Continuous measurement of dissolved sulfide in sewer systems

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ABSTRACT

Sulfides are particularly problematic in the sewage industry. Hydrogen sulfide causes corrosion of concrete infrastructure, is dangerous at high concentrations and is foul smelling at low concentrations. Despite the importance of sulfide monitoring there is no commercially available system to quantify sulfide in waste water. In this article we report on our use of an *in situ* spectrometer to quantify bisulfide in waste water and additional analysis with a pH probe to calculate total dissolved sulfide. Our results show it is possible to use existing commercially available and field proven sensors to measure sulfide to mg/l levels continuously with little operator intervention and no sample preparation.

Key words | *In-situ*, online, real-time, septic sewage, sulfide

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INTRODUCTION

Hydrogen sulfide (H_2S) is generated in the aqueous phase of wastewater by bacterial reduction of sulfate under anaerobic conditions (Tanaka *et al.* 2000). Accumulation of hydrogen sulfide in sewers poses significant problems in wastewater transport and treatment systems. Bacterial oxidation of hydrogen sulfide on pipe walls exposed to atmospheric oxygen produces sulphuric acid, which actively destroys concrete structures and pipes at a corrosion rate of several millimetres a year (Vincke *et al.* 1999). The gas is

also toxic to humans in even relatively low concentrations and poses a health risk to sewage workers (Querellou *et al.* 2005). At even lower concentrations hydrogen sulfide is foul smelling, and has a significant adverse impact on any exposed communities (Gostelow *et al.* 2001).

Hydrogen sulphide production occurs in the sewage system on the Gold Coast of Australia. Approximately 2800 km of sewer mains (60% pressure 40% gravity) are distributed across a large low lying coastal area with

significant canal and broad water frontage. Sea water ingress results in high sulphate concentrations, which is subsequently exposed to reducing conditions and high retention times during long journeys through pressure mains to (one of) only four wastewater treatment plants (WWTPs). The combination of geographical features and year round warm climate combines to produce high corrosion and odour potential environments.

There are a large number of sensor systems available to measure hydrogen sulfide concentration in gas phase. However such instruments are not suitable for measurement of sulfide dissolved in wastewater and particularly in rising mains, which is of particular interest on the Gold Coast. Technologies such as chalcogenide glass chemical sensors (Miloshova *et al.* 2003) and flurometric optode membranes (Shamsipur *et al.* 2005; Choi 1998) are emerging as having potential for detection of sulfide species dissolved in water. Currently, however, the standard method in industry and research for measurement of dissolved sulfide concentration in wastewater is by collection of samples and subsequent analysis by analytical chemistry.

In aqueous systems the bisulfide ion (HS^-) is in equilibrium with hydrogen sulfide and absorbs light directly in the ultra-violet wavelengths (Goldhaber & Kaplan 1975). Recent advances in real-time UV-VIS spectroscopy of seawater have shown the potential use of UV-VIS spectroscopy for detection of the bisulfide ion (Guenther *et al.* 2001; Johnson & Coletti 2002) and hence hydrogen sulfide. In this work, a method for measuring the dissolved sulfide in sewage in real-time using a field UV-VIS spectrometer and a pH probe is developed. This methodology uses existing commercially available sensors designed for immediate deployment in waste water treatment systems without further research and development of sensor hardware. The methodology is demonstrated and validated through field studies.

MATERIALS AND METHODS

Instrument

The spectrometer (spectro::lyser, s::can Messtechnik GmbH) used in this work is an *in situ* probe about 0.6m in length and 50 mm in diameter. The spectrometer measures the attenuation of light in the UV-VIS spectrum between 200 and 750 nm. In this field work the path length was 2.0 mm. Various 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 automatically cleaned by a compressed air system and data is logged on a control computer so the system can operate independently for long periods of time. For more information see Langergraber *et al.* (2003).

Historical data and calibration method

A large dataset of UV-VIS absorption spectra of sewage and other wastewaters was already available from other research projects. These earlier projects were undertaken by DCM Process Control Ltd. with submersible spectrometers. The projects aimed to quantify wastewater parameters such as nitrate (NO_3) and chemical oxygen demand (COD) by employing a similar methodology to that reported in published trials (e.g. Rieger *et al.* 2004; Langergraber *et al.* 2003).

Analysis of this historic data set revealed an unexpected signal in the ultraviolet spectrum of sewage at a variety of sites. This absorption peak was observed to be centred about 230 nm (Figure 1) which is consistent with the bisulfide absorption found in literature. The presence of the signal at these sites was anecdotally linked to observations of foul odours, corrosion problems and/or independently reported elevated hydrogen sulfide levels.

Since other components of sewage also absorbs strongly in the ultraviolet region a curve-fitting and Partial Least Squares (PLS) algorithm was developed to separate the amplitude of the bisulfide peak from the background signals of other wastewater constituents.

Curve fitting was used to generate a preliminary estimate of bisulfide concentration. Equations of the form given in Equation 1 have already been shown to be suitable to account for the majority of the background absorption in some waters and wastewaters (Bricaud *et al.* 1981; Huber & Frost 1998). We found that these equations were also valid for our waste water under the conditions that nitrates or other strongly absorbing distinct contaminants were absent from the sewage. These conditions were always
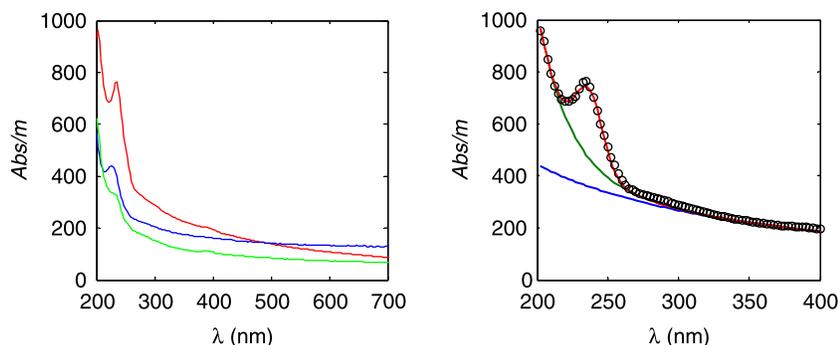
Figure 1 │ Left: Characteristic UV/VIS spectra from three different sites. The bisulfide signal is clearly visible around 230 nm. Right: Curve fitting to isolate the amplitude of the bisulfide signal.

satisfied in our experiments; in particular in septic sewage, nitrate does not normally co-exist with sulphides (Hobson & Yang 2000). After accounting for the background absorption a Gaussian was used to model the bisulfide absorption (Equation 2). Constants were found by sequentially minimising the summed square of the residual for Equations 1 and 2 and raw data over specific regions of the spectrum with a similar scheme to Guenther *et al.* (2001). An example of a resulting fit is given in Figure 1.

$$Abs/m_{(background)} = c_1 \lambda^{c_2} + c_3 e^{c_4(\lambda + c_5)} \qquad (1)$$

$$Abs/m_{(HS^-)} = c_6 e^{(\lambda - c_7)^2/c_8{}^2} \qquad (2)$$

The peak amplitude of the Gaussian, c_6 in Equation 2, was calibrated by linear regression to give mg/l bisulphide based on spectroscopic measurement of standards. Standards were generated using sodium sulfide nonohydrate prepared in oxygen free reverse osmosis water and stabilising sodium hydroxide solution. Samples were standardised by the ion-chromatography method (Keller-Lehman *et al.* 2006). The calibration factor is consistent with the order of magnitude of, but slightly lower than, those calculated from charts found in literature (Table 1).

Table 1 │ Values for bisulfide absorption calculated from literature and found in analytical testing during this study. Values are reported in *Abs/m* per mg/l HS⁻ to match readings obtained directly from the field spectrometer

Source	(*Abs/m*)/(mg/l)
Giggenbach *et al.* 1971	21.4–25
Goldhaber *et al.* 1975	23.2–24.7
Guenther *et al.* 2001	25
this study	19.4

A PLS solution was desirable for operational and robustness reasons. The spectrometer control system is already equipped to analyse spectra in real time with PLS coefficients and a PLS solution is less computationally costly for such a field computer. Curve fitting solutions could also be problematic in the presence of unexpected compounds if exceptions are not programmed for (which in turn increases computational time requirements). A PLS calibration comprising of several different wavelengths was subsequently obtained with standard PLS techniques using the Gaussian amplitude, c_6, and the spectral data as the input. Additional spectra from sites with non-zero nitrate concentrations were added to increase the specificity of the calibration. The PLS bisulfide concentration matched the curve fitting concentration up to a negligible error for all cases tested. A multi wavelength PLS solution (and hence a spectrometer) was necessary for determining the concentration of bisulfide. Single wavelength calibrations were unable to differentiate the large variation in absorption caused by solid material and other UV-absorbing components from the often minor signal of bisulfide.

Bisulfide and hydrogen sulfide exist in an equilibrium that is primarily driven by pH (Equation 3) (Goldhaber & Kaplan 1975). At pH levels above 8 the majority of the sulfide in solution is present as bisulfide and the total dissolved sulfide (TDS) can be directly detected by the spectrometer. In sewers the pH will not necessarily be above 8 so sulfide may not be totally ionised to bisulfide. Two methods are available to determine TDS. The simpler of the two is to determine the equilibrium position by measurement of physical and chemical properties of the

waste and thus mathematically determine the invisible sulfide stored as hydrogen sulfide. We chose to test this method in this work. Alternatively a sample can be automatically drawn and the pH adjusted.

$$H_2S \overset{pK_a \simeq 7}{\rightleftharpoons} H^+ + HS^- \tag{3}$$

Conductivity and temperature measurement allow calculation of the equilibrium point (K_a) of the hydrogen sulfide/bisulfide equilibrium (ASCE 1989). With the bisulfide concentration obtained from the UV/VIS measurements and the pH, it is then possible to calculate the TDS concentration.

The error associated with calculating the TDS concentration can be estimated by taking the error in our estimate of the equilibrium position and bisulphide measurement into account with standard error analysis techniques (Equation 4). Away from the equilibrium point the first term accounting for uncertainty on the equilibrium position is negligible and the error in TDS is dependent on the accuracy of the spectrometer and bisulfide calibration alone. Near the equilibrium the first term is not negligible and creates an upward perturbation in the uncertainty. Below the equilibrium point the uncertainty is very high because very little bisulphide is visible, hence uncertainty on the small visible fraction propagates to make determination of TDS inaccurate.

$$\sigma_{[HS^- + H_2S]} = \sqrt{\left(\frac{\sigma_k}{k(k+1)}\right)^2 + \left(\frac{\sigma_{[HS^-]}}{[HS^-]}\right)^2} \tag{4}$$

When using the equilibrium determination calculation method, accurate pH measurements and higher waste water pH levels result in the most accurate determination of TDS. If the pH is close to or below the equilibrium point it may be desirable to increase the pH of a small sample of waste water to maximise the bisulfide signal and thus reduce the error in the measurement of TDS. With the automated addition of a strong base to an automatically extracted sample the hydrogen sulfide in the sample can be totally ionised to bisulfide, eliminating the error associated with calculation of TDS. For this method a pH probe could be omitted if it is not desirable to know the equilibrium position of the hydrogen sulfide/bisulfide ion.

Calibration validation

Two field sites of the Gold Coast City Council were chosen to validate the bisulfide calibration and pH equilibrium calculation method. The sites were known to have different levels of dissolved sulfide and different flow patterns. The sites are summarised in Table 2. A spectrometer and a pH probe were installed at each site (except for site 3 where pH was tested by spot measurement when samples were drawn), with some spectrometer locations as shown in Figure 2. Conductivity and temperature was also monitored with a combination of spot sampling and online sensors.

At Site 5 a data logger failed and pH data was lost for the sampling period. It was observed that at this site the pH followed a diurnal pattern so a standard diurnal pH pattern was constructed from the remaining data and used for the equilibrium calculations during the validation sampling.

A parallel manual sampling campaign was undertaken at each site. Samples collected were analysed for TDS using a new and highly accurate analytical method developed by the University of Queensland, Advanced Waste Water Management Centre (Keller-Lehman *et al.* 2006). This method involves increasing the pH of the sample, so it was not possible to analytically determine bisulfide concentration. Hence the *in-situ* results for total dissolved sulfide, calculated from determining the equilibrium position, were used to validate the online methodology.

RESULTS AND DISCUSSION

Results correlated well with the offline analytical testing (Figures 3 and 4). In the field sulphide and pH levels were

Table 2 | Site summary

Site	Site description	Installation method
1	Rising main at entry to Elanora WWTP	Tapping and bypass fitting
2	Inlet channel at Coombabah WWTP	*In-situ*
3	Wet well	*In-situ*
4a	Wet well	*In-situ*
4b	Rising main	Tapping and bypass fitting
5	Rising main at entry to Elanora WWTP	Tapping and bypass fitting

Figure 2 | Deployment of the spectrometer. Site 1: in a bypass fitting, Site 2: installed in a sealed box channel and Site 3: hidden from view at the bottom of a wet well.

observed to fluctuate within minutes which made the timing of sampling difficult. From a total sample of 137 validation samples, six were discarded because it appeared there was a timing mismatch between when the sample was drawn and when the instrument measurement was recorded. Regression returned a line of best fit which was slightly different from the calibration initially generated from analysis of standard solutions, however the discrepancy was small. The online predictions were slightly higher, so it is possible that some sulphide was lost from the samples in the delay between sampling and laboratory analysis.

After regression and outlier elimination a prediction error of better than $\pm 1.2 \text{mgL}^{-1}$ with 95% confidence over the tested range was calculated.

The pH variability resulted in a variation in the fraction of TDS present as visible bisulfide from approximately 50 to 90%. Hence online measurement of pH in the liquid phase with the *in situ* pH probe proved essential for the correct determination of the total dissolved sulfide. The lowest pH observed in this study was 6.9, which is approximately the equilibrium position of bisulfide/hydrogen sulfide. The data set was not large enough data set for rigorous analysis to determine σ_k and $\sigma_{[\text{HS}^-]}$ in Equation 4. It was not possible to detect a significant variation in distribution of the residual of total dissolved sulphide as a function of pH. This suggests that the error from the equilibrium calculation was somewhat uniform regardless of pH and hence we both determined the pH with high enough accuracy that the first
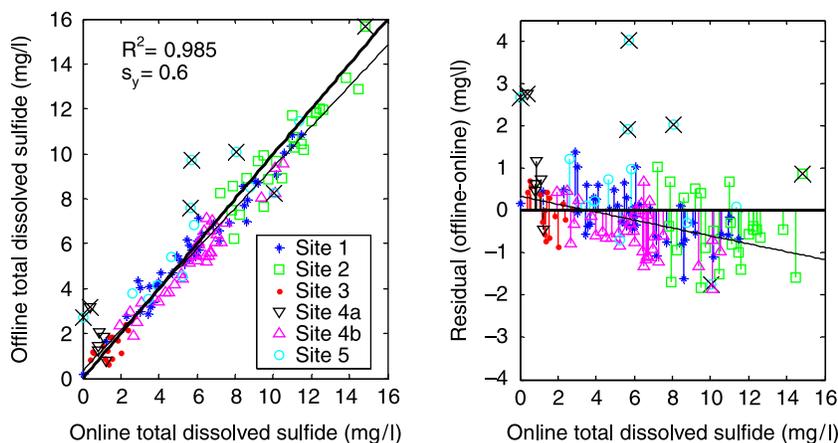

Figure 3 | Field validation results. 95% confidence limits on the regression and future predictions indicated with dashed lines. Six outliers were eliminated and are indicated with a cross.
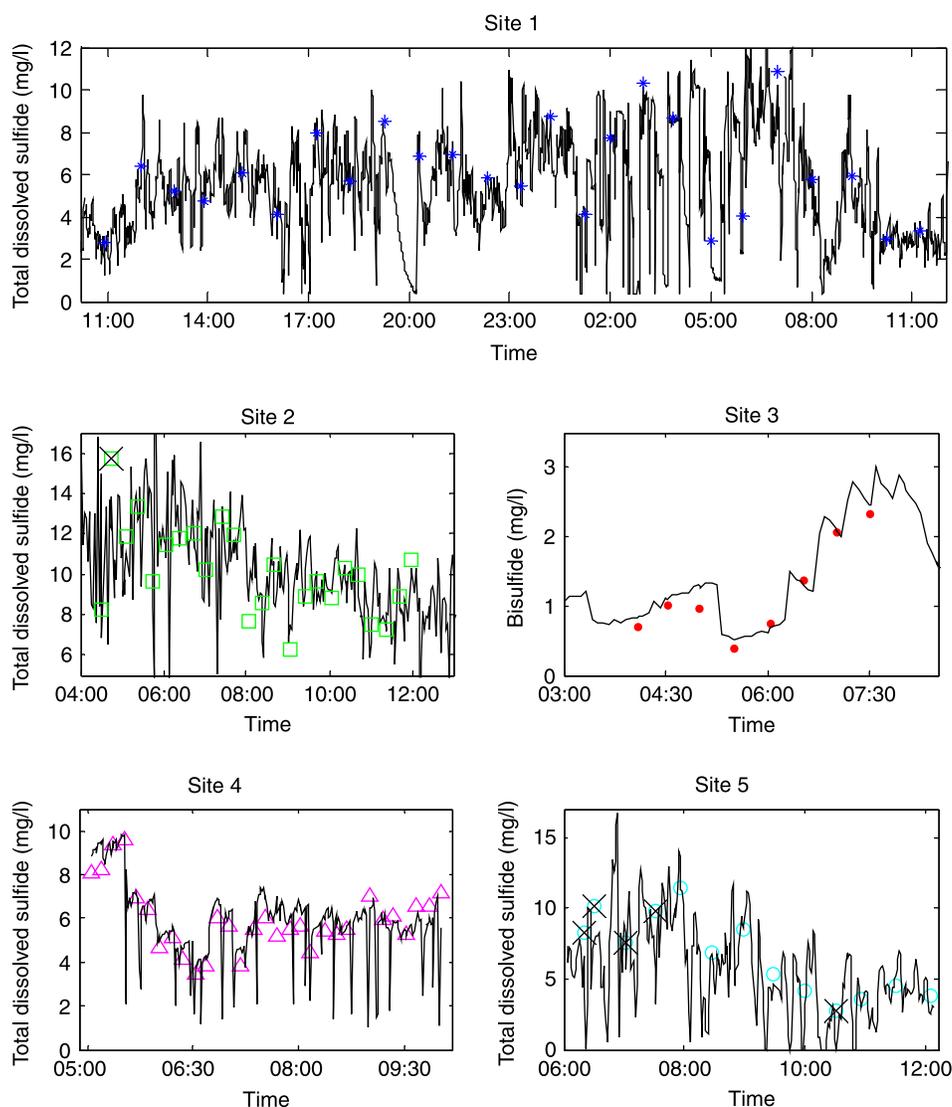
Figure 4 | Characteristic online time series and corresponding offline laboratory samples. At Site 3 no online pH information was recorded, so the analytical bisulphide concentration was determined by an equilibrium calculation based on spot pH sampling. The eliminated outliers are indicated with a cross.

term in Equation 4 was not very strong or that other errors, such as sampling error, were more significant.

The accuracy of the methodology is inevitably worse on a per-sample basis than can be achieved with laboratory methods. The online sensor package however, can monitor with much higher temporal resolution for a much longer duration (indeed almost indefinitely with regular maintenance) than traditional grab sampling and laboratory methods. This is essential for providing data for process control systems or input into sewer models. In particular it is questionable whether grab sampling, regardless of

the accuracy of individual samples, could provide insight into the variability in sulphide concentrations observed in these trials.

The generation of an initial calibration from a curve fitting solution proved to be advantageous for several reasons. Firstly all the data collected during field work formed a validation data set and the calibration can be considered rigorous and free from any researcher bias which might result in tuning for these samples but reduce future predictive power. Additionally, the immediate availability of a calibration allowed the prediction of sulfide concentrations

from the outset of field work. This expedited the preliminary experimental testing: initially our laboratory results disagreed with the online determination of total dissolve sulfide. The discrepancy was traced to a malfunctioning pH probe, and hence an incorrect equilibrium calculation. If these samples had been included in the generation of a PLS solution the problem might not have been detected.

CONCLUSION

We have developed and validated a method to measure TDS and hydrogen sulfide concentrations in real time using a spectrometer and pH, conductivity and temperature probes. Such probes are already deployed to monitor wastewater quality parameters at many other sites so a number of end users will be able to upgrade their existing sensor systems to employ our methodology with just a software patch. The method provides reliable and accurate measurement of sulfide in the field under real conditions, as confirmed by the offline analytical laboratory tests. Compared to labour intensive continuous sampling campaigns, this technique is faster (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).

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