

# *In Situ* 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 foul smelling at low concentrations. Despite the importance of sulfide monitoring there is no commercially available system to quantify sulfide *in situ* in waste water. In this article we report on our use of an *in situ* spectrolyser<sup>TM</sup> 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.

**Keywords:** In-situ, on-line, sulfide, septic sewage, real-time

## INTRODUCTION

Hydrogen sulfide (H<sub>2</sub>S) 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 it is foul smelling, which has a significant adverse impact on the exposed community (Gostelow *et al.*, 2000).

Hydrogen sulphide build up is observed in the sewage system on the Gold Coast of Australia where approximately 2800km of sewer mains (60% pressure 40% gravity) are distributed across a large low lying coastal area with significant canal and boardwater 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 Waste Water 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 *et al.*, 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 ( $\text{HS}^-$ ) is in equilibrium with hydrogen sulfide and absorbs light directly in the ultra-violet wavelengths (Goldhaber *et al.*, 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 *et al.*, 2002) and hence hydrogen sulfide. In this work, a method for measuring the dissolved sulfide *in situ* and in real-time in sewage using an ocean UV-VIS spectrophotometer and a Züllig 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 METHOD

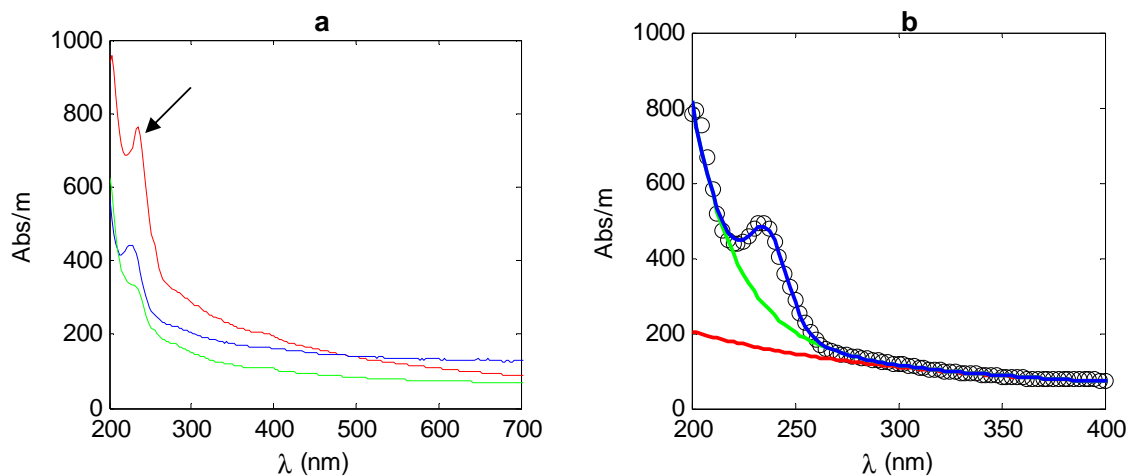
### Instrument

The spectrometer (spectrophotometer, Ocean Messtechnik GmbH) used in this work to detect bisulfide is an *in situ* probe about 0.6m in length and 50mm in diameter. The ocean spectrophotometer measures the attenuation of light in the UV-VIS spectrum between 200 and 750nm. In these experiments the path length was 2.0mm. 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. More information regarding the ocean spectrophotometer can be found in other works (e.g. 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 ocean spectrophotometers. The projects aimed to quantify wastewater parameters such as nitrate ( $\text{NO}_3$ ) 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 230nm (Figure 1a) which is consistent with the bisulfide absorption found in literature.



**Figure 1 a:** Characteristic UV/VIS spectra from three different sites. The bisulfide signal is clearly visible around 230nm (arrow). **b:** Curve fitting to isolate the amplitude of the bisulfide signal. The curves are added together to minimise the difference between the model and observed data.

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 absorb 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 1.1 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 *et al.*, 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 satisfied in our experiments; in particular in septic sewage, nitrate does not normally co-exist with sulphides (Hobson *et al.*, 2000). After accounting for the background absorption a Gaussian was used to model the bisulfide absorption (1.2). Constants were found by sequentially minimising the summed square of the residual for equations 1.1 and 1.2 and raw data over specific regions of the spectrum (Figure 1b).

$$Abs / m_{(background)} = c_1 \lambda^{c_2} + c_3 e^{c_4(\lambda+c_5)} \quad (1.1)$$

$$Abs / m_{(HS^-)} = c_6 e^{\frac{(\lambda-c_7)}{c_8^2}} \quad (1.2)$$

The peak amplitude of the Gaussian (1.2.c<sub>6</sub>) was calibrated by linear regression to give mg/L total dissolved sulfide (Figure 2). Calibration factors were based on spectroscopic measurement of bisulfide 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).

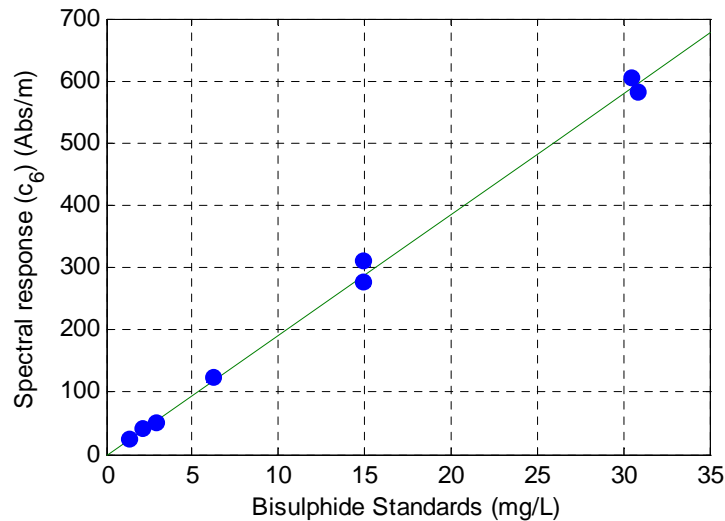


Figure 2. Calibration curve of bisulfide standards vs spectral response.

A PLS solution was desirable for operational and robustness reasons. The standard spectrolyser 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 increased 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. We found a multi wavelength PLS (and hence spectrometer) to be essential for determining the concentration of bisulfide, as a single wavelength calibration would be unable to differentiate the large variation in absorption caused by solid material and other UV-absorbing components from the often minor signal from bisulfide.

**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 s::can spectro::lyser.**

| Source                          | $\frac{Abs/m}{mg/L}$ |
|---------------------------------|----------------------|
| Giggenbach <i>et al.</i> , 1971 | 21.4-25              |
| Goldhaber <i>et al.</i> , 1975  | 23.2-24.7            |
| Guenther <i>et al.</i> , 2001   | 25                   |
| this study                      | 19.4                 |

Bisulfide and hydrogen sulfide exist in an equilibrium that is primarily driven by pH (2.1) (Goldhaber *et al.*, 1975). At pH levels above 8 the majority of the sulfide in solution is present as bisulfide and the total dissolved sulfide and Hydrogen sulfide 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 total dissolved sulfide. 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.

Conductivity and temperature measurement allow calculation of the equilibrium point ( $K_a$ ) of the hydrogen sulfide/bisulfide equilibrium (ASCE, 1989) (2.2). Knowing the bisulfide concentration from the UV/VIS measurements and the pH from an in-situ sensor it is then possible to calculate the total dissolved sulfide and dissolved hydrogen sulfide concentrations by rearranging equation 2.2 to get equations 2.3 and 2.4.



$$K_a = \frac{[H^+][HS^-]}{[H_2S]} \quad (2.2)$$

$$k = \frac{K_a}{[H^+]} \quad (2.3)$$

$$[H_2S + HS^-] = \frac{k+1}{k} [HS^-] \quad (2.4)$$

The error associated with calculating the total dissolved sulfide 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 (2.5). More than one pH unit above or below the equilibrium point the first term accounting for uncertainty on the equilibrium position is negligible and the error in total dissolved sulfide is dependent on the accuracy of the spectrometer and bisulfide calibration alone. Less than one pH unit above or below 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 total dissolved sulphide inaccurate.

$$\sigma_{[HS^-+H_2S]} = \sqrt{\left(\frac{\sigma_k}{k(k+1)}\right)^2 + \left(\frac{\sigma_{[HS^-]}}{[HS^-]}\right)^2} \quad (2.5)$$

This analysis shows that when using the equilibrium determination calculation method accurate pH measurements and higher waste water pH levels obtain the most accurate determination of total dissolved sulfide. 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 total dissolved sulfide. 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 total dissolved sulfide. 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. A scan spectrometer and Züllig pH probe were installed at both sites to log the UV-VIS spectrum and pH of the sewage every 30 seconds. Preliminary site investigations found the variability in salinity and temperature to be second order at these sites for the purpose of calculation of total dissolved sulphide, and hence constants for the equilibrium calculations were determined from spot sampling.

**Site 1** is the inlet to the Elanora WWTP fed by a rising main (#C27) of length 9.2 km carrying an average dry weather flow of 16 ML/day. The retention time in the rising main is known from flow studies to be in the range of 3-4 hours. The scan spectrometer was installed in a flow through bypass fed by a hose from a tapping directly off the rising main. The Züllig pH probe was also inserted into the fitting. Particular care was taken to prevent aeration of the wastewater between the tapping and the measurement gap, as this could result in loss of sulfide from solution through stripping or oxidation.



Figure 3. Deployment of the spectrometer. Site 1: in a bypass fitting and Site 3: installed in a sealed box channel.

**Site 2** 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 sulfide 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 scanning spectrolyser and Züllig pH probe was installed on a stainless steel mounting bracket directly in the flow of the convergent channel.

A parallel manual sampling campaign was undertaken at each site. Samples collected were analysed for total dissolved sulfide 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). As 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.

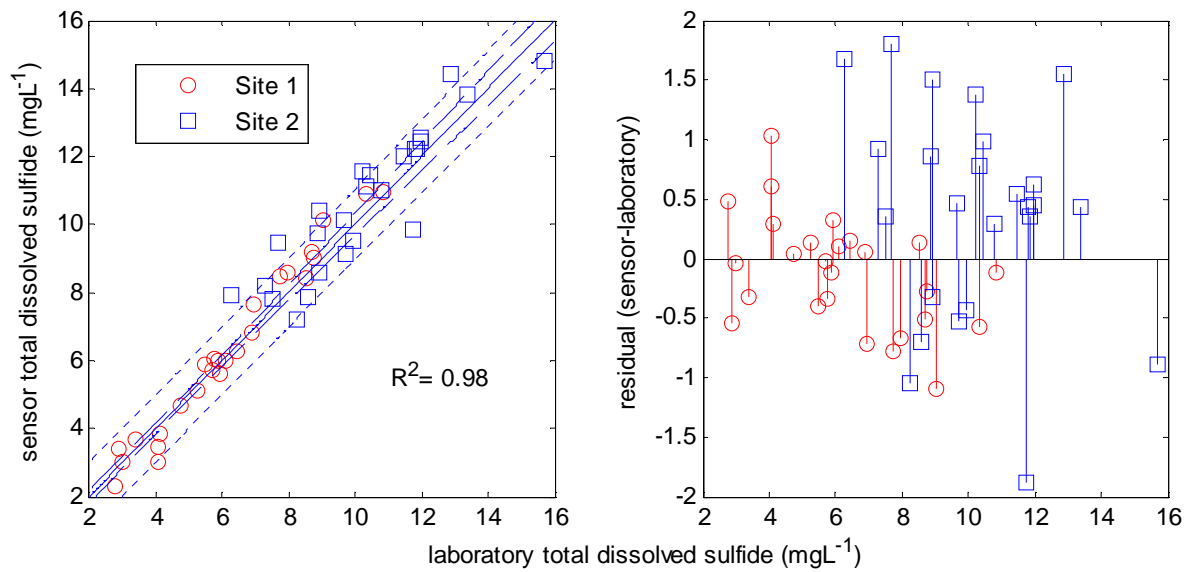
## RESULTS AND DISCUSSION

Results correlated very well with the off-line analytical testing returning a prediction error of better than  $\pm 1.2 \text{mgL}^{-1}$  with 95% confidence over the tested range of  $2\text{-}16 \text{mgL}^{-1}$  total dissolved sulfide and pH of 7.1 to 8.0. In the field sulphide and pH levels were observed to fluctuate within minutes (Figure 5), which made the timing of sampling difficult. It is possible that timing difficulties have contributed to the spread of the calibration plot (Figure 4). The pH variability resulted in a variation in the fraction of total dissolved sulfide present as visible bisulfide from approximately 50 to 90%. Hence 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 sulfide.

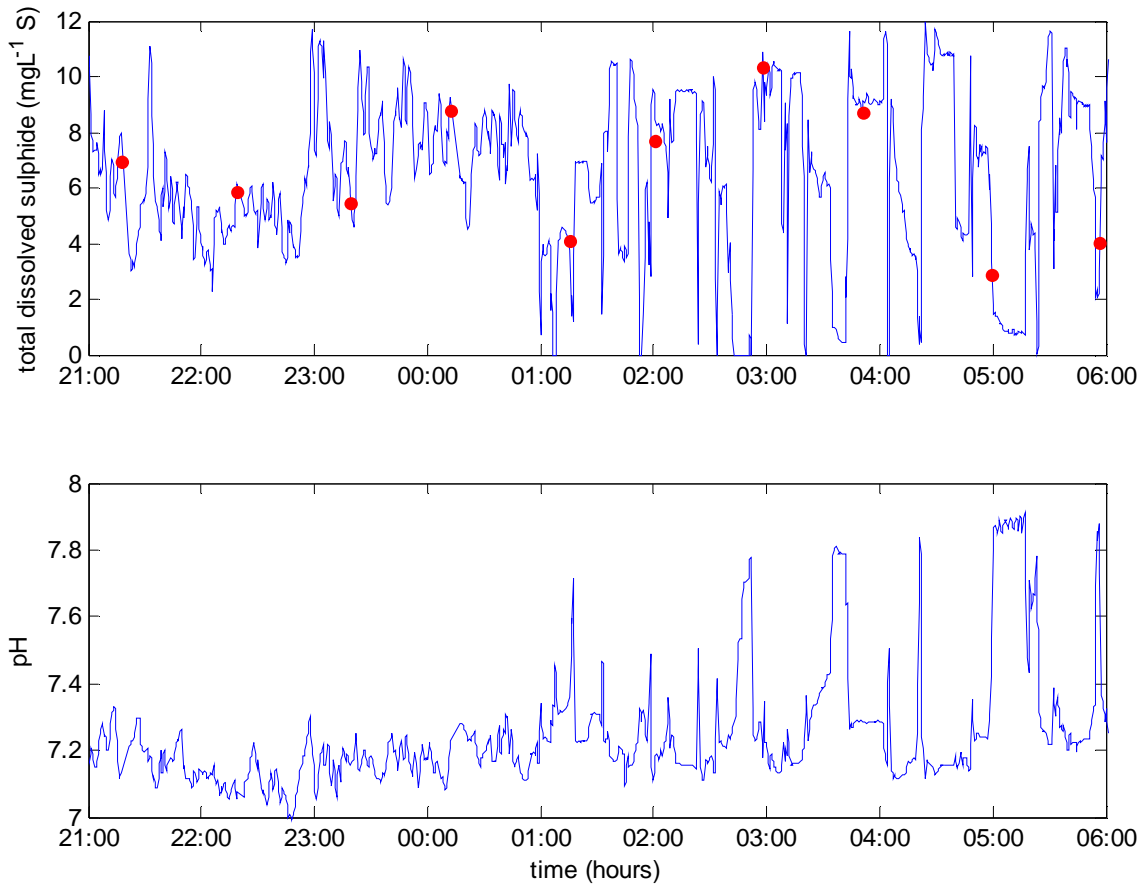
The lowest pH observed in this study was 7.1, which is near the equilibrium position of bisulfide/hydrogen sulfide. We did not have a large enough data set for rigorous analysis to determine  $\sigma_k$  and  $\sigma_{[\text{HS}^-]}$  in equation 2.5. We could not detect a significant variation in distribution 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 term in equation 2.5 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 much longer (indeed almost indefinitely with regular maintenance) than traditional grab sampling/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 useful 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 us to predict sulfide levels from the outset of field work. This expedited the preliminary work. For example initially our laboratory results disagreed with the on-line determination of total dissolved 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 we might not have detected the problem until much later.



**Figure 4. Field validation results. Dotted lines are 95% confidence on prediction and confidence of line of best fit. Higher residuals were observed at Site 2, where samples were taken directly from the channel, not a bypass fitting as at Site 1.**



**Figure 5. An example of a time series obtained with the online methodology, with laboratory validation samples overlaid. Highly variable sulfide and pH illustrate the importance of a high sampling frequency to accurately characterise the total dissolved sulfide concentration.**

## CONCLUSION

We have developed and validated a method to measure total dissolved sulfide and hydrogen sulfide concentrations in real time using an s::can UV-VIS spectrometer and a pH probe. 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 off-line 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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