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Sulphide Occurence in Sewer Networks

- a New Topic in MOUSE Trap

by

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Abstract

Sulphide build-up in gravity sewers takes place mainly in large, slow flowing, pipes with insufficie aeration at relatively-high temperatures and in pressure mains, when the residence time of the waste more than 1-2 hours. Also, industrial wastewater with a high content of organic matter and sulphur contribute to sulphide build-up.

In Denmark build-up of sulphide in bulk water in gravity sewers is rare but in Danish pressure mai up of sulphide can occur - typically up to 10 mg S/l. Significantly higher concentrations are reporte countries.

Sulphide production is of interest due to the problems it may result in; these being e.g. noxious odo health risk, corrosion of concrete and metal constructions and inhibition of sewer treatment process

A new topic has now been developed in MOUSE Trap. The new topic is designed to analyse variati build-up of sulphide in the sewer network during diurnal equilibrium. The testing of the model has promising results in projecting the sulphide concentrations, visualised by an example from Lindköb Sweden.

Introduction

Sewage normally has a high content of various organic and inorganic components, which are easily by different types of microorganisms. The microbial transformation of organic compounds starts in sewer network, where significant amounts of organic matter may be removed during transport /1/. the sewer must be regarded as an integral part of the wastewater treatment system.

The dominating type of microbial activity in the sewer network will be determined by the composit the concentration of the various components in the sewage, especially the concentration of electron acceptors (biological oxidants). The various available electron acceptors are utilised according to th sequence; oxygen for aerobic respiration, nitrate for denitrification, organic compounds for ferment sulphate for sulphate reduction (sulphide production) and carbon dioxide for methanogenesis. Diss oxygen, ammonium, sulphate and organic compounds are natural components in sewage, while nitr usually not present in significant concentrations in domestic sewage /2/.

Sulphide production resulting from a sulphate reduction in gravity sewers takes place mainly in larg flowing, pipes with insufficient re-aeration at relatively-high temperatures and in pressure mains w residence time for the wastewater is more than 1-2 hours (the total residence time for the wastewate under anaerobic conditions). Sulphide in bulk water in gravity sewers in Denmark is rare, probably the low temperatures, but in Danish pressure mains build-up of sulphide can occur, typically up to S/l /1/. In other countries with longer pressure mains or higher temperatures, significantly higher concentrations are reported.

In pressure mains with small diameters the production of sulphide mainly takes place in the biofilm surface of the pipe, whereas in sewers with large diameters anaerobic activity in the bulk liquid will of importance for the total generation of sulphide. The biological activity in the sediment in the sew network can also be significant to the build-up of sulphide /2/.

Sulphide production is of interest because an enhanced sulphide production can result in a number problems, these being noxious odours, health risk, corrosion of concrete and metal constructions in sewer network and inhibition of sewage treatment processes /2/. Also, the content of sulphide may for fish in streams affected by overflow events /1/.

The following table can be used as a guideline for the different problems that the presence of sulphi result in.

Table 1: *Assumable effects due to different sulphide concentrations /3/.*

Content of H_2S in the air [PPM]	Human reaction
< 0,13	Odourless
1	Minor odour
5	Distinct odour
10	Hygiene limit for one working day
10-50	Minor irritation of the eye
30	Strong obnoxious smell
50-100	Minor problems with eyesight and shortness of breath after just on hour
100-200	Problems witk eyesight and coughing. Sense of smell disappears after 2-15 minutes and dizziness occures after 14-30 minutes
500-1000	Rapid unconsciousness and death

Model Concept

Investigations of sulphide formation in sewer systems have been carried out in the past and several predictive empirical models have been proposed. For models describing sulphide production in pre mains the important parameters to quantify the sulphide production rate are the concentrations of s the concentrations of organic matter and the temperature. Organic matter is the key parameter beca sulphate concentration in wastewater is normally not the limiting factor for sulphide production /4/. concentrations of sulphate and sulphide in (Danish) raw wastewater are approximately 20-100 mg/l respectively 0.1 mg/l /5/.

Table 2: Empirical equations for forecasting sulphide production rates in pressure mains. Unit fo *g/m²/h*$^{*)}$.

Equation no.		Referenc
1.	$r_a = 0.5\times10^{-3}\cdot u\cdot\left(C_{\mathrm{BOD}_{\mathrm{total}}}\right)^{0.8}\cdot\left(C_{\mathrm{SO}_4^{2-}}\right)^{0.4}\cdot1.139^{(T-20)}$	Thistlethwayte, 197
2.	$r_a = 0.228\times10^{-3}\cdot \mathrm{C}_{\mathrm{COD}_{\mathrm{total}}}\cdot1.07^{(T-20)}$	Boon & Lister, 197
3.	$r_a = 1\times10^{-3}\cdot C_{\mathrm{BOD}_{\mathrm{total}}}\cdot1.07^{(T-20)}$	Pomeroy & Parkhurst, 197
4.	$r_a = k^{**)}\times10^{-3}\cdot\left(C_{\mathrm{COD}_{\mathrm{soluble}}}-50\right)^{0.5}\cdot1.07^{(T-20)}$	Nielsen & Hvitved-Jacobsen 198

$^{*)}$ Can be expressed as g/m³/h by dividing with the hydraulic radius (V/A).

$^{**)}$ k = 1.5 for Danish domestic wastewater, 3 for wastewater with some contribution from food ind 6 for easily degradable wastewater from food industry.

Different empirical models are listed in table 2. Equations 2, 3 and 4 assume that the sulphate conc is high and non-limiting, which usually is the case for concentrations above 4-5 mg SO_4-S/l. In equ and 3 the rate of sulphide production depends only on the concentration of total organic matter in t wastewater and the temperature, whereas equation 1 also includes sulphate concentration and mean velocity.

Equations 1 and 2 estimate maximum possible rates and they are a conservative result of measurem made in many pressure mains /1/. This also accounts for equation 3, which is widely used in USA. equation has been based on measurements from several sewer systems and it estimates the sulphide production rate under worst-case conditions /6/.

Equation 4 is useful for predicting variations in the sulphide production rate in a pressure main wh known which type of wastewater is going to be modelled. It has proven suitable for estimating diu seasonal variations in sulphide production in many Danish combined or separate pressure mains /1 Equation 4 has one major advantage, i.e. dissolved COD is used in the expression and dissolved C modelled in the existing MOUSE Trap. Moreover, it is more correct to apply dissolved COD in the expression as the bacteria utilise this fraction of COD.

The new topic in MOUSE Trap includes the empirical equations for sulphide build-up described ab possible to select any of the four equations depending on the situation that needs to be analysed anc depending on the available measured data. The data available is important due to the each of the foı equations being dependent upon different measures of organic load.

Furthermore, equation no.1 depends on measurements of sulphate while the mean-flow velocity, wł enters the equation, is calculated in MOUSE. In equations nos.1, 2 and 3 no calibration constants aı applied, while equation no.4 includes a constant that represents the quality of the wastewater under In table no.2 some guidelines are mentioned and also /4/ suggests that the sulphide production rate increased according to the following order (no. 1 has the largest rate while no. 3 has the lowest rate)

1. wastewater from mainly food industries.
2. wastewater from mixed municipal and industrial (food) sources.
3. typical Danish domestic wastewater with little or no content of industrial sewage.

The empirical models described above have limitations in describing the sulphide production and n fundamental (deterministic) models are required if the processes are to be described in more detail / figure 1 the basic model concept is described.

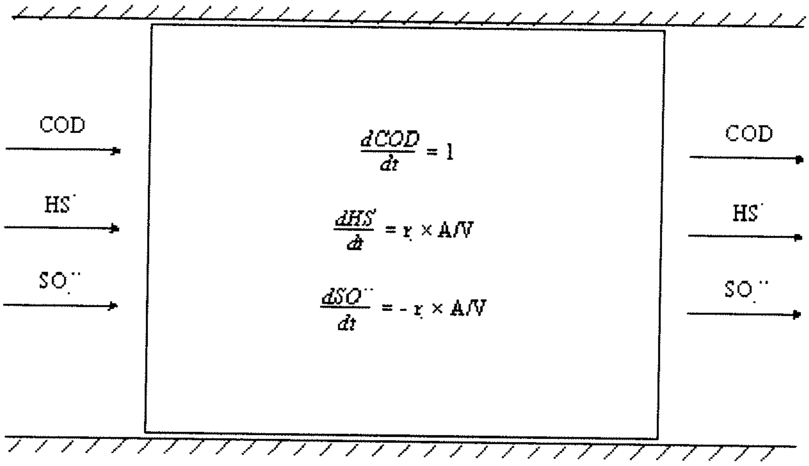


Figure 1: The basic model concept for the new sulphide module (HS-module).

One interesting thing to analyse, while computing sulphide build-up, is which initiatives are effecti decreasing the possibility of having sulphide build-up at all. One of these initiatives, which can be ε with this new module, could be to decrease the diameter of the pressure main and thereby increase ı velocity and decrease the retention time.

Another initiative could be the adding of oxygen either as dissolved oxygen or as other components nitrate. To be able to analyse these situations a variation of the module described above is develope variation includes a simplified expression for the wastewater oxygen demand in the pressure main. oxygen demand is described by a zero order expression including the temperature and a Michaelis-l expression:

$$OD = K \cdot COD \cdot \Theta^{(T-20)} \cdot \frac{DO}{DO + K_{m,DO}}$$

where K is the oxygen decay rate [1/day]

COD is the actual concentration of COD [g/m³]

DO is the actual concentration of dissolve oxygen [g/m³]

$K_{m,\,DO}$ is the half-saturation concentration, DO [g/m³]

Θ is the Arrhenius temperature coefficient

By including this wastewater oxygen demand and a few extra Michaelis-Menten expressions the ful sulphide module can be described as in figure 2.

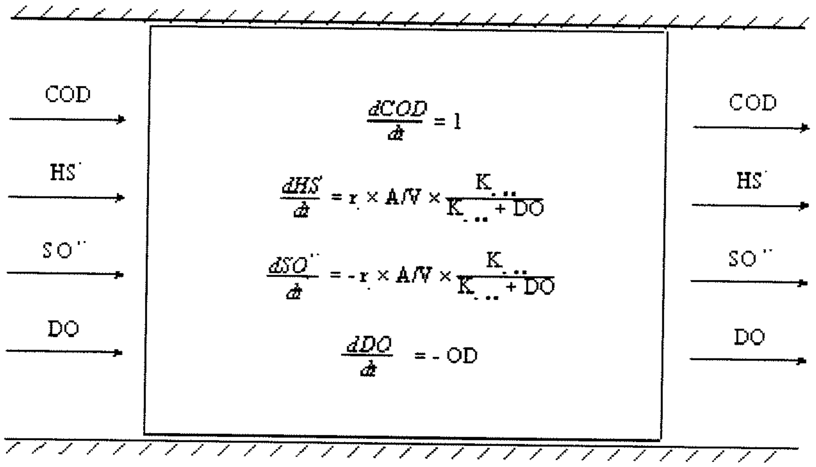


Figure 2: *The full model concept for the new sulphide module (HS-module).*

Hydrogen Sulphide

The model described in the previous section computes sulphide build-up as the total sum of sulphid hydrogen sulphide. To compute the concentration of the toxic gas hydrogen sulphide, the pH is of g importance. pH is not yet included in the new sulphide module, but it will be in the near future.

Hydrogen sulphide is in chemical equilibrium with sulphide according to the following equation:

$$H_2S \leftrightarrow HS^- + H^+ \leftrightarrow S^{2-} + 2H^+$$

The chemical equilibrium between these three fractions is strongly dependent on pH. In wastewater is normally between 6.6 – 7.2 and within this range the chemical equilibrium between H_2S and HS^- sensitive. A change within this interval of ΔpH = 0.2 will create a change in the hydrogen sulphide concentration of about 30 % /3/.

It is not yet possible to distinguish between HS^- and H_2S in the new HS-module, but this is easily d manually, see box 1.

BOX 1: Calculating the chemical equilibrium between sulphide (HS^-) and hydrogen sulphide (H_2S) /5/.

The chemical reaction: $H_2S \leftrightarrow HS^- + H^+$

Equilibrium is calculated as

$$\frac{[HS^-]\cdot[H^+]}{[H_2S]} = K$$

where $[HS^-]$ is the concentration of sulphide

$[H^+]$ is the concentration of hydrogen

$[H_2S]$ is the concentration of hydrogen sulphide

K is the equilibrium constant ($K = 9.12 \times 10^{-8}$ at 25 °C)

Equilibrium is then dependent upon temperature and pH, as $pH = -\log[H^+]$. The temperature dependency is described as

$$\ln(\frac{K(T)}{K(T_0)} = \frac{\Delta H}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

where R is the gas constant, $R = 8.3144$ J/mole/K

T is the actual temperature [K]

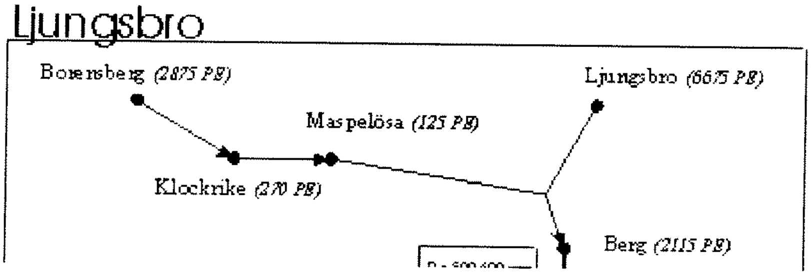
T_0 is the temperature where K is known (25 °C)

$\Delta H = \Delta HS^- - \Delta H_2S = -16.3 + 38.6 = 22{,}3$ [KJ/mole]

Model Set-up, Lindköbing, Sweden

In the following the setup used for testing the module is shortly described. The setup is found in the of the city of Lindköping, Sweden. The example was found in /3/ and it covers the pressure main in Ljungsbro.

A schematic description of the pressure main is shown in figure 3, while the technical data are outli table 3. In the example the wastewater was treated with calcium nitrate to avoid sulphide build-up. been attempted to incorporate this in the model by adding oxygen and thereby delaying the build-u sulphide.



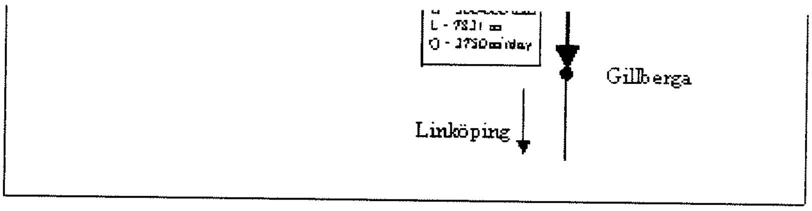


Figure 3: *A schematic overview of the model setup area.*

Table 3: The technical data used in the set-up /3/.

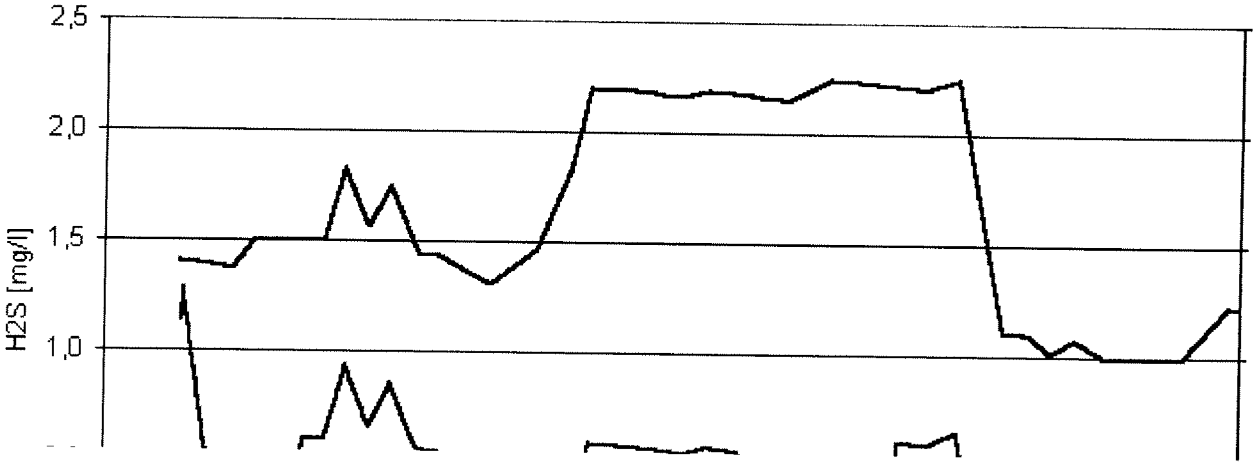
L	*7831 m*
D	*500-600 mm*
Q	*3750 m³*
Retention time	*11,4 hours*
BOD	*360 g/m³*

The experiments carried out in /3/ showed that the concentration of H_2S varies both during the day during the year. The yearly variations are greatly dependent upon the temperature variations while t diurnal variations depend on the loads from households and industrys. Also precipitation events inf the diurnal variations if the wastewater system is a combined system. The variations caused by prec however, are short-term variations.

Only yearly-average loads of BOD and sulphate are available for testing the model, while some dail averages of temperature and pH are available. Therefore, only the yearly variations in the sulphide b are expected to be modelled.

Preliminary Test Results

The preliminary results from the test of the new sulphide module are presented in this section. Mod was used in this example, see table 2. The temperature has an effect on the yearly fluctuations of su build-up, as mentioned in the above section, and these variations in the temperature can be seen in simulated concentrations of sulphide, see figure 4, but obviously other conditions also have an imp sulphide concentrations.



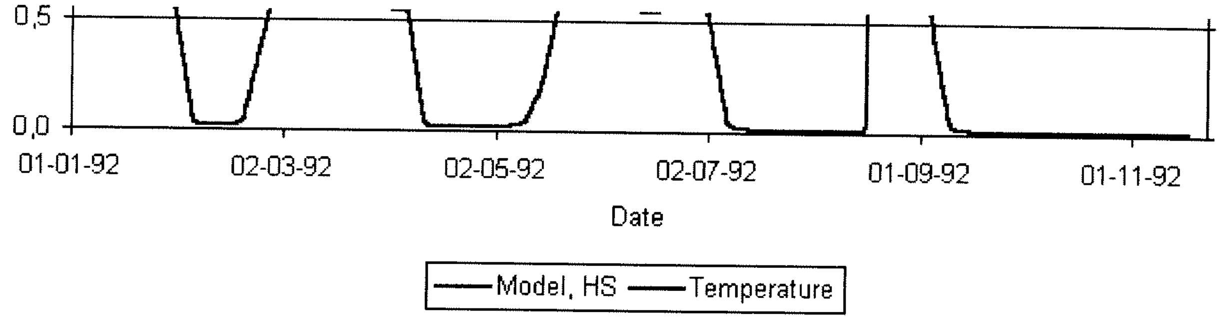


Figure 4: *Temperature used in the testing of the sulphide module and the simulated concentration sulphide (model no.2).*

In the example from Lindköping oxygen was added to prevent sulphide build-up. This explains sorr deviations in the modelled sulphide concentrations compared to the temperature. Also, the concentr sulphide drops in July. This is caused by a decrease in the concentration of BOD as a factory in the closes that month, and this influences the load drastically /3/.

The build-up of hydrogen sulphide is presented in figure 5. The concentrations of hydrogen sulphid calculated using the temperature and pH as described in box 1.

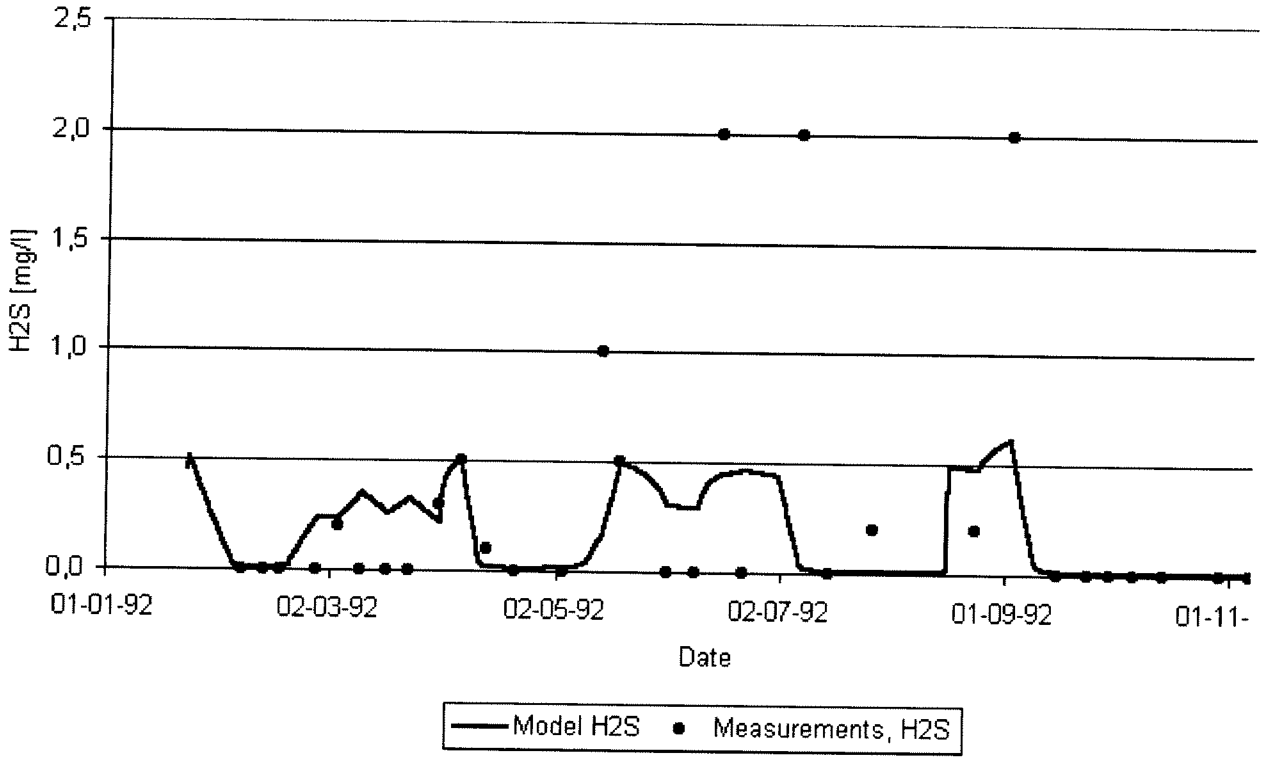


Figure 5: *Simulated and measured concentrations of hydrogen sulphide.*

The concentrations of hydrogen sulphide are successfully modelled compared to the measured data. periods the computed concentrations are within the same range as the measured data, while the moc some difficulty in predicting some of the peaks, which appear in the measured data.

Conclusion

The model presented in this paper is the first draft of a new series of anaerobic models. The model existing empirical equations with little or no possibility of performing a calibration of the model.

Moreover, the data available for creating a test set-up for the sulphide model was scarce. Only yearl averages of BOD and sulphate were available and therefore the model had difficulty in predicting s peaks in the hydrogen sulphide concentrations.

The overall hydrogen sulphide concentrations covering one year of simulations are, however, projec successfully, also taking the limited data into account. Some improvements have been identified an will be incorporated in the ongoing development of the present sulphide model.

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