

WATS – Wastewater Aerobic/Anaerobic Transformations in Sewers

MIKE ECO Lab Template

Scientific Description



DHI headquarters

Agern Allé 5
DK-2970 Hørsholm
Denmark

+45 4516 9200 Telephone
mike@dhigroup.com
www.mikepoweredbydhi.com

Company Registration No.: DK36466871

CONTENTS

WATS – Wastewater Aerobic/Anaerobic Transformations in Sewers MIKE ECO Lab Template Scientific Description

1	Introduction	1
2	Applications.....	3
2.1	Background	3
3	Mathematical Formulations	5
3.1	WATS Conceptual Process Model.....	5
3.2	Overview WATS MIKE ECO Lab Template	5
3.3	The WATS Process Matrix.....	7
3.4	State variables.....	9
3.5	Constants	10
3.6	Forcings.....	13
3.7	Auxiliaries	14
3.8	Derived outputs	17
3.9	Processes.....	17
3.9.1	Process 1: Growth of heterotrophic biomass in bulk liquid	21
3.9.2	Process 2: Growth of heterotrophic biomass in biofilm.....	21
3.9.3	Process 3: Maintenance of heterotrophic biomass under aerobic and anoxic conditions	22
3.9.4	Process 4: Hydrolysis (fast), particulate organic matter in the bulk liquid (n = 1)	22
3.9.5	Process 5: Hydrolysis (slow), particulate organic matter in the bulk liquid (n = 2).....	23
3.9.6	Process 6: Re-aeration of dissolved oxygen.....	24
3.9.7	Process 7: Anaerobic decay of heterotrophic biomass, X_{HW}	24
3.9.8	Process 8: Fermentation in the bulk liquid	25
3.9.9	Process 9: H ₂ S Formation	25
3.9.10	Process 10: Chemical Oxidation of sulphide	25
3.9.11	Process 11: Biological oxidation of sulphide	26
3.9.12	Process 12: Oxidation of sulphide in biofilm	26
3.9.13	Process 13: Emission of hydrogen sulphide to gaseous phase	27
3.9.14	Process 14: Precipitation of Iron Sulphide (FeS)	28
3.9.15	Process 15: Reduction of Iron (III) to Iron (II).....	30
3.10	Nomenclature	30
4	Data Requirements.....	35
5	References.....	37

1 Introduction

MIKE ECO Lab is a numerical laboratory for Ecological Modelling. It is a generic and open tool for customising aquatic ecosystem models to describe e.g. water quality and eutrophication. DHI's expertise and knowhow concerning ecological modelling has been collected in predefined ecosystem descriptions (MIKE ECO Lab templates), ready to be loaded and used in MIKE ECO Lab.

The MIKE ECO Lab templates describe physical, chemical and biological processes related to environmental problems and water pollution. The following is a description of the DHI WATS – Wastewater Aerobic/anaerobic Transformations in Sewers – MIKE ECO Lab model.

The WATS MIKE ECO Lab template supports investigations of the risk of formation of hydrogen sulphide in sewerage systems and for assessing various mitigation options. The WATS modelling approach can be applied in studies considering:

- Risk mapping of formation of hydrogen sulphide in collection systems (sanitary and combined) for entire sewer networks
- Odour and corrosion mapping including risk mapping of hazardous working areas for maintenance crew
- Hydrogen sulphide mitigation options including chemical dosing, air injection, optimal operation of pump and chemical dosing

The aim of using the WATS model as an instrument in impact assessment studies of the formation hydrogen sulphide is to obtain, most efficiently in relation to economy and technology, the optimal solution in regards to minimise the sewer infrastructure maintenance cost due to corrosion, minimise odour nuisances and ensure a safe working environment for maintenance crew.

The WATS model describes the biological processes in the sewerage system in one single model to determine how the transformation of organic matter and electron acceptors (oxygen, nitrate, sulphate) interact in sewers with special emphasis to determine the degree of hydrogen sulphide production (H_2S) in the sewer liquid phase.

The model results describe all the processes included in the WATS conceptual model over time. In addition, a number of relevant derived variables are computed stored, such as retention time ("water age").

The WATS model is integrated with the advection-dispersion module in MIKE 1D, which describes the physical transport processes at each grid-point covering the area of interest. The data required are wastewater flows from pollution sources and concentrations of relevant wastewater constituents, water temperature and pH.

2 Applications

The DHI WATS model template can be applied in a range of studies involving:

- Studies of the risk of formation of hydrogen sulphide causing odour and corrosion in wastewater collection systems
- Studies involving assessment of the wastewater point sources (industries, residential, commercial etc.) impact on the formation of hydrogen sulphide
- Studies with the aim of optimising the various mitigation options to control and minimise the risk of formation of hydrogen sulphide. Mitigation options may include chemical dosing, air injection, optimal pump operation, point source assessment
- Studies evaluating the potential human health risk for maintenance crew working within the collection system environment
- Studies focused on optimising the operation and infrastructure maintenance cost effectively
- Studies involving analysis of wastewater quality at inflows to wastewater treatment plants.

2.1 Background

In sewer systems numerous of processes are occurring due the fact that wastewater consists of nutrients, bacteria and plenty of organic matter. During the transport of wastewater to the wastewater treatment plant the wastewater is transformed by ongoing biological processes. Aerobic heterotrophic activity results in growth of biomass, which attach to the sewer walls as biofilm and starts to consume oxygen dissolved in the sewer liquid. Anaerobic conditions may occur in pressure mains, giving rise to bacteria species that convert sulphate to sulphide. Sulphide, when it takes the gas form hydrogen sulphide (H_2S) may be released to the sewer atmosphere, causing odour and corrosion problems.

The running water stream in gravity sewers re-aerates the wastewater flow, which keeps the oxygen concentration at a certain level and inhibits sulphide formation. An approach to determine the effect of all the interactions has been described in the model concept named **WATS** - Wastewater Aerobic/anaerobic Transformations in Sewers originally proposed by Aalborg University /1/. The purpose of collecting all biological processes in one single model complex is to determine how the transformation of electron donors (organic matter) and electron acceptors (oxygen, nitrate, sulphate) interact in sewers with special emphasis to determine the degree of hydrogen sulphide production (H_2S) in the water.

H_2S is a major problem in many sewer systems where wastewater is warm, the content of organic matter is high or the sewer system is designed in a way that quickly results in anaerobic condition (e.g. pressure mains). In countries with a hot climate (Middle East, Australia, USA, South East Asia etc. – in some cases even in Denmark) the H_2S formation problem is well known and causes severe economic cost in maintaining the infrastructure due to corrosion, odour nuisances and dangerous working environment conditions requiring expensive mitigation actions.

One way to prevent H₂S formation to take place in existing sewer systems is to add chemicals to the wastewater that either prevent sulphide to be produced or prevent the hydrogen sulphide gas to be released to the atmosphere after the sulphide has been generated. Chemical dosing solutions are already being sold commercially, but it can be difficult to know the impacts (operational and economical) of a certain dosing solution strategy since the chemical consumption is highly dynamic and depends on wastewater composition, hydraulic conditions, water age / retention time and the design of the sewer system.

3 Mathematical Formulations

3.1 WATS Conceptual Process Model

This MIKE ECO lab template is based on the WATS (**W**astewater **A**erobic/anaerobic **T**ransformation in **S**ewers) model, which is a flexible and conceptual model for simulation of sewer processes and thereby a predictive tool in terms of which problems may arise. This principle relies on collecting and integrating those segments of model-formulated details that in an actual case describes the relevant processes, the related in-sewer impacts, and their control.

The WATS model, expressed as mass balances via relevant coupled differential equations, is thereby ready for a numerical computation and simulation according to an actual objective, /1/.

Included in the WATS conceptual model is:

- The sulphur cycle
- Aerobic, heterotrophic transformations of organic matter
- Aerobic transformations of organic carbon and sulphur
- Anoxic, heterotrophic transformations of organic matter
- Aerobic and anaerobic transformations of organic carbon and sulphur

3.2 Overview WATS MIKE ECO Lab Template

The WATS MIKE ECO Lab template includes by the following components listed in Table 3.1:

Table 3.1 Overview of WATS MIKE ECO Lab template

Overview	Number
State variables ¹	14
Constants	47
Forcings	7
Auxiliaries	41
Processes ²	42
Derived outputs	1

- 1) 12 out of 14 state variables are subject to both transformation and transport processes, Temperature and acidity are only subject to transport
- 2) 21 out of 42 processes actually participate in transformations. The remaining 21 processes represent either several instances of the same process, or are introduced for some other practical reasons.

3.3 The WATS Process Matrix

The model matrix, Table 3.2, provides an overview of the included processes and their impacts on various state variables.

Table 3.2 The WATS process matrix

No	Process	Process code	X _{HW}	S _F	S _A	X _{S1}	X _{S2}	S _O	S _{NO3}	S(-II)	S _{SO4}	HS-	Fe(II)	Fe(III)	FeS	Process Rate	
1	Growth of biomass in bulk water phase	Aerobic: AGBW	1	$-\frac{1}{Y_{HW}}$				$-\frac{1 - Y_{HW}}{Y_{HW}}$									eq. 5.1
		Anoxic: AXBW	1	$-\frac{1}{Y_{HW}}$					$-\frac{1 - Y_{HW,NO3}}{2.86 \cdot Y_{HW,NO3}}$								eq. 5.28
2	Growth of biomass in biofilm	Aerobic: AGBF	1	$-\frac{1}{Y_{Hf}}$				$-\frac{1 - Y_{Hf}}{Y_{Hf}}$									eq. 5.3
		Anoxic: AXBF	1	$-\frac{1}{Y_{Hf}}$					$-\frac{1 - Y_{Hf,NO3}}{2.86 \cdot Y_{Hf,NO3}}$								eq. 5.30
3	Maintenance energy requirement	Aerobic: MAEN	-1 ^a	-1				-1								eq. 5.2	
		Anoxic: AXMA	-1 ^a	-1					$-\frac{1}{2.86}$							eq. 5.29	
4	Hydrolysis, fast	Aerobic: AEHF		1		-1										eq. 5.4, n=1	
		Anoxic: ANHF		1		-1										eq. 5.31 / eq. 6.21, n=1	
5	Hydrolysis, slow	Aerobic: AEHS		1			-1									eq. 5.4 n=2	
		Anoxic: ANFS		1			-1									eq. 5.31 / eq. 6.21, n=2	
6	Reaeration	REAE						1								eq. 4.39 + eq. 6 in table 4.3 ^b	

No	Process	Process code	X _{HW}	S _F	S _A	X _{S1}	X _{S2}	S _O	S _{NO3}	S(-II)	S _{SO4}	HS-	Fe(II)	Fe(III)	FeS	Process Rate
7	Decay of biomass, X _{HW}	DEBM	-1				1									eq. 6.23
8	Fermentation in the water phase	FEBW		-1	1											eq. 6.22
9	H ₂ S formation	HSFO		-2	-2	-2				1	-1					eq. 6.24
10	Chemical oxidation of sulphide	COSU						$-\frac{1}{R_{Cwc}^c}$		-1	1					eq. 5.13 & 5.14
11	Biological oxidation of sulphide	BOSU						$-\frac{1}{R_{Cwb}}$		-1	1					eq. 5.13 & 5.15
12	Oxidation of sulphide in biofilm	OXSB						$-\frac{1}{R_{Cfb}}$		-1	1					eq. 5.16
13	H ₂ S emission	HSRE								-1						eq. 4.40 & eq. 6 (table 4.3)
14	Iron Precipitation	PRFE										-1	-YFeS++ pH >= 8: YFeS = 1.75g/gS pH < 8: YFeS = -2.28*pH+20		88/32	
15	Fe ⁺⁺⁺ oxidation	REFE											1	-1		

^a If S_F + S_A is not sufficiently available to support the biomass maintenance energy requirement

^b Unit used: day⁻¹

^c Unit of R_c is here gSgO₂⁻¹

^d Equation numbering for process rates refers to the numbering in the book reference \1).

3.4 State variables

State variables represent various constituents and properties of wastewater, which may vary both spatial and temporal. All state variables are subject to the Advection-Dispersion transport mechanisms, and all of them, except acidity and temperature, are subject to transformation processes described in the WATS model.

The State Variables defined in the WATS MIKE ECO Lab template are listed in Table 3.3. A description, unit and expression is provided for each of the state variables.

Table 3.3 State Variables used in the WATS MIKE ECO Lab template

State Variable	Description	Unit	Expression
S_F	Fermentable and readily biodegradable organic products	mg/L	$\frac{dS_F}{dt} = -\frac{1}{Y_{HW}} * (AGBW + AXBW) - \frac{1}{Y_{Hf}} * (AGBF + AXBF) - MAEN - AXMA + AEHF + AEHS + ANHF + ANHS - FEBW - 2 * HSFO$
S_A	Organic fermentation products	mg/L	$\frac{dS_A}{dt} = -\frac{1}{Y_{HW}} * (AGBW + AXBW) - \frac{1}{Y_{Hf}} * (AGBF + AXBF) - MAEN - AXMA + AEHF + AEHS + FEBW - 2 * HSFO$
X_Hw	Heterotrophic active biomass in water phase	mg/L	$\frac{dX_{Bw}}{dt} = AGBW + AXBW + AGBF + AXBF - MAEN - AXMA - DEBM$
X_S1	Fast hydrolysable organic substrate	mg/L	$\frac{dX_{S1}}{dt} = -AEHF - ANHF - 2 * HSFO$
X_S2	Slowly hydrolysable organic products	mg/L	$\frac{dX_{S2}}{dt} = -AEHS - ANHS + DEBM$
S_O	Dissolved oxygen	mg/L	$\frac{dS_O}{dt} = -\frac{1 - Y_{HW}}{Y_{HW}} * AGBW - \frac{1 - Y_{Hf}}{Y_{Hf}} * AGBF - MAEN - \frac{1}{Rcwc} * COSU - \frac{1}{Rcwb} * BOSU - \frac{1}{Rcwb} * OXSB + REAE$

State Variable	Description	Unit	Expression
S_II	Total S H ₂ S+HS-	mg/L	$\frac{dS_{II}}{dt} = HSFO - COSU - BOSU - OXSB - HSRE - PRFE$
S_NO3N	Nitrate concentration in water phase	mg/L	$\frac{dS_{NO3N}}{dt} = -\frac{1 - Y_{HW,NO3}}{2.86 \cdot Y_{HW,NO3}} AXGW - \frac{1 - Y_{Hf,NO3}}{2.86 \cdot Y_{Hf,NO3}} AXBF - \frac{1}{2.86} AXMA$
S_SO4S	Sulphate concentration in water phase	mg/L	$\frac{dS_{SO4S}}{dt} = -HSFO + COSU + BOSU + OXSB$
X_Fe2	Fe ⁺⁺ concentration in water phase	mg/L	$pH < 8: \frac{dX_{Fe2}}{dt} = REFE - (-2.2823 \cdot pH + 20) \cdot PRFE$ $pH \geq 8: \frac{dX_{Fe2}}{dt} = REFE - 1.7416 \cdot PRFE$
X_Fe3	Fe ⁺⁺⁺ concentration in water phase	mg/L	$\frac{dX_{Fe3}}{dt} = - REFE$
X_FeS	Iron sulphide concentration in water phase (suspended)	mg/L	$\frac{dX_{FeS}}{dt} = 2.7416 \cdot PRFE$
pH	Acidity	pH	$\frac{dpH}{dt} = 0$
Temperature	Water temperature	deg. C	$\frac{dTemperature}{dt} = 0$

3.5 Constants

Constants are main controls of the process rate. Each of the processes includes at least one constant.

The constants defined in the WATS MIKE ECO Lab template are listed in Table 3.4. Each constant is provided with a default value, unit of value (for non-dimensionless constants) and description. Default values for the constants have been set according to the recommendations and suggestions found in available literature. Users must be aware that the default values may not be appropriate for the actual application and should be subject to a critical evaluation, mainly based on the wastewater composition.

All constants except **dt** (time step) and **dx** (distance between grid points in a conduit) are user defined and their values can be changed by the user during a calibration process. The values of **dt** and **dx** are provided by the hydraulic engine, MIKE 1D.

Table 3.4 Constants used in the WATS MIKE ECO Lab template

Constant ID	Default value	Unit	Description
A	0.013	$\text{g}^n/\text{m}^n \cdot \text{hour}$	Rate constant for sulfide formation
a_0	3e-010	m	Ion radius
alpha_f	1.05	-	Temperature coefficient for aerobic biofilm processes
alpha_oxygen	0.95	-	Correction factor for oxygen mass transfer dependency on wastewater constituents
alpha_sulfide	0.6	-	Correction factor for hydrogen sulfide mass transfer dependency on wastewater constituents
alpha_Sf	1.03	-	Temperature coefficient for sulfide formation in the biofilm
alpha_r	1.024	-	Temperature coefficient for reaeration
alpha_w	1.07	-	Temperature coefficient for heterotrophic, aerobic water phase processes
beta_reae	0.86	-	Correction factor equal to the ratio of solubility of O ₂ in wastewater to that of clean water
d_H_ana	0.4	day^{-1}	Decay rate constant for the aerobic heterotrophic under anaerobic condition
dH_FeS	-11000	Joule/mol	
Dt	Built-in	S	Time step (provided by hydraulic model)
Dx	Built-in	M	Grid spacing (provided by hydraulic model)
E_0	8.8542e-012	F/m	Permittivity of vacuum
E_a	0.15	gCOD/m^3	Efficiency constant for the biofilm biomass under aerobic conditions
E_an	0.15	-	Efficiency constant for the biofilm biomass under anaerobic conditions
e_charge	1.6022e-019	C	Elementary charge
Fe_mw	55.847	g/mol	Iron molar weight
H2S_to_O2_diff	0.92	-	Ratio of overall mass transfer of H ₂ S and O ₂
K_b	1.3806e-023	Joule/K	Boltzmanns constant
K_fe	20	gCOD/m^3	Saturation constant for fermentation. No scientific reference available. Suggested value (20)
K_Fe3	10	$\text{g Fe}^{+++}/\text{m}^3/\text{d}$	Rate of iron 3 reduction to iron 2
kFeS	0.3	$\text{m}^3 \cdot \text{gFe} \cdot \text{d}^{-1}$	Rate constant for precipitation of FeS
K_FeS25C	891.25	L/mol	Equilibrium concentration at 25 degrees
k_h1	5	day^{-1}	Hydrolysis rate constant, fast hydrolysable fraction
k_h2	0.5	day^{-1}	Hydrolysis rate constant, slowly hydrolysable fraction

Constant ID	Default value	Unit	Description
k_half	4	$\text{gO}_2^{0.5}/\text{m}^{0.5} \cdot \text{day}^{-1}$	Half order rate constant for aerobic growth in the biofilm
k_half_NO3	3	$\text{gNO}_3\text{-N}^{0.5}/\text{m}^{0.5} \cdot \text{day}^{-1}$	Half order rate constant for anoxic growth in biofilm
K_NO3	0.75	gN/m^3	Saturation constant for nitrate
K_O	0.1	gO_2/m^3	Saturation constant for dissolved oxygen
K_Sf	5	gCOD/m^3	Saturation constant for readily biodegradable substrate ($S_S=S_F+S_A$) in the biofilm
K_SO4	5	-	Constant for inhibition of sulfide production due to sulfate deficiency
K_Sw	1	gCOD/m^3	Saturation constant for readily biodegradable substrate ($S_S=S_F+S_A$) in the water phase
K_X1	1.5	gCOD/gCOD	Saturation constant for hydrolysis, fast hydrolysable fraction
K_X2	0.5	gCOD/gCOD	Saturation constant for hydrolysis, slowly hydrolysable substrate.
kH2Sc	0.04	$(\text{gSm}^{-3})(\text{gO}_2\text{m}^{-3}) \cdot \text{hour}^{-1}$	Rate constant for chemical sulfide oxidation of molecular sulfide H_2S
kHSc	0.5	$(\text{gSm}^{-3})(\text{gO}_2\text{m}^{-3}) \cdot \text{hour}^{-1}$	Rate constant for chemical sulfide oxidation of ionic sulfide, HS^-
kSIlb_opt	0.83	$(\text{gSm}^{-3})(\text{gO}_2\text{m}^{-3}) \cdot \text{hour}^{-1}$	Maximum rate constant for biological sulfide oxidation at the optimal pH = 8
kSIloxf	0.5	$(\text{gSm}^{-3})^{0.5} (\text{gO}_2\text{m}^{-3})^{-0.5} \text{m} \cdot \text{hour}^{-1}$	Rate constant for sulfide oxidation
mu_h	4.5	day^{-1}	Maximum specific growth rate for heterotrophic biomass
my_h_NO3	4	day^{-1}	Maximum specific anoxic growth rate for heterotrophic biomass in water phase
n_fe	0.14	-	Anaerobic hydrolysis reduction factor
n1	0.9	-	Reaction order (S) for chemical oxidation of sulfide.
n2	0.15	-	Reaction order (O) for chemical oxidation of sulfide.
OSIlb	25	-	Constant that determines the shape of the activity curve for sulfide oxidation versus pH.
P_atm	760	mmHg	Atmospheric pressure
pHopt	8	pH	optimum pH value for activity of sulfide oxidation
q_fe	3	day^{-1}	Maximum rate for fermentation
q_m	1	day^{-1}	Maintenance energy requirement rate constant
q_m_NO3	0.5	day^{-1}	Anoxic maintenance energy requirement rate constant
R	8.314	$\text{J}/(\text{K mol})$	
Rcwb	2	$\text{molS} / \text{mol O}_2$	Reaction coefficient for biological sulfide oxidation in bulk water and in biofilm
Rcwc	0.85	$\text{molS} / \text{molO}_2$	Reaction coefficient for chemical sulfide oxidation in bulk water

Constant ID	Default value	Unit	Description
X_Bf	10	gCOD/m ²	Heterotrophic active biomass in biofilm
Y_Hf	0.55	gCOD / gCOD	Biofilm yield constant for heterotrophic biomass
Y_Hf_NO3	0.35	gCOD / gCOD	Biofilm anoxic yield constant for heterotrophic biomass
Y_Hw	0.55	gCOD / gCOD	Suspended biomass yield constant for heterotrophic biomass
Y_Hw_NO3	0.35	gCOD / gCOD	Yield constant for anoxic growth of heterotrophic biomass in the water phase
Z_Fe	2	-	Iron ion valence
Z_HS	1	-	HS ion valence

3.6 Forcings

Forcings are external geometric and/or hydraulic variables associated with computational points (i.e. are spatially fixed), but variable in time, which affect some of the processes acting on the state variables.

The Forcings defined in the WATS MIKE ECO Lab template are listed in Table 3.5. All forcings are provided by the MIKE 1D hydraulic engine.

Table 3.5 Forcing - WATS MIKE ECO Lab template

Forcing	Description	Unit
Vraw	Water volume, represents bulk volume belonging to a grid cell	m ³
u	Flow velocity	m/s
Slope	Water surface slope	m/m
Surface_width	Water surface width	m
F_Area	Flow area	m ²
Rel_Depth	Relative depth, ratio between the actual depth (or pressure) and pipe diameter	[-]
Bed_Area	Wetted area belonging to a grid cell, represents active area of biofilm	m ²

3.7 Auxiliaries

The auxiliaries are variables defined to make equations more structured and easier readable. Selected auxiliaries defined in the WATS MIKE ECO Lab template are listed in Table 3.6.

Table 3.6 Auxiliaries - WATS MIKE ECO Lab template

Auxiliaries	Description	Unit	Expression
S_S	Readily biodegradable substrate	g/m ³	$S_S = (S_A + S_F)$
A_wp	Biofilm area, wet perimeter	m ²	$A_{wp} = \text{Bed_Area}$
d_m	Mean hydraulic depth	m	$d_m = \text{IF} \left(\frac{F_{\text{Area}}}{\text{Surface_width}} < 0.0001 \right) \left\{ \begin{array}{l} \text{THEN } \frac{0.001}{F_{\text{Area}}} \\ \text{ELSE } \frac{F_{\text{Area}}}{\text{Surface_width}} \end{array} \right.$
WaterVolume	Bulk water volume	m ³	$\text{WaterVolume} = V$
Fr	Froude Number	[-]	$Fr = \frac{u}{\sqrt{9.81 * d_m}}$
P	Changing unit of P_atm from mm.Hg to atm	atm	$P = \frac{P_{\text{atm}}}{760}$
ftemp_alphaT	Temperature correction for reaeration process	[-]	$f_{\text{temp_alphaT}} = \alpha_T(\text{Temperature} - 20)$
ftemp_alphaW	Temperature correction for heterotrophic, aerobic water phase processes	[-]	$f_{\text{temp_alphaW}} = \alpha_w(\text{Temperature} - 20)$
ftemp_alphaf	Temperature correction for aerobic biofilm processes	[-]	$f_{\text{temp_alphaf}} = \alpha_f(\text{Temperature} - 20)$
Tk	Temperature Kelvin	degree Kelvin	$Tk = (\text{Temperature} + 273.15)$
T2	Square temperature in degree Celsius	degree Celsius	$T2 = \text{Temperature}^2$
Tk2	Square temperature in degree kelvin	degree Kelvin	$Tk2 = Tk^2$
S_Os	Dissolved oxygen saturation concentration at T	gO ₂ /m ³	See Eq. (3.1) below this table

Auxiliaries	Description	Unit	Expression
K_La	Oxygen mass transfer coefficient	hour ⁻¹	$K_{La} = \frac{24 * 0.86 * (1+0.2*Fr^2) * ABS(slope * u)^{\frac{3}{8}}}{d_m}$
k_t	J coefficient	[-]	$k_t = 0.0000000912 * e^{\frac{0.0223}{8.3144} * \left(\frac{1}{298.15} - \frac{1}{(Temperature+273.15)} \right)}$
J	Proportion of H2S in dissolved sulphide	[-]	$j = \frac{\frac{10^{-pH}}{k_t} * 1}{\left(1 + \frac{10^{-pH}}{k_t} \right)}$
SulfideDis	Dissolved sulphide	gS/m ³	SulfideDis = MAX(0, S_II)
H2Sconc	H ₂ S Concentration	gH ₂ S/m ³	$H2Sconc = \frac{\frac{10^{-pH}}{k_t} * SulfideDis * 1}{\left(1 + \frac{10^{-pH}}{k_t} \right)}$
HSconc	HS concentration	gHS/m ³	HSconc = (SulfideDis - H2Sconc)
fsat1_SO	Oxygen inhibition	[-]	$fsat1_{SO} = IF((K_O+S_O) < 0.00001) \left\{ \begin{array}{l} THEN \quad 0 \\ ELSE \quad \frac{S_O}{(K_O+S_O)} \end{array} \right.$
fsat2_SO	Oxygen inhibition2	[-]	$fsat2_{SO} = IF((K_O+S_O) \leq 0) \left\{ \begin{array}{l} THEN \quad 0 \\ ELSE \quad \frac{K_O}{(K_O+S_O)} \end{array} \right.$
f_S1	Saturation function 1n	[-]	$f_{S1} = \frac{\frac{X_{S1}}{X_{Bw}}}{\left(K_{X1} + \frac{X_{S1}}{X_{Bw}} \right)}$
f_S2	Saturation function S2	[-]	$f_{S2} = \frac{\frac{X_{S2}}{X_{Bw}}}{\left(K_{X2} + \frac{X_{S2}}{X_{Bw}} \right)}$
f_BW_E_a	f_BW_E_a	[-]	$f_{BW_E_a} = IF(V \leq 0) \left\{ \begin{array}{l} THEN \quad 0.00001 \\ ELSE \quad \left(X_{Bw} + \frac{E_a * X_{Bf} * A_{wp}}{V} \right) \end{array} \right.$
f_BW_E_an	f_BW_E_an	[-]	$f_{BW_E_an} = IF(V \leq 0) \left\{ \begin{array}{l} THEN \quad 0.00001 \\ ELSE \quad \left(X_{Bw} + \frac{E_{an} * X_{Bf} * A_{wp}}{V} \right) \end{array} \right.$
Anox_sat1	Anox_sat1	[-]	$Anox_sat1 = IF((K_{NO3}+S_{NO3N}) \leq 0) \left\{ \begin{array}{l} THEN \quad 0 \\ ELSE \quad \frac{S_{NO3N}}{(K_{NO3}+S_{NO3N})} \end{array} \right.$
Anox_sat2	Anox_sat2	[-]	$Anox_sat2 = IF((K_{NO3}+S_{NO3N}) \leq 0) \left\{ \begin{array}{l} THEN \quad 0 \\ ELSE \quad \frac{K_{NO3}}{(K_{NO3}+S_{NO3N})} \end{array} \right.$

Auxiliaries	Description	Unit	Expression
Ka1	The first dissociation constant for sulphide 25C	[-]	$Ka1 = 10^{-7.1}$
kSIIC	pH dependent rate constant for chemical sulphide oxidation	[-]	$kSIIC = \frac{\left(kH2Sc + \frac{kHSc * Ka1}{10^{-pH}}\right)}{\left(1 + \frac{Ka1}{10^{-pH}}\right)}$
pHdif	Difference in pH between optimal pH and actual pH	[-]	$pHdif = IF((pHopt - pH) < 0) \begin{cases} THEN & (pH - pHopt) \\ ELSE & (pHopt - pH) \end{cases}$
kSIIB	pH dependent rate constant for biological sulphide oxidation	[-]	$kSIIB = \frac{kSIIB_{opt} * OSIIB}{(OSIIB + 10^{pHdif - 1})}$
Anox_sat3	Inhibition of sulphide production due to deficiency of sulphate	[-]	$Anox_{sat3} = IF((S_{SO4S} - K_{SO4}) \leq 0) \begin{cases} THEN & 0 \\ ELSE & \frac{S_{SO4S}}{(K_{SO4} + S_{SO4S})} \end{cases}$
fSIIB_pH	Factor for relative pH dependency	[-]	$fSIIB_{pH} = \frac{OSIIB}{(OSIIB + 10^{pHdif - 1})}$
ftemp_alphaSf	Temperature correction for sulphide formation process in biofilm	[-]	$ftemp_{alphaSf} = alpha_{Sf}^{(Temperature - 20)}$
Flow_Area	Flow_area_for output	m ²	$Flow_Area = F_Area$
Relative_depth	Relative depth for output	[-]	$Relative_depth = Rel_Depth$
Velocity	Velocity for output	m/s	$Velocity = u$
Surf_Width	Surface width for output	m	$Surf_Width = Surface_width$
Surface_slope	Slope for output	1/1	$Surface_slope = slope$

$$\begin{aligned}
 & P * e^{(7.7117 - 1.31403 * \ln((T + 45.93)))} * \left(1 - e^{\left(\frac{11.8571 - \frac{3840.7}{Tk} - \frac{216961}{Tk^2}}{P} \right)} \right) \\
 & \frac{(1 - (9.75 * 10^{-4} - 1.426 * 10^{-5} * T + 6.436 * 10^{-8} * T^2)) * P}{\left(1 - e^{\left(\frac{11.8571 - \frac{3840.7}{Tk} - \frac{216961}{Tk^2}}{P} \right)} \right)} \\
 S_{0s} = & \frac{\hspace{10em}}{(1 - 9.75 * 10^{-4} - 1.426 * 10^{-5} * T + 6.436 * 10^{-8} * T^2)} \tag{3.1}
 \end{aligned}$$

3.8 Derived outputs

Derived output are user specified variables, calculated out of state variables.

TotalCOD is defined as a sum of five constituents:

$$\text{TotalCOD} = S_F + S_A + X_Hw + X_S1 + X_S2$$

3.9 Processes

The processes implemented include sulphur transformation, precipitation, aeration, electron acceptor transformation and transformation of organic matter. The processes implemented in the current version, describe sulphur cycle in the water phase, both under aerobic and anoxic/anaerobic conditions. A complete overview of the transformation processes of the integrated aerobic-anoxic-anaerobic concept is illustrated in a principle diagram (**Error! Reference source not found.**).

Further in the chapter, description of all individual processes in full detail is provided.

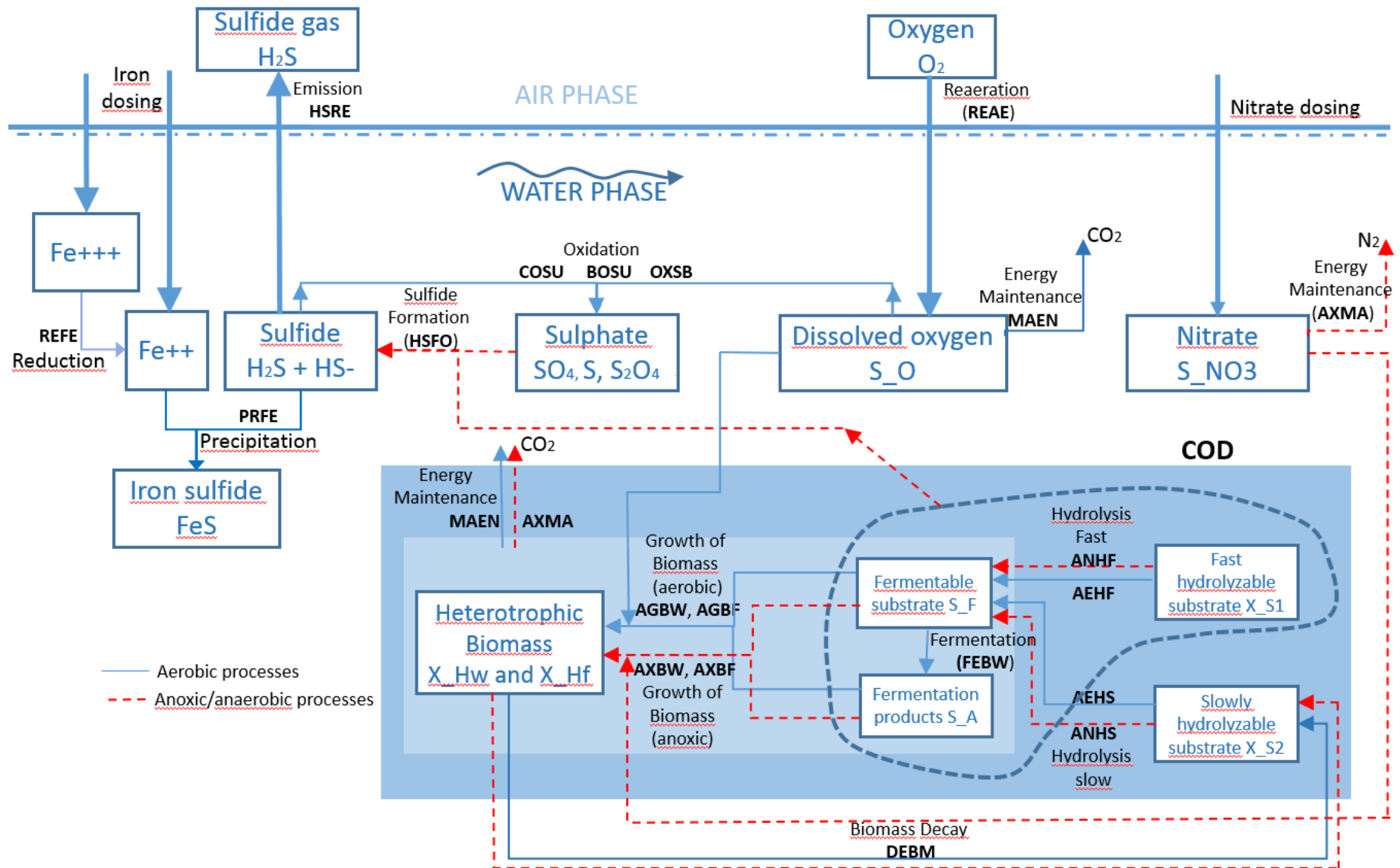


Figure 3.1 Actual implementation of the integrated wastewater aerobic-anaerobe WATS model concept for microbiological transformations of organic carbon and sulphur in sewers water phase

3.9.1 Process 1: Growth of heterotrophic biomass in bulk liquid

Growth of suspended heterotrophic biomass in bulk water under the limiting conditions of organic substrate and dissolved oxygen follows the classic Monod formulation. For this process to occur, fermentation products (S_A) and fermentable readily biodegradable substrate (S_F) are required in the sewage, as well as sufficient concentration of dissolved oxygen. The process intensifies by higher sewage temperatures. The main calibration parameter is the maximum specific growth rate constant (μ_{H,O_2}).

Aerobic growth rate (**AGBW**), adapted from /1/, eq.5.1:

$$r_{grw} = \mu_{H,O_2} \frac{S_F + S_A}{K_{S_w} + (S_F + S_A)} \frac{S_O}{K_O + S_O} X_{Hw} \alpha_w^{(T-20)} \quad (3.2)$$

The anoxic growth of heterotrophic biomass in bulk water is similar to the aerobic growth. The difference between the two processes is just that the terminal electron acceptor is nitrate instead of dissolved oxygen and the presence oxygen of oxygen will inhibit anoxic growth. Anoxic growth will have a specified maximum rate constant (μ_{H,NO_3}), which will be lower than the aerobic maximum specific growth rate constant (μ_{H,O_2}).

Anoxic growth rate (**AXBW**), adapted from /1/, eq.5.28:

$$r_{grw,anox} = \mu_{H,NO_3} \frac{S_F + S_A}{K_{S_w} + (S_F + S_A)} \frac{S_{NO_3}}{K_{NO_3} + S_{NO_3}} \frac{K_O}{K_O + S_O} X_{Hw} \alpha_w^{(T-20)} \quad (3.3)$$

3.9.2 Process 2: Growth of heterotrophic biomass in biofilm

Aerobic growth of biofilm, i.e. release of biomass from the biofilm to bulk liquid is mainly dependent on the dissolved oxygen content (0.5 order dependency). For this process to occur, fermentation products (S_A) and fermentable readily biodegradable substrate (S_F) are required in the sewage. The process is intensified by higher sewage temperatures. Biofilm yield (g_{COD} per g_{COD}) is considered as constant, i.e. biofilm is not changing. This process is associated with growth in biofilm area, but eq. (3.4) relates the process to the change of concentration in bulk water, in consistency with other equations.

The main calibration parameter is the half order rate constant for aerobic growth, $k_{1/2, NO_3}$.

Aerobic process rate (**AGBF**), adapted from /1/, eq.5.3:

$$r_{grf} = k_{1/2} S_O^{0.5} \frac{Y_{Hf}}{1 - Y_{Hf}} \frac{S_F + S_A}{K_{sf} + (S_F + S_A)} \frac{A}{V} \alpha_f^{(T-20)} \quad (3.4)$$

As with biomass growth in bulk water, anoxic process rate is similar to aerobic growth, just with nitrate as the terminal electron acceptor, instead of dissolved oxygen and the presence oxygen of oxygen will inhibit anoxic heterotrophic growth. The anoxic half-order rate constant $k_{1/2, NO_3}$ will be lower than the aerobic half-order rate constant.

Anoxic process rate (**AXBF**), adapted from /1/, eq.5.30:

$$r_{grf,anox} = k_{1/2,NO_3} S_{NO_3}^{0.5} 2.86 \frac{Y_{Hf,NO_3}}{1 - Y_{Hf,NO_3}} \frac{S_F + S_A}{K_{sf} + (S_F + S_A)} \frac{K_O}{K_O + S_O} \frac{A}{V} \alpha_f^{(T-20)} \quad (3.5)$$

3.9.3 Process 3: Maintenance of heterotrophic biomass under aerobic and anoxic conditions

Energy maintenance of heterotrophic biomass is proportional to the actual contents of the heterotrophic biomass and will occur under anoxic and aerobic conditions. The aerobic process slows down when dissolved oxygen decrease and stops fully under anoxic conditions.

The anoxic maintenance process slows down when nitrate decreases and stops fully under aerobic conditions. The process is intensified by higher sewage temperatures. The maintenance processes will initially degrade S_F and S_A and when the sum of these substrates gets low (set to 0.5 mg/L in the template), the maintenance process will use the biomass itself X_{HW} as carbon source.

The main calibration parameters is the maintenance energy requirement rate constants, q_{m, o_2} and q_{m, NO_3} .

Aerobic process rate (**MAEN**), adapted from /1/, eq.5.2:

$$r_{maint} = q_m \frac{S_O}{K_O + S_O} X_{Hw} \alpha_w^{(T-20)} \quad (3.6)$$

Anoxic process rate (**AXMA**), adapted from /1/, eq.5.29:

$$r_{maint,anox} = q_{m,NO_3} \frac{S_{NO_3}}{K_{NO_3} + S_{NO_3}} \frac{K_O}{K_O + S_O} X_{Hw} \alpha_w^{(T-20)} \quad (3.7)$$

3.9.4 Process 4: Hydrolysis (fast), particulate organic matter in the bulk liquid (n = 1)

Hydrolysis of particulate organic substrates produces readily biodegradable organic substrate important for the growth of the biomass. Fast aerobic hydrolysis is proportional to a combined content of heterotrophic biomass in bulk water and in biofilm (the latter corrected by the efficiency factor and converted to bulk water terms).

The fast hydrolysis processes of particulate organic matter occur under aerobic, anoxic and anaerobic conditions – each with a specific rate expressions as described below.

The main calibration parameter is the hydrolysis rate constant k_{hn} .

Aerobic process rate (**AEHF**), adapted from /1/, eq.5.4:

$$r_{hydr} = k_{hn} \frac{X_{Sn} / X_{Hw}}{K_{Xn} + X_{Sn} / X_{Hw}} \frac{S_O}{K_O + S_O} \left(X_{Hw} + \varepsilon X_{Hf} \frac{A}{V} \right) \alpha_w^{(T-20)} \quad (3.8)$$

Anoxic process rate (**ANFH**), adapted from /1/, eq.5.31:

$$r_{hydr,anox} = \eta_{h,anox} k_{hn} \frac{X_{Sn} / X_{Hw}}{K_{Xn} + X_{Sn} / X_{Hw}} \frac{S_{NO_3}}{K_{NO_3} + S_{NO_3}} \cdot \left(X_{Hw} + \varepsilon X_{Hf} \frac{A}{V} \right) \frac{K_O}{K_O + S_O} \alpha_w^{(T-20)} \quad (3.9)$$

Anaerobe process rate, adapted from /1/, eq.6.21:

$$r_{hydr,an} = \eta_{h,an} k_{hn} \frac{X_{Sn} / X_{Hw}}{K_{Xn} + X_{Sn} / X_{Hw}} \frac{K_O}{K_O + S_O} \frac{K_{NO_3}}{K_{NO_3} + S_{NO_3}} \cdot \left(X_{Hw} + \varepsilon X_{Hf} \frac{A}{V} \right) \alpha_w^{(T-20)} \quad (3.10)$$

3.9.5 Process 5: Hydrolysis (slow), particulate organic matter in the bulk liquid (n = 2)

Hydrolysis of particulate substrates produces readily biodegradable substrate important for the growth of the biomass. Slow aerobic hydrolysis is proportional to a combined content of heterotrophic biomass in bulk water and in biofilm (the latter corrected by the efficiency factor and converted to bulk water terms).

The slow hydrolysis processes of particulate organic matter occur under aerobic, anoxic and anaerobic conditions – each with a specific rate expressions as described below.

The main calibration parameter is the hydrolysis rate constant k_{hn} .

Aerobic process rate (**AEHS**), adapted from /1/, eq.5.4:

$$r_{hydr} = k_{hn} \frac{X_{Sn} / X_{Hw}}{K_{Xn} + X_{Sn} / X_{Hw}} \frac{S_O}{K_O + S_O} \left(X_{Hw} + \varepsilon X_{Hf} \frac{A}{V} \right) \alpha_w^{(T-20)} \quad (3.11)$$

Anoxic process rate (**ANHS**), adapted from /1/, eq.5.31:

$$r_{hydr,anox} = \eta_{h,anox} k_{hn} \frac{X_{Sn} / X_{Hw}}{K_{Xn} + X_{Sn} / X_{Hw}} \frac{S_{NO_3}}{K_{NO_3} + S_{NO_3}} \cdot \left(X_{Hw} + \varepsilon X_{Hf} \frac{A}{V} \right) \frac{K_O}{K_O + S_O} \alpha_w^{(T-20)} \quad (3.12)$$

Anaerobe process rate), adapted from /1/, eq. 6.21:

$$r_{hydr,an} = \eta_{h,an} k_{hn} \frac{X_{Sn} / X_{Hw}}{K_{Xn} + X_{Sn} / X_{Hw}} \frac{K_O}{K_O + S_O} \frac{K_{NO_3}}{K_{NO_3} + S_{NO_3}} \cdot \left(X_{Hw} + \varepsilon X_{Hf} \frac{A}{V} \right) \alpha^{(T-20)} \quad (3.13)$$

3.9.6 Process 6: Re-aeration of dissolved oxygen

The dissolved oxygen (**DO**) mass balance, and thereby the redox potential, of wastewater in sewer systems is fundamental for the course and extent of the microbial processes. The low solubility of oxygen in water, illustrated by a very high Henry's law constant, a relatively high resistance to mass transfer across the air-water interface, and a potential high removal rate of **DO** in wastewater are the major reasons why **DO** is often a limiting factor for the aerobic microbial processes.

A quantification of oxygen transfer across the air-water interface in a sewer, taking into account both process and system relevant parameters, is highly important and central for a quantification of the microbial processes.

In addition to the temperature, the oxygen transfer (i.e., the reaeration) is highly affected by the turbulence level of the wastewater, and the flow regime thereby also becomes an important factor [1].

The reaeration (**REAE**) can be expressed by the following equations, eq. (3.14), adapted from [1], eq.4.39, and eq. (3.15), adapted from [1] eq. 6 in Table 4.3:

$$F = \alpha K_{L,O_2}(20) \cdot (\beta \cdot S_{OS} - S_O) \cdot \alpha_r^{T-20} \quad (3.14)$$

$$K_L a(20) = K_{L,O_2}(20) = 0.86 \cdot (1 + 0.20 \cdot Fr^2) \cdot (s \cdot u)^{3/8} * d_m^{-1} \quad (3.15)$$

$$Fr = u \cdot (g \cdot d_m)^{-0.5} \quad (\text{Froude's number}) \quad (3.16)$$

3.9.7 Process 7: Anaerobic decay of heterotrophic biomass, X_{Hw}

The endogenous decay of biomass is, under aerobic conditions, expressed as a maintenance energy requirement. When it comes to anaerobic conditions decay or inactivation of the biomass may still be relevant to consider - but, typically, only if the biomass is exposed to long-term anaerobic conditions and the decay will use heterotrophic biomass as carbon source while producing particulate organic substrate (X_{S2}). The following expression for decay of biomass follows 1-order kinetics in the heterotrophic biomass concentration.

Rate of biomass decay (**DEBM**), adapted from [1], eq. 6.23:

$$r_d = d_{H,an} \frac{K_O}{K_O + S_O} \frac{K_{NO_3}}{K_{NO_3} + S_{NO_3}} X_{Hw} \alpha^{(T-20)} \quad (3.17)$$

3.9.8 Process 8: Fermentation in the bulk liquid

The anaerobic fermentation rate in the water phase and in the biofilm is expressed based on Monod kinetics for the fermentable substrate, S_F /1/.

Anaerobe process rate (**FEBW**) adapted from /1/, eq. 6.22:

$$r_{ferm} = q_{ferm} \frac{S_F}{K_{ferm} + S_F} \frac{K_O}{K_O + S_O} \frac{K_{NO_3}}{K_{NO_3} + S_{NO_3}} \left(X_{Hw} + \varepsilon X_{Hf} \frac{A}{V} \right) \alpha^{(T-20)} \quad (3.18)$$

3.9.9 Process 9: H₂S Formation

The biofilm sulphide formation rate transferred as a flux to the corresponding water phase is shown in eq. 6.24. The formulation of the rate expression follows 1/2-order kinetics (half-order kinetics depending on the sum of S_F , S_A and X_{S1}). The hydrogen sulphide formation is inhibited by the presence of oxygen and nitrate.

Biofilm hydrogen sulphide formation rate (**HSFO**) adapted from /1/, eq. 6.24:

$$r_a = a \sqrt{S_F + S_A + X_{S1}} \frac{K_O}{K_O + S_O} \frac{K_{NO_3}}{K_{NO_3} + S_{NO_3}} \frac{A}{V} \alpha^{(T-20)} \quad (3.19)$$

3.9.10 Process 10: Chemical Oxidation of sulphide

The reaction kinetics with respect to both sulphide and **DO** is at constant temperature and **pH** for both biological and chemical sulphide oxidation described by power functions. When appropriate, the indices c and b are used to describe chemical oxidation and biological oxidation, respectively /1/.

Rate of chemical sulphide oxidation (**COSU**); adapted from /1/, eq. 5.13:

$$r_{S(-II)c} = k_{S(-II)c} (C_S)^{n1} (C_O)^{n2} \quad (3.20)$$

The molecular form of sulphide (**H₂S**) is oxidized with a lower rate than the ionic form (**HS⁻**). This fact must be included in the formulation of the overall rate for chemical sulphide oxidation. In mathematical terms, this rate is therefore proportional with the sum of the oxidation rates for each of these two compounds.

The pH effect on the sulphide oxidation rate in wastewater is therefore closely related to the distribution between **H₂S** and **HS⁻**.

Referring to eq. (3.20), the rate constant for chemical oxidation, $k_{S(-II)c,pH}$, at varying pH values is formulated as, adapted from /1/, eq. 5.14:

$$k_{S(-II)c,pH} = \frac{k_{H_2S_c} + k_{HS^-c} \frac{K_{a1}}{10^{-pH}}}{1 + \frac{K_{a1}}{10^{-pH}}} \quad (3.21)$$

3.9.11 Process 11: Biological oxidation of sulphide

The reaction kinetics with respect to both sulphide and **DO** is at constant temperature and pH for both biological and chemical sulphide oxidation described by power functions. When appropriate, the indices **c** and **b** are used to describe chemical and biological oxidation, respectively /1/:

Rate of biological sulphide oxidation (**BOSU**), adapted from /1/, eq. 5.13:

$$r_{S(-II)} = k_{S(-II)} (C_S)^{n1} (C_O)^{n2} \quad (3.22)$$

$$k_{S(-II)b,pH} = k_{S(-II)b,pH_{opt}} f_{S(-II),pH} = k_{S(-II)b,pH_{opt}} \frac{\omega_{S(-II)b}}{\omega_{S(-II)b} + 10^{|pH_{opt}-pH|} - 1} \quad (3.23)$$

The kinetics of sulphide oxidation is complex. Eq. (3.22) is, in this respect, simple since - for biological oxidation - it does not include the biomass.

3.9.12 Process 12: Oxidation of sulphide in biofilm

Biological sulphide oxidation follows the half-order kinetics in terms of both sulphide and **DO** in the bulk water phase. At constant temperature and pH, the rate equation is therefore formulated as follows /1/:

Rate of oxidation of sulphide in biofilm (**OXSB**), adapted from /1/, eq. 5.16:

$$r_{S(-II),ox,f} = k_{S(-II),ox,f} S_{S(-II)}^{0.5} S_O^{0.5} \quad (3.24)$$

The temperature dependency of the sulphide oxidation rate in biofilms follows the Arrhenius equation with a temperature coefficient $\alpha = 1.03$. As also observed for the heterotrophic oxidation of organic matter, the temperature coefficient in biofilms is relatively low (limited by diffusion) compared with the corresponding value in the suspended water phase. The **pH** dependency of sulphide oxidation in biofilms is expressed in terms of a pH dependency factor, **fS(-II), pH**. The values of both **pHopt** and $\omega_{S(-II)b}$ is assumed to follow those for sulfide oxidation in the water phase /1/.

3.9.13 Process 13: Emission of hydrogen sulphide to gaseous phase

The mass transfer rate can be determined for an arbitrary volatile substance (e.g. such as H_2S), as given in eq. 24, or any similar expressions describing the exchange of volatile substances between the water phase and the gas phase. This process is a term that is a central element in any sewer process model including the sewer atmosphere. Examples where the emission plays a central role are hydrogen sulphide-induced concrete corrosion and odour problems related to VOC formation in collection systems.

It is important that the ratio between the mass transfer coefficients of two volatile substances is constant. This ratio relates to the corresponding diffusion coefficients for the two substances. In this respect, oxygen plays a central role as a reference substance, since an extensive knowledge on behaviour of oxygen has been accumulated through systematic reaeration experiments, which allows for a simple determination of the mass transfer coefficient for an arbitrary volatile substance.

Rate of sulphide emission (**HSRE**), adapted from /1/, eq. 4.40:

$$F = \alpha_{H_2S} K_{L,H_2S} (C_{L,H_2S} - H_{H_2S} C_{G,H_2S}) \cdot \alpha_r^{T-20} \quad (3.25)$$

Where, adapted from /1/, Example 4.5:

$$K_{L,H_2S}(20) = 0.92 \cdot K_{L,O_2}(20) \quad (3.26)$$

It is important to note that the concentration of sulphide in the air is assumed to be zero, thus reducing the eq. (3.25) in the actual implementation to:

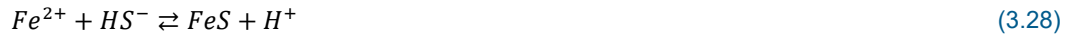
$$F = \alpha_{H_2S} K_{L,H_2S} C_{L,H_2S} \cdot \alpha_r^{T-20} \quad (3.27)$$

i.e. the sulphide emission is only made dependent on the actual sulphide concentration in the water phase. This simplification is a consequence of the fact that calculation of the sulphide concentration in the air phase is not included in the current WATS implementation in MIKE URBAN ECO Lab, and has been assumed zero. This does not compromise the importance of the sulphide emission process, as the computed scale of local sulphide emissions represent an important indicator for corrosion and odour-related problems.

For the temperature correction of sulphide emission process, the same value of α_r is applied as for reaeration (1.024). Researchers have found it vary between 1.021 (pH 7.0) and 1.029 (pH 6.5).

3.9.14 Process 14: Precipitation of Iron Sulphide (FeS)

Precipitation of FeS occurs through the following reaction:



Which can be described through the following equilibrium equations:

$$K_{FeS,25C} = \frac{\gamma_1[H^+]}{\gamma_2[Fe^{2+}]\gamma_1[HS^-]} = \frac{10^{-pH}}{\gamma_2[Fe^{2+}]\gamma_1[HS^-]} = 891.25 \frac{L}{mol} \quad (3.29)$$

$$C_{Fe,tot} = [Fe^{2+}] + [FeS] \quad (3.30)$$

If the calculated K , in the given conditions described by the water temperature and the concentrations of Fe^{++} and HS^- is smaller than the equilibrium value, the precipitation will occur.

If the calculated K exceeds the equilibrium value, there is no precipitation and FeS can be dissolved again. FeS dissolution is a slow process and will not be considered further.

The symbols in eq. (3.29) are:

[] : molar concentration of the ions
 γ_z : activity coefficient for the ion with valence z .

This is calculated as follows:

$$\log(\gamma) = -\frac{Az^2\sqrt{I}}{1 + Ba_0\sqrt{I}} \quad (3.31)$$

$$A = \frac{e^2 B}{2,303 \cdot 8\pi\epsilon_0\epsilon_r k_b T} \quad (3.32)$$

$$B = \sqrt{\frac{2e^2 N_A}{\epsilon_0\epsilon_r k_b T}} \quad (3.33)$$

$$I = \frac{1}{2} \sum c_i z_i^2 \quad (3.34)$$

Where:

a_0 ion radius (~0.3 nm)
 e elementary charge ($1.6022 \cdot 10^{-19}$ C)
 ϵ_0 permittivity in vacuum ($8.8542 \cdot 10^{-12}$ F/m)
 ϵ_r water relative permittivity (temperature-dependent but has value 78.4 at 25C)

Temperature dependency for clean water describes with the following equation, which is assumed to be an acceptable approximation:

$$\epsilon_r = 2.4921 \cdot 10^2 - 7.9069 \cdot 10^{-1}T + 7.2997 \cdot 10^{-4}T^2 \quad (3.35)$$

k_b Boltzmann's constant ($1.3806 \cdot 10^{-23}$ J/K)
 T absolute temperature (K)

N_A	Avogadro's constant ($6.022 \cdot 10^{23} \text{ mol}^{-1}$)
I	Ion strength
c_i	molar concentration (M) of ion i
z_i	valence of ion i

Equilibrium is corrected for the actual temperature:

$$K_{FeS,T} = K_{FeS,25C} \exp \left(-\frac{\Delta H_{FeS}}{R} \left(\frac{1}{T} - \frac{1}{(273.14 + 25)K} \right) \right) \quad (3.36)$$

where:

ΔH_{FeS}	-11000 (J/mol)
R	8.314 (J/(K mol))
T	absolute temperature (K)

FeS Precipitation Kinetics

Precipitation of FeS is a very fast, practically instantaneous process.

However, in presence of Fe^{+++} , the slow reduction of Fe^{+++} to Fe^{++} will control the rate of FeS precipitation. Consequently, assumption of the instantaneous precipitation is only valid for cases where Fe^{++} is applied.

In the current implementation, FeS precipitation achieves equilibrium in each time step. I.e., this means:

$K < K_{FeS} \Rightarrow$ precipitation until $K = K_{FeS}$

When $K > K_{FeS}$ the process reverses and FeS is dissolved back to Fe^{++} and HS^- . However, as indicated above, this process is slow and the precipitation is considered irreversible. A correct description of this process requires knowledge of its kinetics, which in turn is governed by the (unknown) particle size of the precipitated FeS . In the absence of reliable description of the process' empery it is practically impossible to describe this process correctly. A possible alternative would be to allow the re-dissolution occur immediately (as the precipitation).

Stoichiometry of the Fe^{++} precipitation

In the above equations it is assumed that the stoichiometry of the Fe^{++} precipitation is 1:1 (i.e. one Fe per one S). This is theoretically correct, but practical studies have shown that it is not always the case. The reason for this is not clear, but it may be assumed that iron precipitates also with other substances than sulfide.

There is clear dependency of the reaction yield with pH , for pH values above 8. In the current implementation the following dependency (in terms of weights) rules:

IF $pH > 8$ **THEN** $Fe^{++} / HS^- = 1.74$ **ELSE** $Fe^{++} / HS^- = -2.28 * pH + 20$

The number 1.74 is the ratio of atom weights of iron and sulfur.

Practical issues

Inclusion of the instantaneous precipitation in the overall process computation is implemented as follows:

1. Precipitation is considered to occur independently of the other processes affecting sulfide concentration. I.e. the concentrations of total sulfide and iron supplied by the transport model are first subject to precipitation until equilibrium is achieved.
2. As result of the precipitation, iron (Fe^{++}) is consumed to the level governed by the possible equilibrium, and a corresponding level of FeS is generated
3. Ionised part of total sulfide (HS^-) participates in the precipitation and is reduced to the possible equilibrium. After the precipitation, HS^- and H_2S remain in the same proportion as before the precipitation, which is controlled by the actual pH of wastewater.
4. The final sulfide concentration is calculated on the basis of remaining sulfide and the action of other relevant processes.
5. The process is automatically activated when Fe^{++} and HS^- are present in water in non-equilibrium concentrations. This can be achieved by adding Fe^{++} (MIKE ECO Lab state variable **X_Fe2**) or Fe^{+++} (MIKE ECO Lab state variable **X_Fe3**) through model boundaries into the water containing hydrogen sulfide.

3.9.15 Process 15: Reduction of Iron (III) to Iron (II)

Iron(III) (Fe^{+++}) does not participate in the precipitation of sulphide directly. However, if added to wastewater, Fe^{+++} will gradually transform into Fe^{++} .

The process rate (**REFE**) is assumed proportional to the concentration of Fe^{+++} and the process rate constant K_{Fe3} .

$$r_{re,Fe3+} = K_{Fe3} \cdot X_{Fe2} \quad (3.37)$$

3.10 Nomenclature

[x]	Molar concentration of x
α_{O_2}	Correction factor for wastewater constituents (-)
α_f	Temperature coefficient for the biofilm process (-)
α_{H_2S}	Correction factor for sulphide mass transfer dependency on wastewater constituents (-)
α_{O_2}	Correction factor for oxygen mass transfer dependency on wastewater constituents (-)
α_r	Temperature coefficient for reaeration and sulphide emission (-)
α_w	Temperature coefficient for the water phase process (-)
β	Correction factor equal to the ration of solubility of O_2 in wastewater to that of clean water (-)

γ_z	activity coefficient for the ion with valence z
ε	Relative efficiency constant for hydrolysis of the biofilm biomass (-)
ε_0	permittivity in vacuum ($8.8542 \cdot 10^{-12}$ F/m)
ε_r	Water relative permittivity (temperature-dependent but has value 78.4 at 25C)
$\eta_{h,anox}$	Efficiency constant for anoxic hydrolysis (-)
$\eta_{h,an}$	Efficiency constant for anaerobic hydrolysis relative to aerobic hydrolysis(-)
μ_{H,O_2}	Maximum specific growth rate (day^{-1})
μ_{H,NO_3}	Maximum anoxic specific growth rate (day^{-1})
$\omega_{S(-II)b}$	Constant that determines the shape of the activity curve for sulphide oxidation versus pH (-)
a	Rate constant for sulphide formation ($\text{g}^{0.5} \text{m}^{-0.5} \text{h}^{-1}$)
a_0	ion radius (~ 0.3 nm)
A	Wetted area associated with computational cell (m^2)
A/V	Wetted sewer pipe surface area divided by the water volume, i.e., R^{-1} , where R is the hydraulic radius (m^{-1})
$C_{L,A}$	Concentration of A in the water phase (g mL^{-3})
$C_{G,A}$	Concentration of A in the gas phase (g m^{-3})
C_O	Concentration of DO (g m^{-3})
C_S	Concentration of dissolved sulphide (g m^{-3})
d_m	Hydraulic mean depth (m)
e	Elementary charge ($1.6022 \cdot 10^{-19}$ C)
F	Rate of mass transfer of a volatile substance A ($\text{g A m}^{-3} \text{s}^{-1}$)
Fr	Froude number (-)
$f_{S(-II),pH}$	Factor for relative pH dependency (-)
g	Gravitational constant (ms^{-2})
H_A	Henry's law constant for arbitrary substance A (-)
$k_{1/2}$	$\frac{1}{2}$ -order rate constant per unit area of biofilm surface ($\text{g O}_2^{0.5} \text{m}^{-0.5} \text{day}^{-1}$)
$k_{1/2,NO_3}$	$\frac{1}{2}$ -order reaction rate constant per unit area of biofilm surface ($\text{g NO}_3\text{-N}^{0.5} \text{m}^{-0.5} \text{h}^{-1}$)
k_b	Boltzmann's constant ($1.3806 \cdot 10^{-23}$ J/K)
K_{Fe3}	Rate constant for iron(III) oxidation (day^{-1})
k_{hn}	Hydrolysis rate constant, fraction n (day^{-1})
k_{HS-c}	Rate constant for chemical sulphide oxidation of ionic sulphide, HS^- ($(\text{g S m}^{-3})^{1-n1c} (\text{g O}_2 \text{m}^{-3})^{-n2c} \text{h}^{-1}$)
k_{H_2Sc}	Rate constant for chemical sulphide oxidation of molecular sulphide, H_2S ($(\text{g S m}^{-3})^{1-n1c} (\text{g O}_2 \text{m}^{-3})^{-n2c} \text{h}^{-1}$)

$k_{S(-II)}$	Rate constant (unit depends on the values of n_1 and n_2)
$k_{S(-II)b,pH}$	pH-dependent rate constant for biological sulphide oxidation $((\text{g S m}^{-3})^{1-n_1b} (\text{g O}_2 \text{ m}^{-3})^{-n_2b} \text{h}^{-1})$
$k_{S(-II)b,pH_{opt}}$	Maximum rate constant for biological sulphide oxidation at the pH_{opt} value $((\text{g S m}^{-3})^{1-n_1b} (\text{g O}_2 \text{ m}^{-3})^{-n_2b} \text{h}^{-1})$
$k_{S(-II)c,pH}$	pH-dependent rate constant for chemical sulphide oxidation $((\text{g S m}^{-3})^{1-n_1c} (\text{g O}_2 \text{ m}^{-3})^{-n_2c} \text{h}^{-1})$
$k_{S(-II),ox,f}$	Rate constant for sulphide oxidation $((\text{g S m}^{-3})^{0.5} (\text{g O}_2 \text{ m}^{-3})^{-0.5} \text{m h}^{-1})$
K_{a1}	The first dissociation constant for sulphide: $K_{a1} = 10^{-7.1}$ (25°C)
K_{ferm}	Saturation constant for fermentation (g COD m^{-3})
K_{La}	($K_{La} = K_{L,O_2}$) Overall mass transfer coefficient for volatile substance a (s^{-1})
K_{NO_3}	Saturation constant for nitrate ($\text{g NO}_3\text{-N m}^{-3}$)
$K_{O_2 m}$	Saturation constant for DO ($\text{g O}_2 \text{ m}^{-3}$)
K_{sf}	Saturation constant for readily biodegradable substrate in the biofilm (g COD m^{-3})
K_{Sw}	Saturation constant for readily biodegradable substrate in the water phase $(\text{g O}_2 \text{ m}^{-3})$
K_{Xn}	Saturation constant for hydrolysis, fraction n (g COD g COD^{-1})
$n = n_1 + n_2$	Reaction order (unit dependent on n_1 and n_2)
pH	Wastewater acidity (-)
pH_{opt}	Optimum pH value for activity of sulphide oxidation (-)
q_{ferm}	Fermentation rate constant (day^{-1})
q_m	Maintenance energy requirement rate constant (day^{-1})
q_{m,NO_3}	Anoxic maintenance energy requirement rate constant (day^{-1})
r_a	Biofilm surface formation rate for sulphide ($\text{g S m}^{-3} \text{h}^{-1}$)
r_{ferm}	Fermentation rate ($\text{g COD m}^{-3} \text{day}^{-1}$)
r_{grf}	Growth rate of heterotrophic biomass in a biofilm ($\text{g COD m}^{-3} \text{day}^{-1}$)
$r_{grf,anox}$	The anoxic growth rate of heterotrophic biomass in a biofilm $(\text{g COD m}^{-3} \text{day}^{-1})$
r_{grw}	Growth rate of heterotrophic biomass in suspension $(\text{g COD m}^{-3} \text{day}^{-1})$
$r_{grw,anox}$	The anoxic growth rate of heterotrophic biomass in suspension $(\text{g COD m}^{-3} \text{day}^{-1})$
r_{hydr}	Rate of hydrolysis ($\text{g COD m}^{-3} \text{day}^{-1}$)
$r_{hydr,anox}$	Rate of anoxic hydrolysis in the water phase and in the biofilm $(\text{gCOD m}^{-3} \text{day}^{-1})$

$r_{hydr,an}$	Rate of anaerobic hydrolysis in the water phase and in the biofilm (g COD m ⁻³ day ⁻¹)
r_{maint}	Rate of maintenance energy requirement for biomass in suspension (g COD m ⁻³ day ⁻¹)
$r_{maint,anox}$	Rate of anoxic maintenance energy requirement for biomass in suspension (gCODm ⁻³ day ⁻¹)
$r_{S(-II)}$	Rate of sulphide oxidation (g S m ⁻³ day ⁻¹)
$r_{S(-II),ox,f}$	Biofilm surface specific sulphide oxidation rate (g S m ⁻³ h ⁻¹)
S	Water surface slope (m/m)
S_A	Volatile (fermentable) biodegradable substrate (g O ₂ m ⁻³)
S_F	Readily specific growth rate (day ⁻¹)
S_{NO_3}	Nitrate concentration in the water phase (g NO ₃ -N m ⁻³)
S_O	Dissolved oxygen (DO) concentration in bulk water phase (g O ₂ m ⁻³)
S_{OS}	DO concentration saturation concentration in bulk water phase (in equilibrium with the atmosphere) (g O ₂ m ⁻³)
$S_{(-II)}$	Dissolved sulphide concentration
T	Temperature (°C)
u	Mean flow velocity (m/s)
V	Bulk water volume, associated with computational cell (m ³)
Y_{Hf}	Biofilm yield constant (aerobe) for readily biodegradable substrate in biofilm (g COD / g COD)
Y_{Hf,NO_3}	Biofilm yield constant (anoxic) for heterotrophic biomass (g COD / g COD)
X_{Hf}	Heterotrophic biomass in the biofilm (g COD m ⁻²)
X_{Hw}	Heterotrophic biomass concentration in the water phase (g COD m ⁻³)
X_{Me}	Concentration of metal added to precipitate S
X_{MeS}	Concentration of precipitated Me
X_{Sn}	Hydrolysable substrate, fraction # n; $\sum n$ typically equals 2 or 3: n = 1 (fast degradable), n = 2 (slowly degradable)

4 Data Requirements

In order to apply the WATS template for the assessment of hydrogen sulfide formation in a sewer network the following is required:

- A calibrated hydraulic MIKE URBAN MIKE 1D model.
Correct description of the flow hydraulics (loads by wastewater and any other flow amount and its temporal variation, realistic pumping operations and description of the flow dynamics in gravitational network) is essential basis for the correct description of the advection-dispersion transport processes (mixing, dilution, resident time) and the transformation processes on the state variables.
- Definition of AD-components corresponding to the WATS template state variables:
 - Temperature
 - SO₄ (sulphate)
 - DO (dissolved oxygen)
 - Total HS
 - SF (Fermentable and readily biodegradable products)
 - SA (Fermentation products)
 - X_Bw (Heterotrophic active biomass in water phase)
 - X_S1 (Fast hydrolysable substrate)
 - X_S2 (Slowly hydrolysable products)
 - pH
 - NO₃_N (nitrate)
 - Fe₂ (2-valent iron)
 - Fe₃ (3-valent iron)
 - FeS (iron sulphide)

NOTE: AD-components naming is free, but the AD-components must be linked to the WATS template state variable

- General wastewater characteristics at the source (as constant or as time-variable wastewater boundary values):
 - Total COD, defined by its constituents:
 - SF (Fermentable and readily biodegradable products)
 - SA (Fermentation products)
 - X_Bw (Heterotrophic active biomass in water phase)
 - X_S1 (Fast hydrolysable substrate)
 - X_S2 (Slowly hydrolysable products)
 - pH
 - Temperature
 - SO₄ (sulphate)
 - DO (dissolved oxygen)
 - Total HS

If any of these wastewater constituents in the definition of the wastewater boundary are omitted, the model will assume a zero value.

Note that the definition of Total HS at a wastewater boundary is only relevant at places with inputs of wastewater already loaded with HS.

- Identification of any substantial point source discharging wastewater with significantly different characteristics, and its wastewater characteristics (as above)
- Chemical dosing (nitrate), as constant or as time-variable boundary values at the point(s) of dosing
 - NO₃_N (nitrate)
- Chemical dosing (iron) as constant or as time-variable boundary values at the point(s) of dosing
 - Fe₂ (2-valent iron) and/or Fe₃ (3-valent iron)

NOTE: boundary conditions describing dosing of nitrate and iron must be associated with a stream of water (default item). This should be made sufficiently small, so that it does not affect significantly the water volume balance and water quality characteristics of the sewer flow.

Application of MIKE ECO Lab WATS template with default values of process constants will provide a detailed insight to the locations and zones in the sewer network, which are at imminent risk of H₂S emissions, and as such subject to the corrosion and odour problems. The simulated concentrations of HS in water phase, as well as the H₂S emissions must be taken with due care, and treated as qualified estimates, rather than as correct absolute values. This is because the correct simulation of the actual conditions in the sewer network depends on the choice of the key parameters, whose optimal value may be different than default values provided may be significantly different than those applicable for the actual system.

Simulating addition (dosing) of nitrate as effective measure for prevention of sulphide formation and or addition of iron for sulphide precipitation, will provide an useful and very detailed information on the dosing effects and chemical residuals.

If the simulation results are to be used for the quantitative estimate of the relevant variables and serve as a decision basis for the implementation of mitigation measures, the model should be reasonably calibrated. For this purpose, a comprehensive program of field measurements and samplings/lab analyses should be designed and implemented, including:

- Measurements of hydrogen sulphide in the gaseous phase in the sewer atmosphere (e.g. inside pumping station wet wells, in gravity sewers immediately downstream long pressure mains, etc.). Please note that the actual concentrations are results of local H₂S release, transport of H₂S from adjacent locations in the sewer by the air movement and local ventilation conditions. As MIKE URBAN simulates only the local H₂S emissions (air movement, ventilation and any other relevant process in the air phase is not included), measurements of H₂S concentrations in the air cannot be directly used in the calibration, but only as indicators.
- Measurement / Lab analysis of hydrogen sulphide in the bulk liquid (e.g. in pumping station wet wells, in gravity sewers immediately downstream long pressure mains, etc.)
- Any other measurement or experience of locations of odour and corrosion in the system should be considered for usefulness and applied as appropriate.

By comparing the simulation results with measurements, the key constants may be adjusted so that the simulated result approach the measured values.

Please note that in the current implementation, values of the process constants may be adjusted only globally, i.e. affecting the entire model domain.

5 References

- /1/ /1/ Sewer Processes. Microbiological and Chemical Process Engineering of Sewer Networks, Second Edition. Thorkild Hvitved-Jacobsen, Jes Vollertsen, Asbjørn Haaning Nielsen, 2013. ISBN-13: 978-1-4398-8178-1

