

# ***In Situ* Continuous Monitoring of Dissolved Sulphide in Sewer Systems**

Luke Sutherland-Stacey, University of Auckland & DCM Process Control, [luke@dcmprocesscontrol.com](mailto:luke@dcmprocesscontrol.com)

Shaun Corrie, Gold Coast City Council, [scorrie@goldcoast.qld.gov.au](mailto:scorrie@goldcoast.qld.gov.au)

Alan Neethling, DCM Process Control, [alan@dcmprocesscontrol.com](mailto:alan@dcmprocesscontrol.com)

Ian Johnson, Gold Coast City Council, [ijohnson@goldcoast.qld.gov.au](mailto:ijohnson@goldcoast.qld.gov.au)

Oriol Gutierrez, Advanced Wastewater Management Centre, University of Queensland,

[oriol@awmc.uq.edu.au](mailto:oriol@awmc.uq.edu.au)

Rob Dexter, DCM Process Control, [rob@dcmprocesscontrol.com](mailto:rob@dcmprocesscontrol.com)

Zhiguo Yuan, Advanced Wastewater Management Centre, University of Queensland,

[zhiguo@awmc.uq.edu.au](mailto:zhiguo@awmc.uq.edu.au)

Jürg Keller, Advanced Wastewater Management Centre, University of Queensland,

[j.keller@awmc.uq.edu.au](mailto:j.keller@awmc.uq.edu.au)

Geoff Hamilton, Gold Coast City Council, [ghamilton@goldcoast.qld.gov.au](mailto:ghamilton@goldcoast.qld.gov.au)

## **INTRODUCTION**

Hydrogen sulphide (H<sub>2</sub>S) is generated in the aqueous phase of wastewater by bacterial reduction of sulphate under anaerobic conditions. Accumulation of hydrogen sulphide in sewers poses significant problems in wastewater transport and treatment systems. Bacterial oxidation of hydrogen sulphide on pipe walls exposed to atmospheric oxygen produces sulphuric acid, which actively destroys concrete structures and pipework at an annual corrosion rate of several millimetres a year. The gas is also toxic to humans in even relatively low concentrations and poses a health risk to sewerage workers. At even lower concentrations it is foul smelling, and has a significant impact on the exposed community.

On the Gold Coast considerable effort and money is directed toward combating the effects of sulphide generation in rising mains. Around \$1M is spent annually by the Gold Coast City Council to mitigate the impact of sulphide on both assets (corrosion) and the local community (odour). For over 15 years Gold Coast Water (GCW) has employed the use of Oxygen Injection (OI) as a control strategy for sulphide suppression. Through the injection of pure oxygen at wastewater pump stations, OI is thought to prevent the formation of anaerobic conditions in the sewer and hence reduce or eliminate sulphide production.

A history of persistent odour and corrosion problems within GCW infrastructure has led to the belief that the current OI strategy is not cost effective. In some cases OI is thought to have exacerbated corrosion in rising mains at high points where un-dissolved oxygen has accumulated. Until now, it has been very difficult for managers to fully understand the dynamics of sulphide occurrence in rising mains, and as a result they are unable to take informed and effective actions to remedy the problem.

While a large number of sensor systems are available to measure hydrogen sulphide concentration in gas phase, these instruments are not suitable for measurement of sulphide dissolved in wastewater and particularly in rising mains. Monitoring sulphide levels in wastewater has only been possible by collection of samples and their subsequent off-line measurement in analytical laboratories.

The bisulphide ion (HS<sup>-</sup>) is associated with hydrogen sulphide in aqueous systems and absorbs light directly in the ultra-violet wavelengths (Goldhaber *et al.*, 1975; Guenther *et al.*, 2001). Recent advances in real-time UV-VIS spectroscopy of seawater and sewage

have shown the potential use of UV-VIS spectroscopy for detection of the bisulphide ion (Johnson *et al.*, 2002) and hence hydrogen sulphide. In this work, a method for measuring the dissolved sulphide on-line and in real-time in sewage using a UV-VIS spectrometer assisted with a pH probe is developed. The method is demonstrated through both field and laboratory studies.

## MATERIALS AND METHOD

### The s::can UV-VIS spectro::lyzer

The spectrometer used to detect bisulphide is an *in situ* probe about 0.6m in length and 50mm in diameter (Figure 1). The s::can spectro::lyzer measures the attenuation of light in the UV-VIS spectrum between 200 and 730nm across a measurement gap of between 0.5 and 2mm. Different components of wastewater absorb light in different regions of the UV-VIS spectrum, and the spectrometer can detect the total absorption from all the compounds present. Each measurement takes about 15 seconds. The probe is kept clean automatically with a compressed air system and data is logged on a control computer and hence can operate independently for long periods of time.



Figure 1 The s::can spectro::lyzer

### Historical data and preliminary calibration

A large dataset of UV-VIS measurements in sewage and other wastewaters was already available from other research projects. These earlier projects were undertaken by DCM Process Control with an s::can UV-VIS submersible spectro::lyzer. The projects aimed to quantify wastewater parameters such as nitrate ( $\text{NO}_3$ ), chemical oxygen demand (COD) and total suspended solids (TSS) with a similar methodology to that reported in published trials (e.g. Rieger *et al.*, 2004; Langergraber *et al.*, 2003).

Analysis of this historic data revealed a signal in the ultraviolet spectrum of sewage at a variety of sites that was consistent with the bisulphide absorption found in literature. The presence of the signal was anecdotally linked to observations of foul odours, corrosion problems or even independently reported elevated hydrogen sulphide levels.

Since other components of sewage also absorb strongly in the ultraviolet region a curve-fitting and PLS algorithm was developed to quantify the amplitude of the bisulphide peak and eliminate the background signals of other wastewater constituents. Beer's law states that absorption strength is related directly to concentration so the peak amplitude was calibrated by linear regression to give mg/L total dissolved sulphide. The calibration factors were based on testing of standard samples generated from sodium sulphide nonohydrate in the University of Queensland lab. The calibration factor obtained matched that expected from literature (Goldhaber *et al.*, 1975; Guenther *et al.*, 2001; Giggenbach, 1971).

Bisulphide and hydrogen sulphide exist in an equilibrium that is primarily driven by pH. At pH levels above 8.0 the majority of the sulphide in solution is present as bisulphide (Goldhaber *et al.*, 1975) and the total dissolved sulphide can be directly detected by the spectrometer. In sewers the pH will not necessarily be above 8 so sulphide may not be totally ionised to bisulphide. pH, conductivity and temperature measurement allow calculation of the percent of total dissolved sulphide stored as bisulphide (ASCE, 1989). Hence knowing the bisulphide concentration from the UV/VIS measurements and the pH it is possible to calculate the total dissolved sulphide and dissolved hydrogen sulphide concentrations.

## Field Work

Three field sites of the Gold Coast City Council were chosen to validate the calibration. The sites were known to have different levels of dissolved sulphide and different flow patterns, allowing the sensor system to be verified under a variety of conditions.

At each site the spectrometer was set to operate continuously, recording the full UV-VIS spectrum every 30 seconds or 2 minutes depending on storage requirements. Simultaneously an onboard computer analysed the UV-VIS spectrum and calculated the bisulphide concentration based on the preliminary calibration. At sites 1 and 3 an *in situ* Züllig pH probe was also deployed to allow continuous calculation of total sulphide from the measured bisulphide ion concentration.

A parallel, manual sampling campaign was undertaken at each site. Samples collected were analysed for total dissolved sulphide using a new and highly accurate analytical method developed by the University of Queensland, Advanced Waste Water Management Centre (UQ-AWMC) (Keller-Lehman *et al.*, 2006). The aim of the sampling was to evaluate the calibration constructed from the historical data. Gold Coast City Council (GCCC) personnel collected samples for sulphide analysis and took spot measurements of pH, conductivity and temperature.

The validation tests were blinded: analytical results were not available to the group working with the online instruments until the predictions of sulphide concentration had been made available to the analytical group. The calibration of the spectrometer was not altered over the course of the trial.

These sites are described below:

**Site 1** is the inlet to a Wastewater Treatment Plant (WWTP) located at Elanora and fed by a rising main (C27) of significant length (9.2 km) carrying an average load of 16 ML/day Average Dry Weather Flow (ADWF). The retention time in the rising main is known from flow studies to be in the range of 3-4 hours. The probe was installed in a flow through bypass fed by a hose from a tapping directly off the C27 rising main. Particular care was taken to prevent aeration of the wastewater between the tapping and the measurement gap, as this could result in loss of sulphide from solution through stripping or oxidation.

**Site 2** is the CO16 wet well located in the Coomera Waters development. Sulphide levels were known from analytical grab samples to be significantly lower than at Site 1. The sensor probe was installed directly in the sewage below the lowest sewage level in the wet well. Because of the remoteness of the site mains power was unavailable so a solar panel and battery pack was used to power the system and a compressed air bottle supplied air for cleaning.

**Site 3** is in the inlet structure of the Coombabah WWTP. The rising mains feeding the plant are much longer than Site 1. The total flow and sulphide load at this site result from four different mains injecting into the inlet structure. Retention time in the different mains varies between 2 and 4 hours. The spectrometer was installed on a stainless steel mounting bracket directly in the flow of the convergent channel.

The trial at Site 3 coincided with oxygen injection from two pump stations (Figure 3) located on separate mains, approximately 3 km away from the WWTP. The flow from these two mains combines with two other larger mains at the inlet structure of the WWTP,

and then converges into a single flow channel at the test site. Data was collected for two weeks before the oxygen injection system was initialised (a control or baseline sampling period) and for two months after initialisation (the test period).

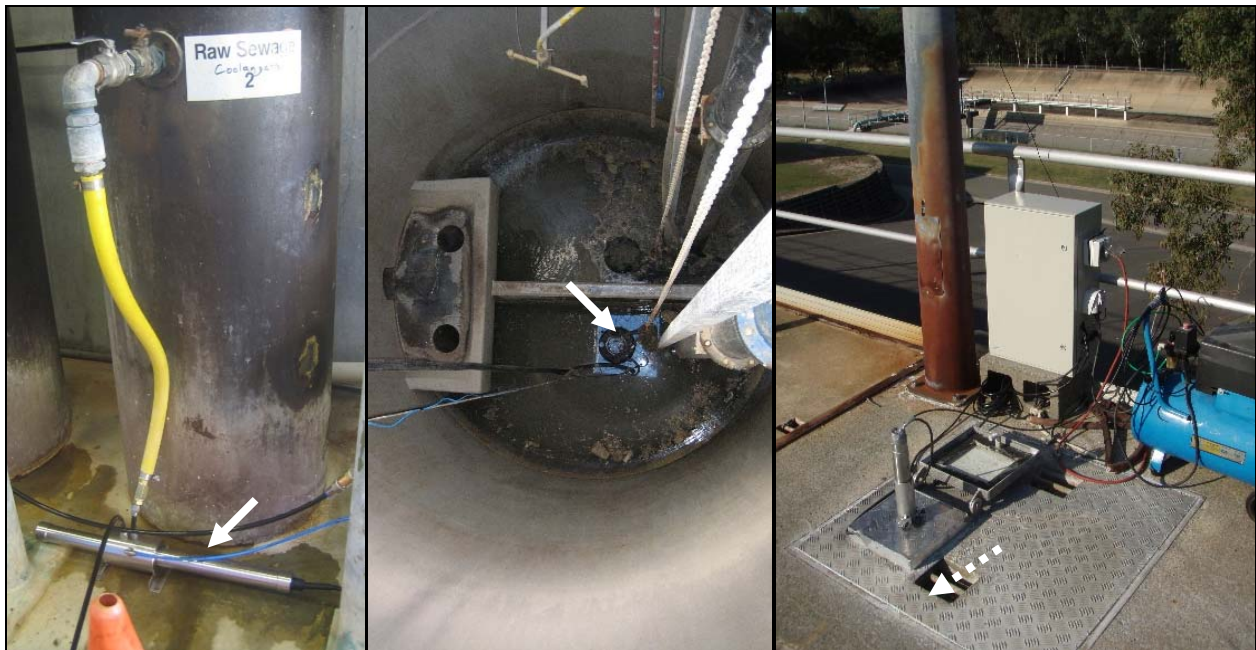


Figure 2 Deployment of the spectrometer (left to right) Site 1: in a bypass fitting, Site 2: suspended in a wet well and Site 3: installed in a sealed box channel. The location of the spectrometer is indicated with an arrow. In the right most picture the spectrometer is hidden from view 2m under the metal plate.



Figure 3 An oxygen injection station

### Laboratory Work

A spectrometer was also deployed to a laboratory scale sewer system at the University of Queensland (Gutierrez *et al.*, 2006). The spectrometer was integrated into the plant with a bypass system. A small flow was diverted out of the pilot plant and through the measurement gap in the spectrometer. Because the volume of the pilot plant was fixed the sample was then recycled back into the reactor. Sulphide production was monitored with

the spectrometer and a pH probe and samples were extracted for analytical analysis. An indicative picture of the laboratory scale system and bypass fitting is given in Figure 4.

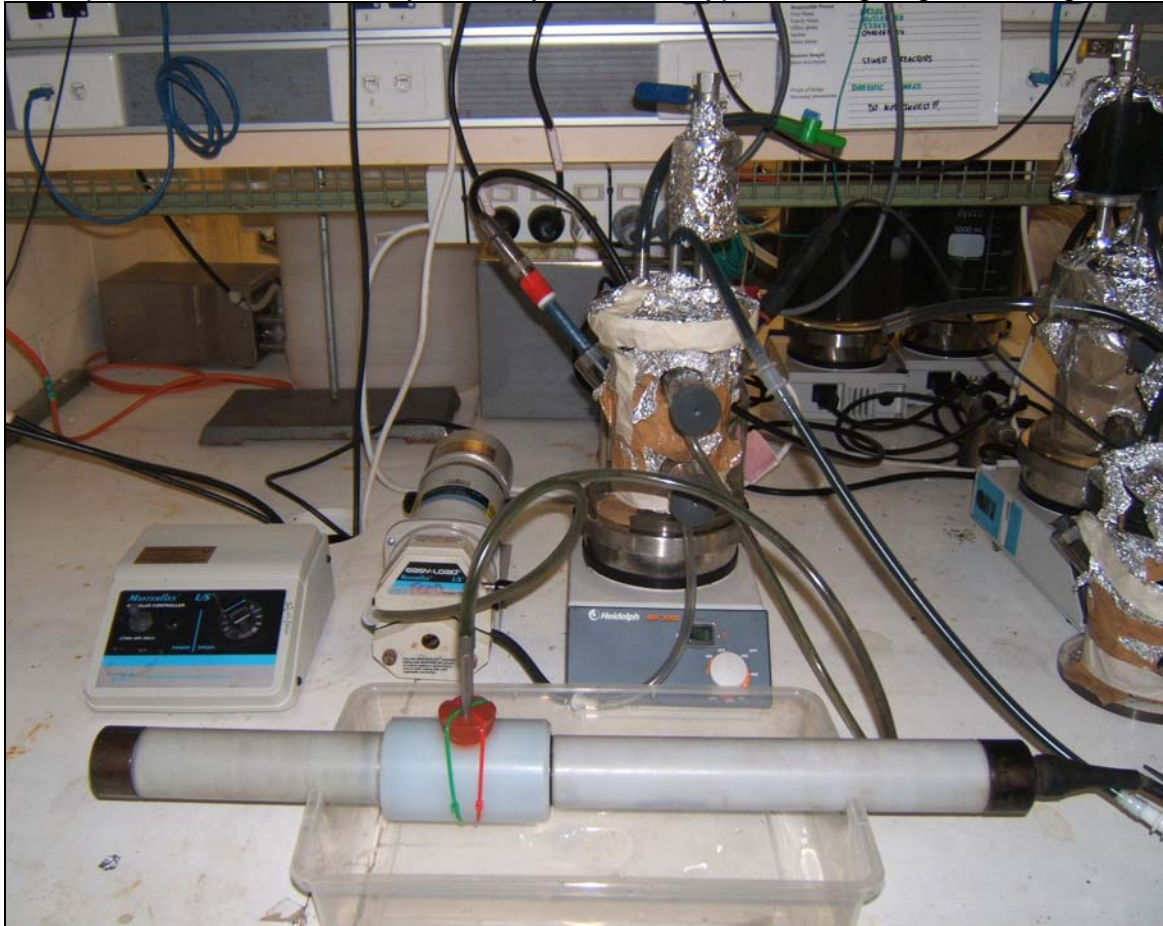


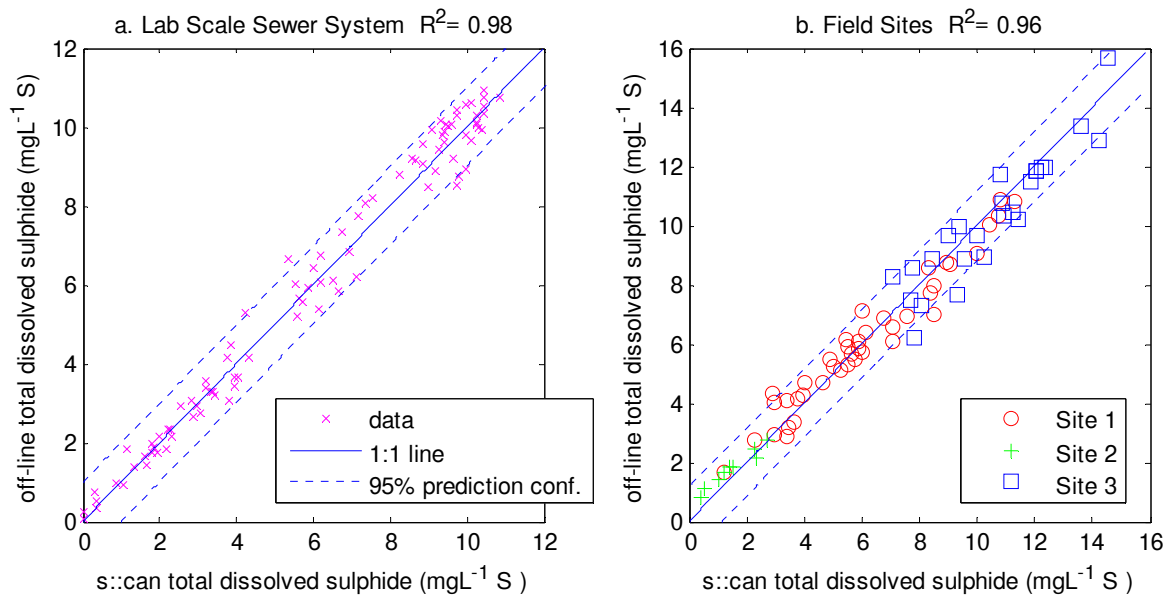
Figure 4 Laboratory scale sewer system and associated equipment, with the scan spectrometer in the foreground.

## RESULTS AND DISCUSSION

Over the field and laboratory work a significant quantity of data was collected spanning several months of online measurement. Simultaneously hundreds of comparison samples were collected for validation of the spectrometer calibration.

In the laboratory scale sewer system the validation results (Fig 5a) show that the new online method can predict total sulphide concentrations to better than  $\pm 1.0 \text{ mgL}^{-1}$  with 95% confidence over the tested range of 0-11  $\text{mgL}^{-1}$ .

Results from the field were also observed to correlate very well with the off-line analytical testing (Fig 5b) returning a prediction error of better than  $\pm 1.2 \text{ mgL}^{-1}$  with 95% confidence over the tested range of 0-16  $\text{mgL}^{-1}$ . As will be further discussed below, in the field sulphide levels were observed to fluctuate within minutes, which made the timing of sampling difficult, contributing to the larger confidence interval. On-line measurement of pH in the liquid phase with the *in situ* Züllig pH probe proved essential for the correct determination of the total dissolved sulphide.



**Figure 5 Total dissolved sulphide measured off-line vs. total dissolved sulphide measured using an s::can and a pH probe. (a) lab-sewer samples; (b) field samples.**

The high sampling frequency of the *in situ* automatic measurements allowed a detailed analysis of variation in sulphide levels over time. It was found that sulphide levels can vary considerably on a time scale of minutes in both wet wells and at the plant inlet. The high variability observed with online methods was verified by offline sampling (Figure 6). This variability has significant implications for sampling programs as it indicates it is a very difficult task to capture the sulphide dynamics using a manual sampling program. The dynamic variation of sulphide concentration may likely be underestimated using offline methods.

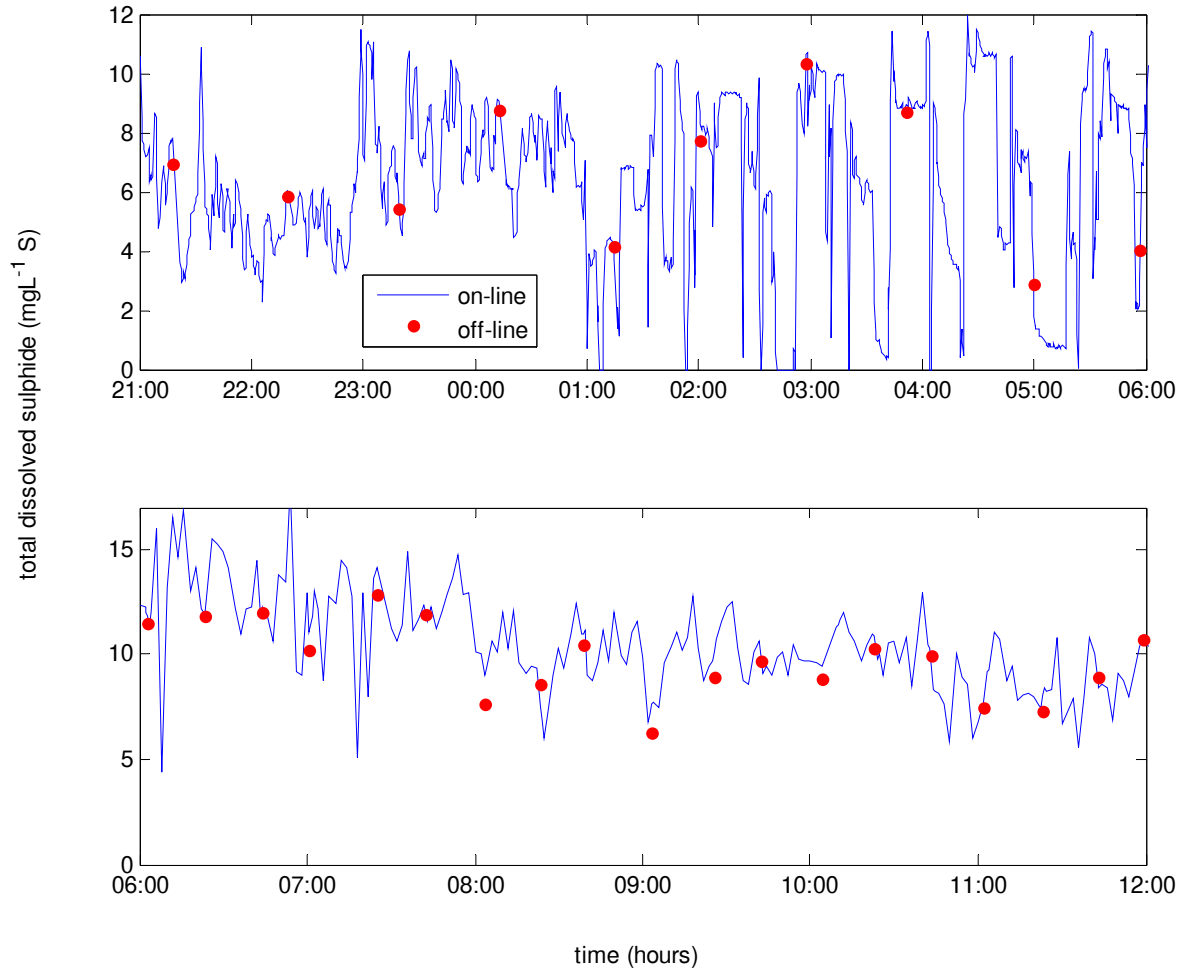


Figure 6 Total dissolved sulphide measurement at the inlets of two different a WWTPs (top: Site 1 and bottom: Site 3)

### Oxygen Injection Results

No significant difference in sulphide concentration was detected between the control period with no oxygen injection and the test period with oxygen injection (Figure 7).

However, the contribution from the mains receiving oxygen injection represented only approximately 20% of the total flow past the monitoring point. Hence the total dissolved sulphide level at the monitoring point could still remain high even if the OI strategy was successful in controlling the sulphide levels in the two treated mains. Detailed investigation of the effectiveness of OI on sulphide control requires monitoring the sulphide levels in individual mains, which is being carried out currently.

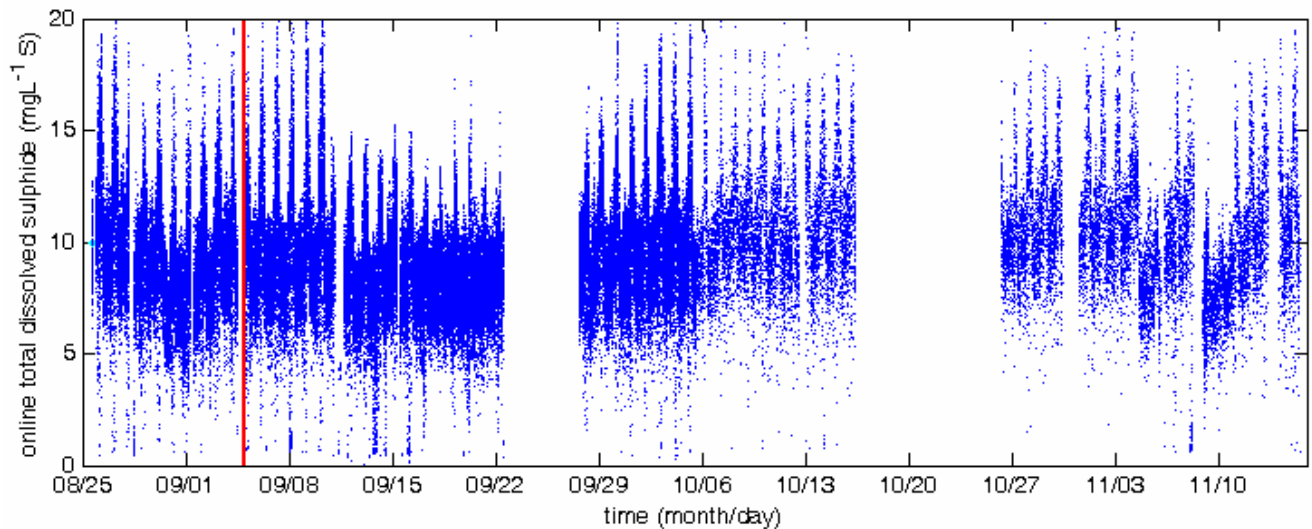


Figure 7 Total dissolved sulphide measurement at the inlet of a WWTP with OI (Site 3). There is high variability in sulphide concentration, but this is not instrument noise (also see Figure 6). The data to the left of the red line was recorded before the oxygen injection system was initialised; the data to the right was recorded after initialisation. The gaps in the data are due to an intermittent site power problem.

## CONCLUSION

We have developed a method to measure total dissolved sulphide and hydrogen sulphide concentrations in real time using a scan UV-VIS spectrometer and a pH probe. The method provides reliable and accurate measurement of sulphide in both field and laboratory conditions, as confirmed by the off-line laboratory tests. Compared to labour intensive continuous sampling campaigns, this technique is quicker (in real time), safer (requiring less contact with sewage and time spent in high risk areas) and much more cost effective (running without operator intervention for significant lengths of time),

Use of this technique has revealed that the sulphide concentration can vary very rapidly over even relatively short time periods, highlighting the need for online measurement tools when the dynamics of a system need to be known.

The application of this method allowed GCW to fully quantify the presence of sulphide, and therefore assess the impacts of oxygen injection as a sulphide control strategy. Future studies using the same direct online monitoring of dissolved sulphide will assist in the optimisation of this strategy.

## ACKNOWLEDGEMENTS

The first author wishes to acknowledge the generous support of the Tertiary Education Commission of New Zealand through the Enterprise Scholarship scheme. We also wish to thank the staff at the Elanora and Coombabah WWTPs for supporting this study, and the GCW staff responsible for after-hours sampling. The project was partially funded by the Australian Research Council through the Linkage Project LP0454182 with the Gold Coast City Council and the Sydney Water Corporation as industry partners.

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