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Comparison of H_2S Gas Sensors: A Sensor Management Procedure for Sewer Monitoring

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Abstract: Hydrogen sulphide (H_2S) emissions are one of the major problems associated with sewer networks. This gas, with its characteristic smell of rotten eggs is highly toxic and leads to the corrosion of sewer infrastructures. To protect cities and ensure the safety of sewer workers, sewers are commonly monitored using H_2S gas sensors. In this work, three commercial H_2S gas sensors for air quality monitoring were compared at two different sites in Berlin, Germany. Two of the sensors provide online access to data, while the other one is a data logger. Moreover, based on statistical measures (RMSE, MAE, MB, and a graphical analysis), we evaluated whether a rotation/exchange between data logger (reference) and online sensors is possible without significant differences in the gas measurements. Experimental evaluation revealed that measurement differences are dependent on the H_2S concentration range. The deviation between sensors increases as the H_2S concentration rises. Therefore, the interchange between reference and online sensors depends on the application site and the H_2S levels. At lower ranges (0–10 ppm) there were no observed problems. Finally, to support practitioners on-site, a management procedure in the form of a decision-making tool is proposed for assessing whether gas sensors should be exchanged/rotated.

Keywords: air quality monitoring; decision making tool; gas sensors; hydrogen sulphide; sewer systems

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1. Introduction

Hydrogen sulphide (H_2S) is one of the major concerns in sewer networks. It is a malodorous gas with the characteristic smell of rotten eggs, highly toxic, and it is corrosive to concrete and metal [1,2]. This gas is formed in the liquid phase under anaerobic conditions; however, its effects are noticeable when released in the gas phase into the sewer and the urban atmosphere [3]. In the liquid phase, under anaerobic conditions, sulfate ($SO_4{}^{2-}$) is biologically reduced by anaerobic bacteria (e.g., Desulfovibrio) to sulphide (S^{2-}) (Equation (1)). Moreover, during the biochemical oxidation of organic matter, hydrogen ions are removed and react with a hydrogen acceptor, sulphide, to form hydrogen sulphide (Equation (2)) [1].

$$SO_4^{2-} + \text{organic matter} \xrightarrow{\text{anaerobic bacteria}} S^{2-} + H_2O + CO_2 \quad (1)$$

$$S^{2-} + 2H^+ \longrightarrow H_2S \quad (2)$$

When released into the sewer gas atmosphere, the effects of H_2S become noticeable already at low concentrations (>0.5 ppm), causing unpleasant and strong malodors. Moreover, irritation and nausea are expected at concentrations above 10 ppm, as well as respiratory and eye injuries at above 50 ppm. Between 300 and 500 ppm, exposure to H_2S becomes life-threatening, and concentrations above 700 ppm are known to be lethal [2].

Moreover, the U.S. Environmental Agency [4] states that "deaths due to hydrogen sulphide intoxication, which are reported regularly, are usually associated with exposure under occupation-related circumstances". Therefore, due to the extreme toxicity of hydrogen sulphide, protective measures must be taken when working in its environment. For this aim, the European Commission Directive 2009/161/EU [5] proposes an indicative occupational exposure limit values (IOELV) for H_2S of 10 ppm for a short-term exposure limit (~15 min) and of 5 ppm for an eight-hour exposure. In order to protect sewer workers' health from H_2S exposure, as well as protecting urban areas from malodor and corrosion, monitoring of the sewer air quality must be a priority. In addition, the accuracy and performance of the sensors are crucial to save lives, and consequently, they are required to be outstanding without exception [6].

As a common practice in sewer systems, H_2S is monitored by the installation of gas sensors in manholes used to identify sources "hotspots" of corrosion and odour as well as provide information on the type and severity of the problems. Frequently, H_2S levels have been recorded using OdaLog sensors [7], which have been applied in several studies worldwide [8,9]. Monitoring of the sewer atmosphere is often challenging because of its harsh environment, associated with high humidity [10] and toxicity. Therefore, H_2S gas sensors need to be robust and should meet the following requirements: easy installation and operation, easy calibration, low power consumption, fast response and low limits of detection [6,11]. To date, several sensor types have been developed for this kind of application, and the most common ones are: electrochemical sensors, optical sensors, sensor arrays and metal oxide-semiconductor-materials-based sensors [6,11].

To ensure high-quality measurements, sensors need to be maintained properly and regularly calibrated [12]. Moreover, some sensors need to be rotated at intervals because of recommended refreshment periods due to the harsh environmental conditions. In some applications, sensors might be scarce and need to be rotated between monitoring points. When these problems arise, some questions should be asked: Are the sensor measurements accurate? Is a sensor interchange possible without significant differences? How should H_2S sensors for sewer monitoring be managed?

Until now, these questions seem to remain unanswered in the literature. A similar study was published recently on the same topic, but focusing on a comparison of H_2S liquid phase monitoring sensors [13]. Since 2004 several papers have been published centered around the use of different materials and techniques for developing H_2S sensors [14,15]. Recent ones (e.g., [6,11,16].) have reviewed the development and availability of H_2S gas sensor methods. Hoewever, these studies do not provide detailed information on the practical application and continuous use of gas sensors in sewer systems. Therefore, a practical comparison of H_2S gas sensors addressing the importance of managing and maintaining them is missing.

Therefore, in this work, we compare three commercial H_2S gas sensors for air quality monitoring in two different sewer installations in Berlin, Germany. Moreover, based on performance criteria, we evaluate the possibility of a rotation/exchange between a reference and two online sensors without significant differences in the gas measurements. Last, we define a framework of possible guidelines to improve the management of H_2S gas sensors for continuous, reliable measurements by proposing a decision-making tool for comparing gas sensors and assessing whether they should be rotated/exchanged.

2. Materials and Methods

2.1. Sensors

Three different H_2S gas sensors were evaluated in this work. A short description of the sensors is provided below and their technical data are summarised in Table 1.

- OdaLog® Logger L2 (Thermo Fisher Scientific Australia Pty Ltd., Scoresby, Australia): Is an electrochemical gas data-logger with a measuring range between 0 and 200 ppm. It is compact and portable (L = 196 mm, Ø 62 mm, w = 420 g) and is widely used in wastewater and sewer applications [17]. For humid environments (>80% relative humidity), regular refreshment periods are recommended by the manufacturer [17].

This specific sensor is not provided with remote site logging; however, newer versions of the sensor offer this feature. In this work, this sensor is used as a reference.

- SulfiLogger™ S1/X1-1020 (SulfiLogger™, Arhus, Denmark): Is a micro-electrochemical sensor that can be used as a water sensor in the liquid phase or as a gas sensor in the gas phase. Its measuring range is 0–1000 ppm in the gas phase and enables continuous online monitoring as well as remote site logging. According to the manufacturer, this sensor does not require refreshment periods. This sensor is also portable (L = 240 mm, Ø 48.3 mm) and light weight (840 g) [18].
- MyDatasensH2S1000 BLE (Microtronics Engineering GmbH, Ruprechtshofen, Austria): Is equipped with an electrochemical sensor for measuring H_2S gas in different wastewater applications. This sensor is also portable (height = 169 mm, width = 106 mm, depth = 61 mm) with a measuring range of 0–200 ppm. According to the manual, this sensor does not require refreshment periods [19]. However, if the sensor is placed in a site with high H_2S exposure, the manufacturer recommends (telephone conversation on 20 August 2021) refreshing the sensor to extend its lifetime. The sensor can only be calibrated by the manufacturer or a service partner and should be calibrated at least once every six months. Indeed, the calibration procedure includes a refreshing period while travelling to the manufacturer. Data can be monitored online through a Bluetooth connection that provides access to the gas measurements [19].

Table 1. Summary of the sensors' technical data.

	OdaLog® Logger L2 [17]	**Sulfilogger™** [18]	**MyDatasensH2S1000 BLE** [19]
Sensor Type	Electrochemical	Microelectrochemical	Electrochemical
Measuring Range	0–200 ppm	0–1000 ppm	0–200 ppm
Measuring Intervals	1 s to 1 h intervals	1 s	Adjustable, e.g., 1 min
Accuracy	±1% of full range	±5% of actual value	1% of signal [20]
Humidity range	15–90% non condensing	0–100%	15–90% non condensing
Battery Life	>8 months (logging)	~3 months (6 h transmission) [21]	~2 years (1 min measurement)
Data Logging or Transmission	1 min logging = 29 days 5 min logging > 6 months	6 h transmission [21]	~3 h transmission
ATEX Certified	Yes II 1 G, Ex ia IIC T4 Ga	Yes II 1G Ex ia IIC T4 Ga	Yes II 2G Ex ib IIB T3 Gb

2.2. Sites and Conditions of Experimental Work

Sensor performance was evaluated at two sites: a local sewer manhole with variable hydrodynamic conditions and a sewer pilot plant with both controlled flow and pumping events. Both sites are located at the pumping station Neukölln II (Berlin, Germany), owned by the Berlin water utilities (Berliner Wasserbetriebe, Berlin, Germany).

2.2.1. Sewer Manhole

The manhole has a 90 cm diameter at the top which widens at a lower depth. It is 4.6 m deep and is connected to a gravity sewer leading to the pumping station Neukölln II (Figure S1). This sewer receives combined municipal wastewater from the surrounding district. During the experimental time, the pH ranged between 6.39 and 9.43 with a mean pH of 7.93 and the temperature between 10.91 and 19.08 °C with a mean value of 16.09 °C. Sensors were installed for a two-week period at two depths: 2.5 m and 0 m (just below the manhole cover). Due to refreshment recommendation of the sensors, two different OdaLogs® and other two MyDatasensH2S1000 BLE were used at each depth. As Sulfilogger™ does not require refreshment periods, only one sensor was used. All measurements were recorded at one-minute intervals. Before each experiment, OdaLog®

and Sulfilogger™ were manually calibrated on-site, while the MyDatasensH2S1000 BLE were calibrated once by the manufacturer before the experimental work.

2.2.2. Sewer Pilot Plant

The sewer pilot plant (Figure 1A) is fed with wastewater from the pumping station Neukölln II according to previously set pumping cycles (intermittent pumping). Typically, the pH at this site ranges between 6.5 and 8, with a median value of approximately 7.5. The water is transported into a pressure pipe and later on into a gravity pipe, where H_2S gas is released into the sewer atmosphere. The gravity pipe is set at a 1.18% slope and has two manholes for gas measurements. All sensors were installed together for four days in manhole B at 16 cm above the water level. Prior to the installation, the OdaLog® and the Sulfilogger™ were calibrated on-site, and all sensors were set to record at one-minute intervals.

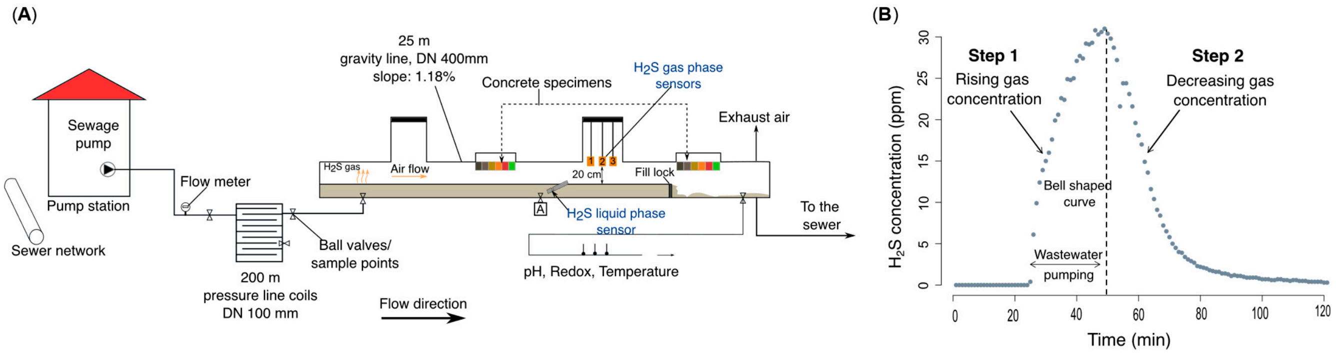

Figure 1. (**A**) Schematic layout of the sewer pilot plant located at the pumping station Neukölln II in Berlin, Germany. Owned by the Berlin water utilities (Berliner Wasserbetriebe). (**B**) Bell shaped horizontal H_2S gas transport in a sewer headspace.

2.2.3. H_2S Gas Development in Sewer Systems

Formation of H_2S in sewer systems occurs under anaerobic conditions. These conditions are usually present in pressure pipes and full-flowing gravity sewers; however, partially filled pipes as well as sewer structures with a free water surface may also be prone to H_2S emissions [2]. During a pumping event, the wastewater is transported from the pressure pipe into the gravity one, where the H_2S is released into the headspace of the pipe. According to Matos et al. 2019 [22], if ventilation is present, the horizontal H_2S gas transport follows a bell-shaped curved (Figure 1B) that can be explained in two steps. First, the gas concentration rises because H_2S is being formed and released due to the pumping event. Second, after the pumping event, the H_2S concentration decreases as it is being outgassed and flushed out through the ventilation system [22]. This concentration profile is also observed in the gas measurements carried out at the sewer pilot plant. Here, ventilation is forced by an air suction system to ensure the researchers' safety.

2.3. Control Test (Response Test)

To verify that all sensors were working correctly and that the recorded measurements were credible, a control or response test was made to evaluate their response when exposed to a known H_2S gas concentration (article number: 14431, Siegrist GmbH, Karlsruhe, Germany) and also to determine how close the measurements were to the known concentration. Often, this test is carried out by comparing the sensor measurements with a standard analysis such as gas chromatography (GC). However, this paper intends to propose practical procedures suitable for fieldwork. Therefore, a control test was made using a calibration gas with a given concentration. To perform the test, we attached a flow cell to the measuring point of the sensors and supplied a flow of H_2S calibration gas with a 50 ppm concentration (article number: 14431, Siegrist GmbH) for five minutes. Each test was carried out in a sealed chamber to ensure that sensors were exposed to similar conditions. Moreover, we performed the tests under ambient and extremely moist environments with relative humidity (RH) levels of 46% and >93%, respectively, and temperatures ranging between 26 and 28 °C. It is important to test the sensors under extreme conditions as those typical in sewer environments that may affect the sensors when wet, which could affect the readings as well [23]. To achieve and control the relative humidity above 90% in the chamber, we connected a continuous steam feed produced from a water bath (Figure S2). At the end of each test, we flushed the chamber, the flow cell and the sensor with air and allowed the sensor to refresh and stabilize before performing a subsequent test. RH and temperature in the chamber were continuously monitored during the test using a hygrometer (Inkbird IBS-TH1 Bluetooth Hygrometer/Thermometer, Inkbird, London, UK).

Sensors' performance was evaluated by determining the accuracy of the sensors during the control test. The accuracy is expressed as a percentage of the actual reading and is computed as the difference between the actual (50 ppm, calibration gas) and the measured value [24].

2.4. Statistical Analyses

Comparison of the sensors was assessed in two different ways. First, quality performance criteria were computed and, second, graphical analyses were carried out.

2.4.1. Data Overview and Handling

As the pilot plant is operated under controlled conditions and previously set pumping cycles, data were divided into two sets: gas transport and no transport. The first one includes both steps involved in the horizontal gas transport (Figure 1B): the H_2S build-up (step 1) when wastewater is pumped for 30 min, and the H_2S decrease (step 2) after the pumping event (30 min). The second data set includes the remaining measurements where there is no horizontal gas transport. This division allows the assessment and comparison under different conditions. Moreover, during this experiment, a zero offset was observed in the data recorded by the Sulfilogger™. This offset was corrected prior to the sensor comparison, and a detailed description of the correction procedure is provided in the Supplementary Materials.

In the manhole, the variable hydrodynamics conditions do not favour the division of the data into two sets, therefore this procedure was not carried out. Sensor data were smoothed with a centered rolling average using a five value window.

2.4.2. Quality Performance

Quality performance was evaluated by three different criteria: the root mean square error (RMSE), the mean absolute error (MAE) as well as the mean bias (MB), whose equations are presented in the Appendix A (Table A1). All criteria are computed by comparing sensor measurements with a reference. The oldest sensor used at this site is the OdaLog® and is considered as the reference device in this work. It must be noted that this is one of the standard sensors used in sewer applications and has been used worldwide in a large number of studies such as [9] (Canada), [8] (Denmark) and [25] (Australia).

- Root Mean Square Error (RMSE): Measures the average magnitude of the differences between the online sensor and the reference sensor [26]. Its optimum value is 0.0.
- Mean Absolute Error (MAE): Measures the mean of the absolute differences between the measurements of the reference sensor and the online sensor. It varies between 0.0 and a large positive value, with 0.0 being the optimum value.
- Mean Bias (MB): Is similar to the MAE, with the only difference being that the Mean Bias takes the direction of the differences into account. The optimal value of MB is also 0.0, meaning that both sensors measure on average equally. A positive value indicates an underestimation of the online sensor. On the contrary, a negative value means that the online sensor overestimates the measurements with respect to the reference sensor.

To evaluate the performance criteria, we defined a rating system based on practical experience (Table 2). According to this rating system, two sensors show no significant differences/are exchangeable if at least three of the criteria are rated good or better.

Table 2. Rating of the performance criteria.

	RMSE (ppm)	∣MAD∣ (ppm)	MB (ppm)	Graphical Analysis (Points within the 0–5 ppm Range) (%)
Very good	<3	<1	<1	100–85
Good	3–8	1–3	1–3	85–70
Satisfactory	8–15	3–5	3–5	70–66
Unsatisfactory	≥15	>5	>5	<66

2.4.3. Graphical Comparison—Difference Plot with Respect to the Line of Equality

In this work, we propose a graphical method to easily analyze and compare the measurements of two H_2S gas sensors. The method is a simplified difference plot (Figure 2B) based on the one proposed by Bland and Altman 1999 [27] (Figure 2A). In this plot, the sensor differences (Reference Sensor-Online Sensor, y-axis) are plotted over the experimental time (x-axis). As stated before, the OdaLog® is used as the reference sensor. The main advantage of this new plot is that it does not require a normal distribution of the differences since the limits of agreement are not calculated based on the data distribution. Moreover, plotting the data over the time series eases the visualization of the differences and also accounts for changes and robustness of the methods over time.

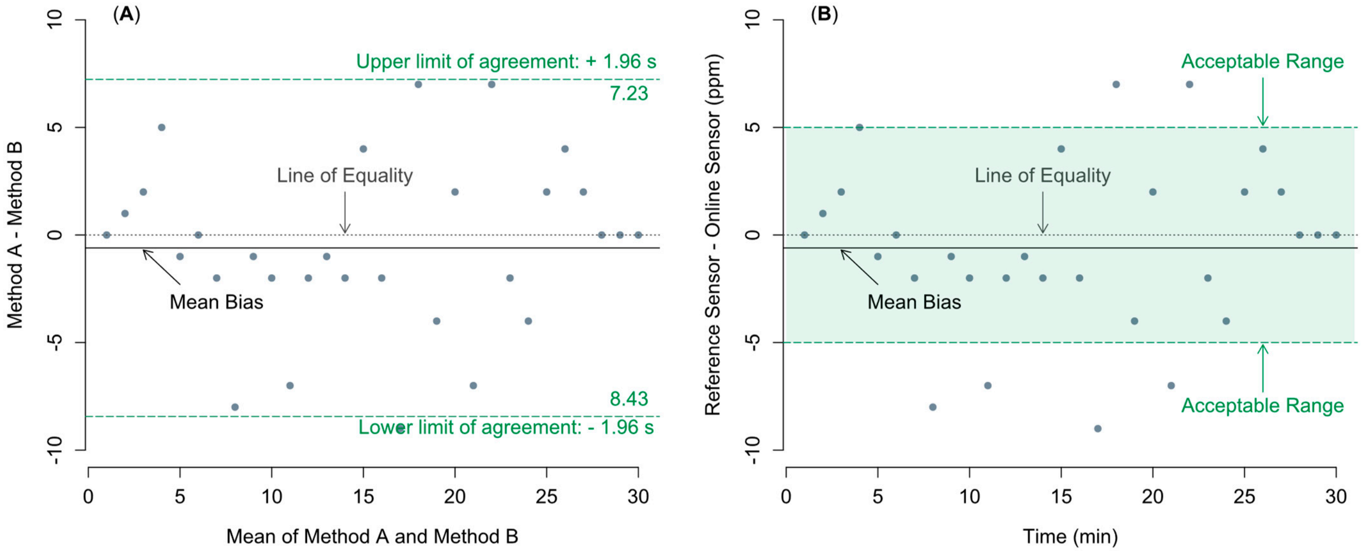

Figure 2. A comparison: (**A**) Bland–Altman plot with limits of agreement; (**B**) Simplified difference plot with acceptable range.

3. Results and Discussion

3.1. Sewer Manhole

Figure 3 shows the computed difference plots of the gas measurements recorded at the sewer manhole. Plots (A)–(B) present the results obtained at 2.5 m depth, and plots (C)–(D) those at 0 m, below the manhole cover. Gas concentrations measured at this site were relatively low, which might be attributed to the high pH levels (mean 7.93) observed.

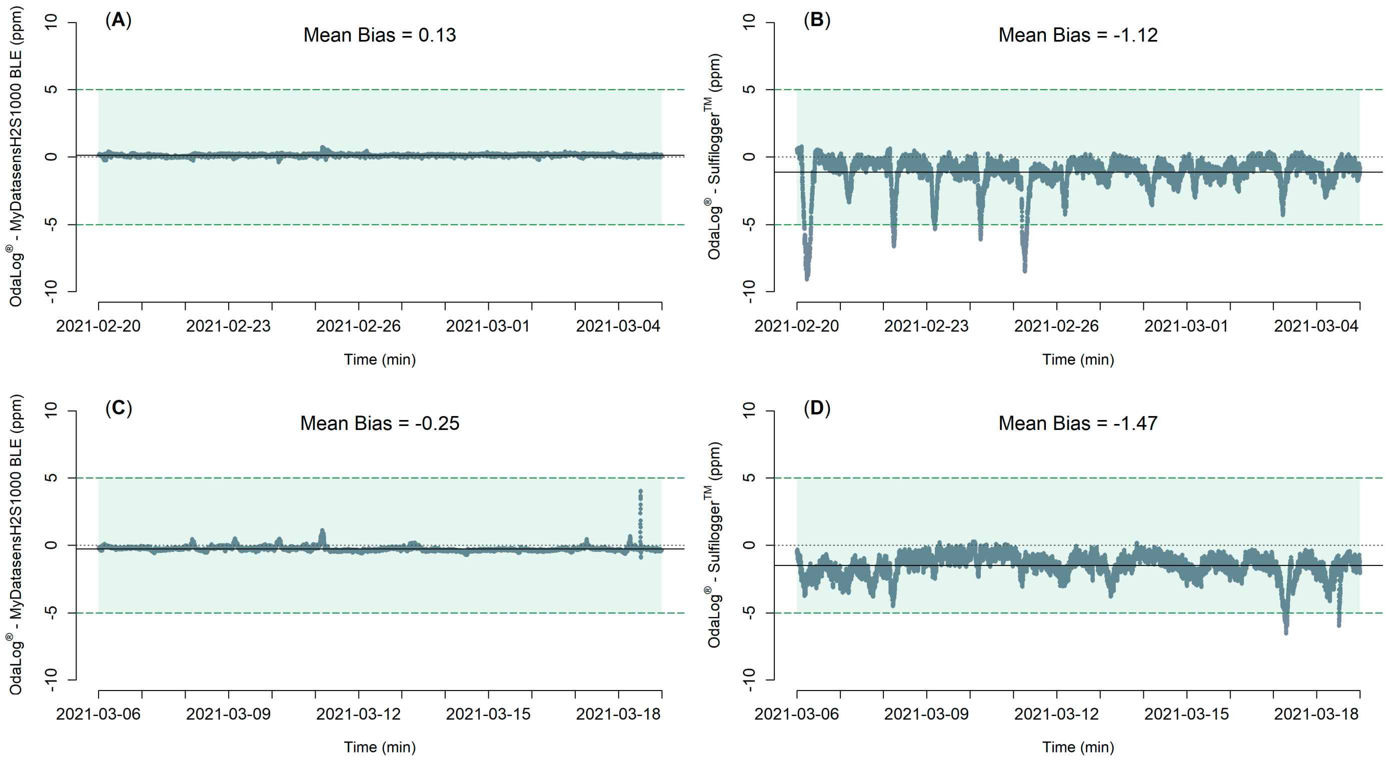

Figure 3. Difference plots (reference—online sensor) computed with the measurements recorded at the sewer manhole at 2.5 m (**A**,**B**) and at 0 m (**C**,**D**) below the manhole cover.

First, the results at 2.5 m depth are analyzed. At this depth, the average H_2S concentration was 1.2 ppm and the maximum 7 ppm, with the air temperature ranging between 11.10 and 14.90 °C. The plots show the difference between the measurements recorded by the reference (OdaLog®) and the online sensors MyDatasensH2SBLE 1000 (Figure 3A) and Sulfilogger™ (Figure 3B). MyDatasensH2SBLE 1000 shows the closest agreement with the reference sensor, 99.95% of the measuring points lie within the acceptable range, the mean bias being 0.13 ppm. Sulfilogger™ measurements are also in good agreement with the reference sensor; however, Sulfilogger™ tends to underestimate the H_2S concentration (mean bias—1.12 ppm). The difference plot also reveals a fluctuating pattern caused probably by intermittent pumping events, where differences increase during H_2S concentration peaks and may lie outside the acceptable range (±5 ppm). At 2.5 m depth, the sensor performance could have been affected by a higher humidity level, as the relative humidity increases with depth [22]. Nevertheless, Sulfilogger performed rather well evene below its detection limit (1% of full range, 0–1000 ppm) [18].

According to the presented criteria Table 1, the MyDatasensH2SBLE 1000 sensor performs very well in all categories, while the Sulfilogger™ is rated as very good in the RMSE (1.69 ppm) and graphical analysis (96.76%), and as good in the remaining ones. According to this rating system, when two sensors show no significant differences in at least three of the criteria, rating good or better, they are exchangeable. In this case, both sensors meet the above criteria, so they are exchangeable with the reference one.

Second, the performance of the sensors just below the manhole cover (0 m) is described. Here, the measured H_2S concentration was on average 0.77 ppm with a maximum of 32 ppm, and the air temperature ranged between 8.46 and 14.30 °C. Both online sensors present behaviours similar to those observed at the previous depth. In this case, the mean bias for MyDatasensH$_2$SBLE 1000 is −0.25 ppm and for Sulfilogger™ −1.47 ppm, indicating that both sensors tend to underestimation. Two possible explanations for this behaviour are: (a) the sensors are located directly underneath the ground surface and can be influenced by open-air conditions; (b) in cold weather, H_2S tends to accumulate at the deepest manhole point due to its higher density [28].

Regarding the difference points, at least 98% lie within the acceptable range for both sensors. As in the previous case, both sensors can be exchanged with the reference one, as both are rated as good or better in at least three of the criteria (Table 3).

Table 3. Performance criteria computed with the sensor measurements at the sewer manhole at 2.5 and 0 m above the water level.

	2.5 m				**0 m**			
	RMSE (ppm)	**∣MAD∣ (ppm)**	**MB (ppm)**	**Graph. Analysis (%)**	**RMSE (ppm)**	**∣MAD∣ (ppm)**	**MB (ppm)**	**Graph. Analysis (%)**
OdaLog®-MyDatasensH2SBLE 1000	0.16	0.14	0.13	99.95	0.31	0.28	−0.25	99.95
OdaLog®-Sulfilogger™	1.69	1.14	−1.12	96.76	1.70	1.48	−1.47	98.15

3.2. Sewer Pilot Plant

H_2S concentrations measured at the sewer manhole ranged between 0 and 10 ppm, indicating low exposure to H_2S. Therefore, to test the sensors' performance at higher concentrations, they were installed for four days in the gravity pipe of the sewer pilot plant. At this site, the H_2S concentration can be partially controlled by previously set pumping cycles, which are used to regulate the wastewater residence time in the system, a key parameter for H_2S generation. During this control experiment, the H_2S concentration in the gas phase ranged between 0–146 ppm and the temperature between 11.4–17.8 °C. Figure 4 shows the measurements recorded by the sensors. All sensors were able to correctly identify the periods where gas transport was taking place (concentration peaks) and those where there was no transport (flat lines).

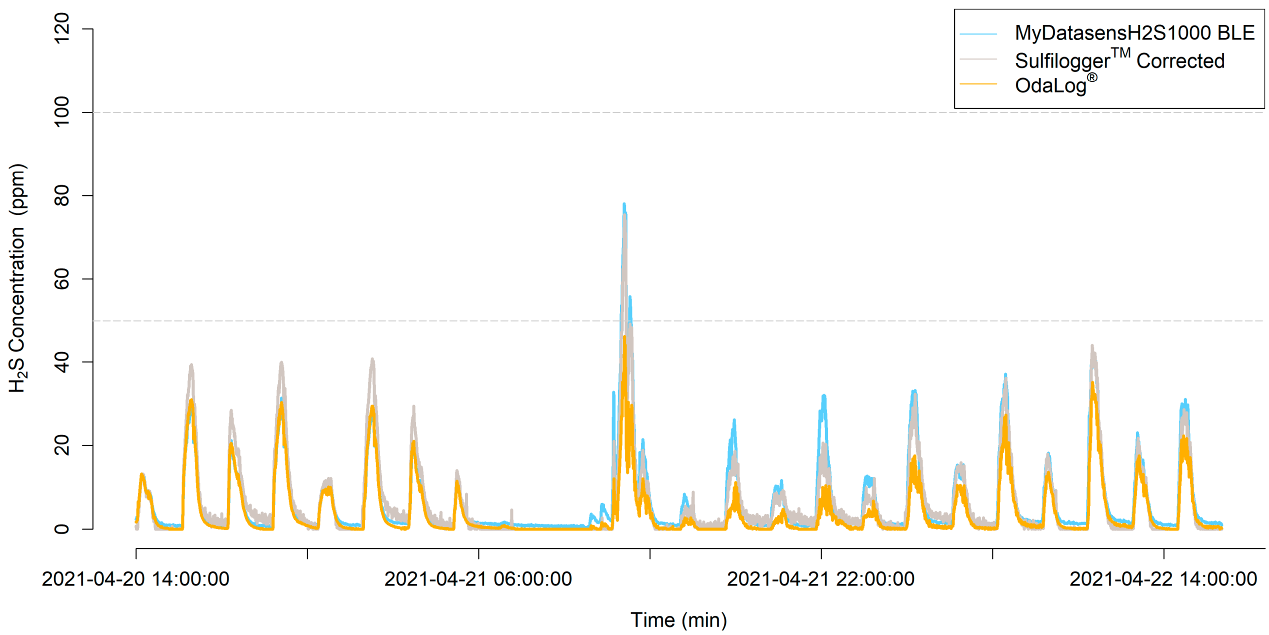

Figure 4. Two-day H_2S gas measurements recorded at the sewer pilot plant between 21–22 April 2021.

In addition, it can be observed that the Sulfilogger^{TM} had a zero offset throughout the experiment, which was corrected later on during the data analysis as described in the Supplementary Materials. The zero offset prevented the sensor from measuring zero even when there was no H_2S in the gravity pipe and this decreased over time. Possible causes for this could be: (a) blockage of the sensor by sanitary solids that accumulated at the measuring tip for an extensive period (at least 3 days) during previous liquid phase monitoring studies; (b) Although not stated by the manufacturer, the possible missing refreshment period before changing phases could explain the decreasing offset as an indication of a sensor adjustment to the new environment. After correction of the data, the Sulfilogger^{TM} measurements show a good agreement with those from the OdaLog® and the MyDatasensH2S1000 BLE sensor. The results presented here were computed using the corrected values.

To evaluate the performance of the sensors, difference plots (Figure 5) and criteria (Table 4) were computed as in the previous site. Furthermore, the sensor's response was evaluated under two different conditions (gas transport and no transport) as both are present in sewer systems and need to be jointly monitored.

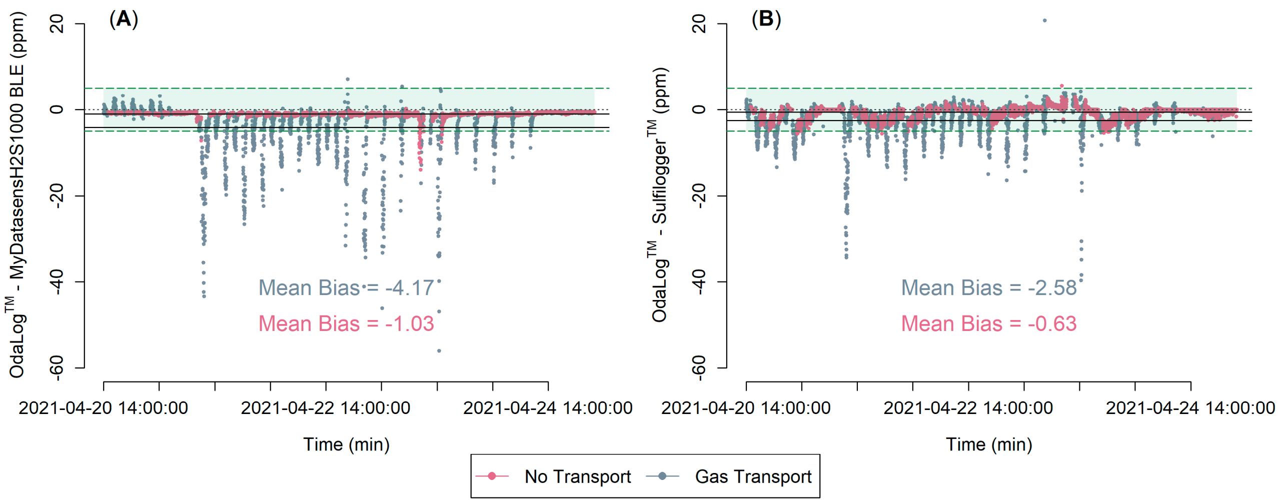

Figure 5. Difference plots computed with the H2S gas measurements from the sewer pilot plant. (**A**) OdaLog®-MyDatasensH2S1000 BLE. (**B**) OdaLog®-Sulfilogger^{TM}.

Table 4. Performance criteria computed with the sensor measurements at the sewer manhole.

	Gas Transport				No Transport			
	RMSE (ppm)	**∣MAD∣ (ppm)**	**MB (ppm)**	**Graph. Analysis (%)**	**RMSE (ppm)**	**∣MAD∣ (ppm)**	**MB (ppm)**	**Graph. Analysis (%)**
OdaLog®-MyDatasensH2S	8.29	4.29	−4.17	75.98	1.21	1.03	−1.03	99.51
OdaLog®-SulfiLogger^{TM} Corrected	4.88	2.93	−2.58	81.29	1.45	0.95	−0.63	99.56

Starting with "no transport" conditions, Figure 5A,B show that over 99% of the measured differences for both online sensors are within the acceptable range (0 ± 5 ppm). MyDatasensH2S1000 BLE (Figure 5A) overestimates the H_2S measurements constantly with a mean bias of −1.03 ppm, while the Sulfilogger^{TM} (Figure 5B) shows a fluctuating pattern with a mean bias of −0.63 ppm.

Second, the computed differences are larger for both sensors under gas transport conditions than in the no transport case. This behaviour appears at higher H_2S concentrations, where both sensors overestimate the gas concentration with respect to the reference one (OdaLog™). Under these conditions, Sulfilogger^{TM} also shows a better agreement with the reference (MB = −2.58 ppm) than MyDatasensH2S1000 BLE (MB = −4.17 ppm).

Third, Table 4provides an overview of the computed results for the performance criteria. According to the ranking system, two sensors are exchangeable if at least three criteria are rated good or better. On the one hand, the OdaLog® can be exchanged for the SulfiLogger^{TM}, since all criteria are rated good or very good during both gas transport and no transport conditions. On the other hand, MyDatasensH2S1000 BLE does not meet these criteria for gas transport conditions, as only the graphical analysis is rated as good, while the remaining criteria are rated as unsatisfactory. This might be attributed to the fact that this sensor could not be calibrated on-site because only the manufacturer is allowed to perform callibrations. Under the no transport conditions, the results are in agreement with those from the sewer manhole, where H_2S concentrations were lower. Therefore, MyDatasensH2S1000 BLE would only be suitable for interchange in sites where low H_2S emissions are expected.

At this site, Sulfilogger^{TM} shows the closest agreement with the reference sensor. Nevertheless, it should be noted that the SulfiLogger^{TM} measurements were corrected previously because of the zero offset.

Last, we evaluated the mean absolute error (Figure 6A) as well as the percentage of points within the previously defined acceptable range (Figure 6B) at different H_2S concentration levels. At lower concentrations (0–10 ppm), the agreement between online sensors and reference sensor is good for the MAE, with both values below 2 ppm, and very good for the graphical analysis, with over 95% of the measured differences within the ±5 ppm range. As the H_2S concentration rises, the agreement between the sensors decreases. For higher concentrations (10–20 ppm), the agreement between the sensors is already considered unacceptable for both criteria. At a concentration higher than 50 ppm, the mean absolute error for MyDatasensH2S1000 BLE is 34.03 ppm, which is twice as high as the one for SulfiLogger^{TM} (15.37 ppm). In addition, the percentage of measured differences within the acceptable range is 4% for MyDatasensH2SBLE 1000 and 21% for SulfiLogger^{TM}. According to these results, an exchange between reference and online sensors is only recommended in the lower range (0–10 ppm).

These results highlight the need to evaluate each sensor's performance at different concentration levels. High accuracy and a close agreement between sensors are crucial in the lower range to comply with the occupational health and safety exposure limit values (10 ppm, 8 h exposure) and to minimize fatalities [6]. Furthermore, a low accuracy in the higher H_2S concentration range can lead to an erroneous strategy for odour and corrosion mitigation plans. For example, it can lead to chemicals overdosing for H_2S control when the overestimated H_2S measurements recorded by the sensor are accepted.

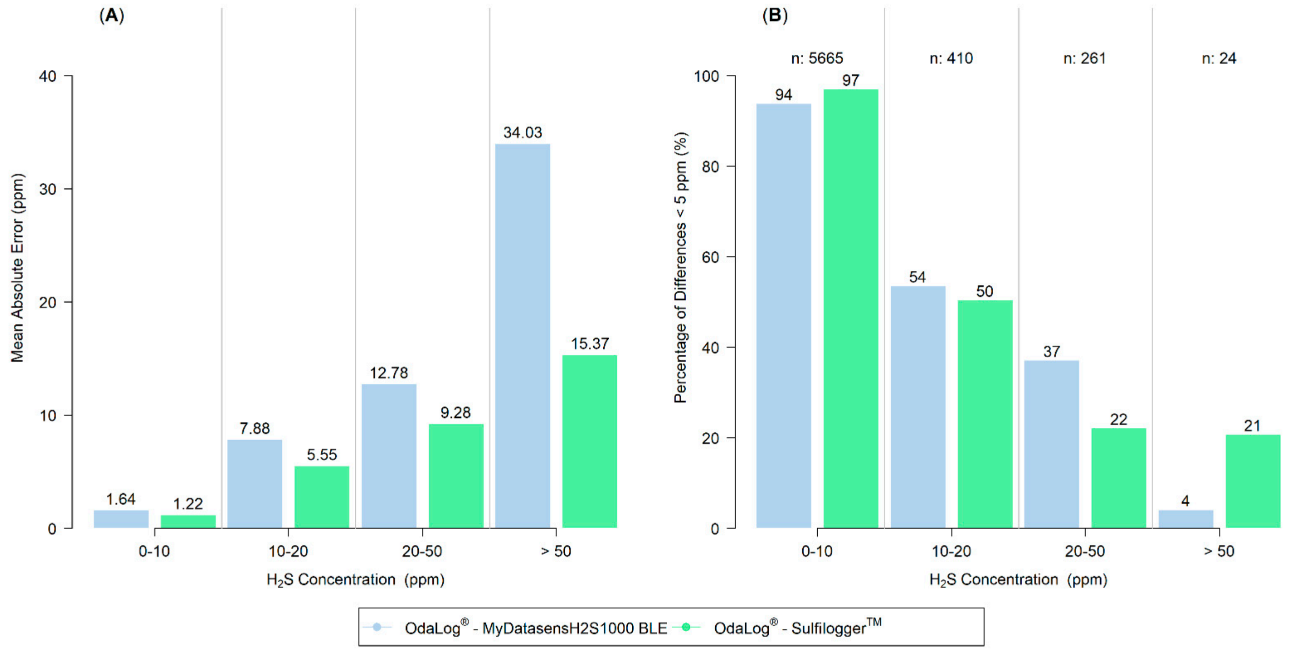

Figure 6. Distribution of the mean absolute error (**A**) and of the percentage differences within the acceptable range (**B**) according to different concentration levels.

3.3. Control Test Results

Figure 7A shows the sensors control test curves at a 50 ppm H_2S concentration and a relative humidity of ~46% (ambient conditions). This concentration was supplied by a calibration gas (article number: 14431, Siegrist GmbH, Karlsruhe, Germany) and is used in this test as the actual value. This concentration was chosen as the measured H_2S concentrations in this study were mostly in the lower and medium range. According to the figure, all sensors, with exception of the SulfiLogger™, reached a nearly constant concentration after three minutes. The final results (5 min) reveal that SulfiLogger™ had the lowest bias (0.1 ppm) with respect to the known gas concentration (50 ppm) and, therefore, also the best accuracy (0.18%). Moreover, it can be observed that the SulfiLogger's control test curve does not start near zero—this might have been caused by some remaining H_2S gas in the flow cell. OdaLog® sensors over- and underestimated the known concentration with a mean bias of 1.9 ppm and an average accuracy of 3.8%. Both MyDatasensH2S1000 BLE sensors showed the same behaviour, underestimating the H_2S concentration with a mean bias of 7.1 ppm and an average accuracy of 14.16%. The computed accuracy values for OdaLog® and SulfiLogger™ are in agreement with those stated by their manufacturers: 5% of full range [17] and 1% of actual value [18], respectively. Regarding the MyDatasensH2S1000 BLE sensors, the observed accuracy is lower than that described by the manufacturer (1% of signal, [19]). This observation can be explained by the fact that these sensors were not calibrated before the control test since this can only be carried out by the manufacturer or a service partner.

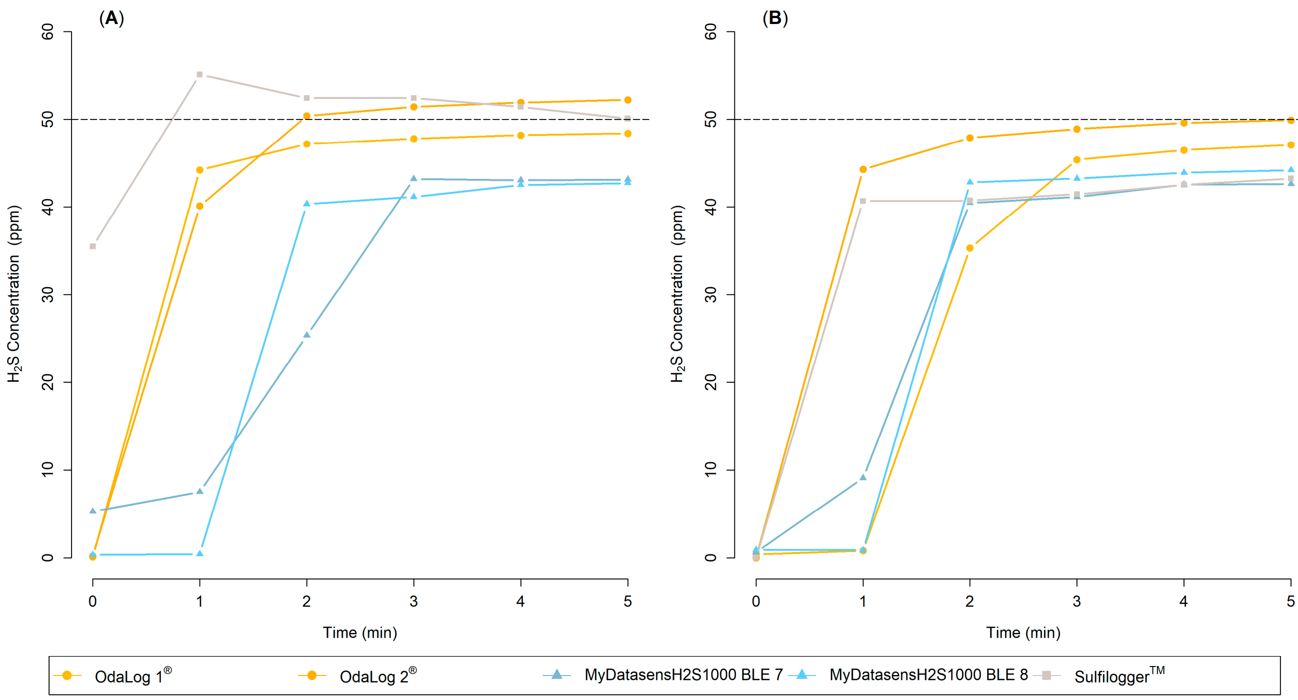

Figure 7. Control test of the sensors using a 50 ppm H2S concentration gas under different conditions: (**A**) relative humidity ~46% and (**B**) relative humidity >90%.

Moreover, poorly ventilated sewer systems are known to be humid environments (RH 80–100%), which can affect the sensor measurements and their accuracy [10]. Therefore, a second control test (50 ppm) was carried out under extreme humid conditions (RH > 90%). Figure 7B shows the control test curves under these conditions. In this case, the sensors were prone to underestimation. Four out of five sensors maintained or improved their response during the short term exposure. OdaLog® sensors were measured with the lowest mean bias (1.5 ppm) and the highest mean accuracy (3%), indicating a slightly improved performance. A similar behavior was observed by MyDatasensH2S1000 BLE, which also showed a slight improvement in the computed mean bias (6.58 ppm) and accuracy (13.16%). These results indicate that the performance of both sensors is not affected by short term exposure to extreme humid conditions.

On the contrary, SulfiLogger™ performed as well as MyDatasensH2S1000 BLE; however, its performance was affected by the high relative humidity, with an increase of the mean bias of 6.65 ppm and a decrease in the accuracy of 12.98%. According to the manufacturer, this sensor should operate for long time periods under a 100% RH as it is designed to be submerged in the liquid phase as well. Nevertheless, this behavior could not be verified in the short term exposure of the control test.

As a final observation, this control test only shows results for a short term exposure. According to Thermo Fisher Scientific Australia Pty Ltd. [17], continuous exposure to high humidity levels may lead to their sensor picking up water or leaking acid. Therefore, before their installation in extreme humid environments, long term exposure of the sensors to these conditions should be evaluated. Should this be the case, the robustness of the sensor can be improved by increasing the sensor's surface temperature, as proposed by Liu et al. [10].

3.4. Challenges, Advantages and Disadvantages of the H_2S Gas Sensors

Compared to H_2S liquid phase sensors, fewer challenges are related to the use and maintenance of gas phase sensors as they are naturally prevented from clogging and fouling as well as from the accumulation of grease and/or sanitary solids that occur in the wastewater (liquid phase) [13]. However, some sensor-specific challenges were observed during this work.

When using the SulfiLogger™ at the sewer pilot plant, a zero offset was observed in the recorded measurements. Based on our experience using the sensor for liquid phase monitoring before this study was undertaken, we presume that the offset could have been caused by changing the sensor from the liquid into the gas phase without a refreshing time. Moreover, long-term measurements in the liquid phase could have also affected the sensor measurements due to clogging, the accumulation of sanitary solids, and/or grease at the tip of the sensor [13]. To correct this problem, a zero calibration is required and recommended before installing the sensor in the gas phase. Moreover, during the experimental period, the data transmission to the server usually suffered from delays and needed to be manually activated on-site. However, the manufacturer claims that this problem has been already solved.

Regarding the OdaLog®, it is a data logger and, therefore, real-time connectivity is missing. The sensor requires regular refreshment periods and maintenance by a practitioner, who downloads the data manually on-site. Consequently, it cannot be used for early warning systems nor online monitoring. However, an online version of this sensor is also available (OdaLog® RTx).

The major challenge when measuring with the MyDatasensH2S1000 BLE sensor is that it cannot be calibrated on-site by a practitioner, only by the manufacturer. This missing feature does not allow users to check the performance and accuracy of the sensor before being installed. In addition, should the sensor not be working correctly, it could not be calibrated on-site to assess the problem.

Furthermore, all sensors evaluated in this work also share some main advantages: they are portable, ATEX proofed, provide continuous measurements, and do not require chemical agents. However, each sensor also has its disadvantages. Therefore, to help practitioners and researchers on the field, a summary table with the observed advantages and disadvantages of the sensors is provided in Table 5.

Table 5. Advantages and disadvantages of the gas phase H_2S sensors used in the study.

	Advantages	Disadvantages
OdaLog® Logger L2	• Easy calibration • Easy installation • Battery Life (>6 months)	• No online access to data • Regular refreshment periods are recommended • Database required for long-term monitoring and data visualization (only shows data for given measured period)
SulfiLogger™	• Gas and liquid phase measurements • Easy calibration • High measuring range 0–1000 ppm	• Additional installation accessories (Sensor + Power Combox) required • Battery life (~3 months, 6 h transmission rate) without power supply • During this experiment, delayed data transmission to server • During this experiment, offset when changing phases (liquid to gas)
MyDatasensH2S1000 BLE	• Easy installation • Reliable data transmission to server • Battery Life ~3 years	• Calibration only by the manufacturer • Refreshment periods are recommended when measuring at high concentrations • Decreasing accuracy when the sensor is not calibrated regularly

Finally, from an economic point of view, the OdaLog® is the cheapest sensor (EUR ~1800), followed by MyDatasensH2S1000 BLE at a total price of EUR ~4300 including maintenance service. The SulfiLogger™ is the most expensive one with an estimated overall price of EUR 6000 including installation accessories.

3.5. Flowchart

The results presented in this paper show that there can be significant differences between the measurements of two different H_2S gas sensors. Nevertheless, for sewer and air quality management, an exchange and/or rotation of sensors is required. Especially if the employed sensors need refreshment periods or if only a limited number of sensors is available. If any of these cases occur, a management plan for sensor rotation/exchange should be established. To ensure high quality and accurate measurements within the management plan, measurement differences between sensors need to be evaluated previously. Therefore, we propose an on-field procedure in the form of a decision-making chart (Figure 8) for comparing gas sensors and assessing whether and when they should be rotated/exchanged.

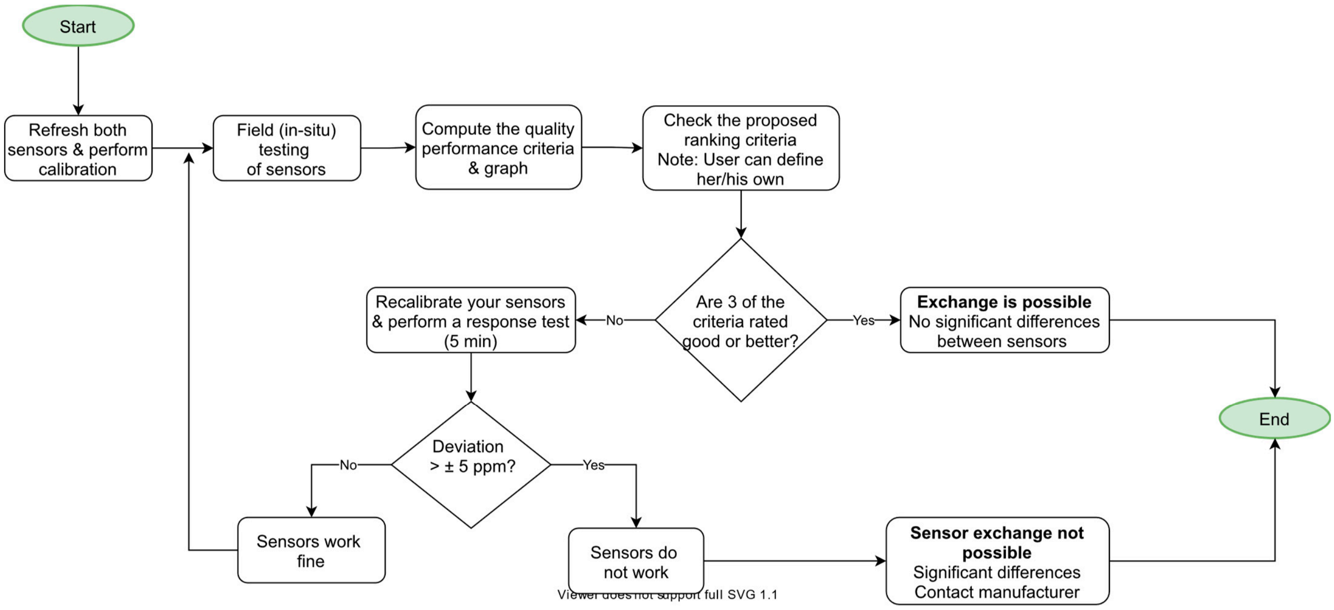

Figure 8. Decision-making chart for evaluating if an exchange of sensors is possible without significant differences.

The decision-making chart is designed to help practitioners on-site to easily and quickly assess if an exchange/rotation of sensors is possible. The key points in the chart are: calibration of the sensors, in situ testing, as well as computing and checking the quality performance criteria.

For future investments, if more than two sensors are being compared, a ranking system can be established to assess which sensor is best suited for the studied application. For this work, we proposed a ranking system based on three main categories: mode of operation, reliability and economic aspect. More information on the ranking system as well as on its results is provided in the Supplementary Materials.

4. Conclusions

The two main objectives of this work were to compare the performance of three H_2S commercial sensors for air quality monitoring in sewer systems and to assess whether they can be rotated/exchanged without showing significant differences in the measurements.

Regarding the first objective, the comparison displayed that all sensors have advantages and disadvantages. The SulfiLogger™ showed the best accuracy (0.18%) during the control test under normal conditions; however, its accuracy decreased (13.52%) under extremely humid conditions (RH > 90%). On the other hand, the OdaLog® performed better with a high humidity level (3% accuracy) than under normal conditions (3.8%). MyDatasensH2S1000 BLE had a similar behavior, although it performed the worst with an average accuracy of 14.18% under normal conditions.

Concerning the second objective, the experimental results confirm that measurement differences between sensors do exist and that they are dependent on the H_2S concentration level. Deviation between sensors increases as the H_2S concentration rises. Under no transport conditions as well as under low concentrations (0–10 ppm) the OdaLog® sensor is exchangeable with both SulfiLogger™ and MyDatasensH2S1000 BLE. However, under gas transport conditions as well as with high H_2S concentrations, an exchange without significant differences is only possible with the SulfiLogger™.

We also propose that sensor exchange, when necessary according to the H_2S concentration, would be the result of our designed decision making tool shown in Figure 8.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/su131910779/s1, Figure S1: Installation of the sensors in the manhole used for comparing the sensors; Figure S2: Set-up of the control test; Table S1: List and description of the performance indicators; Table S2: Example of the sensor ranking according to the results from the performance indicators; Table S3: Sensor ranking based on the performance indicators described in Table S2.

Author Contributions: M.P.F., conceived and designed the experiments; M.P.F. and D.D. performed the experiments; M.P.F. performed data analysis and visualization; M.P.F. and D.D. wrote the draft paper; M.P.F. finalized the paper; all authors edited and revised the paper; M.B. supervised the project. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study is available upon request from the corresponding author.

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Appendix A

Table A1. Criteria used for evaluating the sensors' performance. n is the sample size, RM is the H_2S measurement of the reference sensor in (ppm), M is the H_2S measurement of the online sensor in (ppm).

Criteria	Short Name	Formula
Root Mean Square Error	RMSE	$=\sqrt{\frac{1}{n}\sum_{i=1}^{n}(RM-M)^2}$
Mean Absolute Error	MAE	$=\frac{1}{n}\sum_{i=1}^{n}\lvert RM-M\rvert$
Mean Bias	MB	$=\frac{1}{n}\sum_{i=1}^{n}(RM-M)$

References

1. United States Environmental Protection Agency. Design: ManualOdor and Corrosion Control in Sanitary Sewarage Systems and Treatment Plants, pub. 10.1985; Last Revised November, 2017. Available online: https://nepis.epa.gov/Exe/ZyPDF.cgi/300045C6.PDF?Dockey=300045C6.PDF (accessed on 2 July 2021).
2. Hvitved-Jacobsen, T.; Vollertsen, J.; Nielsen, A.H. *Sewer Processes: Microbial and Chemical Process Engineering of Sewer Networks*; CRC Press: Boca Raton, FL, USA, 2001; pp. 65–129. ISBN 978-1-4200-1266-8.

3. Matias, N.; Matos, R.V.; Ferreira, F.; Vollertsen, J.; Matos, J. Release of hydrogen sulfide in a sewer system under intermittent flow conditions: The Ericeira case study, in Portugal. *Water Sci. Technol.* **2017**, *75*, 1702–1711. [CrossRef] [PubMed]
4. United States Environmental Protection Agency. Hydrogen Sulfide, Report by the Subcommittee on Hydrogen Sulfide, Committee on Medical, Biological Effects on Environmental Pollutants, National Research Council, pub. 02.1978. Available online: https://nepis.epa.gov/Exe/ZyPDF.cgi/9100B2YD.PDF?Dockey=9100B2YD.PDF (accessed on 28 July 2021).
5. *Commission Directive 2009/161/EU of 17 December 2009. Establishing a Third List of Indicative Occupational Exposure Limit Values in Implementation of Council Directive 98/24/EC and Amending Commission Directive 2000/39/ECText with EEA Relevance*; Official Journal of the European Union; European Union: Maastricht, The Netherlands, 2009; p. 3.
6. Ali, F.I.M.; Awwad, F.; Greish, Y.E.; Mahmoud, S.T. Hydrogen Sulfide (H2S) Gas Sensor: A Review. *IEEE Sens. J.* **2019**, *19*, 2394–2407. [CrossRef]
7. Jiang, G.; Sun, J.; Sharma, K.; Yuan, Z. Corrosion and odor management in sewer systems. *Curr. Opin. Biotechnol.* **2015**, *33*, 192–197. [CrossRef] [PubMed]
8. Vollertsen, J.; Nielsen, A.H.; Jensen, H.S.; Wium-Andersen, T.; Hvitved-Jacobsen, T. Corrosion of concrete sewers—The kinetics of hydrogen sulfide oxidation. *Sci. Total. Environ.* **2008**, *394*, 162–170. [CrossRef] [PubMed]
9. Guo, S.; Qian, Y.; Zhu, D.Z.; Zhang, W.; Edwini-Bonsu, S. Effects of Drop Structures and Pump Station on Sewer Air Pressure and Hydrogen Sulfide: Field Investigation. *J. Environ. Eng.* **2018**, *144*, 04018011. [CrossRef]
10. Liu, Y.; Sharma, K.; Murthy, S.; Johnson, I.; Evans, T.; Yuan, Z. On-line monitoring of methane in sewer air. *Sci. Rep.* **2014**, *4*, 6637. [CrossRef] [PubMed]
11. Pandey, S.K.; Kim, K.-H.; Tang, K.-T. A review of sensor-based methods for monitoring hydrogen sulfide. *TrAC Trends Anal. Chem.* **2012**, *32*, 87–99. [CrossRef]
12. Calibrating and Testing Direct-Reading Portable Gas Monitors | Occupational Safety and Health Administration. Available online: https://www.osha.gov/publications/shib093013 (accessed on 10 September 2021).
13. Despot, D.; Fernández, M.P.; Barjenbruch, M. Comparison of Online Sensors for Liquid Phase Hydrogen Sulphide Monitoring in Sewer Systems. *Water* **2021**, *13*, 1876. [CrossRef]
14. Wagh, M.; Patil, L.; Seth, T.; Amalnerkar, D. Surface cupricated SnO2–ZnO thick films as a H2S gas sensor. *Mater. Chem. Phys.* **2004**, *84*, 228–233. [CrossRef]
15. Jain, G.; Patil, L.; Wagh, M.; Patil, D.; Amalnerkar, D. Surface modified BaTiO3 thick film resistors as H2S gas sensors. *Sens. Actuators B Chem.* **2006**, *117*, 159–165. [CrossRef]
16. Mirzaei, A.; Kim, S.S.; Kim, H.W. Resistance-based H2S gas sensors using metal oxide nanostructures: A review of recent advances. *J. Hazard. Mater.* **2018**, *357*, 314–331. [CrossRef] [PubMed]
17. Hermo Fisher Scientific Australia Pty Ltd. Odalog Gas L2 Logger Manual Thermo Fisher Scientific Australia Pty Ltd. 2018. Available online: https://assets.thermofisher.com/TFS-Assets/ANZ/manuals/odalog-gas-l2-logger-manual.pdf (accessed on 17 June 2021).
18. SulfiloggerA/S. SulfiLoggerTM User Manual; Sulfilogger A/S. 2020. Available online: https://sulfilogger.com/wp-content/uploads/2020/09/SulfiLogger_Manual_EN_204.pdf (accessed on 17 June 2021).
19. Microtronics Engineering GmbH. User Manual MyDatasensH2S1000 BLE; Microtronics Engineering GmbH. 2017. Available online: https://support.microtronics.com/manuals/myDatasensH2S1000_BLE_ATEX_Zone1_Manual_en.pdf (accessed on 17 June 2021).
20. City Technology Engineering Safety. Product Datasheet 7H Hydrogen Sulfide Sensor. City Technology Engineering Safety. 2017. Available online: https://support.microtronics.com/datasheet/7H_CiTiceL_Datasheet_en.pdf (accessed on 20 August 2021).
21. Madsen, P.S. PowerCom Box. Available online: https://sulfilogger.com/powercom-box/ (accessed on 2 August 2021).
22. Matos, R.V.; Ferreira, F.; Gil, C.; Matos, J.S. Understanding the effect of ventilation, intermittent pumping and seasonality in hydrogen sulfide and methane concentrations in a coastal sewerage system. *Environ. Sci. Pollut. Res.* **2018**, *26*, 3404–3414. [CrossRef] [PubMed]
23. Alwis, L.S.M.; Bustamante, H.; Roth, B.; Bremer, K.; Sun, T.; Grattan, K. Evaluation of the Durability and Performance of FBG-Based Sensors for Monitoring Moisture in an Aggressive Gaseous Waste Sewer Environment. *J. Light. Technol.* **2016**, *35*, 3380–3386. [CrossRef]
24. Mukhopadhyay, S.C. *Intelligent Sensing, Instrumentation and Measurements*; Springer Science and Business Media LLC: Berlin/Heidelberg, Germany, 2013; p. 23.
25. Sun, X.; Jiang, G.; Bond, P.L.; Keller, J.; Yuan, Z. A novel and simple treatment for control of sulfide induced sewer concrete corrosion using free nitrous acid. *Water Res.* **2015**, *70*, 279–287. [CrossRef] [PubMed]
26. Brito, R.S.; Pinheiro, H.; Ferreira, F.; Matos, J.; Lourenco, N. In situUV-Vis spectroscopy to estimate COD and TSS in wastewater drainage systems. *Urban Water J.* **2013**, *11*, 261–273. [CrossRef]
27. Bland, J.M.; Altman, D.G. Measuring agreement in method comparison studies. *Stat. Methods Med Res.* **1999**, *8*, 135–160. [CrossRef] [PubMed]
28. Occupational Safety and Health Branch, Labour Department. Prevention of Gas Poisoning in Drainage Work. Occupational Safety and Health Branch. 2007. Available online: https://www.labour.gov.hk/eng/public/oh/Drainage.pdf (accessed on 11 August 2021).