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**Modelling Formation and Emission of Odourous Compounds
in Anaerobic Digesters**

by

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A thesis submitted under the supervision of Dr. Wayne Parker

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Abstract

A structured mathematical model of the formation of odourous compounds in anaerobic digesters has been developed in this study. The model describes the general mechanisms for the formation of four ubiquitous sulfur odorous compounds in anaerobic digesters: methyl mercaptan (MT), dimethyl sulfide (DMS), dimethyl disulfide (DMDS) and hydrogen sulfide (H_2S), in addition to VFA and ammonia (NH_3).

In anaerobic environments, the formation of VFA and NH_3 are generally produced by the fermentation processes. However, the formations of sulfur-containing odourous compounds are identified by six specific mechanisms, i.e. degradation of sulfur-containing amino acids, sulfate reduction, methylation reactions, MT oxidation to DMDS, degradation of VOSC and sulfide precipitation. For each process, the kinetic rate equations and kinetic coefficients are discussed. The model includes multiple-reaction stoichiometry, microbial growth kinetics and conventional material balances for an ideally mixed reactor.

Three physico-chemical processes, i.e. acid-base dissociation, liquid-gas mass transfer and liquid-solid partitioning, are addressed in the odour model. Dynamic rate equations are applied to describe the three physico-chemical processes.

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Nomenclature

AA	Amino acids
AB	Acetogenic bacteria
ADM1	Anaerobic Digestion Model No. 1
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
FB	Fermentative bacteria
DMDS	Dimethyl disulfide
DMS	Dimethyl sulfide
HRT	Hydraulic retention time
LCFA	Long chain fatty acids
MA	Methylation reaction
MAC	Methylated aromatic compounds
MB	Methanogenic bacteria
MS	Monosaccharides
MT	Methyl mercaptan
MW	Molecular Weight
SAA	Sulfur-containing amino acids
SR	Sulfate reduction
SRB	Sulfate reducing bacteria
VFA	Volatile fatty acids
VOA	Volatile organic acids
VOL	Volumetric organic loading
VOSC	Volatile organic sulfur-containing odourous compounds
VSS	Volatile suspended solids
WWTP	Wastewater treatment plant

List of Variables

Variables	Description	Units
S_{aa}	Amino acids	kg COD.m ⁻³
S_{hac}	Acetate acid	kg COD.m ⁻³
S_{ac^-}	Ionic acetate acid	kg COD.m ⁻³
S_{an}	Anions	M
S_{hbu}	Butyrate acid	kg COD.m ⁻³
S_{bu^-}	Ionic butyrate acid	kg COD.m ⁻³
S_{cat}	Cations	M
S_{ch4}	Methane	kg COD.m ⁻³
S_{co2}	Carbon dioxide	M
S_{hco3^-}	Bicarbonate	M
S_{DMDS_liq}	DMDS in liquid phase	M
S_{DMDS_sol}	DMDS in solid phase	M
S_{DMS_liq}	DMS in liquid phase	M
S_{DMS_sol}	DMDS in solid phase	M
S_{fa}	Long chain fatty acids	kg COD.m ⁻³
S_{h2}	Elemental hydrogen	kg COD.m ⁻³
S_{h^-}	Hydrogen ion	M
S_{oh^-}	Hydroxide ion	M
S_{H2S}	Hydrogen sulfide	mol S l ⁻¹
S_{HS^-}	Ionic hydrogen sulfide	mol S l ⁻¹
S_{pro^-}	Propionate acid	kg COD.m ⁻³
S_{hpro}	Ionic propionate acid	kg COD.m ⁻³
S_{va^-}	Valerate acid	kg COD.m ⁻³
S_{hva}	Ionic valerate acid	kg COD.m ⁻³
S_I	Soluble inerts	kg COD.m ⁻³
S_{MAC}	Methylated aromatic acids	kg COD.m ⁻³
S_{MIS}	Metal sulfides	M
S_{met}	Equivalent concentrations of total heavy metal which can precipitate hydrogen sulfide, such as Fe, Cu	M
S_{MT_liq}	MT in liquid phase	M
S_{MT_sol}	MT in solid phase	M
S_{nh3}	Ammonia	M
S_{nh4^-}	Ammonium	M
S_{SO4^-}	Sulfate	M
S_{su}	Monosaccharides	kg COD.m ⁻³
X_{aa}	Amino acid degrading organisms	kg COD.m ⁻³
X_{ac}	Acetate acid degrading organisms	kg COD.m ⁻³
X_C	Complex particulates	kg COD.m ⁻³
X_{C4}	Butyrate and valerate degrading organisms	kg COD.m ⁻³
X_{ch}	Particulate carbohydrates	kg COD.m ⁻³
X_{fa}	Long chain fatty acid degrading organisms	kg COD.m ⁻³

List of Variables

Variables	Description	Units
X_{h_2}	Hydrogen degrading organisms	kg COD.m ⁻³
X_I	Particulate inerts	kg COD.m ⁻³
X_{li}	Lipids	kg COD.m ⁻³
X_{pr}	Proteins	kg COD.m ⁻³
X_{pro}	Propionate acid degrading organism	kg COD m ⁻³
X_{SRB_ac}	SRB_ac degrading organisms	kg COD.m ⁻³
X_{SRB_pro}	SRB_pro degrading organisms	kg COD.m ⁻³
X_{SRB_ac}	SRB_h2 degrading organisms	kg COD.m ⁻³
X_{su}	Monosaccharide degrading organisms	kg COD.m ⁻³

Chapter 1: Introduction

1.1 Background Information

Anaerobic digestion consists of the solubilization and reduction of complex organic substances by microorganisms in the absence of oxygen. The biogas produced during anaerobic digestion can replace fossil fuel sources and therefore reduce the emission of greenhouse gas into the air, which will ensure the ongoing and popularity of anaerobic digestion processes for waste treatment in the future.

However, anaerobic conditions will always have some odours emitted. Many different compounds have been associated with odours from wastewater treatment plant (WWTP) and biosolids facilities. It is generally considered that odour emission is related to the formation of sulfur and nitrogen containing odourous compounds, such as hydrogen sulfide, VOSC, ammonium and amines. Other organic compounds, including volatile organic acids (VOA), aldehydes and ketones, can also contribute to the odour but to a much less level compared with sulfur and nitrogen odourants. Table 1.1 lists the most prevalent odour causing compounds from WWTP and biosolids facilities. From Table 1.1, there are mainly three groups of odourous compounds emitted from WWTP facilities, i.e. sulfur containing odourous compound, nitrogen containing odourous compounds and other volatile organic compounds. It is commonly believed that sulfur containing compounds are the most common odourous compounds released from WWTP and biosolids facilities, followed by nitrogen containing compounds and other organic

Table 1.1: Characteristics and thresholds of most prevalent odourants (Vincent and Hobson, 1998)

Substances	Compound	Odour description	Odour threshold (ppb)
Sulfurous	Hydrogen sulfide	Rotten eggs	0.5
	Methyl mercaptan	Decayed cabbage, garlic	0.0014-18
	Ethyl mercaptan	Decayed cabbage	0.02
	Sulfur dioxide	Pungent, acidic	
	Dimethyl sulfide	Decayed vegetables .	0.12-0.4
	Dimethyl disulfide	Putrefaction	0.3-11
Nitrogenous	Ammonia	Sharp, pungent	130-15300
	Methylamine	Fishy, rotten	0.9-53
	Ethylamine	Ammonical	2400
	Dimethylamine	Fish	23-80
	Pyridines	Disagreeable, irritating	
	Scatole	Faecal, repulsive	0.002-0.6
Others	Indole	Faecal, repulsive	1.4
	Acetic	Vinegar	16
	Butyric	Rancid	0.09-20
	Valeric	Sweat	1.8-2630
	Formaldehyde	Acid, suffocating	370
	Acetaldehyde	Fruit, apple	0.005-2
	Butyraldehyde	Rancid, sweaty	4.6
	Isobutyraldehyde	Fruit	4.7-7
	Valeraldehyde	Fruit, apple	0.7-9
	Acetone	Fruit sweet	4580
	Butanone	Green apple	270

compounds. Digester offgas typically has the highest hydrogen sulfide and VOSCs concentration of any gas stream at a WWTP and biosolids treatment plant. The release of unpleasant odours from waste treatment facilities can have an impact on the local

population. Public concerns over the release of odours from these facilities have increased in recent years. Consequently, careful management is required to avoid the creation and release of annoyance odours during waste treatment.

To avoid the formation of odourous compounds requires an understanding of the processes involved. To control and prevent their release, the mechanisms by which odours are formed and then released into the atmosphere must be understood. Anaerobic digestion takes place in a complex system and proceeds in one or more of the three phases: the wastewater (liquid) phase, the suspended solid phase and the gas phase and by exchange of relevant substances between these phases. Processes that participate in anaerobic digestion are shown in Figure 1.1.

Figure 1.1 Processes participating in anaerobic digesters

Although the odour phenomenon and associated control strategies for many years have been of concern when dealing with wastewater and biosolids collection and treatment, the pathways and conditions for odour formation in anaerobic digestion system have not been addressed at a detailed level. No conceptual basis for a general description of odour formation and corresponding formation modeling exists. Therefore, there is a need to develop an odour model, which can correctly describe the pathways of the formation and degradation of odourous compounds and partitioning of the odourous compounds between the three phases in anaerobic digestion systems.

In order to develop an odour model, Anaerobic Digestion Model Number 1 (ADM1) as a common platform for anaerobic process modelling and simulation is introduced. ADM1 is the outcome of general anaerobic process analysis, modeling and simulation done by a number of international experts. However, the specific pathways of the formation and degradation of the main odourants and partitioning of these odourants between the three phases are not described in ADM1. In this study, a structured mathematical model of the odourants formation and partitioning between the liquid, solid and gas phases will be presented.

1.2 Objectives of the Study

The main objective of this study is to develop a mathematical model, which can correctly describe the pathways of formation and degradation of the odourous compounds and

partitioning of these odourants between the liquid, solid and gas phases in anaerobic digesters. Once developed, the following actions were taken:

- Identifying the sensitivity of parameters used in the odour model
- Analyzing the effect of the environmental factors, such as Temperature, HRT and VOL, on the odour model.

Chapter 2: Literature Review

2.1. Introduction

This study would focus on modelling the formation and partitioning between the liquid-gas phase and liquid-solid phases of odourous compounds in anaerobic digestion of municipal sludges. Therefore, the main purposes of the literature review were (1) to define the odourous compounds emitted from anaerobic digesters, (2) to identify the pathways of formation of the odourous compounds under anaerobic conditions, (3) to describe the partitioning between the three phases (gas, liquid and solid).

2.2 Original Components of Wastewater

The compounds contributing to the smell of WWTP and biosolid facilities come from the original components in wastewater, the biochemical changes that take place and the chemicals that may be added as part of the treatment processes. The smell of fresh wastewater results from its components, which consists of a mixture of discharges from toilets, baths, sinks, dishwashers and washing machines, and industrial wastes. Fresh wastewater rarely causes a major odour problem unless potential complainants are located very close to an open discharge. The mixture of odourous chemicals typically contains:

- A wide range of aliphatic, aromatic and chlorinated hydrocarbons derived from cleaning agents used in the home (such as toluene, limonene, aromatic benzene derivatives, saturated aliphatic hydrocarbons C9 and C14, xylene, phenol),
- Solvents (such as chlorinated hydrocarbons),
- Petrol derivatives (such as benzene),
- Odours associated with human wastes such as urea and ammonia from urine and skatole and indole (breakdown products of tryptophan) from faeces.

Most volatile organic carbons (VOC), originating from discharges of solvents or petrochemicals, have a relatively low solubility. Therefore, some VOC will be adsorbed onto primary sludge and may be released during subsequent mesophilic anaerobic digestion and other heated processes. Other components of the wastewater may also increase the potential for generation of odours in downstream treatment process. Adverse discharges are:

- Strong, putrescible wastes from the food industry,
- Sulfate-containing wastewater or infiltrated ground water,
- Seawater infiltration (due to its high content of sulfate and the presence of essential trace nutrients),

Typically, sulfur and nitrogen-containing compounds are the significant sources of odour emitted from WWTP and biosolid facilities. The studies of Boon (1995) and Cheremisinoff (1988) show that domestic wastewater typically contains about 3-6 mg/l organic sulfur, derived mainly from proteinaceous material, and can contain further

organic sulfur in form of sulfonates (about 4 mg/l), derived from household detergents. Inorganic sulfur, in the form of sulfate, is present in quantities depending on the hardness of the water, typically in concentrations of 30-60 mg/l. Considerable higher concentrations of sulfate may result from infiltration water or industrial sources (Harkness, 1980). Nitrogen sources in domestic wastewater are urine, proteins and amino acids (Bonnin *et al.*, 1990).

The literature indicates that the original components of wastewater have a great potential to produce odorous compounds. Under aerobic and anoxic conditions, malodorous compounds are oxidized, which rarely cause a major odour problem. Under anaerobic conditions, the potential odorous-producing compounds precede a series of complex biological reaction and emit odourants into the gas phase.

2.3 Odorous Compounds

A number of organic compounds known as potential odour-producing substances have been identified in wastewater and biosolids. Odour emissions from anaerobic digesters are a function of a variety of chemical, biological and physical processes. In general, these processes either generate the odorous compounds or alter the form or rate of emissions. The offgas from anaerobic digesters can emit a wide variety of odorous compounds. Many papers in the literature review address the odourants emitted from WWTP and biosolids facilities. Typically, these odorous compounds are sulfur and nitrogen-containing compounds, volatile organic acids, aldehydes and ketones. Vincent and Hobson (1998) summarize the main odorous compounds emitted from WWTP and

biosolids facilities in Table 1.1. The specific odourous compounds studied in this project were selected from Table 1.1.

A survey performed by Islam *et al.* (1998) indicated that sulfur-containing compounds were the most prevalent odourous components emitted from WWTP and biosolids processing facilities. They measured 16 sulfur and nitrogen-containing compounds in liquids from various processes in WWTP and biosolids treatment plants in Japan. As expected, anaerobic conditions promoted higher concentrations of these compounds and sulfur-containing compounds were more prevalent than nitrogen-containing compounds. The sulfur-containing odourous compounds in the offgas from anaerobic digesters are measured and documented in many papers (such as WEF MOP 22, 1995; Huang, 1993 and Higgins *et al.*, 2002). Studies from Clanton and Schmidt (2000) and Nakasaki *et al.* (1998) revealed that most of the emanating sulfurs were in the forms of H_2S , MM, DMS and DMDS. From their research, the amount of these four sulfur compounds emitted was over 96% of the total emanating sulfurs. Therefore, these four ubiquitous sulfur-containing odorous compounds were identified as the main odourous compounds evaluated in this study.

Ammonia is one of the odourous gases produced from anaerobic digestion. Besides creating an odour problem, ammonia volatilization has become a major ecological concern because volatilized ammonia tends to be oxidized by various oxidants in the air to produce nitrous oxides, which are widely recognized as being major contributors to acid rain (Xue *et al.*, 1998). It is because of this problem that the escape of ammonia is severely restricted in some parts of the world. VFA, i.e. valerate (HV_a), butyrate (HBu),

propionate (HPr), and acetate (HAc) are normally produced as metabolic intermediates or end-products of degradation of proteins. They normally don't cause serious odour problem because VFA have a relatively high threshold value (Table 1.1) and a relatively low tendency to be emitted at a neutral pH value. However, since VFA and ammonia are generally associated with anaerobic treatment and in particular with the treatment of sewage sludge (Bonnie *et al.*, 1990), VFA and ammonia, in addition to the four-sulfur containing odourous compounds, were selected as the subjects of this odour model.

2.4 Basic Anaerobic Microbial Processes

Anaerobic digestion is typically carried out in a completely mixed reactor. The organic material entering anaerobic digesters is a mixture of primary settled and activated sludges. The role of microorganisms in anaerobic digestion is mainly the removal of BOD, the coagulation of nonsettleable colloidal solids and the stabilization of organic matter (Tchobanoglous and Burton, 1991). Meanwhile, the odourous compounds are also produced by the activity of these microorganisms. Anaerobic digestion systems are dominated by the activity of heterotrophic microorganisms. The presence of the heterotrophic biomass in biosolids is central to the biochemical processes in anaerobic digesters. The heterotrophic biomass make use of the organic matter in the sludge for two fundamental purpose: the organic matter is the carbon source for formation of cell material and it is – as an electron donor – the energy source need for the growth process and for maintenance of the fundamental functions of the existing biomass.

The common biological conversion of organic matter in treatment plant sludges is considered to occur in three steps (Figure 2.1). These processes are normally catalyzed by

intra- or extracellular enzymes and act on the pool of available organic material. Referring to Figure 2.1, the first step involves the enzyme-mediated transformation (hydrolysis) of higher-molecular-mass compounds into compounds suitable for use as a source of energy and cell carbon. The second step (acidogenesis and acetogenesis) involves the bacterial conversion of the compounds resulting from the first step into lower-molecular-mass intermediate compounds. The third step (methanogenesis) involves the bacterial conversion of the intermediate compounds into simpler products, principally methane and carbon dioxide.

Figure 2.1: Schematic diagrams of the patterns of carbon flow in anaerobic digestion

In a digester, a consortium of anaerobic organisms work together to bring about the conversion of organic sludges and wastes. One group of organisms is responsible for hydrolyzing organic polymers and lipids to monosaccharides, amino acids and related compounds. A second group of anaerobic bacteria ferments the breakdown products to simple organic acids. These microorganisms are often identified in the literature as “acidogens”. A third group of microorganisms converts the hydrogen and acetic acid formed by the acidogens to methane gas and carbon dioxide. The bacteria responsible for this conversion are strict anaerobes and are called “methanogens”.

The three steps are the basic and most important microbial processes occurring during anaerobic digestion. All other microbial processes are either based on or incorporated with these three steps. Therefore, most of the mathematical models developed for anaerobic digestions focus on describing the three basic steps. ADM1, developed by the IWA task group, provides a platform for further developing the odour model.

2.5 ADM1

The IWA Anaerobic Digestion Model No. 1 (ADM1) is the outcome of an intensive and fruitful collaboration among a number of international experts in anaerobic process analysis. ADM1 tries to be as widely applicable as possible for anaerobic processes so that it could provide a common basis for further model development (Batstone, *et al.*, 2002).

In this study, ADM1 was coded in the program of AQUASIM 2.0. The program AQUASIM is a computer program designed for the identification and simulation of aquatic systems in laboratory, technical plants and in nature. It was provided by the Swiss Federal Institute for Environmental Science and Technology (EAWAG). The intention behind the design of the program AQUASIM is to provide a universal identification and simulation tool for the important aquatic systems in the environmental sciences. An additional important criterion of AQUASIM is user-friendliness, which is achieved not only by providing a graphical user interface, but also by utilizing a communication “language” familiar to environmental scientists. AQUASIM is extremely flexible in allowing the user to specify transformation processes, and, in addition to perform simulations for the user-specified model, it provides elementary methods for parameters identification analysis, parameters estimation and uncertainty analysis. AQUASIM performs four tasks: simulation, identifiability analysis, parameter estimation and uncertainty analysis. Identifiability and uncertainty analysis are combined to yield sensitivity analysis. (Reichert, 1998)

ADM1 simulates the basic processes occurring during anaerobic digestion and was coded using the program AQUASIM software. In this study, an AQUASIM file containing the ADM1 model was downloaded from the website: http://www.awmc.uq.edu.au/download/ADM1_0_5.zip, along with a steady state excel file (using solver in the Vessels and MB plane) for verification.

2.5.1 Model Structure

ADM1 is a structured model with disintegration and hydrolysis, acidogenesis, acetogenesis and methanogenesis steps. The COD flow chart as used in ADM1 is shown in Figure 2.2.

Figure 2.2: Schematic diagram of COD flux used in ADM1

Referring to Figure 2.2, the COD partitioning and flux could change considerably for different primary components or for different product fractions from monosaccharide and amino acid acidogenesis. The values presented in Figure 2.2 are typical values. Comparing Figure 2.1 and Figure 2.2, it can be seen that ADM1 addressed the three basic processes occurred in anaerobic digestions. The only difference between Figure 2.1 and Figure 2.2 is that ADM1 increased a disintegration step before the hydrolysis occurred. Extracellular solubilization steps in ADM1 are divided into disintegration and hydrolysis, of which the first is a largely non-biological step and converts composite particulate substrate to inerts, particulate carbohydrates, proteins and lipids. The second is enzymatic hydrolysis of particulate carbohydrates, proteins and lipids to monosaccharides, amino acids and long chain fatty acids (LCFA), respectively. Disintegration is mainly included in the degradation of composite particulate material with lumped characteristics (such as primary or waste-activated sludge), while the hydrolysis steps describe well defined, relatively pure substrates (such as cellulose, starch and protein feeds).

2.5.2 Kinetic Rate

The disintegration and hydrolysis processes are represented in ADM1 by first order kinetics, which can be expressed as:

$$r_{dis} = k_{dis} \cdot X_C \quad (2.1)$$

Where,

r_{dis} = the rate of disintegration ($\text{kg COD m}^{-3} \text{ d}^{-1}$)

k_{dis} = first order disintegration coefficient of complex particulate, 0.5 d^{-1} .

X_C = concentration of complex particulate (kg COD m^{-3})

$$r_{hyd,i} = k_{hyr} \cdot X_i \quad (2.2)$$

Where,

$r_{hyr,i}$ = the rate of hydrolysis of particulate component i (i represent carbohydrate, proteins and lipids) (kg COD m⁻³ d⁻¹)

k_{hyr} = first order hydrolysis coefficient , the value of which is same for all components, 10 d⁻¹.

X_i = concentration of particulate component i (kg COD m⁻³)

Substrate-based uptake Monod-type kinetics are used as the basis for all intracellular biochemical reactions in ADM1, which can be expressed as:

$$r_i = k_{m,i} \cdot \frac{S_i}{K_s + S_i} \quad (2.3)$$

Where,

r_i = Monod uptake rate of component i (kg COD m⁻³ d⁻¹)

$k_{m,i}$ = Monod maximum specific uptake rate (d⁻¹)

S_i = concentration of substrata i (kg COD m⁻³)

$K_{s,i}$ = half saturation constant of substrate i (kg COD m⁻³)

Death of biomass is represented by first order kinetics, and dead biomass is maintained in the system as composite particulate material.

$$r_{dec,i} = k_{dec} \cdot X_i \quad (2.4)$$

Where,

$r_{dec,i}$ = the decay rate of biomass i, (kg COD m⁻³ d⁻¹)

k_{dec} = first order decay coefficient , the value of which is same for all biomass, 0.02 d⁻¹.

X_i = concentration of biomass i (kg COD m^{-3})

Inhibition functions in ADM1 include pH (all groups), hydrogen (acetogenic groups) and free ammonia (acetoclastic methanogens). The biochemical rate coefficients ($v_{i,j}$) and kinetic rate equations (r_j) used in ADM1 are presented in Appendix A.

2.5.3 Formation of VFA and NH_3

The formation processes of VFA and NH_3 are described in ADM1. From Figure 2.2, it could be seen that VFA and NH_3 are generated from the degradation of monosaccharides, amino acids and long chain fatty acids. Acidogenesis (fermentation) is generally defined as an anaerobic acid-producing microbial process without an additional electron acceptor or donor (Gujer and Zehner, 1983). This includes the degradation of soluble sugars and amino acids to a number of simpler products. The most important products of the degradation of monosaccharides are listed in Table 2.1.

Table 2.1 Main reactions of monosaccharides degradation

Products	Reaction	
Acetate Acid	$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH + 2CO_2 + 4H_2$	(2.5)
Propionate Acid	$C_6H_{12}O_6 + 2H_2 \longrightarrow 2CH_3CH_2COOH + 2CO_2 + 4H_2O$	(2.6)
Acetate Acid Propionate Acid	$C_6H_{12}O_6 \longrightarrow 4CH_3CH_2COOH + 2CH_3COOH + 2CO_2 + 2H_2O$	(2.7)
Butyrate Acid	$C_6H_{12}O_6 \longrightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$	(2.8)

There are 18 common amino acids, the relative yields of amino acids produced from the hydrolysis of protein are dependent on the protein primary structure (Bonnin *et al.*,1990). The degradation of amino acids is a complicated process, of which a large number of intermediates can be produced. The end products of degradation of amino acids are typically VFA, CO₂, H₂ as well as NH₃, which can be expressed as:

The degradation of LCFA and higher acids to acetate is an oxidation reaction with an external electron acceptor and is therefore included in acetogenesis (as opposed to acidogenesis). The organisms oxidizing the organic acid are required to use an additional electron acceptor such as hydrogen ion or carbon dioxide to produce hydrogen gas or formate respectively. The final carbon-containing product of fatty acids with even number of carbon atoms is acetate only. When the fatty acid has an odd number of carbon atoms (e.g. valerate acid, C₅), one mole of propionate is produced per mole of substrate. Most naturally occurring LCFA have an even number of carbon atoms (Gunstone, 1996) and acetate can be regarded as the major carbon product from this substrate.

2.5.4 Physico-Chemical Processes

The physical-chemical system can be defined as non-biologically mediated processes that commonly occur in anaerobic reactors. Mechanisms included to describe physico-chemical processes in ADM1 are acid-base reactions (to calculate concentration of

hydrogen ions, free ammonia and carbon dioxide), and non-equilibria liquid-gas transfer. Liquid-solid partitioning and solid precipitation has not been included in ADM1.

ADM1 has been developed as a generic model for anaerobic processes, therefore, the most common anaerobic processes, such as hydrolysis, acetogenesis and methanogenesis, are assessed in ADM1. It provides a useful tool for engineers to develop some specific model of anaerobic processes for certain applications. The odour model developed in this study is based on the ADM1 model.

2.6 Formation of Odourous Compounds

The formation of VFA and NH_3 has been addressed in ADM1. Hence, this section focuses on the formations of the four sulfur-containing odourous compounds. Kadota and Ishida (1972), Ferchichi *et al.* (1985), Oho *et al.* (2000) and Persson *et al.* (1990) revealed the pathways of formation of sulfur-containing odourous compounds under anaerobic conditions. Here, these papers are summarized and the main pathways of formation of sulfur odourous compounds are presented in Figure 2.3.

Figure 2.3: Schematic diagram of the main pathways of sulfur odourants in anaerobic digesters

According to Figure 2.3, there are six biochemical processes involved in the formation of sulfur-containing odourous compounds in anaerobic digesters: (1) the degradation of sulfur-containing amino acids; (2) sulfate reduction process; (3) methylation reaction; (4)

oxidation MT to DMDS; (5) sulfide precipitation; and (6) the degradation of VOSC. The final production of each sulfur-containing odourous compound is a combined effect of the six biochemical processes.

2.6.1 Degradation of Sulfur-Containing AA

Hydrolysis of proteins leads to the production of sulfur containing amino acids, i.e. methionine $[\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{CH}_2\text{SCH}_3]$ and cysteine $(\text{SHCH}_2\text{CH}_2\text{NH}_2\text{COOH})$. Under anaerobic conditions, the degradation of cysteine and methionine leads to the production of both hydrogen sulfide and VOSC (Oho *et al.*, 2000).

The studies of Kadota and Ishida (1972), Ferchichi *et al.* (1985), Marshall (1990), Taylor and Kiene (1989) and Higgins *et al.* (2002) indicate that methionine is mainly converted to MT, with some DMS and DMDS. A large number organisms that are involved in VOSC production from methionine, such as *Aspergillus sp*, *Aspergillus oryzae* and *Fusarium culmorum* etc. have been isolated from activated sludge (Tomita *et al.*, 1987).

Microbial processes for MT formation from methionine under anaerobic conditions are summarized in Table 2.2. Three different mechanisms have been detected. Methionine γ -lyase catalyzes the simultaneous $\alpha\gamma$ -elimination of NH_3 and MT from methionine (Table 2.2, reaction 2.10). Methionine γ -lyase has been purified from several species including aerobes and anaerobes. There is evidence for a pathway with deamination of methionine prior to reductive demethiolation (Table 2.2, reaction 2.11). There have been reports for

2-aminobutyrate and MT formation from methionine, indicating reductive demethiolation without the elimination of ammonia (Table 2.2, reaction 2.12).

Table 2.2 Microbial processes for MT formation from methionine (Taylor, 1989)

$\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{SH} + \text{NH}_3 + \text{CH}_3\text{CH}_2\text{COCOOH} \quad (2.10)$	
	2-Ketobutyrate
$\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{SCH}_2\text{CH}_2\text{COCOOH} + \text{NH}_3 + 2\text{H}^+ \quad (2.11)$	
	2-keto-4-methiobutyrate
$\text{CH}_3\text{SCH}_2\text{CH}_2\text{COCOOH} + 2\text{H}^+ \longrightarrow$	$\text{CH}_3\text{SH} + \text{CH}_3\text{CH}_2\text{COCOOH}$
2-keto-4-methiobutyrate	2-Ketobutyrate
$\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH} + 2\text{H}^+ \longrightarrow \text{CH}_3\text{SH} + \text{CH}_3\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH} \quad (2.12)$	
	2-Aminobutyrate

Methionine as a precursor for DMS and DMDS has been reported in some papers. However, the specific microbial processes for the formation of DMS and DMDS from methionine are not well addressed. Generally, there are two pathways for the formation of DMS and DMDS during degradation of methionine (Figure 2.4). Comparing the pathways in Figure 2.4, the first pathway considers MT as a direct precursor for the formation of both DMS and DMDS. It is generally agreed that DMDS arises from MT by oxidation which can probably occur both chemically and biochemically. However, no objective data on the formation of DMDS from MT have been reported. In order to simplify the degradation process of sulfur-containing amino acids, the second pathway was selected in this study to describe the degradation of sulfur-containing odorous compounds.

(1)

(2)

Figure 2.4: Formation of DMS and DMDS from methionine

Cysteine, as another sulfur containing amino acids, is mainly converted to hydrogen sulfide under anaerobic conditions (Gostelow, *et al.*, 2000; Kadota and Ishida, 1972; Lomans *et al.*, 2001). Organisms associated with formation of hydrogen sulfide from cysteine, such as *Pseudomonas sp.* and *Escherichia coli*, have been found in activated

sludges. A simplified pathway for the hydrolysis of cysteine is shown below (Harkness, 1980):

The literature review on the degradation of sulfur containing amino acids reveals that the formation of VOSC results mainly from the degradation of methionine and the formation of hydrogen sulfide results mainly from the degradation of cysteine. Both methionine and cysteine have been shown to be present in proteins extracted from activated sludges and anaerobically digested sludges (Higgins and Novak, 1997; Dignac *et al.*, 1998). Meanwhile, organisms associated with the formation of VOSC and H₂S from methionine and cysteine have been isolated from biosolids. Therefore, the offgas from anaerobic digesters will inevitably contain H₂S and VOSC.

2.6.2 Sulfate Reduction

The reduction of sulfates by sulfate-reducing bacteria (SRB) with the production of hydrogen sulfide is the most important process of the odour-generating reactions. SRB are heterotrophic bacteria, which “respire” sulfate to provide energy for the dissimilation of organic matter and release sulfides into solution (Postgate 1959, 1984). They are strict anaerobes, which grow at a slower rate than aerobic microorganisms. While oxygen or nitrate is present, SRB cannot function. However, they can survive adverse conditions of temperature, aerobic, salinity and pressure, and are ready to become active whenever

local conditions become anaerobic (Lens *et al.*, 1995). SRB are present within wastewater, sludges and in anaerobic digestion processes.

In anaerobic reactors treating sulfate-containing wastewater or biosolids, both sulfate reduction and methanogenesis can be the final steps in the degradation process. Substrate competition in anaerobic digesters is possible on three levels: competition between SRB and FB for sugars and amino acids; competition between SRB and acetogenic bacteria (AB) for VFA and ethanol; and competition between SRB and MB for acetate and hydrogen. A study by Widdel (1998) showed that the competition for the first level is won by the very fast growing FB and sulfate reduction with sugars and amino acids plays an unimportant role. Therefore, reduction of sulfate using sugars as its substrates was not considered in this study. Thermodynamic and Monod-kinetic data of SRB, AB and MB for growth on VFA and hydrogen indicate that SRB should be able to out-compete AB and MB (Houten *et al.* 1994). This prediction has been confirmed experimentally for hydrogen (Alphenaar *et al.* 1993; Mulder 1984; Houten *et al.* 1994) and for VFA (Alphenaar *et al.* 1993; 1997; Visser *et al.* 1993). Because there are many kinds sulfate reducing bacteria in anaerobic digesters, which can use various VFA and H_2 as their substrates to produce H_2S , it was not possible for the odour model to describe all the pathways of sulfate reduction. Hence, propionate, acetate and hydrogen, three common products under anaerobic conditions, were selected as the substrates used by SRB to produce H_2S . Correspondingly, there will be three groups of SRB (i.e. SRB1, SRB2 and SRB3) to use propionate ($CH_3CH_2CH_2COOH$), acetate (CH_3COOH) and hydrogen (H_2), respectively, were identified to form H_2S . The general simplified reaction sequence by

which the chosen substrates are transformed by the different groups of SRB can be presented as (on a molar basis):

Thus, according to the stoichiometric scheme (Equations 2.14-2.16), the conversion process is carried out by three trophic bacteria groups: the group SRB1 contains all propionate-degrading sulfate-reducing bacteria; SRB2, all acetotrophic sulfate-reducing bacteria; and SRB3, all hydrogenotrophic sulfate-reducing bacteria.

Excellent papers (i.e. Kalyuzhnyi *et al.*, 1998; Vincent, 2001; Higgins *et al.*, 2002) are published on the production of hydrogen sulfide by sulfate reducing bacteria. The pathways and conditions of formation of H_2S by SRB are described in these papers. The literature review on production of H_2S by SRB gave the best and most accurate information of those obtained by this literature review.

2.6.3 Methylation Reaction

The term methylation originally defines a process whereby living organisms cause a methyl group to become directly bonded through a carbon atom to one or more heavy

elements (Fatoki, 1997). In this study, it is used to refer to when organisms use sulfide as the methyl group acceptor, resulting in the formation of MT and DMS, respectively. The methylation reaction is a mechanism of formation of VOSC that has been discovered relatively recently. Several authors (Drotar *et al.* 1987; Bak and Finster, 1992; Lomans *et al.*, 2001) have observed formation of MT and DMS during degradation of methoxylated aromatic compounds and concluded that this was caused by the methylation of sulfide and MT. Drotar *et al.* (1987) demonstrated that MT could be formed enzymatically from sulfide by many heterotrophic bacteria in different habitats. Bak and Finster (1992) reported that anaerobic enrichment cultures (such as samples from freshwater and marine sediments) supplemented with methoxylated aromatic acids (3,4,5-trimethoxybenzoic acid or syringic acid) generated intense MT and DMS production. Two strictly anaerobic rod-shaped bacteria, which produced DMS and MT during growth on methoxylated aromatic compounds, were isolated in their studies. Formation of MT and DMS was not observed when the same organisms were cultivated with aliphatic substrates or aromatic substrates lacking methoxyl groups (e.g., pyruvate, phloroglucinol or gallic acid). In addition, during growth on sulfide-free dithionite-reduced medium, DMS and MT were not produced. Therefore, methoxylated aromatic compounds are especially important precursors for MT and DMS. A study of Lomans *et al.* (2001) showed various anaerobic bacteria performing sulfide-mediated O-demethoxylation, which result in VOSC formation, have been isolated from various habitats. In contrast to other homoacetogenic bacteria, which transfer the methyl groups of methoxylated aromatic compounds to CO to produce acetate, these organisms can also use sulfide and MT as the methyl group acceptors, resulting in the formation of MT and DMS, respectively. Since methoxylated

aromatic compounds are degradation products of lignin, a common compound in wastewaters and biosolids, this mechanism for VOSC production is likely to be important in anaerobic digestion systems.

During methylation reactions, organisms can transfer the methoxyl group to H_2S and MT to form MT and DMS, respectively. MT may occur only transiently and in significantly lower concentrations. The appearance of MT only as an intermediate indicates a stepwise methylation of hydrogen sulfide with MT as a first reaction product (Bak and Finster, 1992) (R= aromatic residue):

1. Methylation of sulfide:

2. Methylation of MT:

Sum:

The reaction that will dominate the methylation processes depends on the available sulfur pools of the habitats. For example, marine sediments are characterized by high sulfate concentrations that can contribute to a high rate of sulfate reduction, which sometimes results in substantial accumulation of H_2S . Therefore, the methoxyl group will be preferentially captured by H_2S that is present in excess. Only occasionally will some of the formed MT react with the methyl-group donor to form DMS. In contrast, H_2S concentrations in freshwater sediments are often undetectable. The majority of the

formed MT can be methylated to DMS because H₂S is limiting. This explains why marine sediments mainly produce MT and freshwater sediments produced DMS.

Most research on methylation that was reviewed in this study was performed in the anoxic sediments (i.e. freshwater and marine sediments), but the bacteria isolated from these habitats are anaerobic organisms. Therefore, it is reasonable to assume that these bacteria can also exist in anaerobic digesters. Since methoxylated aromatic compounds are common in biosolids, the formation of VOSCs by methylation reactions is likely to occur in anaerobic digesters and to be as important as the pathways of degradation of sulfur containing amino acids. Methylation reactions provide a reasonable mechanism for the formation of VOSCs, but the biochemical pathways and the enzymes involved in these methylation reactions are not well understood. Very few papers reported the kinetic data on the methylation reaction and the information provided by these papers was generated in anoxic sediments. Therefore, the methylation mechanism is relatively poor in understood.

2.6.4 MT Oxidation to DMDS

During their studies of methylation reaction, Lomans, *et al.*, (1997) and Bak and Finster (1992) indicated that small quantities of DMDS were produced. The presence of DMDS always coincided with high concentration of MT, which can be expressed as:

It is generally agreed that DMDS arises from MT by an oxidation, which probably occurs both chemically and biochemically. Taylor and Kiene (1989) observed variation in the relative rates of MT and DMDS production during growth of different bacteria. Presumably, some species enzymatically catalyzed the conversion of MT to DMDS. However, no known microbial pathway (in non-marine systems) has been found for the production of DMDS. Data suggests that the oxidation of MT to DMDS can be catalyzed by metals such as copper and iron under both aerobic and anaerobic conditions. Since these metals are often presented in biosolids, it is likely that DMDS formation can be through this type of reaction.

2.6.5 VOSCs Degradation

The formation of VOSC is in all cases followed by intense formation of methane, indicating that degradation of VOSCs occurs as rapidly as their formation. Several papers in this study reported that anaerobic degradation of VOSC has been mainly attributed to the activity of methanogens, SRB, anoxygenic phototrophs and denitrifying bacteria. Because the last two groups of bacteria are not likely to exist in the anaerobic digesters, they were not considered in this study. Zinder and Brock (1978) first illustrated methanogenic conversion of VOSC to methane and carbon dioxide in lake sediment slurries. Later, a study of Kiene *et.al.* (1986) on catabolism of MT, DMS and DMDS confirmed that addition of VOSC to a diversity of anoxic aquatic sediments (e.g. fresh water, eaturine, alkaline) stimulated methane production. Bak and Finster (1992) succeeded in isolating a methanogenic bacterium in pure culture that was able to grow

with MT as sole source of energy and carbon and confirmed that methanogens contribute to the degradation of VOSC. Lomans *et al.* (2001) reported that several methanogens, such as *Ms. siciliae* and *Ms. acetivorans*, were able to use DMS as a substrate. These organisms were isolated from marine, estuarine and salt lake habitats. They also isolated a DMS-degrading bacterium (*Ms. barkeri*) from anaerobic wastewater digesters, indicating that the degradation of VOSC may occur in anaerobic digestion systems.

Although it has been demonstrated that methanogens played an important role in catabolism of VOSC, the pathways for the degradation of DMS and DMDS are not clear. Kinene *et al.* (1986) discovered that MT was produced as a consequence of DMS and DMDS metabolism in their study of metabolism of VOSC. Therefore, two possible pathways can occur during the degradation of DMS and DMDS (Figure 2.5).

Figure 2.5: Pathways of the degradation of DMS and DMDS

In pathways (1) (Figure 2.5), methanogens first reduce DMS and DMDS to MT and methane, and then MT is subsequently degraded to CO₂ and H₂S. In order to simplify the process, the second pathway was selected in this study to describe the degradation of DMS and DMDS.

The stoichiometric conversions of VOSC are as following:

1. Degradation of MT:

2. Degradation of DMS:

3. Degradation of DMDS:

The possible role of SRB in the degradation of DMS and MT mainly originates from inhibitor studies. From inhibitor studies with marine and estuarine sediments, Kiene *et al.* (1986) concluded that methanogenic and sulfate-reducing bacteria competed for DMS at concentrations lower than 10 µM, while methanogens dominated DMS degradation at higher concentrations. Only one pure culture of a sulfate reducing bacterium growing on DMS has been isolated from a thermophilic digester by the study of Tanimoto and Bak (1994). The strain oxidizes DMS to CO₂ and sulfide. The reaction was as following:

Because the degradation of VOSCs by SRB is not as important as that performed by methanogens and only few papers provided information on VOSC degradation by SRB, the degradation of VOSC by SRB was not included in this study.

The literature review indicated that methanogens play an important role in the degradation of VOSC. In the following studies, methanogens were selected as the only organisms that degraded VOSC. The degradation of VOSC reported in papers generally occurred in an anoxic environment. Therefore, the kinetic data used to develop the odor model may not exactly reflect the degradation processes of VOSC in anaerobic digesters.

2.6.6 Sulfide Precipitation

Sulfide precipitation is often used as a strategy to control odour emissions. Ferric chloride (FeCl_3) can be added to wastewater to precipitate sulfide and prevent H_2S from being available for odour production (Higgins et al., 2002). In this study, sulfide precipitation referred to the precipitation of sulfide by heavy metals in the biosolids.

Heavy metals (e.g. Fe^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} , Cu^+) have a strong effect on odour emissions from anaerobic digesters. Heavy metals can chemically combine with dissolved sulfide to form relatively insoluble metal sulfides, which precipitate from the liquid phase. The precipitation process can be expressed as:

Approximately 0.5 mg of sulfide is needed to precipitate 1 mg of heavy metals (Malina, 1992; Parkin and Owen, 1986). Concentrations of heavy metals in municipal sludge may vary widely according to the upstream wastewater treatment processes. Table 2.3 indicated the typical heavy metal content in municipal sludge.

Table 2.3: Typical heavy metal content in wastewater sludge (EPA, 1984)

Metal	Dry sludge mg/kg	
	Range	Median
Cadmium	1-3410	10
Chromium	10-99000	500
Copper	84-17000	800
Iron	1000-154000	17000
Zinc	101-49000	1700

2.7 Odour Emission

This section will discuss the most important physico-chemical processes occurring in anaerobic digesters. Generally, three major physico-chemical phenomena must be dealt with in anaerobic digestions:

- Acid-base association/dissociation
- Liquid-gas mass transfer process
- Liquid-solid partitioning process

The physico-chemical system is important when modelling anaerobic systems because:

- A number of biological inhibition factors can be expressed (such as pH, free acids and bases, concentrations of soluble gases in the liquid phase);
- Major performance variables such as gas flow and the concentrations of odourous compounds in the gas phase are dependent on correct estimation of physico-chemical processes

The theory on acid-base dissociations and the mass transfer between the liquid and gas phase have been addressed in many books and papers. However, the theory on the more complicated partitioning process (i.e. liquid-solid partitioning) is not fully developed.

2.7.1 Acid-Base Dissociation

The acid-base dissociation process can significantly affect the concentrations of odourous compounds in the gas phase because only the molecular form is released to the gas phase and the acid-base dissociation constant can determine the ratio of the concentrations of odourous compound between its molecular and ionized form at steady state. Table 2.4 presents the acid-base dissociation coefficients for the selected odourous compounds in this study.

Table 2.4: Acid-base equilibrium coefficients (pKa)^a

Acid	Acid-Base Equation	pKa (298K)
HAc	$\text{HAc} \longrightarrow \text{H}^+ + \text{Ac}^-$	4.76
HPro	$\text{HPro} \longrightarrow \text{H}^+ + \text{Pro}^-$	4.88
HBu	$\text{HBu} \longrightarrow \text{H}^+ + \text{Bu}^-$	4.82
HVa	$\text{HV a} \longrightarrow \text{H}^+ + \text{Va}^-$	4.86
H ₂ S	$\text{H}_2\text{S} \longrightarrow \text{H}^+ + \text{HS}^-$	7.05
NH ₄	$\text{NH}_4^+ \longrightarrow \text{H}^+ + \text{NH}_3$	9.25
CO ₂ (aq)	$\text{H}_2\text{CO}_3 \longrightarrow \text{H}^+ + \text{HCO}_3^-$	6.35
H ₂ O	$\text{H}_2\text{O} \longrightarrow \text{H}^+ + \text{OH}^-$	14.0

Note: ^a Lide, (2001).

From Table 2.4, it could be seen that organic acids have pKa values of approximately 4.8, the H₂S/HS⁻ acid-base pair has a pKa of 7.05 while the NH₄⁺/NH₃ acid-base pair has a K_a of 9.25. The pKa values of these compounds are generally close to the operating pH (6.8-7.4) of anaerobic digestion systems.

Association/dissociation processes occur so rapidly that they are often referred to equilibrium processes (Musvoto et al. 2000a). At steady state, the ratio between the concentrations (S) can be expressed:

$$\frac{S_i}{S_{i^-}} = \frac{S_{\text{H}^+}}{K_{a,i}} \quad (2.26)$$

Where,

S_i = concentration of compound i in the non-dissociated molecular form (kgCOD/m³)

S_{i⁻} = concentration of compound i in the dissociated ion form (kgCOD/m³)

K_{a,i} = acid-base dissociation coefficient of component i (M)

The release of the odourous compounds to the gas phase is therefore strongly dependent on the acid-base dissociation coefficient and the pH in anaerobic digesters.

2.7.2 Liquid-Gas Mass Transfer

If the gas and liquid phase are in contact for an extended period, the partitioning of a substrate between the phases will reach steady state with respect to each other. Henry's law is most widely used to describe the liquid-gas mass transfer under equilibrium condition:

$$K_{H,i} = \frac{S_{l,i}}{P_i^i} \quad (2.27)$$

Where,

$K_{H,i}$ = Henry's law constant for compound i ($M \text{ bar}^{-1}$). Here, the definition of Henry's law constant is incorporated in ADM1.

P_i^i = Partial pressure of compound i (bar)

$S_{l,i}$ = Mole concentration of compound i in the liquid phase (M)

Henry's law defines under equilibrium conditions and at constant temperature the relative amount of a volatile compound in the gas phase as a function of the relative concentration in the water phase: i.e. Henry's law quantifies the degree of tendency of a volatile compound to escape the liquid phase. The law applies for dilute solutions of a compound, i.e. for solutions where the mole fraction of compound is close to zero provided that it does not dissociate or react in the water phase. The values of K_H for selected odourous compounds are shown in Table 2.5. Referring to Table 2.5, the K_H values of sulfur-containing odourous compounds are two to four orders of magnitude smaller than that of

VFA and NH₃, which indicate sulfur-containing odourous compounds have a great potential to release from the liquid phase to the gas phase and cause odour problems.

Table 2.5: Henry's law coefficients of selected odourous compounds (Thibodeaux, 1979; Sander, 2000)

Compound	K_H (M/bar)	K_H^{-1} (bar/M)
H ₂ S	0.099	10.13
MT	0.28	3.60
DMS	0.51	1.98
DMDS	0.88	1.13
HA _c	882	1.13E-03
HPro	1852	5.40E-04
HBu	1852	5.40E-04
HVa	2222	4.50E-04
NH ₃	65.9	0.02

Counlson and Richardson (1993) and Pauss *et al.* (1990) reported in their studies of anaerobic digesters that the gases in anaerobic digester may be supersaturated to a significant degree in relation to effluent organics and total COD balance. Therefore, dynamic gas transfer equations should be used to describe liquid-gas transfer. The most common equation follows the two-film theory of Whitman (1923). Derivation is described by Stumm and Morgan (1996) and the mass flux is a combination of the driving force and the rate equation:

$$\rho_i = k_L a_i (S_{l,i} - K_{H,i} P_i) \quad (2.28)$$

Where,

$k_L a_i$ = the volume-specific liquid-gas transfer coefficient (d⁻¹)

ρ_i = the specific mass transfer rate for compound I

A major problem in the quantification of water-air transport phenomena, in term of the rate expression (Eq. 2.28), is to find appropriate values for $k_L a$. Values for $k_L a$ vary a great deal depending on mixing, temperature and liquid properties. The $k_L a$ value is a function of the molecular diffusion coefficient (D), the liquid laminar layer (d_l) and the gas-liquid contact surface (a) [i.e. ($k_L a = D/d_l \cdot a$)]. Since the values of the liquid laminar layer and the liquid-gas contact surface should be the same for all compounds in a system, then the $k_L a$ value of compound i can be estimated from a reference compound (ideally easily measured substances). The following expression is used to calculate the mass transfer coefficients ($k_L a$) for compound i :

$$k_L a_i = k_L a_r \times \frac{D_i}{D_r} \quad (2.29)$$

Where,

$k_L a_i$ = the volume-specific gas-liquid transfer coefficient of compound i (d^{-1})

$k_L a_r$ = the volume-specific gas-liquid transfer coefficient of the reference compound (d^{-1})

D_i = Diffusivity coefficient of compound i in the liquid phase ($cm^2 s^{-1}$)

D_r = Diffusivity coefficient of the reference compound in the liquid phase ($cm^2 s^{-1}$)

Oxygen is generally considered to be an ideal reference compound for most systems because many experiments have been done to measure the $k_L a_{O_2}$ value in different systems. However, oxygen is not a perfect reference for anaerobic systems. Siegrist *et al.* (2002) used CO_2 as the reference compound in their studies on modeling of anaerobic sewage sludge. They measure the $k_L a_{CO_2}$ value in their laboratory digesters and found a

value of approximately 100 d⁻¹. In this study, carbon dioxide was selected as the reference compound. Most odourous compounds, especially VOSC, were not the common chemicals of interest before, so some of their physical-chemical data (such as diffusivity constant, K_{ow}, etc.) could not be found in the published references. Othmer and Thakar (1953) provide a semi-empirical method to obtain solution phase diffusivities of organic molecules:

$$D_i = \frac{13.26 \times 10^{-5}}{\mu^{1.14} \times (V)^{0.589}} \quad (2.30)$$

Where,

μ = the solution viscosity in centipoises (10⁻² g.cm⁻¹.s⁻¹) at the temperature of interest

V = the molar volume of the chemical (cm³.mol⁻¹)

The primary environmental determinant of solution diffusivities is the viscosity of water.

From Eq. 2.30, the following expression can be derived to estimate the solution phase diffusivity from a reference compound.

$$\frac{D_i}{D_r} = \left(\frac{V_r}{V_i} \right)^{0.589} \quad (2.31)$$

The reference compound selected here was carbon dioxide and its diffusivity coefficient can be obtained from the reference books. The diffusivities of the odourous compounds were then computed with Eq. 2.31. Table 2.6 shows the physical and chemical data for some selected odourous compounds in anaerobic digesters.

Table 2.6: Physical and Chemical data for some selected odourous compounds.

Compound	Formula	V (cm ³ .mol ⁻¹)	D (10 ⁻⁵ cm ² .s ⁻¹)	k _L a (d ⁻¹)
Carbon dioxide	CO ₂	27.5	1.91 ^a	100 ^c
Hydrogen sulfide	H ₂ S	21	1.36 ^a	71 ^b
MT	CH ₃ SH	41.5	1.45 ^b	76 ^b
DMS	CH ₃ SCH ₃	62	1.18 ^b	62 ^b
Acetate	CH ₃ COOH	52	1.31 ^b	69 ^b
Propionate	CH ₃ CH ₂ COOH	72.5	1.08 ^b	57 ^b
Butyrate	CH ₃ (CH ₂) ₂ COOH	93	0.93 ^b	49 ^b
Valerate	CH ₃ (CH ₂) ₃ COOH	113.5	0.83 ^b	43 ^b
Ammonia	NH ₃	11.7	1.5 ^a	78 ^b

Note: ^a Lide, (2001)

^b the values are calculated from the reference compound of CO₂

^c Siegrist *et al.* (2002)

2.7.3 Liquid-Solid Processes

The process by which chemicals become associated with solid phases is generally referred to as sorption (either as adsorption onto a two-dimensional surface, or absorption into a three-dimensional matrix). Sorption on solids is one of the fundamental processes controlling the quantitative emission of odourous compounds from anaerobic digesters. A study of Petrasek *et. al* (1983) and Jelus *et. al* (1986) provided evidences that organic compounds accumulated in sludges at concentrations several orders of magnitude greater than liquid concentrations. The fate of hydrophilic organic pollutants in water systems is

highly dependent upon their sorptive behavior. The degree of sorption not only affects a chemical's mobility, but also a dominant factor in fate processes such as volatilization and biodegradation (Dobbs *et al.*, 1989). Therefore, it is important to investigate the sorptive properties of wastewater solids in order to better understand the role of this removal mechanism in wastewater and biosolids treatments. However, only few studies of sorption on wastewater solids have been reported.

Solids in wastewater streams consist of a mixture of materials from the originating waste stream and biomass that is grown in any biological processes. In dilute systems typical of most environmental situations, the partitioning coefficient K_p for sorption on wastewater solids can be defined as (Dobbs *et al.*, 1989):

$$K_{P,i} = \frac{S_{S,i}}{S_{L,i}} \quad (2.32)$$

Where,

$K_{P,i}$ = the liquid-solid partitioning coefficient of compound i (L/Kg)

$S_{S,i}$ = the mass concentration of compound i in solid phase (g/kg)

$S_{L,i}$ = the mass concentration of compound i in the liquid phase (g/L)

To calculate the total concentration of compound i in suspended wastewater, the following expression has been employed:

$$S_{T,i} = S_{L,i} + K'_{P,i} \cdot X_C \cdot S_{L,i} \quad (2.33)$$

Where

$S_{T,i}$ = total concentration of compound i in the suspended water phase (g/l)

$S_{L,i}$ = concentration of the compound i in liquid phase (g/l)

$K'_{P,i}$ = the partitioning coefficient for compound i in the wastewater solids (L/g COD).

X_C = concentration of volatile suspended solids (VSS) in wastewater (g COD/l)

A challenge with applying the linear model is that values for the partitioning coefficient are not available for most odourous compounds. In addition, no references in the literature review gave a common agreeable formula to calculate the values of the liquid-solid partitioning coefficients. A study of Dobbs *et.al* (1989) developed a relationship between partitioning coefficients and the octanol-water coefficients in municipal wastewater. The equation can be expressed as following:

$$\log K'_{P,i} = 1.14 + 0.58 \log K_{ow,i} \quad (2.34)$$

Where,

$K_{ow,i}$ = the octanol-water partitioning coefficient for compound i (mol/L octanol/mol/L water)

Since Eq. 2.34 is empirical in nature and was developed from the study of toxic organic compounds in municipal wastewater solids, it was not be a suitable formula for the inorganic odourous compounds (e.g. NH_3 and H_2S) and VFA. The liquid-solid partitioning in this study only includes the partitioning processes of VOSC.

Table 2.7 presented the values of octanol-water partitioning coefficients and the calculated K_P' values of VOSC. Referring to the values in Table 2.7, the solid phase concentrations of VOSC can be computed with Eq. 2.33. However, the accuracy of the

estimated solid phase concentration was uncertain since this equation was not developed with any of the odourous compounds.

Table 2.7: Octonal-water coefficient and liquid-solid partitioning coefficients of VOSC

Compounds	$\log K_{ow}$	$\log K_p'$	K_p'
MT	0.66 ^a	1.52	23.0
DMS	1.20	1.84	47.3
DMDS	1.77 ^b	2.17	101.2

Note: ^a. SRC (Syracuse research corporation calculated values) (1988)

^b. Schwarzenbach (1993)

2.8 Conclusion

From the literature review, the following important information was identified:

- The most prevalent odours compounds in biosolids offgases are H₂S, MT, DMS, DMDS, NH₃ and VFA and these will be the subjects discussed in the odor model.
- The main pathways of formation of the selected odourous compounds in anaerobic digesters were identified.
- The most important physical-chemical process for odour emission, i.e. acid-base dissociation, mass transfer between liquid-gas phase and partitioning between liquid-solid phases, were defined.

Because the odor emission is a new subject, the information and data obtained may not be very accurate. However, the literature review still provided a theoretical basis to develop the odour model.

Chapter 3: Model Development

3.1 Introduction

The literature review provided a theoretical foundation to develop an odour model. In addition, ADM1 provided a structural basis to build up the odour model. The common anaerobic processes, such as fermentation, acidogenesis, acetogenesis and methanogenesis, were addressed in ADM1. However, the processes related to odour formation were not included in ADM1. In this chapter, the main pathways of formation of the selected odourous compounds were specified and the kinetic rate expression for each specific process was identified. Furthermore, the dynamic rates for the physico-chemical processes, i.e. acid-base dissociation, liquid-gas mass transfer and liquid-solid partitioning, were also identified. Therefore, a mathematical model for emission of odourous compounds from anaerobic digesters was developed.

The key rate equation in this study is substrate uptake, which is based on substrate level Monod-type kinetics. Biomass growth is implicit in substrate uptake. First order kinetics is applied to describe the processes of disintegration, hydrolysis and endogenous decay. The dynamic kinetic rates were taken to formulate most of the physico-chemical processes.

The main purpose of this chapter is to develop an odour model to predict the concentrations of odourous compounds in anaerobic digesters. Since only limited

information of odour compounds was obtained from references, most kinetics and physico-chemical data for the odourous compounds were unavailable. Hence, subsequent chapters address an uncertainty analysis of the model.

3.2 Conversion Processes

Conversion processes in anaerobic digestion can be divided into two main types, i.e. biochemical processes and physico-chemical processes. Biochemical processes are normally catalyzed by intra- or extracellular enzymes and act on the pool of available organic and inorganic material. Disintegration of composites (such as dead biomass) to particulate constituents and their subsequent enzymatic hydrolysis to soluble monomers are extracellular processes. Digestion of soluble materials mediated by organisms is intracellular and this process results in biomass growth and decay. The physico-chemical processes include acid-base dissociation, gas-liquid mass transfer and liquid-solid phase partitioning.

Figure 3.1 presented an outline of the biochemical and physico-chemical processes occurring in anaerobic digestions. Referring to Figure 3.1, the biochemical processes in the odour model included nine main biochemical processes: disintegration, hydrolysis, acidogenesis, acetogenesis, methanogenesis, sulfate reduction, methylation reactions, MT oxidation to DMDS and sulfide precipitation. The first five processes were already incorporated in the ADM1 model. However, the formation of sulfur containing odourous compounds was not included. The hydrolysis of protein releases sulfur-containing amino

Figure 3.1.1: Conversion processes in anaerobic digesters

acids, which are shown as SAA in Figure 3.1. Degradation of these sulfur-containing amino acids not only produced VFA and NH_3 but also generated sulfur-containing odourous compounds, i.e. H_2S , MT, DMS and DMDS. Sulfate reducing bacteria could grow under anaerobic conditions; therefore, inorganic sulfate (SO_4^{2-}) can be used by SRB as an electronic donor to generate H_2S . A new substrate group - methoxylated aromatic compounds (MAC) – was introduced in this odour model to describe methylation reactions. The particulate MAC was defined as a component from the disintegration of complex particulates, first hydrolyzed to soluble methyl groups (R-CH_3). These soluble methyl groups were then transferred to sulfide or MT by organisms to produce MT and DMDS, respectively. The presence of DMDS has been found to coincide with the high concentration of MT, and hence it is believed MT can be oxidized to DMDS either by chemical reaction or by organisms. Heavy metals presented in biosolids would bind together with sulfide to form extremely insoluble metal sulfides and precipitate from liquid phase to sediments. Methanogens play an important role in the degradation of VOSC. Some methanogens can grow on VOSC to produce hydrogen sulfide and methane. In general, the emission of odourous compounds from anaerobic digesters is the result of these interrelated processes.

Three main physico-chemical processes were presented in Figure 3.1. The three physico-chemical processes play an important role for the odour emissions. First, the acid-bas dissociation coefficients control the ratio of odourous compounds between their molecular form and ionic form; second, the liquid-solid partitioning coefficients determined the ratio of the concentrations of odourous compounds between the liquid

phase and solid phase; and third, the values of Henry's law coefficients determines the concentrations of odourous compounds in the gas phase.

3.3 Biochemical Processes

Biochemical equations are the core of the model and it is possible to represent an anaerobic system using only these equations. However, to describe the effect of the physico-chemical state (such as pH and gas concentrations) on biochemical reactions, physico-chemical conversions must be included as well.

An overview of the structure of the biochemical processes was shown in Figure 3.2. Referring to Figure 3.2, complex composite particulates were assumed to be homogeneous, which disintegrated to carbohydrate, protein, lipid and MAC. Here, MAC is a specific odour-producing group. The complex particulate pool is also used as a pre-lysis repository of dead biomass. Therefore, the disintegration step is intended to include an array of steps such as lysis, non-enzymatic decay, phase separation and physical breakdown (e.g. shearing).

All extracellular steps were assumed to be first order, which was an empirical function reflecting the cumulative effect of a multi-step process (Eastman and Ferguso, 1981). Cellular kinetics were described by three expressions (uptake, growth and decay). Substrate-based Monod-type kinetics were used as the basis for all intracellular biochemical reactions, which were incorporated in ADM1. Death of biomass was

Figure 3.2: Schematic diagrams of the main pathways of odorous compounds

represented by first order kinetics and dead biomass were maintained in the system as composite particulate material. Inhibition functions included pH (all groups), hydrogen (acetogenic groups), free ammonia (aceticlastic methanogens), hydrogen (all groups) and hydrogen sulfide (SRB groups). Inhibition functions were not included in the processes related to the formation of VOSC processes, because the influence of the inhibitors on these biochemical processes is unknown.

3.3.1 Disintegration and Hydrolysis of MAC

Disintegration and hydrolysis are extracellular biological and non-biological processes mediating the breakdown and solubilization of complex organic material to soluble substrates. The disintegration process of the ADM1 model is extended in the odour model by creating a specific odour-producing group – MAC – as one of the components from the disintegration of the complex composites.

MAC is mainly released from the decomposition of lignin (Bak and Finster, 1992). Because lignin is the most recalcitrant component of the plant cell wall, it is widespread in nature. Lignin degradation is primarily an aerobic process, and in an anaerobic environment, lignin can persist for very long periods (Van, 1994). Some organisms, particularly fungi, have developed the necessary enzymes to break lignin apart (Kirk and Farrell, 1987). Lignin is particularly difficult to biodegrade and the retention time required for biodegradation of lignin under anaerobic conditions is 40 days. Therefore, lignin should be included in the inert part of the disintegration of composites (Figure 3.1).

Table 3.1 shows the content of lignin in different organic materials. Referring to Table 3.1, lignin mainly exists in plant-related materials, such as newsprint, wheat straw and wood chips. The content of lignin in poultry manure is about 2%. The composition of poultry manure is relatively similar to that of the municipal biosolids. Kayhanian (1995) found that the content of lignin is typically 4% (based on COD) in a higher-solids anaerobic digester. In this study, it was assumed that the content of MAC resulting from the disintegration of complex composites is 4%.

All the literature models described the disintegration process with first order kinetics as:

$$r_{dis} = k_{dis} \times X_c \quad (3.1)$$

Where,

k_{dis} = first order disintegration coefficient of complex particulate, 0.5 d^{-1} .

X_c = concentration of complex particulate (kg COD m^{-3})

The stoichiometric coefficient for the yield of MAC from disintegration process of complex particulates was 4%.

Table 3.1 Content of lignin in the selected organic materials (Kirk and Farrell, 1987)

Material	Carbon (%) (total)	Carbon (%) (biodegradable)	Lignin (%) (dry basis)	Cell wall (%) (dry basis)
Newsprint	39.3	18.4	20.9	97.0
Wheat straw	51.1	33.6	23.0	95.0
Manure, poultry	43.3	41.8	2.0	38.0
Wood chips, maple	49.7	43.8	12.7	32.0

The hydrolysis step is a complex multi-step process for carbohydrates, proteins, lipids and MAC, which may include multiple enzyme production, diffusion, adsorption, reaction and enzyme deactivation steps. However, the most common kinetic relationship to describe the hydrolysis processes is first order (Eastman and Ferguson, 1981). The hydrolysis processes of carbohydrates, proteins and lipids have been addressed in ADM1. Here, the hydrolysis of MAC is expressed as:

$$r_{hyd_MAC} = k_{hyr_MAC} \times X_{MAC} \quad (3.2)$$

Where,

r_{hyd_MAC} = the first order rate of hydrolysis of MAC (d^{-1}) ;

X_{MAC} = the concentration of MAC degrading organisms ($kgCOD/m^3$)

k_{hyd_MAC} = first order hydrolysis coefficient of MAC, $10 d^{-1}$ (from ADM1)

In ADM1, an overall hydrolysis coefficient is used for carbohydrates, proteins and lipids.

Therefore, the same hydrolysis constant was selected for MAC in the odour model.

3.3.2 Uptake of Amino Acids

There are commonly 18 different kinds of amino acids derived from the hydrolysis of proteins, and only two out of them, i.e. cysteine ($SHCH_2CH_2NH_2COOH$) and methionine ($CH_3SCH_2CH_2NH_2COOH$), contain sulfur (Table 3.2). The literature review in chapter two confirmed that the degradation of cysteine ($SHCH_2CH_2NH_2COOH$) leads to the production of H_2S ; however, the degradation of methionine ($CH_3SCH_2CH_2NH_2COOH$) leads to production of VOSC in addition to VFA and NH_3 . After studying nine types of

manures, Banwart and Bremmer (1975) indicated that all nine types released H_2S , MT, DMS under anaerobic conditions, while some released DMDS, carbonyl sulfide (COS), and carbon disulfide (CS_2). H_2S and MM accounted for 70 to 97% of the total sulfur volatilized. Beard and Guenzi (1983) studied beef-cattle slurry under anaerobic digestion and reported most of the emanating of sulfur was in the forms of H_2S (39%), MM (34%), DMS (21%) and other sulfur compounds (6%). Assuming that the remaining sulfur compounds were in the form of DMDS, in this study the ratio of formation of MT, DMS and DMDS was estimated as 0.56:0.34:0.1. This sulfur distribution ratio will be used in the odour model for calculating the production of VOSC from degradation of amino acids (Appendix B). The specific pathway and stoichiometric yield of odourous compounds from degradation of amino acids is presented in Figure 3.3.

Figure 3.3: Specific pathways and stoichiometric for degradation of amino acid

Legend: ——— basic degradation of Amino acids to form VFA and NH_3
 - - - - - pathways of degradation of AA to form H_2S and VOSC
 pathways of biomass growth

Referring to Figure 3.3, $f_{i,aa}$ represents the generated fraction of odourous compounds i from the degradation of amino acids (based on 1 kg COD of amino acids). Y_{aa} is the yield coefficient of biomass from degradation of amino acids. N_{bio} and S_{bio} are the content of nitrogen and sulfur in biomass. The calculation of these stoichiometric yields was presented in Appendix B.

Monod-type kinetic rates are used to describe the uptake process of amino acids:

$$r_{aa} = k_{m,aa} \frac{S_{aa}}{K_S + S_{aa}} X_{aa} I_{pH} I_{IN,lim} I_{H_2S} \quad (3.3)$$

Where,

$k_{m,aa}$ = Monod maximum specific uptake rate of amino acids, 50 d^{-1} (the value obtained from ADM1)

K_S = half saturation constant for amino acids degradation, 0.3 kgCOD m^{-3} (the value obtained from ADM1)

S_{aa} = concentration of amino acids in the liquid phase, kgCOD m^{-3}

X_{aa} = concentration of amino acids degrading organisms, kgCOD m^{-3}

I_{pH} , $I_{IN,lim}$, I_{H_2S} = the inhibitions from pH, free ammonium and hydrogen sulfide on the uptake amino acids process (Appendix A)

Since the production of odourous compounds are the main interests in this study, referring to Figure 3.3, the corresponding yield for each odourous compound (except NH_3 and H_2S) can be expressed as:

$$r_{i,aa} = f_{i,aa} (1 - Y_{aa}) r_{aa} \quad (3.4)$$

Where,

$r_{i,aa}$ = yield rate of odourous compound i from the degradation of amino acids (d^{-1})

$f_{i,aa}$ = the stoichiometric yield of odourous compound i from degradation of amino acid, gCOD/gCOD (VFA), mol/gCOD (VOSC).

Y_{aa} = yield coefficient of biomass on amino acids, 0.08 kg COD/kg COD (from ADM1)

The yield for ammonia can be expressed as:

$$r_{NH_3,aa} = (f_{IN,aa} - N_{bio} Y_{aa}) r_{aa} \quad (3.5)$$

Where,

N_{bio} = nitrogen content in biomass, 0.00625 kmol N/kg COD (from ADM1)

The yield for H_2S can be expressed as:

$$r_{H_2S,aa} = [f_{H_2S,aa} (1 - Y_{aa}) - S_{bio} Y_{aa}] r_{aa} \quad (3.6)$$

Where,

S_{bio} = Sulfur content in biomass, 7.5E-05 kmol/ kg COD (Appendix B)

Ramsay (1997) compiled a spreadsheet that can be used to predict the products of amino acids (Table 3.2). In Table 3.2, the contents of beef flesh and casein in percentage of total amino acids were given to predict the stoichiometric yields (i.e. $f_{i,aa}$) from a mixture of proteins. The detailed calculation leading to Table 3.3 are presented in Appendix B. Table 3.3 presented the calculated stoichiometric yields of odourous compounds from the degradation of amino acids.

Table 3.2: Products from amino acids based on Stickland reactions (Ramsay 1997)

Amino acid	Molecular formula	HAc	HPe	HBu	HVa	IN	IC	Other	H ₂	H ₂ S	MT	DMS	DMDS	ATP	Beef flesh	Casein ¹
Arginine	C ₆ H ₁₄ O ₂ N ₄	0.5	0.5	0	0.5	4	1		-1	0	0	0	0	1	5.40	2.80
Histidine	C ₆ H ₉ O ₂ N ₃	1	0	0.5	0	3	1	1	0	0	0	0	0	2	2.40	2.60
Lysine	C ₆ H ₁₄ O ₂ N ₂	1	0	1	0	2	0	0	0	0	0	0	0	1	7.20	6.40
Tyrosine	C ₉ H ₁₁ O ₃ N	1	0	0	0	1	1	0.882	1	0	0	0	0	1	2.70	4.30
Tryptophan	C ₁₁ H ₁₂ O ₃ N	0	0	0	0	1	1	1.471	2	0	0	0	0	1	0.90	0.80
Phenylalanine	C ₉ H ₁₁ O ₂ N	0	0	0	0	1	1	1.176	2	0	0	0	0	1	3.60	4.00
Cysteine	C ₃ H ₆ O ₂ NS	1	0	0	0	1	1	0	0.5	1	0	0	0	1	1.50	0.10
Methionine	C ₅ H ₁₁ O ₂ NS	0	1	0	0	1	1	0	1	0	0.56	0.34	0.1	1	2.00	2.50
Threonine	C ₄ H ₉ O ₃ N	1	0	0.5	0	1	0	0	-1	0	0	0	0	1	4.80	3.90
Serine	C ₃ H ₇ O ₃ N	1	0	0	0	1	1	0	1	0	0	0	0	1	5.70	7.60
Leucine	C ₆ H ₁₃ O ₂ N	0	0	0	1	1	1	0	2	0	0	0	0	1	14.40	14.20
Valine	C ₅ H ₁₁ O ₂ N	0	0	1	0	1	1	0	2	0	0	0	0	1	6.50	6.70
Glutamine	C ₅ H ₉ O ₄ N	1	0	0.5	0	1	1	0	0	0	0	0	0	2	13.50	19.20
Aspartate	C ₄ H ₇ O ₄ N	1	0	0	0	1	2	0	2	0	0	0	0	2	8.80	6.40
Glycine	C ₂ H ₅ O ₂ N	1	0	0	0	1	0	0	-1	0	0	0	0	0	8.40	3.00
Alanine	C ₃ H ₇ O ₂ N	1	0	0	0	1	1	0	2	0	0	0	0	1	8.40	4.00
Proline	C ₅ H ₉ O ₂ N	0.5	0.5	0	0.5	1	0	0	-1	0	0	0	0	0	4.00	11.40
Total																

Basic units of mole product/mole amino acids.

¹. Units of mole % total amino acids.

Table 3.3: Calculated products from amino acids.

Source	Acetate f _{ac,aa}	Propionate f _{pro,aa}	Butyrate f _{bu,aa}	Valerate f _{va,aa}	IN f _{in,aa}	H ₂ f _{H2,aa}	H ₂ S f _{H2S,aa}	MT f _{MT,aa}	DMS f _{DMS,aa}	DMDS f _{DMDS,aa}
Casein	0.31	0.05	0.27	0.28	0.009	0.07	1.1E-04	7.9E-05	4.8E-05	1.4E-05
Beef flesh	0.28	0.07	0.28	0.30	0.008	0.08	6.7E-06	9.4E-05	5.7E-05	1.7E-05
ADM1	0.40	0.05	0.26	0.23	0.007	0.06				
Odour Model	0.40	0.05	0.26	0.23	0.007	0.06	1.1E-04	7.9E-05	4.8E-05	1.4E-05

3.3.3 Sulfate Reduction

The study of Kalyuzhnyi *et al.* (1998) on modelling the competition between sulfate reduction and methanogenesis in anaerobic reactors provided well defined information on kinetics and parameters for sulfate reduction. The kinetic rates were based on the following assumptions and considerations:

- Uptake of biomass proceeds according to Monod kinetics with simultaneous inhibition by undissociated H₂S.
- The direct effect of pH on the growth rates is not included to avoid an excessive complexity of the model.
- Undissociated H₂S inhibition proceeds according to first order inhibition kinetics (Levenspiel, 1980)
- Bacterial decay is described by first order kinetics.

The substrate uptake rate equations for propionate, acetate and hydrogen are based on substrate level Monod-type kinetics:

$$r_{i,SR} = k_{m_{i-SR}} \times \frac{S_i}{K_{S_{i-SR}} + S_i} \times \frac{S_{SO4-ion}}{K_{S_{SO4-i}} + S_{SO4-ion}} \times X_{i-SRB} \times I_{H2S-i-SRB} \quad (3.4)$$

Where,

$r_{i,SR}$ = Rate of sulfate reduction due to use of compound i (kg COD m⁻³ d⁻¹). Here, the compound i represented acetate, propionate or hydrogen.

S_i = Concentration of substrate i in liquid phase (kgCOD/m³)

$K_{S_i_SR}$ = half saturation constant of substrate i for sulfate reduction process (kgCOD/m³)

S_{SO4_ion} = Concentration of SO_4^{2-} in liquid phase (M)

$K_{S_SO4_i}$ = half saturation constant of SO_4^{2-} (M)

X_{i_SRB} = Concentration of SRB using i as its substrate (kgCOD/m³)

$k_{m_SR_i}$ = (μ_m/Y) Monod maximum specific uptake rate of substrate i on sulfate reduction process (kg COD kgCOD⁻¹ d⁻¹)

μ_m = Monod maximum specific growth rate (d⁻¹)

Y = Yield of biomass on substrate (kg COD kg COD⁻¹)

$I_{H2S_i_SR}$ = H₂S inhibition for sulfate reduction using compound i as substrate

$$I_{H2S_i_SR} = 1 - \frac{S_{H2S}}{K_{I,i}} \quad (3.5)$$

Where,

S_{H2S} = Concentration of undissociated H₂S (M)

$K_{I, H2S}$ = the inhibition coefficient of H₂S in sulfate reduction process

The values of the parameters have been chosen in a range consistent with the experimental study of Alphenaar *et al.* (1994) and Kalyuzhnyi (1997). Table 3.4 showed the values of the parameters. The substrates uptaken by SRB in this study are propionate, acetate and hydrogen.

Table 3.4 Kinetic parameters used in the model (Alphenaar *et al.* (1993) and Kalyuzhnyi (1997))

Bacteria groups	μ_m (d ⁻¹)	$K_{s,i}$ (kgCOD/m ³)	K_{s,SO_4} (M)	K_{I,H_2S} (M)	$Y(\text{kgCOD}_X / \text{kgCOD}_S)$	K_m (d ⁻¹)	b (d ⁻¹)
SRB1 ^a	0.81	0.295	7.7E-05	0.0089	0.051	15.88	0.018
SRB2 ^a	0.51	0.024	2.0E-04	0.0089	0.059	8.644	0.025
SRB3 ^a	5.0	0.00005	9.4E-06	0.017	0.112	44.64	0.03
X ₁ ^a	8.0	0.028	-	0.017	0.062	129	0.056
X ₂ ^b	0.16	0.247	-	0.0067	0.026	6.15	0.018
X ₃ ^c	0.24	0.056	-	0.0089	0.038	6.32	0.0155
X ₄ ^d	1.0	0.00013	-	0.0067	0.026	38.46	0.05

Note: ^a SRB1, SRB2 and SRB3 refers to propionate-degrading SRB, acetate-degrading SRB and hydrogen-degrading SRB, respectively

^b.bacteria group X₁ contains all fermentative bacteria.(FB)

^c bacteria group X₂ contains all propionate-degrading acetogenic bacteria (AB)

^d bacteria group X₃ contains all actetrophic methanogenic bacteria (MB)

^e bacteria group X₄ contains all hydrogentrophic methanogenic bacteria (MB)

The general reaction sequence for sulfate reduction by different bacteria group can be presented (on a molar basis) as:

Since the concentrations of organic contaminants in the odour model are expressed in kg COD/m³, sulfates and sulfides in M, the stoichiometric schemes (3.6-3.8) can be presented in COD coefficients. The conversion factors are presented in Table 3.5.

Table 3.5: Conversion factors for sulfate reduction.

Conversion factor	value	Basis
m1 (gCOD/mol)	112	C ₂ H ₅ COOH
m2 (gCOD/mol)	64	CH ₃ COOH
m3 (gCOD/mol)	16	H ₂
m4 (mol/mol)	1	SO ₄ ²⁻
m5 (mol/mol)	1	S ²⁻
m6 (gCOD/mol)	0	CO ₂

Therefore, sulfate reduction on a COD basis can be expressed as:

Equations 3.9-3.11 showed the stoichiometric yields ($f_{\text{H}_2\text{S},i_SR}$) of H₂S on a COD basis due to the use of different compounds. For propionate, the stoichiometric yield of H₂S is 0.75/112; for acetate, 1/64; and for hydrogen, 1/64. The yield of H₂S from sulfate reduction due to use of different compounds can be expressed as:

$$r_{\text{H}_2\text{S},i_SR} = [f_{\text{H}_2\text{S},i_SR} \times (1 - Y_{i_SR}) - S_{bio} \times Y_{i_SR}] r_{i_SR} \quad (3.12)$$

Where,

r_{H_2S, i_SR} = the yield kinetic rate of H_2S from sulfate reduction due to use of compound i

(kmol Sulfide kg COD⁻¹ d⁻¹)

f_{H_2S, i_SR} = the stoichiometric yields of H_2S from sulfate reduction due to use compound i,

(k mol H_2S kg COD⁻¹).

Y_{i_SR} = Yield coefficient of biomass due to use of compound i, (kg COD kgCOD⁻¹ d⁻¹)

(the value of Y_{i_SR} can be found in Table 3.5)

S_{bio} =sulfur content in biomass, 7.5E-05 mol/gCOD (Appendix B)

In anaerobic reactors, substrate competition is possible on two levels: competition between SRB and MB for acetate and hydrogen; and competition between SRB and AB for VFA. Table 3.6 presented the kinetic data used for SRB, MB and AB in the odour model. Referring to Table 3.6, it could be seen that SRB should be able to out-compete MB and AB. However, the advantage of SRB over MB and AB is small since there is no big difference between their kinetics

Table 3.6: Kinetics of SRB, AB and MB in the odour model

Bacteria group	k_m (d ⁻¹)	K_s (kg COD m ⁻³)	Y (g COD/g COD)
SRB_ac	8.644	0.024	0.059
MB_ac	8	0.15	0.05
SRB_h2	44.64	5.0E-05	0.112
MB_h2	35	7.0E-06	0.06
SRB_pro	15.88	0.295	0.051
AB_pro	13	0.1	0.04

3.3.4 Methylation Reactions

Methylation reactions are another source for the formation of VOSC in anaerobic digestion. The methylation reaction occurs when organisms use sulfide and MT as the methyl group acceptors, resulting in the formation of MT and DMS, respectively. The literature on methylation reactions supports the theory that methylation reactions occur in two steps: (1) bacteria transfer methyl groups from methylated aromatic compounds to H_2S to form MT; (2) bacteria transfer methyl groups from MAC to MT to form DMS. However, no papers provided kinetic data for the second step. Since the formation of MT and DMS is observed concomitantly, the two steps of forming DMS were combined together in the odour model. Figure 3.6 presented the specific pathways of the methylation reaction in the odour model.

Figure 3.4: Pathways of methylation reactions in the odour model

Since methylation reactions are relatively recently discovered pathway for the formation of VOSC, the information on kinetic data in this aspect was limited. Therefore, the

following assumptions were considered for the kinetic rate to avoid excessive complexity:

- No biomass growth was produced by the methylation reactions
- Organisms, which can mediate the methylation reactions, are normally acetogenic organisms. Therefore, instead of creating a new bacteria group, acetogenic organisms were selected to describe the kinetic rate.
- No inhibition was considered for the methylation reaction process.

The Monod-type uptake rate for MAC to produce MT and DMS can be expressed:

$$r_{MAC,i} = k_{m_MAC_i} \times X_{VFA} \times \frac{S_{MAC}}{K_{S_MAC} + S_{MAC}} \times \frac{S_{H_2S}}{K_{S_H_2S} + S_{H_2S}} \quad (3.13)$$

Where,

$k_{m_MAC_i}$ = Monod maximum specific MAC uptake rate to form compound i

(kg COD kgCOD⁻¹ d⁻¹). Here, Compound i is MT or DMS.

X_{VFA} = Total acetogenic organisms (kg COD m⁻³). In the odour model,

$$X_{VFA} = X_{fa} + X_{va} + X_{bu} + X_{pro}.$$

K_{S_MAC} = half saturation constant of MAC (kg COD m⁻³)

$K_{S_H_2S}$ = half saturation constant of H₂S (M)

S_{MAC} = MAC concentration in liquid phase (kg COD m⁻³)

S_{H_2S} = the concentration of HS⁻¹ in liquid phase (M)

Lomans *et al.* (1997,2001) found four different bacteria groups (strain SYR1, strain SA2, *Sporobacter termitidis* and *Holophaga foetida*), which could use MAC as their substrates

to form VOSC under anaerobic or anoxic conditions. The samples used in their laboratory were collected from freshwater sediments and salt slurries. The kinetic data obtained from their experiments were presented in Table 3.7. Kreft and Schink (1997) studied a strictly anaerobic homoacetogenic bacteria group, *Holophaga foetida*, which could use MAC as a substrate to generate VOSC in freshwater sediments. The kinetic data of *Holophaga foetida* from their experiments were presented in Table 3.7. Bache and Pfennig (1981) isolated another bacteria group, *acetobacterium woodii*, from freshwater mud and sewage sludge samples, which could growth on methoxylated aromatic acids to form VOSC. The kinetic data from their studies were also presented in Table 3.7. Table 3.7 summarized the kinetic data of different bacteria groups obtained from these studies. From Table 3.7, it could be seen that the data of different bacteria groups varied significantly and the kinetic data for each bacteria group was not completed. Therefore, it was difficult to use these data to develop the methylation processes.

In order to correctly reflect the methylation process, the parameter estimation function in AQUASIM was run to adjust the kinetic coefficients. The process for parameter estimation was performed in three steps. First, based on Table 3.7, the range of the parameter values was defined, such as the largest value of the parameter was 10 times greater than the value in Table 3.7; the smallest value was 10 times less than the values in Table 3.7. Then, the gas-phase concentrations for sulfur-containing odorous compounds were fixed according to the values from papers or from experimental data. The last step was to run the parameter estimation function and to determine the value for each parameter so that the output data predicted by the odour model was as close as possible to the given values.

In this study, the output data used to calibrate the parameters were from the study of Griffith and Alvarez (2002) and from data that was obtained from bench scale digesters that were operating at Carleton University (Table 3.8). The raw sludge in the study of Griffith and Alvarez was a mixture of primary sludge and thickened waste activated sludge. The samples of the municipal sludge in the Carleton study were obtained from the Ottawa wastewater treatment plant. However, in both cases, the input data for the feed sludge were not available. Therefore, in this study, the input data were from the study of Siegrist *et al.* (2002).

After running the parameter estimation function in AQUASIM, the resulting kinetic coefficients used in the odour model were presented in Table 3.9. Comparing the values of the Monod maximum specific uptake rate of MAC (k_{m_MAC}) in Table 3.9 and the values calculated from Table 3.7, there was a 10000-time difference between these values. In this study, instead of creating a specific acetogenic bacteria group for methylation reaction, it was assumed that the total acetogenic bacteria group were responsible for the degradation of MAC to form VOSC. Therefore, the kinetic rate for methylation reaction is proportional to the concentration of total acetogenic bacteria (X_{VFA}) (Eq. 3.13). However, from the literature review, only some specific acetogenic bacteria could use MAC as substrates to produce VOSC. The value calculated from Table 3.7 represented the Monod maximum specific uptake rate of MAC (k_{m_MAC}) for some specific acetogenic bacteria, which can degrade MAC to produce VOSC. Therefore, the Monod maximum specific uptake rates of MAC (k_{m_MAC}) obtained from parameter estimation function in AQUASIM were much smaller than the values calculated from Table 3.7.

Table 3.7: Kinetic data for different bacteria groups mediating methylation reactions

Bacteria group	Source	Environment	Products of VOSC	U_{max}^1 (h^{-1})	$K_{S_{H_2S}}^2$ (μM)	$K_{S_{MAC}}^3$ (mM)	Y_s^4 ($gCOD\ X/gCOD\ S$)	Reference
Strain SYR1	Freshwater sediments	Anaerobic	MT/DMS	0.2	200-400	2.5		Lomans, <i>et al.</i>
Strain SA2	Freshwater sediments	Anaerobic	MT/DMS	0.10				Lomans, <i>et al.</i>
<i>Sporobacter termitidis</i>	Freshwater sediments	Anaerobic	MT/DMS	0.05				Lomans, <i>et al.</i>
<i>Holophaga foetida</i>	Freshwater sediments	Anaerobic	MT/DMS	0.06				Lomans, <i>et al.</i>
<i>Holophaga foetida</i>	Freshwater sediments	Anoxic	MT/DMS	0.085			0.0722 ⁵	Keref and Schink
<i>acetobacterium woodii</i> ,	Freshwater sediments/sewage sludge	Anaerobic	MT/DMS				$Y_{s_MT} = 0.033^6$ $Y_{s_DMS} = 0.066^7$	Bache and Pfennig

¹. Monod maximum specific growth rate

². Half saturation value for H_2S

³. Half saturation value for aromatic methoxylated compounds

⁴. The yield coefficient on substrate

⁵. The yield coefficient on substrate to produce MT

⁶. The yield coefficient on substrate to produce DM

Table 3.8: Output data used for parameter estimation.

Compound	Unit	Value
H ₂ S	ppm	16.8 ^a
MT	ppm	0.09 ^b – 0.26 ^a
DMS	ppm	0.03 ^b -0.26 ^a
DMDS	ppm	0.25 ^a

Note: ^a. Griffith and Alvarez (2002)

^b. Carleton digesters (2003)

Table 3.9: Kinetic data of methylation reaction used in the odour model

Products	k _{m_MAC} (kg COD kg COD ⁻¹ .d ⁻¹)	K _{S_MAC} (kg COD m ⁻³)	K _{S_H2S} (M)	Source
MT	0.0074	0.15	0.0001	Model estimation
DMS	0.0082	0.15	0.0001	Model estimation

Syringate [C₆H₂OH(OCH₃)₂COO⁻] was often selected as an typical MAC for methylation reactions. Degradation of syringate to form MT and DMS can be expressed by following equations (on molar basis) (Lomans *et al.*, 2001):

Because the units of the concentrations of organic contaminants in the odour model are in kg COD/m³, H₂S and VOSC in M, the stoichiometric schemes (Eq. 3.14-3.15) should be converted to COD coefficients. The conversion factors are presented in Table 3.9.

Table 3.10: Conversion factors for methylation reaction

Conversion factor	Value	Basis
m1 (gCOD/mol)	288	C ₉ H ₁₀ O ₅
m2 (gCOD/mol)	64	CH ₃ COOH
m4 (mol/mol)	1	MT
m5 (mol/mol)	1	DMDS
m6 (mol/mol)	1	H ₂ S

Therefore, Eq. 3.14 and Eq. 3.15 can be expressed as (in COD basis):

From Equations 3.16 and 3.17, the stoichiometric yields ($f_{i,MR}$) for MT and DMS from uptake MAC are both 1/288. The yield for MT and DMS from methylation reaction can be expressed as:

$$r_{i,MR} = f_{i,MR} r_{MAC_i} \quad (3.18)$$

Where,

$r_{i,MR}$ = yield kinetic rate of compound i (i.e. MT or DMS) from methylation reaction

(k mol kgCOD⁻¹ d⁻¹)

$f_{i,MR}$ = stoichiometric yields for MT and DMS from methylation reaction
(k mol kg COD⁻¹)

3.3.5 MT Oxidation to DMDS

Loman *et al.* (1997) and Bak *et al.* (1992) found that the presence of DMDS always coincided with high concentrations of MT in their study of methylation reaction. This indicated that MT could be oxidized to DMDS either by chemical reaction or by organisms. In this study, first order kinetics were used to describe the oxidation reaction:

$$r_{MT_DMDS} = k_{MT_DMDS} S_{MT} \quad (3.19)$$

Where,

r_{MT_DMDS} = kinetic rate for the oxidation process of MT to DMDS (mol/mol d⁻¹)

k_{MT_DMDS} = first order coefficient for the oxidation process of MT to DMDS (7.35 d⁻¹)

S_{MT} = the concentration of MT in liquid phase (M)

Since no data on the kinetics of the oxidation process of MT to DMDS was available, the value of k_{MT_DMDS} was estimated from running the parameter estimation function in AQUASIM. The process for model estimation was described in section 3.3.4 and the data in Table 3.8 were also used to estimate the value of k_{MT_DMDS} . The oxidation process can be expressed by following reaction (on a molar basis):

Therefore, the stoichiometric yield of DMDS from oxidation of MT is 0.5.

Correspondingly, the yield for DMDS can be expressed as:

$$r_{DMDS} = 0.5 r_{MT_DMDS} \quad (3.21)$$

Where,

r_{DMDS} = the yield kinetic rate of DMDS from oxidizing MT, ($\text{mol mol}^{-1} \text{d}^{-1}$)

3.3.6 Degradation of VOSC

Anaerobic degradation of VOSCs has been mainly attributed to the activity of methanogens and sulfate-reducing bacteria (Lomans *et al.*, 2001, 2002). Compared with sulfate-reducing bacteria, methanogens play a dominant role in the anaerobic degradation of VOSCs. In order to simplify the VOSC degradation processes, methanogens were selected as the only bacterial group for the degradation of VOSC in the odour model. The end products of VOSC degradation are mainly hydrogen sulfide and methane. In this odour model, the kinetic rates for degradation of VOSC were based on the following assumptions:

- No biomass growth was considered in the degradation of VOSC
- No inhibition was included in the degradation of VOSC
- Methanogens were considered as the only organisms, which can degrade VOSC to hydrogen sulfide and methane.

In the odour model, a Monod uptake rate for VOSC was developed:

$$r_{i_deg} = k_{m_i_deg} \times X_{ac} \times \frac{S_i}{K_{S_i} + S_i} \quad (3.22)$$

Where,

$k_{m_i_deg}$ = Monod maximum specific uptake rate of compound i (i.e. MT, DMS and DMDS) ($\text{kmol kgCOD}^{-1} \text{d}^{-1}$)

X_{ac} = concentration of acetate acid degrading organisms (kgCOD m^{-3})

K_{S_i} = half saturation constant of compound i (M)

S_i = concentration of compound i in liquid phase (M)

The role of methanogens in the degradation of VOSC has been reported in several studies and some kinetic data were found. Ni and Boone (1999) reported that several methanogens could degrade VOSC in anaerobic medium to produce hydrogen sulfide, methane and carbon dioxide. *Methanlobus siciliae*, a methanogen isolated from an oil well, was inoculated into media with either MT or DMS. The maximum growth rate on MT and DMS were 0.068 h^{-1} and 0.087 h^{-1} , respectively. Finster *et al.* (1992) isolated a marine coccoid methanogenic bacterium (strain MTP4) that was able to grown on MT as sole source of energy. The growth yield was 3.06 g biomass (as $\text{C}_4\text{H}_7\text{O}_3$) per mol of MT, which corresponded to 4.06 kg COD per kmol MT. Kiene *et al.* (1986) and Bak, *et al.* (1992) studied degradation of MT and DMS in a range of anoxic aquatic sediments (e.g. fresh water, estuarine, alkaline/hypersaline). A pure culture of an estuarine methanogen was isolated in their studies, which was capable of growth on DMS. The culture metabolized DMS to yield a CH_4/CO_2 molar ratio of 2.83, which was smaller than the theoretical ratio of 3.0. It is possible that the excess reducing power was used for cell

synthesis. The growth yield on DMS derived from their research was 2.26 g biomass (as $C_4H_7O_3$) per mol DMS, i.e. 3.84 kg COD per kmol DMS. Table 3.10 summarized the kinetic data on MT and DMS obtained from literature review. Based on these data, the Monod specific maximum uptake rates (k_m) for MT and DMS were derived.

Table 3.11: Kinetic data of MT and DMS from literature

Compound	μ_m (h^{-1})	Y (gOCD/mol)	$k_m (\mu_m/Y)$ ($mol\ g\ COD^{-1}\ .d^{-1}$)	Source
MT	0.068	4.06	0.40	Ni and Boone (1999), Finster <i>et al.</i> (1992) Kiene <i>et al.</i> (1986) Bak, <i>et al.</i> (1992)
DMS	0.087	3.84	0.54	

However, no papers reported the saturation constants (K_S) of MT and DMS degradation. Another unknown aspect of the degradation of VOSC was the degradation of DMDS. Based on the information of Table 3.11, the parameter estimation function in AQUASIM was run and the data in Table 3.8 was used to calibrate the value of the parameters. The kinetic parameters used in the odour model were presented in Table 3.12. Referring to Table 3.12, the values of the Monod specific maximum rate (k_m) were about 1000 times different from the values in Table 3.11. In this study, it is assumed that methanogenic bacteria are the only bacteria group responsible for the degradation of VOSC. Instead of creating a specific methanogenic bacteria group for the degradation of VOSC, it is assumed that the kinetic rate of degradation of VOSC is proportional to the total concentration of methanogenic bacteria (X_{ac}) (Eq. 3.22). However, from the literature review, only few methanogenic bacteria can degrade VOSC. The values of the Monod specific maximum rate calculated from Table 3.11 were represented for the specific methanogenic bacteria, which can degrade VOSC. Therefore, the Monod specific

maximum rate (k_m) obtained from the model estimation function is much smaller than the value in Table 3.11.

Table 3.12: kinetic data used in the odour model for VOSC degradation

Compounds	k_m (mol/g COD d ⁻¹)	K_s (M)	Source
MT	0.00016	0.0003	Model estimation
DMS	0.00064	0.0001	Model estimation
DMDS	0.00176	0.0025	Model estimation

The stoichiometric equation for degradation of VOSC are expressed as (on a molar basis):

From Eq. 3.23-3.25, the stoichiometric yield of H_2S from the degradation of MT, DMS and DMDS are 1,1, and 2, respectively. The yield of H_2S from degradation of VOSC can be expressed as:

$$r_{\text{H}_2\text{S}_i} = f_{\text{H}_2\text{S}_i} \times r_{i_{\text{deg}}} \quad (3.26)$$

Where,

$r_{\text{H}_2\text{S}_i}$ = the yield kinetic rate of H_2S from the degradation of VOSC (mol mol⁻¹ d⁻¹)

$f_{\text{H}_2\text{S}_i}$ = the stoichiometric yield of H_2S from the degradation of VOSC (mol mol⁻¹)

3.3.7 Sulfide Precipitation

Heavy metals, such as Fe^{2+} , Cu^{2+} , Cr^{2+} and Zn^{2+} , in biosolids can bind together with sulfide to form extremely insoluble sulfide metals that precipitate from the liquid phase (Speece, 1996). The reaction of sulfide precipitation can be expressed as:

Sulfide precipitation is a chemical reaction. Since it has a significant effect on the biochemical formation of sulfur containing odourous compounds, sulfide precipitation was put into the biochemical processes in this chapter. First order kinetics were used to describe sulfide precipitation with respect to both the concentrations of heavy metals and the concentration of sulfide in the reactor:

$$r_{S_Pre} = k_{Pre} \times S_{met} \times S_{H_2S} \quad (3.28)$$

Where,

r_{S_Pre} = the kinetic rate of sulfide precipitation (M d^{-1})

k_{pre} = the precipitation coefficient ($10^6 \text{ M}^{-1} \text{ d}^{-1}$)

S_{met} = the total equivalent heavy metal concentration (M)

S_{H_2S} = hydrogen sulfide concentration (M)

Since sulfide precipitation is a chemical reaction, it occurred very rapidly in the anaerobic digester. Hence, the value of precipitation coefficient is set to $10^6 \text{ M}^{-1} \text{ d}^{-1}$.

3.3.8 Modelling of Inhibition

The formation of odourous compounds, especially sulfur-containing odourous compounds, are complicated processes and the information obtained in this area was very limited, therefore, inhibition functions, except for sulfate reduction, was not considered in the formation of sulfur-containing odour compounds processes. The inhibition in this study was incorporated in ADM1, which mainly came from pH, free ammonia, hydrogen and hydrogen sulfide. Non-competitive inhibition was used in general, because it is the most commonly used form in the literature. Table 3.5 summarized the inhibition forms used in the odour model.

pH inhibition is a combination of disruption of homeostasis and increased weak acids concentration at low pH and affects all organisms to some degree. pH inhibition is used for all intracellular processes in the ADM1, with different parameters for acetogens and acidogens, hydrogen-utilising methanogens and acetoclastic methanogens. Apart from pH inhibition, hydrogen inhibition of acetogenic bacteria and free ammonia inhibition of acetoclastic methanogens are included in the odour model, both described by non-competitive functions. First order inhibition kinetics (Levenspiel, 1980) were applied to undissociated H_2S inhibition. Hydrogen sulfide inhibition was only applied to sulfate reduce bacteria.

Tables 3.6-3.8 summarized all the biochemical kinetic rate equations (r_j) and kinetic coefficients ($v_{i,j}$) used to describe the odour model.

Table 3.13: Inhibition forms

Description	Equation	Used for	Processes
Non-competitive Inhibition	$I = \frac{1}{1 + S_I^a / K_I^a}$	Free ammonia and hydrogen inhibition	Uptake LCFA, valerate, butyrate and propionate and acetate
Empirical upper and lower inhibition	$I = \exp \left[-3 \left(\frac{pH - pH_{UL}^b}{pH_{UL} - pH_{LL}} \right)^2 \right]$	pH inhibition when only low pH inhibition occurs. If pH > pH _{UL} , I=1	Uptake Sugars, AA, LCFA, valerate, butyrate, propionate, acetate and hydrogen
Secondary substrate	$I = \frac{1}{1 + S_I / K_I}$	Inorganic nitrogen inhibition	Uptake Sugars, AA, LCFA, valerate, butyrate, propionate, acetate and hydrogen
First order inhibition ^c	$I = 1 - \frac{S_I}{K_I}$	Hydrogen sulfide	Sulfate reduction process

Note: ^a K_I is the inhibition constant (kgCOD/m³ or M), S_I is inhibitor concentration

^b pH_{UL} is the pH level where there is no pH inhibition; pH_{LL} is the pH level where there is a full pH inhibition

^c Levenspiel (1980)

Table 3.14: Biochemical kinetic rate equations (r_j) in the odour model

j	Process	Rate
1	Disintegration	$k_{dis}X_c$
2	Hydrolysis carbohydrate	$k_{hydr}X_{ch}$
3	Hydrolysis proteins	$k_{hydr}X_{pr}$
4	Hydrolysis Lipids	$k_{hydr}X_{li}$
5	Hydrolysis of MAC	$k_{hydr_MAC}X_{MAC}$
6	Uptake of sugar	$r_{su} = k_{m,su} \frac{S_{su}}{K_s + S_{su}} X_{su} I_1$ <p>Yield of Butyrate: $r_{bu,su} = f_{bu,su} * (1 - Y_{su}) * r_{su}$</p> <p>Yield of Propionate: $r_{pro,su} = f_{pro,su} * (1 - Y_{su}) * r_{su}$</p> <p>Yield of Acetate: $r_{ac,su} = f_{ac,su} * (1 - Y_{su}) * r_{su}$</p>
7	Uptake of AA	$r_{aa} = k_{m,aa} \frac{S_{aa}}{K_s + S_{aa}} X_{ad} I_1$ <p>Yield of VFA and VOSC: $r_{i,aa} = f_{i,aa} (1 - Y_{aa}) r_{aa}$</p> <p>Yield of NH_3: $r_{NH3,aa} = (f_{IN,aa} - N_{bio} Y_{aa}) r_{aa}$</p> <p>Yield of H_2S: $r_{H2S,aa} = [f_{H2S,aa} (1 - Y_{aa}) - S_{bio} Y_{aa}] r_{aa}$</p> <p>Yield of MT: $r_{MT,aa} = f_{MT,aa} * (1 - Y_{aa}) * r_{aa}$</p> <p>Yield of DSM: $r_{DMS,aa} = f_{DMS,aa} (1 - Y_{aa}) * r_{aa}$</p>

		Yield of DMDS: $r_{DMDS,aa} = f_{DMDS,aa} (1 - Y_{aa})^* r_{aa}$
8	Uptake of LCFA	$r_{fa} = k_{m,fa} \frac{S_{fa}}{K_s + S_{fa}} X_{fa} I_2$
9	Uptake of Valerate	Yield of Acetate: $r_{ac,fa} = 0.7 * (1 - Y_{fa})^* r_{fa}$ $r_{va} = k_{m,C4} \frac{S_{va}}{K_s + S_{va}} X_{C4} \frac{1}{1 + S_{bu} / S_{va}} I_2$
		Yield of Acetate: $r_{ac,va} = 0.31 * (1 - Y_{C4})^* r_{va}$
10	Uptake of Butyrate	Yield of Propionate: $r_{pro,va} = 0.54 * (1 - Y_{C4})^* r_{va}$ $r_{bu} = k_{m,C4} \frac{S_{bu}}{K_s + S_{bu}} X_{C4} \frac{1}{1 + S_{va} / S_{bu}} I_2$
11	Uptake of propionate	Yield of Acetate: $r_{ac,bu} = 0.8 * (1 - Y_{C4})^* r_{bu}$ $r_{pro} = k_{m,pro} \frac{S_{pro}}{K_s + S_{pro}} X_{pro} I_2$
12	Uptake of acetate	Yield of Acetate: $r_{ac,pro} = 0.57 * (1 - Y_{pro})^* r_{bu}$ $r_{ac} = k_{m,ac} \frac{S_{ac}}{K_s + S_{ac}} X_{ac} I_3$
13	Uptake of hydrogen	$k_{m,h2} \frac{S_{h2}}{K_s + S_{h2}} X_{h2} I_1$
14	Uptake of propionate by SRB	$r_{pro_SRB} = k_{m_pro_SR} \times \frac{S_{ac}}{K_{S_pro_SR} + S_{ac}} \times \frac{S_{SO4_ion}}{K_{S_SO4_pro} + S_{SO4_ion}} \times X_{pro_SRB} \times I_{H2S_pro_SRB}$

15	Uptake of acetate by SRB	Yield of H_2S : $r_{H_2S,pro_SR} = [f_{H_2S,pro_SR} \times (1 - Y_{pro_SR}) - S_{bio} \times Y_{pro_SR}] r_{pro_SR}$ $r_{ac_SRB} = k_{m_ac_SR} \times \frac{S_{ac}}{K_{S_ac_SR} + S_{pro}} \times \frac{S_{SO4_ion}}{K_{S_SO4_ac} + S_{SO4_ion}} \times X_{ac_SRB} \times I_{H_2S_ac_SRB}$
16	Uptake of hydrogen by SRB	Yield of H_2S : $r_{H_2S,ac_SR} = [f_{H_2S,ac_SR} \times (1 - Y_{ac_SR}) - S_{bio} \times Y_{ac_SR}] r_{ac_SR}$ $r_{H_2_SRB} = k_{m_H_2_SR} \times \frac{S_{H_2}}{K_{S_H_2_SR} + S_{H_2}} \times \frac{S_{SO4_ion}}{K_{S_SO4_H_2} + S_{SO4_ion}} \times X_{H_2_SRB} \times I_{H_2S_H_2_SRB}$
17	Uptake of MAC and H_2S to produce MT	Yield of H_2S : $r_{H_2S,H_2_SR} = [f_{H_2S,H_2_SR} \times (1 - Y_{H_2_SR}) - S_{bio} \times Y_{H_2_SR}] r_{H_2_SR}$ $r_{MAC_MT} = k_{m_MAC_MT} \times X_{VFA} \times \frac{S_{MAC}}{K_{S_MAC} + S_{MAC}} \times \frac{S_{H_2S}}{K_{S_H_2S} + S_{H_2S}}$
18	Uptake of MAC and H_2S to produce DMS	Yield of MT: $r_{MT,MR} = f_{MT,MR} r_{MAC_MT}$ $r_{MAC_DMS} = k_{m_MAC_DMS} \times X_{VFA} \times \frac{S_{MAC}}{K_{S_MAC} + S_{MAC}} \times \frac{S_{H_2S}}{K_{S_H_2S} + S_{H_2S}}$
19	MT oxidation to DMDS	Yield of DMS: $r_{DMS,MR} = f_{DMS,MR} r_{MAC_DMS}$ $r_{MT_DMDS} = k_{MT_DMDS} S_{MT}$
20	Uptake of DMS (DMS degradation)	Yield of DMDS: $r_{DMDS} = 0.5 r_{MT_DMDS}$ $r_{DMS_deg} = k_{m_DMS_deg} \times X_{ac} \times \frac{S_{DMS}}{K_{S_DMS} + S_{DMS}}$

		Yield of H ₂ S: $r_{H2S_DMS} = f_{H2S_DMS} \times r_{DMS_deg}$
21	Uptake of MT (MT degradation)	$r_{MT_deg} = k_{m_MT_deg} \times X_{ac} \times \frac{S_{MT}}{K_{S_MT} + S_{MT}}$
22	Uptake of DMDS (DMDS degradation)	Yield of MT: $r_{H2S_DMS} = f_{H2S_DMS} \times r_{DMS_deg}$ $r_{DMDS_deg} = k_{m_DMDS_deg} \times X_{ac} \times \frac{S_{DMDS}}{K_{S_DMDS} + S_{DMDS}}$
23	Sulfide Precipitation	Yield of DMDS: $r_{H2S_DMDS} = f_{H2S_DMDS} \times r_{DMDS_deg}$
24	Decay of SRB_pro	$r_{S_Pre} = k_{Pre} \times S_{met} \times S_{H2S}$
25	Decay of SRB_ac	$r_{dec-SRB_pro} = k_{dec} \times X_{SRB_pro}$
26	Decay of SRB_h2	$r_{dec-SRB_ac} = k_{dec} \times X_{SRB_ac}$ $r_{dec-SRB_H2} = k_{dec} \times X_{SRB_H2}$
27	Decay of X _{su}	$k_{dec} X_{su}$
28	Decay of X _{aa}	$k_{dec} X_{aa}$
29	Decay of X _{fa}	$k_{dec} X_{fa}$
30	Decay of X _{c4}	$k_{dec} X_{c4}$
31	Decay of X _{pro}	$k_{dec} X_{pro}$
32	Decay of X _{ac}	$k_{dec} X_{ac}$
33	Decay of X _{h2}	$k_{dec} X_{h2}$
		Inhibition Factors: $I_1 = I_{pH} I_{IN,lim}$ $I_2 = I_{pH} I_{IN,lim} I_{h2}$ $I_3 = I_{pH} I_{IN,lim} I_{Nh3,Xac}$

Table 3.15: Biochemical stoichiometric coefficients ($v_{i,j}$) for soluble components in the odour model (1)

Component → i	1	2	3	4	5	6	7	8	9	10
j Process ↓	S_{su}	S_{aa}	S_{fa}	S_{va}	S_{bu}	S_{pro}	S_{ac}	S_{h2}	S_{ch4}	S_{ic}
1 Disintegration										
2 Hydrolysis carbohydrate	1									
3 Hydrolysis proteins		1								
4 Hydrolysis Lipids	$1-f_{fa,li}$		$f_{fa,li}$							
5 Hydrolysis of MAC										
6 Uptake of sugar	-1				$(1-Y_{su})f_{bu,su}$	$(1-Y_{su})f_{pro,su}$	$(1-Y_{su})f_{ac,su}$	$(1-Y_{su})f_{h2,su}$		$-\Sigma C_i V_{i,5}$ I=1-9, 11-24
7 Uptake of AA		-1		$(1-Y_{aa})f_{va,aa}$	$(1-Y_{aa})f_{bu,aa}$	$(1-Y_{aa})f_{pro,aa}$	$(1-Y_{aa})f_{ac,aa}$	$(1-Y_{aa})f_{h2,aa}$		$-\Sigma C_i V_{i,6}$ I=1-9, 11-24
8 Uptake of LCFA			-1				$(1-Y_{fa})0.7$	$(1-Y_{fa})0.3$		
9 Uptake of Va.				-1		$(1-Y_{ca})0.54$	$(1-Y_{ca})0.31$	$(1-Y_{ca})0.15$		
10 Uptake of Bu.					-1		$(1-Y_{ca})0.8$	$(1-Y_{ca})0.2$		
11 Uptake of propionate						-1	$(1-Y_{pro})0.57$	$(1-Y_{pro})0.43$		$-\Sigma C_i V_{i,10}$ I=1-9, 11-24
12 Uptake of acetate							-1		$1-Y_{ac}$	$-\Sigma C_i V_{i,11}$ I=1-9, 11-24
13 Uptake of hydrogen								-1	$1-Y_{h2}$	$-\Sigma C_i V_{i,12}$ I=1-9, 11-24
14 Uptake propionate by SRB						-1				
15 Uptake acetate by SRB										
16 Uptake H ₂ by SRB										
17 Uptake of MAC and H ₂ S to produce MT										
18 Uptake of MAC and H ₂ S to produce DMS										

Table 3.15: Biochemical stoichiometric coefficients (v_{ij}) for soluble components in the odour model (2)

Component → i	11	12	13	14	15	16	17	18	19	20
j Process ↓	S_{IN}	S_I	S_{MAC}	S_{H_2S}	S_{MT}	S_{DMS}	S_{DMDS}	S_{SO_4}	S_{Metal}	S_{MS}
1 Disintegration		$f_{SI, Xc}$								
2 Hydrolysis carbohydrate										
3 Hydrolysis proteins										
4 Hydrolysis Lipids										
5 Hydrolysis of MAC			1							
6 Uptake sugar	$-(Y_{su}) N_{bio}$									
7 Uptake AA	$N_{aa} - (Y_{aa}) N_{bio}$			$(1 - Y_{aa}) f_{H_2S, aa} \cdot S_{bio} Y_{aa}$	$(1 - Y_{aa}) f_{MT, aa}$	$(1 - Y_{aa}) f_{DMS, aa}$	$(1 - Y_{aa}) f_{DMDS, aa}$			
8 Uptake of LCFA	$-(Y_{fa}) N_{bio}$									
9 Uptake of Valerate	$-(Y_{c4}) N_{bio}$									
10 Uptake of Butyrate	$-(Y_{c4}) N_{bio}$									
11 Uptake of propionate	$-(Y_{pro}) N_{bio}$									
12 Uptake of acetate	$-(Y_{ac}) N_{bio}$									
13 Uptake of hydrogen	$-(Y_{H_2}) N_{bio}$									
14 Uptake of propionate by SRB				$0.75/112 \cdot (1 - Y_{pro, SRB}) \cdot S_{bio} Y_{pro, SRB}$				$-0.75/112 \cdot (1 - Y_{pro, SRB})$		
15 Uptake of acetate by SRB				$1/64 \cdot (1 - Y_{ac, SRB}) \cdot S_{bio} Y_{ac, SRB}$				$-1/64 \cdot (1 - Y_{ac, SRB})$		
16 Uptake of H_2 by SRB				$1/64 \cdot (1 - Y_{H_2, SRB}) \cdot S_{bio} Y_{H_2, SRB}$				$-1/64 \cdot (1 - Y_{H_2, SRB})$		
17 Uptake of MAC and H_2S to produce MT			-1	$-1/288$	$1/288$					
18 Uptake of MAC and H_2S to produce DMS			-1	$-1/288$		$1/288$				
19 MT oxidation to DMS				-2		1				
20 Uptake of DMS			1		-1					
21 Uptake of MT			1	-1						

Table 3.16: Biochemical stoichiometric coefficients ($v_{i,j}$) for particulate components in the odour model (1)

Component $\rightarrow$ i	21	22	23	24	25	26	27	28	29	30
j Process $\downarrow$	X_C	X_{ch}	X_{pr}	X_{ij}	X_{su}	X_{aa}	X_{fa}	X_{c4}	X_{pro}	X_{ac}
1 Disintegration	-1	$f_{ch,Xc}$	$f_{pr,Xc}$	$f_{ij,Xc}$						
2 Hydrolysis carbohydrate		-1								
3 Hydrolysis proteins			-1							
4 Hydrolysis Lipids				-1						
5 Hydrolysis of MAC										
6 Uptake of sugar					Y_{su}					
7 Uptake of AA						Y_{aa}				
8 Uptake of LCFA							Y_{fa}			
9 Uptake of Va.								Y_{c4}		
10 Uptake of Bu.								Y_{c4}		
11 Uptake of propionate									Y_{pro}	Y_{ac}
12 Uptake of acetate										
13 Uptake of hydrogen					-1					
14 Uptake of propionate by SRB						-1				
15 Uptake of acetate by SRB							-1			
16 Uptake of H_2 by SRB										
17 Uptake of MAC and H_2S to produce MT								-1	-1	
18 Uptake of MAC and H_2S to produce DMS										
19 MT oxidation to DMS										
20 Uptake of DMS										
21 Uptake of MT										
22 Uptake of DMDS										
23 Sulfide precipitation										
24 Decay of SRB_pro										
25 Decay of SRB_ac										

Table 3.16: Biochemical stoichiometric coefficients ($v_{i,j}$) for particulate components in the odour model (2)

j	Component → i	31	32	33	34	35	36
j	Process ↓	X_{h2}	X_i	$X_{pro,SRB}$	$X_{ac,SRB}$	$X_{h2,SRB}$	X_{MAC}
1	Disintegration						0.04
2	Hydrolysis carbohydrate						
3	Hydrolysis proteins						
4	Hydrolysis Lipids						
5	Hydrolysis of MAC						-1
6	Uptake of sugar						
7	Uptake of AA						
8	Uptake of LCFA						
9	Uptake of Va.						
10	Uptake of Bu.						
11	Uptake of propionate						
12	Uptake of acetate						
13	Uptake of hydrogen						
14	Uptake of propionate by SRB			$Y_{pro,SRB}$			
15	Uptake of acetate by SRB				$Y_{ac,SRB}$		
16	Uptake of H ₂ by SRB					$Y_{h2,SRB}$	
17	Uptake of MAC and H ₂ S to produce MT						
18	Uptake of MAC and H ₂ S to produce DMS						
19	MT oxidation to DMDS						
20	Uptake of DMS						
21	Uptake of MT						
22	Uptake of DMDS						
23	Sulfide precipitation						
24	Decay of SRB_pro						
25	Decay of SRB_ac						
26	Decay of SRB_h2						
27	Decay of X_{su}						
28	Decay of X_{aa}						
29	Decay of X_{fa}						

30	Decay of X_{C4}					Particulate MAC (kgCOD/m3)
31	Decay of X_{pro}					SRB_h2 degraders (kgCOD/m3)
32	Decay of X_{ac}					SRB_ac degraders (kg COD/m3)
33	Decay of X_{h2}			-1		SRB_pro degraders (kgCOD/m3)
						Particulate Inerts (kgCOD/m3)
						Hydrogen Degraders (kgCOD/m3)

3.4 Physico-Chemical Processes

The physico-chemical system can be defined as non-biologically mediated processes that commonly occurred in anaerobic digesters. Three important processes were addressed in the odour model, i.e. acid-base dissociation, liquid-gas mass transfer and liquid-solid partitioning. The first two processes have been addressed in some anaerobic models. However, odourous compounds were not addressed in these models. This section will identify the kinetic rates for the three most important physico-chemical processes.

Since VOSC are very weak acids, they were not included in the acid-base dissociation process. Liquid-solid partitioning is a complicated process and an empirical equation (Eq. 2.15) employed to calculate the partitioning coefficient for the VOSC, therefore, the liquid-solid in this study only includes VOSC. Dynamic kinetic rates were employed to describe the three physico-chemical processes. Figure 3.5 demonstrated the mass balance of odourous compounds and the physico-chemical processes in a completely mixed anaerobic digester.

Referring to Figure 3.5, the odourous compounds generated from the biochemical reactions were assumed to be: VFA and NH_3 in their ionic form (i.e. VFA^- and NH_4^+), H_2S and VOSC in their molecular form. The molecular forms of VFA and NH_3 could be produced from their ionic forms by acid-base dissociation and the kinetic rate is expressed as $r_{\text{B/A}}$ (i.e. from base to acid reaction). The ionic form H_2S will be converted from its molecular form by acid-base dissociation and the kinetic rate is $r_{\text{A/B}}$ (i.e. from acid to base reaction). The molecular form of VOSC will partition to the solid phase and the kinetic rate is $r_{\text{L/S}}$ (i.e. from liquid to solid phase partitioning). Only the molecular

form of odourous compounds in the liquid phase can be finally emitted into gas phase and the kinetic rate for this process is $r_{L/G}$ (i.e from liquid to gas phase partitioning). In this section, the kinetic rates for the physico-chemical processes will be addressed and the mass balance of odourous compounds in three phases will be discussed.

Figure 3.5: Mass flow of selected compounds in the odour model

3.4.1 Acid-Base Dissociation

Acid-base dissociation is critical when modelling the emission of odourous compounds in anaerobic digesters, because acid-base dissociating can predict both the molecular concentrations of odourous compounds and the pH values in the reactors. Generally, only the molecular form of odourous compounds are emitted from the liquid phase to the gas

phase and the pH in reactors can effect both chemical and biochemical reactions.

Therefore, acid-base dissociation is a key process for modelling anaerobic digestion.

In this odour model, a dynamic process was applied to address acid-base dissociations;

the two dynamic mass balance equations for S_{VFA} , and S_{VFA}^- respectively are:

$$\frac{dS_{liq,VFA^-}}{dt} = -\frac{Q_{out}S_{liq,VFA^-}}{V_{liq}} + \sum r_j v_{i,j} - r_{B/A,VFA} \quad (3.31)$$

and

$$\frac{dS_{liq,VFA}}{dt} = -\frac{Q_{out}S_{liq,VFA}}{V_{liq}} + r_{B/A,VFA} - r_{L/G,VFA} \quad (3.32)$$

Where,

$dS_{liq,VFA^-}/dt$ = the dynamic rate of ionic VFA in the liquid phase ($\text{kgCOD m}^{-3} \text{d}^{-1}$)

Q_{out} = the output sludge flow ($\text{m}^3 \text{d}^{-1}$)

$\sum r_j v_{i,j}$ = the sum of the specific kinetic rates for biochemical process j multiplied by the stoichiometric coefficient ($v_{i,j}$) of ionic VFA in process j.

$r_{B/A,VFA}$ = the kinetic rate for base to acid reaction of VFA ($\text{kgCOD m}^{-3} \text{d}^{-1}$)

$dS_{liq,VFA}/dt$ = the dynamic concentration rate of molecular VFA in the liquid phase ($\text{kgCOD m}^{-3} \text{d}^{-1}$)

$r_{L/G,i}$ = the kinetic rate for liquid to gas partitioning of VFA ($\text{kgCOD m}^{-3} \text{d}^{-1}$)

(Section 3.4.2)

The two dynamic mass balance equations for $S_{NH_4^+}$, and S_{NH_3} , respectively, are:

$$\frac{dS_{liq,NH_4^+}}{dt} = \frac{Q_{in}S_{in,NH_4^+}}{V_{liq}} - \frac{Q_{out}S_{liq,NH_4^+}}{V_{liq}} + \sum r_j v_{i,j} - r_{A/B,NH_4^+} \quad (3.33)$$

and
$$\frac{dS_{liq,NH_3}}{dt} = -\frac{Q_{out}S_{liq,NH_3}}{V_{liq}} + r_{A/B,NH_4^+} - r_{L/G,NH_3} \quad (3.34)$$

The two dynamic mass balance equations for S_{H_2S} , and S_{HS^-} , respectively, are:

$$\frac{dS_{liq,H_2S}}{dt} = -\frac{Q_{out}S_{liq,H_2S}}{V_{liq}} + \sum r_j v_{i,j} - r_{A/B,H_2S} - r_{L/G,H_2S} \quad (3.35)$$

and
$$\frac{dS_{liq,HS^-}}{dt} = -\frac{Q_{out}S_{liq,HS^-}}{V_{liq}} + r_{A/B,H_2S} \quad (3.36)$$

The dynamic mass balance equation for S_{VOSC} is:

$$\frac{dS_{liq,VOSC}}{dt} = -\frac{Q_{out}S_{liq,VOSC}}{V_{liq}} + \sum r_j v_{i,j} - r_{L/G,H_2S} - r_{L/S,VOSC} \quad (3.37)$$

Where,

$r_{L/S,VOSC}$ = the kinetic rate for liquid to solid partitioning of VOSC ($M d^{-1}$) (section 3.4.3)

Acid-base dissociation describes the ratio of odourous compounds between their molecular form and the ionic form in the liquid phase. At steady state, the acid-base dissociation equation for the selected odourous compounds can be expressed as:

$$K_a S_{SS,i} - S_{SS,i}^- S_{H^+} = 0 \quad (3.38)$$

Where,

K_a = the acid-base dissociation coefficient (M)

$S_{SS,i}$ = the molecular concentration of component i at steady state (M)

$S_{SS,i}^-$ = the ionized concentration of component i at steady state (M)

S_{H^+} = the concentration of hydrogen ion. (M)

The dynamic kinetic rate of VFA for the base to acid reaction can be expressed as:

$$r_{B/A,VFA} = K_{B/A,VFA} (S_{VFA^-} S_{H^+} - K_{a,VFA} S_{VFA}) \quad (3.39)$$

Where,

$r_{B/A,VFA}$ = the production rate of the molecular VFA from their ionic form ($M d^{-1}$)

$K_{A/B,i}$ = dynamic rate coefficient for base to acid reaction, initially set to $10^8 M^{-1} d^{-1}$

The dynamic kinetic rate of NH_4^+ in the acid to base reaction can be expressed as

$$r_{A/B,NH_4^+} = K_{A/B,NH_4^+} (S_{NH_3} S_{H^+} - K_{a,NH_4^+} S_{NH_4^+}) \quad (3.40)$$

The dynamic kinetic rate of H_2S in the acid to base reaction can be expressed as:

$$r_{A/B,H_2S} = K_{A/B,H_2S} (S_{HS^-} S_{H^+} - K_{a,H_2S} S_{H_2S}) \quad (3.41)$$

The stoichiometric yield from acid to base or from base to acid is 1, therefore, the relationship of the kinetic rate of component i between its acid to base reaction and base to acid reaction can be expressed as:

$$r_{A/B,i} = -r_{B/A,i} \quad (3.42)$$

The stoichiometry and kinetic rate equations for acid-base reaction in the odour model were presented in Table 3.16.

Acid base dissociation can also be employed to assisting model a charge balance. The charge balance can be expressed as:

$$\sum S_{C^+} - \sum S_{A^-} = 0 \quad (3.43)$$

Where,

$\sum S_{C^+}$ = the total cationic equivalents concentration

$\sum S_{A^-}$ = the total anionic equivalents concentration

The equivalent concentration is its valence multiplied by molar concentrations. Implemented in the odour model, the charge balance is as follows (denominators for organic acids represented the g COD content per charge):

$$S_{Cat^+} + S_{NH_4^+} + S_{H^+} - S_{HCO_3^-} - \frac{S_{ac^-}}{64} - \frac{S_{pro^-}}{112} - \frac{S_{bu^-}}{160} - \frac{S_{va^-}}{208} - S_{HS^-} - S_{OH^-} - S_{An^-} = 0 \quad (3.44)$$

Where, S_{cat^+} , S_{An^-} represent metallic ions such as Na^+ and Cl^- , which can be treated as inert compounds with no consumption or reaction terms. LCFA were not included in the acid-base system because the number of charged sites per COD is small. Amino acid acid-base reactions were also not included because of their low concentrations in the reactor (due to high acidogenesis rates).

If the acid base reaction for H_2O is implemented, the hydroxide can be calculated as:

$$S_{OH^-} - \frac{K_w}{S_{H^+}} = 0 \quad (3.45)$$

Where,

K_w = the equilibrium coefficient for water, 10^{-14} M

Eq. 3.45 (for S_{OH^-}) was substituted into the charge balance, and S_{H^+} became the only unknown in the charge balance equation (Eq. 3.44). Therefore, the pH in the reactors was predicted by acid-base dissociation.

Table 3.17: Stoichiometry and kinetic rate equations for acid to base reactions in the odour model

Component → i	Process ↓	1a	1b	2a	2b	3a	3b	4a	4b	5a	5b	6a	6b	Rate (r _i , kg COD m ³ d ⁻¹ or M d ⁻¹)
		S _{hac}	S _{ac-}	S _{hPro}	S _{pro-}	S _{hbu}	S _{bu-}	S _{hva}	S _{va-}	S _{H2S}	S _{HS-}	S _{NH4}	S _{NH3}	
1	Acetate base-acid	1	-1											$K_{B/A,ac} (S_{ac-} S_{H^+} - K_{a,ac} S_{hac})$
2	Propionate base-acid			1	-1									$K_{B/A,pro} (S_{pro-} S_{H^+} - K_{a,pro} S_{hpro})$
3	Butyrate base-acid					1	-1							$K_{B/A,bu} (S_{bu-} S_{H^+} - K_{a,bu} S_{hbu})$
4	Valerate base-acid							1	-1					$K_{B/A,va} (S_{va-} S_{H^+} - K_{a,va} S_{hva})$
5	Hydrogen sulfide acid- base									1	-1			$-K_{B/A,H2S} (S_{HS-} S_{H^+} - K_{a,H2S} S_{H2S})$
6	Ammonia base-acid											1	-1	$-K_{B/A,NH3} (S_{NH3} S_{H^+} - K_{a,NH3} S_{NH4^+})$
														<i>Kinetic parameters:</i> k _{A/B,i} rate coefficient for the base to acid reaction. Set to 10 ⁸ M ⁻¹ d ⁻¹

3.4.2 Liquid-Gas Mass Transfer

The gas phase rate equations were similar to the liquid phase equations, except there was no advective influent flow, and only dynamic state components. The dynamic mass balance equations for gas phase with a constant gas volume are:

$$\frac{dS_{gas,i}}{dt} = -\frac{Q_{gas}S_{gas,i}}{V_{gas}} + r_{L/G,i} \frac{V_{liq}}{V_{gas}} \quad (3.46)$$

Where,

$dS_{gas,i}/dt$ = the dynamic concentration rate of component i in gas phase

(for VFA, kgCOD m⁻³ d⁻¹; for NH₃, H₂S and VOSC, M d⁻¹)

$S_{gas,i}$ = the gas phase concentration of component i

(for VFA, kgCOD m⁻³; for NH₃, H₂S and VOSC, M)

Q_{gas} = gas flow emitted from anaerobic digesters (m³ d⁻¹)

V_{gas} , V_{liq} = the volume of gas phase and liquid reactor, respectively (m³)

Compared with the gas phase concentrations of CH₄, CO₂ and H₂, which are the main biogases emitted from anaerobic digesters, the gas phase concentrations of odourous compounds are negligible. The total dry gas flow Q_{gas} (m³ d⁻¹) was calculated with a pressure control loop that kept the sum of the simulated partial gas press ($\Sigma p_i = p_{CH_4} + p_{CO_2} + p_{H_2}$) as close as possible to the effective total dry gas pressure ($p_{atm} - p_{H_2O}$) in the gas bubble. The expression of gas flow was calculated as (Batstone, 2002 and Siegrist *et al.*, 2002):

$$Q_{gas} = k_p \frac{(p_{CH_4} + p_{CO_2} + p_{H_2} + p_{H_2O} - p_{atm})}{p_{atm}} V_{liq} \quad (3.47)$$

Where,

k_p = the proportional control constant, 10000 d⁻¹ (if $\sum p_i < p_{atm} - p_{H_2O}$, then $k_p = 0$)

$p_{CH_4}, p_{CO_2}, p_{H_2}$ = gas phase concentration of CH₄, CO₂ and H₂ in pressure (bar)

p_{H_2O} = the water vapour pressure, which can be assumed to be saturated in the reactor headspace (bar)

p_{atm} = the external (atmospheric) pressure (normally 1.013 bar)

The pressure (in bar) of each gas component was calculated using the ideal gas law from their concentrations in kg COD m⁻³:

$$p_{gas, H_2} = S_{gas, H_2} RT / 16 \quad (3.48a)$$

$$p_{gas, CH_4} = S_{gas, CH_4} RT / 64 \quad (3.48a)$$

$$p_{gas, CO_2} = S_{gas, CO_2} RT \quad (3.48a)$$

Where, the factors in denominators were COD equivalences of the gases.

The temperature dependence of water vapour pressure can be calculate as (Lide,2001):

$$p_{gas, H_2O} = 0.0313 \exp \left(5290 \left(\frac{1}{298} - \frac{1}{T} \right) \right) \quad (3.49)$$

Where, T is the temperature in K.

The liquid-gas transfer rate for VFA was expressed as:

$$r_{L/G,VFA} = k_L a_{VFA} (S_{liq,VFA} - f_{COD} K_{H,VFA} p_{gas,VFA}) \quad (3.50)$$

Where,

$r_{L/G, VFA}$ = the dynamic liquid-gas transfer rate of VFA ($\text{kg COD m}^{-3} \text{d}^{-1}$)

$k_L a_{VFA}$ = volume-specific gas-liquid transfer coefficient (d^{-1})

f_{COD} = the COD equivalent per mol of VFA (for HAC, f is 64; for HPro, f is 112; for HBU, f is 160; and for HVa, f is 208).

$K_{H,VFA}$ = Henry's law coefficient for VFA ($\text{M}_{liq} \text{bar}_{gas}^{-1}$)

The liquid-gas transfer for NH_3 , H_2S and VOSC can be expressed as:

$$r_{L/G,i} = k_L a_i (S_{liq,i} - K_{H,i} p_{gas,i}) \quad (3.51)$$

The stoichiometry and kinetic rate equations for liquid-gas transfer in the odour model were presented in Table 3.17.

Table 3.18: Stoichiometry and kinetic equations for liquid-gas transfer in a dynamic process (1)

Process	S_{H_2S} (M)	P_{H_2S} (bar)	S_{MT} (M)	P_{H_2S} (bar)	S_{DMS} (M)	P_{DMS} (bar)	S_{DMDS} (M)	P_{DMDS} (bar)	S_{NH_3} (M)	P_{NH_3} (bar)	Rate
H ₂ S stripping	-1	1									$r_{L/G,H_2S} = k_L a_{H_2S} \times (S_{liq,H_2S} - K_{H,H_2S} \times p_{gas,H_2S})$
MT stripping			-1	1							$r_{L/G,MT} = k_L a_{MT} \times (S_{liq,MT} - K_{H,MT} \times p_{gas,MT})$
DMS stripping					-1	1					$r_{L/G,DMS} = k_L a_{DMS} \times (S_{liq,DMS} - K_{H,DMS} \times p_{gas,DMS})$
DMDS stripping							-1	1			$r_{L/G,DMDS} = k_L a_{DMDS} \times (S_{liq,DMDS} - K_{H,DMDS} \times p_{gas,DMDS})$
NH ₃ stripping									-1	1	$r_{L/G,NH_3} = k_L a_{NH_3} \times (S_{liq,NH_3} - K_{H,NH_3} \times p_{gas,NH_3})$

Table 3.18: Stoichiometry and kinetic equations for liquid-gas transfer in a dynamic process (2)

Process	S_{HAc}	P_{HAc}	S_{HPro}	P_{HPro}	S_{HBu}	P_{HBu}	S_{HVa}	P_{HVa}	Kinetic expression
HAc stripping	-1	1							$r_{L/G,HAc} = k_L a_{HAc} \times (S_{liq,HAc} - 64K_{H,HAc} \times p_{gas,HAc})$
HPro stripping			-1	1					$r_{L/G,HPro} = k_L a_{HPro} \times (S_{liq,HPro} - 112K_{H,HPro} \times p_{gas,HPro})$
HBu stripping					-1	1			$r_{L/G,HBu} = k_L a_{HBu} \times (S_{liq,HBu} - 160K_{H,HBu} \times p_{gas,HBu})$
HVa stripping							-1	1	$r_{L/G,HVa} = k_L a_{HVa} \times (S_{liq,HVa} - 208K_{H,HVa} \times p_{gas,HVa})$
	kg COD m ⁻³	bar	kg COD m ⁻³	bar	kg COD m ⁻³	bae	kg COD m ⁻³	bar	

3.4.3 Solid-Liquid Partitioning

Normally the concentration mentioned in the liquid phase is composed of liquid and solid phase concentration. The main reason for excluding the liquid-solid partitioning kinetics from most existing models is the complexity of the process. However, in order to effectively model the physico-chemical behaviour, the partitioning mechanisms of VOSC were included in this study. The empirical equation from the study of Dobbs *et al.* (1989) was taken to formulate the liquid-solid phase partitioning coefficients of VOSC at equilibrium. A kinetic rate was employed in the odour model to describe the liquid-solid partitioning process.

In general, the liquid-solid partitioning process is similar to liquid-gas phase mass transfer. The differential mass balance equations for liquid-solid partitioning can be expressed as (assumed that the solid phase volume is equal to the liquid phase volume):

$$\frac{dS_{sol,i}}{dt} = -\frac{Q_{out}S_{sol,i}}{V_{liq}} + r_{L/S,i} \quad (3.52)$$

$dS_{sol,i}/dt$ = the dynamic concentration change rate in solid phase ($M d^{-1}$)

$S_{sol,i}$ = the concentration of component i in solid phase (M)

$r_{L/S,i}$ = the kinetic rate for liquid-solid partitioning ($M d^{-1}$)

At steady state, the ratio between the solid phase concentration and liquid phase concentration of VOSC can be expressed by the empirical equation of Dobbs *et al.* (1989):

$$\frac{S_{sol,i}}{S_{liq,i}} = K_p' X_C \quad (3.53)$$

Where,

$S_{sol,i}$ = solid phase concentration of component i (M)

K_p' = Partitioning coefficient for compound i in the wastewater solids (L/g COD)

X_C = concentration of volatile suspended solids (VSS) in wastewater (g COD/l)

$S_{liq,i}$ = liquid phase concentration of component i (M)

The dynamic rate for liquid-solid partitioning was expressed as:

$$r_{L/S,i} = K_{L/S,i} (K_p' X_C S_{liq,i} - S_{sol,i}) \quad (3.54)$$

Where,

$r_{L/S,i}$ = kinetic rate for the liquid to solid partitioning of component i (M d⁻¹)

$K_{L/S,i}$ = rate coefficient for the liquid to solid partitioning, initially set to 10¹⁰ d⁻¹.

The liquid-solid partitioning coefficients of VOSC were presented in Table 2.7. The stoichiometry and kinetic rate equations for liquid-solid partitioning in the odour model were presented in Table 3.18.

Table 3.19: Stoichiometry and kinetic equations for liquid-solid partitioning in a dynamic process

Process	$S_{liq,MT}$ (M)	$S_{sol,MT}$ (M)	$S_{liq,DMS}$ (M)	$S_{sol,DMS}$ (M)	$S_{liq,DMS}$ (M)	$S_{sol,DMS}$ (M)	Rate (M d ⁻¹)
MT liqui-Solid partitioning	-1	1					$r_{L/S,MT} = K_{L/S,MT}^a \times (K_P' X_C S_{liq,MT} - S_{sol,MT})$
DMS liqui-Solid partitioning			-1	1			$r_{L/S,DMS} = K_{L/S,DMS}^a \times (K_P' X_C S_{liq,DMS} - S_{sol,DMS})$
DMDS liqui-Solid partitioning						-1	$r_{L/S,DMDS} = K_{L/S,DMDS}^a \times (K_P' X_C S_{liq,DMDS} - S_{sol,DMDS})$

Note: ^a $K_{L/G,i}$ is the rate coefficient for the liquid to solid partitioning of compound i. Set to $1 \times 10^{10} \text{ d}^{-1}$.

3.5 Model Verification

Model verification was conducted to ensure that the model has been assembled properly and to check for errors in coding in the program AQUASIM. In ADM1, the verification was conducted in an excel file. In this file, the concentrations of the variables in anaerobic digesters were calculated by excel at steady state and the results were compared with the output data of ADM1. Since the values from the calculation of excel were fit well with the output data of ADM1, it proved that the processes in ADM1 were correctly built in the program AQUASIM. The mass balances for COD, N and C for each process were also calculated in ADM1.

For the odour model, the verification was also conducted with an excel file in a simpler fashion. The mass balance for COD for most of the processes and the mass balance for C, N and S for each process were calculated. The results of the mass balance showed that the processes of the odour model were correctly coded in the program AQUAIM.

3.6 Conclusion

The odour model developed in this study identified the pathways, kinetic rates and stoichiometric coefficients for the formation of selected odourous compounds in anaerobic digesters. In the odour model, the formation of the hydrogen sulfide comes from the degradation of sulfur-containing amino acids, sulfate reduction and the degradation of VOSC. VOSC are produced from degradation of sulfur-containing amino acids and methylation reactions. VFA and NH_3 are generated from the degradation of amino acids.

Generally, the literature on sulfate reduction provided the well-defined and complete kinetic data to develop a kinetic model. However, the kinetic data for methylation reactions and degradation of VOSC were generally uncertain and from anoxic conditions. This may cause the errors in the model predictions.

The physical and chemical processes described in this odour model included acid-base reactions, liquid-gas mass transfer and liquid-solid partitioning. The three physico-chemical processes are important for modelling anaerobic digesters, since all of them may significantly affect the concentration of odourous compounds emitted in the gas phase. Three dynamic rate equations were employed to describe these physico-chemical processes. An acid-base dissociation was also employed to formulate a charge balance to predict the pH in the digesters.

In general, the odour model provides a tool to predict concentrations of the odourous compounds in the gas phase in anaerobic digesters. However, this odour model may contain some errors in its outputs because some kinetic data used in the process rates were uncertain.

Chapter 4: Sensitivity Analysis

4.1 Introduction

In order to develop the odour model, a large number of parameters have been introduced to describe the formation of odourous compounds in anaerobic digesters. These parameters could more or less affect the production of each individual odourous compound in anaerobic digesters. A sensitivity analysis was performed to compare the effects of parameters on the production of the odourous compounds. The goal of the sensitivity analysis was to identify the most significant parameters in the formation of odourous compounds in anaerobic digesters. Some of the parameters were significant to all odourous compounds. There were other parameters, which were only critical to the formation of one specific odourous compound. Therefore, the sensitivity analysis combined the tasks of the general sensitivity analysis and the individual sensitivity analysis. The general sensitivity analysis was to identify the most significant parameters for all odourous compounds. The individual sensitivity analysis was to identify the most significant parameters for the formation of each individual odourous compound. The results of the sensitivity analysis provide insight into the model and can be used to direct future laboratory work.

In this chapter, the suggested parameter values of a base odour model were first discussed. Then, a mass balance for sulfur was used to check the correctness of the basic odour model. The sensitivity analysis in this study included two parts: the general sensitivity analysis and the individual sensitivity analysis.

4.2 Suggested Parameter Values

Biochemical parameter estimation for anaerobic models was one of the areas in which the literature was less developed. The strategies for parameter estimation used in this study were: (a) taking those with detailed information, such as parameters related to the sulfate reduction, from literature values, (b) taking those with limited information, such as parameters related to the methylation reaction and degradation of sulfur-containing odorous compounds, from studies with similar conditions, (c) taking those with no information, such as K_{MT_DMDS} , K_{P_MT} , K_{P_DMS} and K_{P_DMDS} from either calculation or assumption. The suggested parameter values were summarized in Table 4.1.

Referring to Table 4.1, 70 new parameters were introduced in this odour model. The quantitative emission of odorous compounds was a combined effect of all these parameters. However, the role, which each individual parameter played in the behavior of the odorous compounds in anaerobic digesters, was different. The sensitivity analysis was used to identify the importance of the role of each parameter. Because the emission of odourants from anaerobic digesters is a new interest for environmental engineering, research or experimental data in this area was limited. Therefore, most of the parameter values in Table 4.1 were either from studies of similar situations or from assumptions. The sources of these parameters were described in Table 4.1.

Table 4.1: Suggested parameter values for mesophilic anaerobic digesters

Parameter	Unit	Value	Description	References
Disintegration process				
1.f_aro_xc		0.04	Yield of methylated aromatic compounds from disintegration of complex particulates	Kayhanian (1995)
Hydrolysis Process				
2.khyd_aro	d ⁻¹	10	Methylated aromatic compounds hydrolysis first order constant	Estimated from ADM1
Uptake Amino Acids Process				
3.f_aa_DMDS	mol DMDS/gCOD AA	1.17E-005	Yield of DMDS from amino acids degradation	Ramsay (1997) and Appendix B
4.f_aa_DMS	mol DMS/gCOD AA	4.10E-005	Yield of DMS from amino acids degradation	
5.f_aa_MT	mol MT/gCOD AA	6.64E-005	Yield of MT from amino acids degradation	
6.Sul_aa	mol S/gCOD AA	2.08E-004	Sulfur content in amino acids	
7.Sul_biom	mol S/gCOD	6.25E-005	Sulfur content in biomass	
8.Sul_Xc	mol S/gCOD	6.25E-005	Sulfur content in complex particulate	
Sulfate Reduction Process				
9.km_SRB_ac	kgCOD ac/kgCOD X	8.644	Maximum uptake rate of acetate for sulfate reduction	Kalyuzhnyi and Fedorovich, (1998)
10.Ks_so4_ac	M	0.0002	Half saturation constant of sulfate for sulfate reduction using acetate as substrate	
11.Ks_SRB_ac	kgCOD/m ³	0.024	Half saturation constant of acetate for sulfate reduction	
12.Y_SRB_ac	kgCOD/kgCOD	0.059	Yield of sulfate reduction bacteria on uptake of acetate	
13.KI_H2S_SRB_ac	M	0.0089	H ₂ S inhibitory concentration of acetate for sulfate reduction	
14.km_SRB_pro	kgCOD pro/kgCOD X	15.88	Maximum uptake rate of propionate for sulfate reduction	
15.Ks_so4_pro	M	7.71E-005	Half saturation constant of sulfate for sulfate reduction using propionate as substrate	
16.Ks_SRB_pro	kgCOD/m ³	0.295	Half saturation constant of propionate for sulfate reduction	
17.Y_SRB_pro	kgCOD/kgCOD	0.051	Yield of sulfate reduction bacteria on uptake of propionate	
18.KI_H2S_SRB_pro	M	0.0089	H ₂ S inhibitory concentration for propionate for sulfate reduction	
19.km_SRB_h2	kgCOD h ₂ /kgCOD X	44.64	Maximum uptake rate of hydrogen for sulfate reduction	
20.Ks_so4_h2	M	9.38E-006	Half saturation constant of hydrogen for sulfate reduction using acetate as substrate	
21.Ks_SRB_h2	kgCOD/m ³	5E-005	Half saturation constant of hydrogen for sulfate reduction	
22.Y_SRB_h2	kgCOD/kgCOD	0.112	Yield of sulfate reduction bacteria on uptake of hydrogen	

23.KI_H2S_SRB_h2	M	0.0172	H ₂ S inhibitory concentration of hydrogen for sulfate reduction	
Methylation reaction				
24.km_MAC_MT	kgCOD MAC/kgCOD X.d	0.0074	Maximum uptake rate for MAC to produce MT	Lomans <i>et al.</i> (1997,2001); Kreft and Schink (1997); Bache and Pfennig (1981)
25.Ks_MAC	kgCOD/m ³	0.1504	Half saturation constant for MAC to produce VOSC	
26.Ks_H2S_MT	M	0.0001	Half saturation constant of hydrogen sulfide for methylation reaction to produce MT	
27.km_MAC_DMS	kgCOD MAC/kgCOD X.d	0.008226	Maximum uptake rate for MAC to produce DMS	
28.Ks_MAC	kgCOD/m ³	0.1504	Half saturation constant for MAC to produce VOSC	
29.Ks_H2S_DMS	M	0.0001	Half saturation constant of hydrogen sulfide for methylation reaction to produce DMS	
Decay of sulfate reducing bacteria				
30.kdec_xSRBac	d ⁻¹	0.02	Decay rate for sulfate reducing bacteria using acetate as substrate	Kalyuzhnyi and Fedorovich, (1998)
31.kdec_xSRBpro	d ⁻¹	0.02	Decay rate for sulfate reducing bacteria using propionate as substrate	
32.kdec_xSRBh ₂	d ⁻¹	0.02	Decay rate for sulfate reducing bacteria using hydrogen as substrate	
Decay of VOSC				
33.km_MT	kmol MT/kg COD X _{ac} .d	0.00016	Maximum uptake rate of MT to produce H ₂ S	Lomans <i>et al.</i> (2001, 2002); Ni and Boone (1999); Finster <i>et al.</i> (1992); Kiene <i>et al.</i> (1986)
34.Ks_MT	M	3.17E-004	Half saturation constant of MT degradation	
35.km_DMS	kmol DMS/kg COD X _{ac} .d	6.4E-004	Maximum uptake rate of MT to produce H ₂ S	
36.Ks_DMS	M	1.43E-004	Half saturation constant of MT degradation	
37.km_DMDS	kmol DMDS/kg COD X _{ac} .d	0.00176	Maximum uptake rate of MT to produce H ₂ S	
38.Ks_DMDS	M	0.0025	Half saturation constant of MT degradation	
Chemical reaction from MT to produce DMDS				
39.kMT_DMDS	d ⁻¹	7.35	First odor relationship between MT and DMDS	Assumed
Precipitation of H ₂ S				
40.kpre_H ₂ S	d ⁻¹	1.0E006	First order constant for precipitation reaction for H ₂ S	Assumed
Acid base partitioning				
41.pKa _{ac}		4.76	- log ₁₀ (k _{a_ac}) at 308K	Sillen and Martel (1964)
42.pKa _{pro}		4.88	- log ₁₀ (k _{a_pro}) at 308K	
43.pKa _{bu}		4.84	- log ₁₀ (k _{a_bu}) at 308K	
44.pKa _{va}		4.80	- log ₁₀ (k _{a_va}) at 308K	
45.pKa _{nh₃}		8.95	- log ₁₀ (k _{a_nh₃}) at 308K	Lide (2001)
46.pKa_H ₂ S		7.05	- log ₁₀ (k _{a_H₂S}) at 308K	Lide(2001)
Gas liquid phase partitioning				
47.KH_DMDS	M liq/M gas	22.53	non-dimensional Henry's law constant at 308 K	Thibodeaux (1991) and

48.KH_DMS	M liq/M gas	12.93	non-dimensional Henry's law constant at 308 K	Sander (2000)
49.KH_MT	M liq/M gas	7.114	non-dimensional Henry's law constant at 308 K	
50.KH_H2S	M liq/M gas	2.53	non-dimensional Henry's law constant at 308 K	
51.KH_nh3	M liq/M gas	1.69E-003	non-dimensional Henry's law constant at 308 K	
52.KH_hac	M liq/M gas	2.26E-004	non-dimensional Henry's law constant at 308 K	
53.KH_hpro	M liq/M gas	4.74E-004	non-dimensional Henry's law constant at 308 K	Assuming the same K_H value as K_H hbu
54.KH_hbu	M liq/M gas	4.74E-004	non-dimensional Henry's law constant at 308 K	Thibodeaux (1991) and Sander (2000)
55.KH_hva	M liq/M gas	5.69E-004	non-dimensional Henry's law constant at 308 K	Chapter two
56.kLa_DMS	d ¹	54	Volume-specific liquid gas transfer coefficient for DMS at 308K	
57.kLa_DMS	d ¹	62	Volume-specific liquid gas transfer coefficient for DMS at 308K	
58.kLa_MT	d ¹	76	Volume-specific liquid gas transfer coefficient for MT at 308K	
59.kLa_H2S	d ¹	71	Volume-specific liquid gas transfer coefficient for H ₂ S at 308K	
60.kLa_nh3	d ¹	78	Volume-specific liquid gas transfer coefficient for nh3 at 308K	
61.kLa_hac	d ¹	69	Volume-specific liquid gas transfer coefficient for hac at 308K	
62.kLa_hpro	d ¹	57	Volume-specific liquid gas transfer coefficient for hpro at 308K	
63.kLa_hbu	d ¹	49	Volume-specific liquid gas transfer coefficient for hbu at 308K	
64.kLa_hva	d ¹	26	Volume-specific liquid gas transfer coefficient for hva at 308K	
Solid-liquid partitioning				
65.logKow_DMS	(mol.L ⁻¹ octanol)/(mol.L ⁻¹ water)	1.77	log (Kow_DMS)	Hansch and Leo (1979)
66.logKow_DMS	(mol.L ⁻¹ octanol)/(mol.L ⁻¹ water)	1.2	log (Kow_DMS)	
67.logKow_MT	(mol.L ⁻¹ octanol)/(mol.L ⁻¹ water)	0.646	log (Kow_DMS)	SRC (SYRACUSE RESEARCH CORPORATION CALCULATED VALUES) (1988)
68.Kp_DMS	m3/kgCOD Xc	101.21	liqui-solid phase partitioning coefficient for DMS	Dobbs <i>et.al</i> (1989)
69.Kp_DMS	m3/kgCOD Xc	47.28	liqui-solid phase partitioning coefficient for DMS	
70.Kp_MT	m3/kgCOD Xc	22.98	liqui-solid phase partitioning coefficient for MT	

4.3 Input and Output Data for the Odour Model

The basic odour model was developed based on the suggested parameter values in table

4.1. In this section, the input and output data were presented and discussed.

4.3.1 Input Data

From the report of Siegrist, *et al* (2002), the measured total COD of the municipal sludge was divided into the following model components: 40% inert particulate COD (X_{in}), 30% particulate degradable COD (X_S) and 30% hydrolysis products that were divided into: 9% amino acids (S_{aa}), 6% sugars (S_{su}), 13.5% LCFA (S_{fa}), 1.5% inert soluble COD (S_{in}). The average composition of the raw sludges was 40 g of total COD L^{-1} , 4.5 g dissolved COD L^{-1} , 1.5 g of acetate L^{-1} (i.e. 1.6 g COD L^{-1}), 0.9 g propionate L^{-1} (i.e. 1.06 g COD L^{-1}), 0.4 g NH_4-N L^{-1} , 1.6 g of N_{tot} L^{-1} , and pH 6.8. The particulate COD was estimated to be 50-70% degradable and 30-50% inert organic material. Based on the above information, the input data for anaerobic digesters were summarized in Table 4.2.

4.3.2 Output data

The output of the odour model at steady state was presented in Table 4.3. The concentrations of odourous compounds in all three phases (i.e. liquid, solid and gas phases) were described. Referring to Table 4.3, the concentrations of the organic sulfur-containing odourous compounds (i.e. MT, DMS and DMDS) in the solid phase were one to two orders magnitudes greater than those in the liquid phase. Because only the

Table 4.2 Input data used in the odourous model

Variables	Unit	Values	Description
Q_{in_ss}	m^3/d	1.5	Input flow at steady state
S_{aa_in}	kg COD/ m^3	3.6	Concentration of amino acids in feed sludge
S_{fa_in}	kg COD/ m^3	6.3	Concentration of fatty acids in feed sludge
S_{su_in}	kg COD/ m^3	2.4	Concentration of monosaccharides in feed sludge
$S_{metal_ion_in}$	M	0.0008	Equivalent concentration of metal ions, such as Fe^{2+} , Cu^{2+} , which can precipitate of H_2S
S_{SO4_in}	M	0.000328	Concentration of inorganic sulfate in feed sludge
X_{C_in}	KgCOD/ m^3	12	Concentration of complex particulates in feed sludge
X_{I_in}	KgCOD/ m^3	16	Concentration of inert particulates in feed sludge
T	K	308	Temperature of the anaerobic digester
V	m^3	28	The volume of reactor of anaerobic digester
HRT	d^{-1}	18-20	Hydraulic retention time

odourous compounds in the liquid phase could release to the gas phase, the liquid-solid partitioning process was therefore an important process for the emission of the odourous compounds. Correspondingly, the liquid-solid partitioning coefficients became one of the most significant parameters in the odour model. Table 4.3 showed that a large fraction of the VFA and NH_3 were in dissociated ionic forms instead of their non-dissociated molecular forms in the liquid phase. The ratio between the concentrations of the molecular form and ionic form could be expressed by the following acid-base dissociation equations:

The acid-base dissociation constants, K_{a_VFA} , determined the ratio between the concentrations, S, at steady state:

$$\frac{S_{VFA}}{S_{VFA^-}} = \frac{S_{H^+}}{K_{s_VFA}} \quad (4.5)$$

Where,

S_{VFA} = Concentration of VFA in non-dissociated the molecular form (i.e. HAc, Hpro,

HBu, HVa) (kgCOD/m³)

S_{VFA^-} = Concentration of VFA in the dissociated ion form (i.e. Ac⁻, Pro⁻, Bu⁻ and Va⁻)

(kgCOD/m³)

The release of the VFA to the gas phase was thereby strongly dependent on the pH because only the molecular and not the dissociated forms would substantially partition to the gas phase. At pH of about 7.2, approximately 99.5% of the VFA's were in their ionic form.

The acid-base dissociation for ammonia was as following:

The ratio between the concentrations of ammonia and ammonium (S) at equilibrium:

$$\frac{S_{NH_4^+}}{S_{NH_3}} = \frac{S_{H^+}}{K_{a_NH_3}} \quad (4.7)$$

At pH of 7.2, approximately 99% amount of ammonia was in the dissociated ionic form (i.e. ammonium), which could not emit to the gas phase.

For sulfur-containing odourous compounds, except H₂S, all the others (i.e. MT, DMS, DMDS) were very weak acids, therefore, the effects of pH on MT, DMS and DMDS was not considered in this study. H₂S dissociated according to the following equations:

The ratio between the concentrations of H₂S and HS⁻ at equilibrium:

$$\frac{S_{H_2S}}{S_{HS^-}} = \frac{S_{H^+}}{K_{a_H_2S}} \quad (4.9)$$

At pH of 7.2, approximate 40% amount of H₂S was in the non-dissociated molecular form, which could lead to odour emissions. Compared with VFA and NH₃, the ratio of the concentration of H₂S between the molecular form and the ionic form were much greater, which indicated that H₂S could much easier lead to a serious odour problem.

Table 4.3: Output concentrations of odorous compounds in three phases in anaerobic digesters

Compounds	Output concentration (pH=7.2)				Threshold in gas phase (ppb)	Values from literature
	Liquid phases (M)	Solid phase (M)	Gas phase (M)	Gas phase (ppm)		
Hydrogen Sulfide (H ₂ S)	5.7E-06		2.3E-06	49.5	0.5	16.8 ^a
Hydrogen sulfide ion (HS ⁻)	8.4E-07					
Methyl mercaptan (MT)	2.5E-06	7.2E-05	3.6E-07	9.3	0.0014-18	0.26 ^a
Dimethyl sulfide (DMS)	2.8E-06	1.7E-04	2.2E-07	5.5	0.12-0.4	0.25 ^a
Dimethyl disulfide (DMDS)	1.9E-06	2.3E-04	8.3E-08	2.2	0.3-11	0.25 ^a
Ammonia (NH ₃)	5.8E-04		3.4E-07	8.8	130-15300	
Ammonium (NH ₄ ⁺)	3.1E-02					
	Liquid phase (kgCOD/m ³)		Gas phase (kgCOD/m ³)	Gas phase (ppm)		
Acetate acid (HAc)	1.7E-04		7.4E-09	3.0E-03	16	
Acetate (Ac ⁻)	4.8E-02					
Propionate acid (HPro)	8.2E-05		1.7E-09	4.0E-04	0.09-20	
Propionate (Pro ⁻)	1.8E-02					
Butyrate acid (HBu)	6.2E-05		1.3E-09	2.1E-04	0.09-20	
Butyrate (Bu ⁻)	1.5E-02					
Valerate acid (HVa)	4.5E-05		7.8E-10	9.7E-05	1.8-2630	
Valerate (Va ⁻)	1.2E-02					

Note: ^a Griffith and Alverez (1999)

The concentrations of the sulfur-containing odorous compounds in the gas phase in Table 4.3 were three to five orders of magnitude greater than those of VFA, which further proved that sulfur-containing odorous compounds were the most prevalent odorous compounds emitted from anaerobic digesters. When compared with the thresholds of the odorous compounds, it was obvious that the concentrations of sulfur-containing odorous compounds in the gas phase were much greater than their threshold values while the VFA's and NH_3 were under or close to their threshold values. Therefore, the emission of VFA and NH_3 from anaerobic digesters should not cause odour problems. On the contrary, the emission of sulfur-containing odorous compounds can lead to serious odour problems.

The literature values presented in Table 4.3 were from the studies of Griffith and Alvarez (1999) on the mesophilic and thermophilic anaerobic digesters. The predicted values were generally one order magnitude greater than the literature values. In the studies of Griffith and Alvarez, hydrogen sulfide in the gas phase was controlled by the aggressive dosing of iron salts to the collection system and to the primary sludge. Therefore, it is reasonable that the predicted H_2S concentration in the gas phase was higher than the literature value. The quantity of H_2S in anaerobic digesters would affect the production of other sulfur-containing odorous compounds because sulfide in H_2S can be used in methylation reactions to produce MT and DMS. Therefore, while the gas phase concentrations of odorous compounds predicted by the odour model did not fit well with the literature values, if further information on the metals content of the specific sludges were available, the model predictions could be improved.

4.4 Sulfur Mass Balance

Mass balances were used to check the correctness of a model. Since the data for COD balance was not complete, a mass balance on sulfur was chosen to check the correctness of the odour model. The theory of mass balance is that the total mass of the sulfur in the input data should equal the total mass of the sulfur in the output flows. Figure 4.1 showed the mass flow of sulfur in the input and output of the odour model.

The feed sludge in this study was assumed to be a mixture of primary and waste activated sludge and it was assumed that all inorganic sulfur in the feed sludge existed as sulfate. Referring to Figure 4.1, both amino acids and complex particulates (X_c) contributed to the organic sulfur in the feed sludge. Table 3.2 showed that two kinds of AA (methionine and cysteine) out of the 17 basic AA contained sulfur and the mole fraction of sulfur in

Figure 4.1: Mass Balance of Sulfur in the Odour Model

the total AA in beef flesh and casein is around 2.5%. The disintegration of complex particulates would lead to the production of AA (Figure 3.2), so the complex particulates also contained sulfur. The calculation of the sulfur content in the AA and complex particulates was discussed in appendix B. The sulfur released in the anaerobic digesters existed in three phases: sulfur in the gas phase, sulfur in the liquid phase and sulfur in the solid phase. The mass balance of sulfur in the odour model is expressed in equation 4.10:

$$Q_{in} \sum Sul_{i_in} = Q_{out} \sum Sul_{i_liq} + Q_{out} \sum Sul_{i_sol} + Q_{gas} \sum Sul_{i_gas} + Q_{out} Sul_{pre} \quad (4.10)$$

Where,

Q_{in} = input sludge flow ($m^3.d^{-1}$)

Sul_{i_in} = sulfur concentration of compound i in the input sludges (M)

Q_{out} = output sludge flow ($m^3.d^{-1}$).

Sul_{i_liq} = sulfur concentration of compound i in the liquid phase in output sludge flow (M)

Sul_{i_sol} = sulfur concentration of compound i in the solid phase in output sludge flow (M)

Q_{gas} = the output gas flow ($m^3.d^{-1}$)

Sul_{i_gas} = sulfur concentration of compound i in the output gas flow (M)

Sul_{pre} = sulfur concentration in the precipitates (M)

The results of the mass balance on sulfur between the input and output flow for the base case model were shown in Table 4.4

Table 4.4: Mass balance for sulfur in the odour model

Input Sulfur						
Parameters	M	f_sul_i ^a	Sul_i (M)	Q _{in} (m ³ /d)	Sulfur (mol/d)	Sulfur Fraction (%)
SO ₄	3.3E-04	1.0	3.3E-04	1.5	0.492	18
S_aa	0.021	0.035	7.5E-04	1.5	1.125	41
S_Xc	12 (kgCOD/m ³)	6.25E-05	7.5E-04	1.5	1.125	41
Total					2.742	100
Output sulfur in liquid, solid and gas phases						
Parameters	S (M)	f_sul_i ^a	Sul_i (M)	Q _{in} (m ³ /d)	Sulfur (mol/d)	Sulfur Fraction (%)
SO ₄	5.5E-05	1.0	5.5E-05	1.5	0.083	3.0
HS_ion_out	8.4E-07	1.0	8.4E-07	1.5	0.013	0.5
H ₂ S_out	5.7E-06	1.0	5.7E-06	1.5	0.009	0.3
H ₂ S_gas	2.3E-06	1.0	2.3E-06	16.6	0.037	1.4
Sul_pre	7.9E-04	1.0	7.9E-04	1.5	1.189	43.4
S_MT_liq	2.5E-06	1.0	2.5E-06	1.5	0.004	0.1
S_MT_sol	7.2E-05	1.0	7.2E-05	1.5	0.108	3.9
S_MT_gas	3.6E-07	1.0	3.6E-07	16.6	0.006	0.2
S_DMS_liq	2.8E-06	1.0	2.8E-06	1.5	0.004	0.2
S_DMS_sol	1.7E-04	1.0	1.7E-04	1.5	0.248	9.1
S_DMS_gas	2.2E-07	1.0	2.2E-07	16.6	0.004	0.1
S_DMDS_liq	1.9E-06	2.0	3.7E-06	1.5	0.006	0.2
S_DMDS_sol	2.3E-04	2.0	4.7E-04	1.5	0.703	25.6
S_DMDS_gas	8.3E-07	2.0	1.7E-06	16.6	0.003	0.1
	kgCOD/m³		M	m³/d	mol/d	%
S_aa_out	0.006	0.035	1.3E-06	1.5	0.002	0.1
X_pr_out	0.019	0.035	3.8E-06	1.5	0.006	0.2
X_c_out	1.2	6.25E-05	7.8E-05	1.5	0.117	4.3
X_bio_out ^b	2.1	6.25E-05	1.3E-04	1.5	0.201	7.3
Total					2.741	100
Mass Balance = Total sulfur in input flow - Total sulfur in output flow = 2.742-2.741= 0.001 mol/d						
Error = Δ(mass balance for sulfur between input and output flow)/ total in put sulfur = 0.001/2.742= 0.04%						

Note: ^a The mole fraction of sulfur in the compounds.

^b sulfur in the biomass in the output sludge flow.

Referring to Table 4.4, organic sulfur occupied 82% of the total sulfur in the input data; i.e. 41% from amino acids and 41% from complex particulates. Inorganic sulfur (sulfate) only occupied 18% of the total input sulfur. Therefore, the sulfur-containing odourous compounds in anaerobic digesters result mainly from the degradation of amino acids. Sulfur discharged from anaerobic digesters distributes into three phases: solid, liquid and gas phase. The model predicted that 43% of the output sulfur were precipitated with heavy metals. A total of 39% of the output sulfur was sorbed onto the organics in the solid phase: i.e. 4% sulfur as MT, 9% sulfur as DMS and 26% sulfur as DMDS adsorbed to the solid phase. Therefore, a total of 82% of sulfur discharged from the anaerobic digester stayed in the solid phase. From Table 4.4, it could be seen that 16.2% of the sulfur in the outflow remained in the liquid phase. Only 1.8% of the sulfur was emitted into the gas phase: i.e. 1.4% sulfur as H_2S , 0.2% sulfur as MT, 0.1% sulfur as DMS and 0.1% sulfur as DMDS. However, the 1.8% sulfur in the gas phase can cause serious odour problems.

Referring to Table 4.4, the calculated difference of sulfur between the input and output flow was 0.001 mole/d and the calculated error of the mass balance was 0.04 %. The value of the error (0.04%) indicated that the odour model developed in this study correctly reflected the mass transfer among the three phases (i.e. liquid, solid and gas) in anaerobic digesters and that it was able to track all of the sulfur through the digesters.

4.5 Sensitivity Analysis

The sensitivity analysis in this study included a general sensitivity analysis and individual sensitivity analyses. The general sensitivity analysis was employed to identify the common significant parameters for all odourous compounds. Since the pathways for the formation of each individual compound were different, the most significant parameters for each individual odourous compound are different. The individual sensitivity analyses were employed to identify the most significant parameters for each individual odourous compound.

The general sensitivity analysis was performed in four steps. First, the sensitivity function in AQUASIM was run on each individual odourous compound for all parameters in the odour model. Then, by analyzing the results, the effects of the parameters on each individual odourous compound were ranked. Ten common significant parameters were identified according to their ranks. Third, the general sensitivity analysis was performed on the ten common significant parameters by using the relative-relative and relative-absolute sensitivity functions. Finally, the three common most significant parameters were identified for all odourous compounds.

The process used for individual sensitivity analysis was similar to the process of general sensitivity analysis. First, the sensitivity function in AQUASIM was run for each individual odourous compound for all parameters in the odour model and the rank of the parameters was presented. Then, the ten most significant parameters for each individual odourous compound were identified. In order to obtain the detailed information on

sensitivity analysis, the individual sensitivity analysis was performed on the ten most significant parameters by using the absolute-relative sensitivity function. Finally, the five most significant parameters for each individual odourous compound were identified.

Based on ADM1, the odour model introduced 70 new parameters (Table 4.1) to describe the formation processes of the odourous compounds in anaerobic digesters. The following sensitivity analysis focused on the introduced 70 parameters.

4.5.1 Theory of Sensitivity Analysis

The sensitivity functions considered for use in this study were defined by the following equations (Reichert, 1998):

$$\delta_{y,p}^{a,a} = \frac{\partial y}{\partial p} \quad (4.11a)$$

$$\delta_{y,p}^{r,a} = \frac{1}{y} \frac{\partial y}{\partial p} \quad (4.11b)$$

$$\delta_{y,p}^{a,r} = p \frac{\partial y}{\partial p} \quad (4.11c)$$

$$\delta_{y,p}^{r,r} = \frac{p}{y} \frac{\partial y}{\partial p} \quad (4.11d)$$

In these functions, y was a response variable (i.e. the concentration of the odourous compound in the gas phase) calculated by the odour model and p was a model parameter represented by a constant variable. The absolute-absolute sensitivity function (Eq 4.11a) measured the absolute change in y per unit of change in p , the relative-absolute sensitivity function (Eq. 4.11b) measured the relative change in y per unit of change in p , the absolute-relative sensitivity function (Eq. 4.11c) measured the absolute change in y per unit of a 100 % change in p , and the relative-relative sensitivity function (Eq. 4.11d) measured the relative change in y per unit of a 100 % change in p . All these changes

were calculated in linear approximation only. The most useful sensitivity functions were the absolute-relative sensitivity function (Eq. 4.11c) and relative-relative sensitivity function (Eq. 4.11d), because their units did not depend on the units of the parameters. This made quantitative comparisons of the effect of different parameters p on a common variable y possible. Because the relative-relative sensitivity function (Eq. 4.11d) was non-dimensional, this sensitivity function could not only be used to compare the effect of different parameters on a common variable, but also the effects of different parameters on different variables. However, the disadvantage of the relative-relative comparison was that it gave not very useful results if the value of the variable y became small during a simulation (because large relative changes of a value that was close to zero were not relevant). Figure 4.2 illustrates the meaning of the absolute-relative sensitivity function (Eq. 4.11c). The linear approximation to the change in y for a 100 % change in p can be easily constructed with the aid of the tangent to the function of $y(p)$ in p .

Figure 4.2: Interpretation of the absolute-relative sensitivity function $\delta_{y,p}^{a,r} = p \frac{\partial y}{\partial p}$

In this odour model, the suggested parameter values listed in Table 4.1 were first reduced to half of the tabulated values and then increased to double of these values. Under these two conditions, the sensitivity functions could be expressed as follows:

$$\delta_{y,p}^{r,a} = \frac{\partial y}{p - 0.5p} = \frac{\partial y}{0.5p} \quad (4.11a')$$

or
$$\delta_{y,p}^{a,a} = \frac{\partial y}{2p - p} = \frac{\partial y}{p} \quad (4.11a')$$

$$\delta_{y,p}^{r,a} = \frac{1}{y} \frac{\partial y}{p - 0.5p} = \frac{1}{y} \frac{\partial y}{0.5p} \quad (4.11b')$$

or
$$\delta_{y,p}^{a,a} = \frac{1}{y} \frac{\partial y}{2p - p} = \frac{1}{y} \frac{\partial y}{p} \quad (4.11b')$$

$$\delta_{y,p}^{a,r} = p \frac{\partial y}{p - 0.5p} = \frac{\partial y}{0.5} \quad (4.11c')$$

or
$$\delta_{y,p}^{a,r} = p \frac{\partial y}{2p - p} = \partial y \quad (4.11c')$$

$$\delta_{y,p}^{r,r} = \frac{p}{y} \frac{\partial y}{p - 0.5p} = 2 \frac{\partial y}{y} \quad (4.11d')$$

or
$$\delta_{y,p}^{r,r} = \frac{p}{y} \frac{\partial y}{2p - p} = \frac{\partial y}{y} \quad (4.11d')$$

The relative-absolute sensitivity function (Eq. 4.11b') indicated the relative change of concentration of each odourous compound ($\delta y/y$) per 0.5 unit or per unit change in the parameter (p). Referring to Equation 4.11b', the relative-absolute sensitivity function (Eq. 4.11b') was not dependent on the unit of the response variable (y), therefore, the effects of each individual parameters on total odourous compounds could be compared (i.e. the general sensitivity analysis). The absolute-relative sensitivity equation (Eq. 4.11c')

showed that the change of the concentration of the odourous compounds (δy) was not dependent on the unit of the parameter. Therefore, the absolute-relative sensitivity analysis could be used to compare the effects of different parameters on a common variable (i.e. the individual sensitivity analysis).

4.5.2 General Sensitivity Analysis

The odourous compounds studied in this model were sulfur containing odourous compounds (i.e. H_2S , MT, DMS and DMDS), VFA (i.e. HAc, HPro, HBu and HVa) and ammonia (NH_3). The general sensitivity analysis was conducted to identify the most significant parameters for all odourous compounds. Both the relative-absolute sensitivity function (Eq. 4.11b') and the relative-relative sensitivity function (Eq. 4.11d') can be used for general sensitivity analysis, because they do not depend on the units of the response variables (i.e. y). The relative-relative sensitivity function (Eq. 4.11d') is non-dimensional; therefore, it can also be used to compare the effects of different parameters on different variables. In this study, the two sensitivity functions were selected to perform the general sensitivity analysis.

In this odour model, a large number of parameters were used to describe the formation of odourous compounds in anaerobic digesters. The emissions of odourous compounds from anaerobic digesters were a combined effect of all these parameters. It was difficult to identify the most common significant parameters for all odourous compounds from these huge number parameters. Fortunately, AQUASIM itself had a sensitivity analysis function. For each individual odourous compound, the effects of 100 parameters were

analyzed by the sensitivity function of AQUASIM. By comparing and analyzing the results, the ranks of the relatively important parameters were presented in Table 4.5. Referring to Table 4.5, it could be seen that the most significant parameter for different compounds were different; for example, the effect of k_{dis} ranked No. 1 for H_2S but No.14 for HPro. However, in general k_{dis} , Y_{aa} and Y_{ac} were important parameters for all odourous compounds since the ranks of them were all high among the 100 parameters.

Because sulfur-containing odourous compounds were the main interest in this study, an additional five significant parameters for sulfur-containing odourous compounds were identified. Table 4.6 presented the ranks of the important parameters for sulfur-containing odourous compounds. Referring to Table 4.6, the rank of the presented parameters was generally high among the 100 parameters, which indicated that they were important parameters for the formation of sulfur-containing odorous compounds. However, the most sensitivity response of different compounds varied. In general, the liquid-solid partitioning parameters and the degradation kinetics of DMS were significant for sulfur-containing odourous compounds since the ranks of them were high out of the 100 parameters. Therefore, the three liquid-solid partitioning parameters of VOSC and two kinetic parameters (i.e. k_{m_DSM} and K_{S_DMS}) were selected as the common significant parameters for all sulfur-containing odourous compounds.

Another method to identify the most significant parameters for all odourous compounds involved applying the relative-relative sensitivity analysis ($\delta y/y$). Because the relative-relative sensitivity function was non-dimensional, the value of $\delta y/y$ could be used to compare the effect of different parameters on different variables. In Appendix C and D,

the processes used to calculate the general sensitivity analysis were described in detail. Table 4.7 summarized the results of relative-relative sensitivity analysis for all odourous compounds. Referring to Table 4.7, the effects of k_{dis} on sulfur-containing odourous compounds was more significant than other three presented parameters; the effect of Y_{ac} on HAc was much more significant than other parameters; because the values of $\delta y/y$ in these two cases were much greater than other values of $\delta y/y$ in Table 4.7. Compared with $k_{m_{aa}}$, the effects of k_{dis} , Y_{ac} , Y_{aa} on all odourous compounds were more significant, it could be seen from Table 4.7 that the values of $\delta y/y$ of k_{dis} , Y_{ac} , Y_{aa} were greater than that of $k_{m_{aa}}$. It further proved that k_{dis} , Y_{ac} , Y_{aa} were the important parameters for all odorous compounds. Table 4.8 presented the results of relative-relative sensitivity analysis for sulfur-containing odourous compounds. From the values of $\delta y/y$ presented in Table 4.8, it could be seen the effects of the first five parameters were more significant than other parameters. Therefore, K_{P_DMS} , K_{P_MT} , K_{P_DMDS} , k_{m_DMS} and K_{S_DMS} were selected as the additional five significant parameters for sulfur-containing odourous compounds.

Table 4.7 gives an outline of the effects of the three most significant parameters on all odourous compounds. Referring to Table 4.7, the responses of sulfur-containing odourous compounds were more sensitive to k_{dis} than to Y_{ac} and Y_{aa} ; Y_{ac} had a substantial impact on the formation of HAc, while the effect of Y_{aa} was relatively even to all odourous compounds. The above phenomena are reasonable. Disintegration of complex particulates is the first biochemical step that occurs in anaerobic digesters (Figure 3.2). All other processes such as hydrolysis and acetogenesis are dependent on the disintegration process; therefore, the disintegration parameter (k_{dis}) was important for all

Table 4.5: Results of AQUASIM sensitivity analysis for all odorous compounds

Parameters Rank	k _{dis}	Y _{ac}	Y _{aa}	k _{m,aa}	k _{m,ac}	k _{m,MAC,DMS}	k _{m,MAC,MT}	k _{m,DMS}	K _{S,DMS}
H ₂ S	1 ^a	2	16	39	19	13	10	3	6
MT	2	9	6	41	27	19	4	9	10
DMS	1	5	13	46	19	6	14	3	4
DMDS	1	3	9	42	26	19	8	12	13
HAc	7	2	5	36	1	45	36	32	33
HPto	14	9	11	45	16	36	44	48	50
HBu	11	6	7	38	13	35	44	46	38
HVa	11	6	7	38	13	35	44	46	38
NH ₃	8	1	4	25	15	43	49	51	52

Note: ^a . the number represented the rank of the parameter out of 100 parameters.

Table 4.6: Results of AQUASIM sensitivity analysis for sulfur-containing odorous compounds

Parameter Rank	K _{P,DMS}	K _{P,MT}	K _{P,DMS}	k _{m,DMS}	K _{S,DMS}	k _{m,MAC,DMS}	k _{m,MAC,MT}	k _{m,DMS}	K _{S,DMS}	k _{MT,DMS}	k _{M,SRB,ac}	K _{S,SO4,AC}
H ₂ S	7 ^a	23	8	3	6	15	10	4	5	31	9	12
MT	13	3	11	10	12	19	3	7	8	1	16	18
DMS	2	22	11	3	4	6	14	9	10	31	15	18
DMDS	14	7	2	12	13	19	8	4	5	6	17	21

Note: ^a . the number represented the rank of the parameter out of 100 parameters.

Table 4.7: Relative-relative sensitivity analysis ($\delta y / y_p$) for the parameters for all odorous compounds

Compounds Parameters $\delta y / y_p$	H ₂ S	MT	DMS	DMDS	NH ₃	HAc	HPto	HBu	HVa
k_{dis}	1.92	0.35	0.88	1.56	0.06	0.01	-0.01	0.00	-0.01
Y_{ac}	0.63	-0.05	-0.48	-0.12	-0.19	-2.61	0.03	0.03	0.03
Y_{aa}	0.70	-0.09	-0.06	-0.11	-0.16	-0.01	0.05	0.05	0.03
$k_{m_{aa}}$	0.01	-0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.00

Table 4.8: Relative-relative sensitivity analysis ($\delta y / y_p$) for the parameters for sulfur-containing odorous compounds

Compounds Parameters $\delta y / y_p$	K_{P_DMS}	K_{P_MT}	K_{P_DMDS}	k_{m_DMS}	K_{S_DMS}	$k_{m_MAC_DMS}$	$k_{m_MAC_MT}$	k_{m_DMDS}	K_{S_DMDS}
H ₂ S	-1.17	-0.12	-0.46	1.17	-1.14	-0.20	-0.27	0.50	-0.46
MT	-0.05	-0.23	-0.02	0.05	-0.05	-0.01	0.04	0.02	-0.02
DMS	-0.87	-0.01	-0.03	-0.46	0.45	0.08	-0.02	0.03	-0.03
DMDS	-0.04	-0.16	-1.39	0.03	-0.02	-0.01	0.03	-0.06	0.08

responses. Because the amount of acetate degraders (X_{ac}) is proportional to the uptake rate of HAc, with the increase of the yield coefficient of acetate degraders (Y_{ac}), more HAc will be consumed. Therefore, the effect of Y_{ac} on HAc is much more significant than any other odourous compounds. Since HAc can be used by SRB to form H_2S and the amount of acetate degraders (X_{ac}) is proportional to the degradation rates of VOSC (Table 3.3), the effects of Y_{ac} on sulfur-containing odorous compounds is also significant. The degradation of amino acids is one of the most important processes for the formation of all odourous compounds; therefore, the effects of Y_{aa} on all odourous compounds are important.

Figure 4.3 presented the effect of k_{dis} on all the odourous compounds. The steepness of the slope reflects the response of each odourous compound to k_{dis} . The steeper the slope is, the more sensitive the response of the odourous compound to k_{dis} is. Referring to Figure 4.3, H_2S was the most sensitive odourous compounds to k_{dis} , followed by DMDS, DMS and MT. Compared with sulfur-containing odourous compounds, the responses of VFA and NH_3 were relatively insensitive. With the increase of the k_{dis} value, all sulfur-containing odourous compounds increased. As the value of the disintegration coefficient (k_{dis}) increased, more precursors of odourous compounds, such as protein, LCFA and MAC, are produced in anaerobic digesters. Correspondingly, the emission of odourous compounds increases. k_{dis} had a fundamental effect on all odourous compounds in anaerobic digesters.

Figure 4.4 presented the effects of Y_{ac} on all odourous compounds. Referring to Figure 4.4, the response of HAc to Y_{ac} was much more sensitive than any other odourous compound. The responses of sulfur-containing odourous compounds and NH_3 to Y_{ac} were also sensitive, however, the responses of HPro, HBu and HVa were relatively insensitive. With the increase of the Y_{ac} value, the concentration of HAc and VOSC in the gas phase decreased, however, the concentration of H_2S in the gas phase increased. The increase of Y_{ac} leads to a higher concentration of acetate degraders (X_{ac}) in anaerobic digesters. The amount of acetate degraders in anaerobic digesters is proportional to the degradation rates of HAc and VOSC. When the amount of acetate degraders increases, more HAc and VOSC will be consumed. Correspondingly, the emission of HAc and VOSC from anaerobic digesters will decrease. The degradation of VOSC releases H_2S and, therefore, the emission of H_2S from anaerobic digesters increases.

Figure 4.5 presented the effects of Y_{aa} on all odorous compounds. Referring to Figure 4.5, the response of H_2S to Y_{aa} was much more sensitive than all other odourous compounds, which can be reflected by the magnitude of its slope. The responses of other odourous compounds to Y_{aa} were similar because their slopes were close, which further proved Y_{aa} has a relatively even effect on all odourous compounds. With the increase of Y_{aa} value, the emission of H_2S increased, however, the emissions of VOSC, HAc and NH_3 decreased. The degradation of amino acids is a control process for anaerobic digestion, with a number of intermediate, such as HAc and HPro, produced from this process. The degradation of these intermediates will also affect the formation of odourous

compounds. Therefore, the final emissions of the odourous compounds will be a balance among the effects of these processes.

Figure 4.3: Relative-Absolute Sensitivity Analysis of k_{dis}

Figure 4.4: Relative-Absolute Sensitivity Analysis of Y_{ac}

Figure 4.5: Relative-Absolute Sensitivity Analysis for Y_{aa}

The formation processes for sulfur-containing odourous compounds are quite different from the formation processes for VFA and NH_3 . Since the odour emissions are mainly from the sulfur-containing odourous compounds, it is more useful to identify the most significant parameters for all sulfur-containing odourous compounds. Therefore, five additional significant parameters for sulfur-containing odourous compounds were selected and studied. Tables 4.8 and Figures 4.7-4.11 presented the effects of the five additional significant parameters on all sulfur-containing odourous compounds.

Table 4.8 shows the effects of the five most significant parameters for the sulfur-containing odourous compounds using the relative-relative sensitivity function (Eq. 4.11d'). Referring to Table 4.8, the effects of liquid-solid partitioning coefficients (K_p) on sulfur-containing odourous compounds were generally more significant than the effects of the biochemical parameters. The liquid-solid partitioning coefficients (K_p) affect the

mass transfer between the liquid and solid phase and the mass transfer process occurs much more rapidly than the biochemical processes. Therefore, the responses of sulfur-containing odourous compounds were more sensitive to K_P than to biochemical parameters. Except the solid-liquid partitioning coefficients, k_{m_DMS} and K_{S_DMS} were the most significant parameters for all sulfur containing odourous compounds. The response of H_2S to k_{m_DMS} and K_{S_DMS} was most sensitive among the sulfur-containing odourous compounds, followed by DMS, MT and DMDS. The formation of sulfur-containing odourous compounds is interrelated to each other, which can be expressed in Figure 4.6.

Figure 4.6: Microbial cycling processes for sulfur-containing odourous compounds

Referring to Figure 4.6, H_2S is a critical component for the microbial cycling process for sulfur-containing odourous compounds, because the formation of VOSC is dependent on H_2S . Therefore, the responses of H_2S are generally sensitive to all parameters related to the formation of sulfur containing odourous compounds. Since k_{m_DMS} and K_{S_DMS} are related to the uptake rate of DMS and the uptake of DMS leads to production of H_2S ,

k_{m_DMS} and K_{S_DMS} will also affect the production of MT and DMDS in anaerobic digesters.

Figures 4.7-4.9 presented the effects of the liquid-solid partitioning coefficients of VOSC (i.e. K_{P_MT} , K_{P_DMS} , K_{P_DMDS}) on the concentrations of sulfur-containing odourous compounds in the gas phase. Referring to Figures 4.7-4.9, with the increase of each K_P value, the emissions of all the sulfur-containing odourous compounds decreased. The response of H_2S was sensitive to all three partitioning coefficients, which can be reflected by the steepness of the slopes of H_2S in Figures 4.7-4.9. However, the response of MT was only sensitive to K_{P_MT} ; the response of DMS was only sensitive to K_{P_DMS} ; and the response of DMDS was sensitive to K_{P_DMDS} and K_{P_MT} . The values of K_{P_DMS} affect the partitioning of DMS between the solid and liquid phases. With the increase of K_{P_DMS} values, the amount of DMS partitioning to the solid phase increased. Therefore, less DMS remained in the liquid phase. Since only DMS in the liquid phase can emit to the gas phase, DMS in the gas phase will also decrease. With the decrease of DMS in the liquid phase, the amount of H_2S produced by the degradation of DMS decreases. Correspondingly, the production of MT and DMDS in anaerobic digesters will also decrease with the decrease of H_2S (Figure 4.6). Therefore, with the increase of the K_{P_DMS} value, the concentration of all sulfur-containing odourous compounds in the gas phase decrease. For the same reasons, an increase of K_{P_DMDS} and K_{P_MT} values, results in a decrease in the concentrations of all sulfur-containing odourous compounds in the gas phase.

Figures 4.10 and 4.11 show the effects of k_{m_DMS} and K_{S_DMS} on the concentrations of sulfur-containing odorous compounds in the gas phase. Referring to Figure 4.10 and Figure 4.11, the response of H_2S was most sensitive to both k_{m_DMS} and K_{S_DMS} , followed by the response of DMS; while the responses of MT and DMDS were relatively insensitive to k_{m_DMS} and K_{S_DMS} . Referring to Figure 4.10, with an increase of k_{m_DMS} value, the emission of DMS decreased and the emissions of H_2S , MT and DMDS increased. The degradation rate of DMS is proportional to the value of k_{m_DMS} . With the increase of k_{m_DMS} values, more DMS will be degraded. Therefore, the production of H_2S by the degradation of DMS increased. Correspondingly, the production of MT and DMDS increased (Figure 4.6). Referring to Figure 4.11, with the increase of K_{S_DMS} values, the concentration of DMS in the gas phase increased, however, the concentrations of H_2S , MT and DMDS decreased. The degradation rate of DMS is inversely proportional to the value of K_{S_DMS} . With the increase of K_{S_DMS} value, less DMS is degraded. Therefore, less H_2S is generated by the degradation of DMS. Correspondingly, the production MT and DMDS decreased (Figure 4.6).

Figure 4.7: Relative_Absolute Sensitivity Analysis for K_{P_DMS}

Figure 4.8: Relative-Absolute Sensitivity Analysis for K_{P_DMS}

Figure 4.9: Relative-Absolute Sensitivity Analysis for K_{P_MT}

Figure 4.10: Relative-Absolute Sensitivity Analysis for k_{m_DMS}

Figure 4.11: Relative-Absolute Sensitivity Analysis for K_{S_DMS}

4.5.3 Individual Sensitivity Analysis

In this section, the effects of the parameters on each individual odourous compound were studied. First, the sensitivity analysis function in AQUASIM was run for each individual odourous compound for the 100 parameters. Then, by ranking the effects of the 100 parameters on each individual odourous compound, the 10 most significant parameters for each individual odourous compound were identified (Appendix E). Finally, the individual sensitivity analysis was performed on these selected parameters in order to obtain detailed information on sensitivity.

The absolute-relative sensitivity function (Eq. 4.11c') was used for the individual sensitivity analysis because it is independent of the units of the parameters. In Appendix E, the 10 most significant parameters for each individual sulfur-containing odorous compound, NH_3 and HAc were analyzed, calculated and ranked. Then, the effects of the five most significant parameters for each individual sulfur-containing odorous compound are discussed in this section. In the Figures, the steepness of the slopes can be used to compare the effect of the parameters on a common odorous compound. The steeper the slope is, the more significant the effect of the parameter is.

Figure 4.12 presented the effects of the five most significant parameters on the concentration of H_2S in the gas phase. Referring to Figure 4.12, the most significant parameter to H_2S was the maximum uptake parameter of DMS (k_{m_DMS}), followed by K_{S_DMS} , K_{P_DMS} , $K_{S_SO4_ac}$ and $k_{m_SRB_ac}$. Generally, the response of H_2S was sensitive to all these parameters. With the increase of k_{m_DMS} and $k_{m_SRB_ac}$ values, the concentration of H_2S in the gas phase of anaerobic digesters increased. Both the uptake of DMS and the uptake of HAc for sulfate reduction lead to the formation of H_2S (Eq. 2.10 and 2.15). Therefore, with the increase of k_{m_DMS} and $k_{m_SRB_ac}$ values, more H_2S was produced in the digesters. Figure 4.12 also showed that with increases of K_{S_DMS} , K_{P_DMS} and $K_{S_SO4_ac}$ values, the concentration of H_2S in the gas phase decreased. The effect of K_{P_DMS} on the concentration of DMS in the gas phase was explained in the general sensitivity analysis section. K_{S_DMS} and $K_{S_SO4_ac}$ are inversely proportional to the maximum uptake rate of DMS and HAc for sulfate reduction, respectively. With an increase of K_{S_DMS} and

$K_{S_SO4_ac}$ values, the uptake rates of DMS and HAc decrease. Therefore, the amount of H_2S produced by the uptake process decreases.

Figure 4.12: Sensitivity of Gas Phase H_2S to Model Parameters

Figure 4.13 presented the effects of the five most significant parameters on the concentration of MT in the gas phase. Referring to Figure 4.13, the slope of the sensitivity of K_{MT_DMDS} was much more steeper than any other parameter, which indicates the response of MT to K_{MT_DMDS} was most sensitive among these parameters. MT can be converted to DMDS either by chemical reaction or by biochemical reaction and the transfer process occurs rapidly. Therefore, the value of K_{MT_DMDS} affects the amount of MT in anaerobic digesters. The effect of K_{P_MT} on MT was the second most significant influence, followed by k_{m_DMS} , K_{S_DMS} and K_{P_DMS} . From Figure 4.13, it can be seen that the effects of k_{m_DMS} , K_{S_DMS} and K_{P_DMS} on MT were similar because the steepness of

their slopes were close. As the value of K_{MT_DMDS} increased, the concentration of MT in the gas phase dramatically decreased. With an increase of K_{MT_DMDS} values, the rate of the concentration of MT to DMDS will increase. Therefore, the amount of MT remaining in the digester decreases.

The values of K_{P_MT} , K_{P_DMS} and K_{S_DMS} had a negative effect on the concentration of MT in the gas phase. With increases of K_{P_MT} , K_{P_DMS} and K_{S_DMS} values, the concentration of MT in the gas phase decreased. As the value of K_{S_DMS} increased, the maximum uptake rate of DMS decreases, therefore, the production of H_2S by the degradation of DMS decreases. Correspondingly, the production of MT by methylation reactions was reduced (Figure 4.6). Therefore, with the increase of K_{S_DMS} values, the production of MT decreased. The effect of the maximum specific uptake parameter for DMS (k_{m_DMS}) on MT was positive. The uptake of DMS leads to production of H_2S , which can be used by methylation reactions to produce MT. Therefore, with an increase of k_{m_DMS} value, the production of MT in anaerobic digesters increased.

Figure 4.13: Sensitivity of gas phase MT to Model Parameters

Figure 4.14 presented the effects of the five most significant parameters on the concentration of DMS in the gas phase. Referring to Figure 4.14, the most significant parameter to DMS was K_{P_DMS} , followed by k_{m_DMS} , K_{S_DMS} , $K_{S_H2S_DMS}$ and $k_{m_MAC_DMS}$. With an increase of K_{P_DMS} , K_{m_DMS} and $K_{S_H2S_DMS}$ values, the concentrations of DMS in the gas phase decreased. The liquid-solid partitioning coefficient of DMS (K_{P_DMS}) affects the partitioning between the liquid and solid phases and hence the availability for substance for biodegradation and liquid-gas mass transfers.

The maximum uptake parameter of DMS (k_{m_DMS}) is proportional to the uptake rate of DMS. With an increase of the k_{m_DMS} value, the uptake rate of DMS increases. Correspondingly, the amount of DMS in the liquid phase decreases. $K_{S_H2S_DMS}$ is defined as the half saturation parameter of H_2S for the methylation reaction to produce DMS (Table 3.1). As $K_{S_H2S_DMS}$ increased, the maximum specific uptake rate of MAC to produce DMS ($k_{m_MAC_DMS}$) decreases. Hence, the formation of DMS in anaerobic digesters decreases.

The effects of K_{S_DMS} and $k_{m_MAC_DMS}$ on DMS were positive. The larger the values of K_{S_DMS} and $k_{m_MAC_DMS}$, the larger the concentration of DMS in the gas phase. K_{S_DMS} is inversely proportional to the maximum uptake rate of DMS. As the value of K_{S_DMS} increases, the maximum uptake rate of DMS decreases. Therefore, more DMS will remain in the digesters. $k_{m_MAC_DMS}$ is proportional to the maximum uptake rate of MAC to produce DMS. With the increase of $k_{m_MAC_DMS}$ value the maximum uptake rate of MAC increases, therefore, more DMS is produced.

Figure 4.14: Sensitivity of Gas Phase DMS to Model Parameters

Figure 4.15 presented the effects of the five most significant parameters on the concentration of DMDS in the gas phase of anaerobic digesters. Referring to Figure 4.15, K_{P_DMDS} had the most significant effect on the concentration of DMDS in the gas phase, followed by K_{MT_DMDS} , k_{m_DMDS} , K_{S_DMDS} and k_{m_DMS} . Both K_{P_DMDS} and K_{MT_DMDS} had a much more significant effect on DMDS than any other parameters. The importance of K_{P_DMDS} on DMDS is that its value controls the partitioning between the liquid and solid phases. When the value of K_{P_DMDS} increased, the amount of DMDS partitioning to the solid phase increased and hence reduced its availability for biochemical and liquid-gas mass transfer processes.

The conversion of MT to DMDS is the main process for the formation of DMDS in anaerobic digesters. Therefore, the value of K_{MT_DMDS} determines the rate of DMDS production. The production of DMDS is inversely proportional to the maximum uptake parameter of DMDS (k_{m_DMDS}). An increase of k_{m_DMDS} value results in more DMDS degradation. K_{S_DMDS} and k_{m_DMS} had a positive effect on the concentration of DMDS in the gas phase in anaerobic digesters. The half saturation parameter of uptake of DMDS (K_{S_DMDS}) was inversely proportional to the uptake rate of DMDS. Therefore, with an increase of K_{S_DMDS} values, the concentration of DMS increases. k_{m_DMS} expresses the maximum uptake parameter for DMS. The larger the k_{m_DMS} value, the more DMS consumed. Therefore, with an increase in the k_{m_DMS} value, H_2S production by uptake of DMS increases.

Figure 4.15: Sensitivity of Gas Phase DMDS to Model Parameters

4.6 Conclusion

In this chapter, a sensitivity analysis was applied to identify the most significant parameters for the odourous compounds in the gas phase of anaerobic digesters. In order to proceed with the sensitivity analysis, a base odour model was first developed on the basis of suggested parameter values. A mass balance for sulfur in anaerobic digesters was then applied to check the correctness of the base model. Finally, the sensitivity analysis was performed in two parts: the general sensitivity and the individual sensitivity analysis. In the general sensitivity analysis, the three most significant parameters for all odourous compounds were identified (i.e. k_{dis} , Y_{ac} , and Y_{aa}). Since sulfur-containing odourous compounds were the main interest for this study, five additional significant parameters for all sulfur-containing odourous compounds were identified (i.e. K_{P_DMS} , K_{P_DMDS} , K_{P_MT} , k_{m_DMS} and K_{S_DMS}). In the individual sensitivity analysis, the five most significant parameters of each individual odourous compound were identified, presented and discussed. The results of the sensitivity analysis can be used to direct future research.

Chapter 5: Factors Affecting Odour Emission

5.1 Introduction

Many factors may affect the emissions of odourous compounds from anaerobic digesters. These could include process loading factors such as HRT and VOL, environmental factors such as temperature and pH, and operational factors such as the characteristics of the sludge being treated. In this study, the effects of these parameters on the formation of odourous compounds were evaluated with the model. It was expected that changes in these factors would have an influence on the total anaerobic system. Therefore, the overall effect on the system due to changes in these parameters was more important than changes in biochemical parameters, which had been analyzed in chapter four. A thorough understanding of these factors was considered important when developing strategies to control odour emissions.

Four program parameters, i.e. temperature, HRT, VOL and solid characteristics, were considered as the most important factors for odour emissions. Since the content of heavy metals and sulfate in biosolids significantly affect the formation of sulfur-containing odourous compounds in anaerobic digesters, the biosolids characteristics was subdivided into the effects from heavy metal and sulfate. Table 5.1 summarized the values of these program factors used in the base model.

Table 5.1: Program parameter values used in the base model

Program Parameters	Units	Values
Temperature	C	35
HRT	d ⁻¹	20
VOL	kg COD m ⁻³ .d ⁻¹	2
Heavy Metal	M	0.0008
Sulfate	M	0.000328

This chapter describes model simulations where these program factors were varied. The corresponding output concentrations of odourous compounds were predicted and explanations for observed responses are discussed.

5.2 Temperature

5.2.1 Variation of Biochemical Parameters with Temperature

As with all biochemical processes, the performance of anaerobic processes is significantly affected by operating temperature. The best performance is typically obtained by operation in the optimal temperature ranges, i.e. 30°C to 40°C for mesophilic or 50°C to 60°C for thermophilic, and most anaerobic processes are designed to do so. These two regions generally represent the optima for growth of the bacteria. Because biochemical reaction rates increase with temperature, doubling with every 10°C rise in the temperature until a limiting temperature is reached, thermophilic digestion is much faster than mesophilic digestion (Tchobanoglous and Burton, 1991).

A commonly used expression for the temperature effects in the environmental engineering literature:

$$K_2 = K_1^{\theta(T_2-T_1)} \quad (5.1)$$

Where,

K = the temperature dependent rate coefficient

θ = The temperature coefficient in the mesophilic (30-40 °C) and thermophilic (50-60°C) temperature range

All kinetic coefficients for thermophilic conditions can be calculated based on the mesophilic values. Therefore, the same base set of kinetic parameters is valid for mesophilic and thermophilic. Because of the uncertainty associated with the impact of temperature on yield coefficient, most engineers assume it to be independent of temperature, thereby, allowing the same temperature coefficient to be used for both growth and substrate utilization. Because factors contributing to decay are the same as those contributing to growth, it is logically to expect temperature to have similar effects on k_{dec} and μ (Grady *et al.*, 1999). In ADM1, a unique value of k_{dec} at mesophilic and thermophilic conditions, respectively, is used for all biomass decay processes, i.e. at mesophilic condition (35 °C), the value of k_{dec} is 0.2 d⁻¹; at thermophilic condition (55 °C), the value of k_{dec} is 0.4 d⁻¹. After substituting the two k_{dec} values into Eq. 5.1, the θ value for biomass decay in ADM1 can be calculated:

$$\theta = \ln \frac{k_2}{k_1} \cdot \frac{1}{T_2 - T_1} = \ln \frac{0.4}{0.2} \cdot \frac{1}{55 - 35} = 0.035$$

No papers related to the influence of temperature on the formation of odourous compounds under anaerobic conditions were found in this study, therefore, the θ value for biomass decay were used to calculate the growth rate kinetics of odourous compounds at thermophilic conditions. Table 5.2 presented the values of biochemical parameters under mesophilic and thermophilic conditions in anaerobic digestion.

Table 5.2: Kinetic values of the mesophilic (35 °C) and thermophilic (55 °C) temperature.

Process	Coefficient	Unit	Mesophilic (35 °C)	Thermophilic (55 °C)	θ (°C ⁻¹)	Source
Disintegration	k_{dis}	d ⁻¹	0.5	1.0	0.034	ADM1
Hydrolysis	k_{hyd}	d ⁻¹	10	10		ADM1
Decay of all organisms	K_{dec_all}	d ⁻¹	0.02	0.04	0.035	ADM1
Uptake of carbohydrate	k_{m_su}	COD/COD.d	30	70	0.042	ADM1
	K_{S_su}	kg COD/m ³	0.5	1	0.035	ADM1
	Y_{su}	COD/COD	0.10	0.10		ADM1
Uptake of amino acid	k_{m_aa}	COD/COD.d	50	70	0.016	ADM1
	K_{S_aa}	kg COD/m ³	0.3	0.3		ADM1
	Y_{aa}	COD/COD	0.08	0.08		ADM1
Uptake of LCFA	k_{m_fa}	COD/COD.d	6	10	0.026	ADM1
	K_{S_fa}	kg COD/m ³	0.4	0.4		ADM1
	Y_{fa}	COD/COD	0.06	0.06		ADM1
Uptake of butyrate and valerate	K_{m_C4+}	COD/COD.d	20	30	0.02	ADM1
	K_{S_C4+}	kg COD/m ³	0.2	0.4	0.035	ADM1
	Y_{C4+}	COD/COD	0.03	0.03		ADM1
Uptake of propionate	k_{m_pro}	COD/COD.d	13	20	0.022	ADM1
	K_{S_pro}	kg COD/m ³	0.1	0.3	0.055	ADM1
	Y_{pro}	COD/COD	0.04	0.05	0.011	ADM1
Uptake of acetate	K_{m_ac}	COD/COD.d	8	16	0.035	ADM1
	K_{S_ac}	kg COD/m ³	0.15	0.3	0.035	ADM1

	Y_{ac}	COD/COD	0.05	0.05	0.05	ADMI
Uptake of H_2	$k_{m_{H_2}}$	COD/COD.d	35	35	35	ADMI
	$K_{S_{H_2}}$	kg COD/m ³	$7 \cdot 10^{-6}$	$5 \cdot 10^{-5}$		ADMI
	Y_{H_2}	COD/COD	0.06	0.06	0.06	ADMI
Uptake MAC to produce MT	$k_{m_{aro_MT}}$	d ⁻¹	71.6	138	0.035	Assumed
	$\mu_{max_aro_DMS}$	d ⁻¹	2.37	4.57	0.035	Assumed
	Y_{aro_MT}	gCOD_X/gCOD_S	0.033	0.033		Assumed
	$K_{S_{aro}}$	kgCOD/m ³	0.36	0.36		Assumed
	$K_{S_{H_2S}}$	kgS/m ³	0.0096	0.0096		Assumed
Uptake of MAC to produce DMS	$k_{m_{aro_DMS}}$	d ⁻¹	36.59	70.62	0.035	Assumed
	$\mu_{max_aro_DMS}$	d ⁻¹	2.37	4.57	0.035	Assumed
	Y_{aro_DMS}	gCOD_X/gCOD_S	0.066	0.066		Assumed
	$K_{S_{aro}}$	kgCOD/m ³	0.36	0.36		Assumed
	$K_{S_{H_2S}}$	kgS/m ³	0.0096	0.0096		Assumed
Uptake of acetate by SRB	$k_{m_{ac_SRB}}$	d ⁻¹	15.88	30.65	0.035	Assumed
	Y_{ac_SRB}	COD_X/gCOD_S	0.051	0.051		Assumed
	$K_{S_{ac_SRB}}$	kgCOD/m ³	0.30	0.30		Assumed
	$K_{S_{SO4_ac}}$	kg/m ³	0.0074	0.0074		Assumed
	$K_{I_{ac_H_2S}}$	kgS/m ³	0.29	0.29		Assumed
Uptake of propionate SRB	$k_{m_{pro_SRB}}$	d ⁻¹	8.644	16.67	0.035	Assumed
	Y_{ac_SRB}	COD_X/gCOD_S	0.059	0.059		Assumed
	$K_{S_{pro_SRB}}$	kgCOD/m ³	0.024	0.024		Assumed
	$K_{S_{SO4_pro}}$	kg/m ³	0.019	0.019		Assumed
	$K_{I_{pro_H_2S}}$	kgS/m ³	0.29	0.29		Assumed

Uptake of hydrogen by SRB	$k_{m_H2_SRB}$	d^{-1}	44.64	86.15	0.035	Assumed
	Y_{H2_SRB}	$kgCOD/m^3$	0.112	0.0112		Assumed
	$K_{S_H2_SRB}$	kg/m^3	$5 \cdot 10^{-6}$	$5 \cdot 10^{-6}$		Assumed
	$K_{S_SO4_H2}$	kg/m^3	0.0009	0.0009		Assumed
	$K_{L_H2_H2S}$	kgS/m^3	0.55	0.55		Assumed
Uptake of DMS (degradation of DMS)	$k_{m_DMS_deg}$	d^{-1}	33.65	64.94	0.035	Assumed
	$\mu_{max_DMS_deg}$	d^{-1}	2.09	4.03	0.035	Assumed
	Y_{DMS_deg}	$gCOD_X/gCOD_S$	0.062	0.062		Assumed
	K_{S_DMS}	kg/m^3	0.019	0.019		Assumed
Uptake MT of (degradation of MT)	$k_{m_MT_deg}$	d^{-1}	19.31	37.27	0.035	Assumed
	$\mu_{max_MT_deg}$	d^{-1}	1.632	3.15	0.035	Assumed
	Y_{MT_deg}	$gCOD_X/gCOD_S$	0.085	0.085		Assumed
	K_{S_MT}	kg/m^3	0.016	0.016		Assumed
MT oxidation to DMDS	k_{MT_DMDS}	d^{-1}	7.35	7.35		Assumed
Precipitation of sulfide	k_{pre_H2S}	d^{-1}	10^6	10^6		Assumed

5.2.2. Variation of Physico-Chemical Parameters with Temperature

Changes in temperature have a fundamental influence on physical-chemical systems, mainly because of changes in equilibrium coefficients. The van't Hoff equation describes the variation of equilibrium coefficients with temperature:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (5.3)$$

Where,

ΔH° = heat of reaction at standard temperature and pressure (J mole⁻¹)

R = gas law constant, 8.314 J mole⁻¹ K⁻¹

K_1 = the known equilibrium coefficient at reference temperature T_1 (K)

K_2 = the unknown coefficient at temperature T_2 (K)

If it is assumed that $T_1 \times T_2 \approx T_1^2$ and θ is substituted for $(\Delta H^\circ / R T_1^2)$, Eq. 5.3 reduces to the following commonly used form (Siegrist *et al.*, 1993; Vavilin *et al.*, 1997):

$$K_2 = K_1 e^{\theta(T_2 - T_1)} \quad (5.4)$$

Between 273 K (0°C) and 333 K (60°C), Eq. 5.4 is effective for all equilibrium coefficients in the odour model, except for the organic acids. However, the K_a values for the organic acids vary a small amount in this temperature range, and can be assumed to be constant. Since no references reported the temperature influence on liquid-solid partitioning coefficients, they were assumed to be constant in this study. Tables 5.3 - 5.6

summarized the characteristics of odorous compounds at mesophilic and thermophilic temperatures.

Table 5.3: Acid-base equilibrium coefficient at mesophilic and thermophilic conditions

Compounds	T=35°C		T=55°C		θ (°C ⁻¹)	Source
	Ka	pKa	Ka	pKa		
HAc	1.74E-05	4.76	1.74E-05	4.76	n/a	Lide (2001)
HPro	1.32E-05	4.88	1.32E-05	4.88	n/a	Lide (2001)
HBu	1.45E-05	4.84	1.45E-05	4.84	n/a	Lide (2001)
HVa	1.58E-05	4.80	1.58E-05	4.80	n/a	Lide (2001)
NH ₃	1.11E-09	8.95	4.51E-09	8.35	0.07	Lide (2001)
H ₂ S	8.91E-08	7.05	1.59E-07	6.80	0.03	Lide (2001)
H ₂ O	2.08E-14	13.68	9.51E-14	13.02	0.08	Lide (2001)

Table 5.4: Henry's law coefficients under mesophilic and thermophilic conditions

Compounds	T=35 °C	T=55 °C	θ (°C ⁻¹)	Source
	K _H (M/Bar)	K _H (M/Bar)		
HAc	882	469	-0.032	Lide (2001)
HPro	1852	776	-0.043	Lide (2001)
HBu	1852	620	-0.055	Lide (2001)
HVa	2222	625	-0.063	Lide (2001)
NH ₃	65.9	38.5	-0.027	Lide (2001)
H ₂ S	0.099	0.068	-0.019	Lide (2001)
MT	0.28	0.28	-0.0003	Assumed
DMS	0.51	0.50	-0.0003	Schwarzenbach, <i>et al.</i> (1992)
DMDS	0.88	0.87	-0.0003	

Table 5.5 Volume-specific liquid-gas mass transfer coefficients under mesophilic and thermophilic conditions

Compounds	T=35 °C	T=55 °C	θ (°C ⁻¹)	Source
	k_{La} (d ⁻¹)	k_{La} (d ⁻¹)		
HAc	69	126	0.03	Siegrist <i>et al.</i> , (2002)
HPro	49	89	0.03	
HBu	57	104	0.03	
HVa	43	78	0.03	
NH ₃	78	142	0.03	
H ₂ S	71	129	0.03	
MT	76	138	0.03	
DMS	62	113	0.03	
DMDS	54	98	0.03	

Table 5.6: Liquid-solid partitioning coefficients at mesophilic and thermophilic conditions

Compounds	T=35 °C	T=55 °C	Source
	K_p (m ³ /kg COD)	K_p (m ³ /kg COD)	
MT	22.98	22.98	Assumed
DMS	47.28	47.28	Assumed
DMDS	101.21	101.21	Assumed

A thermophilic odour model was developed on the basis of the thermophilic parameters values. Table 5.7, Figures 5.1 and 5.2 compared the concentrations of odourous compounds in the gas phase under mesophilic and thermophilic conditions.

Table 5.7: Concentrations of odorous compounds at mesophilic and thermophilic conditions

Compounds	Phases	Units	Mesophilic T=35°C	Thermophilic T=55°C	Values from literature ^a T=35°C T=55°C		Threshold (ppb)
H ₂ S	Gas	ppm	49.5	206.8	1.68	25.0	0.5
	Gas	M	1.9E-06	7.6E-06			
	H ₂ S_ion_r	M	7.3E-07	5.0E-05			
	H ₂ S_r	M	4.9E-06	1.4E-05			
MT	Gas	ppm	9.3	11.3	0.26	0.77	0.0014-18
	Gas	M	3.6E-07	4.1E-07			
	Liquid	M	2.6E-06	3.1E-06			
	Solid	M	7.4E-05	4.9E-05			
DMS	Gas	ppm	5.5	7.5	0.25	0.28	0.12-0.4
	Gas	M	2.2E-07	2.8E-07			
	Liquid	M	2.8E-06	3.8E-06			
	Solid	M	1.6E-04	1.2E-04			
DMDS	Gas	ppm	2.2	4.2	0.25	0.25	0.3-11
	Gas	M	8.4E-08	1.5E-07			
	Liquid	M	1.9E-06	3.7E-06			
	Solid	M	2.4E-04	2.5E-04			
NH ₃	Gas	ppm	8.8	79.4			13-15300
	Gas	M	3.4E-07	3.1E-06			
	NH ₄ ⁺ _r	M	3.1E-02	3.2E-02			
	NH ₃ _r	M	5.8E-04	3.3E-03			
	Gas	ppm	3.0E-03	8.2E-03			16

HAc	Gas	M	7.4E-09	2.2E-08			
	Ac_r	M	4.8E-02	9.7E-02			
	HAc_r	M	1.7E-04	2.4E-04			
	Gas	ppm	4.0E-04	2.7E-03			0.09-20
	Gas	M	1.7E-09	1.1E-08			
HPro	Pro_r	M	1.8E-02	7.1E-02			
	HPro_r	M	8.2E-05	2.4E-04			
	Gas	ppm	2.1E-04	8.0E-04			0.09-20
	Gas	M	1.3E-09	4.7E-09			
	Bu_r	M	1.5E-02	2.6E-02			
	HBu_r	M	6.2E-05	8.0E-05			
	Gas	ppm	9.7E-05	4.4E-04			1.8-2630
	Gas	M	7.8E-10	3.4E-09			
HVa	Va_r	M	1.2E-02	2.1E-02			
	HVa_r	M	4.5E-05	5.8E-05			
pH			7.2	7.4	7.3	7.6	
Xc		kg COD m ⁻³ d ⁻¹	1.3	0.7			

Note: ^a Griffith and Alvarez (2002).

^b Vincent and Hobson (1998)

Figure 5.1: Gas phase concentration vs temperature

Figure 5.2 Gas phase concentrations of VFA vs temperature

Referring to Table 5.7, with an increase of temperature, the concentrations of odourous compounds in the liquid and gas phases increased, however, the concentrations in the solid phase slightly decreased. These phenomena were reasonable because with an increase of temperature, the degradation rates of organic compounds increased. Therefore, more odourous compounds would be generated in the digesters. With temperature increase, Henry's law coefficients (M bar^{-1}) decreased and the volumetric-specific liquid-gas transfer coefficients increased. Both situations caused the emission of odorous compounds increased from digesters. Although the solid-liquid partitioning coefficient was assumed to be the same at both mesophilic and thermophilic temperatures, with an increase of temperature, the concentration of complex particulate (X_C) in the digesters decreased, which could cause the decrease of the partitioning from liquid phase to solid phase (Eq. 2.33). Hence, the solid phase concentration of odourous compounds slightly decreased.

Referring to Figure 5.1 and 5.2, the increases in concentrations of H_2S and NH_3 were much greater than other odourous compounds. The concentration of H_2S under thermophilic conditions was triple that under mesophilic conditions and the concentration of NH_3 was 8 times greater under thermophilic as compared to mesophilic conditions. The dramatically increased concentrations of H_2S and NH_3 would contribute significantly to odour. Comparing with NH_3 and H_2S , the increased concentrations of MT, DMS and DMDS were slight. Although the concentrations of the VFA increased 2 to 5 times under thermophilic conditions, the concentrations of VFA in the gas phase were still below their thresholds. Therefore, the emission of VFA under thermophilic conditions would not

cause a serious odour problem. In general, the odour emissions under thermophilic conditions were much more serious than under mesophilic conditions.

The pH value increased slightly in the thermophilic digester due to the enhanced protein decomposition in thermophilic digestion. pH had a significant impact on the performance of anaerobic processes. A pH range of 6.8 to 7.4 generally provides optimum conditions for the methanogens (Grady *et al.*, 1999). As the pH deviates from an optimum value, the activity decreases. This effect is particularly significant for anaerobic processes because the methanogens are affected to a greater extent than the other microorganisms in the microbial community. The pH values under both mesophilic and thermophilic conditions were in the optimum ranges. With the increase of pH, the emission of NH_3 was enhanced (Eq. 4.7), however, the emission of H_2S decreased (Eq. 4.9). Since the difference of pH values between mesophilic and thermophilic conditions was only 0.136, the impact of pH on the emission of odourous compound under thermophilic conditions was not significant. The increased emissions of odourous compounds were mainly from the increased biochemical reaction rates with the temperature increase, such as the enhanced protein decomposition, the increased rate of amino acids degradation and methylation reaction. All these processes would lead to increases in the emission of odourous compounds.

Table 5.7 also compared the emissions of odourous compounds under mesophilic and thermophilic conditions with the data from the literature review. The values predicted by the odour model were generally about one order of magnitude greater than the literature data. One main reason was that hydrogen sulfide in the literature study was controlled by

the aggressive dosing of iron salts to the collection and to the primary sludge (Griffith and Alvarez, 2002). Therefore, the emission of H₂S was controlled in the literature study. The production of H₂S in anaerobic digestion had a strong impact on the formation of other sulfur-containing odourous compounds because the sulfur used for methylation reactions to produce MT and DMS is originally from H₂S. With the increased emission of H₂S, the emissions of MT, DMS and DMDS correspondingly increased. The increased emissions of NH₃ and VFA were mainly from the enhanced decomposition rates of proteins, amino acids and LCFA with the increase of temperature.

5.3 Hydraulic Retention Time

Hydraulic retention time (HRT) is the mean residence time of feed sludge in an anaerobic digester, and can be expressed as:

$$HRT = \frac{V_r}{Q_{in}} \quad (5.1)$$

Where,

V_r = volume of the anaerobic reactor (m³)

Q_{in} = the input flow of feed sludge (m³/d)

HRT exerts a dominant effect on controlling the performance of anaerobic processes. HRT controls the types of microorganisms that could grow in a process, as well as their activity, thereby determines the effluent quality. Hydrolysis of particulate carbohydrates and proteins to produce simple sugars and amino acids is a relatively rapid reaction, which is essentially complete for HRT values in excess of about 3 days. In contrast, the

hydrolysis of lipids to form long chain fatty acids and other soluble reaction products is a much slower reaction that does not generally occur for HRT values less than 6 days. A significant difference also exists for the various acidogenic reactions that convert the hydrolysis products into acetic acid and hydrogen. Fermentation of amino acids and simple sugars occur very rapidly and generally would not be rate limiting. In contrast, the anaerobic oxidation of fatty acids to acetic acid and hydrogen is much slower. The oxidation of propionic acid is particularly slow in comparison to the other anaerobic oxidations. Hydrogen oxidizing methanogens can grow very rapidly; a complete population of such organism would develop for HRT values in excess of 1.5 days. In contrast, the acetoclastic methanogens grow much more slowly and would not generally be present unless the SRT is in excess of about 12 days (Grady *et al.*, 1999). Generally, a minimum HRT of about 10 days is specified to ensure the main biochemical processes complete in anaerobic digesters under mesophilic conditions.

In this study, the input of HRT ranging from 3 to 40 days on the predicted gas phase concentrations of odorous compounds was assessed. Table 5.8 and Figure 5.3 summarized the concentrations of odorous compounds at the different HRT values.

Referring to Table 5.8, generally, the gas flow increased with the increase of HRT. At an HRT of 3 days, the gas flow was only 1.417 m³/d, which indicated that the production of methane (the main biogas from anaerobic digestion systems) was very small. On the contrary, at an HRT of 10 days, the gas flow was 15.57 m³/d, which was one order of

Table 5.8: Concentrations of odourous compounds at different HRT values.

Compounds	Phases	Units	HRT (d)						
			3	5	10	20	30	40	
H ₂ S	Gas	ppm	50.3	4.7	9.1	49.5	127.1	164.7	
	Gas	M	2.0E-06	1.8E-07	3.5E-07	1.9E-06	5.0E-06	6.4E-06	
	H2S_ion_r	M	9.1E-08	5.9E-07	1.3E-06	7.3E-07	1.9E-05	2.5E-05	
	H2S_r	M	5.0E-06	4.7E-07	9.0E-07	4.9E-06	1.3E-05	1.6E-05	
MT	Gas	ppm	9.4	11.1	11.4	9.3	7.2	6.1	
	Gas	M	3.7E-07	4.3E-07	4.4E-07	3.6E-07	2.8E-07	2.4E-07	
	Solid	M	2.9E-04	2.5E-04	1.5E-04	7.4E-05	3.8E-05	2.5E-05	
	Liquid	M	2.6E-06	3.1E-06	3.2E-06	2.6E-06	2.0E-06	1.7E-06	
DMS	Gas	ppm	1.9	2.6	7.1	5.5	6.9	7.7	
	Gas	M	7.3E-08	1.0E-07	2.8E-07	2.2E-07	2.7E-07	3.0E-07	
	Solid	M	2.2E-04	2.2E-04	2.0E-04	1.6E-04	1.4E-04	1.2E-04	
	Liquid	M	9.5E-07	1.3E-06	2.0E-06	2.8E-06	3.5E-06	3.9E-06	
DMDS	Gas	ppm	0.2	0.4	1.0	2.2	3.9	4.8	
	Gas	M	8.1E-09	1.5E-08	3.9E-08	8.4E-08	1.4E-07	1.9E-07	
	Solid	M	8.9E-05	1.2E-04	1.8E-04	2.4E-04	2.6E-04	2.7E-04	
	Liquid	M	1.8E-07	3.4E-07	8.7E-07	1.9E-06	3.2E-06	4.3E-06	
NH ₃	Gas	ppm	0.1	6.6	7.8	8.8	9.7	10.2	
	Gas	M	4.6E-09	2.6E-07	3.1E-07	3.4E-07	3.8E-07	4.0E-07	
	NH ₄ ⁺ _r	M	3.4E-02	2.7E-02	2.9E-02	3.1E-02	3.3E-02	3.5E-02	
	NH ₃ _r	M	7.7E-06	4.3E-04	5.1E-04	5.8E-04	6.4E-04	6.7E-04	

HAc	Gas	ppm	15.8	0.02	6.1E-03	3.0E-03	2.0E-03	1.6E-03
	Gas	M	4.0E-05	5.8E-08	1.5E-08	7.4E-09	4.9E-09	4.0E-09
	Ac_r	M	3.2	3.3E-01	9.5E-02	4.8E-02	3.3E-02	2.7E-02
	HAc	M	0.9	1.3E-03	3.4E-04	1.7E-04	1.1E-04	9.0E-05
HPro	Gas	ppm	1.9	2.8E-03	8.0E-04	4.0E-04	2.6E-04	2.1E-04
	Gas	M	8.1E-06	1.2E-08	3.5E-09	1.7E-09	1.1E-09	9.0E-10
	Pro_r	M	1.0	1.1E-01	3.5E-02	1.8E-02	1.2E-02	1.0E-02
	HPro_r	M	0.4	5.8E-04	1.7E-04	8.2E-05	5.4E-05	4.3E-05
HBu	Gas	ppm	1.2	9.0E-04	3.8E-04	2.1E-04	1.4E-04	1.2E-04
	Gas	M	7.2E-06	5.6E-09	2.4E-09	1.3E-09	8.9E-10	7.3E-10
	Bu_r	M	1.0	1.1E-01	2.6E-02	1.5E-02	1.0E-02	8.7E-03
	HBu_r	M	0.3	5.8E-04	1.1E-04	6.2E-05	4.2E-05	3.5E-05
HVa	Gas	ppm	0.5	4.1E-04	1.7E-04	9.7E-05	6.6E-05	5.4E-05
	Gas	M	3.7E-06	3.3E-09	1.4E-09	7.8E-10	5.4E-10	4.4E-10
	Va_r	M	6.8E-01	4.3E-02	2.0E-02	1.2E-02	8.3E-03	6.9E-03
	HVa_r	M	2.1E-01	1.9E-04	8.1E-05	4.5E-05	3.1E-05	2.5E-05
pH			5.3	7.2	7.2	7.2	7.2	7.2
Gas flow		m ³ /d	1.4	13.5	15.6	16.6	17.2	17.6
X _C		kgCOD m ³ d ⁻¹	4.9	3.5	2.1	1.3	0.82	0.64

Figure 5.3: Gas phase concentrations vs HRT

magnitude greater than that at HRT of 3 days. There was little difference between the gas flows when the HRT value was greater than 10 days, which proved that the minimum HRT of about 10 days was needed to complete the main biochemical processes in anaerobic digestion. At an HRT of 3 days, hydrogen-oxidizing methanogens would convert hydrogen into methane. Since only limited amounts of hydrogen were produced through fermentation reactions, the quantity of methane would be small. Hydrolysis of carbohydrates and proteins would be generally completed at an HRT of 3 days, and the simple sugars and amino acids produced would be converted into acetic acid, other volatile acids and hydrogen. Therefore, VFA accumulated in the anaerobic reactor, and the concentrations of the VFA in both liquid phase and gas phase became significantly high (Table 5.8). Because the gas phase concentrations of VFA at an HRT of 3 days were greater than their thresholds (Table 5.8), their emissions could contribute to odour problems. The accumulation of VFA also dropped the pH value in the reactor to 5.3,

which deviated from the optimum pH range for anaerobic digestion. This low pH would inhibit all uptake processes in the digesters. Therefore, the production of the main biogas (i.e. CH_4) was dramatically decreased.

The concentrations of H_2S at an HRT of 3 days in the liquid phase and gas phase were slightly lower than that at HRT of 20 days (the base odour model was developed at an HRT of 20 day). The formation of H_2S in anaerobic digestion results mainly from the degradation of amino acids and sulfate reduction. At an HRT of 3 days, the fermentation of amino acids was not complete, which could reduce the formation of H_2S in the anaerobic digesters. Nevertheless, the low pH value enhanced the free H_2S in the liquid phase (Eq. 4.9), which could be released into the gas phase. Therefore, there was no substantial difference between the concentrations of H_2S at an HRT of 3 days and 20 days.

Referring to Table 5.8 and Figure 5.3, with the increased HRT values, the concentrations of MT in the gas phase slightly dropped and the emission of DMDS slightly increased, which indicated that the transfer of MT to DMDS increased slightly with the increase of HRT. The solid phase concentrations of MT and DMS slightly decreased with an increase of HRT. Since the complex particulate concentration (X_C) decreased in the digesters with an increase of HRT, it would correspondingly decrease the partitioning between the liquid and solid phases (Eq. 2.33). The solid phase concentration of DMDS slightly increased with the increase of HRT, which might be caused by the increased conversion

rate between MT to DMDS. In general, the increase of HRT did not have a strong effect on the formation of MT, DMS, DMDS and NH₃.

5.4 Volumetric Organic Loading Rate

The volumetric organic loading rate (VOL) could be calculated in units of kg COD/(m³.day) as:

$$VOL = \frac{Q_{in} (S_{So} + X_C)}{V_r} \quad (5.2)$$

Where,

VOL = volumetric organic loading rate [kg COD/(m³.d)]

S_{So} = soluble organic matter in the feed sludge (kg COD/m³)

X_C = Particulate organic matter in the feed sludge (kg COD/m³)

S_{So}+X_C = Total COD in the feed sludge (kg COD/m³)

Substitution of Eq. 5.1 into Eq. 5.2 related the VOL to the HRT:

$$VOL = \frac{S_{So} + X_C}{HRT} \quad (5.3)$$

VOL typically ranges from 2 to 8 kg COD /(m³.day) for anaerobic digestion systems. In the base model, the total COD (i.e. S_{So}+X_C) in feed sludge was 40 kg/m³ and HRT was 20 days (Table 4.2), therefore, VOL for the basic odour model was 2 kg COD/(m³.day). Because the total suspended solid in the feed sludge can be controlled by thickening or by varying the proportion of the primary sludge and waste activated sludge in the feed

sludge, the values of the VOL can be adjusted by modifying the operation of the upstream treatment processes. Generally, for the thickening process, the concentration of soluble COD in the thickened sludges will not change while the concentration of particulate COD increases. Table 5.9 presented the corresponding input data that was employed to reflect different VOL values for the thickening process. Table 5.10 and Figure 5.4 compared the concentrations of odourous compounds in the three phases at different VOL values.

Referring to Table 5.10, with the increase of VOL values, the gas flow increased proportionally; the pH value increased only slightly; and the concentrations of odourous compounds in the three phases generally increased. The phenomena are reasonable because with an increase of VOL, the availability of degradable organic compounds increased. The increased concentration of VFA in the gas phase was slight, which indicates that the responses of VFA to VOL are insensitive. Contrarily, the emission of ammonia increased proportionally with the increase of VOL values from 2 to 6.2 kg COD/(m³.day). At VOL of 6.2 kg COD/(m³.day), the gas phase concentration of ammonia was already above its thresholds (Table 5.8). Therefore, with the increase of VOL, the emission of NH₃ might cause odour problems.

From Table 5.10 and Figure 5.4, it could be seen that the emission of H₂S increased significantly with the increase of VOL, which indicated that odour problems become more serious with the increase of VOL values. The solid phase concentrations of VOSC also increased with the increase of VOL, however, only the concentration of MT in the

gas phase increased. The concentrations of DMS and DMDS in gas phase decreased slightly. Although the increase of VOL values enhanced the total production of DMS and DMDS, it also increased the concentration of complex particulate (X_C) in the digesters. The concentration of X_C is proportional to the partitioning rate from the liquid to the solid phase (Eq. 2.33), therefore, more DMS and DMDS would partition to the solid phase, and correspondingly less DMS and DMDS were emitted to the gas phase. The emissions of DMS and DMDS into the gas phase were a combined effect of these parameters.

Table 5.9: Input data at different VOL values

Compounds	Unit	VOL (kgCOD/m ³ .d)				
		0.95	1.3	2.0	3.4	6.2
Q_{in_ss}	m ³ /d	1.5	1.5	1.5	1.5	1.5
S_{aa_in}	kgCOD/m ³	3.6	3.6	3.6	3.6	3.6
S_{fa_in}	kgCOD/m ³	6.3	6.3	6.3	6.3	6.3
S_{su_in}	kgCOD/m ³	2.4	2.4	2.4	2.4	2.4
$S_{metal_ion_in}$	M	0.0008	0.0008	0.0008	0.0008	0.0008
S_{SO4_in}	M	0.000328	0.000328	0.000328	0.000328	0.000328
X_{C_in}	kgCOD/m ³	3	6	12	24	48
X_{I_in}	kgCOD/m ³	4	8	16	32	64
T	K	308	308	308	308	308
V	m ³	30	30	30	30	30
HRT	d ⁻¹	20	20	20	20	20

Note: ^a the VOL value used in the basic odour model.

Table 5.10: Concentrations of odorous compounds in three phases at different VOL values

Compounds	Phases	Units	VOL (kgCOD/m ³ .d)				
			0.95	1.3	2.0	3.4	6.2
H ₂ S	Gas	ppm	3.6	6.0	49.5	205.6	432.8
	Gas	M	1.4E-07	2.3E-07	1.9E-06	8.0E-06	1.7E-05
	H2S_ion_r	M	5.3E-07	8.7E-07	7.3E-07	3.2E-05	8.0E-05
	H2S_r	M	3.5E-07	6.0E-07	4.9E-06	2.0E-05	4.3E-05
MT	Gas	ppm	6.7	7.5	9.3	12.5	16.0
	Gas	M	2.6E-07	2.9E-07	3.6E-07	4.9E-07	6.3E-07
	Liquid	M	1.9E-06	2.1E-06	2.6E-06	3.5E-06	4.5E-06
	Solid	M	1.5E-05	3.1E-05	7.4E-05	1.9E-04	4.9E-04
DMS	Gas	ppm	7.4	6.3	5.5	5.3	4.8
	Gas	M	2.9E-07	2.5E-07	2.2E-07	2.1E-07	1.9E-07
	Liquid	M	3.8E-06	3.2E-06	2.8E-06	2.7E-06	2.4E-06
	Solid	M	6.1E-05	9.6E-05	1.6E-04	3.1E-04	5.6E-04
DMDS	Gas	ppm	4.9	3.2	2.2	1.5	1.1
	Gas	M	1.9E-07	1.2E-07	8.4E-08	6.0E-08	4.3E-08
	Liquid	M	4.3E-06	2.8E-06	1.9E-06	1.4E-06	9.7E-07
	Solid	M	1.5E-04	1.8E-04	2.4E-04	3.3E-04	4.7E-04
NH ₃	Gas	ppm	6.7	7.3	8.8	12.6	22.8
	Gas	M	2.6E-07	2.8E-07	3.4E-07	4.9E-07	8.9E-07
	NH ₄ ⁺ _r	M	2.3E-02	2.6E-02	3.1E-02	4.2E-02	6.4E-02
	NH ₃ _r	M	4.4E-04	4.8E-04	5.8E-04	8.4E-04	1.5E-03

HAc	Gas	ppm	2.7E-03	2.8E-03	3.0E-03	3.2E-03	3.7E-03
	Gas	M	6.7E-09	7.0E-09	7.4E-09	8.0E-09	9.2E-09
	Ac_r	M	4.5E-02	4.6E-02	4.8E-02	5.6E-02	7.7E-02
	HAc	M	1.5E-04	1.6E-04	1.7E-04	1.8E-04	2.1E-04
HPro	Gas	ppm	4.0E-04	4.0E-04	4.0E-04	3.7E-04	3.1E-04
	Gas	M	1.7E-09	1.7E-09	1.7E-09	1.6E-09	1.4E-09
	Pro_r	M	1.8E-02	1.8E-02	1.8E-02	1.8E-02	1.8E-02
	HPro_r	M	8.0E-05	8.2E-05	8.2E-05	7.7E-05	6.4E-05
HBu	Gas	ppm	2.1E-04	2.1E-04	2.1E-04	1.9E-04	1.6E-04
	Gas	M	1.3E-09	1.3E-09	1.3E-09	1.2E-09	1.0E-09
	Bu_r	M	1.5E-02	1.5E-02	1.5E-02	1.5E-02	1.5E-02
	HBu_r	M	6.0E-05	6.2E-05	6.2E-05	5.8E-05	4.9E-05
HVa	Gas	ppm	9.5E-05	9.7E-05	9.7E-05	9.0E-05	7.5E-05
	Gas	M	7.7E-10	7.9E-10	7.8E-10	7.3E-10	6.1E-10
	Va_r	M	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02
	HVa_r	M	4.4E-05	4.5E-05	4.5E-05	4.2E-05	3.5E-05
pH			7.2	7.2	7.2	7.3	7.3
Gas flow		m ³ /d	10.8	12.7	17	24.4	40.1
X_c		kg COD/m ³	0.34	0.64	1.24	2.4	4.8

Note: ^a Griffith and Alvarez, 2002^o.

Figure 5.4: Gas Phase Concentration vs VOL

5.5 Characteristics of Feed Sludge

The characteristics of the feed sludge may significantly affect the formation of odourous compounds in anaerobic digesters. The characteristics of feed sludge that are normally considered in anaerobic digestion include the relative amount of soluble and particulate organic matter, which was similar to VOL. As this model studied the formation of the odourous compounds in anaerobic digestion, the interest was focused on the components in feed sludge that were critical to the formation of odourous compounds. The main processes for the formation of odourous compounds in anaerobic digestion were: the degradation of amino acids, sulfate reduction and the methylation reactions.

Correspondingly, three critical components in feed sludge that related to these three processes were identified: the protein content, the sulfate content and the heavy metal content. As the protein content in municipal sludge is generally constant, the effects of the heavy metal and sulfate content on the formation of odourous compounds in anaerobic digesters were evaluated.

5.5.1 Heavy Metals

Heavy metals (i.e. Fe^{2+} , Zn^{2+} , Cd^{2+} and Cu^{2+}) have a strong effect on anaerobic processes, as is indicated in Table 5.11 by the low concentrations causing 50% inhibition. Fortunately, only the soluble metal ions are inhibitory and the metal sulfides are insoluble, giving residual heavy metal concentrations much less than the concentration in Table 5.11. Consequently, heavy metal inhibition to anaerobic processes is often prevented by the sulfide produced in the process. Furthermore, the concentration of soluble sulfide can be reduced by the addition of iron to the reactor, thereby reducing the emission of H_2S in the gas phase of anaerobic digesters.

Table 5.11: Soluble heavy metal concentrations exhibiting 50% inhibition of anaerobic digesters (Mosey and Hughes, 1975)

Cation	Concentration (mg/l)
Fe^{2+}	1 to 10
Zn^{2+}	10^{-4}
Cd^{2+}	10^{-7}
Cu^{2+}	10^{-12}

In this section, the effect of heavy metals on the formation of odourous compounds was assessed. Different concentrations of heavy metal were given and the corresponding output concentrations of the odourous compounds in the three phases were compared in Table 5.12 and Figure 5.5. Referring to Table 5.12 and Figure 5.5, it can be seen that changes in the heavy metal concentrations significantly affected the concentration of H_2S in the gas phase. The concentration of H_2S in the gas phase varied from 660 to 0.63 ppm as the heavy metal concentration in the reactor changed from 0.0002 to 0.0016 M. The concentrations of MT, DMS and DMDS in all three phases decreased slightly as the formation of the H_2S in the reactor decreased, which resulted from an increase in the heavy metal concentration in the reactor. Because the sulfide used in methylation reactions to form MT and DMS was originally from H_2S , the decrease of H_2S concentration generally led to the decrease of MT and DMS. The changes in heavy metal concentration in the reactor had no influence on the emission of VFA and ammonia. Therefore, the content of heavy metal in the feed sludge had a fundamental impact on the emission of H_2S in anaerobic digesters and a slight effect on the emissions of MT, DMS and DMDS.

Table 5.12: Comparing the concentrations of odorous compounds at different heavy metal concentrations

Compounds	Phases	Units	Heavy Metals (M)				
			0.0002	0.0004	0.0008	0.0012	0.0016
H ₂ S	Gas	ppm	634.8	423.5	49.5	1.3	0.6
	Gas	M	2.5E-05	1.7E-05	1.9E-06	5.1E-08	2.4E-08
	H2S_ion_r	M	9.4E-05	6.2E-05	7.3E-07	1.9E-07	9.0E-08
	H2S_r	M	6.4E-05	4.2E-05	4.9E-06	1.3E-07	6.1E-08
MT	Gas	ppm	11.7	11.1	9.3	9.0	9.0
	Gas	M	4.6E-07	4.3E-07	3.6E-07	3.5E-07	3.5E-07
	Liquid	M	3.3E-06	3.1E-06	2.6E-06	2.5E-06	2.5E-06
	Solid	M	9.3E-05	8.8E-05	7.4E-05	7.1E-05	7.1E-05
DMS	Gas	ppm	8.1	7.4	5.5	5.2	5.2
	Gas	M	3.2E-07	2.9E-07	2.2E-07	2.0E-07	2.0E-07
	Liquid	M	4.1E-06	3.7E-06	2.8E-06	2.6E-06	2.6E-06
	Solid	M	2.4E-04	2.2E-04	1.6E-04	1.5E-04	1.5E-04
DMDS	Gas	ppm	2.6	2.5	2.2	2.5	2.5
	Gas	M	1.0E-07	9.6E-08	8.4E-08	8.2E-08	8.2E-08
	Liquid	M	2.4E-06	2.2E-06	1.9E-06	1.8E-06	1.8E-06
	Solid	M	2.8E-04	2.7E-04	2.4E-04	2.3E-04	2.3E-04
NH ₃	Gas	ppm	9.0	8.8	8.8	8.8	9.0
	Gas	M	3.5E-07	3.4E-07	3.4E-07	3.4E-07	3.5E-07
	NH ₄ ⁺ _r	M	3.1E-02	3.1E-02	3.1E-02	3.1E-02	3.1E-02
	NH ₃ _r	M	5.8E-04	5.8E-04	5.8E-04	5.8E-04	5.8E-04

HAc	Gas	ppm	3.0E-03	3.0E-03	3.0E-03	3.0E-03	3.0E-03
	Gas	M	7.4E-09	7.4E-09	7.4E-09	7.4E-09	7.4E-09
	Ac_r	M	4.9E-02	4.9E-02	4.9E-02	4.9E-02	4.8E-02
	HAc	M	1.7E-04	1.7E-04	1.7E-04	1.7E-04	1.7E-04
HPro	Gas	ppm	4.0E-04	4.0E-04	4.0E-04	3.9E-04	3.9E-04
	Gas	M	1.7E-09	1.7E-09	1.7E-09	1.7E-09	1.7E-09
	Pro_r	M	1.8E-02	1.8E-02	1.8E-02	1.8E-02	1.8E-02
	HPro_r	M	8.2E-05	8.2E-05	8.2E-05	8.2E-05	8.2E-05
HBu	Gas	ppm	2.1E-04	2.1E-04	2.1E-04	2.1E-04	2.1E-04
	Gas	M	1.3E-09	1.3E-09	1.3E-09	1.3E-09	1.3E-09
	Bu_r	M	1.5E-02	1.5E-02	1.5E-02	1.5E-02	1.5E-02
	HBu_r	M	6.2E-05	6.2E-05	6.2E-05	6.2E-05	6.2E-05
HVa	Gas	ppm	9.7E-05	9.7E-05	9.7E-05	9.7E-05	9.7E-05
	Gas	M	7.8E-10	7.8E-10	7.8E-10	7.9E-10	7.9E-10
	Va_r	M	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02
	HVa_r	M	4.5E-05	4.5E-05	4.5E-05	4.5E-05	4.5E-05

Figure 5.5: Gas phase concentrations vs heavy metal concentrations

5.5.2 Sulfate Content

The sulfate concentration in the model input was another critical factor for the emission of sulfur-containing odourous compounds from anaerobic digesters because H₂S can be produced by sulfate reduction. Inorganic sulfur, in the form of sulfate, in the feed sludge is typically found in concentrations of 30-60 mg/l (Boon, 1995; Cheremisinoff). Considerably higher concentrations of sulfate may result from infiltration water or industrial sources (Harkness, 1980). In this section, the effects of sulfate content on the formation of odourous compounds in anaerobic digesters were analyzed by varying the sulfate concentrations in the feed sludge and finding the corresponding changes of the concentrations of odourous compounds in the gas phase. Table 5.13 and Figure 5.6 presented the concentrations of odourous compounds at different inlet sulfate concentrations in anaerobic digesters.

Table 5.13: Concentrations of odourous compounds in three phases at different inlet sulfate concentration

Compounds	Phases	Units	Sulfate Concentrations (M)				
			0	1.64E-04	3.28E-04	6.56E-04	1.31E-03
H ₂ S	Gas	ppm	1.4	3.2	49.5	349	1106
	Gas	M	5.5E-08	1.2E-07	1.9E-06	1.4E-05	4.3E-05
	H ₂ S_ion_r	M	2.1E-07	4.6E-07	7.3E-07	5.1E-05	1.6E-04
	H ₂ S_r	M	1.4E-07	3.1E-07	4.9E-06	3.5E-05	1.1E-04
MT	Gas	ppm	9.0	9.0	9.3	10.8	12.6
	Gas	M	3.5E-07	3.5E-07	3.6E-07	4.2E-07	4.9E-07
	Liquid	M	2.5E-06	2.5E-06	2.6E-06	3.0E-06	3.5E-06
	Solid	M	7.1E-05	7.1E-05	7.4E-05	8.6E-05	1.0E-04
DMS	Gas	ppm	5.2	5.2	5.5	7.1	9.0
	Gas	M	2.0E-07	2.0E-07	2.2E-07	2.8E-07	3.5E-07
	Liquid	M	2.6E-06	2.6E-06	2.8E-06	3.6E-06	4.6E-06
	Solid	M	1.5E-04	1.5E-04	1.6E-04	2.1E-04	2.7E-04
DMDS	Gas	ppm	2.1	2.1	2.2	2.4	2.7
	Gas	M	8.2E-08	8.2E-08	8.4E-08	9.4E-08	1.1E-07
	Liquid	M	1.8E-06	1.8E-06	1.9E-06	2.1E-06	2.4E-06
	Solid	M	2.3E-04	2.3E-04	2.4E-04	2.6E-04	3.0E-04
NH ₃	Gas	ppm	8.8	8.8	8.8	8.8	8.8
	Gas	M	3.4E-07	3.4E-07	3.4E-07	3.4E-07	3.4E-07
	NH ₄ ⁺ _r	M	3.1E-02	3.1E-02	3.1E-02	3.1E-02	3.1E-02
	NH ₃ _r	M	5.8E-04	5.8E-04	5.8E-04	5.8E-04	5.8E-04

HAc	Gas	ppm	3.0E-03	3.0E-03	3.0E-03	3.0E-03	3.0E-03
	Gas	M	7.4E-09	7.4E-09	7.4E-09	7.4E-09	7.4E-09
	Ac_r	M	4.8E-02	4.8E-02	4.8E-02	4.8E-02	4.8E-02
	HAc	M	1.7E-04	1.7E-04	1.7E-04	1.7E-04	1.7E-04
HPro	Gas	ppm	4.0E-04	4.0E-04	4.0E-04	4.0E-04	4.0E-04
	Gas	M	1.7E-09	1.7E-09	1.7E-09	1.7E-09	1.7E-09
	Pro_r	M	1.8E-02	1.8E-02	1.8E-02	1.8E-02	1.8E-02
	HPro_r	M	8.2E-05	8.2E-05	8.2E-05	8.2E-05	8.2E-05
HBu	Gas	ppm	2.1E-04	2.1E-04	2.1E-04	2.1E-04	2.1E-04
	Gas	M	1.3E-09	1.3E-09	1.3E-09	1.3E-09	1.3E-09
	Bu_r	M	1.5E-02	1.5E-02	1.5E-02	1.5E-02	1.5E-02
	HBu_r	M	6.2E-05	6.2E-05	6.2E-05	6.2E-05	6.2E-05
HVa	Gas	ppm	9.7E-05	9.7E-05	9.7E-05	9.7E-05	9.7E-05
	Gas	M	7.8E-10	7.8E-10	7.8E-10	7.8E-10	7.8E-10
	Va_r	M	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02
	HVa_r	M	4.5E-05	4.5E-05	4.5E-05	4.5E-05	4.5E-05

Figure 5.6: Gas phase concentration vs sulfate concentration

Referring to Table 5.13 and Figure 5.6, as the sulfate concentration in the feed sludge varied from 0 to 126 mg/l (i.e. 0 to 0.00131 M), the corresponding H₂S concentrations in the gas phase ranged from 1.4 to 1100 ppm and in the liquid phase from 1.4E-07 to 1.1E-04 M. This indicates that the sulfate concentration had a strong impact on the formation of H₂S in anaerobic digesters. The concentrations of MT and DMS also significantly increased with the increase of sulfate concentrations in the feed sludge, because the increased formation of H₂S provided more sulfides for the methylation reactions to form MT and DMS. The concentration of DMDS was slightly increased with the increase of sulfate concentration. The changes of sulfate concentrations had very little influence on the formation of VFA and ammonia. There was almost no effect of sulfate concentration on gas flow and pH values in the reactor.

5.6 Conclusion

In this chapter, the effect of different digestion parameters on the emission of the odourous compounds in anaerobic digesters was analyzed. These parameters included temperature, process loading parameters (HRT and VOL) and the characteristics of feed sludge (heavy metals and sulfate content). In general, all these parameters significantly impacted the emission of odourous compounds in anaerobic digestion. Under thermophilic conditions, the emission of all odourous compounds increased, especially the emission of H_2S and NH_3 , which further proved that odour emissions under thermophilic conditions were more significant than that under mesophilic conditions. At an HRT of 3 days, the VFA were predicted to accumulate in the reactor, and therefore a large amount of VFA emissions were predicted. The pH values in the reactor dramatically dropped to 5.3, which inhibited the formation of CH_4 . Generally, the longer the HRT values, the more significant the odour emission. With the increase of VOL, the emission of odourous compounds from anaerobic digesters increased. The heavy metal and sulfate content in the feed sludge directly affect the formation of H_2S under anaerobic conditions; hence, they had a significant impact on the formation of sulfur-containing odourous compounds. For VFA and NH_3 , the effects of heavy metal and sulfate content were very slight. The emission of odourous compounds from anaerobic digesters was a combined effect of all these parameters.

Chapter 6: Conclusion and Recommendation

6.1 Conclusion

The odour emissions from wastewater and biosolids treatment facilities have increasingly become an environmental concern in recent years. To control and prevent their release requires an understanding of the process involved. An odour model was developed as a tool to identify the mechanisms by which odour are forms and then released into the atmosphere; and also to predicted the concentrations of odourous compounds emitted from anaerobic digesters. As to achieve these objectives, the following main areas have been addressed in the odour model:

- Defined the selected odorous compounds
- Specified the pathways for the formations of odourous compounds
- Identified the kinetic rates and kinetic coefficients
- Evaluated the three main physico-chemical reactions

Four ubiquitous sulfur-containing odourous compounds (H_2S , MT, DMS and DMDS), as the most prevalent odourous compounds, were selected as the subjects in this study together with VFA (HV_a, HBu, HPro and H_v) and NH_3 .

The formation of VFA and NH_3 are generally from the fermentation processes, which have been addressed in some anaerobic models (such as ADM1). However, information on the formation of sulfur-containing odourous compounds is relatively limited, especially for VOSC. In the odour model, six biochemical processes was specified for the

formation of sulfur-containing odourous compounds: degradation of sulfur-containing amino acids, sulfate reduction, methylation reactions, MT oxidation to DMDS, degradation of VOSC and sulfide precipitation.

For each process, the kinetic rate and kinetic coefficients were evaluated. For the formation processes of VFA and NH_3 , the kinetic rate equations and kinetic coefficients were already incorporated in ADM1. For the formation of sulfur-containing odourous compounds, sulfate reduction had well-defined kinetic data; however, the kinetic data obtained for methylation reactions and VOSC degradation were generally from anoxic environments, such as sediment and estuarine and no data for MT oxidation to DMDS was found in this study. Therefore, there is considerable uncertainty in the developed odour model. This uncertainty may cause some error in the model prediction.

The three physico-chemical processes addressed in this study are very important for modelling the odour emission. Since both acid-base dissociation and liquid-solid partitioning substantially affect the molecular form of odourous compounds in the liquid phase and only the molecular form of odourous compounds in the liquid phase can be released into the gas phase, effectively reflecting the three physico-chemical processes determined the accuracy of the prediction of the model. VOSC are very weak acids, therefore, the acid-base dissociation was not included for VOSC. Because of the complexity of the liquid-solid processes and the limited information in this area, only the partitioning of VOSC was addressed in this study. Three dynamic rate equations are employed to address the three physico-chemical processes.

From the general sensitivity analysis, k_{dis} , Y_{ac} and Y_{aa} are identified as the most significant parameters for all odourous compounds; and K_{P_DMS} , K_{P_MT} , K_{P_DMDS} , k_{m_DMS} and K_{S_DMS} are identified as the most significant parameters for all sulfur-containing odourous compound. From the individual sensitivity analysis, five most significant parameters for each individual odourous compound are identified.

6.2 Recommendation

The odour model developed in this study summarized the most important mechanisms for the formation of odourous compounds under anaerobic conditions. Therefore, it could be used as a tool to predict the concentration of odourous compound emitted from anaerobic digesters. However, the odour model coincidentally brought up some uncertain factors in its development. The main recommendations identified in this study were generally related to future laboratory work.

The kinetic rate equations and kinetic coefficients are considered as the core of mathematic models. However, the kinetic coefficients used to describe the formation processes of sulfur-containing odourous compounds in this study, such as methylation reactions and VOSC degradation, were generally poor. Therefore, it is important to obtain some kinetic data from laboratory experiments in this aspect. In Chapter four of model analysis, the most significant parameters were identified, which can be used to direct the laboratory job. The forms of the kinetic expressions and the selection of mechanisms also need to be evaluated experimentally.

Calibrating and validating the odour model is another recommendation for the future job, which also need the experimental data. After calibrating and validating, the odour model will be more useful and effective in prediction.

Reference

Alphenarr, P.A., Visser, A. and Lettinga, G. (1993) “ The Effect of Liquid Upward Velocity and Hydraulic Retention Time on Granulation in UASB Reactors Treating Waste Water with a High Sulfate Content” *Biores. Technol.*, 43 (3), 249-258

Bache, R. and Pfennig N (1981) “Selective isolation of *Acetobacterium Woodii* on methoxylated aromatic acids and determination of growth yields” *Arch Microbiol* 130, 225-261

Bak, F., Finster, F. and Rothfuss, F. (1992) “Formation of Dimethyl Sulfide and Methanethiol from Methoxylated Aromatic Compounds and Inorganic Sulfide by Newly Isolated Anaerobic Bacteria” *Arch. Microbiol.* 157, 529-534

Banwart, W.L. and Bremmer, J.M. (1975) “Identification of sulfur gases evolved from animal manures slurry” *J. Environ. Qual.* 4 (3): 363 – 366

Batstone, D.J., Keller, J., Angelidaki, I., Kalyuzhnyi, S.V., Pavlostathis, S.G., Rozzi, A., Sanders, W.T.M., Siegrist, H. and Vavilin, V.A. (2002) *Anaerobic Digestion Model No.1* IWA Publishing

Beard, W.E. and Guenzi, W.D. (1983) “Volatile sulfur compounds from a-redox-controlled-manure slurry” *J. Environ. Qual.* 12 (1): 113-116

Bonnin, C., Laborie A. and Paillard H. (1990) “Odour Nuisances Created by Sludge Treatment: Problems and Solutions” *Water Science and Technology* 22, 65-74

Boon, A.G. (1995) “Speticity in Sewer: Causes, Consequences and Containment” *Water Science and Technology* 31(7), 237-253

- Cheremisinoff, P.N. (1998) *Industrial Odour Control* Butterworth-Heinemann Ltd. Oxford
- Clanton, C.J. and Schmidt, D.R. (2000) "Sulfur Compounds in Gases Emitted from Stored Manure" *American Society of Agricultural Engineers* 43(5), 1229-1239
- Coulson, J.M. and Richardson, J.F. (1993) *Chemical Engineering Volume 1: Fluid Flow, Heat Transfer and Mass Transfer* 4th Edition, Pergamon, Oxford
- Dignac, M.F., Urbain, V., Rybacki, D., Bruchet, A., Snidaro, D. and Scribe, P. (1999) "Chemical Description of Extracellular Polymers: Implication on Activated Sludge Floc. Structure" *Water Science and Technology* 38, 39-46
- Dobbs, R.A., Wang, L.P. and Govind, R. (1989) "Sorption of Toxic Organic Compounds on Wastewater Solids: Correlation with Fundamental Properties" *Environ. Sci. Technol.* 23, 1092-1097
- Eastman, J.A. and Ferguson, J.F. (1981) "Solubilization of particulate organic carbon during the acid phase of anaerobic digestion" *J. Wat. Poll. Cont. Fed.* 53, 352-366
- EPA (1984) U.S. Environmental Protection Agency: *Environmental Regulations and Technology, Use and Disposal of Municipal Wastewater Sludge* EPA 625/10-84-003, September 1984
- Fatoki, O.S. (1997) "Biomethylation in the Natural Environmental: A Review" *South African Journal Science* 93, 366-370
- Ferchichi, M., Hemme, D., Nardi, M. and Pamboukian, N. (1985) "Production of Methanethiol from Methionine by *Brevibacterium Linens*" CNRZ 918, *J. Gen. Microbiol.* 131, 175

Finster, K., Tanimoto, Y. and Bak, F. (1992) “ Fermentation of Methanethiol and dimethylsulfide by a newly isolated methanogenic bacterium” *Archives of Microbiology* 157, 425-430

Gostelow, P., Parsons, S.A. and Stuetz, R.M. (2001) “Review Paper: Odour Measurements for Sewage Treatment Works” *Water Resource* 35 (3), 579-597

Graday, C.G.L.Jr., Daigger, G.T. and Lim, H.C. (1999) *Biological Wastewater Treatment*, Marcel Dekker, INC. New York

Griffith, P and Alvarez, M. (2002) “The LACSD Experience with Thermophilic Digestion: Start-up and operation of a Full-Scale Reactor from Mesophilic Conditions” WEFTEC

Gujer, N. and Zehnder, A.J.B. (1983) “Conversion Processes in Anaerobic Digestion” *Water Science and Technology* 15, 127-167

Gunstone, F. (1996) *Fatty acids and Lipid Chemistry* Blackie Academic and Professional, London

Hammer, M.J. and Hammer, Jr. M.J. (1996) *Water and Wastewater Technology* 3rd Ed. Englewood Cliffs, N.J.: Prince-Hall, Inc

Harkness, N. (1980) “Chemistry of septicity” *Effluent Water Treatment* J.20, 16-23

Huang, R.T. (1993) *The Practical Handbook of Compost Engineering* Lewis Publishers

WEF (1995) Water Environmental Federation and American Society of Civil Engineers *Odour Control in Wasterwater Treatment Plant WEF Manual of Practice No.22 and ASCE Manuals and Reports on Engineering Prattice No. 82*. Alexandria, Va: Water Environment Federation and American Society of Civil Engineers.

- Higgins, M.J., Murthy, S.N., Yarosz, D.P., Novak, J.T. and Toffey, W.E. (2002) "Effects of Chemical Addition of Production of Volatile Sulfur Compounds and Odour from Anaerobically Digested Biosolids" WEFTEC
- Higgins, M.J. and Novak, J.T. (1997b) "Characterization of Exocellular Protein and its Role in Bioflocculation" *J. Environ. Engr. ASCE*, 123, 479-485
- Houten, V.R.T., Elferink, O.S.J.W.H., Hamel, V.S.E., Pol H.L.W. and Lettinga, G. (1995) "Sulfate Reduction by Aggregates of Sulfate-Reducing Bacteria and Homo-Acetogenic Bacteria in Lab-Scale Gas-Lift Reactor" *Biotechnol. Bioeng.* 54, 73-79
- Islam, A.K.M.N., Honaki, K and Matsuo, T (1998) "Fate of Dissolved Odourous Compounds in Sewage Treatment Plants" *Water Science and Technology* 38(3), 337-344
- Jelus, M., Cheng, K. and Dobbs, R.A. (1986) "Partitioning of Toxic Organic Compounds on Municipal Wastewater Treatment Plant Solids" EPA/600/D-86/37, July 1986; NTIS PB68-218427
- Kadota, H. and Ishida, Y. (1972) "Production of Volatile Sulfur Compounds by Microorganisms" *Annu. Rev. Microbiol.* 26, 127-137
- Kalyuzhnyi, S.V. and Fedorovich, V.V. (1998) Mathematical Modelling of Competition Between Sulfate Reduction and Methanogenesis in Anaerobic Reactors" *Bioresource Technology* 65, 227-242
- Kalyuzhnyi, S.V., Fedorovich, V.V., Lens, P., Pol, L.H. and Lettinga, G. (1998) "Mathematical modelling as a tool to study population dynamics between sulfate reducing and methanogenic bacteria" *Biodegradation* 9, 187-199

- Kappler, O., Janssen P.H., Kreft, J.U. and Schink, B. (1997) "Effects of alternative methyl group acceptors on the growth energetics of the O-demethylating anaerobic *Holophaga foetida*" *Microbiology* 143, 1105-1114
- Kayhanian, M. (1995) "Biodegradability of the Organic Fraction of Municipal Solid Waste in a high-solids Anaerobic Digester" *Waste Management and Research* 13,123-136
- Kiene, R.P., Oremland, R.S., Catena, A., Miller, L.G. and Capone, D.G. (1986) "Metabolism of Reduced Methylated Sulfur Compounds in Anaerobic Sediments and by a Pure Culture of an Estuarine Methanogen" *Applied and Environmental Microbiology* Nov. 1986, 1037-1045
- Kirk, T.K. and Farrell, R.L. (1987) "Enzymatic 'combustion': the microbial degradation of lignin" *Annu. Rev. Microbiol.* 41,465-505.
- Kreft, J.U. and Schink, B. (1997) "Specificity of O-demethylation in extracts of homoacetogenic *Holophaga foetida* and demethylation kinetics by a coupled photometric assay" *Arch Microbiol* 167, 363-368
- Lens, P.N., Poorter, M.P., Cronenberg, C.C. and Verstraete, W.H. (1995) "Sulfate Reducing and Methane Producing Bacteria in Aerobic Wastewater Treatment Systems" *Water Resource* 29 (3), 871-880
- Levenspiel, O. (1980) "the Monod Equation: a revisit and a generalization to product inhibition situations" *Biotechnol. Bioeng.* 22, 1671-1687
- Lide, D. (2001) *CRC Handbook of Chemistry and Physics* 82nd edition CRC Press Boca Raton, FL.

Lomans, B.P., Drift, C.V.D., Pol, A. and Camp, H.J.M. (2002) "Microbial Cycling of Volatile Organic Sulfur Compounds" *Water Science and Technology* 45 (10), 55-60

Lomans, B.P., Leijdekkers, P., Wesselink, J., Bakkes, P., Pol, A., Driefft, C. and Camp, H.J.M.O. (2001) "Obligate Sulfide-Dependent Degradation of Methoxylated Aromatic Compounds and Formation of Methanethiol and Dimethyl Sulfide by a Freshwater Sediment Isolate, *Parasporobacterium paucivorans* gen.nov., sp.nov." *Applied and Environmental Microbiology* 2001, 4017-4023

Lomans, B.P., Smolders, A.J.P., Intven, L.M., Pol, A., Camp, H.J.M.O. and Drift, C. (1997) "Formation of dimethyl sulfide and methanethiol in Anoxic fresh sediments" *Applied and Environmental Microbiology* Dec. 1997, 4741-4747

Malina, J.F. (1992) "Anaerobic Sludge Digestion" *In Design of Anaerobic Processes for the Treatment of Industrial and Municipal Wastes* Technomic Publishing, Pennsylvania

Marshall, K.C. (1990) *Advances in Microbial Ecology* Volume 11 Plenum Press New York

Mosey, F.E. and Hughes, D.A. (1975) "The toxicity of heavy metal ions to anaerobic digestion" *Water Pollution Control* 74, 18-39

Mulder, A. (1984) "the effect of High Sulfate Concentrations on Methane Fermentation of Waste Water" *Progr. Ind. Microbial* 20,133-143

Nakasaki, K., Kuratomi, H., Wakizaka, H., Hiyama, R. and Akakura, N. (1998) "Quantitative Analysis of Ammonia and Odourous Sulfur Compounds Evolved during Thermophilic Composting" *Waste Management & Research* 16(6), 514-524

- Ni, S.S. and Boone, D.R. (1999) "Catabolism of Dimethyl sulfide and methane thiol by methylotrophic methanogens" *FEMS Microbiol. Ecol.* 29, 341-350
- Oho, T., Satio, T. and Koga, T. (2000) "Formation of Methyl Mercaptan from L-Methionine by *porphyromonas gingivalis*" *Infect. Immun* 68, 6912-6916
- Othmer, D.F. and Thakar, M.S. (1953) "Correlating diffusion coefficients in liquids" *Ind. Eng. Chem.* 45, 589-593
- Parkin, G.F. and Owen, W.F. (1986) "Fundamentals of Anaerobic Digestion of Wastewater Sludges" *Journal of Environmental Engineering* 112, 867-920
- Pauss, A., Andre, G., Perrier, M. and Guiot, S.R. (1990) "Liquid to Gas Mass Transfer in Anaerobic processes: Inevitable Transfer Limitations of Methane and Hydrogen in the Biomethanation Process" *Biotec. Bioeng.* 56, 1636-1644
- Postage, J.R. (1959) "Sulfate reduction bacteria" *A. Rev. Microbiol.* 13, 505-520
- Postage, J.R. (1984) *The Sulfate-reducing Bacteria* Cambridge University Press
- Ramsay, I.R. (1997) *Modelling and Control of High-Rate Anaerobic Wastewater Treatment Systems*, PhD thesis, University of Queensland, Brisbane
- Reichert, P. (1998) *AQUASIM 2.0-User Manual* Swiss Federal Institute for Environmental Science and Technology
- Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M. (1993) *Environmental Organic Chemistry* John Wiley & Sons, Inc. New York
- Speece, R.E. (1996) *Anaerobic Biotechnology: For Industrial Wastewaters* Archace Press Tennessee

- Stumm, W. and Morgan, J.J. (1996) *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters* 3rd Edition McGraw Hill, New York
- Taylor, B.F. and Kiene, R.P. (1989) "Microbial Metabolism Dimethyl Sulfide" *Biogenic Sulfur in the Environment* ACS, Washington DC, 202-217
- Taylor, B.F. "Bacterial Transformations of Organic Sulfur compounds in Marine Environments" *Biogenic Sulfur in the Environment* ACS, Washington DC, 745-773
- Tchobanoglous, G. and Burton, F.L. (1991) *Wastewater Engineering: Treatment, Disposal and Reuse* 3rd McGraw-Hill, Inc. New York
- Tomita, B., Inoue, H., Chaya, K., Nakamura, N., Ueno, K., Watanabe, K. and Ose, Y (1987) "Identification of Dimethyl Disulfide-Forming Bacteria Isolated from Activated Sludge" *Appl. Environ. Microbiol* 53, 1541
- Van, S. P.J. (1994) *The Nutritional Ecology of the Ruminant* 2nd edition Cornell University Press Ithaca, NY
- Vincent, A. J. and Hobson, J. (1998) "Odour Control" *CIWEN Monographs on Best Practice No. 2* Terence Dalton Publishers, London
- Vincent, A.J. (2001) "Sources of Odours in Wastewater Treatment" *Odours IN Wastewater Treatment: Measurement, Modelling and Control* IWA Publishing
- Visser, A (1995) "The Anaerobic Treatment of Sulfate Containing Wastewater" Ph.D thesis Wageningen Agriculture University, the Netherlands
- Widdel, F (1988) "Microbiology and Ecology of Sulfate and Sulfur-Reducing Bacteria" *Biology of Anaerobic Microorganisms* Wiley, New York

Whitman, W.G. (1923) "The Two-Film Theory of Absorption" *Chem. Met. Eng.* 29, 147

Xue, S.K., Chen, S. and Hermanson, R.E. (1998) "Measure Ammonia and Hydrogen Sulfide Emitted from Manure Storage Facilities" *American Society of Agriculture Engineers* 41(4), 1125-1130

Appendix A: Biochemical Kinetic Matrix for ADM1

Table A.1: Biochemical kinetic rate equations (r_i) for ADM1

Process (j)		Rate (kg COD m ⁻³ d ⁻¹)
1	Disintegration	$k_{dis}X_c$
2	Hydrolysis carbohydrate	$k_{hydr}X_{ch}$
3	Hydrolysis proteins	$k_{hydr}X_{pr}$
4	Hydrolysis Lipids	$k_{hydr}X_{li}$
5	Uptake of sugar	$k_{m,su} \frac{S_{su}}{K_s + S_{su}} X_{su} I_1$
6	Uptake of AA	$k_{m,aa} \frac{S_{aa}}{K_s + S_{aa}} X_{aa} I_1$
7	Uptake of LCFA	$k_{m,fa} \frac{S_{fa}}{K_s + S_{fa}} X_{fa} I_2$
8	Uptake of Valerate	$k_{m,C4} \frac{S_{va}}{K_s + S_{va}} X_{C4} \frac{1}{1 + S_{bu}/S_{va}} I_2$
9	Uptake of Butyrate	$k_{m,C4} \frac{S_{bu}}{K_s + S_{bu}} X_{C4} \frac{1}{1 + S_{va}/S_{bu}} I_2$
10	Uptake of Propionate	$k_{m,pro} \frac{S_{pro}}{K_s + S_{pro}} X_{pro} I_2$
11	Uptake of Acetate	$k_{m,ac} \frac{S_{ac}}{K_s + S_{ac}} X_{ac} I_3$
12	Uptake of Hydrogen	$k_{m,h2} \frac{S_{h2}}{K_s + S_{h2}} X_{h2} I_1$
13	Decay of X_{su}	$k_{dec}X_{su}$
14	Decay of X_{aa}	$k_{dec}X_{aa}$
15	Decay of X_{fa}	$k_{dec}X_{fa}$
16	Decay of X_{C4}	$k_{dec}X_{C4}$
17	Decay of X_{pro}	$k_{dec}X_{pro}$
18	Decay of X_{ac}	$k_{dec}X_{ac}$
19	Decay of X_{h2}	$k_{dec}X_{h2}$
		Inhibition Factors: $I_1 = I_{pH} I_{IN,lim}$ $I_2 = I_{pH} I_{IN,lim} I_{h2}$ $I_3 = I_{pH} I_{IN,lim} I_{Nh3,Xac}$

Table A.2: Biochemical rate coefficients ($V_{i,j}$) for soluble components

Table A.2: Biochemical rate coefficients ($V_{i,j}$) for soluble components													
Component $\rightarrow$ i	1	2	3	4	5	6	7	8	9	10	11	12	
j Process $\downarrow$	S_{su}	S_{aa}	S_{fa}	S_{va}	S_{bu}	S_{pro}	S_{ac}	S_{h2}	S_{ch4}	S_{IC}	S_{IN}	S_I	
1 Disintegration												$f_{SI,Xc}$	
2 Hydrolysis carbohydrate	1												
3 Hydrolysis proteins		1											
4 Hydrolysis lipids	$1-f_{fa,li}$		$f_{fa,li}$										
5 Uptake sugar	-1				$(1-Y_{su}) f_{bu,su}$	$(1-Y_{su}) f_{pro,su}$	$(1-Y_{su}) f_{ac,su}$	$(1-Y_{su}) f_{h2,su}$		$-\Sigma C_i V_{i,5}$ $I=1-9, 11-24$	$-(Y_{su}) N_{bac}$		
6 Uptake AA		-1		$(1-Y_{aa}) f_{va,aa}$	$(1-Y_{aa}) f_{bu,aa}$	$(1-Y_{aa}) f_{pro,aa}$	$(1-Y_{aa}) f_{ac,aa}$	$(1-Y_{aa}) f_{h2,aa}$		$-\Sigma C_i V_{i,6}$ $I=1-9, 11-24$	$N_{aa}-(Y_{aa}) N_{bac}$		
7 Uptake LCFA			-1				$(1-Y_{fa}) 0.7$	$(1-Y_{fa}) 0.3$			$-(Y_{fa}) N_{bac}$		
8 Uptake Va.				-1		$(1-Y_{c4}) 0.54$	$(1-Y_{c4}) 0.31$	$(1-Y_{c4}) 0.15$			$-(Y_{c4}) N_{bac}$		
9 Uptake Bu.					-1		$(1-Y_{c4}) 0.8$	$(1-Y_{c4}) 0.2$			$-(Y_{c4}) N_{bac}$		
10 Uptake propionate						-1	$(1-Y_{pro}) 0.57$	$(1-Y_{pro}) 0.43$		$-\Sigma C_i V_{i,10}$ $I=1-9, 11-24$	$-(Y_{pro}) N_{bac}$		
11 Uptake acetate							-1		$1-Y_{ac}$	$-\Sigma C_i V_{i,11}$ $I=1-9, 11-24$	$-(Y_{ac}) N_{bac}$		
12 Uptake hydrogen								-1	$1-Y_{h2}$	$-\Sigma C_i V_{i,12}$ $I=1-9, 11-24$	$-(Y_{h2}) N_{bac}$		
13 Decay of X_{su}													
14 Decay of X_{aa}													
15 Decay of X_{fa}													
16 Decay of X_{c4}													
17 Decay of X_{pro}													
18 Decay of X_{ac}													
19 Decay of X_{h2}													
		Monosaccharides (kgCOD/m ³)	Amino Acids (kgCOD/m ³)	LCFA (kgCOD/m ³)	Total Valerate (kg COD/m ³)	Total Butyrate (kgCOD/m ³)	Total Propionate (kgCOD/m ³)	Total acetate (kgCOD/m ³)	Hydrogen gas (kgCOD/m ³)	Methane Gas (kgCOD/m ³)	Inorganic carbon (kgCOD/m ³)	Inorganic nitrogen (kgCOD/m ³)	Soluble Inerts (kgCOD/m ³)

Table A.3: Biochemical rate coefficients and kinetic rate equations for particulate components

Component $\rightarrow$ i	1	2	3	4	5	6	7	8	9	10	11	12
j Process $\downarrow$	X_c	X_{ch}	X_{pr}	X_{li}	X_{su}	X_{aa}	X_{fa}	X_{c4}	X_{pro}	X_{ac}	X_{h2}	X_l
1 Disintegration	-1	f_{ch}, X_c	f_{pr}, X_c	f_{li}, X_c								f_{Xl}, X_c
2 Hydrolysis carbohydrate		-1										
3 Hydrolysis proteins			-1									
4 Hydrolysis Lipids				-1								
5 Uptake sugar					Y_{su}							
6 Uptake AA						Y_{aa}						
7 Uptake LCFA							Y_{fa}					
8 Uptake Valerate								Y_{c4}				
9 Uptake Butyrate								Y_{c4}				
10 Uptake pro.									Y_{pro}			
11 Uptake acetate										Y_{ac}		
12 Uptake hydraogen											Y_{h2}	
13 Decay of X_{su}	1				-1							
14 Decay of X_{aa}	1					-1						
15 Decay of X_{fa}	1						-1					
16 Decay of X_{c4}	1							-1				
17 Decay of X_{pro}	1								-1			
18 Decay of X_{ac}	1									-1		
19 Decay of X_{h2}	1										-1	
	Composite (kgCOD/m ³)	Proteins (kgCOD/m ³)	Lipids (kgCOD/m ³)	Total Valerate (kg COD/m ³)	Sugar Degraders (kgCOD/m ³)	AA Degraders (kgCOD/m ³)	LCFA de graders (kgCOD/m ³)	Valerate & Butyrate Degraders (kgCOD/m ³)	Propionate Degraders (kgCOD/m ³)	Acetate Degraders (kgCOD/m ³)	Hydrogen Degraders (kgCOD/m ³)	Particulate Inerts (kgCOD/m ³)

Appendix B: Estimating Stoichiometric Yields from Degradation of AA

B.1: Calculate the MW of AA in COD

Assumption:

1. Sulfur in cysteine ($C_3H_6O_2NS$) are all degraded into H_2S
2. Sulfur in Methionine ($C_5H_{11}O_2NS$) are degraded into MT, DMS and DMDS, and MT: DMS: DMDS = 0.56:0.34:0.1
3. The end products of degradation of AA, which can contribute to COD in AA, are HAc, HPro, HBU, HVA and H_2 .

Table B.1: Products from amino acids based on Stickland reaction (Ramsay)

Amino Acid	Formula	HAc	Hpr	Hbu	Hva	IN	IC	H_2S	MT	DMS	DMDS	Other	H_2	ATP	Beef ¹	Casein ¹
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1.Arginine	$C_6H_{14}O_2N_4$	0.5	0.5	0	0.5	4	1	0	0	0	0	0	-1	1	5.4	2.8
2.Histidine	$C_6H_9O_2N_3$	1	0	0.5	0	3	1	0	0	0	0	1	0	2	2.4	2.6
3.Lysine	$C_6H_{14}O_2N_2$	1	0	1	0	2	0	0	0	0	0	0	0	1	7.2	6.4
4.Tyrosine	$C_9H_{11}O_3N$	1	0	0	0	1	1	0	0	0	0	0.882	1	1	2.7	4.3
5.Tryptophan	$C_{11}H_{12}O_3N$	0	0	0	0	1	1	0	0	0	0	1.471	2	1	0.9	0.8
6.Phenylalanine	$C_9H_{11}O_2N$	0	0	0	0	1	1	0	0	0	0	1.176	2	1	3.6	4.0
7.Cysteine	$C_3H_6O_2NS$	1	0	0	0	1	1	1	0	0	0	0	0.5	1	1.5	0.1
8.Methionine	$C_5H_{11}O_2NS$	0	1	0	0	1	1	0	0.56	0.34	0.1	0	1	1	2.0	2.5
9.Threonine	$C_4H_9O_3N$	1	0	0.5	0	1	0	0	0	0	0	0	-1	1	4.8	3.9
10.Serine	$C_3H_7O_3N$	1	0	0	0	1	1	0	0	0	0	0	1	1	5.7	7.6
11.Leucine	$C_6H_{13}O_2N$	0	0	0	1	1	1	0	0	0	0	0	2	1	14.4	14.2
12.Valine	$C_5H_{11}O_2N$	0	0	1	0	1	1	0	0	0	0	0	2	1	6.5	6.7
13.Glutamine	$C_5H_9O_4N$	1	0	0.5	0	1	1	0	0	0	0	0	0	2	13.5	19.2
14.Aspartate	$C_4H_7O_4N$	1	0	0	0	1	2	0	0	0	0	0	2	2	8.8	6.4
15.Glycine	$C_2H_5O_2N$	1	0	0	0	1	0	0	0	0	0	0	-1	0	8.4	3.0
16.Alanine	$C_3H_7O_2N$	1	0	0	0	1	1	0	0	0	0	0	2	1	8.4	4.0
17.Proline	$C_5H_9O_2N$	0.5	0.5	0	0.5	1	0	0	0	0	0	0	-1	0	4.0	11.4
Total															100.2	99.9

Note: Basic units of mole production /mole amino acids. ¹. Units of mole % total amino acids

Base on Table B.1, the mole fraction of HAc, HPr, HBu, and H₂ in 1 mole amino acids can be calculated.

For example, the mole fraction of HAc in Beef flesh is the sum of column 3 times column 16 divided by 100, i.e.

$$\begin{aligned} \text{Mole fraction of HAc} = \\ (0.5*5.4+1*2.4+1*7.2+1*2.7+0*0.9+0*3.6+1*1.5+0*2.0+1*4.8+1*5.7+0*14.4+0*6.5+1*13.5+1*8.8+1*8.4+1*8.4+0.5*4.0)/100 \\ =0.68 \end{aligned}$$

The mole fraction of HPr, HBu, HVa, H₂, IN, H₂S, MT, DMS and DMDS can be calculated by the same method and the value are:

$$\begin{aligned} \text{HPr: } 0.07, \quad \text{HBu: } 0.24, \quad \text{HVa: } 0.19, \quad \text{H}_2: 0.74 \\ \text{IN: } 1.28; \quad \text{H}_2\text{S: } 0.015; \quad \text{MT: } 0.0112; \quad \text{DMS: } 0.0068; \quad \text{DMDS: } 0.002 \end{aligned}$$

Therefore, the following reaction can be obtained from degradation of AA:

Since only HAc, HPr, HBu, HVa and H₂ can contribute COD in amino acids, therefore,

$$\begin{aligned} \text{MW of AA in COD} = 0.681\text{molHAc/mole aa} * 64 \text{ gCOD/mol} + 0.07 \text{ mol HPr/mol aa} * 112 \text{ gCOD/mol} + 0.24 \text{ mol HBu/mol aa} \\ * 192 \text{ gCOD/mole} + 0.19 \text{ mole HVa/mol aa} * 218 \text{ gCOD/mole} + 0.74 \text{ mole H}_2\text{/mol aa} * 16 \text{ gCOD/mol} + 141.10 \\ \text{gCDO/molaa} \end{aligned}$$

According to the molecular weight of AA in COD, the stoichiometric yield ($f_{i,aa}$) can be calculated based on 1kg COD of AA.

For example,

$$f_{HAc,aa} = (0.68 \text{ mole HAc /mole aa} * 64 \text{ gCOD/mole HAc}) / (141 \text{ gCOD/mole aa}) = 43.58/141 = 0.31 \text{ (gCOD HAc/gCOD AA)}$$

$$f_{IN,aa} = (1.28 \text{ mole N/mole aa}) / (141 \text{ gCOD/mole aa}) = 0.009 \text{ (mol N/gCOD AA)}$$

$$f_{H_2S,aa} = (0.015 \text{ mole S/mole aa}) / (141 \text{ gCOD/mole aa}) = 1.1E-04 \text{ (mol S/g COD AA)}$$

$$f_{MT,aa} = (0.0112 \text{ mol MT/mole aa}) / (141 \text{ gCOD/mole aa}) = 7.9E-05 \text{ (mol MT/g COD AA)}$$

$$f_{DMS,aa} = (0.0068 \text{ DMS/mole aa}) / (141 \text{ gCOD/mole aa}) = 4.8E-05 \text{ (mole DMS /g COD)}$$

$$f_{DMDS,aa} = (0.002 \text{ DMDS/mole aa}) / (141 \text{ gCOD/mole aa}) = 1.4E-05 \text{ (mole DMS /g COD)}$$

Table B.2 summarized the calculation of MW in COD and stoichiometric Yield for odorous compounds from degradation of AA.

Table B.2: the MW of AA in COD and the stoichiometric yield ($f_{i,aa}$) of odorous compound in 1kgCOD AA in Beef flesh

	HAc	Hpr	Hbu	HVa	H2	IN	H2S	MT	DMS	DMDS	gCOD/mol AA
mol fraction in beef	0.68	0.07	0.24	0.19	0.74	1.28	0.015	0.0112	0.0068	0.002	
g COD in per mole products	64	112	160	218	16	0	0	0	0	0	141
COD in beef	43.58	7.50	38.48	39.73	11.80	0	0	0	0	0	
$f_{i,aa}$	0.31	0.05	0.27	0.28	0.08	0.009	1.1E-04	7.9E-05	4.8E-05	1.4E-05	

The same method was taken to calculate the MW of AA in COD and the stoichiometric yield of odorous compounds in Casein.

Table B.3: the MW of AA in COD and the stoichiometric yield of odorous compound in 1kgCOD AA in Casein

	HAc	Hpr	Hbu	HVa	H2	IN	H2S	MT	DMS	DMDS	gCOD/mol AA
mole fraction in Casein	0.65	0.10	0.26	0.21	0.66	1.20	0.001	0.014	0.0085	0.0025	
g COD in per mole products	64	112	160	218	16	0	0	0	0	0	
COD	41.3	10.8	41.5	44.3	10.5	0.0	0	0	0.0	0	148
$f_{i,aa}$	0.28	0.07	0.28	0.30	0.07	0.008	6.7E-06	9.4E-05	5.7E-05	1.7E-05	

Table B.4 summarized the stoichiometric yield calculated from beef flesh and casein and presented the calculated values with the values used in ADM1 and the odour model.

Table B.4: Comparing the stoichiometric yields of each odorous compounds in AA (based on COD):

	$f_{hac,aa}$	$f_{hpr,aa}$	$f_{hbu,aa}$	$f_{hva,aa}$	$f_{h2,aa}$	$f_{in,aa}$	$f_{h2s,aa}$	$f_{mt,aa}$	$f_{dms,aa}$
Beef flesh	0.31	0.05	0.27	0.28	0.08	0.009	1.1E-04	7.9E-05	4.8E-05
Casein	0.28	0.07	0.28	0.30	0.07	0.008	6.7E-06	9.4E-05	5.7E-05
ADM1	0.4	0.05	0.26	0.23	0.06				
Odour Model	0.4	0.05	0.26	0.23	0.06	0.007	1.1E-04	7.9E-05	4.8E-05

B.2: Calculate Sulfur Content in Biomass

Assumption:

1. All the sulfur in complex particulates (X_c) converted to sulfur in proteins
2. The sulfur content in biomass is the same as in X_c

The following calculations are based on the sulfur content in beef flesh:

From Table B.1:

Mole fraction of sulfur in 1 mole of AA = $(1.5+2.0)/100 = 0.035$

Therefore, sulfur content in per g COD AA = $0.035/141 = 2.5E-04$ mol S/gCOD AA

Since AA is the only product from protein hydrolysis, the sulfur content in proteins should be the same as in AA (i.e. $2.5E-04$ mol S/g COD Proteins).

Because all sulfur in complex particulates (X_c) converted to proteins during its disintegration and only 30% of X_c was disintegrated to proteins. Therefore, sulfur in X_c = $(0.3 \text{ g COD proteins/gCOD } X_c) * [(2.5E-04) \text{ mole S/gCOD proteins}] = 7.5E-05 \text{ mol S/gCOD } X_c$

Sulfur content in biomass is assumed to be the same as in X_c , therefore,

Sulfur in biomass = sulfur in X_c = $7.5E-05$ mol S/ g COD bio

The same method calculated sulfur in biomass from casein = $0.026/148*0.3 = 5.3E-05$ mol S/g COD bio.

In this study, the sulfur content calculated from beef flesh was used to model the emission of odourous compounds from anaerobic digesters.

The Monod uptake rate for amino acid can be expressed as:

$$r_{aa} = k_m * S_{aa} / (K_S + S_{aa}) * I_{pH} I_{IN,lim} (ADM1)$$

The correspondingly generate rate for odourous compounds can be expressed as:

$$r_{i, aa} = Y_{i,aa} * r_{aa}$$

Where, $r_{i,aa}$ = the yield rate for each odourous compound in degradation of amino acids

$Y_{i,aa}$ = the stoichiometric yield for odourous compounds of degradation of amino acids.

In chapter three, it derived the formula to calculate $Y_{i,aa}$ for each odourous compounds from the degradation of AA, which can be expressed as:

$$Y_{VFA, aa} = f_{VFA,aa} (1 - Y_{aa})$$

$$Y_{IN,aa} = f_{IN,aa} - N_{bio} * Y_{aa}$$

$$Y_{H2S,aa} = f_{H2S,aa} (1 - Y_{aa}) - S_{bio} * Y_{aa}$$

Table B.5 calculated the stoichiometric compounds for each odourous compound from degradation of AA.

Appendix C:

The General Sensitivity Analysis for all Odourous Compounds

As discussed in chapter four, the general sensitivity analysis in this study was performed by using the relative-absolute sensitivity function (Eq. 4.11b) and the relative-relative sensitivity function (Eq. 4.11d).

In the odour model, more than 100 parameters are introduced. Because of the large number of parameters and the different pathways for the formation of odourous compounds, it is difficult to identify the common significant parameters for all odourous compounds. The strategy used in the general sensitivity analysis is: first, the sensitivity function in the AQUASIM was run for each odourous compound for 100 parameters; second, the responses of odourous compounds to the 100 parameter was ranked and by comparing the ranks, 10 common significant parameters for all odourous compounds were selected and presented in Table C.1; third, the relative-relative sensitivity function (4.11d') was performed and the magnitude of $\delta y/y$ can be used to compare the effect of different parameters on all odourous compounds. The values of $\delta y/y$ of parameters were presented in Table C.2.

Table C.1: The rank of some significant parameters from the results of AQUASIM sensitivity analysis

Parameters Rank	k_{dis}	Y_{ac}	Y_{aa}	$k_{m,aa}$	$k_{m,ac}$	k_{dec_xac}	$k_{m_MAC_DMS}$	$k_{m_MAC_MT}$	k_{m_DMS}	K_{S_DMS}
H ₂ S	1 ^a	2	16	39	19	11	13	10	3	6
MT	2	9	6	41	27	22	19	4	9	10
DMS	1	5	13	46	19	8	6	14	3	4
DMDS	1	3	9	42	26	11	19	8	12	13
HAc	7	2	5	36	1	4	45	36	32	33
HPro	14	9	11	45	16	5	36	44	48	50
HBu	11	6	7	38	13	12	35	44	46	38
HVa	11	6	7	38	13	12	35	44	46	38
NH ₃	8	1	4	25	15	8	43	49	51	52

Note: ^a . the number represented the rank of the parameter out of 100 parameters.

Referring to Table C.1, it can be found that the most significant parameters for each individual odorous compound. The rank for the same parameter of different compounds can be greatly different. For example, the rank of k_{dis} is No. 1 for H₂S but 14 for HPro. However, in general, k_{dis} , Y_{ac} and Y_{aa} are the most common significant parameters among the presented parameters since the rank of them are all within 20 out of the 100 parameters. In order to check the corrective of the result, the relative-sensitivity function was run for the parameters presented in Table C.2.

Table C.2: Relative-relative sensitivity function ($\delta y / y_p$) for the parameters.

Parameter $\delta y / y_p$	k_{dis}	Y_{ac}	Y_{aa}	$k_{m,aa}$	$k_{m,ac}$	$k_{dec,xac}$	$k_{m,MAC,DMS}$	$k_{m,MAC,MT}$	$k_{m,DMS}$	$K_{S,DMS}$
H ₂ S	2.24	0.73	0.70	0.01	-0.68	-0.36	-0.23	-0.32	1.36	-1.33
MT	0.35	-0.05	-0.09	-0.01	-0.03	0.00	-0.01	0.04	0.05	-0.05
DMS	0.88	-0.48	-0.06	0.00	-0.05	0.13	-0.08	-0.02	-0.47	0.46
DMDS	1.56	-0.12	-0.11	0.00	-0.02	0.01	-0.01	0.02	0.03	-0.04
HAc	0.06	-2.61	-0.01	0.01	-2.57	0.58	0.00	0.00	0.00	0.00
HPro	-0.01	0.03	0.05	0.01	-0.03	-0.01	0.00	0.00	0.00	0.00
HBu	0.00	0.03	0.05	0.00	-0.03	-0.01	0.00	0.00	0.00	0.00
HVa	-0.01	0.03	0.03	0.00	-0.04	0.01	0.00	0.00	0.00	0.01
NH ₃	0.06	-0.19	-0.16	0.00	0.04	0.04	0.00	0.00	0.00	0.00

Referring to Table C.2, the relative-relative function (4.11d') are used calculated the value of $\delta y / y_p$, which can be expressed as:

$$\delta_{y,p}^{r,r} = \frac{p}{y} \frac{\partial y}{2p - p} = \frac{\partial y}{y} \quad (4.11d')$$

Since the detailed calculation of $\delta y / y_p$ will be presented in the following part of further discussion on the three most significant parameters for all odorous compounds and the program of calculation of $\delta y / y_p$ for the each parameter are the same, therefore, only the result are presented in Table C.2.

From Table C.2, it could be seen that the value of $\delta y / y_p$ varies greatly for the same parameter of different compounds. It is difficult to find the common parameters for all odourous compounds because the formation process for each odourous compound is different. For example, the parameters, such as k_{m_DMS} and K_{S_DMS} , are significant for sulfur-containing odourous compounds but not sensitive to VFA and NH_3 . However, compared the $\delta y / y_p$ values of k_{dis} , Y_{ac} and Y_{aa} with other parameters, the impact of the three parameters are generally significant for most of the odourous compounds. Therefore, k_{dis} , Y_{ac} and Y_{aa} are selected as the most significant parameters for all odourous compounds in this study.

The sensitivity analysis in AQUASIM only presented the result. Therefore, the detailed calculation of the general sensitivity analysis was discussed. Both the relative-absolute sensitivity function and the relative-relative sensitivity function was calculated and presented in Tables and Figures. In the Tables, the ratio of $\delta y / y_p$ was presented in one column, which expressed the relative-relative sensitivity function. The value of $\delta y / y_p$ can be used to compare the effects of different parameters on different odourous compounds. The slope in the figures reflected the relative -absolute sensitive function; therefore, the sharpness of slopes can be used to compare the effect of a common parameter on different odourous compounds. The sharper the slope is, the more sensitive the response of the odourous compounds to the parameter is. Four significant parameters for all odourous compounds were calculated and presented.

Table C.3: The effect of k_{dis} on all odourous compounds

k_{dis}	0.5 (ppm v/v)	1.0 (ppm v/v)	0.25 (ppm v/v)	δy	$\delta y / y_p$	Rank
1	2	3	4	5	6	7
H ₂ S	49.5	121.94	11.14	110.80	2.24	1
S_MT	9.20	10.83	7.61	3.21	0.35	4
S_DMS	5.50	8.39	3.46	4.93	0.88	3
S_DMDS	2.20	4.35	1.05	3.30	1.56	2
S_nh3	8.81	9.01	8.49	0.52	0.06	5
S_hac	2.96E-03	2.98E-03	2.94E-03	4.10E-05	0.014	6
S_hpro	3.95E-04	3.94E-04	3.96E-04	-2.10E-06	-0.005	8
S_hbu	2.09E-04	2.08E-04	2.08E-04	-6.40E-07	-0.003	9
S_hva	9.65E-05	9.62E-05	9.69E-05	-7.02E-07	-0.007	7

Referring to Table C.3, Column 2 presents the concentration of the odourous compound in the gas phase in anaerobic digester at parameter value of p , which is the value used in the base model (for k_{dis} , $p=0.5d^{-1}$). Column 3 presents the concentrations of the odourous compounds in the gas phase in anaerobic digester at parameter value of $0.5p$ (for k_{dis} , $0.5p=0.25 d^{-1}$). Column 4 presents the concentration of the odourous compound in the gas phase in anaerobic digester at parameter value of $2p$ (for k_{dis} , $2p=1.0 d^{-1}$). δy in column 5 is the difference of the concentrations of the odourous compounds at parameters value of $0.5p$ and $2p$, i.e. $\delta y = \text{column 3} - \text{column 4}$. $\delta y/y_p$ in column 6 is column 5 over column 2, represented the relative-relative sensitivity function (Eq. 4.11d'). Therefore, the values of $\delta y/y_p$ can be used to compare the effects of different parameters on different odourous compounds. The rank in column 7 is determined by the values of $\delta y/y_p$. The greater the value of $\delta y / y_p$, the higher the rank of the parameter.

Table C.4: The relative-relative sensitivity analysis (y_i/y_p) of odourants at different k_{dis} values

$\frac{\text{Parameter}}{k_{dis}}$	y_i/y_p	H ₂ S	S _{MT}	S _{DMS}	S _{DMDS}	S _{nh3}	S _{hac}	S _{hpro}	S _{hbu}	S _{hva}
0.25		0.19	0.84	0.62	0.49	0.96	0.99	1.00	1.00	1.00
0.5 ^a		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1.0		2.11	1.19	1.50	2.05	1.02	1.01	1.00	1.00	1.00

Note: ^a the value of k_{dis} used in the base model.

Based on Table C.4, Figure C.1 is presented the effect of k_{dis} on all odourous compounds. The slope in Figure C.1 showed the relative-absolute sensitivity analysis, the sharper the slope is, the more significant the effect of the parameter on the odourous compound is.

Table C.5: The effect of Y_{ac} on all odorous compounds

Y_{ac} (kgCOD/kgCOD)	0.05 (ppm v/v)	0.10 (ppm v/v)	0.025 (ppm v/v)	δy	$\delta y / y_p$	Rank
H_2S	49.5	71.32	35.18	36.14	0.73	2
S_{MT}	9.10	8.76	9.18	-0.42	-0.05	6
S_{DMS}	5.59	4.15	6.85	-2.70	-0.48	3
S_{DMDS}	2.12	1.94	2.20	-0.26	-0.12	5
S_{nh3}	8.81	7.61	9.24	-1.64	-0.19	4
S_{hac}	2.96E-03	1.27E-03	8.99E-03	-7.72E-03	-2.61	1
S_{hpro}	3.95E-04	4.08E-04	3.97E-04	1.17E-05	0.03	8
S_{hbu}	2.09E-04	2.15E-04	2.10E-04	5.56E-06	0.03	9
S_{hva}	9.65E-05	9.98E-05	9.69E-05	2.88E-06	0.03	7

Table C.6: The relative-relative sensitivity analysis (y_i/y_p) of odourants at different Y_{ac} values

Parameter y_i/y_p	H_2S	S_{MT}	S_{DMS}	S_{DMDS}	S_{nh3}	S_{hac}	S_{hpro}	S_{hbu}	S_{hva}
0.025	0.61	1.01	1.23	1.04	1.05	3.04	1.01	1.00	1.00
0.05	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.1	1.23	0.96	0.74	0.92	0.86	0.43	1.03	1.03	1.03

Table C.7: The effect of Y_{aa} on all odorous compounds

Y_{aa} (kgCOD/kgCOD) 1	0.08 (ppm v/v) 2	0.16 (ppm v/v) 3	0.04 (ppm v/v) 4	δy 5	$\delta y / y_p$ 6	Rank 7
H ₂ S	49.5	78.08	37.69	40.38	0.70	1
S _{MT}	9.30	8.78	9.58	-0.80	-0.09	4
S _{DMS}	5.6	5.35	5.66	-0.31	-0.06	5
S _{DMDS}	2.2	1.99	2.23	-0.24	-0.11	3
S _{nh3}	8.8	7.89	9.27	-1.39	-0.16	2
S _{hac}	2.96E-03	2.95E-03	2.99E-03	-3.30E-05	-0.01	9
S _{hpro}	3.95E-04	4.07E-04	3.89E-04	1.83E-05	0.05	7
S _{hbu}	2.09E-04	2.15E-04	2.05E-04	1.06E-05	0.05	6
S _{hva}	9.65E-05	9.87E-05	9.55E-05	3.24E-06	0.03	8

Table C.8: The relative-relative sensitivity analysis (y_i/y_p) of odourants at different Y_{aa} values

Parameter k_{dis} y_i/y_p	H ₂ S	S _{MT}	S _{DMS}	S _{DMDS}	S _{nh3}	S _{hac}	S _{hpro}	S _{hbu}	S _{hva}
0.04	0.65	1.05	1.01	1.05	1.04	1.01	0.98	0.98	0.99
0.08	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.16	1.35	0.97	0.96	0.94	0.90	1.00	1.03	1.03	1.02

Table C.9: The effect of k_{m_aa} on all odorous compound

k_{m_aa}	50 (ppm v/v)	100 (ppm v/v)	25 (ppm v/v)	δy	$\delta y / y_p$	Rank
1	2	3	4	5	6	7
H ₂ S	57.80	49.68	57.34	-7.66	-0.13	1
S_MT	9.10	9.32	9.11	0.21	0.02	8
S_DMS	5.59	5.59	5.58	0.01	0.00	2
S_DMDS	2.12	2.16	2.12	0.04	0.02	5
S_nh3	8.81	8.82	8.80	0.01	0.00	9
S_hac	2.96E-03	2.97E-03	2.96E-03	1.10E-05	0.004	6
S_hpro	3.95E-04	3.94E-04	3.98E-04	-3.60E-06	-0.009	3
S_hbu	2.09E-04	2.10E-04	2.08E-04	1.80E-06	0.009	4
S_hva	9.65E-05	9.70E-05	9.66E-05	3.30E-07	0.003	7

Table C.10: The relative-relative sensitivity analysis (y_i/y_p) of odourants at different k_{m_aa} values

Parameter	H ₂ S	S _{MT}	S _{DMS}	S _{DMDS}	S _{nh3}	S _{hac}	S _{hpro}	S _{hbu}	S _{hva}
k_{dis}	y_i/y_p								
25	0.85	1.02	0.99	1.01	1.00	1.00	1.01	1.00	1.00
50	1.00	1.02	0.99	1.01	1.00	1.00	1.00	1.00	1.00
100	0.86	1.02	1.00	1.02	1.00	1.01	1.00	1.00	1.00

FigureC.1: Relative-Absolute Sensitivity Analysis of k_{dis}

Figure C.2: Relative-Absolute Sensitivity Analysis of Y_{ac}

Figure C.3: Relative-Absolute Sensitivity Analysis for Y_{aa}

Figure C.4: Relative-Absolute Sensitivity Analysis of km_{aa}

Appendix D:

The General Sensitivity Analysis for Sulfur-Containing Odourous Compounds

Because sulfur-containing odourous compounds are the most prevalent odourous compounds and main interests in this study, additional significant parameters for sulfur-containing odourous compounds were presented.

The strategy used here is the same as used for general sensitivity analysis. Table D.1 presented the rank of some common significant parameters for sulfur-containing odourous compounds. Table D.2 presented the values of relative-relative functions ($\delta y/y_p$) of some significant parameters for sulfur-containing odourous compounds.

Table D.1: Results of AQUASIM sensitivity analysis for sulfur-containing odorous compounds

Parameter Rank	K _{P_DMS}	K _{P_MT}	K _{P_DMS}	K _{m_DMS}	K _{S_DMS}	k _{m_MAC_DMS}	k _{m_MAC_MT}	k _{m_DMS}	K _{S_DMS}	k _{MT_DMS}	k _{M_SRB_ac}	K _{S_SO4_AC}
H ₂ S	7 ^a	23	8	3	6	15	10	4	5	31	9	12
MT	13	3	11	10	12	19	3	7	8	1	16	18
DMS	2	22	11	3	4	6	14	9	10	31	15	18
DMDS	14	7	2	12	13	19	8	4	5	6	17	21

Note: ^a the number represented the rank of the parameter out of 100 parameters.

Table D.2: Relative-relative sensitivity analysis ($\delta y/y_p$) for the parameters for sulfur-containing odorous compounds

$\delta y/y_p$	K _{P_DMS}	K _{P_MT}	K _{P_DMS}	k _{m_DMS}	K _{S_DMS}	k _{m_MAC_DMS}	k _{m_MAC_MT}	k _{m_DMS}	K _{S_DMS}	K _{S_DMDS}
H ₂ S	-1.17	-0.12	-0.46	1.17	-1.14	-0.20	-0.27	0.50	-0.46	-0.46
MT	-0.05	-0.23	-0.02	0.05	-0.05	-0.01	0.04	0.02	-0.02	-0.02
DMS	-0.87	-0.01	-0.03	-0.46	0.45	0.08	-0.02	0.03	-0.03	-0.03
DMDS	-0.04	-0.16	-1.39	0.03	-0.02	-0.01	0.03	-0.06	0.08	0.08

Table D.3: the effects of K_{P_DMS} on sulfur-containing odourous compounds

K_{P_DMS}	47.28 (ppm v/v)	94.56 (ppm v/v)	23.64 (ppm v/v)	δy (ppm v/v)	$\delta y / y_p$	Rank
1	2	3	4	5	6	
H ₂ S	57.80	29.47	97.31	-67.84	-1.17	1
S _{MT}	9.10	8.92	9.35	-0.43	-0.05	3
S _{DMS}	5.59	3.41	8.25	-4.84	-0.87	2
S _{DMDS}	2.12	2.09	2.18	-0.09	-0.04	4

Table D.4: The relative gas phase concentrations (y_i/y_p) of sulfur-containing odourous compounds at different K_{P_DMS} values

Compounds K_{P_DMS}	H ₂ S	S _{MT}	S _{DMS}	S _{DMDS}
y_i/y_p				
23.64	1.68	1.03	1.48	1.03
47.28	1.00	1.00	1.00	1.00
94.56	0.51	0.98	0.61	0.99

Figure D.1: Relative_Absolute Sensitivity Analysis for K_{P_DMS}

Table D.5: the effects of K_{P_DMDS} on sulfur-containing odourous compounds

K_{P_DMDS} Parameters y_i	101.21 (ppm v/v)	202.42 (ppm v/v)	50.61 (ppm v/v)	δy (ppm v/v)	$\delta y / y_p$	Rank
H_2S	49.50	48.86	75.23	-26.37	-0.46	2
S_{MT}	9.30	9.04	9.21	-0.17	-0.02	4
S_{DMS}	5.50	5.53	5.71	-0.18	-0.03	3
S_{DMDS}	2.20	1.09	4.03	-2.94	-1.39	1

Table D.6: The relative gas phase concentrations (y_i/y_p) of sulfur-containing odourous compounds at different K_{P_DMS} values

Parameters K_{P_DMS} y_i	H ₂ S	S _{MT}	S _{DMS}	S _{DMS}
50.61	1.30	1.01	1.02	1.90
101.21	1.00	1.00	1.00	1.00
202.42	0.85	0.99	0.99	0.51

FigureD.2: Relative-Absolute Sensitivity Analysis for K_{P_DMS}

Table D.7: the effects of K_{P_MT} on sulfur-containing odorous compounds

Compounds K_{P_MT} y_i	22.98 (ppm v/v)	45.96 (ppm v/v)	11.49 (ppm v/v)	δy	$\delta y / y_p$	Rank
H ₂ S	49.50	53.52	60.56	-7.04	-0.12	3
S _{MT}	9.30	7.82	9.92	-2.10	-0.23	1
S _{DMS}	5.50	5.56	5.61	-0.05	-0.01	4
S _{DMS}	2.20	1.91	2.25	-0.34	-0.16	2

Table D.8: The relative gas phase concentrations (y_i/y_p) of sulfur-containing odourous compounds at different K_{P_MT} values

Compounds K_{P_MT} y_i/y_p	H ₂ S	S _{MT}	S _{DMS}	S _{DMDS}
11.49	1.05	1.09	1.00	1.06
22.98	1.00	1.00	1.00	1.00
45.96	0.93	0.86	0.99	0.90

FigureD.3: Relative-Absolute Sensitivity Analysis for K_{P_MT}

Table D.9: the effects of k_{m_DMS} on sulfur-containing odourous compounds

k_{m_DMS} Parameters y_i	0.00064 (ppm v/v)	0.00128 (ppm v/v)	0.00032 (ppm v/v)	δy (ppm,v/v)	$\delta y / y_p$	Rank
H ₂ S	49.50	90.34	22.92	67.42	1.17	1
S _{MT}	9.30	9.56	9.11	0.46	0.05	3
S _{DMS}	5.50	4.12	6.71	-2.59	-0.46	2
S _{DMDS}	2.20	2.21	2.13	0.07	0.03	4

Table D.10: The relative gas phase concentrations (y_i/y_p) of sulfur-containing odourous compounds at different k_{m_DMS} values

k_{m_DMS} Parameters y_i/y_p	H ₂ S	S _{MT}	S _{DMS}	S _{DMDS}
11.49	1.05	1.09	1.00	1.06
22.98	1.00	1.00	1.00	1.00
45.96	0.93	0.86	0.99	0.90

Figure 4.9: Relative-Absolute Sensitivity Analysis for k_{m_DMS}

Table D.11: the effects of K_{S_DMS} on sulfur-containing odourous compounds

K_{S_DMS} Compounds y_i	0.0001433 (ppm v/v)	0.0002866 (ppm v/v)	0.0000716 (ppm v/v)	δy	$\delta y / y_p$	Rank
H ₂ S	49.50	23.26	89.31	-66.06	-1.14	1
S _{MT}	9.30	9.13	9.56	-0.43	-0.05	3
S _{DMS}	5.50	6.69	4.16	2.54	0.45	2
S _{DMDS}	2.20	2.14	2.20	-0.05	-0.02	4

Table D.12: The relative gas phase concentrations (y_i/y_p) of sulfur-containing odourous compounds at different K_{S_DMS} values

compounds K_{S_DMS} y_i/y_p	H ₂ S	S _{MT}	S _{DMS}	S _{DMDS}
0.0000716	1.55	1.05	0.74	1.04
0.0001433	1.00	1.00	1.00	1.00
0.0002866	0.40	1.00	1.20	1.01

Figure D.5: Relative-Absolute Sensitivity Analysis for K_{S_DMS}

Table D.13: the effects of k_{m_DMDS} on sulfur-containing odourous compounds

k_{m_DMDS} Compound y_i	0.00176 (ppm v/v)	0.00352 (ppm v/v)	0.00088 (ppm v/v)	δy	$\delta y / y_p$	Rank
H ₂ S	49.50	70.01	40.84	29.17	0.50	1
S _{MT}	9.30	9.41	9.25	0.17	0.02	4
S _{DMS}	5.50	5.66	5.47	0.19	0.03	3
S _{DMDS}	2.20	2.08	2.21	-0.13	-0.06	2

Table D.14: The relative gas phase concentrations (y_i/y_p) of sulfur-containing odourous compounds at different k_{m_DMS} values

K_{m_DMS} y_i/y_p	H ₂ S	S _{MT}	S _{DMS}	S _{DMDS}
0.00088	0.71	1.02	0.98	1.04
0.00176	1.00	1.00	1.00	1.00
0.00352	1.21	1.03	1.01	0.98

FigureD.6: Relative-Absolute Sensitivity Analysis for k_{m_DMS}

Table D.15: the effects of K_{S_DMS} on sulfur-containing odourous compounds

K_{S_DMS} Compound y_i	0.0025 (ppm v/v)	0.005 (ppm v/v)	0.00125 (ppm v/v)	δy	$\delta y / y_p$	Rank
H ₂ S	49.50	40.61	66.91	-26.30	-0.46	1
S _{MT}	9.30	9.27	9.41	-0.14	-0.02	4
S _{DMS}	5.50	5.51	5.69	-0.18	-0.03	3
S _{DMDS}	2.20	2.25	2.07	0.18	0.08	2

Table D.16: The relative gas phase concentrations (y_i/y_p) of sulfur-containing odourous compounds at different K_{S_DMS} values

Compound K_{S_DMS} y_i/y_p	H ₂ S	S _{MT}	S _{DMS}	S _{DMDS}
0.00125	1.16	1.03	1.02	0.98
0.0025	1.00	1.00	1.00	1.00
0.005	0.70	1.02	0.98	1.00

Figure D.7: relative-absoloute sensetivity analysis of K_{S_DMS}

Table D 17: the effects of $k_{m_MAC_MT}$ on sulfur-containing odourous compounds

$k_{m_MAC_MT}$ Compound y_i	74.41 (ppm v/v)	148.82 (ppm v/v)	37.21 (ppm v/v)	δy	$\delta y / y_p$	Rank
H ₂ S	49.50	40.36	56.05	-15.70	-0.27	1
S _{MT}	9.30	9.53	9.16	0.37	0.04	2
S _{DMS}	5.50	5.47	5.58	-0.11	-0.02	4
S _{DMDS}	2.20	2.19	2.13	0.06	0.03	3

Table D.18: The relative gas phase concentrations (y_i/y_p) of sulfur-containing odourous compounds at different $k_{m_MAC_MT}$ values

Compound $k_{m_MAC_MT}$ y_i	H ₂ S	S _{MT}	S _{DMS}	S _{DMDS}
37.21	0.97	1.01	1.00	1.01
74.41	1.00	1.00	1.00	1.00
148.82	0.70	1.05	0.98	1.03

Figure D.8: relative-absolute sensetivity analysis of $k_{m_MAC_MT}$

Table D 19: the effects of $k_{m_MAC_DMS}$ on sulfur-containing odourous compounds

Compound $k_{m_MAC_DMS}$ y_i	82.26 (ppm v/v)	164.52 (ppm v/v)	41.13 (ppm v/v)	δy	$\delta y / y_p$	Rank
H ₂ S	49.50	42.61	53.95	-11.34	-0.20	1
S _{MT}	9.30	9.25	9.34	-0.09	-0.01	4
S _{DMS}	5.50	5.80	5.36	0.44	0.08	2
S _{DMDS}	2.20	2.14	2.17	-0.02	-0.01	3

Table D.20: The relative gas phase concentrations (y_i/y_p) of sulfur-containing odourous compounds at different $k_{m_MAC_DMS}$ values

$k_{m_MAC_DMS}$	H ₂ S	S _{MT}	S _{DMS}	S _{DMDS}
41.13	0.93	1.03	0.96	1.02
82.26	1.00	1.00	1.00	1.00
164.52	0.74	1.00	1.04	1.01

Figure D.9: relative-absolute sensetivity analysis of $k_{m_MAC_DMS}$

Table D 21: the effects of k_{m_MT} on sulfur-containing odourous compounds

k_{m_MT} Compound y_i	0.00016 (ppm v/v)	0.00032 (ppm v/v)	0.00008 (ppm v/v)	δy	$\delta y / y_p$	Rank
H ₂ S	49.50	57.82	45.25	12.57	0.22	1
S _{MT}	9.30	9.10	9.40	-0.29	-0.03	2
S _{DMS}	5.50	5.59	5.50	0.08	0.02	4
S _{DMDS}	2.20	2.12	2.17	-0.05	-0.02	3

Table D.22: The relative gas phase concentrations (y_i/y_p) of sulfur-containing odourous compounds at different k_{m_MT} values

Compound k_{m_MT} y_i/y_p	H ₂ S	S _{MT}	S _{DMS}	S _{DMDS}
0.00008	0.78	1.03	0.98	1.02
0.00016	1.00	1.00	1.00	1.00
0.00032	1.00	1.00	1.00	1.00

Figure D.10: relative-absolute sensitivity analysis of k_{m_MT}

Appendix E: Individual Sensitivity Analysis

The individual sensitivity analysis started with running the sensitivity function in AUQASIM. For each individual odourous compound, the sensitivity function was run for 100 parameters. Based on the result of the sensitivity analysis of AQUASIM, the impact of the parameters on each individual odourous compound was ranked, and 10 most significant parameters for each individual odourous compound were identified. In this study, the individual sensitivity analysis was performed on sulfur-containing odourous compounds together with NH_3 and HAc.

The absolute-relative sensitivity function (Eq. 4.11c') was preceded to compare the effects of different parameters on a common variable. Referring to Eq. 4.11c', the results of absolute-relative sensitivity function are only dependent on the change of the variable (i.e. δy). Therefore, the values of δy can be used to compare the effects of different parameters on a common variable. The larger the δy value is, the more significant the parameter is. In the following individual sensitivity analysis, the δy values of the variables to different parameters were calculated. The absolute-relative sensitivity analysis can also be presented by the slopes in the Figures. The sharper the slope is, the more significant the parameter to the variable.

E.1 the Individual Sensitivity Analysis for H₂S

Fifteen significant parameters for H₂S were identified and presented in the Tables E.1, E.2 and Figure E.1.

Table E.1: The effects of different parameters on gas phase H₂S

1 k_{dis} (d ⁻¹)	S_{H_2S} (ppm v/v)
0.25	11.14
0.5	57.8
1	121.94
δS	110.80

2. K_{P_DMS} (m ³ /kgCOD)	S_{H_2S} (ppm v/v)
23.64	97.31
47.28	57.8
94.56	29.47
δS	-67.84

3. k_{m_DMS} (kmolDMS/kgCOD.d)	S_{H_2S} (ppm v/v)
0.00032	22.92
0.00064	57.8
0.00128	90.34
δS	67.42

4. K_{S_DMS} (M)	S_{H_2S} (ppm v/v)
0.0000716	89.31
0.0001433	57.8
0.0002866	23.26
δS	-66.05

9. k_{m_DMDS} (kmolDMDS/kgCod.d)	S_{H_2S} (ppm v/v)
0.00088	40.46
0.00176	57.80
0.00352	70.01
δS	29.55

5. $K_{S_SO4_ac}$ (kgCOD/m ³)	S_{H_2S} (ppm v/v)
0.0001	69.93
0.0002	57.80
0.0004	11.22
δS	-58.71

6. Y_{aa} (kgCOD/kgCOD)	S_{H_2S} (ppm v/v)
0.04	37.69
0.08	57.8
0.16	78.08
δS	40.39

7. $k_{m_SRB_ac}$ (kgCOD/kgCOD d)	S_{H_2S} (ppm v/v)
4.322	33.39
8.644	57.80
17.288	71.91
δS	38.52

8. Y_{SRB_ac} (kgCOD/kgCOD)	S_{H_2S} (ppm v/v)
0.059	57.80
0.04425	33.49
0.118	71.80
δS	38.31

13. k_{dec_Xac} (d ⁻¹)	S_{H_2S} (ppm v/v)
0.02	50.60
0.01	60.66
0.04	35.54
δS	-25.12

10.K _{S_DMDS} (m)	S _{H2S} (ppm v/v)
0.00125	69.98
0.0025	57.80
0.005	40.61
δS	-29.37
11.Y _{ac} (kgCOD/kgCOD)	S _{H2S} (ppm v/v)
0.025	75.23
0.05	57.8
0.1	48.86
δS	-26.37

12.K _{P_DMDS} (m3/kgCOD_X)	S _{H2S} (ppm v/v)
50.61	66.25
101.21	57.80
202.42	40.72
δS	-25.53

14.k _{m_MAC_MT} (kgCOD/kgCOD.d)	S _{H2S} (ppm v/v)
74.41	57.80
37.205	58.33
148.82	39.92
δS	-18.41
15.K _{S_H2S_MT} (M)	S _{H2S} (ppm v/v)
0.0001	57.80
0.00005	40.56
0.0002	58.41
δS	17.85

Table E.2: The gas phase concentration of H₂S at different relative parameter values (p_i/p)

Parameters p/p	y_i	K_{dis}	K_{P_DMS}	k_{m_DMS}	K_{S_DMS}	K_{S_SO4_ac}	Y_{aa}	k_{m_SRB_ac}	Y_{SRB_ac}	k_{m_DMS}	K_{S_DMS}
1	2	3	4	5	6	7	8	9	10	11	
0.5	11.14	97.31	22.92	89.31	69.93	37.69	33.39	57.80	40.46	69.98	
1	57.8	57.8	57.8	57.8	57.80	57.8	57.80	33.49	57.80	57.80	
2	121.94	29.47	90.34	23.26	11.22	78.08	71.91	71.80	70.01	40.61	

Referring to Table E.2, the column 1 presented the relative parameter values, which is non-dimensional. Column 2-11 presented the

gas phase concentrations of H₂S at the parameter values of 0.5p, p and 2p, where p is the parameter value used in the base model. For

example, column 2 presented the gas phase concentrations of H₂S at the k_{dis} values of 0.25 d⁻¹, 0.5 d⁻¹ and 1.0 d⁻¹, where the k_{dis} value

of 0.5 d⁻¹ is used for the base model. Figure E.1 is based on Table C.2. The slope of the line in Figure C.2 can be expressed as:

$$\delta_{y,p}^{a,r} = p \frac{\partial y}{p - 0.5p} = \frac{\partial y}{0.5} \quad (4.11c')$$

or
$$\delta_{y,p}^{a,r} = p \frac{\partial y}{2p - p} = \frac{\partial y}{p} \quad (4.11c')$$

For example, the slope of kdis can be expressed as:

$$S_{kdis1} = (57.8 - 11.4)/0.5 = 92.8 \quad S_{kdis2} = (121.94 - 57.8) = 64.14$$

$$S_{KP_DMS1} = (57.80 - 97.31)/0.5 = -79.02 \quad S_{KP_DMS1} = (29.47 - 57.80) = -28.33$$

By comparing the values of the slopes, the response of H₂S to k_{dis} is more sensitive than that to K_{P_DMS}.

Figure E-1: Sensitivity of Gas Phase H₂S to Model Parameters

E.2 the Individual Sensitivity Analysis for MT

Ten significant parameters for MT was identified and presented in the Tables E.3, E.4 and Figure E.2.

Table E.3: Effects of different parameter on gas phase MT

1 k_{MT_DMS} (d^{-1})	S_{MT} (ppm v/v)
3.675	15.48
7.35	9.10
15.7	4.89
δS	-10.59
2 k_{dis} (d^{-1})	S_{MT} (ppm v/v)
0.3	7.61
0.5	9.1
1	10.83
δS	3.22
3 K_{P_MT} (m3/kgCOD)	S_{MT} (ppm v/v)
11.49	9.92
22.98	9.10
45.96	7.82
δS	-2.10
4 Y_{aa} (kgCOD/kgCOD)	S_{MT} (ppm v/v)
0.04	9.58
0.08	9.1
0.16	8.78
δS	-0.80
5 k_{m_DMS} (kmolDMS/kgCOD.d)	S_{MT} (ppm v/v)
0.32	9.11
0.64	9.10
1.28	9.56
δS	0.45

6 K_{S_DMS} (M)	S_{MT} (ppm v/v)
7.16E-05	9.56
0.000143	9.10
0.000287	9.13
δS	-0.43
7 K_{P_DMS} (m3/kgCOD)	S_{MT} (ppm v/v)
23.64	9.35
47.28	9.10
94.56	8.92
δS	-0.43
8 $k_{m_SRB_ac}$ (kgCOD/kgCOD.d)	S_{MT} (ppm v/v)
4.322	8.99
8.644	9.30
17.288	9.39
δS	0.40
9 $K_{S_SO4_ac}$ (M)	S_{MT} (ppm v/v)
0.0001	9.44
0.0002	9.30
0.0004	9.05
δS	-0.39
10 $k_{m_MAC_MT}$ (kgCOD/kgCOD.d)	S_{MT} (ppm v/v)
74.41	9.30
37.205	9.15
148.82	9.53
δS	0.38

Table E.4: Gas phase concentrations of MT at the different relative parameter values.

Parameters p/p	Gas Phase Concentration (ppm)										
	y_i	K_{MT_DMS}	k_{dis}	K_{P_MT}	Y_{aa}	k_{m_DMS}	K_{S_DMS}	K_{P_DMS}	$k_{m_SRB_ac}$	$K_{S_so4_ac}$	$k_{m_MAC_MT}$
0.5		15.48	7.61	9.92	9.58	9.11	9.56	9.35	8.99	9.44	9.30
1		9.10	9.10	9.10	9.10	9.10	9.10	9.10	9.30	9.30	9.15
2		4.89	10.83	7.82	8.78	9.56	9.13	8.92	9.39	9.05	9.53

Figure E2: Sensitivity of Gas Phase MT to Model Parameters

E.3 the Individual Sensitivity Analysis for DMS

Ten significant parameters for DMS were identified and presented in the Tables E5, E.6 and Figure E.3.

Table E.5: Effects of ten significant parameters for the gas phase DMS

1. K_{P_DMS} ($m^3/kgCOD$)	S_{DMS} (ppm v/v)
23.64	8.25
47.28	5.59
94.56	3.41
δS	-4.84
2. k_{dis} (d^{-1})	S_{DMS} (ppm v/v)
0.5	5.59
0.25	3.46
1	8.39
δS	4.93
3. Y_{ac} ($kgCOD/kgCOD$)	S_{DMS} (ppm v/v)
0.05	5.59
0.025	6.85
0.1	4.15
δS	-2.70
4. k_{m_DMS} ($kmolDMS/kgCOD.d$)	S_{DMS} (ppm v/v)
0.32	6.71
0.64	5.59
1.28	4.12
δS	-2.59
5. K_{S_DMS} (M)	S_{DMS} (ppm v/v)
7.16E-05	4.16
0.000143	5.59
0.000287	6.69
δS	2.53
6. $K_{S_H2S_DMS}$ (M)	S_{DMS} (ppm v/v)
0.00005	6.73
0.0001	5.59
0.0002	5.42
δS	-1.32
7. k_{dec_xac} (d^{-1})	S_{DMS} (ppm v/v)
0.01	5.28
0.02	5.59
0.04	5.98
δS	0.70
8. $k_{m_MAC_DMS}$ ($kgCOD/kgCOD.d$)	S_{DMS} (ppm v/v)
41.13	5.38
82.26	5.59
164.52	5.81
δS	0.43
9. $K_{S_SO4_ac}$ (M)	S_{DMS} (ppm v/v)
0.0002	5.59
0.0001	5.68
0.0004	5.26
δS	-0.43
10. Y_{aa} ($kgCOD/kgCOD$)	S_{DMS} (ppm v/v)
0.08	5.59
0.04	5.66
0.16	5.35
δS	-0.31

Table E.6: Gas phase concentrations of DMS at the different relative parameter values

Parameters		K _{P_DMS}	k _{dis}	Y _{ac}	k _{m_DMS}	K _{S_DMS}	K _{S_H2S_DMS}	k _{dec-xac}	k _{m_MAC_DMS}	K _{S_SO4_ac}	Y _{aa}
p/p	y _i										
	0.5	8.25	3.46	6.85	6.71	4.16	6.73	5.28	5.38	5.68	5.66
	1	5.59	5.59	5.59	5.59	5.59	5.59	5.59	5.59	5.59	5.59
	2	3.41	8.39	4.15	4.12	6.69	5.42	5.98	5.81	5.26	5.35

Figure E.3: Sensitivity of Gas Phase DMS to Model Parameters

E.4 the Individual Sensitivity Analysis for DMDS

Ten significant parameters for DMDS were identified and presented in the Tables E.7, E.8 and Figure E.4.

Table E.7: Effects of ten significant parameters for the gas phase DMDS

1. k_{dis} (d^{-1})	S_{DMDS} (ppm)
0.25	1.05
0.5	212.00
1	4.35
δS	3.30
2. K_{P_DMDS} ($m^3/kgCOD$)	S_{DMDS} (ppm)
50.61	4.03
101.21	2.12
202.42	1.09
δS	-2.94
3. k_{MT_DMDS} (d^{-1})	S_{DMDS} (ppm)
3.675	1.90
7.35	2.12
15.7	2.34
δS	0.43
4. K_{P_MT} ($m^3/kgCOD$)	S_{DMDS} (ppm)
11.49	2.25
22.98	2.12
45.96	1.91
δS	-0.34
5. Y_{aa} ($kgCOD/kgCOD$)	S_{DMDS} (ppm)
0.04	2.23
0.08	2.12
0.16	1.99
δS	-0.24

6. Y_{ac} ($kgCOD/kgCOD$)	S_{DMDS} (ppm)
0.05	2.20
0.025	2.12
0.1	1.94
δS	-0.18
7. k_{m_DMDS} ($kmoldDMDS/kgCOD.d$)	S_{DMDS} (ppm)
0.88	2.20
1.76	2.12
3.52	2.07
δS	-0.13
8. K_{S_DMDS} (M)	S_{DMDS} (ppm)
0.00125	2.08
0.0025	2.12
0.005	2.20
δS	0.12
9. k_{m_DMS} ($kmoldDMS/kgCOD.d$)	S_{DMDS} (ppm)
0.32	2.13
0.64	2.12
1.28	2.21
δS	0.08
10. K_{S_DMS} (M)	S_{DMDS} (ppm)
7.16E-05	2.20
0.000143	2.12
0.000287	2.14
δS	-0.06

Table E.8: Gas phase concentrations of DMDS at the different relative parameter values

Parameters		k_{dis}	K_{P_DMDS}	K_{MT_DMDS}	K_{P_MT}	Y_{aa}	Y_{ac}	k_{m_DMDS}	K_{S_DMDS}	k_{m_DMS}	K_{S_DMS}
p/p	y_i										
0.5		1.05	4.03	1.90	2.25	2.23	2.20	2.20	2.08	2.13	2.20
1		2.12	2.12	2.12	2.12	2.12	2.12	2.12	2.12	2.12	2.12
2		4.35	1.09	2.34	1.91	1.99	1.94	2.07	2.20	2.21	2.14

Figure E.4: Sensitivity of Gas Phase DMDS to Model Parameters

E.5 the Individual Sensitivity Analysis for NH₃

Ten significant parameters for NH₃ were identified and presented in the Tables E.9, E.10 and Figure E.5.

Table E.9: Effects of ten significant parameters for the gas phase NH₃

1. Y_{fa} (kgCOD/kgCOD)	S_{NH3} (ppm)
0.03	9.28
0.06	8.81
0.12	7.57
δS	-1.71
2. Y_{ac} (kgCOD/kgCOD)	S_{NH3} (ppm)
0.025	9.24
0.05	8.81
0.1	7.61
δS	-1.63
3. Y_{aa} (kgCOD/kgCOD)	S_{NH3} (ppm)
0.04	9.15
0.08	8.81
0.16	7.77
δS	-1.38
4. Y_{su} (kgCOD/kgCOD)	S_{nh3}
0.05	9.15
0.1	8.81
0.2	7.77
δS	-1.37
5. Y_{h2} (kgCOD/kgCOD)	S_{NH3} (ppm)
0.03	9.00
0.06	8.81
0.12	8.09
δS	-0.91

6. Y_{c4} (kgCOD/kgCOD)	S_{NH3} (ppm)
0.03	8.91
0.06	8.81
0.12	8.24
δS	-0.66
7. k_{dis} (d ⁻¹)	S_{NH3} (ppm)
0.25	8.49
0.5	8.81
1	9.01
δS	0.52
8. k_{dec_xaa} (d ⁻¹)	S_{NH3} (ppm)
0.01	8.59
0.02	8.81
0.04	8.88
δS	0.29
9. k_{dec_xsu} (d ⁻¹)	S_{NH3} (ppm)
0.01	8.63
0.02	8.81
0.04	8.92
δS	0.29
10. k_{dec_xac} (d ⁻¹)	S_{NH3} (ppm)
0.01	8.60
0.02	8.81
0.04	8.84
δS	0.24

Table E.10: Gas phase concentrations of NH₃ at the different relative parameter values

Parameters p/p	Y _i									
	Y _{fa}	Y _{ac}	Y _{aa}	Y _{su}	Y _{h2}	Y _{c4}	kdis	k _{dec_xaa}	k _{dec_xsu}	k _{dec_xac}
0.5	9.28	9.24	9.15	9.15	9.00	8.91	8.49	8.59	8.63	8.63
1	8.81	8.81	8.81	8.81	8.81	8.81	8.81	8.81	8.81	8.81
2	7.57	7.61	7.77	7.77	8.09	8.24	9.01	8.88	8.92	8.92

Figure E.5: Sensitivity of Gas Phase NH3 to Model Parameters

E.6 the Individual Sensitivity Analysis for HAc

Ten significant parameters for NH_3 were identified and presented in the Tables E.11, E.12 and Figure E.6.

Table E11: Effects of ten significant parameters for the gas phase HAc

1. Y_{ac} (kgCOD/kgCOD)	S_{HAc} (ppm v/v)
0.025	8.99E-03
0.05	2.96E-03
0.1	1.27E-03
δS	-7.72E-03
2. $k_{m,ac}$ (kgCOD/kgCOD.d)	S_{HAc} (ppm v/v)
8	2.96E-03
4	8.86E-03
16	1.27E-03
δS	-7.59E-03
3. $k_{s,ac}$ (kgCOD)	S_{HAc} (ppm v/v)
0.075	1.47E-03
0.15	2.96E-03
0.3	5.97E-03
δS	4.50E-03
4. $k_{dec,ac}$ (d ⁻¹)	S_{HAc} (ppm v/v)
0.02	2.96E-03
0.01	2.45E-03
0.04	4.15E-03
δS	1.70E-03
5. k_{dis} (d ⁻¹)	S_{HAc} (ppm v/v)
0.25	2.94E-03
0.5	2.96E-03
1	2.98E-03
δS	4.10E-05

6. Y_{aa} (kgCOD/kgCOD)	S_{HAc} (ppm v/v)
0.08	2.96E-03
0.04	2.99E-03
0.16	2.95E-03
δS	-3.30E-05
7. $k_{m,aa}$ (kgCOD/kgCOD.d)	S_{HAc} (ppm v/v)
25	2.96E-03
50	2.96E-03
100	2.97E-03
δS	1.10E-05
8. Y_{su} (kgCOD/kgCOD)	S_{HAc} (ppm v/v)
0.1	2.96E-03
0.05	2.96E-03
0.2	2.95E-03
δS	-1.50E-05
9. Y_{h2} (kgCOD/kgCOD)	S_{HAc} (ppm v/v)
0.06	2.96E-03
0.03	2.96E-03
0.12	2.95E-03
δS	-1.20E-05
10. Y_{c4} (kgCOD/kgCOD)	S_{HAc} (ppm v/v)
0.06	2.96E-03
0.03	2.96E-03
0.12	2.97E-03
δS	6.00E-06

Table E.12: Gas phase concentrations of HAc at the different relative parameter values

Parameters		Y_{ac}	k_{m_ac}	K_{S_ac}	$k_{dec-xac}$	k_{dis}	Y_{aa}	k_{m_aa}	Y_{su}	Y_{h2}	Y_{c4}
p_i/p	y_i										
0.25		8.99E-03	8.86E-03	1.47E-03	2.45E-03	2.94E-03	2.96E-03	2.96E-03	2.96E-03	2.96E-03	2.96E-03
0.5		2.96E-03	2.96E-03	2.96E-03	2.96E-03	2.96E-03	2.99E-03	2.96E-03	2.96E-03	2.96E-03	2.96E-03
1		1.27E-03	1.27E-03	5.97E-03	4.15E-03	2.98E-03	2.95E-03	2.97E-03	2.95E-03	2.95E-03	2.97E-03

Figure E.6: Sensitivity of Gas Phase HAc to Model Parameters

Appendix F: Input and Output Data of the Odour Model

Table F1: Input data for the base case odour model partitioning

Variables	Unit	Values	Description
Q_{in_ss}	$m^3 d^{-1}$	1.5	Input flow at steady state
S_{aa_in}	$kg\ COD\ m^{-3}$	3.6	Amino acids in feed sludge
S_{fa_in}	$kg\ COD\ m^{-3}$	6.3	Fatty acids in feed sludge
S_{su_in}	$kg\ COD\ m^{-3}$	2.4	Monosaccharides in feed sludge
S_{NH3_in}	M	0.0038	Inorganic nitrogen in feed sludge
S_{CO2_in}	M	0.005	Inorganic carbon in feed sludge
$S_{metal_ion_in}$	M	0.0008	Equivalent concentration of heavy metal ions, such as Fe^{2+} , Cu^{2+} , which can precipitate H_2S
S_{SO4_in}	M	0.000328	Inorganic sulfate in feed sludge
X_{C_in}	$kg\ COD\ m^{-3}$	12	Complex particulates in feed sludge
X_{I_in}	$kg\ COD\ m^{-3}$	16	Inert particulates in feed sludge
T	K	308	Temperature of the anaerobic digester
V	m^3	30	The volume of reactor of anaerobic digester
HRT	d^{-1}	1.5	Hydraulic retention time

Table F2: Output data for the base case odour model

Variables	Unit	Values	Description
Q_{out}	$m^3 d^{-1}$	1.5	Output flow at steady state
Q_{gas}	$m^3 d^{-1}$	16.59	Output gas flow at steady state
pH		7.22	pH value in anaerobic digester at steady state
COD_{tot}	$kg\ COD\ m^{-3}$	22.29	Total COD in digested sludge
COD_S	$kg\ COD\ m^{-3}$	1.65	Soluble COD in digested sludge
S_{aa}	$kg\ COD\ m^{-3}$	0.006	Amino acids in digested sludge
S_{hac_liq}	$kg\ COD\ m^{-3}$	0.00017	Acetate acid in digested sludge
S_{hac_gas}	$kg\ COD\ m^{-3}$	7.4E-09	Acetate acid in gas phase
S_{ac}^-	$kg\ COD\ m^{-3}$	0.048	Ionic acetate acids in digested sludge
S_{hpro_liq}	$kg\ COD\ m^{-3}$	8.2E-05	Propionate acid in digested sludge
S_{hpro_gas}	$kg\ COD\ m^{-3}$	1.7E-09	Propionate acid in gas phase
S_{pro}^-	$kg\ COD\ m^{-3}$	0.018	Ionic propionate acid in digested sludge
S_{hbu_liq}	$kg\ COD\ m^{-3}$	6.2E-05	Butyrate acid in digested sludge

$S_{\text{hbu_gas}}$	kg COD m ⁻³	1.3E-09	Butyrate acid in the gas phase
S_{bu^-}	kg COD m ⁻³	0.015	Ionic butyrate acid in digested sludge
$S_{\text{hva_liq}}$	kg COD m ⁻³	4.5E-05	Valerate acid in digested sludge
$S_{\text{hva_gas}}$	kg COD m ⁻³	7.8E-10	Valerate acid in the gas phase
S_{va^-}	kg COD m ⁻³	0.012	Ionic valerate acid in digested sludge
$S_{\text{nh3_liq}}$	M	5.8E-04	Ammonia in digested sludge
$S_{\text{nh3_gas}}$	M	3.4E-07	Ammonia in the gas phase
S_{nh4^+}	M	0.031	Ammonium in digested sludge
$S_{\text{H2S_liq}}$	M	5.7E-06	Hydrogen sulfide in digested sludge
$S_{\text{H2S_gas}}$	M	2.3E-06	Hydrogen sulfide in the gas phase
S_{HS^-}	M	8.4E-07	Ionic hydrogen sulfide in digested sludge
$S_{\text{MT_liq}}$	M	2.5E-06	Methyl mercaptan in digested sludge
$S_{\text{MT_sol}}$	M	7.2E-05	Methyl mercaptan in the gas phase
$S_{\text{MT_gas}}$	M	3.6E-07	Methyl mercaptan in digested sludge
$S_{\text{DMS_liq}}$	M	2.8E-06	Dimethyl sulfide in digested sludge
$S_{\text{DMS_sol}}$	M	1.7E-04	Dimethyl sulfide in the gas phase
$S_{\text{DMS_gas}}$	M	2.2E-07	Dimethyl sulfide in digested sludge
$S_{\text{DMDS_liq}}$	M	1.9E-06	Dimethyl disulfide in digested sludge
$S_{\text{DMDS_sol}}$	M	2.3E-04	Dimethyl disulfide in the gas phase
$S_{\text{DMDS_gas}}$	M	8.3E-08	Dimethyl disulfide in digested sludge
$S_{\text{co2_liq}}$	M	0.0081	Carbon dioxide in digested sludge
$S_{\text{co2_gas}}$	M	0.012	Carbon dioxide in the gas phase
S_{hco3^-}	M	0.067	Bicarbonate in digested sludge
$S_{\text{ch4_liq}}$	kg COD m ⁻³	1.65	Methane in digested sludge
$S_{\text{ch4_gas}}$	kg COD m ⁻³	0.055	Methane in the gas phase
$S_{\text{h2_liq}}$	kg COD m ⁻³	1.2E-05	Hydrogen in digested sludge
$S_{\text{h2_gas}}$	kg COD m ⁻³	2.6E-07	Hydrogen in the gas phase
S_{fa}	kg COD m ⁻³	0.11	Long chain fatty acids in digested sludge
S_{I}	kg COD m ⁻³	1.40	Soluble inerts in digested sludge
S_{cat}	M	0.04	Cations in digested sludge
S_{an}	M	0.004	Anions in digested sludge
S_{su}	kg COD m ⁻³	1.24	Monosaccharides in digested sludge
S_{SO4}	M	5.5E-05	Sulfate in digested sludge
S_{MS}	M	7.9E-04	Metal sulfides in digested sludge
X_{C}	kg COD m ⁻³	1.24	Complex particulates in digested sludge
X_{pro}	kg COD m ⁻³	0.069	Propionate acid degrading organism

X_{pr}	kg COD m ⁻³	0.019	Proteins in digested sludge
X_{su}	kg COD m ⁻³	0.39	Monosaccharide degrading organisms in digested sludge
X_{li}	kg COD m ⁻³	0.015	Lipids in digested sludge
X_{SRB_ac}	kg COD m ⁻³	7.9E-04	SRB_ac degrading organisms in digested sludge
X_{SRB_h2}	kg COD m ⁻³	5.739E-06	SRB_h ₂ degrading organisms in digested sludge
X_{SRB_pro}	kg COD m ⁻³	3.22E-06	SRB_pro degrading organisms in digested sludge
X_I	kg COD m ⁻³	17.16	Particulate inerts in digested sludge
X_{h2}	kg COD m ⁻³	0.24	Hydrogen degrading organisms in digested sludge
X_{fa}	kg COD m ⁻³	0.39	Long chain fatty acid degrading organisms in digested sludge
X_{c4}	kg COD m ⁻³	0.17	Butyrate and valerate degrading organisms in digested sludge
X_{aa}	kg COD m ⁻³	0.41	Amino acids degrading organisms in digested sludge
X_{ac}	kg COD m ⁻³	0.51	Acetate acids degrading organisms in digested sludge

Appendix G: Sensitivity Analysis by AUQASIM

AQUASIM Version 2.0 (win/mfc) - Sensitivity Analysis File

Date and time of listing: 10/15/2003 10:26:36

Ranking of mean absolute sensitivities and error contributions:

Calculation Number: 0

Compartment: headspace

Zone: Bulk Volume

Variable: S_ch4

	Parameter:	Sens AR:	Parameter:	Error Contr.:
		[kg COD.m-3]		[kg COD.m-3]
1	input_X_c_in	0.09031	Ka_h2o	16.45
2	Ka_co2	0.02287	Ka_nh4	4.274
3	Y_fa	0.01451	Ka_co2	4.191
4	f_pr_xc	0.0117	f_aa_DMDS	0.05419
5	kdis	0.01038	Y_fa	0.02418
6	input_S_aa_in	0.007293	KI_nh3_ac	0.01818
7	km_ac	0.00574	Ka_H2S	0.01332
8	Y_aa	0.00474	kdis	0.01038
9	Ks_ac	0.004132	input_S_so4_in	0.009873
10	Y_su	0.004121	Ks_SRB_ac	0.008539
11	Y_c4	0.004061	input_X_c_in	0.007526
12	input_S_metal_ion_in			
		0.003443	Ks_h2	0.005218
13	input_S_so4_in	0.00324	Y_su	0.004121
14	Y_h2	0.003025	f_pr_xc	0.003901
15	f_aa_MT	0.001434	Ks_SRB_h2	0.002913
16	km_SRB_ac	0.001177	kdec_xac	0.002672
17	kdec_xac	0.001069	input_S_aa_in	0.002026
18	km_pro	0.0009984	Ks_MAC	0.001819
19	Ks_pro	0.0008549	f_aa_DMS	0.001613
20	f_aa_DMS	0.0006615	kdec_xfa	0.001345
21	f_aa_DMDS	0.0006329	Ks_c4	0.001252
22	khyd_ch	0.000544	kdec_xaa	0.001228
23	kdec_xfa	0.0005381	Ks_su	0.0009263
24	km_MAC_DMS	0.0005364	kdec_xsu	0.0009068
25	Ks_so4_ac	0.000496	kdec_xh2	0.0008329
26	kdec_xaa	0.0004913	km_ac	0.0007175
27	km_su	0.0004741	KI_h2_pro	0.0006811
28	Kpre_H2S	0.0004715	Y_c4	0.0006768
29	Ks_su	0.0004632	Y_aa	0.0005925
30	km_DMDS	0.0004514	Ks_ac	0.0005643
31	Ks_DMDS	0.000449	Ks_fa	0.0005116
32	Kp_DMDS	0.0004361	Y_h2	0.0005042
33	km_MAC_MT	0.0004113	kdec_xpro	0.0004216
34	Y_SRB_ac	0.0004053	kdec_xSRBac	0.0003562
35	Ks_h2	0.0003653	Ks_H2S_DMS	0.0003555

36	kdec_xsu	0.0003627	kdec_xc4	0.0003402
37	Ks_H2S_DMS	0.0003555	Ks_MT	0.0002779
38	kdec_xh2	0.0003332	Ks_H2S_MT	0.0002694
39	Y_ac	0.0003167	kdec_xSRBh2	0.0002612
40	km_SRB_h2	0.0003101	KI_H2S_SRB_ac	0.0002288
41	km_h2	0.000299	Ks_IN	0.0002279
42	km_DMS	0.0002809	f_aa_MT	0.0002161
43	Ks_MAC	0.0002736	Ks_SRB_pro	0.0002147
44	Kp_DMS	0.0002713	Ks_pro	0.0002018
45	Ks_H2S_MT	0.0002694	Ks_DMS	0.0001858
46	km_c4	0.0002688	km_SRB_ac	0.0001361
47	Ks_DMS	0.0002663	Ka_ac	0.0001268
48	km_fa	0.0002566	KI_h2_fa	0.0001267
49	Ks_c4	0.0002504	km_pro	7.68e-005
50	Ks_SRB_ac	0.0002049	Y_SRB_ac	6.869e-005
51	Ks_fa	0.0002046	KI_h2_c4	6.691e-005
52	kdec_xpro	0.0001686	Y_ac	6.335e-005
53	Ks_so4_h2	0.0001634	khyd_ch	5.44e-005
54	kdec_xSRBac	0.0001425	km_DMS	4.388e-005
55	kdec_xc4	0.0001361	input_S_metal_ion_in	4.304e-005
56	Y_pro	0.0001189	km_fa	4.277e-005
57	kLa	0.0001076	kdec_xSRBpro	3.807e-005
58	kdec_xSRBh2	0.0001045	Y_pro	2.972e-005
59	Ka_nh4	9.562e-005	Ks_aa	2.592e-005
60	Kp_MT	9.107e-005	km_DMDS	2.565e-005
61	km_SRB_pro	9.102e-005	Kp_DMDS	2.495e-005
62	Ks_so4_pro	8.454e-005	Ks_so4_ac	2.48e-005
63	Ks_SRB_pro	6.333e-005	KI_H2S_SRB_h2	2.462e-005
64	Y_DMS	5.938e-005	KI_H2S_SRB_pro	2.384e-005
65	khyd_pr	4.792e-005	Ka_pro	2.258e-005
66	km_aa	3.994e-005	km_MT	2.236e-005
67	KMT_DMDS	3.941e-005	Ks_DMDS	1.796e-005
68	km_MT	3.577e-005	km_su	1.58e-005
69	KI_nh3_ac	3.272e-005	km_c4	1.344e-005
70	kLa_hac	2.841e-005	Kp_DMS	1.13e-005
71	Y_DMDS	2.694e-005	Ka_bu	9.542e-006
72	kLa_hpro	2.424e-005	km_h2	8.542e-006
73	Ks_IN	2.279e-005	km_SRB_h2	6.946e-006
74	kLa_hva	1.754e-005	km_MAC_DMS	6.521e-006
75	Ks_aa	1.555e-005	km_SRB_pro	5.732e-006
76	kdec_xSRBpro	1.523e-005	km_MAC_MT	5.528e-006
77	kLa_hbu	1.453e-005	khyd_pr	4.792e-006
78	khyd_li	9.982e-006	Kp_MT	4.035e-006
79	Ks_MT	8.819e-006	Ka_va	2.865e-006
80	kLa_MT	5.313e-006	KMT_DMDS	2.681e-006
81	khyd_aro	4.692e-006	Ks_so4_h2	1.742e-006
82	Y_MT	4.576e-006	Ks_so4_pro	1.097e-006
83	Ka_pro	2.977e-006	khyd_li	9.982e-007
84	KI_H2S_SRB_ac	2.038e-006	km_aa	7.988e-007
85	kLa_H2S	1.683e-006	kLa_hpro	7.131e-007
86	Ka_H2S	1.586e-006	kLa_hac	6.763e-007
87	kLa_DMS	5.491e-007	kLa_hva	6.748e-007
88	Ka_va	4.54e-007	Kpre_H2S	5.836e-007
89	KI_H2S_SRB_h2	4.231e-007	kLa	5.382e-007
90	Ka_ac	2.203e-007	kLa_hbu	4.843e-007

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91 KI_H2S_SRB_pro2.123e-007 khyd_aro 4.692e-007
92 Ks_SRB_h2 1.457e-007 kLa_MT 1.107e-007
93 Ka_bu 1.379e-007 kLa_H2S 2.371e-008
94 kLa_DMDS 1.604e-008 kLa_DMS 1.484e-008
95 Ka_h2o 7.316e-009 Y_MT 1.128e-008
96 KI_h2_pro 2.384e-009 Y_DMDS 4.622e-009
97 KI_h2_c4 6.691e-010 Y_DMS 1.545e-009
98 KI_h2_fa 6.337e-010 kLa_DMDS 4.859e-010
99 kLa_nh3 0 kLa_nh3 0
100 f_aa_H2S 0 f_aa_H2S 0
Variable: S_co2
Parameter: Sens AR: Parameter: Error Contr.:
[M] [M]
1 input_X_c_in 0.001417 Ka_nh4 0.113
2 Ka_co2 0.0003576 Ka_h2o 0.08064
3 Y_fa 0.0002267 Ka_co2 0.06554
4 f_pr_xc 0.0001834 f_aa_DMDS 0.0008502
5 kdis 0.0001622 Y_fa 0.0003778
6 input_S_aa_in 0.000115 KI_nh3_ac 0.0002846
7 km_ac 8.988e-005 Ka_H2S 0.0002068
8 Y_aa 7.428e-005 kdis 0.0001622
9 Ks_ac 6.469e-005 input_S_so4_in 0.0001539
10 Y_su 6.466e-005 Ks_SRB_ac 0.0001333
11 Y_c4 6.341e-005 input_X_c_in 0.0001181
12 input_S_metal_ion_in
5.348e-005 Ks_h2 7.098e-005
13 input_S_so4_in 5.05e-005 Y_su 6.466e-005
14 Y_h2 4.675e-005 f_pr_xc 6.112e-005
15 f_aa_MT 2.283e-005 Ks_SRB_h2 4.554e-005
16 km_SRB_ac 1.837e-005 kdec_xac 4.188e-005
17 kdec_xac 1.675e-005 input_S_aa_in 3.194e-005
18 km_pro 1.565e-005 Ks_MAC 2.825e-005
19 Ks_pro 1.34e-005 f_aa_DMS 2.573e-005
20 f_aa_DMS 1.055e-005 kdec_xfa 2.105e-005
21 f_aa_DMDS 9.93e-006 Ks_c4 1.967e-005
22 khyd_ch 8.516e-006 kdec_xaa 1.928e-005
23 kdec_xfa 8.419e-006 Ks_su 1.45e-005
24 km_MAC_DMS 8.34e-006 kdec_xsu 1.425e-005
25 Ks_so4_ac 7.736e-006 kdec_xh2 1.26e-005
26 kdec_xaa 7.714e-006 km_ac 1.123e-005
27 km_su 7.421e-006 KI_h2_pro 1.068e-005
28 Kpre_H2S 7.366e-006 Y_c4 1.057e-005
29 Ks_su 7.25e-006 Y_aa 9.286e-006
30 km_DMDS 7.093e-006 Ks_ac 8.835e-006
31 Ks_DMDS 7.055e-006 Ks_fa 7.799e-006
32 Kp_DMDS 6.511e-006 Y_h2 7.792e-006
33 km_MAC_MT 6.378e-006 kdec_xpro 6.605e-006
34 Y_SRB_ac 6.317e-006 kdec_xSRBac 5.551e-006
35 kdec_xsu 5.7e-006 Ks_H2S_DMS 5.527e-006
36 Ks_H2S_DMS 5.527e-006 kdec_xc4 5.339e-006
37 kdec_xh2 5.039e-006 Ks_MT 4.436e-006
38 Ks_h2 4.969e-006 Ks_H2S_MT 4.178e-006
39 Y_ac 4.926e-006 kdec_xSRBh2 4.084e-006
40 km_SRB_h2 4.847e-006 Ks_IN 3.598e-006
41 km_DMS 4.533e-006 KI_H2S_SRB_ac 3.573e-006
42 km_h2 4.315e-006 f_aa_MT 3.44e-006

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43	Ks_DMS	4.297e-006	Ks_SRB_pro	3.357e-006
44	Ks_MAC	4.249e-006	Ks_pro	3.165e-006
45	km_c4	4.223e-006	Ks_DMS	2.999e-006
46	Ks_H2S_MT	4.178e-006	km_SRB_ac	2.125e-006
47	Kp_DMS	4.088e-006	Ka_ac	1.979e-006
48	Ks_c4	3.934e-006	KI_h2_fa	1.932e-006
49	km_fa	3.912e-006	km_pro	1.204e-006
50	Ks_SRB_ac	3.198e-006	Y_SRB_ac	1.071e-006
51	Ks_fa	3.12e-006	KI_h2_c4	1.051e-006
52	kdec_xpro	2.642e-006	Y_ac	9.852e-007
53	Ks_so4_h2	2.553e-006	khyd_ch	8.516e-007
54	Ka_nh4	2.527e-006	km_DMS	7.083e-007
55	kdec_xSRBac	2.221e-006	input_S_metal_ion_in	6.685e-007
56	kdec_xc4	2.136e-006	km_fa	6.521e-007
57	Y_pro	1.859e-006	kdec_xSRBpro	5.946e-007
58	kdec_xSRBh2	1.633e-006	Y_pro	4.648e-007
59	kLa	1.631e-006	Ks_aa	4.076e-007
60	km_SRB_pro	1.423e-006	km_DMDS	4.03e-007
61	Ks_so4_pro	1.321e-006	Ks_so4_ac	3.868e-007
62	Kp_MT	1.318e-006	KI_H2S_SRB_h2	3.849e-007
63	Ks_SRB_pro	9.902e-007	KI_H2S_SRB_pro	3.729e-007
64	Y_DMS	9.278e-007	Kp_DMDS	3.725e-007
65	KMT_DMDS	8.61e-007	km_MT	3.57e-007
66	khyd_pr	7.536e-007	Ka_pro	3.523e-007
67	km_aa	6.251e-007	Ks_DMDS	2.822e-007
68	km_MT	5.711e-007	km_su	2.474e-007
69	KI_nh3_ac	5.124e-007	km_c4	2.111e-007
70	kLa_hac	4.438e-007	Kp_DMS	1.702e-007
71	Y_DMDS	4.209e-007	Ka_bu	1.488e-007
72	kLa_hpro	3.789e-007	km_h2	1.233e-007
73	Ks_IN	3.598e-007	km_SRB_h2	1.086e-007
74	kLa_hva	2.741e-007	km_MAC_DMS	1.014e-007
75	Ks_aa	2.446e-007	km_SRB_pro	8.96e-008
76	kdec_xSRBpro	2.379e-007	km_MAC_MT	8.572e-008
77	kLa_hbu	2.27e-007	khyd_pr	7.536e-008
78	khyd_li	1.58e-007	KMT_DMDS	5.857e-008
79	Ks_MT	1.408e-007	Kp_MT	5.841e-008
80	kLa_MT	8.292e-008	Ka_va	4.465e-008
81	khyd_aro	7.288e-008	Ks_so4_h2	2.724e-008
82	Y_MT	7.149e-008	Ks_so4_pro	1.714e-008
83	Ka_pro	4.645e-008	khyd_li	1.58e-008
84	KI_H2S_SRB_ac	3.182e-008	km_aa	1.25e-008
85	kLa_H2S	2.614e-008	kLa_hpro	1.114e-008
86	Ka_H2S	2.463e-008	kLa_hac	1.057e-008
87	kLa_DMS	8.692e-009	kLa_hva	1.054e-008
88	Ka_va	7.077e-009	Kpre_H2S	9.117e-009
89	KI_H2S_SRB_h2	6.615e-009	kLa	8.156e-009
90	Ka_ac	3.44e-009	kLa_hbu	7.566e-009
91	KI_H2S_SRB_pro	3.321e-009	khyd_aro	7.288e-009
92	Ks_SRB_h2	2.277e-009	kLa_MT	1.727e-009
93	Ka_bu	2.15e-009	kLa_H2S	3.682e-010
94	kLa_DMDS	3.455e-010	kLa_DMS	2.349e-010
95	KI_h2_pro	3.738e-011	Y_MT	1.763e-010
96	Ka_h2o	3.587e-011	Y_DMDS	7.222e-011
97	KI_h2_c4	1.051e-011	Y_DMS	2.414e-011

98 KI_h2_fa 9.661e-012 kLa_DMDS 1.047e-011
 99 kLa_nh3 0 kLa_nh3 0
 100 f_aa_H2S 0 f_aa_H2S 0

Variable: S_h2

	Parameter:	Sens AR:	Parameter:	Error Contr.:
		[kg COD.m-3]		[kg COD.m-3]
1	km_h2	1.212e-005	Ka_h2o	2.29
2	Ks_h2	1.173e-005	Ks_h2	0.0001675
3	Y_h2	1.085e-005	Ka_nh4	0.0001182
4	kdec_xh2	3.003e-006	Ka_co2	8.389e-006
5	kLa	1.577e-006	kdec_xh2	7.509e-006
6	input_X_c_in	8.04e-007	Y_h2	1.808e-006
7	input_S_aa_in	3.049e-007	Ks_IN	3.924e-007
8	kdis	1.26e-007	km_h2	3.464e-007
9	f_pr_xc	6.815e-008	f_aa_DMDS	1.63e-007
10	Y_su	5.193e-008	kdis	1.26e-007
11	Y_aa	4.61e-008	input_S_aa_in	8.47e-008
12	Ka_co2	4.578e-008	input_X_c_in	6.7e-008
13	Y_ac	4.522e-008	KI_nh3_ac	6.435e-008
14	Ks_IN	3.924e-008	Ks_SRB_ac	5.853e-008
15	Y_fa	2.768e-008	Y_su	5.193e-008
16	km_fa	2.227e-008	Y_fa	4.614e-008
17	km_ac	2.017e-008	Ks_fa	4.508e-008
18	Ks_fa	1.803e-008	Ka_H2S	4.122e-008
19	km_pro	1.707e-008	Ks_SRB_h2	2.322e-008
20	Ks_ac	1.448e-008	Ks_c4	2.281e-008
21	Ks_pro	1.446e-008	f_pr_xc	2.272e-008
22	Y_c4	1.401e-008	kdec_xaa	1.899e-008
23	Kpre_H2S	1.141e-008	kdec_xsu	1.763e-008
24	input_S_metal_ion_in	1.053e-008	kdec_xac	1.506e-008
25	km_SRB_ac	7.856e-009	input_S_so4_in	1.25e-008
26	kdec_xaa	7.597e-009	KI_h2_pro	1.199e-008
27	kdec_xsu	7.05e-009	KI_h2_fa	1.126e-008
28	kdec_xac	6.024e-009	Ks_SRB_pro	1.061e-008
29	km_c4	4.8e-009	kdec_xfa	9.679e-009
30	Ks_c4	4.562e-009	Y_ac	9.045e-009
31	km_SRB_pro	4.332e-009	kLa	7.887e-009
32	f_aa_MT	4.293e-009	kdec_xc4	5.846e-009
33	input_S_so4_in	4.102e-009	Y_aa	5.762e-009
34	kdec_xfa	3.872e-009	Ks_MAC	5.649e-009
35	Ks_SRB_pro	3.13e-009	Ks_su	4.674e-009
36	Ks_so4_ac	2.767e-009	km_fa	3.712e-009
37	Y_pro	2.751e-009	Ks_pro	3.414e-009
38	khyd_ch	2.737e-009	KI_H2S_SRB_ac	2.919e-009
39	km_SRB_h2	2.66e-009	kdec_xSRBac	2.673e-009
40	Ka_nh4	2.645e-009	km_ac	2.521e-009
41	km_su	2.505e-009	kdec_xpro	2.508e-009
42	khyd_li	2.486e-009	Y_c4	2.335e-009
43	khyd_pr	2.456e-009	Ks_ac	1.977e-009
44	kdec_xc4	2.338e-009	KI_H2S_SRB_pro	1.807e-009
45	Ks_su	2.337e-009	kdec_xSRBpro	1.787e-009
46	Ks_so4_h2	2.035e-009	kdec_xSRBh2	1.752e-009
47	f_aa_DMDS	1.904e-009	f_aa_DMS	1.601e-009
48	Ks_so4_pro	1.861e-009	Ks_MT	1.384e-009
49	km_DMS	1.74e-009	Ks_aa	1.324e-009

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50 km_MAC_DMS 1.677e-009 km_pro 1.313e-009
51 Ks_DMS 1.645e-009 KI_h2_c4 1.243e-009
52 Kp_DMS 1.615e-009 Ks_DMS 1.148e-009
53 km_DMDS 1.487e-009 Ks_H2S_DMS 1.104e-009
54 Ks_DMDS 1.479e-009 km_SRB_ac 9.088e-010
55 Ks_SRB_ac 1.405e-009 Ks_H2S_MT 8.165e-010
56 Kp_DMDS 1.4e-009 Y_pro 6.878e-010
57 km_MAC_MT 1.254e-009 f_aa_MT 6.469e-010
58 Y_SRB_ac 1.237e-009 KI_H2S_SRB_h2 4.679e-010
59 km_aa 1.224e-009 khyd_ch 2.737e-010
60 Ks_H2S_DMS 1.104e-009 km_SRB_pro 2.728e-010
61 kdec_xSRBac 1.069e-009 km_DMS 2.718e-010
62 Ka_h2o 1.019e-009 Ka_ac 2.625e-010
63 kdec_xpro 1.003e-009 khyd_li 2.486e-010
64 Ks_MAC 8.497e-010 khyd_pr 2.456e-010
65 Ks_H2S_MT 8.165e-010 km_c4 2.4e-010
66 Ks_aa 7.946e-010 Y_SRB_ac 2.097e-010
67 kdec_xSRBpro 7.149e-010 Ka_pro 2.054e-010
68 kdec_xSRBh2 7.009e-010 Ks_so4_ac 1.383e-010
69 f_aa_DMS 6.567e-010 input_S_metal_ion_in
1.316e-010
70 kLa_hac 6.216e-010 km_MT 1.117e-010
71 Kp_MT 4.98e-010 km_DMDS 8.447e-011
72 kLa_hpro 4.582e-010 Ka_bu 8.419e-011
73 kLa_hva 3.875e-010 km_su 8.35e-011
74 kLa_hbu 3.116e-010 Kp_DMDS 8.01e-011
75 km_MT 1.787e-010 Kp_DMS 6.724e-011
76 KI_nh3_ac 1.158e-010 km_SRB_h2 5.958e-011
77 KMT_DMDS 1.068e-010 Ks_DMDS 5.915e-011
78 kLa_MT 8.596e-011 Ka_va 4.13e-011
79 Y_DMS 4.83e-011 km_aa 2.447e-011
80 Ks_MT 4.393e-011 Ks_so4_pro 2.414e-011
81 Ka_pro 2.707e-011 Kp_MT 2.206e-011
82 KI_H2S_SRB_ac 2.599e-011 Ks_so4_h2 2.17e-011
83 Y_DMDS 2.008e-011 km_MAC_DMS 2.039e-011
84 khyd_aro 1.865e-011 km_MAC_MT 1.686e-011
85 KI_H2S_SRB_pro 1.609e-011 kLa_hva 1.49e-011
86 kLa_DMS 1.542e-011 kLa_hac 1.48e-011
87 KI_H2S_SRB_h2 8.042e-012 Kpre_H2S 1.413e-011
88 Ka_va 6.546e-012 kLa_hpro 1.348e-011
89 kLa_H2S 5.2e-012 kLa_hbu 1.039e-011
90 Ka_H2S 4.909e-012 KMT_DMDS 7.266e-012
91 Y_MT 3.296e-012 khyd_aro 1.865e-012
92 Ka_bu 1.217e-012 kLa_MT 1.791e-012
93 Ks_SRB_h2 1.161e-012 kLa_DMS 4.169e-013
94 Ka_ac 4.561e-013 kLa_H2S 7.324e-014
95 kLa_DMDS 3.314e-013 kLa_DMDS 1.004e-014
96 KI_h2_fa 5.628e-014 Y_MT 8.125e-015
97 KI_h2_pro 4.197e-014 Y_DMDS 3.446e-015
98 KI_h2_c4 1.243e-014 Y_DMS 1.257e-015
99 kLa_nh3 0 kLa_nh3 0
100 f_aa_H2S 0 f_aa_H2S 0
Variable: S_nh3
Parameter: Sens AR: Parameter: Error Contr.:
[M] [M]
1 input_S_aa_in 5.472e-007 Ka_nh4 4.043e-005

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2	input_X_c_in	1.918e-007	Ka_h2o	6.274e-006
3	Y_ac	8.565e-008	Ka_co2	5.464e-006
4	Y_fa	7.547e-008	input_S_aa_in	1.52e-007
5	Y_su	5.861e-008	Y_fa	1.258e-007
6	Y_aa	5.858e-008	Y_su	5.861e-008
7	Y_h2	3.781e-008	f_aa_DMDS	5.197e-008
8	Y_c4	3.001e-008	kdec_xac	4.512e-008
9	Ka_co2	2.982e-008	kdec_xfa	3.32e-008
10	kdis	2.051e-008	kdec_xaa	3.26e-008
11	kdec_xac	1.805e-008	kdec_xsu	3.239e-008
12	f_pr_xc	1.403e-008	kdis	2.051e-008
13	kdec_xfa	1.328e-008	kdec_xh2	1.937e-008
14	kdec_xaa	1.304e-008	KI_nh3_ac	1.804e-008
15	kdec_xsu	1.295e-008	Y_ac	1.713e-008
16	Y_pro	1.157e-008	input_X_c_in	1.598e-008
17	kdec_xh2	7.747e-009	kdec_xc4	1.383e-008
18	km_ac	5.707e-009	Ka_H2S	1.286e-008
19	kdec_xc4	5.533e-009	input_S_so4_in	8.637e-009
20	Ks_ac	4.107e-009	Y_aa	7.323e-009
21	input_S_metal_ion_in	3.3e-009	Ks_SRB_ac	7.289e-009
22	khyd_pr	3.139e-009	kdec_xpro	6.449e-009
23	input_S_so4_in	2.834e-009	Y_h2	6.301e-009
24	kdec_xpro	2.579e-009	Y_c4	5.002e-009
25	kLa	2.516e-009	f_pr_xc	4.677e-009
26	km_fa	1.966e-009	Ks_fa	3.923e-009
27	Ks_fa	1.569e-009	Ks_c4	3.245e-009
28	km_pro	1.568e-009	Y_pro	2.893e-009
29	f_aa_MT	1.384e-009	Ks_SRB_h2	2.531e-009
30	Ks_pro	1.341e-009	Ks_h2	2.461e-009
31	km_aa	1.001e-009	Ks_MAC	1.768e-009
32	km_SRB_ac	9.916e-010	Ks_aa	1.644e-009
33	Ks_aa	9.867e-010	f_aa_DMS	1.369e-009
34	Ka_nh4	9.045e-010	Ks_su	1.343e-009
35	khyd_ch	7.921e-010	KI_h2_pro	1.069e-009
36	km_c4	6.919e-010	KI_h2_fa	9.645e-010
37	km_su	6.858e-010	km_ac	7.133e-010
38	Ks_su	6.714e-010	Ka_ac	6.543e-010
39	Ks_c4	6.491e-010	Ks_ac	5.609e-010
40	f_aa_DMDS	6.069e-010	kdec_xSRBac	5.109e-010
41	f_aa_DMS	5.615e-010	kdec_xSRBh2	4.109e-010
42	Y_SRB_ac	5.315e-010	Ks_H2S_DMS	3.412e-010
43	km_MAC_DMS	5.172e-010	Ks_MT	3.28e-010
44	km_DMDS	4.58e-010	km_fa	3.277e-010
45	Ks_DMDS	4.555e-010	Ks_pro	3.166e-010
46	Ks_so4_ac	4.31e-010	khyd_pr	3.139e-010
47	Kp_DMDS	4.218e-010	Ks_IN	3.131e-010
48	km_MAC_MT	4.003e-010	Ks_H2S_MT	2.611e-010
49	Kpre_H2S	3.678e-010	Ks_SRB_pro	2.256e-010
50	Ks_H2S_DMS	3.412e-010	Ks_DMS	2.188e-010
51	km_DMS	3.31e-010	f_aa_MT	2.086e-010
52	Ks_DMS	3.135e-010	KI_H2S_SRB_ac	1.83e-010
53	Kp_DMS	3.002e-010	kdec_xSRBpro	1.769e-010
54	km_SRB_h2	2.699e-010	KI_h2_c4	1.733e-010
55	Ks_MAC	2.66e-010	km_pro	1.206e-010
56	Ks_H2S_MT	2.611e-010	km_SRB_ac	1.147e-010

57	khyd_li	2.439e-010	Y_SRB_ac	9.008e-011
58	km_h2	2.311e-010	Ka_pro	8.826e-011
59	kdec_xSRBac	2.044e-010	khyd_ch	7.921e-011
60	Ks_SRB_ac	1.749e-010	km_DMS	5.171e-011
61	Ks_h2	1.723e-010	input_S_metal_ion_in	4.125e-011
62	kdec_xSRBh2	1.644e-010	km_c4	3.46e-011
63	Ks_so4_h2	1.369e-010	Ka_bu	3.139e-011
64	km_SRB_pro	9.561e-011	km_MT	2.643e-011
65	Kp_MT	8.453e-011	km_DMDS	2.602e-011
66	Ks_so4_pro	8.041e-011	khyd_li	2.439e-011
67	kdec_xSRBpro	7.075e-011	Kp_DMDS	2.413e-011
68	Ks_SRB_pro	6.655e-011	KI_H2S_SRB_pro	2.343e-011
69	KMT_DMDS	5.032e-011	km_su	2.286e-011
70	km_MT	4.228e-011	Ks_so4_ac	2.155e-011
71	Y_DMS	3.999e-011	KI_H2S_SRB_h2	2.113e-011
72	KI_nh3_ac	3.247e-011	km_aa	2.001e-011
73	Ks_IN	3.131e-011	Ks_DMDS	1.822e-011
74	kLa_hac	2.184e-011	kLa	1.258e-011
75	kLa_hpro	1.885e-011	Kp_DMS	1.25e-011
76	Y_DMDS	1.744e-011	Ka_va	6.813e-012
77	kLa_hva	1.403e-011	km_h2	6.602e-012
78	Ka_pro	1.163e-011	km_MAC_DMS	6.287e-012
79	kLa_hbu	1.092e-011	km_SRB_h2	6.047e-012
80	Ks_MT	1.041e-011	km_SRB_pro	6.021e-012
81	khyd_aro	4.542e-012	km_MAC_MT	5.379e-012
82	kLa_MT	3.172e-012	Kp_MT	3.745e-012
83	Y_MT	3.096e-012	KMT_DMDS	3.423e-012
84	KI_H2S_SRB_ac	1.63e-012	Ks_so4_h2	1.46e-012
85	kLa_H2S	1.627e-012	Ks_so4_pro	1.043e-012
86	Ka_H2S	1.531e-012	kLa_hpro	5.545e-013
87	Ka_ac	1.137e-012	kLa_hva	5.397e-013
88	Ka_va	1.08e-012	kLa_hac	5.2e-013
89	Ka_bu	4.538e-013	Kpre_H2S	4.552e-013
90	kLa_DMS	4.488e-013	khyd_aro	4.542e-013
91	KI_H2S_SRB_h2	3.631e-013	kLa_hbu	3.64e-013
92	KI_H2S_SRB_pro	2.086e-013	kLa_MT	6.609e-014
93	Ks_SRB_h2	1.266e-013	kLa_H2S	2.292e-014
94	kLa_DMDS	1.914e-014	kLa_DMS	1.213e-014
95	KI_h2_fa	4.823e-015	Y_MT	7.633e-015
96	KI_h2_pro	3.74e-015	Y_DMDS	2.992e-015
97	Ka_h2o	2.791e-015	Y_DMS	1.04e-015
98	KI_h2_c4	1.733e-015	kLa_DMDS	5.8e-016
99	kLa_nh3	0	kLa_nh3	0
100	f_aa_H2S	0	f_aa_H2S	0

Variable: S_H2S

Parameter:	Sens AR:	Parameter:	Error Contr.:
	[kmol S.m-3]		[kmol S.m-3]

1	input_S_metal_ion_in	2.999e-005	Ka_h2o	0.0004211
2	input_S_aa_in	1.486e-005	f_aa_DMDS	0.0003501
3	f_aa_MT	1.324e-005	Ka_H2S	0.0001751
4	input_S_so4_in	1.243e-005	Ka_nh4	0.0001447
5	f_pr_xc	1.141e-005	Ka_co2	0.0001347
6	input_X_c_in	6.917e-006	input_S_so4_in	3.788e-005
7	kdis	6.823e-006	Ks_SRB_ac	1.968e-005

8	f_aa_DMS	4.809e-006	f_aa_DMS	1.173e-005
9	Y_ac	4.786e-006	kdis	6.823e-006
10	f_aa_DMDS	4.088e-006	Ks_MAC	6.361e-006
11	km_DMS	3.201e-006	input_S_aa_in	4.127e-006
12	km_DMDS	3.155e-006	f_pr_xc	3.804e-006
13	Ks_DMDS	3.136e-006	kdec_xac	3.771e-006
14	Ks_DMS	3.008e-006	KI_nh3_ac	3.476e-006
15	Kp_DMS	2.946e-006	Ks_MT	3.089e-006
16	Kp_DMDS	2.94e-006	Ks_DMS	2.099e-006
17	km_SRB_ac	2.522e-006	Y_fa	2.019e-006
18	km_MAC_MT	2.016e-006	f_aa_MT	1.996e-006
19	kdec_xac	1.508e-006	Ks_H2S_MT	1.324e-006
20	Ks_so4_ac	1.359e-006	Ks_h2	1.304e-006
21	Ks_H2S_MT	1.324e-006	kdec_xSRBac	1.27e-006
22	Y_SRB_ac	1.323e-006	Y_su	1.084e-006
23	km_MAC_DMS	1.286e-006	Y_ac	9.571e-007
24	Y_fa	1.212e-006	Ks_H2S_DMS	8.439e-007
25	Y_su	1.084e-006	Ks_SRB_h2	6.429e-007
26	Y_aa	1.014e-006	input_X_c_in	5.764e-007
27	Ks_MAC	9.567e-007	km_DMS	5.001e-007
28	Ks_H2S_DMS	8.439e-007	input_S_metal_ion_in	3.748e-007
29	Ka_co2	7.352e-007	Ks_fa	3.377e-007
30	km_ac	6.63e-007	KI_H2S_SRB_ac	3.359e-007
31	Kp_MT	6.072e-007	Ks_SRB_pro	3.304e-007
32	Y_h2	5.895e-007	km_SRB_ac	2.918e-007
33	Kpre_H2S	5.678e-007	km_MT	2.51e-007
34	kdec_xSRBac	5.078e-007	Ks_c4	2.253e-007
35	Y_c4	5.005e-007	Y_SRB_ac	2.242e-007
36	Ks_SRB_ac	4.724e-007	kdec_xaa	1.903e-007
37	Ks_ac	4.682e-007	km_DMDS	1.793e-007
38	km_MT	4.015e-007	Kp_DMDS	1.682e-007
39	KMT_DMDS	2.565e-007	kdec_xsu	1.644e-007
40	Y_pro	2.061e-007	kdec_xfa	1.446e-007
41	km_fa	1.689e-007	Y_aa	1.268e-007
42	km_pro	1.465e-007	Ks_DMDS	1.254e-007
43	km_SRB_pro	1.444e-007	Kp_DMS	1.226e-007
44	Ks_fa	1.351e-007	kdec_xSRBpro	1.049e-007
45	kLa	1.341e-007	Y_h2	9.825e-008
46	Ks_pro	1.226e-007	KI_h2_pro	9.799e-008
47	Ks_so4_pro	1.151e-007	kdec_xh2	9.155e-008
48	km_SRB_h2	1.081e-007	KI_h2_fa	8.418e-008
49	Ks_MT	9.803e-008	Y_c4	8.341e-008
50	Ks_SRB_pro	9.748e-008	km_ac	8.287e-008
51	Ks_h2	9.131e-008	Ks_so4_ac	6.793e-008
52	khyd_pr	9.002e-008	kdec_xSRBh2	6.667e-008
53	kdec_xaa	7.613e-008	kdec_xc4	6.417e-008
54	Ks_so4_h2	7.418e-008	Ks_ac	6.395e-008
55	km_h2	7.374e-008	Ks_su	5.848e-008
56	kdec_xsu	6.578e-008	Y_pro	5.152e-008
57	km_c4	5.982e-008	kdec_xpro	5.002e-008
58	kdec_xfa	5.784e-008	Ks_aa	4.981e-008
59	km_aa	5.246e-008	KI_H2S_SRB_pro	2.922e-008
60	km_su	4.533e-008	Ks_pro	2.895e-008
61	Ks_c4	4.505e-008	km_fa	2.815e-008
62	kdec_xSRBpro	4.196e-008	km_MAC_MT	2.709e-008

63	khyd_ch	3.771e-008	Kp_MT	2.69e-008
64	kdec_xh2	3.662e-008	Ks_IN	2.533e-008
65	kLa_hac	3.435e-008	KMT_DMDS	1.745e-008
66	kLa_hpro	3.103e-008	km_MAC_DMS	1.564e-008
67	kLa_H2S	3.065e-008	KI_h2_c4	1.279e-008
68	Ks_aa	2.988e-008	km_pro	1.127e-008
69	Ks_su	2.924e-008	Ka_ac	9.76e-009
70	kdec_xSRBh2	2.667e-008	km_SRB_pro	9.095e-009
71	kdec_xc4	2.567e-008	khyd_pr	9.002e-009
72	khyd_li	2.381e-008	KI_H2S_SRB_h2	8.848e-009
73	Ka_H2S	2.085e-008	khyd_ch	3.771e-009
74	kLa_hbu	2.06e-008	Ka_pro	3.038e-009
75	kdec_xpro	2.001e-008	km_c4	2.991e-009
76	kLa_hva	1.912e-008	km_SRB_h2	2.421e-009
77	khyd_aro	1.625e-008	khyd_li	2.381e-009
78	kLa_MT	1.278e-008	km_h2	2.107e-009
79	KI_nh3_ac	6.256e-009	Ka_bu	2.06e-009
80	Y_DMS	5.009e-009	khyd_aro	1.625e-009
81	Ka_nh4	3.238e-009	km_su	1.511e-009
82	KI_H2S_SRB_ac	2.992e-009	Ks_so4_pro	1.494e-009
83	Ks_IN	2.533e-009	km_aa	1.049e-009
84	Y_DMDS	1.992e-009	Ka_va	9.814e-010
85	kLa_DMS	6.583e-010	kLa_hpro	9.127e-010
86	Ka_pro	4.005e-010	kLa_hac	8.179e-010
87	Y_MT	3.267e-010	Ks_so4_h2	7.912e-010
88	KI_H2S_SRB_pro	2.603e-010	kLa_hva	7.354e-010
89	Ka_va	1.555e-010	Kpre_H2S	7.027e-010
90	KI_H2S_SRB_h2	1.521e-010	kLa_hbu	6.868e-010
91	kLa_DMDS	5.398e-011	kLa	6.704e-010
92	Ks_SRB_h2	3.215e-011	kLa_H2S	4.317e-010
93	Ka_bu	2.977e-011	kLa_MT	2.662e-010
94	Ka_ac	1.696e-011	kLa_DMS	1.779e-011
95	KI_h2_fa	4.209e-013	kLa_DMDS	1.636e-012
96	KI_h2_pro	3.43e-013	Y_MT	8.055e-013
97	Ka_h2o	1.873e-013	Y_DMDS	3.418e-013
98	KI_h2_c4	1.279e-013	Y_DMS	1.303e-013
99	kLa_nh3	0	kLa_nh3	0
100	f_aa_H2S	0	f_aa_H2S	0

Variable: S_hac

	Parameter:	Sens AR:	Parameter:	Error Contr.:
		[kg COD.m-3]		[kg COD.m-3]
1	Ka_co2	4.554e-007	Ka_h2o	0.000107
2	km_ac	2.623e-008	Ka_co2	8.346e-005
3	Y_ac	2.412e-008	Ka_nh4	3.988e-007
4	Ks_ac	1.883e-008	Ka_ac	1.856e-007
5	kdec_xac	6.887e-009	KI_nh3_ac	8.431e-008
6	input_S_aa_in	4e-009	kdec_xac	1.722e-008
7	input_X_c_in	3.833e-009	Y_ac	4.825e-009
8	Y_aa	5.08e-010	km_ac	3.279e-009
9	Y_su	4.854e-010	Ks_ac	2.571e-009
10	kdis	3.857e-010	input_S_aa_in	1.111e-009
11	Ka_ac	3.226e-010	f_aa_DMDS	8.809e-010
12	f_pr_xc	2.868e-010	Ks_IN	8.6e-010
13	Y_h2	2.778e-010	Y_su	4.854e-010
14	Y_fa	2.536e-010	Y_fa	4.226e-010
15	KI_nh3_ac	1.518e-010	kdis	3.857e-010

16	Y_c4	1.368e-010	input_X_c_in	3.194e-010
17	kdec_xaa	9.859e-011	kdec_xaa	2.465e-010
18	kdec_xfa	9.623e-011	kdec_xfa	2.406e-010
19	kdec_xsu	9.518e-011	kdec_xsu	2.379e-010
20	Ks_IN	8.6e-011	Ka_H2S	1.676e-010
21	Y_pro	7.213e-011	Ks_SRB_ac	1.642e-010
22	kdec_xh2	5.87e-011	kdec_xh2	1.468e-010
23	km_fa	3.98e-011	input_S_so4_in	1.074e-010
24	kdec_xc4	3.948e-011	kdec_xc4	9.87e-011
25	input_S_metal_ion_in	3.931e-011	f_pr_xc	9.561e-011
26	kLa	3.764e-011	Ks_fa	8.035e-011
27	input_S_so4_in	3.523e-011	Ks_h2	7.507e-011
28	Ks_fa	3.214e-011	f_aa_DMS	6.526e-011
29	km_SRB_ac	2.694e-011	Y_aa	6.349e-011
30	f_aa_DMS	2.676e-011	Y_h2	4.63e-011
31	Y_DMS	2.548e-011	Ks_MAC	3.794e-011
32	f_aa_MT	2.511e-011	Ks_SRB_h2	3.718e-011
33	khyd_pr	2.207e-011	kdec_xpro	3.448e-011
34	Kpre_H2S	1.666e-011	Ks_c4	3.384e-011
35	km_pro	1.607e-011	Y_c4	2.28e-011
36	kdec_xpro	1.379e-011	KI_h2_fa	2.043e-011
37	Ks_pro	1.321e-011	Y_pro	1.803e-011
38	Y_DMDS	1.14e-011	Ks_SRB_pro	1.378e-011
39	f_aa_DMDS	1.029e-011	KI_h2_pro	1.141e-011
40	Ka_nh4	8.924e-012	Ks_aa	1.137e-011
41	km_DMS	8.761e-012	Ks_su	1.037e-011
42	Ks_DMS	8.229e-012	Ks_MT	9.615e-012
43	Kp_DMS	8.144e-012	KI_H2S_SRB_ac	7.53e-012
44	Ks_so4_ac	7.966e-012	km_fa	6.633e-012
45	km_MAC_MT	7.948e-012	kdec_xSRBac	6.608e-012
46	km_c4	7.316e-012	Ks_DMS	5.743e-012
47	Ks_aa	6.821e-012	Ks_H2S_MT	4.151e-012
48	Ks_c4	6.768e-012	f_aa_MT	3.784e-012
49	km_aa	6.767e-012	kdec_xSRBh2	3.253e-012
50	km_MAC_DMS	6.606e-012	Ks_pro	3.12e-012
51	Y_SRB_ac	6.509e-012	km_SRB_ac	3.117e-012
52	khyd_ch	5.951e-012	kdec_xSRBpro	2.55e-012
53	Ks_MAC	5.706e-012	Ks_H2S_DMS	2.475e-012
54	km_SRB_pro	5.661e-012	KI_H2S_SRB_pro	2.436e-012
55	km_su	5.419e-012	khyd_pr	2.207e-012
56	Ks_h2	5.255e-012	KI_h2_c4	1.924e-012
57	Ks_su	5.184e-012	Ka_pro	1.751e-012
58	km_DMDS	4.782e-012	km_DMS	1.369e-012
59	Ks_DMDS	4.753e-012	km_pro	1.236e-012
60	Kp_DMDS	4.514e-012	Y_SRB_ac	1.103e-012
61	km_h2	4.207e-012	Ka_bu	7.937e-013
62	Ks_H2S_MT	4.151e-012	km_MT	7.812e-013
63	khyd_li	4.142e-012	khyd_ch	5.951e-013
64	Ks_SRB_pro	4.065e-012	input_S_metal_ion_in	4.914e-013
65	Ks_SRB_ac	3.942e-012	KI_H2S_SRB_h2	4.798e-013
66	km_SRB_h2	3.921e-012	khyd_li	4.142e-013
67	Ks_so4_h2	2.885e-012	Ks_so4_ac	3.983e-013
68	Ks_so4_pro	2.688e-012	km_c4	3.658e-013
69	kdec_xSRBac	2.643e-012	km_SRB_pro	3.565e-013

70	Ks_H2S_DMS	2.475e-012	Kp_DMS	3.391e-013
71	Y_MT	1.965e-012	km_DMDS	2.717e-013
72	kdec_xSRBh2	1.301e-012	Kp_DMDS	2.582e-013
73	km_MT	1.25e-012	Ka_va	2.086e-013
74	Kp_MT	1.194e-012	Ks_DMDS	1.901e-013
75	kdec_xSRBpro	1.02e-012	kLa	1.882e-013
76	kLa_hac	9.129e-013	km_su	1.806e-013
77	kLa_hpro	5.971e-013	km_aa	1.353e-013
78	kLa_hbu	4.547e-013	km_h2	1.202e-013
79	kLa_hva	4.211e-013	km_MAC_MT	1.068e-013
80	KMT_DMDS	3.432e-013	km_SRB_h2	8.783e-014
81	Ks_MT	3.051e-013	km_MAC_DMS	8.03e-014
82	kLa_MT	2.875e-013	Kp_MT	5.29e-014
83	Ka_pro	2.308e-013	Ks_so4_pro	3.487e-014
84	khyd_aro	1.986e-013	Ks_so4_h2	3.077e-014
85	KI_H2S_SRB_ac	6.706e-014	KMT_DMDS	2.334e-014
86	Ka_h2o	4.759e-014	kLa_hac	2.173e-014
87	Ka_va	3.306e-014	Kpre_H2S	2.062e-014
88	kLa_H2S	2.659e-014	khyd_aro	1.986e-014
89	KI_H2S_SRB_pro	2.169e-014	kLa_hpro	1.756e-014
90	Ka_H2S	1.996e-014	kLa_hva	1.62e-014
91	Ka_bu	1.147e-014	kLa_hbu	1.516e-014
92	kLa_DMS	1.015e-014	kLa_MT	5.99e-015
93	KI_H2S_SRB_h2	8.247e-015	Y_MT	4.845e-015
94	Ks_SRB_h2	1.859e-015	Y_DMDS	1.956e-015
95	kLa_DMDS	2.426e-016	Y_DMS	6.628e-016
96	KI_h2_fa	1.021e-016	kLa_H2S	3.745e-016
97	KI_h2_pro	3.993e-017	kLa_DMS	2.743e-016
98	KI_h2_c4	1.924e-017	kLa_DMDS	7.35e-018
99	kLa_nh3	0	kLa_nh3	0
100	f_aa_H2S	0	f_aa_H2S	0

Variable: S_hbu

Parameter:	Sens AR:	Parameter:	Error Contr.:	
	[kg COD.m-3]		[kg COD.m-3]	
1	km_c4	1.526e-009	Ka_h2o	2.695e-005
2	Ks_c4	1.431e-009	Ka_co2	1.062e-007
3	Y_c4	1.346e-009	Ka_nh4	1.456e-008
4	Ka_co2	5.793e-010	Ka_bu	1.251e-008
5	input_S_aa_in	4.028e-010	Ks_c4	7.154e-009
6	kdec_xc4	3.737e-010	kdec_xc4	9.342e-010
7	Ka_bu	1.809e-010	Ks_h2	5.571e-010
8	input_X_c_in	1.025e-010	KI_h2_c4	3.829e-010
9	Y_fa	7.513e-011	Y_c4	2.244e-010
10	f_pr_xc	6.781e-011	Y_fa	1.252e-010
11	Y_ac	6.256e-011	input_S_aa_in	1.119e-010
12	Y_aa	4.286e-011	f_aa_DMDS	1.092e-010
13	km_h2	4.004e-011	km_c4	7.628e-011
14	Ks_h2	3.9e-011	Ks_IN	5.016e-011
15	Y_su	3.028e-011	KI_nh3_ac	3.729e-011
16	kdis	1.426e-011	kdec_xac	3.405e-011
17	kdec_xac	1.362e-011	Y_su	3.028e-011
18	km_ac	1.177e-011	Ka_H2S	2.714e-011
19	Y_h2	1.165e-011	f_pr_xc	2.26e-011
20	Y_pro	8.612e-012	kdec_xfa	2.148e-011
21	kdec_xfa	8.594e-012	kdec_xsu	2.137e-011
22	kdec_xsu	8.548e-012	kdec_xaa	2.1e-011

23 Ks_ac 8.466e-012 input_S_so4_in1.929e-011
 24 kdec_xaa 8.401e-012 Ks_SRB_ac 1.697e-011
 25 input_S_metal_ion_in
 6.901e-012 kdis 1.426e-011
 26 input_S_so4_in6.331e-012 Y_ac 1.251e-011
 27 kLa 5.915e-012 kdec_xh2 1.25e-011
 28 Ks_IN 5.016e-012 input_X_c_in 8.545e-012
 29 kdec_xh2 5e-012 Ks_SRB_h2 5.859e-012
 30 f_aa_MT 2.929e-012 Y_aa 5.357e-012
 31 khyd_pr 2.841e-012 kdec_xpro 4.953e-012
 32 km_pro 2.487e-012 Ks_MAC 3.757e-012
 33 km_SRB_ac 2.328e-012 f_aa_DMS 3.155e-012
 34 Ks_pro 2.128e-012 Ks_su 2.667e-012
 35 kdec_xpro 1.981e-012 Ks_fa 2.389e-012
 36 khyd_ch 1.589e-012 Y_pro 2.153e-012
 37 km_su 1.36e-012 Y_h2 1.942e-012
 38 Ks_su 1.333e-012 KI_h2_pro 1.695e-012
 39 f_aa_DMS 1.294e-012 Ka_ac 1.594e-012
 40 f_aa_DMDS 1.276e-012 Ks_aa 1.533e-012
 41 km_fa 1.204e-012 km_ac 1.471e-012
 42 Kpre_H2S 1.179e-012 Ks_ac 1.156e-012
 43 km_MAC_DMS 1.096e-012 km_h2 1.144e-012
 44 Ks_so4_ac 9.735e-013 kdec_xSRBac 7.65e-013
 45 Ks_fa 9.557e-013 Ks_H2S_DMS 7.191e-013
 46 km_aa 9.489e-013 kdec_xSRBh2 6.605e-013
 47 km_DMDS 9.299e-013 Ks_MT 6.132e-013
 48 Ks_DMDS 9.25e-013 KI_h2_fa 5.891e-013
 49 Ks_aa 9.197e-013 Ks_H2S_MT 5.467e-013
 50 Y_SRB_ac 8.63e-013 Ks_pro 5.024e-013
 51 Kp_DMDS 8.547e-013 KI_H2S_SRB_ac 4.584e-013
 52 km_MAC_MT 8.438e-013 f_aa_MT 4.415e-013
 53 Ks_H2S_DMS 7.191e-013 Ks_SRB_pro 4.39e-013
 54 km_DMS 6.244e-013 Ks_DMS 4.128e-013
 55 km_SRB_h2 6.112e-013 khyd_pr 2.841e-013
 56 Ks_DMS 5.916e-013 km_SRB_ac 2.693e-013
 57 Ks_MAC 5.65e-013 Ka_pro 2.306e-013
 58 Kp_DMS 5.645e-013 km_fa 2.007e-013
 59 Ks_H2S_MT 5.467e-013 km_pro 1.913e-013
 60 Ks_SRB_ac 4.072e-013 kdec_xSRBpro 1.62e-013
 61 Ks_so4_h2 3.406e-013 khyd_ch 1.589e-013
 62 Ka_nh4 3.258e-013 Y_SRB_ac 1.463e-013
 63 kdec_xSRBac 3.06e-013 km_DMS 9.756e-014
 64 kdec_xSRBh2 2.642e-013 input_S_metal_ion_in
 8.626e-014
 65 khyd_li 2.007e-013 Ka_va 6.25e-014
 66 km_SRB_pro 1.892e-013 km_DMDS 5.284e-014
 67 Ks_so4_pro 1.858e-013 KI_H2S_SRB_h2 5.048e-014
 68 Kp_MT 1.77e-013 km_MT 4.936e-014
 69 Ks_SRB_pro 1.295e-013 KI_H2S_SRB_pro 4.899e-014
 70 KMT_DMDS 1.091e-013 Kp_DMDS 4.89e-014
 71 km_MT 7.898e-014 Ks_so4_ac 4.868e-014
 72 kLa_hac 6.943e-014 km_su 4.534e-014
 73 KI_nh3_ac 6.711e-014 Ks_DMDS 3.7e-014
 74 kdec_xSRBpro 6.482e-014 kLa 2.958e-014
 75 kLa_hpro 5.392e-014 Kp_DMS 2.35e-014
 76 Y_DMS 5.007e-014 khyd_li 2.007e-014

77	kLa_hbu	3.777e-014	km_aa	1.898e-014
78	kLa_hva	3.433e-014	km_SRB_h2	1.369e-014
79	Ka_pro	3.039e-014	km_MAC_DMS	1.332e-014
80	Y_DMDS	2.287e-014	km_SRB_pro	1.192e-014
81	kLa_MT	2.213e-014	km_MAC_MT	1.134e-014
82	Ks_MT	1.946e-014	Kp_MT	7.84e-015
83	Ka_h2o	1.199e-014	KMT_DMDS	7.421e-015
84	khyd_aro	9.917e-015	Ks_so4_h2	3.633e-015
85	Ka_va	9.906e-015	Ks_so4_pro	2.411e-015
86	KI_H2S_SRB_ac	4.082e-015	kLa_hac	1.653e-015
87	Y_MT	3.873e-015	kLa_hpro	1.586e-015
88	KI_h2_c4	3.829e-015	Kpre_H2S	1.46e-015
89	kLa_H2S	3.418e-015	kLa_hva	1.321e-015
90	Ka_H2S	3.233e-015	kLa_hbu	1.259e-015
91	Ka_ac	2.769e-015	khyd_aro	9.917e-016
92	kLa_DMS	1.067e-015	kLa_MT	4.611e-016
93	KI_H2S_SRB_h2	8.677e-016	kLa_H2S	4.814e-017
94	KI_H2S_SRB_pro	4.363e-016	kLa_DMS	2.885e-017
95	Ks_SRB_h2	2.929e-016	Y_MT	9.55e-018
96	kLa_DMDS	4.226e-017	Y_DMDS	3.924e-018
97	KI_h2_pro	5.934e-018	Y_DMS	1.303e-018
98	KI_h2_fa	2.946e-018	kLa_DMDS	1.281e-018
99	kLa_nh3	0	kLa_nh3	0
100	f_aa_H2S	0	f_aa_H2S	0

Variable: S_hpro

Parameter:	Sens AR:	Parameter:	Error Contr.:	
	[kg COD.m-3]		[kg COD.m-3]	
1	km_pro	6.028e-009	Ka_h2o	1.423e-005
2	Y_pro	5.354e-009	Ka_co2	3.816e-007
3	Ks_pro	5.144e-009	Ka_nh4	5.198e-008
4	Ka_pro	2.935e-009	Ka_pro	2.227e-008
5	Ka_co2	2.082e-009	Ks_h2	6.078e-009
6	kdec_xpro	1.503e-009	KI_h2_pro	4.105e-009
7	input_S_aa_in	1.33e-009	kdec_xpro	3.757e-009
8	input_X_c_in	4.338e-010	Y_pro	1.339e-009
9	km_h2	4.313e-010	Ks_pro	1.215e-009
10	Ks_h2	4.254e-010	km_pro	4.637e-010
11	Y_h2	2.983e-010	Y_fa	4.525e-010
12	Y_fa	2.715e-010	f_aa_DMDS	3.946e-010
13	Y_ac	2.269e-010	input_S_aa_in	3.694e-010
14	Y_su	1.398e-010	kdec_xh2	2.229e-010
15	Y_aa	1.327e-010	Ks_IN	2.082e-010
16	f_pr_xc	1.117e-010	Ks_SRB_ac	1.496e-010
17	Y_c4	9.231e-011	Y_su	1.398e-010
18	kdec_xh2	8.915e-011	KI_nh3_ac	1.391e-010
19	kdis	5.932e-011	kdec_xac	1.229e-010
20	kdec_xac	4.915e-011	Ka_H2S	9.833e-011
21	km_ac	4.193e-011	kdec_xfa	7.804e-011
22	kdec_xfa	3.122e-011	kdec_xsu	7.706e-011
23	kdec_xsu	3.082e-011	kdec_xaa	7.646e-011
24	kdec_xaa	3.058e-011	input_S_so4_in	7.027e-011
25	Ks_ac	3.016e-011	kdis	5.932e-011
26	input_S_metal_ion_in	2.493e-011	Y_h2	4.972e-011
27	input_S_so4_in	2.306e-011	Y_ac	4.537e-011
28	kLa	2.13e-011	f_pr_xc	3.722e-011

29	Ks_IN	2.082e-011	input_X_c_in	3.615e-011
30	km_SRB_ac	1.754e-011	kdec_xc4	3.297e-011
31	kdec_xc4	1.319e-011	Ks_SRB_pro	3.178e-011
32	km_SRB_pro	1.259e-011	Ks_c4	2.158e-011
33	f_aa_MT	1.058e-011	Ks_SRB_h2	2.115e-011
34	Ks_SRB_pro	9.374e-012	Y_aa	1.659e-011
35	Kpre_H2S	9.328e-012	Y_c4	1.539e-011
36	khyd_pr	8.697e-012	Ks_MAC	1.362e-011
37	khyd_ch	5.386e-012	km_h2	1.232e-011
38	Ks_so4_ac	4.796e-012	f_aa_DMS	1.14e-011
39	f_aa_DMS	4.673e-012	Ks_su	8.894e-012
40	f_aa_DMDS	4.609e-012	Ks_fa	8.637e-012
41	km_su	4.577e-012	KI_H2S_SRB_ac	6.529e-012
42	km_c4	4.516e-012	Ka_ac	5.725e-012
43	Ks_su	4.447e-012	KI_H2S_SRB_pro	5.665e-012
44	km_fa	4.347e-012	km_ac	5.241e-012
45	Ks_c4	4.315e-012	kdec_xSRBpro	4.99e-012
46	km_MAC_DMS	3.97e-012	Ks_aa	4.674e-012
47	Y_SRB_ac	3.76e-012	Ks_ac	4.119e-012
48	Ks_so4_pro	3.667e-012	kdec_xSRBac	3.688e-012
49	Ks_SRB_ac	3.592e-012	Ks_H2S_DMS	2.602e-012
50	Ks_fa	3.455e-012	kdec_xSRBh2	2.377e-012
51	km_DMDS	3.359e-012	Ks_MT	2.215e-012
52	Ks_DMDS	3.341e-012	KI_h2_fa	2.129e-012
53	Kp_DMDS	3.087e-012	km_SRB_ac	2.029e-012
54	km_MAC_MT	3.058e-012	Ks_H2S_MT	1.979e-012
55	km_aa	2.888e-012	f_aa_MT	1.595e-012
56	Ks_aa	2.805e-012	Ks_DMS	1.492e-012
57	Ks_H2S_DMS	2.602e-012	KI_h2_c4	1.188e-012
58	km_DMS	2.256e-012	khyd_pr	8.697e-013
59	km_SRB_h2	2.215e-012	km_SRB_pro	7.925e-013
60	Ks_DMS	2.138e-012	km_fa	7.244e-013
61	Ks_MAC	2.048e-012	Y_SRB_ac	6.372e-013
62	Kp_DMS	2.04e-012	khyd_ch	5.386e-013
63	kdec_xSRBpro	1.996e-012	km_DMS	3.525e-013
64	Ks_H2S_MT	1.979e-012	Ka_bu	3.171e-013
65	Ks_so4_h2	1.571e-012	input_S_metal_ion_in	3.116e-013
66	kdec_xSRBac	1.475e-012	KI_H2S_SRB_h2	2.527e-013
67	Ka_nh4	1.163e-012	Ks_so4_ac	2.398e-013
68	kdec_xSRBh2	9.507e-013	km_c4	2.258e-013
69	Kp_MT	7.425e-013	km_DMDS	1.909e-013
70	khyd_li	7.366e-013	km_MT	1.784e-013
71	kLa_hac	4.861e-013	Kp_DMDS	1.766e-013
72	KMT_DMDS	3.943e-013	km_su	1.526e-013
73	kLa_hpro	3.652e-013	Ks_DMDS	1.336e-013
74	kLa_hva	2.959e-013	kLa	1.065e-013
75	km_MT	2.854e-013	Ka_va	1.063e-013
76	KI_nh3_ac	2.505e-013	Kp_DMS	8.494e-014
77	kLa_hbu	2.422e-013	khyd_li	7.366e-014
78	Y_DMS	1.807e-013	km_aa	5.776e-014
79	Y_DMDS	8.232e-014	km_SRB_h2	4.962e-014
80	kLa_MT	8.022e-014	km_MAC_DMS	4.827e-014
81	Ks_MT	7.03e-014	Ks_so4_pro	4.757e-014
82	KI_H2S_SRB_ac	5.814e-014	km_MAC_MT	4.11e-014
83	KI_H2S_SRB_pro	5.046e-014	Kp_MT	3.29e-014

84	khyd_aro	3.629e-014	KMT_DMDS	2.682e-014
85	Ka_va	1.685e-014	Ks_so4_h2	1.676e-014
86	KI_h2_pro	1.437e-014	kLa_hac	1.157e-014
87	Y_MT	1.396e-014	Kpre_H2S	1.154e-014
88	kLa_H2S	1.24e-014	kLa_hva	1.138e-014
89	Ka_H2S	1.171e-014	kLa_hpro	1.074e-014
90	Ka_ac	9.95e-015	kLa_hbu	8.074e-015
91	kLa_DMS	8.984e-015	khyd_aro	3.629e-015
92	Ka_h2o	6.329e-015	kLa_MT	1.671e-015
93	Ka_bu	4.584e-015	kLa_DMS	2.428e-016
94	KI_H2S_SRB_h2	4.344e-015	kLa_H2S	1.746e-016
95	Ks_SRB_h2	1.058e-015	Y_MT	3.442e-017
96	kLa_DMDS	2.631e-016	Y_DMDS	1.412e-017
97	KI_h2_c4	1.188e-017	kLa_DMDS	7.973e-018
98	KI_h2_fa	1.065e-017	Y_DMS	4.701e-018
99	kLa_nh3	0	kLa_nh3	0
100	f_aa_H2S	0	f_aa_H2S	0

Variable: S_hva

Parameter:	Sens AR:	Parameter:	Error Contr.:	
	[kg COD.m-3]		[kg COD.m-3]	
1	km_c4	9.127e-010	Ka_h2o	1.625e-005
2	Ks_c4	8.615e-010	Ka_co2	6.401e-008
3	Y_c4	8.054e-010	Ka_nh4	8.78e-009
4	Ka_va	5.295e-010	Ks_c4	4.308e-009
5	Ka_co2	3.493e-010	Ka_va	3.341e-009
6	kdec_xc4	2.234e-010	kdec_xc4	5.585e-010
7	input_S_aa_in	1.934e-010	Ks_h2	3.332e-010
8	f_pr_xc	7.234e-011	KI_h2_c4	2.291e-010
9	input_X_c_in	6.427e-011	Y_c4	1.342e-010
10	Y_fa	4.522e-011	Y_fa	7.536e-011
11	Y_ac	3.761e-011	f_aa_DMDS	6.586e-011
12	Y_su	3.028e-011	input_S_aa_in	5.373e-011
13	km_h2	2.396e-011	km_c4	4.564e-011
14	Ks_h2	2.332e-011	Y_su	3.028e-011
15	Y_aa	1.781e-011	Ks_IN	3.001e-011
16	kdis	9.12e-012	f_pr_xc	2.411e-011
17	kdec_xac	8.293e-012	KI_nh3_ac	2.248e-011
18	km_ac	7.093e-012	kdec_xac	2.073e-011
19	Y_h2	6.912e-012	Ka_H2S	1.636e-011
20	kdec_xfa	5.237e-012	kdec_xfa	1.309e-011
21	Y_pro	5.177e-012	kdec_xaa	1.287e-011
22	kdec_xaa	5.149e-012	kdec_xsu	1.285e-011
23	kdec_xsu	5.142e-012	input_S_so4_in	1.163e-011
24	Ks_ac	5.104e-012	Ks_SRB_ac	1.023e-011
25	input_S_metal_ion_in	4.161e-012	kdis	9.12e-012
26	input_S_so4_in	3.817e-012	Y_ac	7.521e-012
27	kLa	3.567e-012	kdec_xh2	7.316e-012
28	Ks_IN	3.001e-012	input_X_c_in	5.356e-012
29	kdec_xh2	2.927e-012	Ks_SRB_h2	3.531e-012
30	f_aa_MT	1.766e-012	kdec_xpro	3.014e-012
31	km_pro	1.499e-012	Ks_MAC	2.264e-012
32	khyd_pr	1.431e-012	Y_aa	2.226e-012
33	km_SRB_ac	1.403e-012	f_aa_DMS	1.902e-012
34	Ks_pro	1.282e-012	Ks_fa	1.436e-012
35	kdec_xpro	1.206e-012	Y_pro	1.294e-012

36	f_aa_DMS	7.801e-013	Y_h2	1.152e-012
37	f_aa_DMDS	7.691e-013	KI_h2_pro	1.021e-012
38	km_fa	7.242e-013	Ks_su	9.624e-013
39	Kpre_H2S	7.076e-013	Ka_ac	9.608e-013
40	km_MAC_DMS	6.607e-013	km_ac	8.866e-013
41	Ks_so4_ac	5.869e-013	Ks_aa	7.793e-013
42	Ks_fa	5.745e-013	Ks_ac	6.97e-013
43	khyd_ch	5.659e-013	km_h2	6.845e-013
44	km_DMDS	5.606e-013	kdec_xSRBac	4.609e-013
45	Ks_DMDS	5.576e-013	Ks_H2S_DMS	4.335e-013
46	Y_SRB_ac	5.201e-013	kdec_xSRBh2	3.984e-013
47	Kp_DMDS	5.153e-013	Ks_MT	3.696e-013
48	km_MAC_MT	5.086e-013	KI_h2_fa	3.542e-013
49	km_su	4.933e-013	Ks_H2S_MT	3.296e-013
50	km_aa	4.845e-013	Ks_pro	3.027e-013
51	Ks_su	4.812e-013	KI_H2S_SRB_ac	2.762e-013
52	Ks_aa	4.676e-013	f_aa_MT	2.662e-013
53	Ks_H2S_DMS	4.335e-013	Ks_SRB_pro	2.649e-013
54	km_DMS	3.764e-013	Ks_DMS	2.488e-013
55	km_SRB_h2	3.684e-013	km_SRB_ac	1.623e-013
56	Ks_DMS	3.566e-013	khyd_pr	1.431e-013
57	Ks_MAC	3.406e-013	Ka_bu	1.429e-013
58	Kp_DMS	3.403e-013	Ka_pro	1.39e-013
59	Ks_H2S_MT	3.296e-013	km_fa	1.207e-013
60	Ks_SRB_ac	2.454e-013	km_pro	1.153e-013
61	Ks_so4_h2	2.053e-013	kdec_xSRBpro	9.746e-014
62	Ka_nh4	1.964e-013	Y_SRB_ac	8.815e-014
63	kdec_xSRBac	1.844e-013	km_DMS	5.881e-014
64	kdec_xSRBh2	1.593e-013	khyd_ch	5.659e-014
65	km_SRB_pro	1.141e-013	input_S_metal_ion_in	5.201e-014
66	Ks_so4_pro	1.119e-013	km_DMDS	3.185e-014
67	Kp_MT	1.066e-013	KI_H2S_SRB_h2	3.043e-014
68	khyd_li	1.013e-013	km_MT	2.976e-014
69	Ks_SRB_pro	7.815e-014	KI_H2S_SRB_pro	2.959e-014
70	KMT_DMDS	6.577e-014	Kp_DMDS	2.948e-014
71	km_MT	4.761e-014	Ks_so4_ac	2.935e-014
72	kLa_hac	4.171e-014	Ks_DMDS	2.231e-014
73	KI_nh3_ac	4.046e-014	kLa	1.784e-014
74	kdec_xSRBpro	3.898e-014	km_su	1.644e-014
75	kLa_hpro	3.245e-014	Kp_DMS	1.417e-014
76	Y_DMS	3.031e-014	khyd_li	1.013e-014
77	kLa_hbu	2.274e-014	km_aa	9.69e-015
78	kLa_hva	2.072e-014	km_SRB_h2	8.254e-015
79	Ka_pro	1.833e-014	km_MAC_DMS	8.032e-015
80	Y_DMDS	1.384e-014	km_SRB_pro	7.188e-015
81	kLa_MT	1.329e-014	km_MAC_MT	6.835e-015
82	Ks_MT	1.173e-014	Kp_MT	4.725e-015
83	Ka_h2o	7.228e-015	KMT_DMDS	4.474e-015
84	khyd_aro	5.976e-015	Ks_so4_h2	2.19e-015
85	KI_H2S_SRB_ac	2.46e-015	Ks_so4_pro	1.452e-015
86	Y_MT	2.345e-015	kLa_hac	9.93e-016
87	KI_h2_c4	2.291e-015	kLa_hpro	9.544e-016
88	Ka_bu	2.065e-015	Kpre_H2S	8.757e-016
89	kLa_H2S	2.061e-015	kLa_hva	7.97e-016
90	Ka_H2S	1.949e-015	kLa_hbu	7.579e-016

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91 Ka_ac      1.67e-015   khyd_aro    5.976e-016
92 kLa_DMS    6.431e-016   kLa_MT     2.769e-016
93 KI_H2S_SRB_h2 5.23e-016   kLa_H2S    2.902e-017
94 KI_H2S_SRB_pro2.635e-016   kLa_DMS    1.738e-017
95 Ks_SRB_h2   1.766e-016   Y_MT       5.78e-018
96 kLa_DMDS    2.548e-017   Y_DMDS     2.375e-018
97 KI_h2_pro   3.575e-018   Y_DMS      7.885e-019
98 KI_h2_fa    1.771e-018   kLa_DMDS   7.72e-019
99 kLa_nh3     0          kLa_nh3     0
100 f_aa_H2S   0          f_aa_H2S    0
Variable: S_MT_liq
Parameter: Sens AR:      Parameter: Error Contr.:
          [kmol .m-3]      [kmol .m-3]
1 KMT_DMDS    3.046e-007   Ka_h2o      5.117e-006
2 f_aa_MT     2.838e-007   Ka_nh4      3.732e-006
3 input_S_aa_in 2.436e-007   f_aa_DMDS   2.201e-006
4 input_S_metal_ion_in
  1.343e-007   Ka_H2S     5.126e-007
5 input_X_c_in 1.318e-007   input_S_so4_in1.558e-007
6 f_pr_xc     1.173e-007   kdis        1.1e-007
7 kdis        1.1e-007   Ks_MAC      7.153e-008
8 Kp_MT       7.329e-008   input_S_aa_in 6.767e-008
9 input_S_so4_in5.112e-008   Ks_MT       6.634e-008
10 km_MAC_MT  4.299e-008   Ks_SRB_ac   6.098e-008
11 Ks_H2S_MT  2.864e-008   f_aa_DMS    5.109e-008
12 f_aa_DMDS  2.571e-008   Ka_co2      4.327e-008
13 Y_aa       2.433e-008   f_aa_MT     4.276e-008
14 f_aa_DMS   2.095e-008   f_pr_xc     3.91e-008
15 km_DMDS    1.505e-008   Ks_H2S_MT   2.864e-008
16 Ks_DMDS    1.497e-008   KMT_DMDS    2.072e-008
17 Y_ac       1.475e-008   input_X_c_in 1.098e-008
18 km_DMS     1.419e-008   KI_nh3_ac   1.085e-008
19 Kp_DMDS    1.403e-008   kdec_xac    9.664e-009
20 Ks_DMS     1.344e-008   Ks_DMS      9.379e-009
21 Kp_DMS     1.306e-008   Y_fa        6.824e-009
22 Ks_MAC     1.076e-008   kdec_xSRBac 6.343e-009
23 km_MT      8.615e-009   km_MT       5.384e-009
24 km_SRB_ac  7.144e-009   Ks_h2       4.528e-009
25 Y_SRB_ac   6.421e-009   Ks_H2S_DMS  4.109e-009
26 Ks_so4_ac  5.951e-009   Y_su        3.709e-009
27 km_MAC_DMS 5.8e-009      Kp_MT       3.247e-009
28 Ks_H2S_DMS 4.109e-009   Y_aa        3.041e-009
29 Y_fa       4.094e-009   kdec_xfa    2.961e-009
30 kdec_xac    3.866e-009   Y_ac        2.951e-009
31 Y_su       3.709e-009   kdec_xaa    2.912e-009
32 kdec_xSRBac 2.537e-009   kdec_xsu    2.856e-009
33 Ks_MT       2.105e-009   km_DMS      2.218e-009
34 Y_h2       2.012e-009   kdec_xh2    1.704e-009
35 km_ac      1.971e-009   input_S_metal_ion_in
  1.679e-009
36 Kpre_H2S   1.875e-009   Ks_SRB_h2   1.36e-009
37 Y_c4       1.681e-009   kdec_xc4    1.216e-009
38 Ks_SRB_ac  1.463e-009   Y_SRB_ac    1.088e-009
39 Ks_ac      1.365e-009   km_DMDS     8.553e-010
40 khyd_pr    1.35e-009   km_SRB_ac   8.265e-010
41 kdec_xfa   1.185e-009   Kp_DMDS     8.027e-010

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42	kdec_xaa	1.165e-009	Ks_aa	7.081e-010
43	kdec_xsu	1.143e-009	Ks_SRB_pro	6.345e-010
44	Y_pro	7.193e-010	Ks_DMDS	5.99e-010
45	kLa_MT	7.15e-010	km_MAC_MT	5.778e-010
46	kdec_xh2	6.816e-010	kdec_xpro	5.55e-010
47	kdec_xc4	4.865e-010	Kp_DMS	5.437e-010
48	Ks_aa	4.249e-010	kdec_xSRBpro	5.059e-010
49	km_aa	4.019e-010	Ks_fa	4.036e-010
50	km_pro	3.925e-010	Y_h2	3.353e-010
51	Ks_so4_pro	3.815e-010	kdec_xSRBh2	3.05e-010
52	kLa	3.544e-010	Ks_so4_ac	2.975e-010
53	Ks_pro	3.206e-010	Y_c4	2.802e-010
54	Ks_h2	3.169e-010	KI_h2_pro	2.558e-010
55	km_SRB_pro	3.032e-010	Ks_c4	2.501e-010
56	km_SRB_h2	2.857e-010	km_ac	2.463e-010
57	Ka_co2	2.361e-010	Ks_ac	1.865e-010
58	Ks_so4_h2	2.327e-010	KI_H2S_SRB_ac	1.854e-010
59	kdec_xpro	2.22e-010	Y_pro	1.798e-010
60	km_h2	2.123e-010	khyd_pr	1.35e-010
61	kdec_xSRBpro	2.024e-010	KI_h2_fa	1.006e-010
62	km_fa	1.998e-010	Ks_pro	7.571e-011
63	Ks_SRB_pro	1.872e-010	km_MAC_DMS	7.051e-011
64	khyd_aro	1.804e-010	Ks_su	6.806e-011
65	Ks_fa	1.614e-010	Ks_IN	6.24e-011
66	kdec_xSRBh2	1.22e-010	km_fa	3.33e-011
67	kLa_hac	9.857e-011	km_pro	3.019e-011
68	Ka_nh4	8.35e-011	km_SRB_pro	1.909e-011
69	kLa_hpro	8.27e-011	khyd_aro	1.804e-011
70	km_c4	7.283e-011	KI_H2S_SRB_pro	1.499e-011
71	kLa_hbu	7.088e-011	kLa_MT	1.489e-011
72	km_su	6.803e-011	KI_h2_c4	1.456e-011
73	kLa_H2S	6.596e-011	KI_H2S_SRB_h2	9.905e-012
74	Ka_H2S	6.106e-011	km_aa	8.038e-012
75	khyd_ch	5.789e-011	km_SRB_h2	6.401e-012
76	Ks_c4	5.002e-011	km_h2	6.066e-012
77	Ks_su	3.403e-011	khyd_ch	5.789e-012
78	khyd_li	3.387e-011	Ks_so4_pro	4.949e-012
79	kLa_hva	3.089e-011	Ka_ac	4.032e-012
80	Y_DMDS	2.297e-011	Ka_bu	3.754e-012
81	KI_nh3_ac	1.953e-011	km_c4	3.642e-012
82	Y_DMS	1.491e-011	khyd_li	3.387e-012
83	Ks_IN	6.24e-012	Ka_pro	2.856e-012
84	KI_H2S_SRB_ac	1.651e-012	Ks_so4_h2	2.482e-012
85	Y_MT	1.033e-012	kLa_hpro	2.432e-012
86	kLa_DMS	9.254e-013	kLa_hbu	2.363e-012
87	Ka_pro	3.765e-013	kLa_hac	2.347e-012
88	Ka_va	2.708e-013	Kpre_H2S	2.321e-012
89	kLa_DMDS	2.328e-013	km_su	2.268e-012
90	KI_H2S_SRB_h2	1.702e-013	kLa	1.772e-012
91	KI_H2S_SRB_pro	1.335e-013	Ka_va	1.709e-012
92	Ks_SRB_h2	6.801e-014	kLa_hva	1.188e-012
93	Ka_bu	5.427e-014	kLa_H2S	9.29e-013
94	Ka_ac	7.008e-015	kLa_DMS	2.501e-014
95	Ka_h2o	2.276e-015	kLa_DMDS	7.056e-015
96	KI_h2_pro	8.954e-016	Y_DMDS	3.941e-015
97	KI_h2_fa	5.029e-016	Y_MT	2.548e-015

98	KI_h2_c4	1.456e-016	Y_DMS	3.879e-016
99	kLa_nh3	0	kLa_nh3	0
100	f_aa_H2S	0	f_aa_H2S	0

Variable: S_DMDS_liq

	Parameter:	Sens AR:	Parameter:	Error Contr.:
		[kmol.m-3]		[kmol.m-3]
1	kdis	3.198e-007	f_aa_DMDS	7.337e-006
2	Kp_DMDS	2.81e-007	Ka_h2o	4.403e-006
3	input_S_aa_in	1.954e-007	Ka_nh4	3.336e-006
4	f_aa_MT	1.879e-007	Ka_co2	4.762e-007
5	input_X_c_in	1.621e-007	Ka_H2S	3.434e-007
6	f_pr_xc	1.265e-007	kdis	3.198e-007
7	input_S_metal_ion_in	8.648e-008	input_S_so4_in	1.004e-007
8	f_aa_DMDS	8.569e-008	input_S_aa_in	5.427e-008
9	Y_ac	6.331e-008	Ks_MAC	4.898e-008
10	km_DMDS	6.198e-008	Ks_MT	4.394e-008
11	Ks_DMDS	6.162e-008	f_pr_xc	4.215e-008
12	KMT_DMDS	5.84e-008	Ks_SRB_ac	3.679e-008
13	Kp_MT	4.888e-008	f_aa_DMS	3.318e-008
14	input_S_so4_in	3.296e-008	kdec_xac	3.237e-008
15	km_MAC_MT	2.898e-008	f_aa_MT	2.831e-008
16	Y_aa	2.539e-008	Ks_H2S_MT	1.898e-008
17	Ks_H2S_MT	1.898e-008	Kp_DMDS	1.607e-008
18	f_aa_DMS	1.361e-008	input_X_c_in	1.351e-008
19	kdec_xac	1.295e-008	Y_ac	1.266e-008
20	km_DMS	9.16e-009	KI_nh3_ac	9.862e-009
21	Ks_DMS	8.674e-009	Y_fa	6.503e-009
22	Kp_DMS	8.429e-009	Ks_DMS	6.053e-009
23	Ks_MAC	7.366e-009	kdec_xSRBac	4.133e-009
24	km_MT	5.705e-009	KMT_DMDS	3.973e-009
25	km_SRB_ac	4.396e-009	kdec_xaa	3.639e-009
26	Y_SRB_ac	3.959e-009	km_MT	3.566e-009
27	km_MAC_DMS	3.931e-009	km_DMDS	3.522e-009
28	Y_fa	3.902e-009	kdec_xsu	3.365e-009
29	Ks_so4_ac	3.748e-009	Y_su	3.191e-009
30	Y_su	3.191e-009	Y_aa	3.174e-009
31	Y_h2	2.961e-009	kdec_xfa	2.882e-009
32	Ks_H2S_DMS	2.751e-009	Ks_H2S_DMS	2.751e-009
33	Ka_co2	2.598e-009	Ks_h2	2.644e-009
34	km_ac	2.195e-009	Ks_DMDS	2.465e-009
35	kdec_xSRBac	1.653e-009	Kp_MT	2.166e-009
36	Ks_ac	1.557e-009	kdec_xh2	2.042e-009
37	Y_c4	1.486e-009	Ks_fa	1.484e-009
38	kdec_xaa	1.456e-009	km_DMS	1.431e-009
39	Ks_MT	1.394e-009	kdec_xc4	1.334e-009
40	kdec_xsu	1.346e-009	input_S_metal_ion_in	1.081e-009
41	kdec_xfa	1.153e-009	Ks_SRB_h2	8.26e-010
42	khyd_pr	1.118e-009	Ks_c4	7.827e-010
43	Kpre_H2S	9.098e-010	Y_SRB_ac	6.71e-010
44	Ks_SRB_ac	8.828e-010	Ks_aa	5.808e-010
45	Y_pro	8.515e-010	km_SRB_ac	5.085e-010
46	kdec_xh2	8.167e-010	Y_h2	4.935e-010
47	km_fa	7.396e-010	kdec_xpro	3.902e-010

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48 Ks_fa      5.936e-010  km_MAC_MT  3.895e-010
49 kdec_xc4   5.336e-010  Ks_SRB_pro 3.641e-010
50 km_aa      4.078e-010  KI_h2_fa   3.638e-010
51 Ks_aa      3.485e-010  Kp_DMS     3.509e-010
52 km_pro     2.967e-010  kdec_xSRBpro 2.944e-010
53 kLa_DMDS   2.826e-010  km_ac      2.744e-010
54 Ks_pro     2.569e-010  Y_c4       2.477e-010
55 kLa        1.881e-010  Y_pro      2.129e-010
56 km_SRB_pro 1.863e-010  Ks_ac      2.126e-010
57 Ks_h2      1.851e-010  KI_h2_pro  1.959e-010
58 km_SRB_h2  1.776e-010  Ks_so4_ac  1.874e-010
59 Ks_c4      1.565e-010  kdec_xSRBh2 1.823e-010
60 kdec_xpro   1.561e-010  Ks_su      1.6e-010
61 km_c4      1.445e-010  km_fa      1.233e-010
62 khyd_aro   1.289e-010  khyd_pr    1.118e-010
63 Ks_so4_pro 1.26e-010  KI_H2S_SRB_ac 1.064e-010
64 kdec_xSRBpro 1.178e-010  Ks_IN      1.045e-010
65 km_h2      1.163e-010  Ks_pro     6.065e-011
66 Ks_so4_h2  1.094e-010  km_MAC_DMS 4.779e-011
67 Ks_SRB_pro 1.074e-010  KI_h2_c4   3.996e-011
68 Y_DMS      9.922e-011  Ka_ac      2.58e-011
69 khyd_ch    9.099e-011  km_pro     2.282e-011
70 Ks_su      7.999e-011  khyd_aro   1.289e-011
71 km_su      7.724e-011  km_SRB_pro 1.173e-011
72 khyd_li    7.486e-011  khyd_ch    9.099e-012
73 Ka_nh4     7.465e-011  KI_H2S_SRB_pro 8.807e-012
74 kdec_xSRBh2 7.293e-011  kLa_DMDS   8.564e-012
75 kLa_hpro   4.894e-011  km_aa      8.155e-012
76 kLa_hac    4.603e-011  khyd_li    7.486e-012
77 kLa_H2S    4.441e-011  km_c4      7.223e-012
78 Ka_H2S     4.091e-011  Ka_pro     5.201e-012
79 Y_DMDS     3.833e-011  KI_H2S_SRB_h2 4.105e-012
80 kLa_hbu    3.012e-011  km_SRB_h2  3.978e-012
81 kLa_MT     2.87e-011  km_h2      3.322e-012
82 KI_nh3_ac  1.775e-011  Ka_bu      2.688e-012
83 kLa_hva    1.189e-011  km_su      2.575e-012
84 Ks_IN      1.045e-011  Ks_so4_pro 1.634e-012
85 Y_MT       4.955e-012  kLa_hpro   1.439e-012
86 KI_H2S_SRB_ac 9.478e-013  Ka_va      1.329e-012
87 Ka_pro     6.856e-013  Ks_so4_h2  1.167e-012
88 kLa_DMS    3.23e-013  Kpre_H2S   1.126e-012
89 Ka_va      2.107e-013  kLa_hac    1.096e-012
90 KI_H2S_SRB_pro 7.843e-014  kLa_hbu    1.004e-012
91 KI_H2S_SRB_h2 7.055e-014  kLa        9.403e-013
92 Ka_ac      4.484e-014  kLa_H2S    6.255e-013
93 Ks_SRB_h2  4.13e-014  kLa_MT     5.979e-013
94 Ka_bu      3.886e-014  kLa_hva    4.573e-013
95 Ka_h2o     1.958e-015  Y_MT       1.222e-014
96 KI_h2_fa   1.819e-015  kLa_DMS    8.731e-015
97 KI_h2_pro  6.858e-016  Y_DMDS     6.576e-015
98 KI_h2_c4   3.996e-016  Y_DMS      2.581e-015
99 kLa_nh3    0          kLa_nh3    0
100 f_aa_H2S  0          f_aa_H2S   0

```

Variable: S_DMS_liq

Parameter: Sens AR:	Parameter: Error Contr.:
[kmol.m-3]	[kmol.m-3]

1	f_aa_DMS	2.449e-007	Ka_h2o	7.085e-006
2	input_S_aa_in	2.059e-007	Ka_nh4	3.213e-006
3	input_S_metal_ion_in	1.898e-007	f_aa_DMDS	3.102e-006
4	kdis	1.883e-007	Ka_co2	1.2e-006
5	Kp_DMS	1.73e-007	Ka_H2S	7.346e-007
6	km_DMS	1.636e-007	f_aa_DMS	5.972e-007
7	Ks_DMS	1.54e-007	input_S_so4_in	2.209e-007
8	Y_ac	1.419e-007	kdis	1.883e-007
9	f_aa_MT	8.305e-008	Ks_DMS	1.074e-007
10	input_S_so4_in	7.25e-008	Ks_MAC	1.037e-007
11	km_MAC_DMS	6.648e-008	kdec_xac	8.654e-008
12	f_pr_xc	6.058e-008	Ks_SRB_ac	8.437e-008
13	Ks_H2S_DMS	4.395e-008	input_S_aa_in	5.72e-008
14	f_aa_DMDS	3.623e-008	Ks_H2S_DMS	4.395e-008
15	kdec_xac	3.462e-008	Y_ac	2.837e-008
16	input_X_c_in	3.449e-008	km_DMS	2.556e-008
17	km_DMDS	2.118e-008	KI_nh3_ac	2.185e-008
18	Ks_DMDS	2.107e-008	f_pr_xc	2.019e-008
19	Kp_DMDS	1.975e-008	Ks_MT	1.965e-008
20	Ks_MAC	1.56e-008	f_aa_MT	1.252e-008
21	Y_aa	1.384e-008	Ks_H2S_MT	9.107e-009
22	km_MAC_MT	1.29e-008	kdec_xSRBac	9.043e-009
23	km_SRB_ac	9.954e-009	Y_fa	8.031e-009
24	Ks_H2S_MT	9.107e-009	Kp_DMS	7.202e-009
25	Y_SRB_ac	8.987e-009	Ks_h2	6.193e-009
26	Ks_so4_ac	8.377e-009	Y_su	3.668e-009
27	Ka_co2	6.549e-009	Ks_fa	3.035e-009
28	km_ac	4.833e-009	input_X_c_in	2.874e-009
29	Y_fa	4.819e-009	input_S_metal_ion_in	2.372e-009
30	Y_h2	4.409e-009	Ks_SRB_h2	1.873e-009
31	Kp_MT	3.867e-009	Y_aa	1.729e-009
32	Y_su	3.668e-009	Ks_c4	1.598e-009
33	kdec_xSRBac	3.617e-009	km_MT	1.584e-009
34	Ks_ac	3.419e-009	Y_SRB_ac	1.523e-009
35	km_MT	2.534e-009	km_DMDS	1.204e-009
36	Ks_SRB_ac	2.025e-009	km_SRB_ac	1.152e-009
37	Kpre_H2S	1.965e-009	Kp_DMDS	1.13e-009
38	Y_c4	1.727e-009	Ks_SRB_pro	8.699e-010
39	KMT_DMDS	1.666e-009	Ks_DMDS	8.429e-010
40	km_fa	1.51e-009	km_MAC_DMS	8.081e-010
41	Ks_fa	1.214e-009	kdec_xfa	7.536e-010
42	Y_pro	1.189e-009	KI_h2_fa	7.455e-010
43	khyd_pr	1.142e-009	Y_h2	7.348e-010
44	Ks_MT	6.237e-010	kdec_xSRBpro	6.946e-010
45	km_pro	6.127e-010	kdec_xaa	6.785e-010
46	Ks_pro	5.322e-010	kdec_xsu	6.327e-010
47	km_SRB_pro	4.362e-010	km_ac	6.041e-010
48	Ks_h2	4.335e-010	Ks_aa	5.926e-010
49	kLa_DMS	4.162e-010	Ks_ac	4.67e-010
50	km_SRB_h2	4.057e-010	kdec_xh2	4.363e-010
51	Ks_so4_pro	3.941e-010	Ks_so4_ac	4.188e-010
52	km_aa	3.635e-010	kdec_xSRBh2	4.178e-010
53	kLa	3.604e-010	KI_h2_pro	4.144e-010
54	Ks_aa	3.556e-010	kdec_xpro	3.472e-010

55	Ks_c4	3.195e-010	Ks_su	3.116e-010
56	km_c4	3.172e-010	Y_pro	2.972e-010
57	kdec_xfa	3.014e-010	Y_c4	2.878e-010
58	kdec_xSRBpro	2.779e-010	km_fa	2.517e-010
59	km_h2	2.768e-010	KI_H2S_SRB_ac	2.476e-010
60	kdec_xaa	2.714e-010	Ks_IN	2.327e-010
61	khyd_aro	2.669e-010	kdec_xc4	1.806e-010
62	Ks_SRB_pro	2.566e-010	km_MAC_MT	1.734e-010
63	kdec_xsu	2.531e-010	Kp_MT	1.713e-010
64	Ks_so4_h2	2.147e-010	Ks_pro	1.257e-010
65	khyd_ch	1.878e-010	khyd_pr	1.142e-010
66	Y_DMS	1.807e-010	KMT_DMDS	1.133e-010
67	kdec_xh2	1.745e-010	KI_h2_c4	8.459e-011
68	kdec_xSRBh2	1.671e-010	Ka_ac	5.787e-011
69	khyd_li	1.639e-010	km_pro	4.713e-011
70	Ks_su	1.558e-010	km_SRB_pro	2.747e-011
71	km_su	1.532e-010	khyd_aro	2.669e-011
72	kdec_xpro	1.389e-010	KI_H2S_SRB_pro	2.42e-011
73	kLa_hpro	1.088e-010	khyd_ch	1.878e-011
74	kLa_hac	9.609e-011	khyd_li	1.639e-011
75	kLa_H2S	9.528e-011	km_c4	1.586e-011
76	kLa_MT	9.066e-011	KI_H2S_SRB_h2	1.221e-011
77	Ka_H2S	8.749e-011	kLa_DMS	1.125e-011
78	Y_DMDS	7.809e-011	Ka_pro	1.113e-011
79	kdec_xc4	7.223e-011	km_SRB_h2	9.088e-012
80	Ka_nh4	7.188e-011	km_h2	7.908e-012
81	kLa_hbu	6.42e-011	km_aa	7.27e-012
82	KI_nh3_ac	3.933e-011	Ka_bu	6.216e-012
83	kLa_hva	2.791e-011	Ks_so4_pro	5.112e-012
84	Ks_IN	2.327e-011	km_su	5.107e-012
85	Y_MT	1.447e-011	kLa_hpro	3.2e-012
86	KI_H2S_SRB_ac	2.205e-012	Kpre_H2S	2.432e-012
87	Ka_pro	1.468e-012	Ka_va	2.345e-012
88	kLa_DMDS	3.791e-013	Ks_so4_h2	2.29e-012
89	Ka_va	3.716e-013	kLa_hac	2.288e-012
90	KI_H2S_SRB_pro	2.156e-013	kLa_hbu	2.14e-012
91	KI_H2S_SRB_h2	2.098e-013	kLa_MT	1.889e-012
92	Ka_ac	1.006e-013	kLa	1.802e-012
93	Ks_SRB_h2	9.365e-014	kLa_H2S	1.342e-012
94	Ka_bu	8.985e-014	kLa_hva	1.074e-012
95	KI_h2_fa	3.727e-015	Y_MT	3.567e-014
96	Ka_h2o	3.152e-015	Y_DMDS	1.34e-014
97	KI_h2_pro	1.451e-015	kLa_DMDS	1.149e-014
98	KI_h2_c4	8.459e-016	Y_DMS	4.702e-015
99	kLa_nh3	0	kLa_nh3	0
100	f_aa_H2S	0	f_aa_H2S	0