm. The concrete coupons were cut from a corroded concrete sewer pipe that was replaced after 70 years of

service in Sydney (Sydney Water Corporation, Australia). The dimensions of each coupon were approximately 100mm (length) × 70 mm (width) × 70 mm (thickness). After cutting, the coupons were washed with tap water to remove surface contaminants and dried in an oven for 3 days (Joseph et al., 2010). Each coupon was partially embedded in a stainless steel casing fixed by epoxy (FGI R180 epoxy & H180 hardener) with the surface that previously formed the ceiling surface of the sewer pipe protruding 10 – 20 mm above the epoxy surface. These coupons were then exposed to the gas phase of the corrosion chamber with the exposure surface facing downwards. This arrangement of concrete coupon is to simulate the position of the concrete in the crown area of real sewer pipes.

Three corrosion chambers were set up with three different H_2S levels (i.e. 5, 15 and 50 ppm) for this study. The relative humidity and temperature of all chambers was controlled at 100% and 22 – 25 °C, respectively. Each chamber contained 2.5 L of domestic sewage (collected from a pumping station in Brisbane, Australia) that was replaced every 14 days. Gaseous H_2S levels in the chambers were achieved and controlled by dosing Na_2S solution into a container located inside the chamber and filled with HCl solution using a solenoid pump (120SP1220-4TP Solenoid Operated Micro-pump, BIO-CHEM Fluidics) controlled by a programmable logic controller (PLC). The chambers were arranged in drawers in a temperature controlled lab (22 – 25 °C). The sewage in the chamber was warmed slightly by recirculating warm water through two glass tubes submerged in it. This arrangement ensures that the relative humidity in the gas phase of the chamber can be maintained at about 100% (Joseph et al., 2010). The relative humidity was determined with wet and dry bulb temperatures measured by resistance temperature detectors.

The concrete coupons were exposed to these corrosion conditions for more than 3 years to establish strong corrosion activity before this study, which was indicated by the visible, active corrosion layer on the surface of the coupons and the measured surface pH of all

coupons being below 4 (measured by surface pH probe with 4 independent measurements on each coupon surface).

2.3. H_2S uptake measurement system

Concrete corrosion in sewers is largely driven by production of sulfuric acid through oxidation of sulfide. The SUR of concrete is shown to be a good indicator to estimate the maximum rate of sulfide induced concrete corrosion (Sun et al., 2014; US Environmental Protection Agency 1974). In this study, the SUR by the concrete coupons was measured using the method modified from that described in Sun et al., (2014) (Figure 1). To briefly describe the method, we use an example to measure the SUR of a concrete coupon at 15 ppm H_2S. A coupon was retrieved from the corrosion chamber and immediately placed into the H_2S uptake reactor where the relative humidity was controlled at 100%. Gaseous H_2S was added from a 50 mL syringe into the H_2S uptake reactor to achieve a reactor concentration of 20 ppm. The H_2S uptake profile of the coupon was recorded using a H_2S detector (App-Tek OdaLog® Logger L2, detection range of 0-200 ppm). The SUR of the coupon at 15 ppm of H_2S was calculated using the monitored H_2S profiles (Sun et al., 2014). To repeatedly measure the SUR at 15 ppm, the addition of gaseous H_2S into the reactor was performed when the monitored H_2S concentration in the reactor gas phase decreased to 10 ppm. A programmable Logic Controller (PLC) was employed to monitor the H_2S concentration inside the reactor and to trigger the syringe pump (NEW Era Model 501 OEM syringe pump with stall detection) to add further gaseous H_2S. The PLC was used to run a pre-determined sequence of low and high H_2S concentrations at a specified frequency. To avoid the build-up of pressure inside the reactor during the dosing of gaseous H_2S, a small gas outlet from the reactor was kept open through a needle (0.5 mm in diameter) inside a rubber stopper with a non-metallic luer-lock connector on the inside of the reactor (to avoid the potential of metal (needle) catalysed sulfide oxidation).

193 [INSERT FIGURE 1]

194 The background uptake rates of H_2S were determined by removing the coupon, resealing the
195 reactor with a piece of foam panel and a stainless steel sheet and repeating the H_2S injection
196 and monitoring process. The background uptake rates of the whole reactor (but without the
197 coupon) were subtracted from the measured SUR with the coupons in place to obtain the net
198 uptake rates for the concrete coupons (see Equation S1 in the Supplementary Information (SI).

199 **2.4.Batch tests**

200 **2.4.1. Effect of H_2S peak concentrations**

201 Two types of H_2S concentration high load scenarios were investigated, i.e. short- and long-
202 term. These were designed to mimic the H_2S fluctuations typically observed in real sewers.

203 The test to identify the effect of short-term high H_2S load conditions on the SUR was carried
204 out on a coupon previously exposed to 15 ppm for 53 months. Gaseous H_2S was
205 intermittently infused into the uptake reactor containing the concrete coupon. The gaseous
206 H_2S concentration in the uptake reactor was maintained between 10 and 20 ppm (averaging
207 15 ppm) for 30 mins. This simulates the historical exposure level (i.e. 15 ppm) of H_2S of the
208 coupon in the corrosion chamber. Based on the temporal H_2S uptake profiles, the SUR of the
209 coupon at 15 ppm after each injection of H_2S was calculated according to methods developed
210 previously (Sun et al., 2014). The average SUR at 15 ppm was termed the baseline SUR.
211 Then, the gaseous H_2S in the uptake reactor was quickly raised to 160 ppm and gradually
212 decreased to baseline level due to the uptake by the coupon. This intends to simulate the
213 short-term high H_2S load event. The duration of the short-term high load event was usually
214 around 7 to 8 mins. Following that, intermittent injection of H_2S at a level between 10 and 20
215 ppm was performed again. The corresponding SUR at 15 ppm was measured and compared
216 with the baseline SUR. To facilitate the comparison of the SUR prior to and after a high H_2S

load, the relative SUR ratio, defined as the SUR divided by the baseline SUR, was calculated. The experiment with H_2S concentration up to 160 ppm was repeated three times. The SUR after each high loading event was calculated and compared with the baseline SUR.

To investigate the influence of the long-term high load of H_2S concentrations on the SUR, one uptake test was carried out on the same coupon after 54 months of corrosion chamber exposure with a similar test procedure. The only difference was that the duration of the high H_2S level was maintained for 20 to 22 mins, which was achieved through intermittent injection of gaseous H_2S to keep the H_2S level between 115 and 160 ppm. The corresponding SUR at 130 ppm was calculated using the monitored H_2S uptake profiles. A control test was carried out on the same coupon through intermittently injecting H_2S to around 10 and 20 ppm for 3 h.

2.4.2. Cumulative inhibition effect of high H_2S load

The post-exposure inhibition effect of high H_2S concentrations on the SUR of the concrete coupon was determined using a coupon previously exposed to 15 ppm H_2S for 42 months in the corrosion chamber. The experiment included two independent H_2S uptake tests with different H_2S exposure profiles but the same average H_2S exposure level.

For the first test, to simulate the historical H_2S exposure level (i.e. 15 ppm) of the coupon in the corrosion chamber, gaseous H_2S was intermittently injected into the uptake reactor to maintain the gaseous H_2S level in the uptake reactor between 10 and 20 ppm for 110 min. The corresponding SUR at 15 ppm after each injection of H_2S was calculated and termed as the baseline SUR. Then, the coupon was exposed to various high loads of H_2S , i.e. H_2S levels between 160 and 180 ppm for about 45 min, between 110 and 130 ppm for about 45 min and between 65 and 85 for about 45 min. The corresponding relative SUR ratio was

240 calculated by dividing the experimental SUR by the baseline SUR, for each high loading
241 event.

242 The second test was carried out in a similar procedure but the exposure H_2S profiles were
243 different. Following the baseline exposure between 10 to 20 ppm H_2S, the coupon was
244 exposed to different, and increasing H_2S levels for 45 minutes in each experiment, namely at
245 65 to 85 ppm, 110 to 130 ppm and 160 to 180 ppm H_2S. The corresponding relative SUR
246 ratio for each experiment was calculated as described above.

247 The duplicate experiment was conducted on a coupon previously exposed to 15 ppm H_2S for
248 38 months in the corrosion chamber.

249 **2.4.3. The effect of H_2S spikes on coupons with different exposure histories**

250 To examine the effect of the high-level H_2S exposure on coupons that had previously been
251 maintained at different H_2S levels, three coupons previously exposed to either 5, 15 and 50
252 ppm were tested. To examine the effect of various H_2S spike scenarios on the overall amount
253 of H_2S taken up, several tests (shown in Table 1) were carried out to compare the amount of
254 H_2S uptake by each coupon at its historical H_2S level (i.e. 'control' test) and various H_2S
255 spike situations (i.e. 'spike' test) over the same exposure time.

256 [INSERT TABLE 1]

257 Over the experimental period of a specific 'spike' test, the mass of H_2S taken up by the
258 concrete coupon surface is termed T_{spike} ((mg-S), see details of calculation in Equation S2 in
259 SI). Over a duration equivalent to that of the specific 'spike' test, the mass of H_2S taken up by
260 the same coupon surface when exposed to the baseline H_2S concentration is termed $T_{baseline}$
261 ((mg-S), see details of calculation in Equation S4 in SI).

Therefore, the ratio (α) is defined for a specific coupon by the mass of H_2S taken up by the concrete coupon in a 'spike' test compared to the uptake by the same concrete coupon when exposed to a constant H_2S level (i.e. historical exposure level) over the same time:

$$\alpha = \frac{T_{spike}}{T_{baseline}} \quad (1)$$

3. Results and discussion

3.1. Effect of high H_2S load

3.1.1. Short-term high load of H_2S

Figure 2A shows the temporal H_2S uptake profiles of a concrete coupon over 3 h and the corresponding SUR measured after each injection of gaseous H_2S. At stage 1, the repeated measurement of SUR of the coupon at its historical exposure level of H_2S (i.e. 15 ppm) was relatively constant, averaging 173 mg-S m^{-2} h^{-1}. Similarly, Figure S2 in SI shows the stability of the SUR during a control experiment, expressed as percentage relative to the baseline SUR. This suggests that the SUR of a specific coupon will be quite constant when the H_2S exposure level is constant. However, immediately after experiencing the first H_2S peak concentration (stage 2), the SUR of the coupon at 15 ppm decreased to 149 mg-S m^{-2} h^{-1}, which was about 14% lower than the baseline SUR (Figure 2B). Following that, the SUR rose gradually to 96% of baseline SUR over about 10-20 minutes. Compared to stage 2, the decrease of SUR after the second (stage 3) and third (stage 4) H_2S peak concentration is similar, but the recovery is less. Especially, no recovery of SUR was observed within about 1 h after the third peak. It seems that there was a temporary inhibition initially, which then became more persistent.

[INSERT FIGURE 2]

The immediate decrease of SUR after the high H_2S load could be explained as follows. Elemental sulfur (S^0) would likely be produced as intermediate product during sulfide

oxidation (Jensen et al., 2009; Nielsen et al., 2014). Part of this S^0 may be directly oxidized to sulfate and hence would compete with sulfide as electron donors for SOB. Another part of this may remain as an intermediate and undergo a slower oxidation process (Jensen et al., 2009; Nielsen et al., 2014). During the high load period, increased amount of S^0 may be produced and stored temporarily in the corrosion layer. Immediately after the high H_2S load, part of the S^0 was further oxidized which could consequently reduce the SUR temporarily. With the ongoing oxidation of S^0 in the corrosion layer after the H_2S loading, the previously accumulated S^0 would be gradually consumed, and the SUR would recover. Under some circumstances, such as after the quick reduction of H_2S peak concentrations by sewer ventilation, some H_2S accumulated in the corrosion layer during the previous high load periods may even diffuse back into the gas phase, resulting in a negative SUR (see details in Table S1 in the SI)).

However, the diminishing recovery capacity of the SUR after several high H_2S loading experiments suggests a possible inhibitive effect of this loading on the SOB activity. The probable inhibition of SOB by high sulfide loads has also been reported in sewer concrete corrosion layers that were periodically exposed to 1000 ppm_v of H_2S and loadings of up to 340 mg-S m^{-2} h^{-1} (Nielsen et al., 2014). In other studies, the inhibitory effect of high sulfide loads onto biological sulfide oxidation activity was detected to occur in denitrifying and sulfide oxidizing conditions (Buisman et al., 1990; Buisman et al., 1991; Cardoso et al., 2006; Mahmood et al., 2008; Wirsen et al., 2002). A possible explanation for this effect could be that the temporary increase in sulfide and hence sulfuric acid formation reduces the pH within the biofilm/corrosion layer temporarily until this is neutralized by the corroding concrete again over time. Further detailed investigations may be necessary to corroborate this hypothetical explanation.

3.1.2. Long-term high load of H_2S

Figure 3A (stage 1) shows that the baseline SUR of the coupon prior to the high load experiments was around 225 mg-S m^{-2} h^{-1} and hence slightly higher than that in the previous test shown in Figure 2A. This difference of the absolute SUR value for the same coupon within about 1 month may be due to various effects, possibly related to the absorbed moisture in the corrosion biofilm. As this study is aimed at identifying the immediate changes of SUR caused by high H_2S load, such variations of the absolute SUR have a negligible impact on the results.

[INSERT FIGURE 3]

Upon long-term exposure to high levels of H_2S (Figure 3A, stage 2), the SUR of the coupon at 15 ppm H_2S immediately decreased by 41%. The SUR gradually recovered to approximately 86% - 92% of the baseline SUR during the following the following 6 – 15 minutes. The observed decreases of the SUR after the 2nd and 3rd long-term high-level exposure (stage 3 & 4) were even slightly larger than that after the 1st long-term exposure and the recovery of the SUR was also slower. Particularly, the final recovery level at stage 4 reached only 87% and 93 % 2h after the end of the high loading, indicating there is some more persistent inhibition, as also observed in the short-term experiments. In addition, during exposure to high H_2S levels, the coupon had a gradual decrease of the SUR at 130 ppm not only within each of the three stages (stage 2, 3 and 4 in Figure 3A) but also from stage 2 to stage 4.

Compared to the effects after the short-term exposure to high H_2S levels, the SUR clearly showed a more significant decrease immediately after the long-term high H_2S load and had a similar extent of recovery although the time required for the recovery of the SUR to a steady level is slightly longer. Consequently, it supports that the longer-term exposure of the coupon to high H_2S levels may result in a greater accumulation of S^0 in the corrosion layer, thus

334 causing a bigger decrease of the SUR after the exposure. In addition, the similar extent of
335 recovery of SUR after short- and long- term high load of H_2S suggests that the
336 duration/length of coupon exposure to high levels of H_2S may affect the rate of the SUR
337 recovery but not the extent of the recovery. This indicates that the activity of the SOB may be
338 inhibited for various lengths depending on the duration of high H_2S load.

339 **3.2. Cumulative inhibitive effect of high H_2S loads**

340 Based on the hypothetical accumulation of S^0 in the corrosion layer discussed above, it would
341 be expected that all prior H_2S loads can have a cumulative effect on the SUR of the concrete
342 coupon unless the recovery time between high load events is sufficient to eliminate the
343 temporarily accumulated elemental sulfur. This was indeed demonstrated in a separate
344 experiment. Figures 4A&B show the results of two tests where the coupon is exposed to
345 various high H_2S load sequences but with the average H_2S concentration of the two tests
346 being similar. In Figure 4A, after exposing the concrete coupon to the baseline H_2S level
347 (stage 1), the relative SUR at 170 ppm from the 1st to the last measurement decreased by
348 about 32% (stage 2) and then the relative SUR was stable during the repeated measurement at
349 both 120 (stage 3) and 70 ppm (stage 4). The relative SUR values of the last measurements at
350 70 ppm H_2S (stage 4), 120 ppm (stage 3) and 170 ppm (stage 1) were 168%, 199% and 238%,
351 respectively. In contrast, Figure 4B shows a gradual decrease of relative SUR during the
352 repeated measurement at 70 ppm (stage 2), 120 ppm (stage 3) and 170 ppm (stage 4) and the
353 relative SUR of the last measurements at stages 2, 3 and 4 were 187%, 210% and 232%,
354 respectively.

355 [INSERT FIGURE 4]

356 The results demonstrate that an abrupt increase of the H_2S level led to gradual decrease of
357 SUR at the elevated H_2S level whereas an abrupt decrease of H_2S resulted to gradual increase

of SUR at the lowered H_2S level. This suggests that during the periods of high load of H_2S various factors, including the storage of S^0 in the corrosion layer and the inhibition of SOB activity due to high H_2S and/or temporary acid surge, may cause the observed gradual decrease of SUR, which is consistent with the results and explanations given in the above sections. The SUR recovery observed after the high load periods could be explained by the gradual consumption of the previously accumulated S^0 and the reduced inhibition of SOB due to the lower H_2S level and/or the neutralisation of acid by alkaline concrete components. Compared to the trend of SUR at stage 2 in Figure 4A, the decrease of SUR at stage 2, 3 and 4 in Figure 4B is much less prominent, indicating that the greater the change of the H_2S levels, the more obvious the change of the SUR at the new higher H_2S level seems to be.

In addition, the relative SUR at both 70 and 120 ppm in Figure 4A were much lower than those shown in Figure 4B (summarized in Figure 4C). Therefore, it is reasonable to speculate that the previous very high load of the coupon with H_2S at stage 2 (Figure 4A) has significantly inhibited the biological sulfide oxidation activity for some extended period (hours), which is also supported by the results shown in the previous sections. Similar phenomena were also observed in a repeat experiment on a pre-corroded coupon with a much higher absolute SUR than the one shown here (Figure S3 in SI).

3.3.Effects of high H_2S loads on coupons with different exposure history

The effects of the high H_2S concentrations on coupons with different H_2S historic exposure levels were compared. Figure 5 shows the values of α (as defined in Equation 4) plotted against the high H_2S level in each uptake test. For all the three coupons, the values of α increased with the increase of the high H_2S load level although the incremental increases of α were smallest and largest for the coupons previously exposed to 50 and 5 ppm of H_2S, respectively. This indicates that the value of α and the historical exposure level of H_2S of

concrete coupons are inversely correlated, partly due to that the baseline SUR is much lower for 5 ppm coupon compared to 50 ppm coupon. In addition, it suggests that the lower the historical exposure level of H_2S, the more sensitive the H_2S uptake of the coupon is towards a high H_2S load. This is reasonable as the SOB adapted to continuously higher levels of H_2S have a much higher activity and therefore are less susceptible to the occasional peak levels of H_2S.

[INSERT FIGURE 5]

Interestingly, the values of α were below 1 for all coupons when the high levels of H_2S were around 1.5 to 2 times of the baseline H_2S levels. This suggests that during the exposure to modest H_2S loads the coupons may actually have a lower H_2S uptake rate compared to that under constant H_2S baseline conditions. Extrapolating this finding to a specific section of real sewer pipe with active corrosion layers, it would suggest that the occurrence of relative low H_2S peak levels due to short-term pumping events may not cause any additional H_2S uptake, but may even result in a slightly lower level of H_2S uptake compared to a situation with a steady H_2S level having the same average H_2S concentration. On the contrary, having periods with high H_2S loads when the baseline levels are low (e.g. 5 ppm), will result in the highest levels of sulfide uptake amounts. Therefore, these conditions with extremely high H_2S levels should be avoided to minimize H_2S flux and thus corrosion activity and prolong sewer life.

3.4. Implications

This study reveals that the presence of occasional high H_2S levels in sewer atmosphere has an inhibitory effect on H_2S uptake by sewer concrete. Estimating the H_2S uptake simply based on the *average* H_2S level will therefore cause an overestimation of the H_2S uptake and hence the corresponding corrosion rate if there are significant fluctuations in the gas phase H_2S concentrations, which is commonly the case. For example, calculating the mass of H_2S taken

406 up by a concrete pipe over 24 h based on the SUR at the *average* H_2S concentration may lead
407 to an overestimation of theH_2S uptake compared to an integration of the *actual* SUR over
408 time. It is due to the following two reasons. First, the SUR follows a n^{th} order relative to the
409 H_2S concentration with n being below 1 (Sun et al., 2014; Vollertsen et al., 2008), which
410 indicates that the average SUR over the 24 h is smaller than the SUR at the average H_2S
411 concentration. Second, the actual average SUR is smaller than the average SUR over 24 h
412 due to the fact that the SUR at low H_2S levels is affected by the inhibition effect from
413 preceding high H_2S load events.

414 The total sulfide uptake by a concrete surface over seven days exposed to Sydney sewers
415 calculated based on the real H_2S profile and the average H_2S level (i.e. 5.2 ppm) was 722 and
416 766 mg-S m^{-2} respectively, suggesting that the calculation from the average H_2S level
417 resulted to an overestimation of at least 5.8%. Therefore, a correction factor will need to be
418 implemented when calculating the H_2S uptake based on SUR at average H_2S level. However,
419 since the reduction in SUR will directly depend on the actual high H_2S load profile and the
420 exposure history of the concrete, the correction factor will need to be determined on a case-
421 by-case basis using the actual or expected H_2S profiles.

422 **4. Conclusions**

423 This study examined the behaviour of H_2S uptake by concrete under various high H_2S load
424 scenarios. The main findings from this work are:

425 • Both short and long high H_2S load events decrease the SUR of concrete coupons. The
426 latter leads to a larger temporary reduction of SUR whereas they cause similar
427 persistent inhibition effects.

- Sequential exposures to elevated H_2S levels create a cumulative effect on the SUR, which is more pronounced if there is a rapid initial increase rather than a gradual increase in H_2S.
- The sensitivity of the H_2S uptake rate by the corrosion layer towards high H_2S loads is largely dependent on the historical H_2S exposure levels. Large H_2S loads on a low baseline concentration have a more pronounced impact on the total sulfide uptake than modest increases on top of higher H_2S levels. However, it has to be considered that for a specific, actively corroding concrete surface higher average H_2S concentrations always create more corrosive conditions than lower levels.
- Due to the rapid decrease and slow recovery effect of H_2S spikes on the SUR, an estimation of the corrosion effect purely on the average H_2S concentrations may result in an overestimation of the total H_2S uptake and thus probably an overestimation of the concrete corrosion rates.

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559

560

Table 1 – Details of three series of H_2S uptake tests performed on three concrete coupons with different historical exposure conditions.

Test serie	Coupon exposure history	Batch tests	H_2S levels (ppm)
1	5 ppm, 22-25°C, 100% RH, 39 months	Control	5
		Spike 1	10 to 5
		Spike 2	15 to 5
		Spike 3	20 to 5
		Spike 4	25 to 5
		Spike 5	50 to 5
		Spike 6	100 to 5
		Spike 7	150 to 5
2	15 ppm, 22-25°C, 100% RH, 39 months	Control	15
		Spike 1	25 to 15
		Spike 2	50 to 15
		Spike 3	75 to 15
		Spike 4	100 to 15
		Spike 5	150 to 15
3	50 ppm, 22-25°C, 100% RH, 39 months	Control	50
		Spike 1	75 to 50
		Spike 2	100 to 50
		Spike 3	125 to 50
		Spike 4	180 to 50

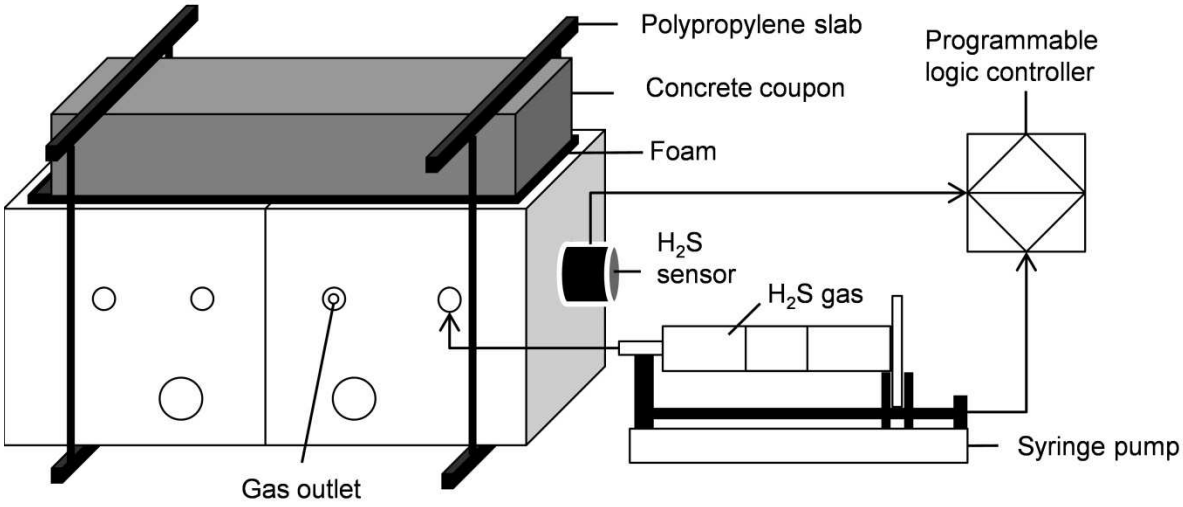


Figure – 1 The schematic diagram of the system used to measure the H_2S uptake by concrete coupons.

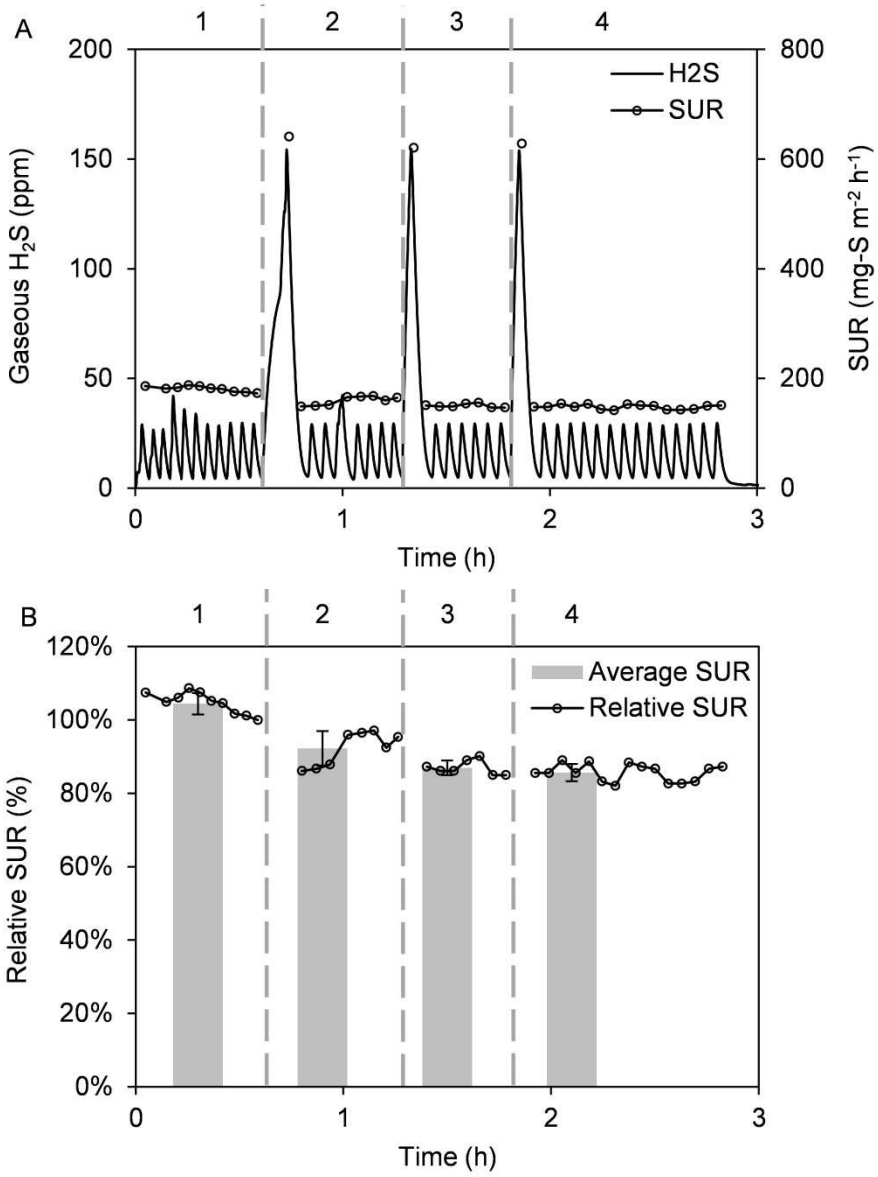


Figure 2 – The temporal H_2S uptake profiles of a coupon (exposure history: 15 ppm H_2S, 22-25 °C, 100% relative humidity for 53 months) and the corresponding SUR at the historical exposure level (i.e. 15 ppm) and peak levels (i.e. 130 ppm) of H_2S are shown in Figure A and the relative SUR and average SUR at various stages shown in Figure B. Different experimental stages (1 to 4) are listed above the plotted data in Figures A and B and the error bars in Figure B represent standard deviations.

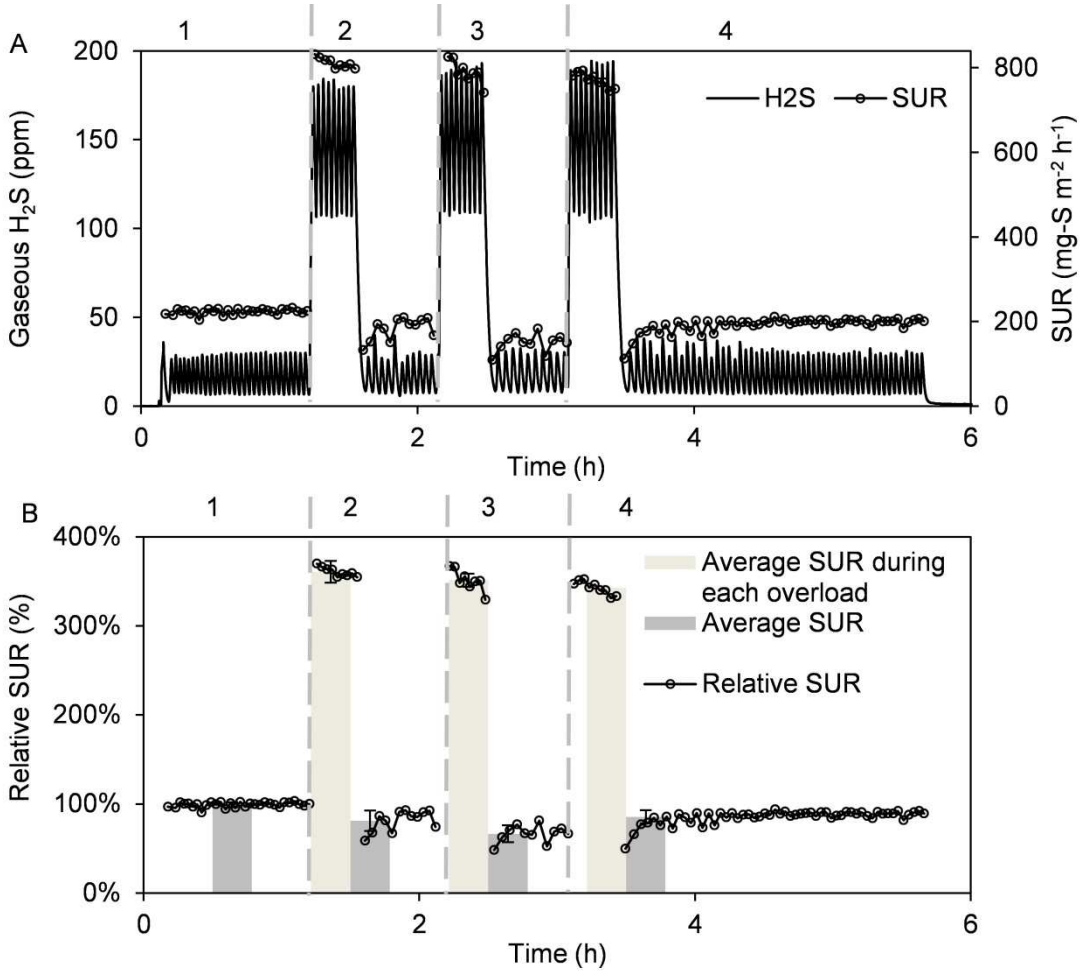
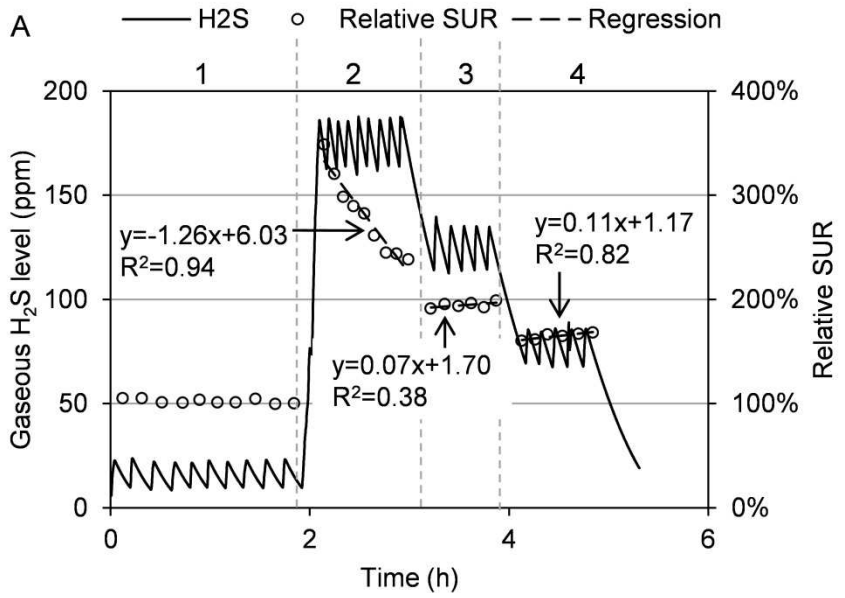
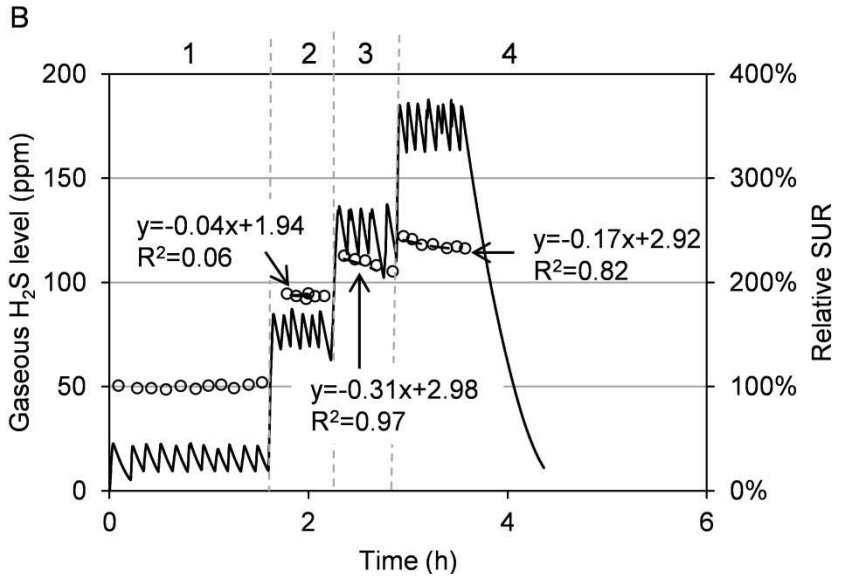


Figure 3 – The H_2S uptake profiles of the coupon (exposure history: 15 ppm H_2S, 22-25 °C, 100% relative humidity for 54 months), the corresponding SUR at its baseline H_2S level (i.e. 15 ppm) and high H_2S levels (i.e. 130 ppm) are shown Figure A and the relative SUR and the average relative SUR at each stage is shown in Figure B. Different experimental stages (1 to 4) are listed above the plotted data in Figures A and B and the error bars in Figure B represent standard deviations.


A
H2S
Relative SUR
Regression
1
2
3
4
Gaseous H2S level (ppm)
Relative SUR
Time (h)
y=-1.26x+6.03
R²=0.94
y=0.07x+1.70
R²=0.38
y=0.11x+1.17
R²=0.82


B
1
2
3
4
Gaseous H2S level (ppm)
Relative SUR
Time (h)
y=-0.04x+1.94
R²=0.06
y=-0.31x+2.98
R²=0.97
y=-0.17x+2.92
R²=0.82

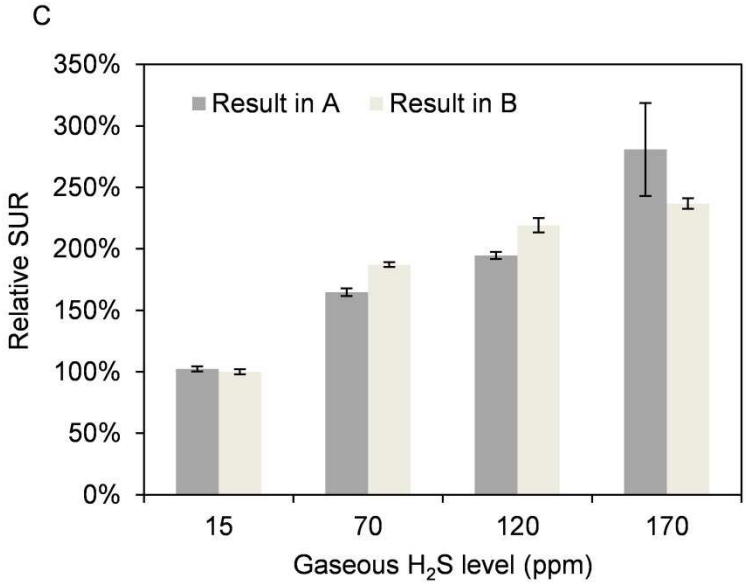

C
Result in A
Result in B
Relative SUR
Gaseous H2S level (ppm)
15
70
120
170

Figure 4 – The H_2S uptake profiles of a coupon (previously exposed to 15 ppm, 100% relative humidity and 22-25°C for 42 months) in a H_2S uptake test with various high loads of H_2S and the corresponding relative SUR at 15, 70, 120 and 170 ppm were shown in Figure A. The H_2S uptake profiles of the same coupon in the other test and the corresponding relative SUR was shown in Figure B. The corresponding relative SUR in Figure A and B against H_2S concentration is shown in Figure C. Different stages of the experiment are listed (1 to 4) above the plotted data on Figure A and B and the linear regression of relative SUR at each stage shown in Figure A and B was also described by the equation aside. The error bars in Figure C represent standard deviations.

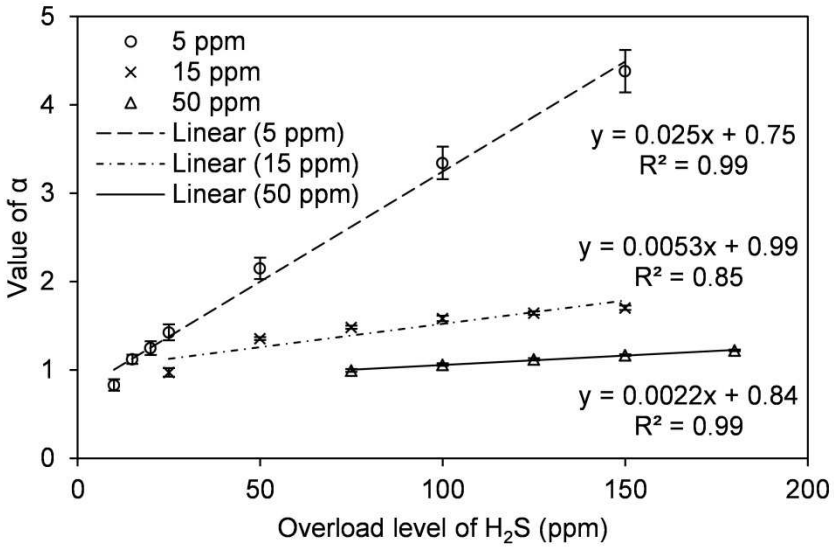


Figure 5 – The α values (dot) of coupons previously exposed to 5, 15 and 50 ppm of H_2S in corrosion chamber for 39 months were plotted against the high level of H_2S in each uptake test. Each line shows the linear regression based on the α values of each coupon and was also described by the equation aside.

Highlights:

- Gaseous H_2S concentration fluctuations in real sewers were detected and analysed
- High H_2S loads affected the H_2S uptake activity of concrete coupon
- The effect associates strongly with the duration and the scale of H_2S load
- The effect correlates with the concrete historical H_2S exposure concentrations
- Our results may facilitate better estimation of the sewer corrosion activity

Supplementary Information for

Impact of fluctuations in gaseous H_2S concentrations on sulfide uptake by sewer concrete: the effect of high H_2S loads

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The background SUR follows first order (R^2=0.9998) towards the gaseous H_2S concentration (also shown in the previous study (Sun et al., 2014)) and can be expressed as:

$$r_{H_2S,background} = k * [H_2S] = a * [H_2S] * 101.325KPa * \frac{32g/mol}{RT} * \frac{V}{S} \quad (\mathbf{S1})$$

$r_{H_2S,background}$ is background SUR (mg-S m^{-2} h^{-1}),), k is rate constant (mg-S m^{-2} h^{-1} ppm^{-1}, k was found to be 0.13 mg-S m^{-2} h^{-1} ppm^{-1} in this study), a is the rate constant with the unit of h^{-1}, $[H_2S]$ is gaseous H_2S concentration in the uptake reactor (ppm), R is the universal gas constant (J k^{-1} mol^{-1}), T is the absolute temperature (K), V is the total gas volume in the reactor (m^3, 0.000145 m^3 in this study), S is the concrete surface exposed to the reactor atmosphere (m^2, 0.00905 m^2 in this study).

$$T_{spike} = ([H_2S]_{spike,e} - [H_2S]_{baseline,e}) * 101.325KPa * \frac{32g/mol}{RT} * V - T_{background} \quad (\mathbf{S2})$$

T_{spike} is the mass of H_2S transfer from reactor atmosphere to the concrete coupon over the experimental period of a specific 'spike' test (mg-S), $[H_2S]_{spike,e}$ is the spike H_2S concentration in the specific 'spike' test (ppm), $[H_2S]_{baseline,e}$ is the historical exposure concentration of H_2S of the coupon (ppm), $T_{background}$ is the mass loss of H_2S due to background H_2S uptake by the reactor alone (without the concrete coupon) over the specific 'spike' test (mg-S, see the details of calculation in Equation S3).

$$T_{background} = \sum_{i=1}^{n} a * ([H_2S]_i + [H_2S]_{i+1}) * 101.325KPa * \frac{32g/mol}{RT} * V * 0.5 * \Delta t \quad (\mathbf{S3})$$

i is i^{th} measurement of gaseous H_2S concentration in uptake reactor in the specific test; $[H_2S]_i$ is the gaseous H_2S concentration in uptake chamber at the i^{th} measurement, n is the number of measurements of gaseous H_2S concentration over the specific test, Δt is the time interval between two measurements of H_2S concentration (h).

$$T_{baseline} = SUR_{baseline} * S * t = r_{baseline} * 101.325KPa * \frac{32g/mol}{RT} * V * t \quad (S4)$$

where $T_{baseline}$ is the mass of H_2S transfer to the same coupon over the periods equivalent to that of the specific 'spike' test and when exposed to historical H_2S exposure levels (mg-S), $SUR_{baseline}$ is the surface specific SUR of the coupon (background SUR had been deducted from it) at its baseline H_2S concentration measured in a 'control' test (mg-S m^{-2} h^{-1}), $r_{baseline}$ is the corresponding H_2S uptake rate of coupon in the unit of ppm h^{-1}, t is the duration of a 'spike' test (h, note here $t = \sum_{i=1}^{n} \Delta t$).

Table S1 Details of H_2S in reactor atmosphere and liquid layer of concrete surface at 15 ppm and 150 ppm of gaseous H_2S

H_2S concentration in atmosphere (ppm)	15	150
H_2S mass in atmosphere (mg-S)	0.029	0.29
H_2S mass in liquid layer H_2S (mg-S)	0.0017	0.017
(H_2S mass in atmosphere)/(H_2S mass in liquid layer and atmosphere)	5.5%	5.5%
H_2S concentration in liquid layer (mg-S L^{-1})	0.049	0.49

The results in Table S1 are based on the assumption that the concrete coupon has a water layer of 5 mm and that the H_2S achieves equilibrium in atmosphere and the corrosion layer.

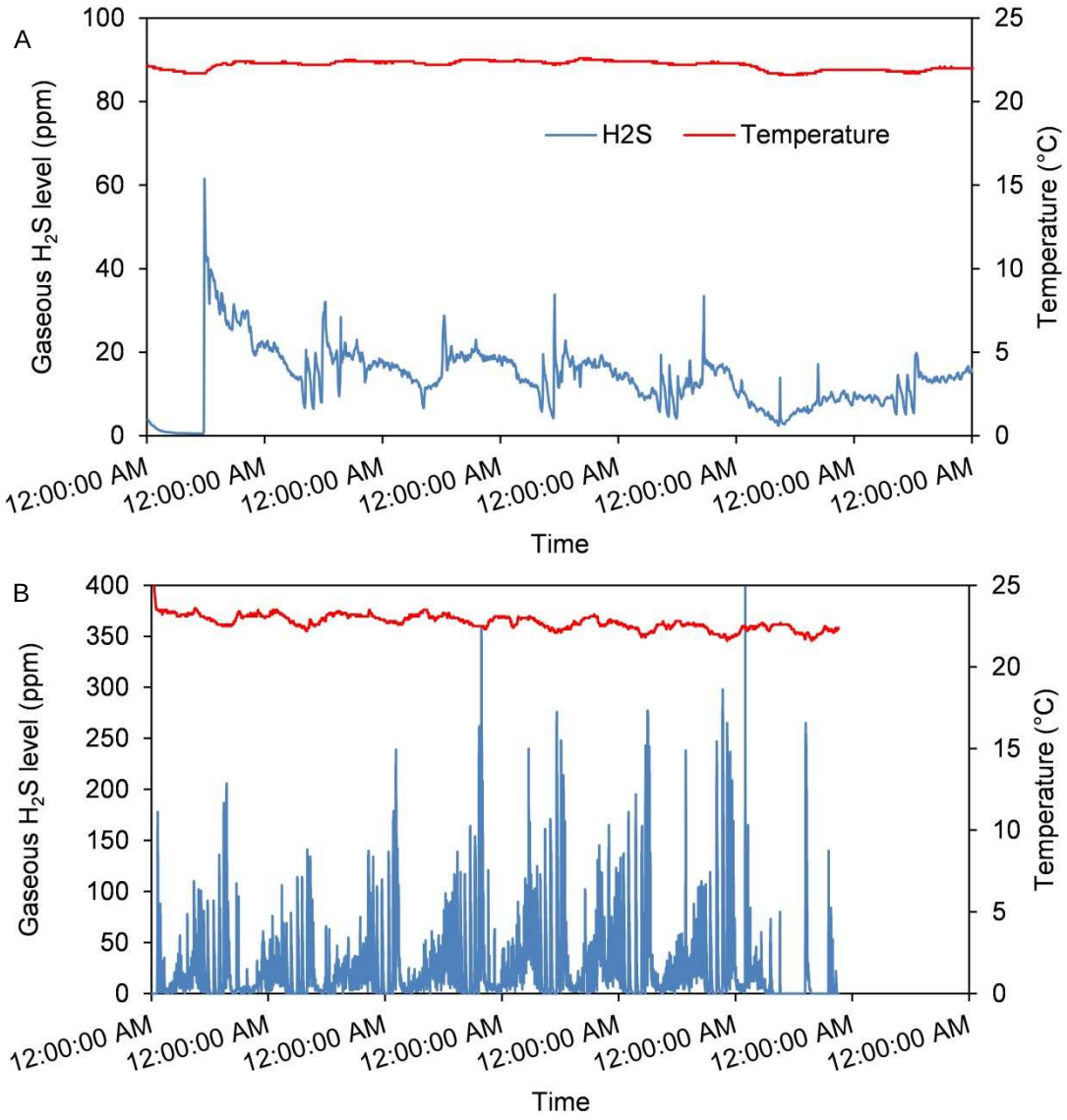


Figure S1 – Gaseous H_2S concentrations monitored in a manhole at Melbourne's Western Trunk Sewer from 5th April 2011 to 11th April 2011 and at Queensland's Sunshine Coast region from 25th June 2014 to 1st July 2014 is shown in Figure A and B respectively.

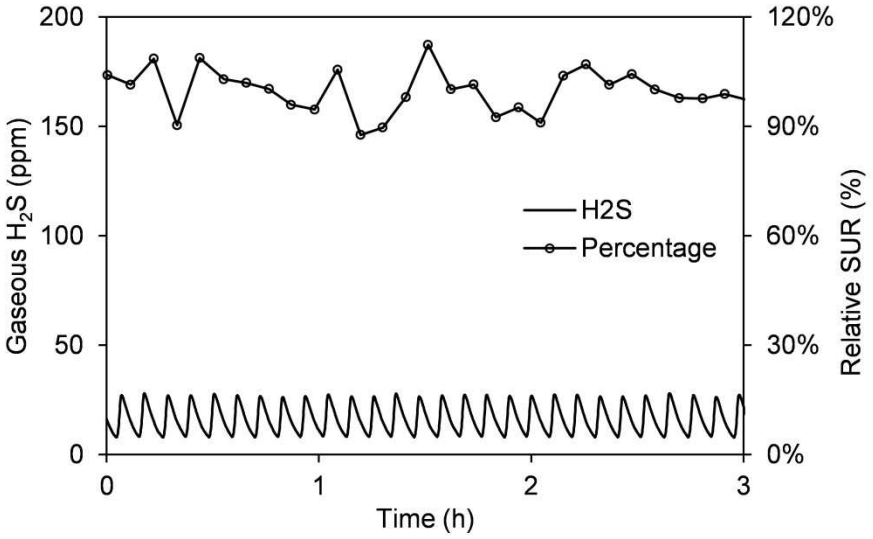
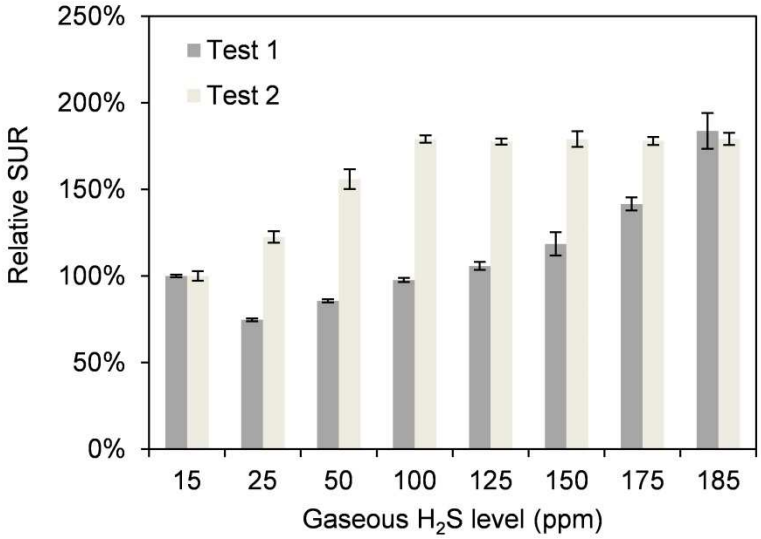


Figure S2 – The temporal H_2S uptake profiles of a coupon (exposure history: 15 ppm H_2S, 22-25 °C, 100% relative humidity for 53 months) and the corresponding relative SUR in a control experiment over 3 h.



68

69 **Figure S3** – The relative SUR of a coupon previously exposed to 15 ppm for 38 months at
70 various H_2S levels against H_2S concentrations in two independent tests (shown as test 1 and
71 2). Test 1 has a rapid initial increase of H_2S concentration whereas test 2 has a gradual
72 increase of H_2S concentration.