

Emission of hydrogen sulfide (H₂S) at a waterfall in a sewer: study of main factors affecting H₂S emission and modeling approaches

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ABSTRACT

Hydrogen sulfide (H₂S) represents one of the main odorant gases emitted from sewer networks. A mathematical model can be a fast and low-cost tool for estimating its emission. This study investigates two approaches to modeling H₂S gas transfer at a waterfall in a discharge manhole. The first approach is based on an adaptation of oxygen models for H₂S emission at a waterfall and the second consists of a new model. An experimental set-up and a statistical data analysis allowed the main factors affecting H₂S emission to be studied. A new model of the emission kinetics was developed using linear regression and taking into account H₂S liquid concentration, waterfall height and fluid velocity at the outlet pipe of a rising main. Its prediction interval was estimated by the residual standard deviation (15.6%) up to a rate of 2.3 g H₂S·h⁻¹. Finally, data coming from four sampling campaigns on sewer networks were used to perform simulations and compare predictions of all developed models.

Key words | emission kinetics, hydrogen sulfide, model, sewer, waterfall

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INTRODUCTION

Hydrogen sulfide (H₂S) is well known to cause harmful effects such as sewer corrosion, odor nuisance and death hazards for people in charge of sewer network maintenance. Hydrogen sulfide originates primarily from anaerobic microbial sulfate respiration in slimes and sediments. It is frequently found in sewer sections where reaeration and ventilation are insufficient or even absent, i.e. in low-slope gravity sewers or in rising mains. In sewer networks, H₂S concerns are today on a constant rise as the current trend is for the building of increasingly large wastewater treatment plants. Therefore wastewater is collected in increasingly extensive sewer networks and water dwells more and more in septic conditions which are favorable to sulfate reduction and sulfide production.

Nowadays, the optimization of sewer design is investigated using many numerical tools including models that are required to identify hotspots of H₂S emission. There

are a number of biochemical models to describe changes in organic matter and sulfide transformation (Yongsiri *et al.* 2003; Lahav *et al.* 2006; Sharma *et al.* 2008). However, we have observed a lack of models for hydrogen sulfide release at a drop structure despite the H₂S emission rate being significant due to the high turbulence occurring at waterfalls. The present study investigates how to model H₂S emission kinetics at a waterfall in order to add a sub-routine onto an ASM- (Activated Sludge Model) based model (like WATS or SeweX models) and to complete the modeling for H₂S release under these special turbulent locations of a sewer network.

This paper has two objectives: (i) development of a regression model of H₂S emission rate from laboratory experiments and its validation with data coming from the sewer; and (ii) using the same field data for benchmarking a new model and the oxygenation models developed for a waterfall, transposed for H₂S emission.

BACKGROUND

Hydrogen sulfide mass transfer

Matias *et al.* (2014) presented the progress status of their works aiming to develop a relationship between H₂S release and physical parameters of free-fall drops. Thanks to an experimental set-up, their investigations were encouraging by several observations on waterfall height, flow rate and oxidation rate impacts on H₂S emission. However, no formula was proposed or evaluated with experimental data. First, they studied the reaeration process at a waterfall in relation to oxygen removed and the air-to-water oxygen mass transfer. They corroborated that the waterfall height increases mass oxygen transfer. This relationship can easily be understood because high waterfall height induces more water turbulence. As shown in Figure 1, transfer mechanisms are indeed boosted and subject to local variations, particularly air entrainment, splashing, and disintegrating droplets.

Oxygenation models

An analogy with mass oxygen transfer is typically applied for mass gas transfer estimation. Based on the two-film theory (Lewis & Whitman 1924), the emission rate is controlled by steady-state molecular diffusion through two thin films, one gas and one liquid, separated by a liquid-gas interface. The mass transfer rate across the liquid-gas interface is often expressed as a function of a global mass transfer coefficient (K_La) driven by the difference between

liquid and gas phase concentrations. According to the two-film theory, the global mass transfer coefficient depends on the resistance of liquid and gas phase. However, resistance is subject to local variations at a waterfall due to hydraulic mechanisms (see Figure 1), inducing several interface forms (water droplets, waterfall film, tailwater surface, and air bubbles). Thus, it is complex to determine a global mass transfer coefficient depending on flow rate and waterfall geometry.

Nevertheless, previous works (Pomeroy & Lofy 1972; Thistlethwayte 1972; Matos 1992; Rame *et al.* 1997) established an oxygen deficit ratio as a function of geometric parameters of a waterfall. The deficit ratio r_i is defined for a specie i at 20 °C such as:

$$r_i = \frac{C_{upstream} - C_S}{C_{downstream} - C_S} \quad (1)$$

with,

C : mass concentration in the gas phase ($\text{g}\cdot\text{m}^{-3}$);

C_S : mass saturation concentration at the liquid-gas interface ($\text{g}\cdot\text{m}^{-3}$).

Table 1 presents these models and their validity domain. These authors agree that waterfall height (H in meters) can be included as a function parameter; some authors also add tailwater depth (D in meters) and/or flow rate (Q in $\text{L}\cdot\text{min}^{-1}$). Pomeroy & Lofy (1972) validated a reaeration coefficient (Equation (2)): $K_H = 0.41 \text{ m}^{-1}$ for a wastewater fall in a sewer with a tailwater depth comprised between 0.3 and 0.76 meters. Thistlethwayte (1972) proposed another reaeration coefficient: $K_H = 0.21 \text{ m}^{-1}$. Such differences are not surprising because of hydraulic complexity occurring at a waterfall. In addition, Thistlethwayte's relationship was deduced from experiments conducted on rivers, whereas other models were based on data analysis coming from a sewer. Rame *et al.* (1997) developed their model from experimental results observed on a pilot unit with wastewater: they studied the tailwater depth between 0.5 and 0.8 meters, and the pipe diameter from 0.145 to 0.295 meters.

Our works investigate how a global mass transfer coefficient ($K_La_{\text{H}_2\text{S}}$) for hydrogen sulfide from an oxygen deficit ratio could be determined as suitable for a waterfall (Table 1). In order to challenge these results, we also dealt with an experimental method to devise a new model for H₂S mass transfer at a waterfall using statistical data analysis.

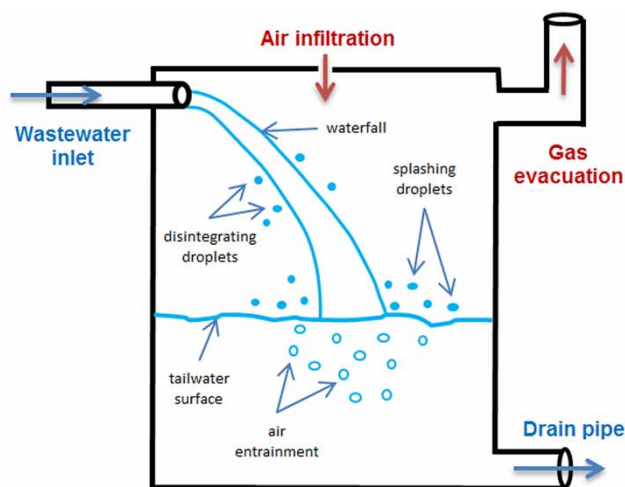


Figure 1 | Mass transfer mechanisms induced at a waterfall.

Table 1 | Models of oxygen uptake rate at a waterfall

	Flow rate (m ³ ·h ⁻¹)	Waterfall height (m)		
Pomeroy & Lofy (1972)	$Q = [2; 16]$	$H = [0.62; 1.52]$	$r_O = e^{0.41H}$	Equation (2)
Thistlethwayte (1972)	u/k	u/k	$r_O = 1 + 0.21H$	Equation (3)
Matos (1992)	u/k	$H < 1.75$	$r_O = e^{0.451H - 0.125H^2}$	Equation (4)
Rame <i>et al.</i> (1997)	$Q \in [2; 16]$	$H \in [0.12; 1.67]$	$r_O = e^{1.081H^{0.784}Q^{-0.139}}$	Equation (5)
Rame <i>et al.</i> (1997)	$Q \in [2; 16]$	$H \in [0.12; 1.67]$	$r_O = e^{1.048H^{0.765}Q^{-0.140}D^{-0.071}}$	Equation (6)

METHODS

Adaptation of oxygenation models

Mass transfer

As reaeration models were devised for gravity sewer by Yongsiri *et al.* (2003), an H₂S mass transfer coefficient can be determined using oxygen uptake model at a waterfall. In any case, the mass transfer rate through the liquid-gas interface is often expressed as:

$$\frac{dC}{dt} = -K_L \cdot \left(\frac{A}{V}\right) \cdot (C - C_S) = -K_L a \cdot (C - C_S) \quad (7)$$

with,

C : mass concentration in the gas phase (g·m⁻³);

C_S : mass saturation concentration at the liquid-gas interface (g·m⁻³);

K_L : global mass transfer rate (m·h⁻¹);

A : surface area of the liquid-gas interface (m²);

V : volume of liquid phase (m³);

$K_L a$: global mass transfer coefficient (h⁻¹);

t : time (h).

From the two-film theory composing the liquid-gas interface (Lewis & Whitman 1924), the liquid-gas mass transfer is driven by molecular diffusion through two steady films – one gaseous, the other liquid – divided by a liquid-gas interface. The global mass transfer rate can be expressed as:

$$\frac{1}{K_L} = \frac{1}{k_L} + 101.32 \frac{k_H R T}{k_G} \quad (8)$$

with,

k_L : mass transfer rate in the liquid phase (m·h⁻¹);

k_G : mass transfer rate in the gas phase (m·h⁻¹);

k_H : Henry's law constant (mol·atm⁻¹·L⁻¹);

R : universal gas constant = 8.3144621 (J·mol⁻¹·K⁻¹);

T : temperature (K).

Using the values k_L and k_G observed by Liss & Slater (1974) for their application to Equation (8), Yongsiri *et al.* (2004) estimated that the film of liquid phase controls more than 95% of the total mass transfer. The smaller the k_H value, the more the gas film resistance might be neglected. Thus, for an application to H₂S and O₂, the resistance of the liquid phase controls more than 98 and 99%, respectively, of the mass transfer process. Therefore, the global mass transfer rate (K_L) is considered equal to the mass transfer rate of liquid phase (k_L).

Molecular diffusion

The diffusion is one key parameter of liquid-gas transfer. It can be described by the first order Fick's law. Based on the two-film theory and Fick's law, mass transfer coefficients of liquid and gas phases are proportional to molecular diffusivity in the same conditions. Equation (9) introduces a relation between $K_L a$ and the molecular diffusion coefficient (D) for H₂S and O₂ in water:

$$\frac{K_L a_{H_2S}}{K_L a_{O_2}} = \frac{D_{H_2S}}{D_{O_2}} \quad (9)$$

with,

$K_L a_{H_2S}$: global mass transfer coefficient of hydrogen sulfide (h⁻¹);

$K_L a_{O_2}$: global mass transfer coefficient of oxygen (h⁻¹);

D_{H_2S} : molecular diffusion coefficient of hydrogen sulfide in water ($m^2 \cdot h^{-1}$);

D_{O_2} : molecular diffusion coefficient of oxygen in water ($m^2 \cdot h^{-1}$).

Yongsiri et al. (2004) studied four empirical equations to estimate molecular diffusion coefficients in wastewater. They demonstrated by a numerical application at 20 °C that:

- $D_{H_2S} = [6.08 \times 10^{-6}; 6.55 \times 10^{-6}](m^2 \cdot h^{-1})$
- $D_{O_2} = [7.06 \times 10^{-6}; 7.63 \times 10^{-6}](m^2 \cdot h^{-1})$

These observations concluded to a median ratio of molecular diffusion coefficients of hydrogen sulfide per oxygen:

$$\frac{K_L a_{H_2S}}{K_L a_{O_2}} = \frac{D_{H_2S}}{D_{O_2}} = 0.86 \quad (10)$$

Hydrogen sulfide deficit ratio

To implement the oxygen uptake models (Table 1), the modeling approach aims to describe a global mass transfer coefficient $K_L a$ according to the most influencing factors. Its formulation can be expressed from Equation (7), assuming that $K_L a$ and C_S are constant values in the steady phase of the experiment (operating conditions):

$$\int_{upstream}^{downstream} \frac{dC}{(C - C_S)} = -K_L a \int_0^t dt \quad (11)$$

$$\ln \left[\frac{C_{downstream} - C_S}{C_{upstream} - C_S} \right] = -K_L a \cdot t \quad (12)$$

$$\ln \left[\frac{C_{upstream} - C_S}{C_{downstream} - C_S} \right] = K_L a \cdot t \quad (13)$$

The term in brackets refers to a chemical deficit ratio r_i . Hydrogen sulfide deficit ratio can be estimated from Equations (1), (10) and (13) with an analogy to oxygen deficit because the emission rate is independent of the time:

$$\frac{\ln(r_{H_2S})}{\ln(r_O)} = \frac{K_L a_{H_2S}}{K_L a_{O_2}} = \frac{D_{H_2S}}{D_{O_2}} \quad (14)$$

$$\ln(r_{H_2S}) = \ln(r_O) \cdot \frac{D_{H_2S}}{D_{O_2}} \quad (15)$$

$$r_{H_2S} = r_O^{D_{H_2S}/D_{O_2}} \quad (16)$$

Hydrogen sulfide transfer rate at a waterfall

The global mass transfer coefficient is specific to the waterfall and its falling time. From Galileo's theory, the waterfall flight time is calculated by the following equation when neglecting air resistance:

$$t_f = 3,600 \sqrt{\frac{2 \cdot H}{g}} \quad (17)$$

with,

t_f : the falling time equal to the vertical motion time of the fluid from its free fall point to its impact point with the water surface (h);

g : gravity acceleration constant = $9.81 \text{ m} \cdot \text{s}^{-2}$.

By analogy with Equation (7), the liquid-gas transfer rate after the waterfall is calculated from the difference of concentrations and the waterfall flight time from the free fall point:

$$\frac{dC}{dt} = \frac{C_{upstream} - C_{downstream}}{t_f} \quad (18)$$

From Equations (7) and (18), the global mass transfer coefficient $K_L a_{H_2S}$ is expressed according to upstream and downstream concentrations:

$$\begin{aligned} \frac{dC}{dt} &= -K_L a_{H_2S} (C_{upstream} - C_S) \\ &= \frac{C_{upstream} - C_{downstream}}{t_f} \end{aligned} \quad (19)$$

$$K_L a_{H_2S} = -\frac{C_{upstream} - C_{downstream}}{t_f (C_{upstream} - C_S)} \quad (20)$$

Using Equation (1) the global mass transfer coefficient $K_L a_{H_2S}$ at 20 °C depends on the hydrogen sulfide deficit ratio r_{H_2S} after algebraic operations:

$$K_L a_{H_2S} = -\frac{C_{upstream} - C_{upstream} - C_S/r_{H_2S} - C_S}{t_f (C_{upstream} - C_S)} \quad (21)$$

$$K_L a_{H_2S} = \frac{1 - r_{H_2S}}{t_f \cdot r_{H_2S}} \quad (22)$$

Temperature compensation is finally applied on $K_L a_{H_2S}$ value. This function is described by the following equation:

$$K_L a_{(T)} = K_L a \cdot \theta^{T-20} \quad (23)$$

with,

T : fluid temperature (°C);

θ : temperature coefficient, usually equal to 1.024.

The hydrogen sulfide transfer rate through the atmosphere can be calculated from Equation (7) thanks to Equations (22) and (23).

New model for H₂S transfer rate

Modeling approach

As in previous works (Matias et al. 2014), our study was based on experimental tests and statistical analysis. The first step was to determine the model's response and which parameters the model was to consist of. The model's response was hydrogen sulfide emission rate (R_{H_2S}) formulated in $gH_2S \cdot h^{-1}$. On the basis of the literature (Yongsiri et al. 2004; Matias et al. 2014) and our knowledge, the following factors were selected due to their presumed influence on hydrogen sulfide transfer: water temperature (T), liquid H₂S concentration (C_S) at pipe outlet, waterfall height (H), tailwater depth (D), and flow (Q). The pipe diameter (ϕ) was also selected as an influencing factor to reach realistic fluid velocities at the outlet pipe according to the flow Q . The fluid velocity (S) at the pipe outlet could be another factor but not included at the beginning of our study. It could be either measured or estimated from pumping flow rate and pipe diameter values. The manhole surface was not studied. The emission rate and water turbulence are assumed to be more highly influenced by mechanisms induced at a waterfall, which are spatially local, than the water surface of the manhole. This work does not focus on gas stratification which is another subject. In this study gas measurements were carried out one meter over the waterfall using a gas sensor. Measurements were made every ten seconds.

The second step aimed to define and devise an experimental design enabling determination of influencing factors after data analysis, independently of previous experiments. The fractional factorial design was used to reduce the number of experiments and to reach the maximum information. 2^{5-1} experiments were selected, which allowed 16 combinations of waterfall (Box et al. 2005). Some assays of reference (center points) and duplications were added to complete the

experimental design and measure the process repeatability. Data analysis was then performed on the entire dataset.

Multiple regression analysis is used to describe the emission rate. The model is formulated as:

$$Y = X \cdot \beta + \varepsilon \quad (24)$$

Y is an $n \times m$ matrix of responses; X is an $n \times p$ matrix, with p the number of terms in the model including the constant (effects and interactions); β is the matrix of regression coefficients; and ε is the matrix of residuals.

Model formulation

For a sewer manhole supplied by a rising main, we assumed that maximum H₂S gas concentration is governed by emission rate, pumping time, and ventilation rate r_v . A ventilation rate had been introduced in order to simulate a more realistic dynamic behavior of the gas concentration. The pump is switched on between the initial time t_i and final time t_f . Hydrogen sulfide emission is taken into account from t_i , and then the simulation starts. Ventilation rate is only taken into account after the end of waterfall, t_f , to simulate gas intake from the manhole headspace to the downstream sewer as a result of wastewater evacuation. Indeed, the downstream pipe is almost always located at the manhole bottom and is therefore under water during the waterfall, as shown in Figure 1. The wastewater existing in the manhole bottom is presumed to create air intake after the waterfall stop. We assume that water volume is replaced by a renewed air volume. During this short moment, the wastewater flow rate is assumed to approximatively govern the ventilation rate r_v . The rate r_v could be defined by Equation (25):

$$r_v = \frac{Q}{v} \quad (25)$$

where Q is the wastewater flow rate and v the air volume of manhole headspace.

Continuous air leakage was not modeled in this work at laboratory scale but an air leakage rate could be added for a prediction of dynamic behavior of gas concentration in a sewer. The dynamics of H₂S gas concentration C_g are defined by Equation (26):

$$\frac{dC_g}{dt} = -r_v C_g \int_0^{+\infty} \delta(t - t_f) \cdot dt + \frac{R_{H_2S}}{v} \int_0^{+\infty} \delta(t - t_i) - \delta(t - t_f) \cdot dt \quad (26)$$

where $t_i < t_f$ and $\delta(t)$ a Dirac function.

This approach will be discussed hereinafter during model validation using the data from a sewer manhole.

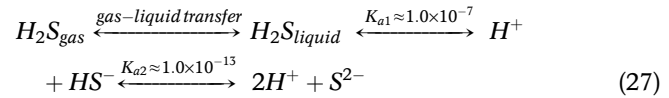
Data collection and analysis

Data collection from an experimental unit

The aims of the laboratory experiments were to determine factor effects and their prioritization in H₂S gas release. An experimental unit was designed at laboratory scale to simulate a waterfall fed with tap water or wastewater, see Figure 2. The experimental design enabled the control and adjustment of the value of each factor studied and measurement of the H₂S emission rate.

Water temperature (TT10 on Figure 2) was controlled from 10 to 30 °C in the 230-liter storage tank (B10) by a heating/cooling device during the effluent preparation step as a result of water recycling (pump P10). Liquid H₂S concentration was set in the storage tank after several steps: first, a solution of sodium sulfide trihydrate (Na₂S, 3H₂O) was added; and second, a solution of hydrochloric acid (HCl) was injected to reach the required amount of hydrogen ions governing sulfur species concentration (H₂S, HS⁻ and S²⁻). In fact, liquid H₂S concentration is difficult to set as the two

equilibria – gas–liquid transfer and sulfur species dissociation – must be controlled, see Equation (27).



The amount of H₂S gas (AT10) was also measured in the storage tank headspace to check mass balance. The reagent amounts were determined by electronic and mass balance. Finally, liquid H₂S concentration was verified using total dissolved sulfide analysis (methylene blue test) and pH measurement (AT11). For each test, waterfall height and tailwater depth were selected according to the experimental design using a set of valves (VI16, VI31 to VI34). A flowmeter (FT10) measured the flow rate which was controlled by a PI (Proportional and Integral) controller to ensure the set point of fluid velocity.

Thus, the experimental unit simulated a discharge manhole (B20), with a surface area of 0.16 m², a height of 0.75 m and made of polyvinylchloride (PVC), that was receiving a constant flow of H₂S. Some online measurements were available to check the mass balance of sulfide:

- H₂S gas measurement (AT40) in the manhole headspace
- H₂S gas measurement (AT40) in the manhole headspace determined H₂S emission rate.

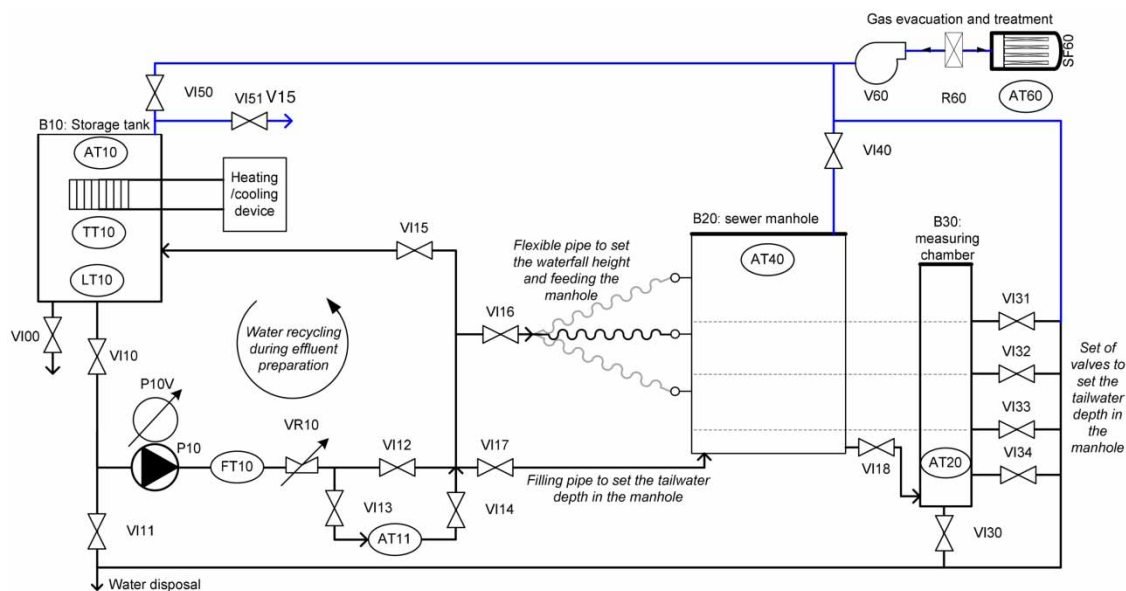


Figure 2 | Experimental unit for effluent preparation and waterfall simulation.

- Temperature, oxygen concentration, pH and HS⁻ concentration (using an UV-VIS spectrometer) were measured (AT20) before and after the waterfall.

Figure 3 describes the main steps of an experiment and the monitoring data. After effluent preparation in the storage tank in terms of temperature and liquid hydrogen sulfide concentration, the manhole bottom was filled (reference time: -6 minutes before the waterfall). The amount of liquid H₂S was calculated from online measurement of HS⁻ by UV-VIS spectrometer, from the temperature and pH. This calculation shows that the manhole received a constant flow of H₂S during waterfall simulation (23 minutes in this example); that is why the sulfide oxidation rate does not interact with model development. In fact, oxygenation of liquid varies according to waterfall height and flow (Pomeroy & Lofy 1972; Thistlethwayte 1972; Matos 1992; Rame et al. 1997) and therefore oxidation rate should also change total sulfide concentration. From the observations in Figure 3 and others tests of the experimental design, the oxidation rate was weak enough to be neglected.

For the test shown in Figure 3, H₂S emission rate was determined in gH₂S·h⁻¹ between two gas measurement intervals (5 and 15 minutes) for an estimation with good confidence interval. The slope was calculated at these points (71 ppm at 5 minutes and 211 ppm at 15 minutes) and the emission rate was determined in gH₂S·h⁻¹ by molar conversion and air temperature compensation. For this example, the numerical application is detailed hereafter

with a drop height of 0.21 meter and air temperature at 20.7 °C.

$$\begin{aligned} R_{H_2S} &= \frac{211 - 71}{10} * \frac{M_{H_2S}}{v_m} * v * 60 \\ &= 14 * \frac{M_{H_2S}}{v_m} * (0.16 * (0.75 - 0.21)) * 60 \\ &= 0.1026 \text{ gH}_2\text{S} \cdot \text{h}^{-1} \end{aligned}$$

with,

M_{H_2S} : molar mass of H₂S (g·mol⁻¹);

v_m : molar volume of gas with temperature compensation (m³·mol⁻¹ at 1 atm);

v : air volume of manhole headspace (m³).

Figure 3 also shows the final step of a test that was to evacuate and treat gas and wastewater.

Data analysis

Following data collection from the experimental unit, the dataset was analyzed in order to generate a regression while taking factor interactions into account. Partial least squared regressions and multiple linear regressions (MLRs) were tested. Due to the experimental design and the probability of finding greater interactions, only first order interactions were considered. Therefore, H₂S emission rate R_{H_2S} model is composed of significant factors and, if necessary, some interactions.

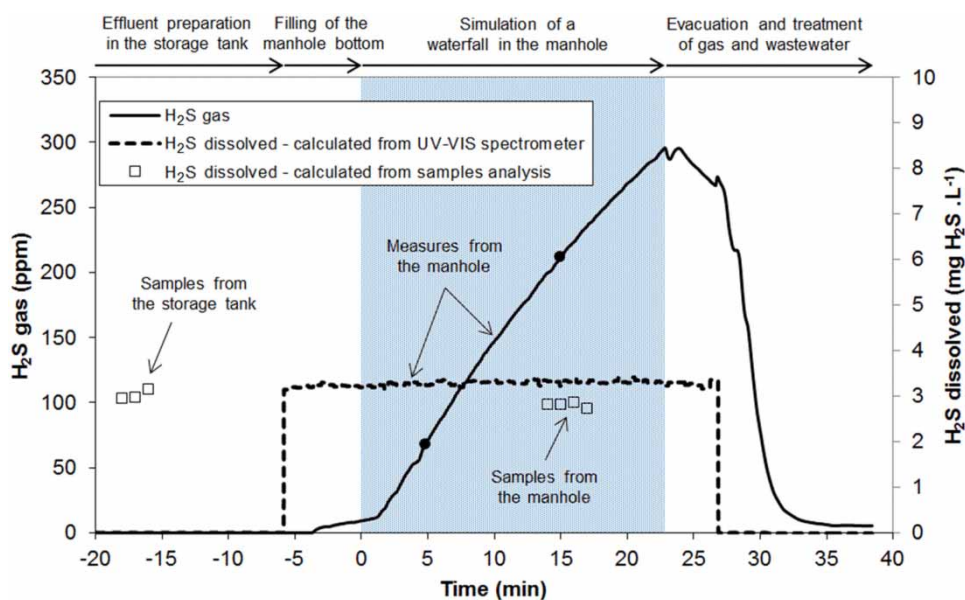


Figure 3 | Description of test steps and data monitoring.

Data collection for model validation

Four sampling campaigns were realized at a discharge manhole of a rising main where a waterfall occurs. Samplings were collected before the waterfall to obtain a more realistic analysis of total sulfide concentration. Two sewers were selected in the south of France. The other two sampling campaigns were performed on a third sewer located in the west of France during June and November: if wastewater temperatures were different, the gas emitted amounts were also different. Wastewater was sampled at the pipe outlet, before the waterfall, in order to determine a representative concentration of liquid hydrogen sulfide. Air and water temperature, pH and H₂S gas concentration were also measured. Pumping time was recorded at the pumping station.

Temporal dynamics of hydrogen sulfide gas were observed in the discharge manhole. For instance, see Figure 4, gas concentration increases each time the pump starts. Naturally occurring ventilation in the sewer headspace decreases hydrogen sulfide level in the headspace to 0 ppm, which in turn increases H₂S emission rate, as transfer potential is higher. This phenomenon was not studied at pilot scale: however, its effect could be modeled by a mass balance (Equation (26)).

The hydrogen sulfide emission rate is determined by the rising curve slope in Figure 4, whereas ventilation rate can be approximated by analysis of data observed after reaching maximum concentration.

RESULTS AND DISCUSSION

Data analysis

Influencing factors

A descriptive statistical analysis highlighted that the dispersion of the response for all tests versus the reference (center point) was more significant, see Figure 5. This means that some factors have a significant effect on H₂S emission rate. With respect to this, the repeatability of the reference test was quite good; therefore, the influencing factors can be analyzed if their intensity is significant enough.

The multiple regression analysis is inefficient in case of collinearity, thus increasing the difficulty of interpreting the linear regression equation (Wold et al. 2001). One approach could be the removal of one of the correlated

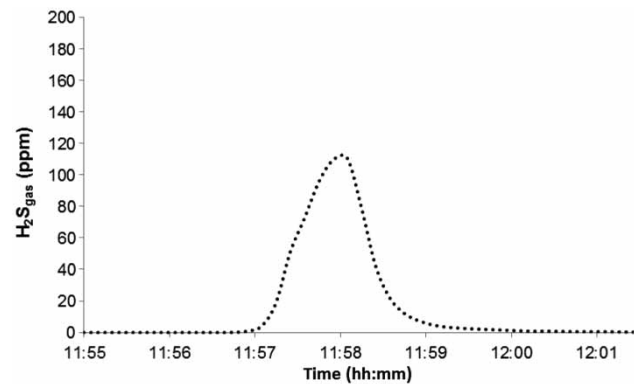


Figure 4 | Change in H₂S gas concentration in a sewer manhole headspace.

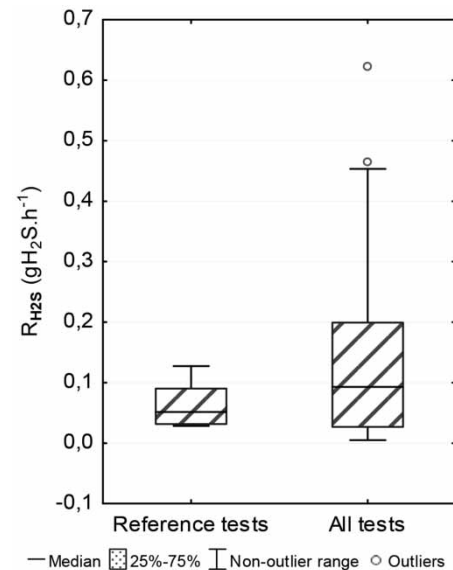


Figure 5 | Descriptive statistical analysis of tests response – all configurations (32 tests) versus reference configuration (15 tests).

factors (in our case: flow rate and pipe diameter – correlation due to fluid velocity effect on water turbulence and water crash) and another could be to use an alternative statistical technique such as the partial least squares (PLS) regression. The PLS is more appropriate to construct predictive models when the factors are numerous and highly collinear. In order to develop a simpler model, we chose to replace the factors such as flow rate and pipe diameter by the fluid velocity at outlet pipe, and redo the analysis. On the other hand we observed visually that fluid velocity impacts directly the water crash and thus water surface turbulence and air entrainment. Therefore we analyzed five factors: water temperature (T), liquid H₂S concentration (C) at pipe outlet, waterfall height (H), tailwater depth

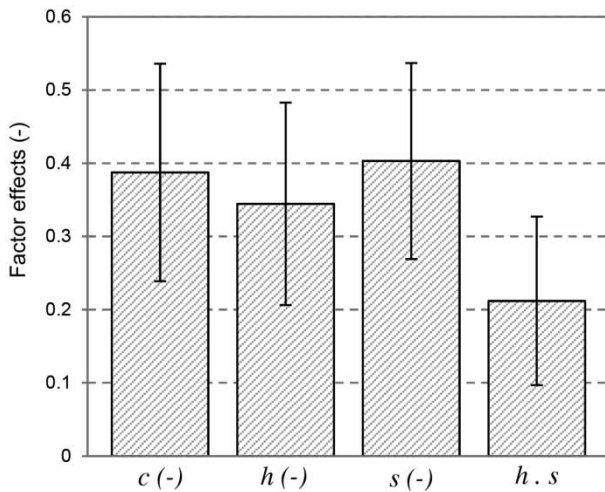


Figure 6 | Factor effects with their uncertainty – c: liquid concentration of hydrogen sulfide; h: waterfall height; s: fluid velocity.

(D), and the fluid velocity (S). Figure 6 displays the intensity of factor effects and the first order interactions obtained by analysis of standardized data.

Liquid H₂S concentration (C), waterfall height (H) and fluid velocity (S) have a significant influence on H₂S emission rate. Waterfall height also interacts with the fluid velocity, which is useful for explaining statistically the water turbulence effect on H₂S released. Given the analytical uncertainty (± 0.12 (-)), no effect of water temperature was detected despite its known effect on saturation concentration. Tailwater depth effect was also not detected. Most factors seemed to have a linear influence in their relevant area of study. These observations confirmed that mass transfer mechanisms are both complex and combined at a waterfall, and that is why it is necessary to include an interaction of waterfall height and fluid velocity in the model. The main conclusion of works by the other authors (Rame et al. 1997) is in keeping with these results: drop height is a factor with great influence on oxygen absorption, and tailwater depth has little effect on oxygen transfer at drop structures. According to our analysis focused on H₂S transfer, the flow rate was also a significant factor; however, our original proposal was to include fluid velocity at the pipe outlet which seemed to be a better factor more closely correlated with water turbulence than the flow rate. For H₂S transfer especially, liquid concentration is a key factor.

Finally, the second experimental design, consisting of some additional tests where emission rate was particularly high, was devised to produce a statistical model able to predict H₂S emission rate.

Prediction model

The model is based on MLR using standardized data from the experimental unit and a transformed response in square root. This kind of response transformation allows getting a better dispersion of observed data in order to improve data analysis. MLR was validated as the factors did not produce strong correlation amongst themselves. The graph of observed and predicted responses of square root of H₂S emission rate is given in Figure 7. Analytical results are concordant: the coefficient of determination ($R^2 = 0.91$) suggests that all factors make it possible to confidently model the observed H₂S emission rate. The residuals follow normal distribution and they are uncorrelated (not shown here). In order to estimate model error as a prediction interval, the residual standard deviation to predictions (RSD = 15.6%) shows the unexplained variations of the model response.

The statistical model is given by Equation (28). The validity domain of the model is reported in Table 2.

$$\sqrt{R_{H_2S}} = a + f(c, h, s, h.s) \quad (28)$$

where a : empirical constant rate ($g^{0.5}H_2S \cdot h^{-0.5}$); c : standardized liquid concentration of hydrogen sulfide (-); h : standardized waterfall height (-); s : standardized fluid velocity at pipe outlet (-).

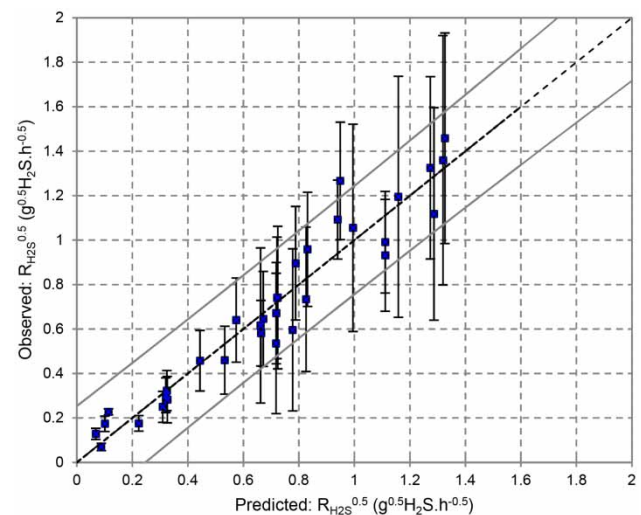


Figure 7 | Observed versus predicted responses of square root of H₂S emission rate ($g^{0.5}H_2S \cdot h^{-0.5}$). Vertical bars represent standard deviation of observed data; grey lines represent prediction interval.

Table 2 | Validity domain of the model

Factors	Symbol	Min	Max
Liquid H ₂ S concentration (mg H ₂ S·L ⁻¹)	<i>C</i>	0.4	5.6
Waterfall height (m)	<i>H</i>	0.05	1.5
Fluid velocity (m·s ⁻¹)	<i>S</i>	0.06	1.2

Model validation

H₂S concentration dynamics in a sewer manhole

As an example (Figure 8), model validation was applied to the waterfall configuration in the sewer in the west of France. Waterfall height was 0.4 meters, tailwater depth was 0.15 meters and fluid velocity was 0.51 meters per second at the pipe outlet. The validation solved Equations (26) and (28) during three pump operations by Euler's numerical solver. Ventilation rate r_v was set using Equation (25): flow rate was 128 cubic meters per hour and the volume of manhole headspace was 1.43 cubic meters. The flow rate was estimated at pumping station by several tests with the reservoir drawdown zone. A data set from the sampling campaign in the west of France provided this simulation. H₂S gas measurement and the model's response, converted to ppm and estimated in the headspace of the sewer manhole, are given in Figure 8.

The dynamics of H₂S gas concentration can be observed for three pumping sequences of 60, 45, and 20 seconds running time. Although calculation of the ventilation rate is roughly estimated by Equation (25), the analytical results of the field study showed that temporal variations in gas hydrogen sulfide concentration can be reasonably well predicted. The numerical results show that the maximum concentration can be approximated.

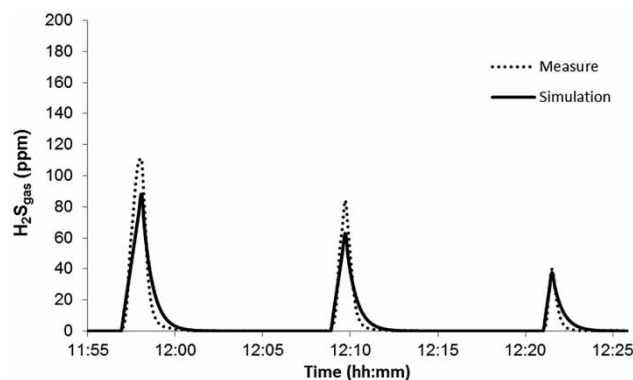


Figure 8 | Dynamics of H₂S gas concentration in a discharge manhole with three pumping sequences, respectively of 60, 45 and 20 seconds running time – Comparison of measured and simulated values.

Models evaluation

Four of the five available models adapted by an analogy between H₂S and O₂ (Pomeroy & Lofy 1972 – Equation (2); Thistlethwayte 1972 – Equation (3); Matos 1992 – Equation (4); Rame et al. 1997 – Equation (5)) and the new model were simulated with data collected from four sampling campaigns. Wastewater quality and pumping time were variable during each campaign. Therefore, pH, wastewater temperature, and the total sulfide concentration allowed us to proceed with several simulations in variable operating conditions at each waterfall. We used 38 observations to evaluate predictions of each model and their robustness. Simulation results are reported in Figure 9 as the residuals mean of the H₂S transfer rate for each sampling campaign.

If we look at Figure 9 we notice that the adapted model from Thistlethwayte (1972) and the new model (introduced in this paper) show a better robustness. Indeed, these two models are highlighted as a result of low mean of residuals at each sampling campaign. The last three sampling campaigns resulting in higher residues were performed during summer season with higher temperature than the first campaign. This could explain higher transfer rate and a weakness of models to compensate wastewater temperature effect. On the other hand, vertical gas stratification in the manhole atmosphere could justify the observed residues particularly in sewer 1 and 2 in the south of France where the waterfall height is higher, 1.2 and 2 meters, respectively. The natural ventilation of the atmosphere was not controlled in a manhole. The intensity and gas velocity gradients depend on hydraulic conditions, weather, and the state of deterioration of the manhole. Thus the gas sensor placement is very decisive for comparing simulation results. We will examine this topic in future studies to

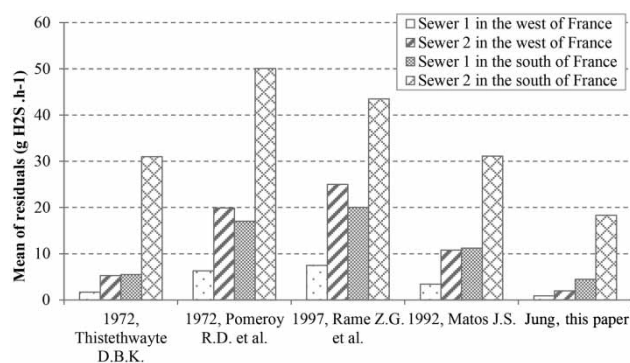


Figure 9 | Mean of residuals for several simulations of H₂S transfer rate (five models) with data from four sewers.

explain gas stratification. Regarding the manhole material, Nielsen *et al.* (2008) studied the adsorption and subsequent oxidation on pipe surfaces in a gravity sewer. They performed tests with plastic (PVC and high-density polyethylene) and concrete pipes. From their simulations they demonstrated that the steady state H₂S gas concentration is significantly affected by the pipe material. This should also be investigated to validate limits of the new model.

CONCLUSIONS

This paper investigates hydrogen sulfide transfer at a waterfall in a sewer manhole in which H₂S emission rate is still largely unexplored and systemic modeling is missing. These works highlight main factors affecting water turbulence and H₂S transfer. A statistical analysis was performed using data from an experimental unit. The most significant factors were highlighted and prioritized: waterfall height, liquid concentration of hydrogen sulfide and fluid velocity play a key role in hydrogen sulfide emission.

A first approach is to model the transfer rate at a waterfall. The objective is to determine a transfer coefficient of H₂S at liquid-gas interface and to solve a mass balance. The H₂S transfer coefficient is calculated from available models predicting a deficit ratio of oxygen as a function of geometric parameters of a waterfall. The second approach is based on experiments and a statistical analysis. This work concludes with a new model of hydrogen sulfide transfer rate dedicated to an ordinary waterfall produced by a rising main. A complete model of gas concentration dynamics is proposed according to emission rate, pumping time, and ventilation rate. The model results in a residual standard deviation of 15.6% up to a rate of 2.3 g H₂S·h⁻¹.

Finally, a simulation benchmark of all models was performed as a result of data from four sampling campaigns on sewer networks. Five models were simulated to compare their predictions and robustness according to variable hydraulic and wastewater characteristics. Two models were highlighted regarding the residuals mean. Some observations suggested that the vertical gas stratification in the manhole atmosphere should be investigated to explain model errors according to gas sensor placement.

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